

**Study of rare earth local moment magnetism and strongly correlated phenomena
in various crystal structures**

by

Tai Kong

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Program of Study Committee:

Paul C. Canfield, Major Professor

Sergey L. Bud'ko

Alan I. Goldman

Rebecca Flint

Sanjeevi Sivasankar

Matthew J. Kramer

Iowa State University

Ames, Iowa

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To Li Kong, Meiyong Liu, Shimin Liu, Lan Liu

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ABSTRACT

Benefiting from unique properties of 4f electrons, rare earth based compounds are known for offering a versatile playground for condensed matter physics research as well as industrial applications. This thesis focuses on three specific examples that further explore the rare earth local moment magnetism and strongly correlated phenomena in various crystal structures.

The first two Chapters of the thesis will be dedicated to general introductions to rare earth physics and to quasicrystals that are related to the forthcoming Chapters. Chapter 3 describes the high-temperature solution growth technique for single crystal synthesis as well as the measurement techniques that were used during the course of this thesis research.

We then look at how local magnetic moments behave in a quasicrystalline lattice. Chapter 4 presents the discovery and characterization of i- R -Cd ($R = \text{Y, Gd-Tm}$), icosahedral quasicrystals, six of which belong to the world's first family of magnetic, binary quasicrystals. We first show how these quasicrystals were discovered via high-temperature solution growth utilized as an exploratory tool. We then present a detailed characterization of i- R -Cd ($R = \text{Y, Gd-Tm}$) by means of x-ray diffraction, temperature-dependent dc and ac magnetization, temperature-dependent resistance and temperature-dependent specific heat measurements. i-Y-Cd is weakly diamagnetic and manifests a temperature-independent susceptibility. i-Gd-Cd can be characterized as a spin-glass below 4.6 K via a dc magnetization cusp, a third order non-linear magnetic susceptibility peak, a frequency-dependent freezing temperature and a broad maximum in the specific heat. i- R -Cd ($R = \text{Ho-Tm}$) is similar to i-Gd-Cd in terms of features observed in thermodynamic measurements. i-Tb-Cd and i-Dy-Cd do not show a clear cusp in their zero-field-cooled dc magnetization data, but instead show a more rounded, broad local maximum. The resistivity for i- R -Cd is of order $300 \mu\Omega \text{ cm}$ and weakly temperature-dependent. The characteristic freezing temperatures for i- R -Cd ($R = \text{Gd-Tm}$) deviate from the de Gennes scaling, consistent with crystal electric field splitting induced local moment anisotropy.

Chapter 5 focuses on the search for a hexagonal system that exhibits a strong planar magnetization with a 6-state-clock, in-plane magnetic anisotropy. In Chapter 5, we look at a specific system, RMg_2Cu_9 . Single crystals of RMg_2Cu_9 ($R=Y, Ce-Nd, Gd-Dy, Yb$) were grown using a high-temperature solution growth technique and were characterized by measurements of room-temperature x-ray diffraction, temperature-dependent specific heat and temperature-, field-dependent resistivity and anisotropic magnetization. YMg_2Cu_9 is a non-local-moment-bearing metal with an electronic specific heat coefficient, $\gamma \sim 15 \text{ mJ/mol K}^2$. Yb is divalent and basically non-moment bearing in $YbMg_2Cu_9$. Ce is trivalent in $CeMg_2Cu_9$ with two magnetic transitions being observed at 2.1 K and 1.5 K. $PrMg_2Cu_9$ does not exhibit any magnetic phase transition down to 0.5 K. The other members being studied ($R=Nd, Gd-Dy$) all exhibit antiferromagnetic transitions at low-temperatures ranging from 3.2 K for $NdMg_2Cu_9$ to 11.9 K for $TbMg_2Cu_9$. Whereas $GdMg_2Cu_9$ is isotropic in its paramagnetic state due to zero angular momentum ($L=0$), all the other local-moment-bearing members manifest an anisotropic, planar magnetization in their paramagnetic states. To further study this planar anisotropy, detailed angular-dependent magnetization was carried out on magnetically diluted $(Y_{0.99}Tb_{0.01})Mg_2Cu_9$ and $(Y_{0.99}Dy_{0.01})Mg_2Cu_9$. Despite the strong, planar magnetization anisotropy, the in-plane magnetic anisotropy is weak and field-dependent. A set of crystal electric field parameters are proposed to explain the observed magnetic anisotropy.

The topic of Chapter 6 switches to strongly correlated phenomena. We study the evolution of the Kondo effect in heavy fermion compounds, $Yb(Fe_{1-x}Co_x)_2Zn_{20}$ ($0 \leq x \leq 1$), by means of temperature-dependent electric resistivity and specific heat. The ground state of $YbFe_2Zn_{20}$ can be well described by a Kondo model with degeneracy $N = 8$ and a $T_K \sim 30 \text{ K}$. In the presence of a very similar total CEF splitting with $YbFe_2Zn_{20}$, the ground state of $YbCo_2Zn_{20}$ is close to a Kondo state with degeneracy $N = 2$ and a much lower $T_K \sim 2 \text{ K}$. Upon Co substitution, the coherence temperature of $YbFe_2Zn_{20}$ is suppressed, accompanied by an emerging Schottky-like feature in specific heat associated with the thermal depopulation of CEF levels upon cooling. For $0.4 \lesssim x \lesssim 0.9$, the ground state remains roughly the same which can be understood by the Kondo effect in the presence of CEF splitting. However, only qualitative information can be obtained in this middle region due to a large substitution level variation. There is no clear

indication of Kondo coherence observable in resistivity within this substitution range down to 500 mK. The coherence re-appears at around $x \gtrsim 0.9$ and the coherence temperature increases with higher Co concentration levels.

CHAPTER 1. BASICS OF THE MAGNETIC PROPERTIES OF RARE EARTH ELEMENTS

If one looks at the periodic table of elements, rare earth elements probably are the most prominent ones since the majority of them (lanthanides) are listed separately across the whole bottom of the periodic table. Scandium and yttrium also belong to the rare earth family since they are often found in the same ore as lanthanide elements with very similar chemistry. Despite the fact that they are called rare earth, the real concentrations of rare earth elements in the crust of earth are actually not low. For example, cerium is as abundant as the well known metal, copper. And most of them are two orders of magnitude more abundant than precious metals, like gold[1]. The reason that they are called rare earths is that most of them are diffuse/dispersed and not often found in concentrated mineral deposits. In the context of current studies, the focus of this chapter will be on the magnetic and electronic properties of rare earth elements, most of which arise from the partially filled 4f-electron shell. Due to the relatively smaller spatial distribution of the un-paired 4f electrons compared to the outer filled shells, the 4f-magnetism can be approximated as a spatially localized moment. In the opposite limit, itinerant magnetism comes from a difference in population in spin orientations, or a spatial modulation of spins, of conduction electrons that are delocalized in real space. In the following sections, I am going to introduce in more detail how 4f electrons behave by themselves as well as collectively in a crystalline lattice.

1.1 4f electrons of rare earth and local magnetism

Most rare earth elements are trivalent in intermetallic compounds. Notable exceptions happen at the two ends of the lanthanide group and in the middle of the series where full/half-full 4f

shell is energetically more favourable. Eu is almost always divalent in intermetallic compounds to achieve a half-filled 4f shell. Eu^{2+} , therefore, has the same 4f electron configuration with Gd^{3+} , whereas contribute one less electron to the conduction band. Ce and Yb sometimes tend to have an empty (Ce^{4+}) or a full 4f shell (Yb^{2+}).

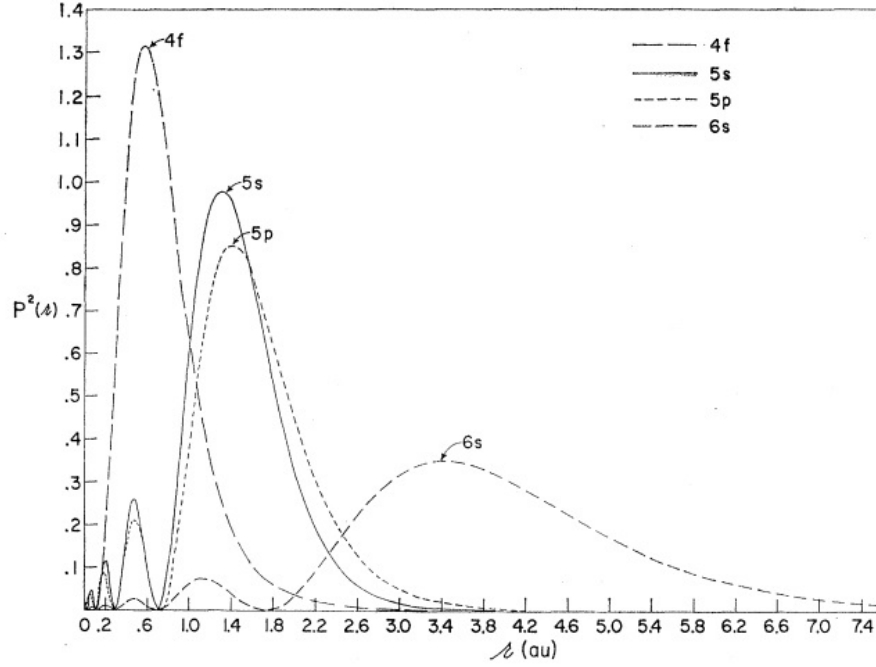


Figure 1.1 Relative radial extent for electrons of Gd^{+} from Hartree-Fock calculations.[2]

As mentioned above, the 4f electrons are closer located near the atomic core than outer-shell electrons. Fig. 1.1 shows the radial extent of some atomic electrons according to Hartree-Fock calculations. It worth pointing that the 4f electrons have a narrower spatial extent than, for instance, 5s and 5p electrons. Note that the 5s and 5p orbitals belong to closed shells, whereas the maximum of the 4f orbital is located inside of those orbitals[2; 3]. Since the overlap between 5d or 6s electrons between atoms are significantly larger than 4f electrons, the conduction band formed by s-d electrons are much wider in energy. Band calculations often show only ~ 50 meV band width for 4f electrons and locate at ~ 10 eV below the 6s-5d conduction bands[3]. In other words, 4f electrons are well localized.

Here, it is necessary to introduce Hund's rules, which explain how to calculate the ground state configuration for an unfilled shell when the total angular momentum is a good quantum number. The Hund's rules are:

- Hund's first rule: The ground state has the largest value of total spin angular momentum S .
- Hund's second rule: The ground state has the largest value of total orbital angular momentum L that is permitted by the first rule.
- Hund's third rule: The total angular momentum $J = |L-S|$ for less than half filled shell and $J = L+S$ for more than half filled shell.

The "energy scale" of these three rules becomes progressively smaller as we go from the first rule to the third. The third rule can be justified by considering spin-orbit coupling, whereas the first two rules are related to exchange energy that is usually much higher in energy. For example, being able to have the maximum spin avoid electrons staying in the same orbit due to Pauli exclusion principle and thus saves Coulomb potential energy. Roughly speaking, the first rule is easily of the order ~ 1 eV. The second is weaker at around 0.1-0.3 eV. And the third rule is even weaker[4].

For most rare earth elements, the three Hund's rules' energy scales are dominant ones as compared to other energy scales, for instance room temperature (~ 25 meV) and crystal electric field splitting (more detail later). The ground state, as shown above, therefore, is well separated from excited states. For rare earth trichlorides, the excited states are at least 0.2 eV higher in energy, except for much lower values for Sm and Eu. Because of the relatively small energy difference between the Hund's rule ground state and the first excited state, Sm sometimes behaves differently from what is expected from the Hund's rule's prediction. Eu is mostly divalent in intermetallics instead of trivalent as been tabulated[5]. In the case other energy scales become more dominant, for example many 3d electrons in the presence of a strong crystalline electric field (CEF) effect, Hund's second and third rule may be violated. For the current study, we won't go into details for such cases.

Hund's rules will specify the ground state J , which still has a degeneracy of $(2J+1)$. In the presence of applied magnetic field, Zeeman splitting will continue lifting the degeneracy. With

a finite thermal excitation due to finite temperature, the magnetization of the ground state J can be written as:

$$M = -\frac{N}{V} g_J \mu_B J B_J(\beta g_J \mu_B J H) \quad (1.1)$$

Where N is the particle number, V is the volume of the sample. g_J is the Landé g factor, $g_J = 1 + \frac{J(J+1)+S(S+1)-L(L+1)}{2J(J+1)}$, μ_B is the Bohr magneton, $\beta = 1/(k_B T)$ and B_J is the Brillouin function. When temperature is much higher than the Zeeman splitting, the magnetic susceptibility can be expressed as:

$$\chi = \frac{\partial M}{\partial H} \sim N_A \frac{(g_J \mu_B)^2 J(J+1)}{3k_B T} = \frac{C}{T} \quad (1.2)$$

This is known as the Curie's law where the Curie constant C is defined as $C = N_A \frac{(\mu_{eff})^2}{3k_B}$ and the effective moment, $\mu_{eff} = g_J \mu_B \sqrt{J(J+1)}$

In a real compound, magnetic interaction produces an effective mean field on the magnetic ions. This additional magnetic field modifies equation (1.2) into:

$$\chi = \frac{C}{T - \theta} \quad (1.3)$$

When θ is positive (negative), the magnetic interaction is ferromagnetic (antiferromagnetic). The addition of the θ term, however does not change the effective moment that is depicted by the Curie constant, C . Since most of the rare earth ions have a well defined effective moment, this can be used to evaluate the concentration of rare earth in a compound, such as a magnetically doped system or a simple binary compound (an example of i - R -Cd will be described in the following chapter), as long as the rare earth ion is the only moment bearing ion in the compound. Useful parameters associated with trivalent rare earth ions are summarized in Table 1.1.

The data in Table 1.1 are for isolated rare earth ions. Magnetic interaction may appear in a solid once multiple magnetic moments are present and able to interact. The most straightforward interaction is via a direct overlap between 4f electrons. Due to the quite small spatial extent of 4f electrons, this type of direct exchange interaction usually does not offer the primary source of interaction in rare earth based intermetallic compounds (or even elements). In a

Table 1.1 Ground state orbital angular momentum L , spin angular momentum S and total angular momentum J as calculated from Hund's rules. Landé factor, $g_J = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$; Saturated magnetic moment, $M_{sat} = g_J J$; Effective magnetic moment, $\mu_{eff} = g_J \sqrt{J(J+1)} \mu_B$ and de Gennes factor, $dG = (g_J - 1)^2 J(J+1)$ of trivalent rare earth ions.

R^{3+}	L	S	J	g_J	M_{sat}	μ_{eff}	dG
Sc	-	-	-	-	-	-	-
Y	-	-	-	-	-	-	-
La	0	0	0	-	-	-	-
Ce	3	0.5	2.5	0.857	2.14	2.54	0.19
Pr	5	1	4	0.800	3.20	3.58	0.80
Nd	6	1.5	4.5	0.727	3.27	3.62	1.84
Pm	6	2	4	0.600	2.40	2.68	3.20
Sm	5	2.5	2.5	0.286	0.71	0.84	4.46
Eu	3	3	0	-	-	-	-
Gd	0	3.5	3.5	2.00	7.00	7.94	15.75
Tb	3	3	6	1.500	9.00	9.72	10.50
Dy	5	2.5	7.5	1.333	10.00	10.64	7.08
Ho	6	2	8	1.250	10.00	10.61	4.50
Er	6	1.5	7.5	1.200	9.00	9.58	2.55
Tm	5	1	6	1.167	7.00	7.56	1.17
Yb	3	0.5	3.5	1.143	4.00	4.54	0.32
Lu	0	0	0	-	-	-	-

metal, the primary interaction between localized 4f electrons is through polarized conduction electrons, an indirect exchange interaction called RKKY interaction. RKKY interaction is named after the scientists who proposed the theory: M. A. Ruderman, C. Kittel, T. Kasuya, K. Yosida[6; 7; 8]. The model starts with a single magnetic impurity embedded in conduction electrons. The spin polarization of the conduction sea will exhibit a Friedel oscillation type spatial modulation, which only arises when a sharp Fermi surface exists. When encountering with another magnetic impurity some distance away, the polarization of conduction electrons will be able to interact with this second magnetic impurity, finishing the indirect interaction between the two magnetic impurities. More detailed mathematical treatment can be found in several books[5; 9]. Since the RKKY interaction is mediated by conduction electrons, the interaction depends on the density of states of electrons at the Fermi energy, the Fermi surface topology and the real space distance between local moments. In addition, depending on the

combination of Fermi surface momentum and the real space spacing, Friedel oscillations can result in different signs for the exchange interaction, which may result in either ferro- and antiferromagnetic interactions between local moments.

If assuming that the interaction between local moments and the conduction electrons, I , does not vary much across the rare earth series, the strength of interaction can be simplified as:

$$H \sim I \mathbf{s} \mathbf{S} \quad (1.4)$$

where $\mathbf{s}$ and $\mathbf{S}$ represent spins for conduction electrons and 4f electrons[10]. For 4f electrons, since $\mathbf{J}$ is a good quantum number, we can project $\mathbf{S}$ back to $\mathbf{J}$ via $\mathbf{S} = (g_J - 1)\mathbf{J}$. Since the conduction electron need to interact with another local moment again to complete the 4f-4f communication, overall the strength of this indirect interaction is proportional to:

$$\sim I^2 (g_J - 1)^2 \mathbf{J}^2 \sim I^2 (g_J - 1)^2 J(J + 1) \quad (1.5)$$

In a mean field theory, the Curie-Weiss temperature as well as the ordering temperature will be proportional to the de Gennes factor (dG): $(g_J - 1)^2 J(J + 1)$. This is called the de Gennes' scaling[11]. Note that for all rare earth trivalent ions listed in Table 1.1, the de Gennes factor reaches its maximum at Gd^{3+} . The de Gennes' scaling is followed for most of the time by heavy rare earth members with possible complication brought in by anisotropy in exchange energy and CEF effects[12; 13]. More examples will be discussed in the following chapters.

1.2 Crystalline electric field effect

The crystalline electric field (CEF) describes the electric field an ion experiences due to its neighboring ions when embedded in a crystalline lattice. The simplest picture depicts an environment where the central ion is surrounded by point charges sitting on neighboring lattice sites. Such an electric field produces an additional Coulomb energy that needs to be taken into account. For 4f electrons, this energy scale is usually smaller than the energy scale of Hund's rules and therefore can be considered as a perturbation. For 3d electrons, as a counter example,

the CEF energy scale can be stronger than the spin-orbit coupling. This means that, for 3d electrons, the total angular momentum J is no longer a good quantum number.

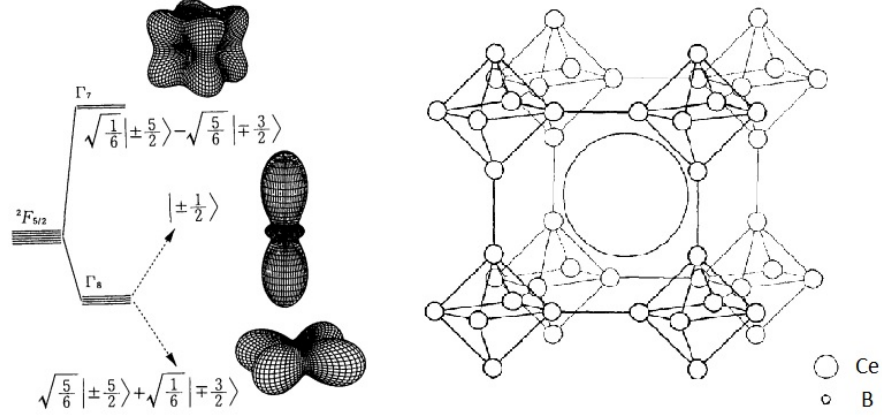


Figure 1.2 Shape of 4f electron clouds of different crystal field levels for Ce in CeB_6 [4]. The structure of CeB_6 is shown on the right[14].

The CEF induced free ion magnetic anisotropy originates from the fact that each occupied orbital has a spatial charge distribution which feels the surrounding crystalline electric field. To minimize the static electric potential energy, certain spatial distributions will be favored and therefore lowered in energy while others will be raised. For rare earths, where the total angular momentum J is a good quantum number, the degeneracy in magnetic orientation is lifted via spin-orbit coupling, and single ion, magnetic anisotropy emerges. Following such an argument, elements with a finite angular momentum will exhibit magnetic anisotropy whereas trivalent Gd and divalent Eu will be isotropic since $L = 0$ (spherical distribution). Note that the magnetic anisotropy can still arise from other contributions, for instance, anisotropic exchange interaction. In any case, there will be anisotropy in the ordered state. Coming back to the single ion CEF picture, Fig. 1.2 shows an example of CeB_6 where Ce^{3+} sits in a cubic symmetry. If assuming that B clusters at the corners of the cube have effectively negative charges, the Γ_7 states with charges distributed towards the corners will be unfavourable in energy. On the other hand, the Γ_8 states, where electron distributions point to the gaps, will be lower in energy.

Some examples of anisotropic magnetization in tetragonal systems are shown in Fig. 1.3[15; 16]. As mentioned above, trivalent Gd is isotropic with $L = 0$. Fig. 1.3(a) shows the temperature-dependent magnetization of GdNi_2Ge_2 . In the paramagnetic state, the anisotropic magnetization data along the two characteristic orientations of a tetragonal system are virtually isotropic as expected. CEF effect can also confine the magnetic moment along the axial or within the basal-plane, leading to an extreme axial or planar magnetization. Fig. 1.3(b)-(d) show examples for these cases. For DyAgSb_2 , the magnetic moments of Dy^{3+} are primarily confined in the basal-plane as shown in Fig. 1.3(b). Y dilution allows a more accurate evaluation of the CEF effect by minimizing the magnetic anisotropy brought in by the anisotropic exchange interaction. TbNi_2Ge_2 , on the other hand, is extremely axial as shown in Fig. 1.3(c)-(d). The c-axis magnetization is an order of magnitude larger than the planar magnetization and deviating from the c-axis, the magnetization decreases rapidly (Fig. 1.3(d)).

To describe the CEF effect quantitatively, based on the idea of point charge model, one can write down the electric potential generated by surrounding point charges at the point $\mathbf{r}$:

$$V = \sum_j \frac{q_j}{|\mathbf{R}_j - \mathbf{r}|} \quad (1.6)$$

where q_j is the charge of the j th neighboring ion (or simplified as a point charge here) at a distance $\mathbf{R}_j$ from the origin. The potential energy of a magnetic ion with charges q_i will then be:

$$W_e = \sum_i q_i V_i = \sum_i \sum_j \frac{q_i q_j}{|\mathbf{R}_j - \mathbf{r}|} \quad (1.7)$$

To expand this equation, different forms can be used. Common straightforward solutions include using Cartesian coordinates or somewhat easier, spherical harmonics. The most convenient and widely used is the formalism set up by Stevens in 1952[17; 18; 19]. Utilizing Wigner-Eckart theorem, Hamiltonian expressed in Cartesian system is converted to operator equivalents so that it is expressed in total angular momentum J . In solving the matrix elements of crystalline electric potential, such operator equivalents requires no additional effort to go back to single electron wavefunctions. These operator equivalents were then named Stevens'

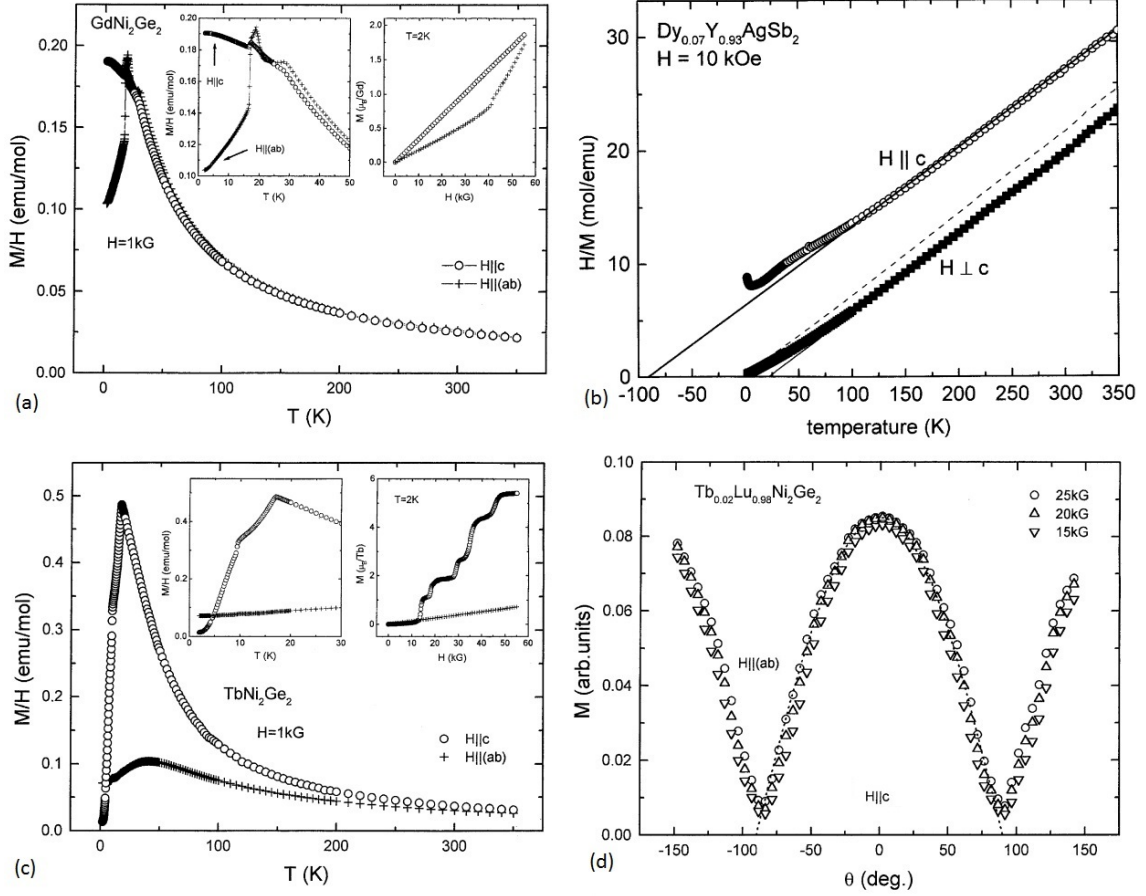


Figure 1.3 Anisotropic, temperature-dependent magnetization of (a) GdNi_2Ge_2 (b) Y diluted DyAgSb_2 and (c) TbNi_2Ge_2 . (d) Angular-dependent magnetization of Lu diluted TbNi_2Ge_2 [15; 16].

operators. With lengthy derivation skipped here, the Hamiltonian of CEF effect can then be simplified as:

$$H_{CEF} = \sum_{n,m} B_n^m O_n^m \quad (1.8)$$

Where O_n^m are Stevens' operators. B_n^m are called CEF parameters which can be dissected into three parts: $B_n^m = A_n^m \langle r^n \rangle \theta_n$. A_n^m is the material-dependent part describing the sign and the strength of the CEF effect. It is only very weakly dependent on the lattice parameter[20] and usually can be considered as a constant in an iso-structural series. $\langle r^n \rangle$ describes the mean value of the nth power of the radial distance of the 4f electrons. θ_n are multiplicative factors that are usually denoted as: $\theta_2 = \alpha_J$, $\theta_4 = \beta_J$ and $\theta_6 = \gamma_J$. Theoretically computed $\langle r^n \rangle$ and the α_J , β_J , γ_J values are tabulated in Table 1.2[21; 22].

Table 1.2 Stevens factors α_j , β_j , γ_j and radial matrix elements $\langle r^l \rangle$ for rare earth ions.

R^{3+}	$\alpha_j \times 10^2$	$\beta_j \times 10^4$	$\gamma_j \times 10^6$	$\langle r^2 \rangle (\text{\AA}^2)$	$\langle r^4 \rangle (\text{\AA}^4)$	$\langle r^6 \rangle (\text{\AA}^6)$
Ce	-5.7143	63.4921	0.0000	0.3666	0.3108	0.5119
Pr	-2.1010	-7.3462	60.9940	0.3350	0.2614	0.4030
Nd	-0.6428	-2.9111	-37.9880	0.3120	0.2282	0.3300
Sm	4.1270	25.0120	0.0000	0.2728	0.1772	0.2317
Tb	-1.0101	1.2244	-1.1212	0.2302	0.1295	0.1505
Dy	-0.6349	-0.5920	1.0350	0.2188	0.1180	0.1328
Ho	-0.2222	-0.3330	-1.2937	0.2085	0.1081	0.1181
Er	0.2540	0.4440	2.0699	0.1991	0.0996	0.1058
Tm	1.0101	1.6325	-5.6061	0.1905	0.0921	0.0953
Yb	3.1746	-17.3160	148.0001	0.1826	0.0854	0.0863

CEF effects in both cubic and hexagonal point symmetry have been well studied by Lea et al. and Segal et al.[23; 24]. For a cubic symmetry, the CEF Hamiltonian can be written as:

$$H_{cubic} = B_4^0 [O_4^0 + 5O_4^4] + B_6^0 [O_6^0 - 21O_6^4] \quad (1.9)$$

For hexagonal symmetry, an ideal closed packing will give the Hamiltonian:

$$H_{hex} = B_4^0 O_4^0 + B_6^0 (O_6^0 + \frac{77}{8} O_6^6) \quad (1.10)$$

It should be noted, though, that for hexagonal systems, deviating from the ideal c/a ratio (1.63), the relative ratio between Stevens' operators will be not fixed and B_2^0 term will have to be considered. In general, the lower the symmetry the more terms there will be in the Hamiltonian. CEF terms that need to be included for each point group can be found, for example, in Table.3 of Ref. [21]. Experimentally, CEF parameters can be obtained by fitting experimental data, e.g. temperature- and field-dependent magnetization and specific heat data or inelastic neutron scattering data, to the calculated values from the CEF Hamiltonian. In uniaxial systems, B_2^0 can be directly determined via anisotropic Curie-Weiss temperatures[25]:

$$B_2^0 = \frac{10}{3(2J-1)(2J+3)} k_B (\Theta_{ab} - \Theta_c) \quad (1.11)$$

In Chapter 5, we will show more examples on how to obtain the CEF parameters from experimental data and how the CEF influences the anisotropic magnetization.

1.3 Kondo effect and heavy fermions

Now we move on to a different type of system where the 4f moments hybridize with conduction electrons. The puzzle started in early 1930s when scientists observed an upturn of resistance in noble metals, like gold, at very low temperatures (see, for example Ref.[26]). This upturn violated the common understanding based on Matthiessens rule, where the residual resistivity, ρ_0 should be additive. It was later realized that the amount of magnetic impurity in the sample modifies the features associated with this mysterious upturn in temperature-dependent resistivity data (see Fig. 1.4)[27]. Whereas the magnetic nature of the impurity was crucial, the right combination of magnetic impurity and host was also important[28].

In 1961, P.W. Anderson proposed a model to understand the conditions needed for a local moment to exist in a host metal by considering the interaction between local spins and the conduction electrons[29]. J. Kondo later successfully explained the logarithmic rise of resistivity at low-temperature using a perturbation theory considering a s-d exchange interaction[27]. The interaction between local moment and conduction electron has to be antiferromagnetic in the model. Historically, however, the calculation by Kondo predicted a non-physical diverging

resistivity at zero temperature, which was later called the "Kondo problem". This problem was solved by K. G. Wilson by using numerical renormalization group theory[30]. In the Kondo model (which is also known as the single ion Kondo model because it deals with well isolated magnetic ions in a metallic host), an energy scale is characterized by a so called "Kondo temperature", $T_K \sim De^{-1/2J_K\rho}$ [31]. Here, D is the band width of conduction electrons, J_K is the antiferromagnetic exchange energy between s-d electrons and ρ is the density of states at the Fermi energy. Below T_K , the entropy that is removed can be approximated by $\gamma T_K = R \ln \Omega$. Here γ is the Sommerfeld coefficient, R is the ideal gas constant and Ω is the degeneracy associated with the local moment. It was taken as $\Omega = 2$ for spin 1/2 in the simplest situations.

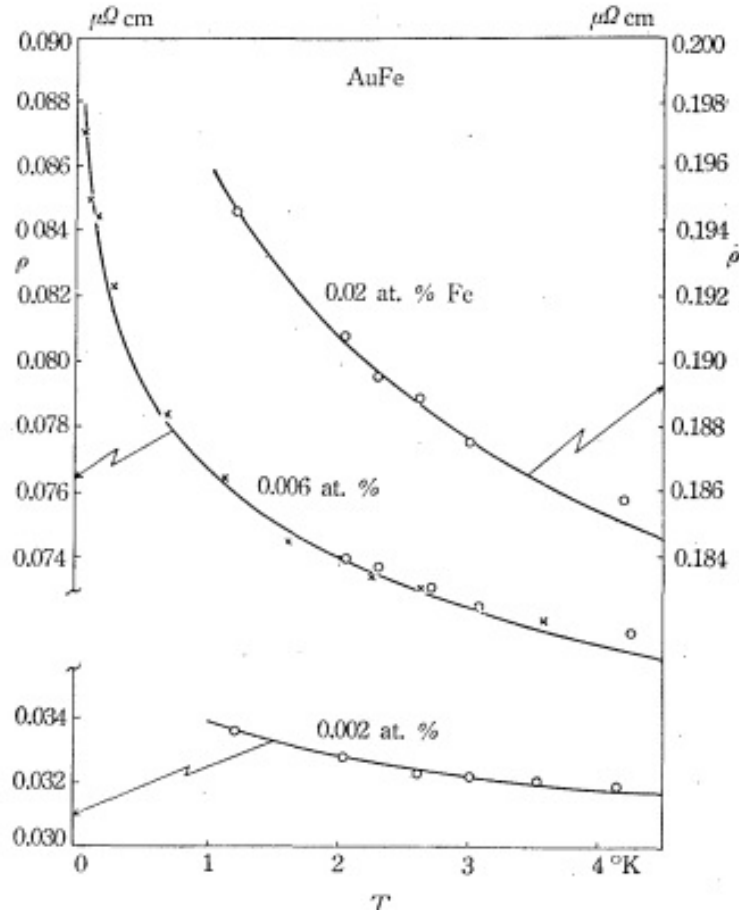


Figure 1.4 Low-temperature resistivity of Au with different Fe impurity concentrations. Solid lines are theoretical fits from J. Kondo[27].

When magnetic impurities get denser, they can ultimately fully occupy a specific lattice site as part of an ordered compound and a new ground state, heavy fermion, can sometimes emerge. The heavy fermion state is very similar to that of a normal metal, however with a very high γ value, for example, ~ 1600 mJ/mol-K² in CeAl₃[32]. In comparison, the γ value is around 1 mJ/mol-K² in most elemental metals[33]. Heavy fermions were later related to the Kondo effect as a concentrated Kondo lattice as opposed to single ion Kondo impurities. A new energy scale, the so called "Kondo coherence temperature", emerges, below which each Kondo impurity starts communicating with other impurities and a coherent state develops. Despite many theoretical, phenomenological studies, it is still not clear how the Kondo temperature and the Kondo coherence temperature are related to each other[34; 35; 36; 37; 38; 39].

As mentioned in the previous sections, the interaction between local moments and conduction electrons will inevitably give rise to an indirect exchange channel which could result in magnetic ordering. On the other hand, the Kondo effect leads to a singlet ground state. Conduction electrons will eventually screen the local moment and end up in a non-magnetic state at low-temperatures. If assuming the interaction between local moment and conduction electron is always antiferromagnetic and is the same for both Kondo and RKKY, Doniach came up with a generic phase diagram that captures the results from the competition between the Kondo effect and the RKKY interaction (see Fig. 1.5). With increasing $|J_K\rho|$, the ground state can evolve from an magnetically ordered state to a non-magnetic state[40]. This phase diagram is of course simplified. It omits many real factors for example different types of interactions between local moments and conduction electrons, leaving only the Kondo type antiferromagnetic exchange interaction. Due to a rising T_K , it also indicates a decreasing γ value as one initially increases $|J_K\rho|$, which will give a higher γ value in the antiferromagnetic regime (This could be explained by including more considerations, for example: short range magnetic correlations[41]). However, the Doniach phase diagram captures the bulk part of the picture and serves as a good guide for material searching.

Kondo physics, including single ion effects, Kondo lattices and the related heavy fermion and quantum critical point, is a very large and currently intensively investigated subject. Many experimental and theoretical reviews have provided detailed descriptions, which will not be

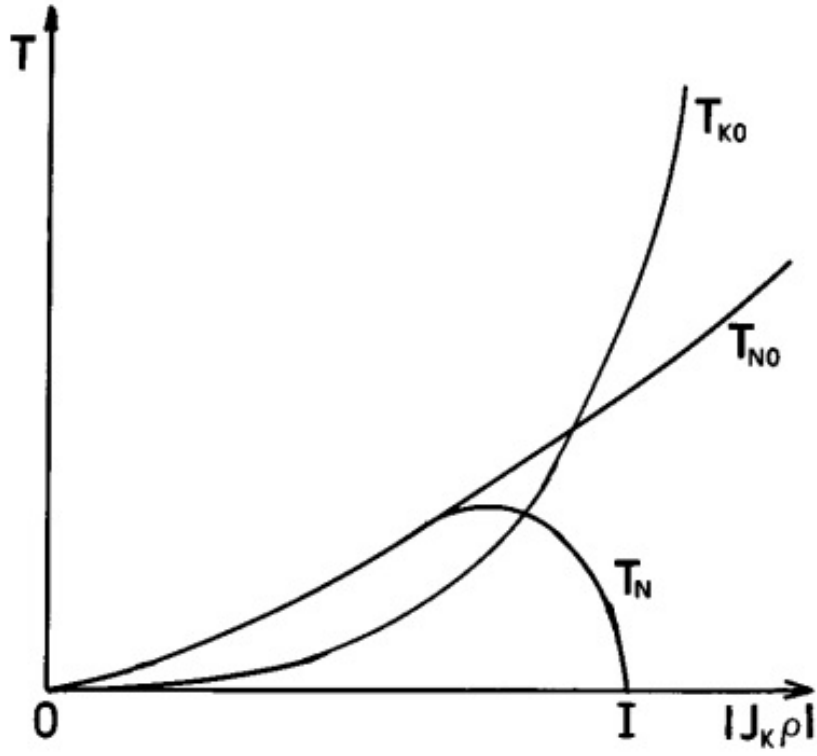


Figure 1.5 Doniach diagram. It shows the strength of Kondo energy scale (T_{K0}) and the RKKY energy scale (T_{N0}) as a function of $|J_K \rho|$. The actual ordering temperature (T_N) shows a dome-like shape due to the competition between the two energy scales[41].

covered here[31; 42; 43; 44; 45]. Several models and results will be mentioned in the context of the work that will be presented in the following chapters.

To date, most of the models and calculations have focused on studying the physical properties of isolated magnetic impurities (single ion Kondo impurity). Coqblin and Schrieffer have mapped out a way to calculate when the local moment has an arbitrary degeneracy instead of the simplest spin 1/2 case[46]. This model was later solved numerically by Rajan for magnetization and specific heat[47].

In real systems, the degeneracy of local moments will be lifted by CEF effects. As temperature decreases, the Kondo behavior will look differently when different CEF levels are populated and interact with conduction electrons. In the presence of CEF splitting, physical quantities such as resistivity[48], thermoelectric power (TEP)[49] have been modelled and calculated. Specific heat of spin 1/2 as well as degenerate cases are solved and scaled with T_K as mentioned ahead[47; 50; 51]. In the presence of CEF splitting, the specific heat in an arbitrary CEF splitting has only been solved for Ce very recently[52]. Yb, having a large degeneracy, is yet to be exactly solved. Only approximation models have been proposed[53] and used to fit Yb-based Kondo systems(see for example Ref.[53; 54]). Another key feature in a real world is anisotropy. Undoubtedly, this brings more complications into the calculation. So far, only anisotropy effects in resistivity have been studied[55; 56; 57].

In the Fermi liquid picture, the coefficient of T^2 dependence in low-temperature resistivity, A , is proportional to m^{*2} . Similarly, the magnetic susceptibility χ and Sommerfeld coefficient γ are all proportional to m^* , where m^* is the quasiparticle effective mass. In a heavy fermion system, these relations still apply. Therefore, the Wilson ratio (χ/γ) [31] and the Kadowaki-Woods ratio (A/γ^2) [58] work for many of the heavy fermion systems. Deviations from the standard numbers will offer additional information about the system. For instance, the generalized Kadowaki-Woods plot can be understood from degeneracy point of view[59], or band structure point of view[60; 61]. The Wilson ratio (WR) was generalized to be $WR = N/(N-1)$ which could also indicate the degeneracy (N) that is associated with the Kondo effect[31]. More examples will be discussed in the following chapters.

1.4 Spin glass

Previous sections have been focusing on well ordered magnetic systems which will end up with either a long range magnetic ordering or a non-magnetic, hybridized, heavy Fermi liquid state. Now we introduce two new concepts: frustration and randomness. Frustration means no spin configuration can simultaneously minimize all the competing interaction terms. For example in a triangular lattice of Ising spins with only a nearest neighbor antiferromagnetic interaction, two nearest spins will be anti-parallel due to antiferromagnetic interaction. However the third spin cannot satisfy the antiferromagnetic interaction on both sides since it cannot be both spin up and spin down. Randomness is mainly about the randomness related to local moments. It could be a randomness in site occupancy where there is a distribution of distance between spins or a randomness of bond where nearest neighbor interactions vary between ferromagnetic coupling and antiferromagnetic coupling. Randomness in these cases will ultimately result in a distribution of exchange interactions experienced by each specific magnetic ion.

If one adds enough frustration and randomness into a long-range magnetically ordered system, it will eventually lose its static long-range magnetic order, leaving only a short range order in a non thermal equilibrium state. In many aspects, this picture is very similar to that of oxide glasses, which describe solid states with only short range structural order below a certain glass transition temperature. A spin glass is thus defined as a magnetic system that can be characterized by a well defined freezing temperature, T_f , below which an irreversible and metastable freezing of spin orientation occurs without long range magnetic ordering[62; 63].

The spin glass state was initially recognized in diluted magnetic alloys, for example AuFe alloy with only a few molar percent of moment-bearing Fe[64]. Later, spin glass states were found in magnetically ordered systems when the magnetic ions were sufficiently diluted by non-magnetic ions. Dilution can create randomness as well as spin configurations that are equally favorable in energy at low temperature[65]. In the following chapter, I will show that, quasicrystals, albeit being an ordered structure, also end up in a spin glass state at low temperature due to a distribution of exchange interaction, and possibly a randomness in site occupancy.

Due to the randomness and non thermal equilibrium nature of the spin glass state, theoretical study is still ongoing, often resorting to large scale numerical simulations. Many review papers have covered the progress on the theoretical side with comparison to the experiments[62; 63; 65]. In the current study, I will be focusing more on the experimental identification of the spin glass state as compared to long range magnetically ordered states[62; 63; 65]:

A spin glass will show time-dependent (ageing process) physical properties due to the fact that spin-glass state is a metastable and non-equilibrium state. It manifests a zero-field-cooled (ZFC) and field-cooled (FC) irreversibility in which a canonical spin glass will have a cusp in the ZFC magnetization data at the freezing temperature, T_f . In addition, the magnetization of spin glass is frequency-dependent. Higher order magnetic susceptibility can also serve as a clear indicator to identify the spin glass state. At T_f , a spin glass will manifest a sharp peak in the third order magnetic susceptibility (χ_3) whereas for ferromagnets, theory predicts a divergence of χ_3 to opposite extremes before and after T_c , and for antiferromagnets, a step-like behavior at T_N [66]. Finally, in specific heat and resistivity, there will be no clear feature that can be associated with magnetic phase transition at T_f . The specific heat data manifest a broad maximum at $\sim 20\%$ above the T_f [62]. The resistivity data can show a variety of temperature-dependences in the vicinity of T_f . Similar to the temperature-dependent specific heat data, the resistivity data sometimes show a broad feature above the T_f . It should be noted that, like the identification of any other phase transitions, all criteria should be considered for consistency and satisfying a single criterion is not sufficient to claim a spin glass state.

Fig. 1.6 shows examples of some spin glass systems to illustrate criteria that are mentioned above. The time-dependence of the magnetization for the icosahedral, quasicrystalline, Tb-Mg-Zn measured at 100 Oe is shown in Fig. 1.6(a). For the ZFC data, the magnetization increased by approximately 10% in 3 days from the time external magnetic field was turned on. On the other hand, the FC data stay fairly constant as a function of time. Fig. 1.6(b) shows the irreversibility between ZFC and FC data for Tb-Mg-Zn measured at 25 Oe. The ZFC data shows a clear cusp at T_f whereas FC data flattens below T_f . The temperature and measurement procedure for the middle curves starts from an initial ZFC down to 2 K, at which temperature 25 Oe was applied and magnetization was measured upon warming up to 2.5 K.

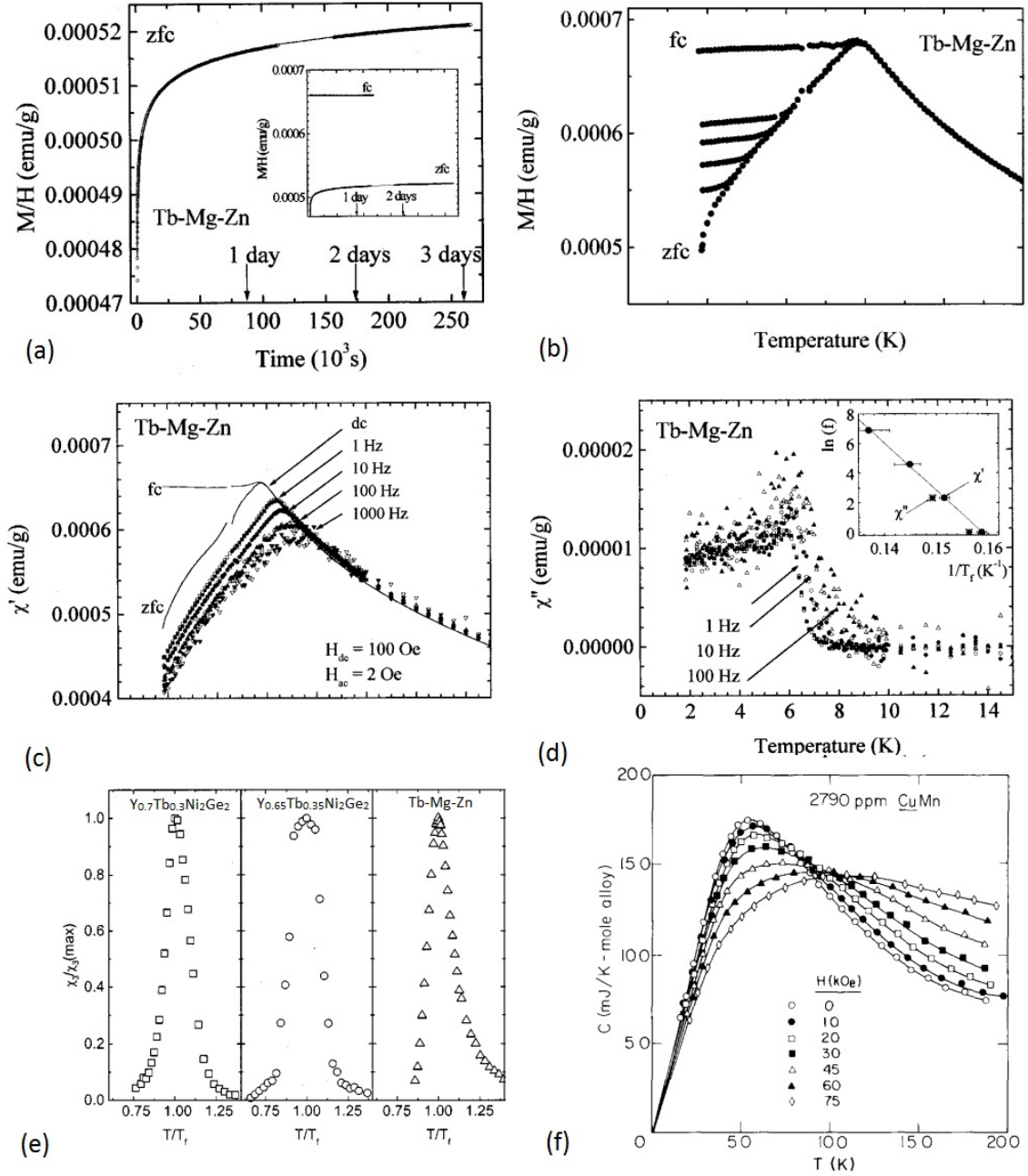


Figure 1.6 Some representative physical properties of a canonical spin glass system. (a)-(d) are data measured on Tb-Mg-Zn icosahedral quasicrystal[67] (a) Time-dependent magnetization measured in 100 Oe at 2 K. (b) Temperature-dependent magnetization measured at 25 Oe. (c)-(d) Real and imaginary part of the ac magnetic susceptibility measured at different frequencies. (e) Third order magnetization of Ising spin glass $Y_{1-x}Tb_xNi_2Ge_2$ with comparison to that of Tb-Mg-Zn quasicrystal[68]. (f) Temperature-dependent specific heat of CuMn alloy measured at different applied magnetic fields[69].

The sample was then cooled back to 2 K with applied field and measured upon warming up to 3.0 K. This is in essence a FC data from 2.5 K. It stays close to constant up to 2.5 K and then falls back onto the pure ZFC data between 2.5 K and 3.0 K. A similar procedure was also carried out for 3.0, 3.5 and 4.0 K. These data provide further evidence for spin-glass freezing and demonstrate that the thermal and magnetic field history affects the observed phenomena for a spin glass. Note that the applied magnetic fields are very small for these measurements. With increasing field, the cusp feature will be rounded and the irreversible temperature will be lower[63].

Fig. 1.6(c) and (d) show real and imaginary part of the ac magnetic susceptibility of Tb-Mg-Zn. With increasing frequency, the T_f is shifted to higher temperatures. For a long range magnetically ordered system, such shift would require several orders of magnitude higher change of measurement frequency[63]. Fig. 1.6(e) shows the normalized third order magnetic susceptibility for two different spin glass systems: Ising-like spin glass achieved by diluting Tb into YNi_2Ge_2 and the aforementioned Tb-Mg-Zn quasicrystal[68]. Both systems show sharp peaks at T_f in their third order magnetic susceptibility data, indicating spin glass states. Fig. 1.6(f) shows the temperature-dependent specific heat data for spin glass system, CuMe alloy, measured at various applied magnetic fields. At zero field, only a broad dome could be observed at a temperature that is slightly above the T_f (3.9 K). This is in contrast to long-range order phase transitions where different sharp features could be observed depending on the order of the phase transition. With increasing field, the specific heat feature for spin glass gets even broader.

CHAPTER 2. BASICS OF QUASICRYSTALS

2.1 Crystalline, non-crystalline and quasicrystal

Prior to the discovery of quasicrystals, the way scientists thought of a space being filled with atoms could be categorized into two types: Crystalline and non-crystalline. In a crystalline solid, an important concept is the existence of "unit cell", which is the building block for the crystal, in analogy to bricks for a building. The crystal is constructed by laying identical unit cells together in a periodic fashion. What is implicitly required is the existence of a translational symmetry and a unique unit cell for a specific crystal. Given a set of basis vectors, any brick in the building can be indexed by a combination of the basis vectors. Physically it means that given an origin point, all atomic positions can be predicted if the lattice is ideal and free from defects. Under the assumption of a translational symmetry, additionally, one can easily derive the rotational symmetry operations that are allowed for a crystalline solid: namely 2, 3, 4 and 6-fold rotations. More intuitively, in two dimensions, this is equivalent as saying one can only tile the floor without leaving empty space if the tile has the shape of a rectangle/triangle/square/hexagon. Other rotational symmetries are thus all called "forbidden" for periodic crystals. Due to the periodicity in the real space, the reciprocal space of a crystal is also periodic.

On the contrary, the structure of a non-crystalline solid is much less restricted. There is no building block to speak of and there is no way one can predict where atoms are given a starting point. Locally, one may still expect to observe some similar motifs (short-range order). However, strong disorder and randomness in atomic tiling leads to the loss of long-range order. (Note: an incommensurate structure is also considered as a crystalline structure. An incommensurate structure has two sublattices that have lattice parameters with an irrational

ratio. However, each of them still has the concept of unit cell and translational symmetry.) As a consequence, no sharp diffraction peak would be expected from a non-crystalline solid with no fixed atomic spacings. It is then obviously a great challenge to explain what was observed by Dan Shechtman in 1984 where sharp diffraction peaks appear for a rotational symmetry that is not 2-fold, 3-fold, 4-fold nor 6-fold, but rather, 5-fold.

This 5-fold symmetry was first observed in a rapidly quenched Al-Mn alloy[70]. The diffraction peaks that represent the reciprocal space of the compound were sharp without exhibiting spatial translational periodicity. A new rule, inflation, was discovered for this 5-fold pattern: the diffraction pattern could be expanded/contracted by a factor of τ^3 (τ is the golden mean which will be discussed more in detail later.). For comparison, in the version for a crystal, the diffraction pattern can map back onto itself by moving a multiple of basis vectors or their combinations. All these facts led to the realization that quasicrystals represent a new way of systematically filling the space with atoms. And Dan Shechtman was awarded the Nobel Prize in Chemistry in 2011 for the discovery of quasicrystals.

2.2 Types of quasicrystals

In the decades since the initial discovery, several different types of quasicrystal have been discovered. If the forbidden symmetry only exists in 2-dimensional (2D) out of the 3D real space, like a periodic packing of quasicrystalline sheets in the third dimension, it is called a 2D quasicrystal. Some of the examples are octagonal in-plane symmetry in Ce-Ni-Si and V-Ni-Si systems[71], decagonal in-plane symmetry in Al-Ni-Co[72] and Al-Fe[73] systems and dodecagonal in-plane symmetry in V-Ni and V-Ni-Si systems[74]. If the quasicrystalline concept happens in 3D, it is called a 3D quasicrystal. All known 3D quasicrystal have an icosahedral symmetry and therefore called i-QCs. If we look deeper into the structure of i-QCs, they can be divided into primitive, body-centered and face-centered, depending on the details of hyper-space that their structure can be derived from. This point will be introduced more in later sections. For our current studies, we focus on 3D quasicrystals, i-QCs.

2.3 How to describe a quasicrystal

In conventional crystallography, 5-fold symmetry is formally forbidden. The solution to the puzzle is: forbidden symmetries can be realized if the prerequisite of translational symmetry is abandoned. And in fact, sharp diffraction peaks only require the existence of well-defined order or rules for packing rather than the periodic translational order. For example, a Penrose tiling in a 2D surface does not have a translational symmetry, yet it features a reciprocal space that reproduces real quasicrystalline materials[75] (Fig. 2.1). A simpler example is given by a 1D Fibonacci sequence. Unlike amorphous solids, here, given a starting sequence, one can uniquely determine the segment at any point[76]. A quasicrystalline solid is thus a solid that is well ordered and predictable in terms of atomic arrangement but without translational symmetry. A quasicrystal is constructed by two or more motifs, or structural units, arranged in a quasiperiodic way. This is in contrast to a conventional crystal where a single building block is arranged periodically throughout the whole space. It is an incommensurate lattice with forbidden rotational symmetry.

For an incommensurate structure to exist, there are many available irrational numbers. But for a quasicrystal to form, only a special class of irrational numbers are allowed, known as algebraic numbers[77]. That means, the irrational number must be a solution to a polynomial equation with integer coefficients. For example the golden mean that we are talking about is a root for the polynomial equation: $\tau^2 - \tau - 1 = 0$

The rotational symmetry will put constraints on the allowed quasiperiodicity. In Fig. 2.2, parallel lines with periodic spacing a are drawn parallel to the edges of a hexagon (Fig. 2.2(a)) and a pentagon (Fig. 2.2(b)). In the case of a hexagon, the intervals between intersection points by set 1&3 and by set 2&3 have the same length. This equivalence in length results from the fact that the whole space can be filled by a periodic stacking of hexagons. On the other hand, if we look at the pentagon, the intervals have different lengths. The ratio between these two segments is exactly the golden ratio. A more rigorous mathematical derivation shows that the quasiperiodic spacing for a pentagonal symmetry must be related to τ in order to make sure the spacing between intersecting point does not go non-physically small[77].

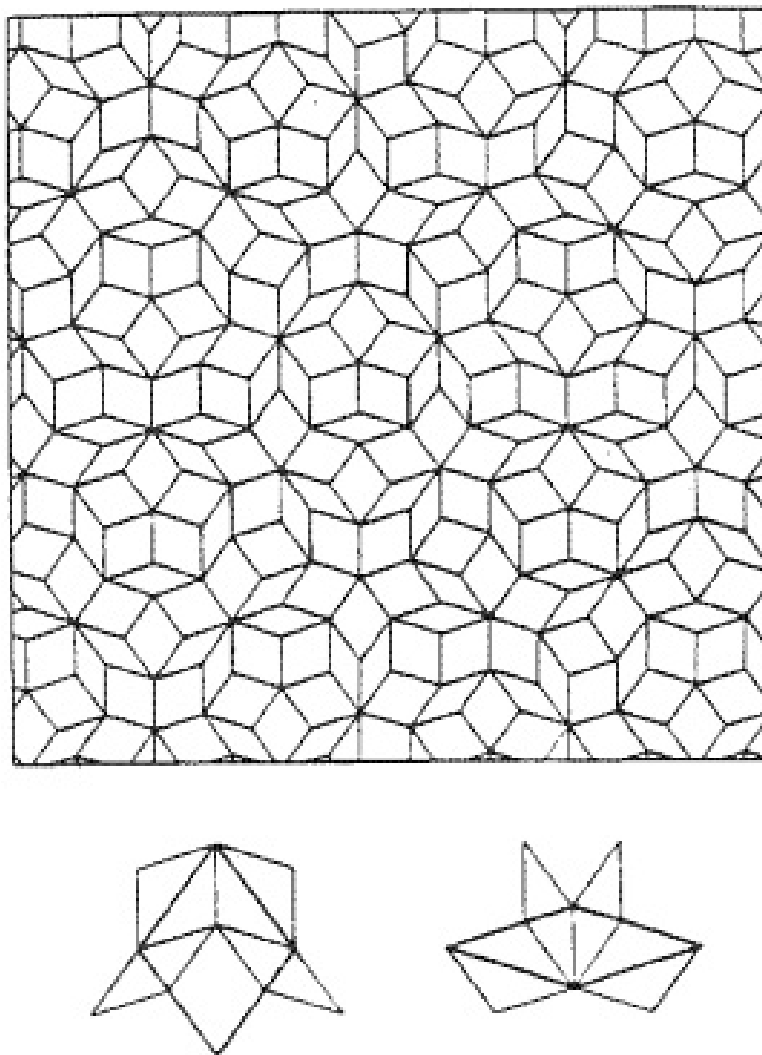


Figure 2.1 Top: Penrose tiling. Bottom: A combination of motifs that if replaced in the original Penrose tiling, will reproduce the Penrose tiling. This illustrates the inflation/deflation rules followed by quasicrystals.[76]

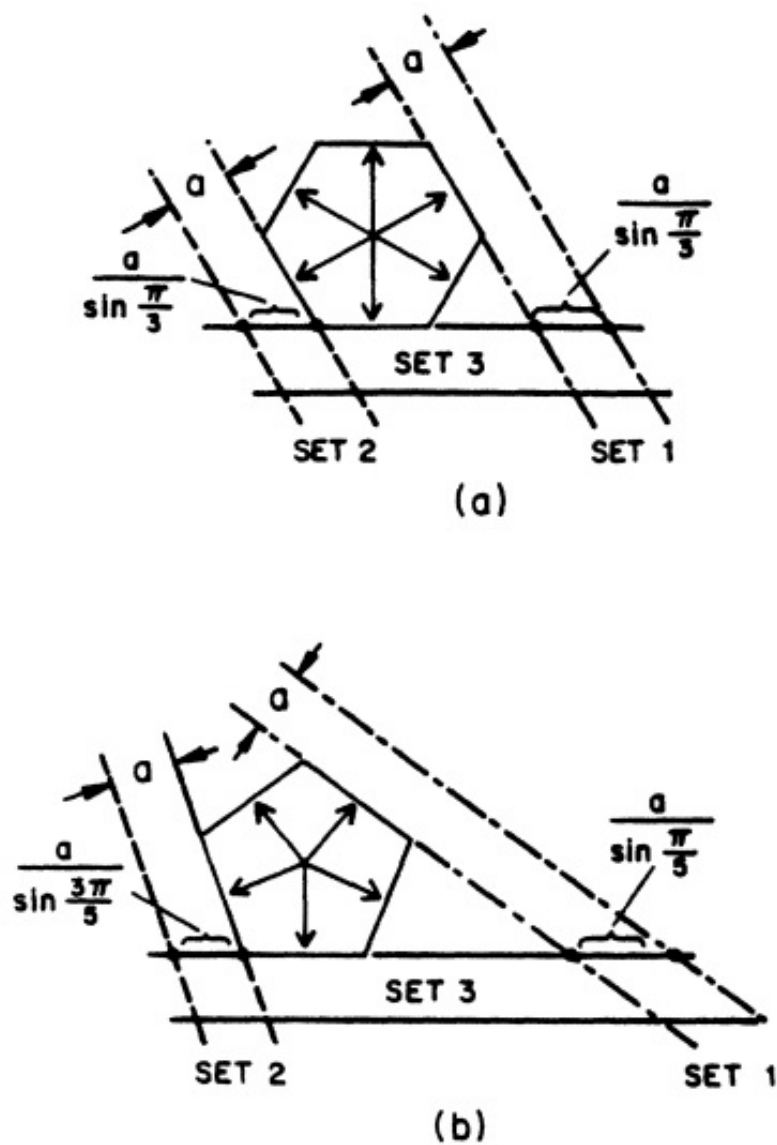


Figure 2.2 Parallel lines with periodic spacing a are drawn parallel to the edges of a (a) hexagon and (b) pentagon.[77].

The simplest incommensurate, aperiodic structure is a Fibonacci sequence. To describe a Fibonacci sequence, one needs to use at least two parameters to denote the two fundamental units. Given the real space arrangement of a Fibonacci sequence, it can be shown that the basis vectors in reciprocal space can be written as[76]:

$$Q_{hh'} = \frac{2\pi\tau^2}{\tau^2 + 1}(h + h'/\tau) \quad (2.1)$$

where h and h' are two integer parameters. And the amplitude of each Fourier component can be written as:

$$F_{h,h'} = \frac{\sin(\frac{\pi\tau}{\tau^2+1}(\tau h' - h))}{(\frac{\pi\tau}{\tau^2+1}(\tau h' - h))} \exp(i\pi \frac{\tau - 2}{\tau + 2}(\tau h' - h)) \quad (2.2)$$

Even though long range translational symmetry is missing, it is clear that the reciprocal space, or diffraction peaks, for a Fibonacci sequence are well-defined, sharp, peaks that can be described by two sets of numbers. Worth noting, the intensity of each diffraction peak is not a simple function of Q (as with traditional crystals), but rather also depends on the ratio of h/h' (Eq.2.2). The most intense peak occurs when h/h' is close to τ . This is reminiscent of what was observed in quasicrystals where the diffraction peaks are densely spaced while neighboring peaks in reciprocal space differ significantly in intensity.

If we use the Miller integer indices to label the atomic orientation or atomic positions, a smart, and now common, way is to invoke a higher dimension and view the real space as a projection space from a hyperspace with more dimensions. For example, if we have a square lattice with an edge length of a, (Fig. 2.3), drawing a line that has a slope of the golden mean and project lattice points onto the line, we will get a Fibonacci sequence. In this manner, the projected point can be traced back to two integer indices that index the original point in the 2D square lattice. Of course, in the real space, the atomic size will determine a lower limit of how close atoms can be. To avoid unphysical results, we can either limit the region where points in the square lattice are allowed to project, or we can define a 'strength of influence' that is represented by a line segment on each lattice point in the square lattice. Whenever the segment crosses the Q_{par} , it will be an atom in the real space.

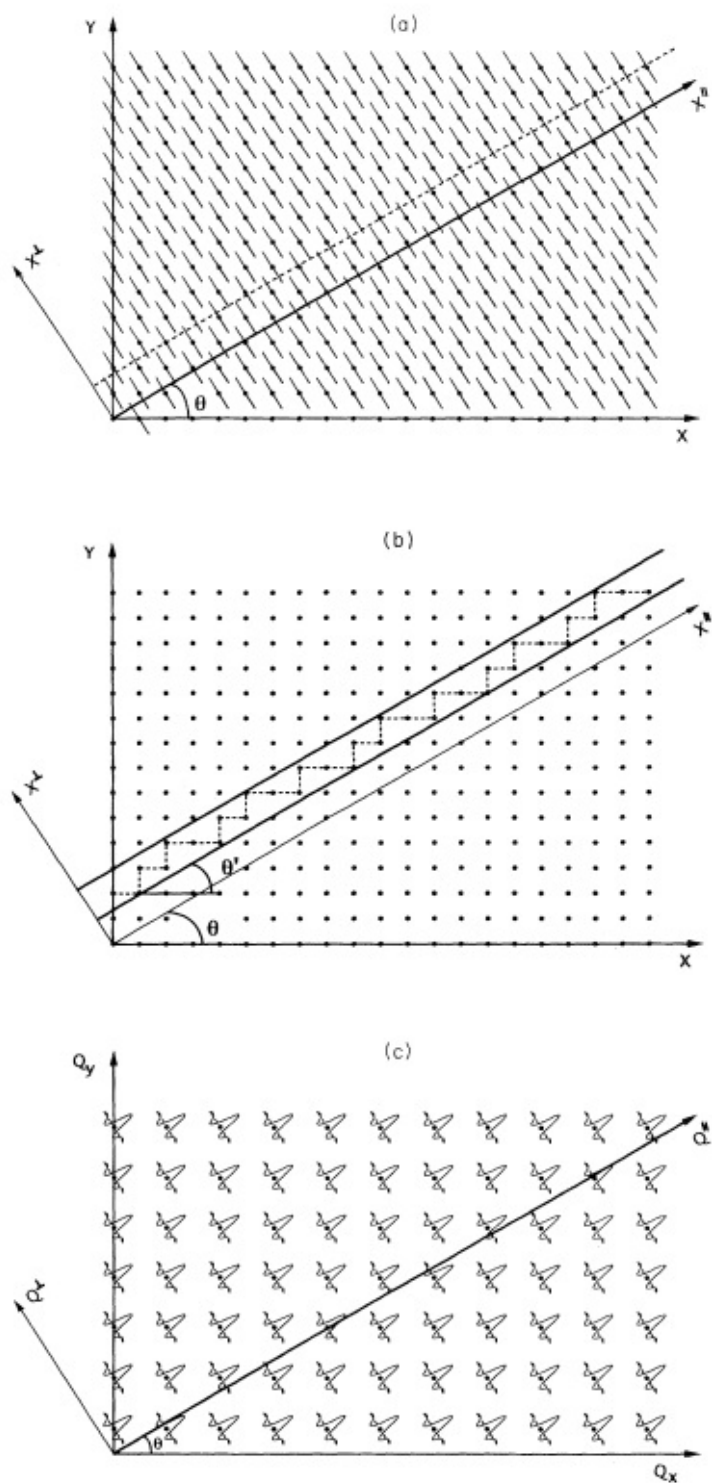


Figure 2.3 Cut and projection method to construct a quasiperiodic order from a higher dimension[78].

In a similar fashion, we can construct the whole 3D atomic tiling by invoking a 6D hyperspace for the i-QCs. This, in principle, is the same as using the vectors point to six five-fold axis. However, to solve a 3D quasicrystal structure, it involves much more complicated expertises. Since it is not the focus of current studies, we are not going into details. More information and examples can be found in Refs.[76; 79; 80]

In Fig. 2.3, the axis where cuts are projected onto, $x^{\parallel}$, can be understood as the axis in real space. On this axis, if the arrangement of atoms were shifted from their designated positions, it is equivalent as dislocations in a conventional crystal. On the other hand, the axis that is perpendicular to $x^{\parallel}$, $x^{\perp}$, is called the phase space. The reason is that if the atom in the hyperspace distorts along the phase space, it will cause the project and cut disrupted which result in a new start of a Fibonacci sequence. This instead of a distortion, is closer to a phase shift in tiling in the real space. And this phase space is what quasicrystals have in addition to a conventional crystal as a "benefit" from more degrees of freedom in describing its structure. Additionally, in a conventional crystalline material, a periodic vibration of atoms in the real space is called a phonon. If vibrations happen in the hyperspace, specifically, in the perpendicular space, that will cause a tiling error/defects in real space. This is called a "phason". Physically, phasons will cause shift/broadening of diffraction peaks that increase with Q_{perp} and independent of Q_{par} .

2.4 Approximant phase

A quasicrystal approximant phase is very similar to a real quasicrystal in terms of their local motifs. One can construct a quasicrystal approximant phase by taking a quasicrystalline cluster and locate the clusters onto a regular Bravais lattice. Thus by definition, the approximant phases have periodic structures that satisfy translational symmetry. Due to the similarities in structure that they share with a real quasicrystal, they serve a very important role for the understanding of how quasicrystal is constructed and why translational symmetry is missing under certain condition of synthesis. The order of an approximant phase is a scale that describes how close it is to a real quasicrystal. It is conventionally expressed in a ratio of p/q , where the closer the number to the golden mean, the closer it is to a real quasicrystal. p and q are chosen

as neighboring numbers in a Fibonacci sequence. The RCd_6 , quasicrystal approximant phase, as will be discussed in Chapter 4, is a $1/1$ approximant phase.

When projecting from the hypercubic lattice to the real 3D space, we will get oblate and prolate rhombohedras. These polyhedrons are the building blocks of an quasicrystal. The edge lengths of the rhombohedras are in analogous to a unit cell length in a traditional crystal with translational symmetry. This edge length, a_R , is therefore called the quasilattice constant. Relating a_R to the lattice parameter of a quasicrystal approximant phase, $a_{q/p}$, we have[78]:

$$a_{q/p} = \frac{2(p + q\tau)a_R}{(2 + \tau)^{1/2}} \quad (2.3)$$

2.5 Ways to prepare quasicrystalline samples

The way quasicrystalline grains grow remains an interesting and open subject. Many models have been put forward[76]. Recently, the growth of decagonal Al-Ni-Co was observed in-situ by high resolution transmission electron microscopy, which suggests phason relaxation plays an important role in quasicrystal's crystallization (see Ref. [81] and references therein). Without understanding the mechanism, quasicrystals have been experimentally discovered and made over the years. The first quasicrystalline sample studied by Dan Shechtman in 1984[70] was made by fast cooling Al-Mn. The fast cooling or rapid solidification of liquid where the cooling rates are in the order of 10^6 K/s can be achieved by using a melt spinning apparatus. Liquid is ejected onto a cold, fast spinning wheel, after which it is rapidly solidified into a solid ribbon. A fast quench does not allow for a careful nucleation of a high temperature stable phase. Therefore, it is often used to produce metallic glasses and metastable phases. In the initial stage of quasicrystal study, quasicrystalline materials produced this way usually have sizes in micron range and are mixed with other phases.

Large single crystals of quasicrystal can also be grown using high-temperature solution growth technique, for example, in the cases of decagonal quasicrystal Al-Ni-Co[82] and icosahedral quasicrystal R -Mg-Zn[83]. These quasicrystals are thought to be thermodynamically stable phases and allow for more physical property measurements, for e.g. powder xray diffraction, neutron diffraction and anisotropic magnetization and transport.

2.6 Physical properties of quasicrystals

One of the most important milestones in condensed matter physics is the concept of reciprocal space and Brillouin zone. However, this key concept fails when one looks at a quasicrystal where no translational symmetry is present. The definition of a Brillouin zone is very difficult for a quasicrystal where, formally, one grain of quasicrystal, even if it is a cubic centimeter in size, is one unit cell. Band structure and density of states are thus usually calculated by looking at high order quasicrystal approximant phases which still contain thousands of atoms[84; 85; 86]. These calculations suggest a small density of states or a pseudogap at the Fermi energy. Such a pseudogap was experimentally observed[87; 88; 89]. In transport measurements, the resistivity along the quasicrystalline, or in other words, quasiperiodic direction can often be characterized as a bad metal or close to a metal insulator transition. At room temperature, the resistivity is of the order of $\text{m}\Omega \text{ cm}$ which is about three orders of magnitude higher than that for a good metal[76]. The resistivity is very weakly temperature-dependent, increasing or decreasing with temperature only slightly, often, non-monotonically. Typical resistivity data can be found, for example, for Al-Pd-Mn[90; 91], Al-Ni-Co[82], *R*-Mg-Zn[67] and Yb-Cd[92]. These resistivity data are consistent with a low density of states at the Fermi energy.

Despite theoretical predications[93; 94; 95; 96], long range magnetic ordering has not yet been observed in any known quasicrystalline systems[97]. All magnetic moment bearing quasicrystals exhibit spin glass behavior[67; 98; 99; 100].

As mentioned above, the approximant phase is structurally very similar to a real quasicrystal. Interestingly, long range magnetic order does exist in approximant phases, for instance, antiferromagnetic RCd_6 [101; 102; 103] and ferromagnetic Gd-Au-Si(Ge) [104; 105]. However, as will be discussed in the next chapter, the corresponding quasicrystal for RCd_6 does not have a long range magnetic order, and the corresponding quasicrystal phase for Gd-Au-Si is yet to be found. It is an interesting subject to understand the evolution of magnetic correlations from a quasicrystal approximant phase to a quasicrystal. This might help to unveil the missing long range magnetic order in the quasicrystals found so far.

CHAPTER 3. EXPERIMENTAL TECHNIQUES

3.1 Crystal growth

For most condensed matter physics experiments, being able to make the condensed matter being studied is the first and necessary step. Material synthesis, therefore, is a vital starting point. For the studies presented in this thesis, bulk, single crystals were prepared and characterized. Single crystals can preserve the anisotropic information about the magnetic and electronic properties of the material. In addition, as compared to polycrystalline samples, single crystals reduce effects associated with grain boundaries and defects that are concomitants of microscopic grains found in polycrystals. Hence, high quality single crystals are important for detailed studies of intrinsic, anisotropic properties of a material. Polycrystals, however, do have their advantages in some cases when a random crystalline orientation is needed. For example: (i) the random orientation in powder x-ray diffraction makes it easier to observe all possible diffraction peaks, and (ii) the polycrystalline averaged temperature-dependent magnetization is closer to an ideal Curie-Weiss behavior even in the presence of a large CEF splitting[106]. It is, though, much easier to make a polycrystalline sample out of a single crystal than the reverse.

Single crystalline samples can be grown by many different techniques. Starting stoichiometry and temperature are controlled to achieve a slow solidification with or without a solution. Czochralski, Bridgeman and floating zone refining methods, for example are commonly used to grow congruently melting compounds. The high-temperature solution technique is the method that was used to prepare samples in this thesis. Its principle is analogous to crystallizing salt out of salty water by cooling. The solubility of one compound in the liquid mixture is a function of temperature. By changing the temperature of a given mixture (fixed stoichiometry),

the desired phase can therefore be crystallized out of the solution. The advantage of the high-temperature solution growth technique, as compared to other aforementioned techniques, is that it requires relatively simple equipment and it can work for either congruent melting or incongruent melting materials. In the following, the high-temperature solution growth technique will be explained in more detail.

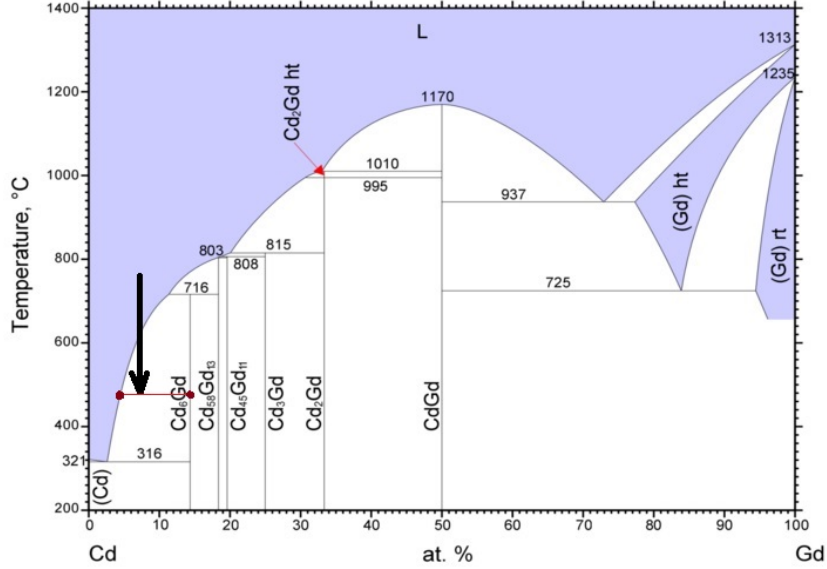


Figure 3.1 Gd-Cd binary phase diagram from ASM alloy phase diagram[107]. Arrow indicates the starting stoichiometry and temperature profile. Brown dots indicate the liquid and solid compositions at the temperature of the red line.

First, I will introduce the principle of the high-temperature solution growth technique from the perspective of a binary phase diagram[108; 109]. The binary phase diagram of Gd-Cd, as it was presented before my research efforts, is shown in Fig. 3.1 and can be used as an example. For the sake of this discussion, we will, for the time being, assume that the phase diagram shown in Fig. 3.1 is accurate. As we will discuss in the next chapter, for the more Cd-rich part of this diagram, this is not actually the case. Blue indicates a single phase regime and white indicates a two-phase regime. The large blue area on the top/left of the phase diagram suggests a homogeneous liquid state. The boundary between the blue, homogeneous liquid region, and the white, two-phase region, is called the liquidus line. A point on the liquidus

line indicates the lowest temperature to have a single phase liquid of that stoichiometry, below which temperature a solid phase should start to precipitate and the melt composition starts to change. For the congruent melting compound, GdCd , melting the solid will result in a liquid with the same chemical composition (GdCd). As mentioned above, Czochralski, Bridgeman and floating zone refining methods often work well for congruent melting compounds since cooling the liquid will yield a solid phase with the same chemical composition as well. For an incongruent melting compound, for example GdCd_6 , cooling a liquid with a composition of GdCd_6 to room temperature will yield multiple phases, including $\text{Gd}_{13}\text{Cd}_{58}$, GdCd_6 and Cd .

To grow a single phase GdCd_6 , one has to start with a more Cd rich composition. When the starting stoichiometry is $\text{Gd}:\text{Cd}=7:93$, a homogeneous, single phase, liquid state can be reached above approximately $600\text{ }^\circ\text{C}$ (Note that elemental Cd boils at $\sim 767\text{ }^\circ\text{C}$. Even with the addition of Gd, caution should be taken to prevent Cd from boiling and thereafter causing an explosion of the sealed ampoule.). Upon cooling, GdCd_6 will be crystallized (precipitates) out from the solution according to its exposed liquidus line. At the temperature of the red line, the equilibrium state consists of two phases as suggested by the white color. Two brown dots at the ends of the red line represent these two phase: GdCd_6 and a more Cd-rich liquid. The relative amount of each can be estimated based on the lever rule[110]. Further cooling will lead to further crystal growth until below $\sim 316\text{ }^\circ\text{C}$, everything solidifies at the eutectic temperature and there is a eutectic decomposition of the solid into Cd and GdCd_6 . To obtain clean single crystals of GdCd_6 in an easier manner, it is then necessary to separate the crystal from the liquid above $316\text{ }^\circ\text{C}$. This can be achieved in a centrifuge where liquid is filtered through a frit/strainer and crystals remain[111]. Of course, in some cases, single crystals can also be obtained after everything solidifies, i.e. when the non-crystalline parts can be etched or washed away (See, for example, KFe_2As_2 single crystal growth with KAs solution. Ethanol can be used to rinse away the non-crystalline materials[112]).

Existing phase diagrams are often good starting points when designing the growth profile (the initial stoichiometry of the melt, temperature profiles and cooling rates). However, for most of the intermetallic compounds with three or more elements, phase diagrams are commonly not available. In such cases, trials and errors, based on knowledge of binary phase diagrams and

other similar, known systems, are often needed to obtain the target compound. Growing crystals from a solution that contains only elements contained in the target crystal itself is commonly called a self-flux. Here, flux has the same meaning as solution. Discussions on choices of flux and solution growth technique can be found in Ref. [83; 108; 111].

After determining the starting stoichiometry, one needs to choose the right container for the melt. For many of the materials studied here, alumina crucibles are stable enough to resist any reaction with the melt below 1200 °C. Crucibles that were made of Ta were also used when some of the starting elements were thought likely to react with alumina, for example, Mg. In addition, Ta can be a good protective layer to protect the outer silica jacket from being attacked by the material vapor (the silica jacket with back filled Ar gas serves as an outer, protective environment against sample and Ta oxidation.). K, for example, will react with silica and thus needs to be contained in a sealed Ta tube (or other sealed container that does not react with it). In Fig. 3.2(c), a Matryoshka-doll-like ampoule that was used to grow $K_2Cr_3As_3$ is shown[113]. Alumina can hold FeAs solution (which Ta tube fails to hold) whereas a Ta tube prevents the K vapor from attacking silica ampoule. Finally, the silica ampoule protects the Ta tube from getting oxidized.

The final step in our standard implementation of the solution growth technique is the separation of the liquid phase from the crystallized solid phase that are both residing at the bottom, or growth, crucible. Traditionally, a reversed crucible filled with silica wool was used to filter the liquid. At the desired temperature, the whole growth ampoule as shown in Fig. 3.2(a) is quickly flipped and placed inside of a centrifuge where the liquid and the solid is separated by filtering. During "the spin", the liquid phase will be spun to the so called "catch crucible" and the solid phase will be left outside of the pack of silica wool. The drawback of using silica wool is that the spun material will inevitably solidify with silica contamination when it gets cold. This makes the re-use of the spun material impossible. Recent development in filtering set-up involves alumina frit with drilled holes[111] (see Fig. 3.2(b)). This frit-disc crucible assembly, also called a "Canfield-Crucible-Set" or CCS, solves the contamination problem of the material due to silica wool. It also allows for a more quantitative analysis of the decanted, liquid phase. Being able to re-use the material in this clean manner can also reduce the cost of material

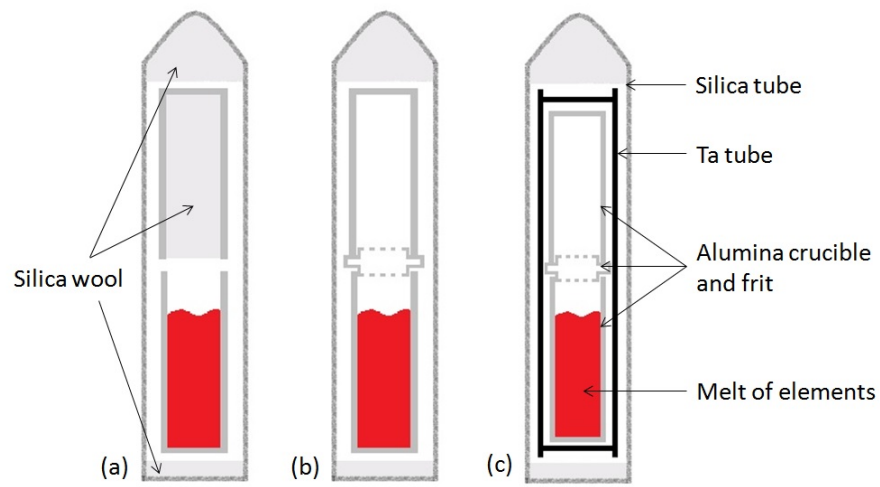


Figure 3.2 Schematics of growth ampoules. Growth and catch alumina crucibles are sealed in a silica tube with (a) silica wool as the filtering material (e.g. for synthesizing BaFe_2As_2 [114]). and (b) alumina frit as a filter (e.g. for synthesizing $\text{YbFe}_2\text{Zn}_{20}$ [115]). (c) An additional sealed Ta tube is added in between the frit-disc alumina crucible set and the silica tube to prevent volatile elements from attacking the silica tube (e.g. for synthesizing $\text{K}_2\text{Cr}_3\text{As}_3$ [113]).

exploration. It is also helpful when re-using the material is necessary, for instance, when using expensive elements as part of the solution. One drawback to the frit-disc is that if the crystals are plate-like and block the holes in the frit, the solution will not be easily separated from the crystal. Silica wool as a filter, in this case, can provide a better separation since it has more porous filtering availabilities.

Going back to the growth of single crystalline GdCd_6 , experimentally, the starting elements were packed in an alumina crucible with a molar ratio $\text{Gd}:\text{Cd} = 7:93$. The starting material and crucible sets were then sealed in a silica ampoule under partial argon atmosphere. Considering the high vapor pressure of Cd, the whole ampoule was heated up to 700°C , dwelt there for 10 hours to achieve a homogeneous liquid state. It was then cooled to 510°C over ~ 40 hours. At 510°C , the ampoule was quickly transferred from the furnace to the centrifuge where crystal and remaining liquid was separated. This process will be discussed again in the following chapter when discussing the discovery of *i-R*-Cd quasicrystals. And detailed growth procedures will be presented in each subsequent chapter.

3.2 Characterization

3.2.1 Powder x-ray diffraction

Powder x-ray diffraction data were measured at room temperature using a Rigaku Miniflex powder diffractometer (Cu K_α). Single crystals were ground into powders. The ground powder was then spread onto a single crystalline Si, zero background sample holder with a thin layer of vacuum grease on top. Typical data were recorded every 0.02° with 1-3 seconds data collecting time at each angle. Longer collecting time was sometimes used to acquire a better signal to noise ratio. For air sensitive samples, the powder x-ray diffraction was performed in a Rigaku Miniflex powder diffractometer that is located in a N_2 glove box. Powder diffraction data were analysed using the General Structure Analysis System (GSAS) software[116; 117]. The refined lattice parameters have a typical instrumental error bar of 0.2%.

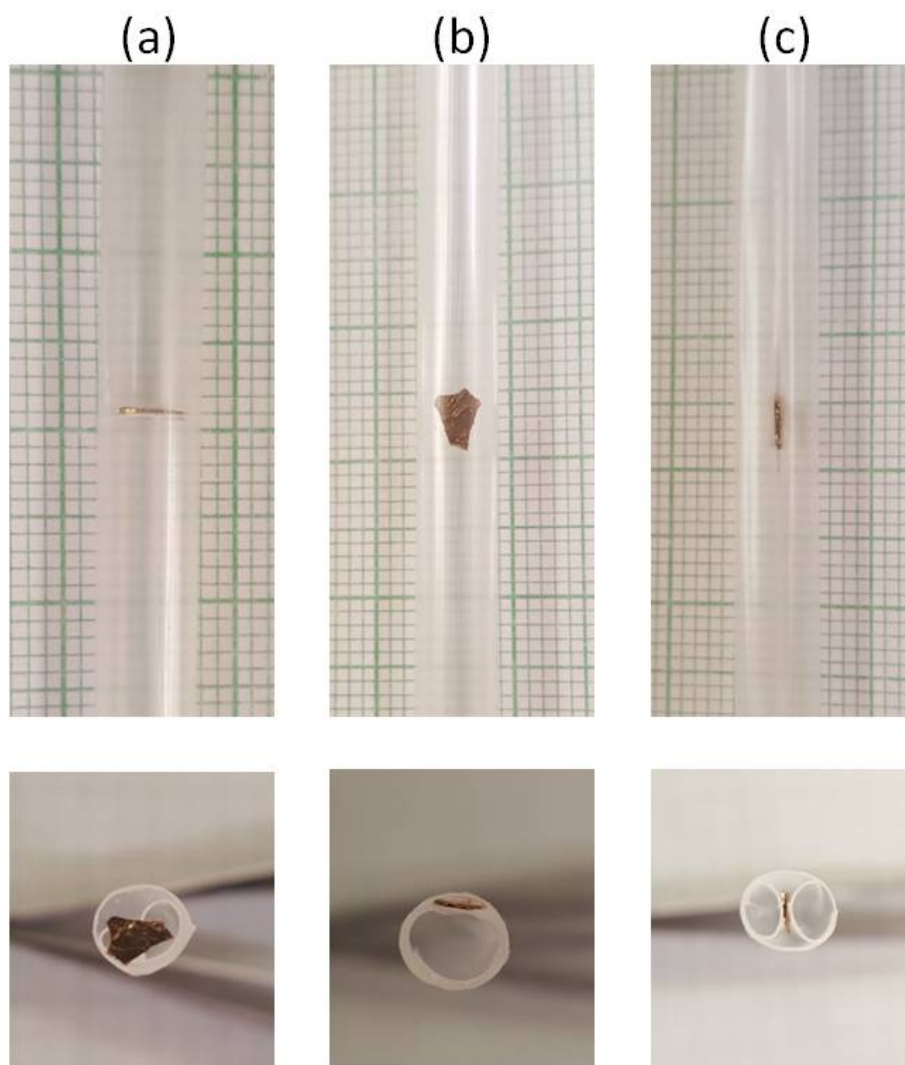


Figure 3.3 Side and top views for some common sample mounting geometries, using transparent drinking straws with (a) sample clamped by two halved straws from top and bottom; (b) sample held in between an inner and an outer straw on the side; and (c) sample held in between two halved straws in the center.

3.2.2 Magnetization

Magnetization measurements were performed in Quantum Design (QD) Magnetic Property Measurement System (MPMS) with superconducting quantum interference device (SQUID) magnetometer over the temperature range of 1.8 - 300 K and field range of 55 kOe (MPMS-5) or 70 kOe (MPMS-7). Samples were mounted by using transparent plastic straws in desired orientation. For plate-like samples, the most commonly used configuration to measure anisotropic magnetization value are shown in Fig. 3.3(a) and (b). If the sample is large and hard enough, the method in Fig. 3.3(c) can sometimes be used, which is advantageous to the configuration shown in (b) due to the fact that the sample is closer to the central axial of the pick-up coil. Deviation from the central axis will lead to a slightly larger, inferred magnetization value due to fitting error[118]. Both (b) and (c) have essentially zero magnetic background signal. In Fig. 3.3(a), since the upper and lower straws leave a gap in the middle for the sample, there will be a small paramagnetic background signal of an order of 10^{-5} emu at 2 K and 50 kOe per 1 mm gap. dc magnetization data down to 500 mK were measured at QD (Japan) using an iHelium3 system. And the ACMS option of a QD Physical Property Measurement System (PPMS) was used to measure ac magnetic susceptibility or dc magnetization up to 140 kOe.

Angular-dependent magnetization was measured using a sample rotating platform with an angular resolution of 0.1° in a QD MPMS. Detailed set-up of the rotator is shown Fig. 3.4. The top clip B (Fig. 3.4(a)) is tightened to a MPMS motor which performs a vertical transport motion to execute the dc magnetization measurement. The top clip A (Fig. 3.4(a)) is tightened to another motor that performs a rotational motion with respect to clip B. The rotation of clip A will lead to to a translational motion of part C via a screw, as shown in Fig. 3.4(d). Part C pulls on the wire (part D shown in Fig. 3.4(e)) which is connected to the bottom spring (part F) of the rod (Fig. 3.4(f)). The wire winds around a pulley/sample-stage assembly (part E) and rotates part E when pulled. In Fig. 3.4(d), two different angles of the sample stage are shown. On the upper panel, the sample-plate that is attached to the stage would rotate with changing in-plane magnetic field orientation. If the sample was to be mounted on the surface of the sample stage shown in the lower panel, the magnetic field orientation could then be rotated

from in-plane to out-of-plane. Samples were glued to the sample stage using the Permabond 910 metal bond, which can be removed by nitromethane. The magnetic background signal of the sample stage is weakly diamagnetic. At 2 K, the magnetization value may be equal to or smaller than the order of 10^{-4} emu at 50 kOe (due to a bad regression fit, the absolute value could not be accurately determined).

3.2.3 Specific heat

Specific heat measurements were carried out in a QD PPMS using a relaxation method[119]. The sample together with the sample platform were heated up by a heat-pulse of a known size and then allowed to cool. The thermal response as reflected by its temperature was recorded and fitted to the relaxation model to determine the heat capacity of the sample plus the sample platform. The background signal from sample platform, measured as an addenda prior to the sample measurement, was subtracted to obtain the heat capacity of the sample. In most of the cases, specific heat data were collected down to 2 K. A ^3He option or, in some cases, a dilution refrigerator option, was used in order to measure specific heat down to 500 mK or 50 mK. Apiezon N grease was used to attach sample to the sample puck. Typical sample mass was ~ 5 mg.

3.2.4 Resistivity

Resistivity data were measured using a standard 4-probe technique. Both DuPont 4929N silver paint and Epotek-H20E silver epoxy were used to attach Pt wires onto polished bar-shape samples. Epotek-H20E silver epoxy needs to be cured at 120°C for 20 minutes. It generally provides a strong mechanical bond between the sample and the contact leads. Silver paint only needs to be air dried for approximately 5-10 minutes. It does not provide as strong of a mechanical bond as Epotek-H20E silver epoxy. However, it is sometimes favorable when the sample is sensitive to air/heat or fixed in position. Contact resistance can be reduced by running an electric current through the contacts. Slowly ramping up the electric current from sub-mA to eventually 10-100 mA range usually works well without damaging the contacts. Common contact resistances are around 1-2 Ω . Resistance data were collected using a QD

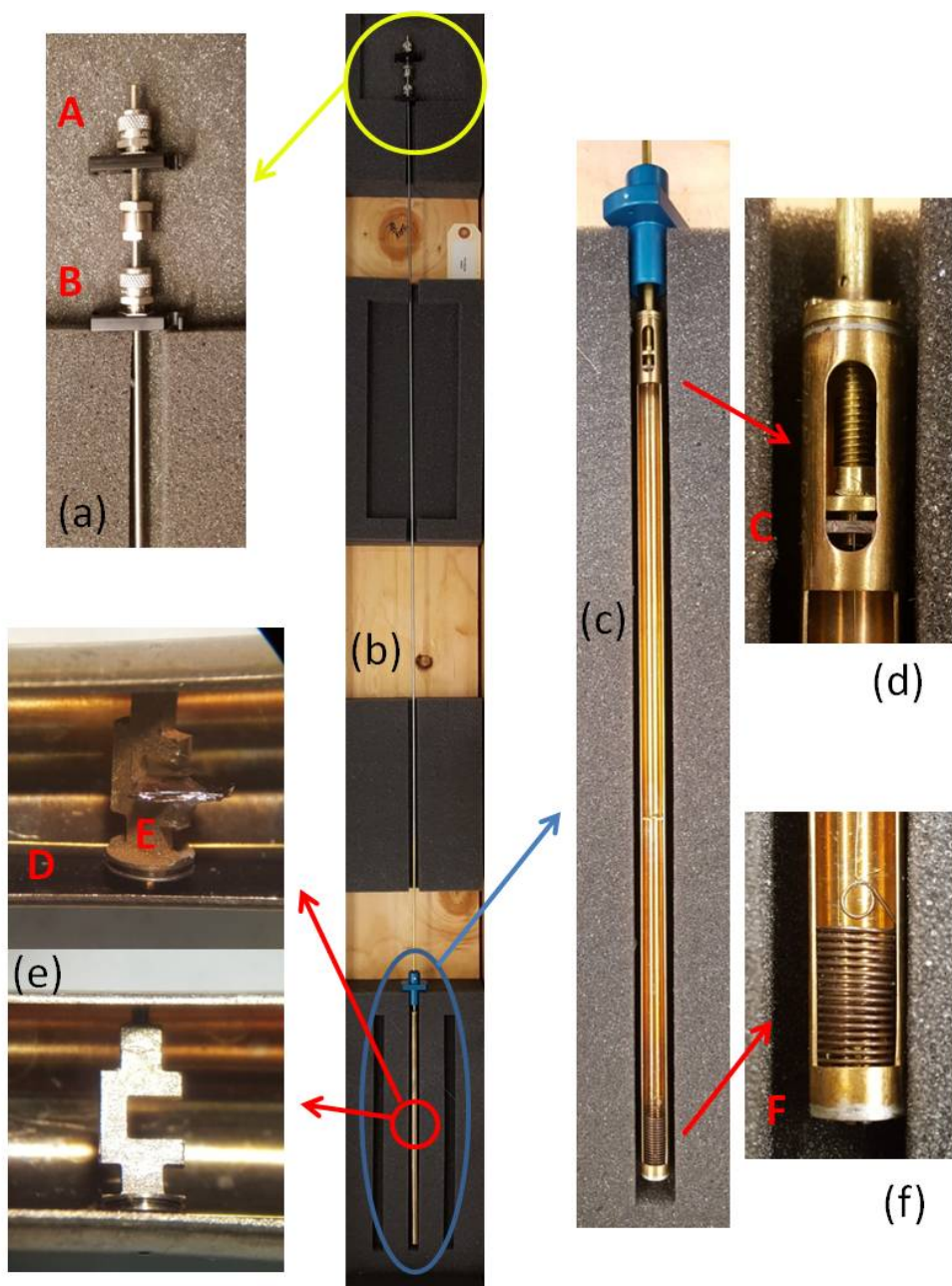


Figure 3.4 Overall and expanded views on the sample rotator rod for magnetization measurements. (a) and (c) are zoom-ins for the top and the bottom of the whole sample rod shown in (b). (d) shows the top screw in the sample space. (e) shows the sample stage in two different angles, with the upper panel showing a sample glued onto the sample stage. (f) shows the bottom spring with the wire attached. Capital red letters represent parts that are described in the text.

PPMS (1.8-300 K, maximum field 90 kOe or 140 kOe, $f = 17$ Hz, $I = 1-3$ mA) or a Linear Research (LR), LR-700 ac resistance bridge ($f=16$ Hz, $I=1-3$ mA). Similar with specific heat measurements, a ^3He or a dilution refrigerator option in PPMS was used to achieve lower temperatures. To prevent sample heating, a much lower electric current was used: typically ~ 0.1 mA for ^3He temperature range (down to 500 mK) and ~ 0.01 mA for dilution refrigerator temperature range (down to 50 mK). An ETO option in PPMS was used to measure resistivity in a dilution refrigerator.

CHAPTER 4. DISCOVERY AND PHYSICAL PROPERTIES OF i - R -Cd ($R = \text{Y, Gd-Tm}$) QUASICRYSTALS

As introduced previously, quasicrystals are intermetallic compounds that manifest aperiodic, rather than periodic, long-range positional order with rotational symmetries (for example, five-fold, ten-fold) that are forbidden for conventional crystals. Forbidden rotational symmetries are achieved in quasicrystals at the expense of translational symmetry, which is implicitly required in conventional crystallography. Since the initial discovery of quasicrystals[70], the search for new quasicrystalline systems, especially thermodynamically stable ones, as well as understanding of their structural and physical properties has been of keen interest to the solid state physics and chemistry communities[76].

One of the interests is to study the magnetic interactions of local moments on an aperiodic lattice. Despite several theoretical predictions[93; 94; 95], no long range magnetic ordering has, as of yet, been discovered in moment-bearing quasicrystals[97]. So far, all of the known quasicrystals with moment-bearing elements exhibit frustration and spin-glass-like behaviour at low temperatures[120; 121]. In the ternary i - R -Mg-Zn and i - R -Mg-Cd icosahedral quasicrystals, for example, d.c.- and a.c.-susceptibility measurements demonstrate spin-glass behaviour[67; 98; 122]. In addition, neutron diffraction measurements on both i - R -Mg-Zn and i - R -Mg-Cd clearly show the presence of only short-range magnetic correlations at low temperatures[123]. Interestingly, the absence of long-range magnetic order also extended to the known crystalline approximant phases as well[91; 124; 125; 126; 127]. Crystalline approximants are periodic crystals with compositions and unit-cell atomic decorations (for example, atomic clusters) that are closely related to their respective quasicrystalline phases[78]. Recently, two exceptions have been identified: ferromagnetic Gd-Au-Si(Ge)[104] and antiferromagnetic (AFM) RCd_6 [101; 102; 103; 128; 129]. The antiferromagnetic RCd_6 compounds, in particular, have attracted

great attention. On one hand, they bring up the possibility of related quasicrystalline phases that could have long-range magnetic ordering. On the other hand, binary compounds, in general, are valuable for studying the chemical and physical properties due to their relative compositional simplicity. Examples of stable binary icosahedral quasicrystals are relatively rare, and, before this work, there were no known examples featuring localized magnetic moments. A moment-bearing binary quasicrystal would represent an ideal model system for attaining a deeper understanding of the nature of magnetic interactions in aperiodic lattices. The RCd_6 crystalline phases, which are isostructural to the approximant ($YbCd_6$) of the non-moment-bearing binary i- $Yb-Cd_{5.7}$ icosahedral phase, have been found to manifest a long-range AFM order at low temperatures based on both thermodynamic and scattering measurements[101; 102; 128]. The observation of AFM order in the RCd_6 approximants, therefore, provided a strong impetus to search for and study a related, moment-bearing, binary icosahedral phase to better understand, or place constraints on, possibilities for the existence of AFM order on an aperiodic lattice[93]. In this chapter, I am going to present the discovery and physical properties of a family of seven rare earth icosahedral binary quasicrystals, i- R -Cd ($R = Y, Gd-Tm$), six of which bear localized magnetic moments. The contents of this chapter are a combination of two publications on the discovery[130] and detailed characterization of i- R -Cd[100].

4.1 Discovery and identification of i- R -Cd quasicrystal

Following the previous proposal that, like icosahedral $Sc_{12}Zn_{88}$ [131], binary quasicrystalline phases may well exist nearby known crystalline approximants, perhaps as incongruent melting compounds with very limited liquidus surfaces, offering very limited ranges of composition/temperature for primary solidification, the new i- R -Cd icosahedral family ($R = Y, Gd-Tm$) was discovered by using the high-temperature solution growth technique[83; 109] as an exploratory synthetic tool.

As explained in Chapter 3, the quasicrystal approximant phase, $GdCd_6$, can be grown from the wide, exposed, liquidus line that spans from $\sim 12\%$ to $\sim 3\%$ at. Gd (Fig. 3.1). In order to verify and/or explore the accuracy of the reported liquidus line, especially in the low-temperature regime, the initial decanting temperature was set to be $340^\circ C$ as opposed to 510

°C that was described in Chapter 3. This decanting temperature is very close to the eutectic temperature, which then allows us to explore potential deep peritectics associated with this liquidus line. In Fig. 4.1, the obtained large single crystal of GdCd_6 is shown on millimeter grid paper. However, in contrast to the known phase diagram, where a single phase GdCd_6 is expected for this growth profile, a conspicuous secondary phase grew on top of the GdCd_6 phase with pentagonal facets clearly visible. It worth noting that since the secondary phase grows on the surface of GdCd_6 , it grows at a relatively lower temperature than GdCd_6 .

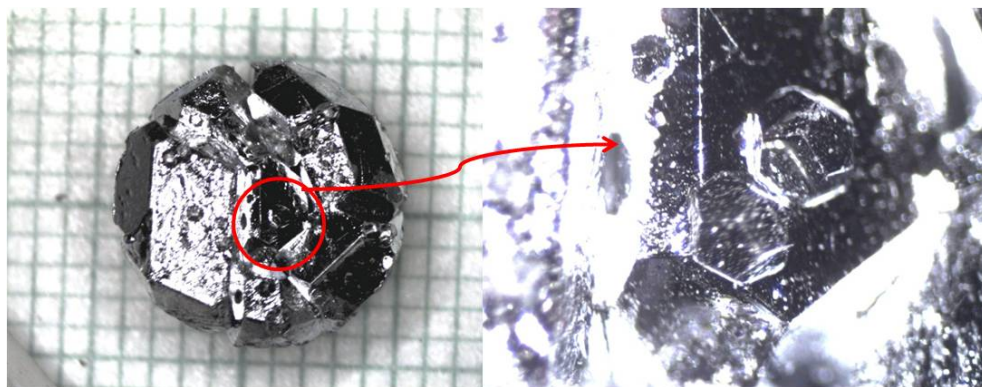


Figure 4.1 A single crystal of GdCd_6 with i-Gd-Cd quasicrystalline grains grow on top.

Apparently, the previous Gd-Cd binary phase diagram is incomplete on the Cd rich side and worth further investigation. The liquidus line for GdCd_6 as well as for the new phase can be determined via solution growth. Based on the mass of starting material and the mass of obtained crystalline phase, the chemical composition of the remaining liquid at various decanting temperatures can be estimated. In Fig. 4.2(a), a revised Gd-Cd binary phase diagram on the Cd rich side is presented. The new phase, as will be shown in detail below to be a binary quasicrystalline phase, is an incongruent melting phase with very limited liquidus range. This range, unfortunately shrinks as we progress from $R = \text{Gd}$ to $R = \text{Tm}$. The middle inset in Fig. 4.2 shows the differential scanning calorimetry (DSC) data, which suggest that the i-Gd-Cd phase decomposes at around 450 °C. Our discovery of this new, more Cd-rich phase, refinement of the binary phase diagram and the new phase's decomposition temperature, were all confirmed by a metallurgical study of the Gd-Cd binary phase diagram submitted one

year after the publication of our discovery[132]. However, Ref. [132] makes no mention of our discovery[133].

Using our redetermined Gd-Cd phase diagram, we were able to grow single-phase *i-R*-Cd for $R = \text{Y, Gd-Tm}$. Single-grain quasicrystals were grown out of Cd-rich binary solutions. A typical procedure involved adding approximately 5 g of Cd (Alfa Aesar, 99.9999% purity) and 0.06 g of rare earth elements (Ames Laboratory Material Preparation Center) into a 2 ml alumina crucible with a molar ratio of $\text{Cd}/R = 99.2:0.8$ ($R = \text{Y, Gd-Dy}$) or $99.4:0.6$ ($R = \text{Ho-Tm}$). The crucible with the starting elements was sealed in a fused-silica ampoule under a partial argon atmosphere, which was then heated up to 700 °C, held at 700 °C for 10 hours, cooled to 455 °C in 3 hours and then slowly (roughly 2 °C h⁻¹) cooled to 335 °C, at which temperature the *R*-depleted, remaining Cd-rich solution was decanted with the assistance of a centrifuge. Clusters of single grains with a mass of about 0.2 g were obtained from each growth[100; 111; 130].

Typical grains of quasicrystal are shown in the inset of Fig. 4.2(a) and also in Fig. 4.2(b). Small, single grains of quasicrystal, like the one shown in the inset of Fig. 4.2(a), usually are well faceted. Much larger grains, as shown for both the front and back sides in Fig. 4.2(b), often form from a single nucleation site, which then follows an initial dendritic growth and followed by faceted growth.

The structure of this new phase was identified as an icosahedral quasicrystalline phase (denoted as *i-R*-Cd, in which 'i' stands for icosahedral.) via x-ray powder diffraction, using a conventional laboratory source, as well as a high-energy x-ray single-grain diffraction technique[134]. The high-energy x-ray measurements were carried out at station 6-ID-D at the Advanced Photon Source in collaboration with Dr. Goldman's neutron and x-ray scattering group at Iowa State University and Ames Laboratory. Detailed experimental methods on the high-energy x-ray experiments can be found in Ref. [100; 130]. The single-grain precession images of *i*-Gd-Cd, shown in Fig. 4.3(a) and (b), were taken with the beam along a five-fold and two-fold axis of the pentagonal faceted grain and show the pattern of diffraction spots characteristic of a primitive (P-type) quasilattice. This was also confirmed for $R = \text{Tb}$ and Tm . The entire sample shown in Fig. 4.2(b) was also surveyed by high-energy x-ray diffrac-

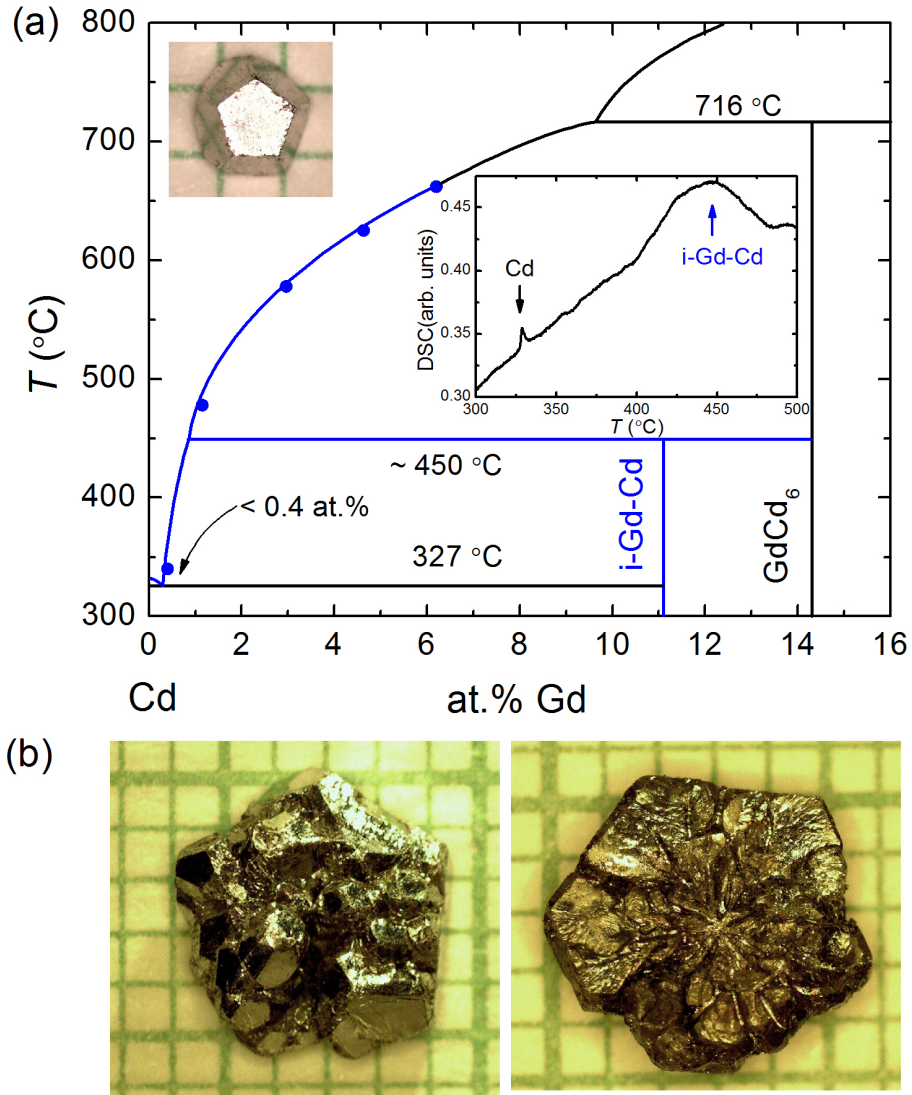


Figure 4.2 (a) Revised Gd-Cd binary phase diagram around the Cd concentrated region. Blue indicates the revised part as compared to the old version shown in Fig. 3.1. Data points on the revised liquidus line were inferred by decanting growths at different temperatures and weighing the obtained crystals. The upper inset shows a single grain of i-Gd-Cd on a millimeter grid paper. The middle inset shows DSC data for i-Gd-Cd. (b) The front and back sides of a larger grain of i-Tb-Cd on a millimeter grid paper.

tion. A series of diffraction patterns were recorded by translating the sample in both directions perpendicular to the beam in a grid-like manner in steps of 1 mm. All recordings showed similar patterns demonstrating the same crystal orientation in each probed sample volume and, therefore, demonstrating that the entire sample shown in Fig. 4.2(b) is a single grain i-Tb-Cd quasicrystal despite the obvious initial dendritic growth.

Likewise, the diffraction pattern from powdered single grains of i-Gd-Cd, shown in Fig. 4.3(c), is well indexed by a primitive icosahedral quasilattice. All peaks for $q < 3 \text{ \AA}^{-1}$, and the prominent peaks for $3 \text{ \AA}^{-1} < q < 5 \text{ \AA}^{-1}$ are indexed either to the icosahedral phase or the residual Cd flux. The labels 2, 3 and 5 denote prominent peaks along the two-fold, three-fold and five-fold directions, respectively. The six-dimensional (6D) lattice constant, a_{6D} , was estimated to be $7.972(4) \text{ \AA}$, using the strongest peak along the five-fold axis (indexed (211111) in Fig. 4.3). No impurity phases, beyond some residual Cd flux at the $<5\%$ level, were found.

The ambient temperature powder x-ray diffraction patterns obtained for all of the i- R -Cd ($R = \text{Y, Gd-Tm}$) are shown in Fig. 4.4. All diffraction patterns are similar to that shown in Fig. 4.3 for i-Gd-Cd. Progressing from $R = \text{Gd}$ to $R = \text{Tm}$, the diffraction peaks shift to slightly higher values of 2θ , reflecting a change in the six-dimensional quasilattice constant, a_{6D} . As the inset of Fig. 4.3(c) shows, our powder diffraction measurements for $R = \text{Gd, Tb, Dy, Ho, Er and Tm}$ shows a smooth decrease of a_{6D} , consistent with the well-known lanthanide contraction.

The composition of the icosahedral phase was inferred from two independent methods: wavelength-dispersive x-ray spectroscopy (WDS) and temperature-dependent magnetization (shown in Fig. 4.5). Compositions, determined from each measurement, are presented with other magnetic and structural data in Table 4.1.

WDS data were collected in the electron probe microanalyser of a JEOL JXA-8200 electron microprobe with a 20 kV beam voltage and a $5\text{-}\mu\text{m}$ spot size. For each sample, the measurement was done at 12 different locations on a polished surface. In order to calibrate the WDS data to the R -Cd system, respective RCd_6 samples were also measured and used as standard materials with known stoichiometry. The WDS data suggest an average composition of i- R -Cd $_{7.55\pm0.3}$ across the series. From Gd to Tm, the Cd concentration decreases continuously with

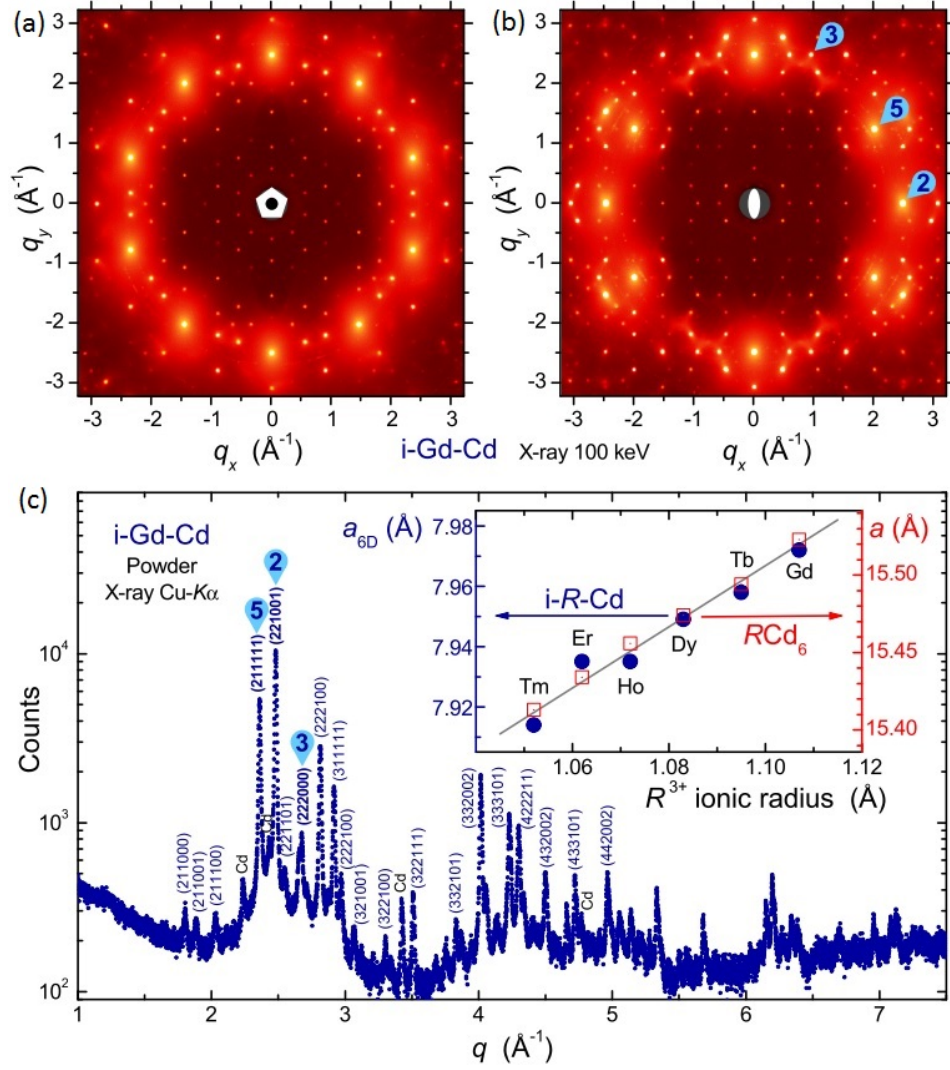


Figure 4.3 High-energy x-ray diffraction patterns from a single grain of i-Gd-Cd were taken with the beam parallel to the five-fold (a) and two-fold (b) axes. The scaling of peak positions along the five-fold axis confirms that the i-Gd-Cd quasicrystals fall within the simple-icosahedral (P-type) structural family. (c), The powder diffraction pattern from i-Gd-Cd. The inset shows the scaling of the 6D quasilattice constants (determined from indexing the patterns) for $R = \text{Gd-Tm}$ as a function of rare earth ionic radius[135] and compares the lattice constant determined from powder measurements of our RCd_6 samples with the values calculated from a_{6D} as described in the text.

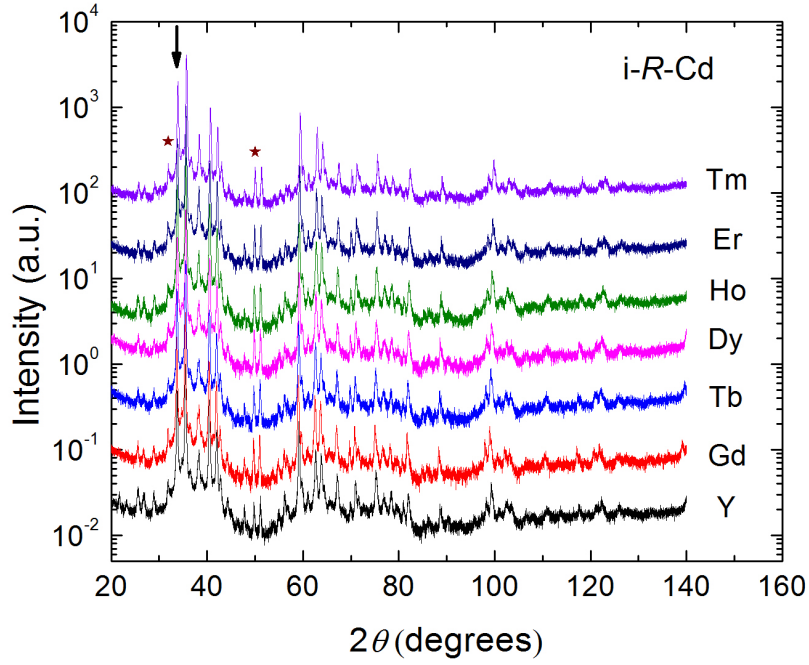


Figure 4.4 Powder diffraction patterns from all of the *i-R-Cd* quasicrystals under investigation. The patterns are normalized to the strongest diffraction peak and offset for clarity. All peaks can be indexed to either the icosahedral phase or residual Cd flux. Stars indicate major diffraction peaks that come from Cd flux. The arrow indicates the (211111) peak, which was used to calculate a_{6D} .

Table 4.1 The composition of the icosahedral phase as inferred from WDS and temperature-dependent magnetization (Fig. 4.5), the value of the Weiss temperature, Θ , and the 6D quasilattice constant, a_{6D} , determined by indexing the powder diffraction patterns from each sample. Errors in parenthesis for x from the WDS measurements and a_{6D} represent one standard deviation in the values. The error in x from the magnetization measurements was estimated from fitting over different temperature ranges and weighing errors.

RCd_x	x (WDS)	x (Magnetization)	Θ (K)	a_{6D} (Å)
Gd	7.88(18)	7.98(7)	-41(1)	7.972(4)
Tb	7.69(17)	7.89(7)	-21(1)	7.958(4)
Dy	7.50(9)	7.51(6)	-11(1)	7.949(5)
Ho	7.60(13)	7.80(9)	-6(1)	7.935(5)
Er	7.34(13)	7.78(5)	-4(1)	7.935(6)
Tm	7.28(6)	7.76(8)	-2(1)	7.914(5)
Y	7.48(16)	-	-	7.955(5)

an exception of Dy. The Cd/Y ratio in i-Y-Cd is close to that of i-Dy-Cd.

The R/Cd ratio was also extracted from the temperature-dependent magnetic susceptibility by assuming that $R = \text{Gd-Tm}$ manifest full, trivalent, local moments and that the temperature-dependent magnetic susceptibility, $\chi(T) = M(T)/H$, could be fitted to a Curie-Weiss law, $\chi(T) = C/(T - \Theta)$. The inverse magnetic susceptibility of i- R -Cd, measured at 5 kOe or 10 kOe are shown in Fig. 4.5. From the fits to the high-temperature $H/M(T)$ data for the moment-bearing samples, it is found that the composition is slightly more Cd rich: i- R -Cd $_{7.75 \pm 0.25}$ than the values obtained from WDS data. The Cd concentration also shows a systematic decrease as observed in the WDS results. For the heaviest rare earth members of the i- R -Cd series, given the shrinking grain size, the R/Cd ratios that were inferred from the magnetization data may become less reliable than the WDS value owing to the increasing significance of the small amount of residual Cd flux on the surfaces of the grains. For example, approximately 5% Cd (by mass) second phase on the i-Tm-Cd quasicrystal can shift the inferred R/Cd ratio from the WDS value of 1:7.28 to the magnetization-derived value of 1:7.76.

Both measurements, however, set compositions for i- R -Cd that: differ significantly from the prototypical i-Yb-Cd $_{5.7}$ icosahedral quasicrystal and RCd_6 cubic approximants; and are close to the stoichiometry of the recently discovered Sc $_{12}$ Zn $_{88}$ (ScZn $_{7.33}$ in the present notation) ico-

hedral phase[131] as will be discussed in detail below. It is worth noting that both measurements suggest the possibility of a slight increase in R content as the rare earth elements become heavier. This phenomenon could be driven by steric (ionic size) constraints as a result of lanthanide contraction.

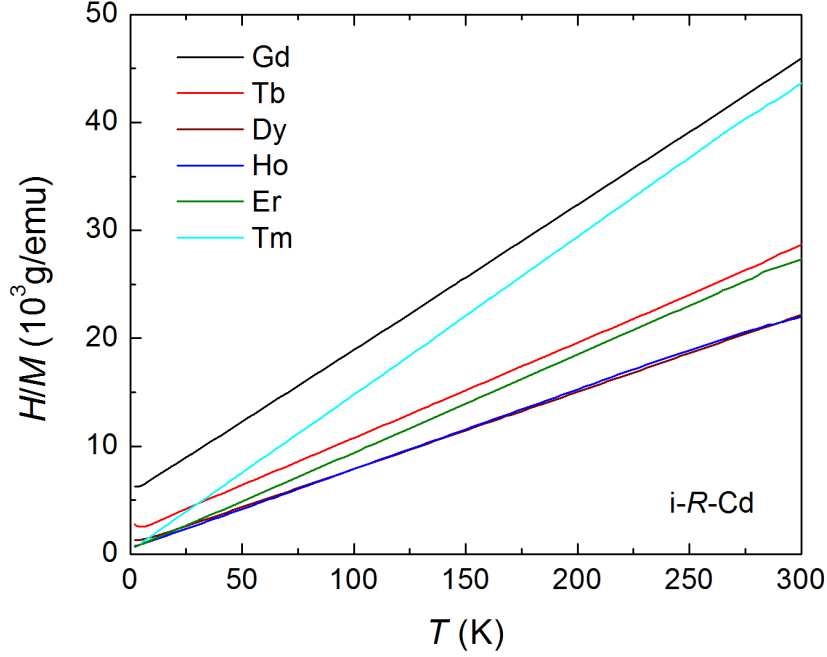


Figure 4.5 Temperature-dependent inverse magnetic susceptibility of i - R -Cd measured at 5 kOe or 10 kOe.

4.2 Structure and lattice parameter

After the initial discovery and identification of this new family of binary quasicrystals, more detailed studies are needed to further characterize their chemical and physical properties. Here we start from the structure of i - R -Cd via x-ray diffraction.

The difference in composition between the new i - R -Cd phase and the i -Yb-Cd_{5.7} quasicrystal, as well as the RCd_6 quasicrystal approximants, raises the question of whether there are fundamental differences between the structures of these systems. The analysis of the structure

of *i-R*-Cd relative to the *i*-Yb-Cd_{5.7} quasicrystal and *RCd*₆ approximants is based on the close association between the atomic motifs in quasicrystals and their associated approximants[78]. The *RCd*₆ cubic approximants may be described as a body-centred cubic packing of interpenetrating rhombic triacontahedral, or Tsai-type clusters[136], which features an icosahedron of 12 *R* atoms comprising the third shell of the cluster. These clusters, situated at the body-centred cubic lattice points are linked along the cubic axes by sharing a face, and interpenetrate neighbouring clusters along the body diagonal[137].

These same clusters have been shown to comprise the backbone of the structure of the icosahedral phase of *i*-Yb-Cd_{5.7}, with the same type of linkages[80]. Indeed, in terms of the higher dimensional description of aperiodic crystals, the atomic structure of the *RCd*₆ approximant can be generated by a rational projection of the 6D representation of the icosahedral phase[80]. However, there is only one crystallographic site for the *R* ion in the approximant structure corresponding to their placement at the vertices of an icosahedron embedded in the rhombic triacontahedral cluster. For *i*-Yb-Cd_{5.7}, on the other hand, approximately 70% of the *R* ions are associated with the embedded icosahedral cluster, whereas 30% are found in the glue that fills the gaps between the rhombic triacontahedral clusters[80; 138].

As a support argument that they belong to the same structural family, we can compare the measured values for a_{6D} to the lattice constant, a , expected for the *RCd*₆ approximant phase through the well-established relation[125]: $a = \sqrt{2}a_{6D}(p + q\tau)/\sqrt{(2 + \tau)}$, where τ is the golden mean, $(\sqrt{5} + 1)/2$, and p and q are indices that label the approximant. For *RCd*₆, a 1/1 approximant phase, $p = q = 1$. For *i*-Gd-Cd, the calculated value of $a = 15.519$ Å, in excellent agreement with our measured lattice parameter for GdCd₆ of 15.523 Å. For *i*-Y-Cd, the lattice constant for the approximant, derived from $a_{6D} = 7.955$ Å (15.483 Å), and the measured value of $a = 15.482$ Å are also in excellent agreement and lie between those values determined for *R* = Dy and Tb. The powder diffraction patterns from the *RCd*₆ approximants were refined using the Rietveld package in GSAS[116] and the results are in good agreement with the published crystallographic data[137]. As the inset of Fig. 4.3(c) shows, excellent agreement between the derived and measured cubic approximant lattice constants is found for all *R* ions in the *i-R*-Cd family. This provides compelling evidence that, despite rather significant differences in

composition, the cluster-based backbone of the icosahedral structure of the *i-R*-Cd quasicrystal is quite similar, if not identical, to that found for *i*-Yb-Cd_{5.7} and the *RCd*₆ cubic approximants.

This is confirmed recently by a full 6D structural refinement of the *i-R*-Cd quasicrystal as was done for *i*-Yb-Cd_{5.7} [80; 139]. In the case of *i-R*-Cd, both the rhombic triacontahedral clusters and the Tsai-type atomic cluster were found to show certain degree of Cd/*R* partial occupancy[139]. The deficiency of *R* in the Tsai-type cluster may result from a deviation of the atomic size ratio between *R* and Cd, from the ideal value for Tsai-type cluster, 1.288[140]. For *i-R*-Cd, this ratio ranges from 1.149 for *i*-Gd-Cd to 1.112 for *i*-Tm-Cd. In the case of *i*-Yb-Cd_{5.7}, where there is a full occupancy of Yb²⁺ in the Tsai-type cluster, the atomic size ration between Yb²⁺ and Cd is ~ 1.237 , a value that is very close to the ideal ratio[139]. The partial occupancy of the *R* sites, especially on the Tsai-type clusters, may have a strong influence on the magnetic ground state of *i-R*-Cd. Neutron scattering experiments are ongoing in searching for this link between rare earth deficiency and the missing of long range magnetic order.

As discussed above, there is a slight change in stoichiometry as *R* changes from Gd to Tm. Phason strain was analysed based on the broadening of powder x-ray diffraction peaks. It was found that the frozen-in phason strain is the key mechanism for structural disorder in these quasicrystalline samples. And there is no significant difference in strain/phason strain between *i*-Gd-Tm and *i*-Tm-Cd[100].

4.3 Magnetic properties of *i-R*-Cd

To further explore the physical properties of *i-R*-Cd, detailed magnetization data were measured in identifying the magnetic ground states. As shown in Fig. 4.5, *i-R*-Cd (*R* = Gd-Tm) binary quasicrystals show Curie-Weiss behavior at high-temperatures, which can be well fitted with local moment behavior of trivalent rare earth elements. Among all binary quasicrystals that were discovered in this study, *i*-Y-Cd is the only non-moment-bearing member due to an empty 4f shell of Y³⁺. Therefore, it serves as a good non-magnetic comparison to the rest of the members.

The temperature-dependent dc magnetization of *i*-Y-Cd and YCd₆ are shown in Fig. 4.6. Both compounds exhibit diamagnetic and essentially temperature-independent behavior with

a value close to -3×10^{-7} emu/g. Compared with other *i-R*-Cd members at room temperature, the absolute value of magnetization for *i-Y*-Cd is about two orders of magnitude smaller. In addition, the sign and order of magnitude of the dc magnetization is close to another Y-based quasicrystal: Y-Mg-Zn[67]. At 2 K, the field-dependent magnetization is negative and close to linear.

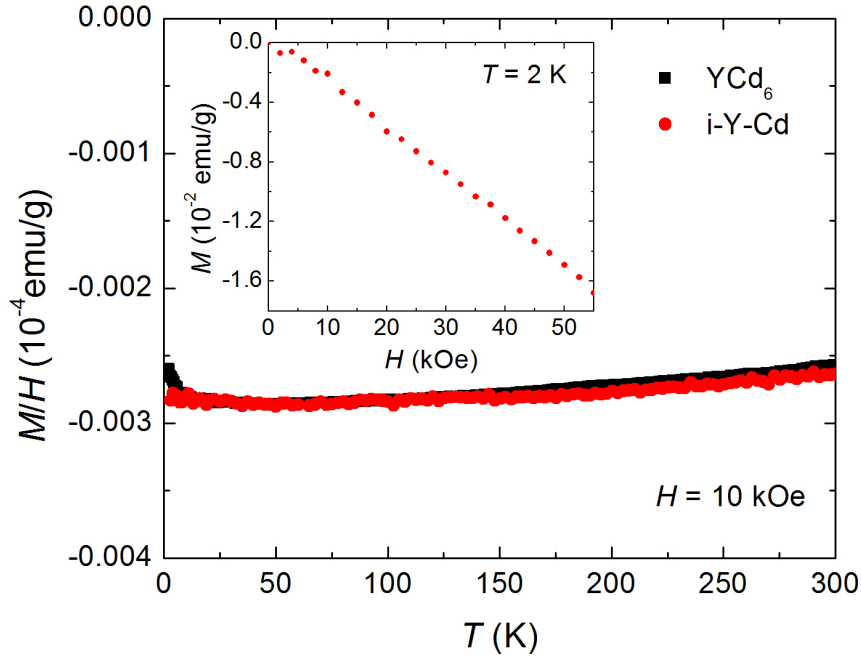


Figure 4.6 Temperature-dependent dc magnetic susceptibility of *i-Y*-Cd and YCd_6 measured at 10 kOe. The inset shows the field-dependent magnetization of *i-Y*-Cd measured at 2 K.

The inverse magnetic susceptibility for *i-Gd*-Cd is linear from 300 K down to about 10 K as shown in the inset of Fig. 4.7. *i-Gd*-Cd exhibits a typical spin glass behavior with a clear cusp at 4.6 K in the zero-field-cooled (ZFC) magnetization data. Below 4.6 K, the field-cooled (FC) magnetization also exhibits a small cusp and then remains almost temperature-independent. Fig. 4.7 shows that the dc magnetization of *i-Gd*-Cd is strongly history-dependent: data were measured following an initial zero-field cooling to 2 K and warming in a 50 Oe field from 2 K to

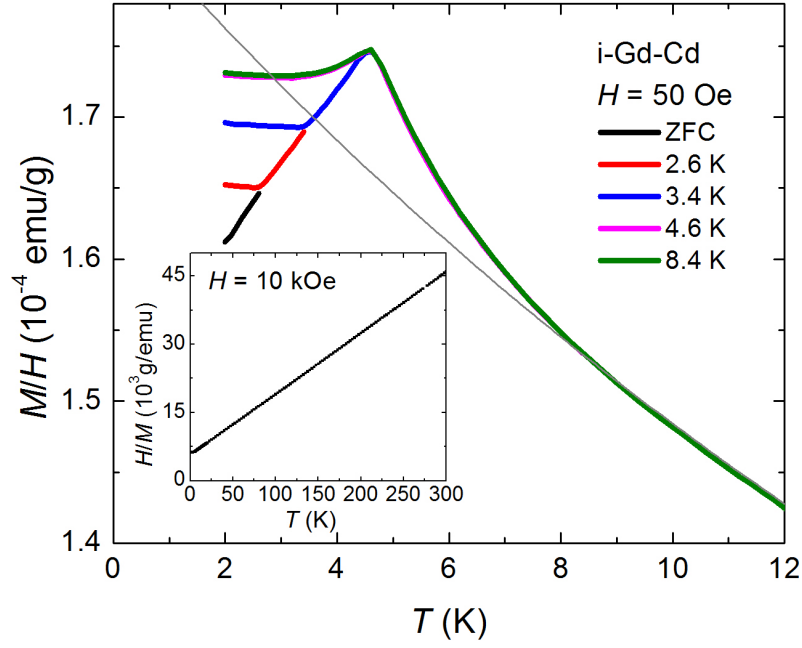


Figure 4.7 Irreversibility of dc magnetization measured at 50 Oe. Different colors indicate different field-cool temperatures (see text). The inset shows temperature-dependent inverse magnetic susceptibility of i-Gd-Cd measured at 10 kOe. The grey line represents Curie-Weiss behavior that is extrapolated from its high-temperature paramagnetic state.

various temperatures, T' . For instance, after ZFC measurement from 2 K to 2.6 K, the sample was cooled with applied field back to 2 K, after which the magnetization data was acquired upon warming from 2 K to 3.4 K. Therefore, the red-line in Fig. 4.7 can be considered as a 2.6 K FC measurement. The magnetization after field-cooling from various T' are essentially temperature-independent up to T' and then fall back onto the ZFC data above T' . Here we define T_{irr} as the highest temperature where ZFC and FC data differ by more than 0.5% and T_{max} as the temperature at which the maximum of ZFC dc magnetization occurs. In the case of i-Gd-Cd, both characteristic temperatures are the same. Above the T_{max} , the FC and ZFC data for i-Gd-Cd are essentially identical. In addition, a Curie-Weiss extrapolation from the high-temperature, paramagnetic state of i-Gd-Cd is plotted in grey solid line in Fig. 4.7. There exists a clear deviation from the Curie-Weiss behavior at a higher temperature than T_{max} . This precursor of spin-glass state may imply a formation of magnetic clusters prior to the spin freezing temperature[62; 67; 141; 142; 143].

The dc magnetization of i-Gd-Cd was also investigated at different applied fields and the results are presented in Fig. 4.8. The applied field has two significant effects on the measured magnetization: the first being that the cusp in ZFC measurement is rounded and broadened and the second is that T_{irr} is shifted to lower temperatures with higher applied fields. A subset of the data is presented in the inset to illustrate these effects. The onset of irreversibility can be associated with de Almeida-Thouless's prediction[144], where the change in T_{irr} with applied field should follow:

$$H(T_{\text{irr}}) = \alpha \left(1 - \frac{T_{\text{irr}}}{T_{\text{f}}}\right)^b \quad (4.1)$$

where T_{f} stands for the spin freezing temperature in zero field which for i-Gd-Cd was taken as 4.6 K, the same value as T_{max} . α is the applied magnetic field, above which the irreversibility phenomenon of spin-glass should be fully suppressed. The data for i-Gd-Cd can be fitted with $\alpha = 3.3(\pm 0.3) \times 10^4$ Oe and $b = 2.5 (\pm 0.1)$. This value of α is close to that found for i-Tb-Mg-Zn which has an $\alpha = 3.5 \times 10^4$ Oe[67]. It should be noted, though, that the original theory was developed for Ising spins with $b = 1.5$. Clearly, this will not be the case for Gd moments. For Heisenberg spins, however, an even smaller value of $b = 0.5$ was predicted[145]

and could not give a reasonable fit to our data. In Ref. [67], the fit could be improved if a larger value of exponent was used. However, it is not clear what causes the difference in the exponent values.

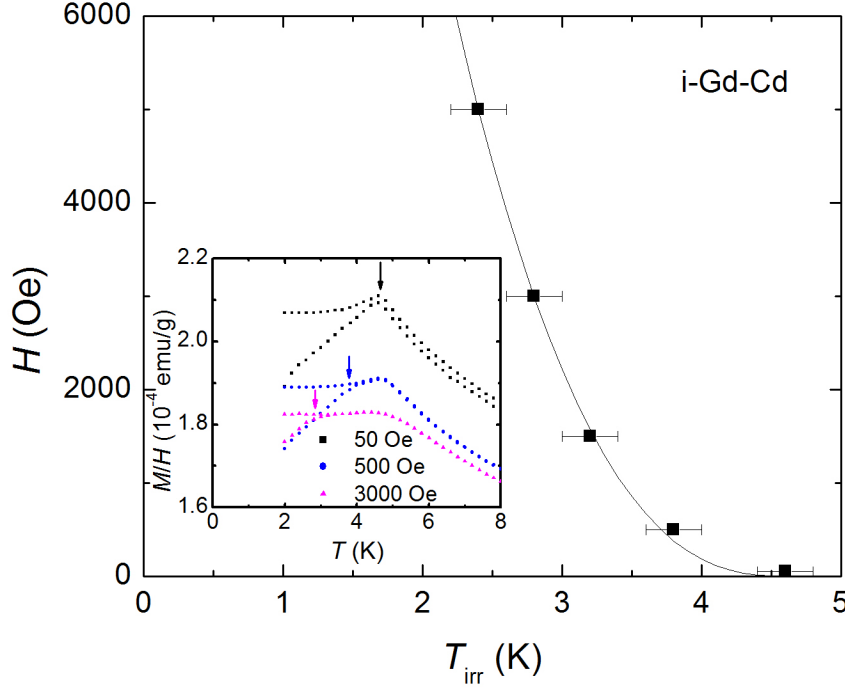


Figure 4.8 The field dependence of T_{irr} for i-Gd-Cd. Fits according to Eq. 4.1 are shown with $b = 2.5$ and $\alpha = 3.3 \times 10^4$ Oe. The inset shows representative ZFC and FC measurements under different applied magnetic field. Arrows indicate T_{irr} for different fields.

Compared with a long-range magnetic ordering, which can be viewed as a thermal equilibrium state during the time scale of measurement, a spin-glass is not in such an equilibrium state. Therefore, the magnetic behavior will depend on the frequency of measurement due to the system's limited ability to respond to the changing applied field. The cusp-temperature in the real part of the ac susceptibility increases by about 0.16 K upon increasing the measurement frequency from 10 Hz to 10000 Hz. This implies about 3% increase of the freezing temperature, which is close to that found for i-Gd-Mg-Zn[146]. $\Delta T_f/[T_f \Delta(\log_{10} f)]$ is about 0.01.

Although the dc magnetization data and the frequency dependence of ac magnetization are consistent with a spin-glass-type freezing of the magnetic moments in i-Gd-Cd, more evidence is required to rule out superparamagnetic-type blocking, or cluster glass, behavior. A convincing way to distinguish between these possibilities is to look at the third order, non-linear magnetic susceptibility, χ_3 , in the vicinity of spin-freezing/blocking temperature[147; 63]. χ_3 is defined in terms of magnetization, M , and applied field, H , as follows,

$$M/H = \chi = \chi_1 + \chi_3 H^2 + \chi_5 H^4 + \dots \quad (4.2)$$

The temperature-dependent χ_3 term will exhibit a much sharper peak in spin-glass systems as compared with a broad feature that is usually observed in superparamagnets[147]. The third order magnetic susceptibility was investigated for i-Gd-Cd and is shown in Fig. 4.9. An ac field with an amplitude of 3 Oe and a frequency of 333.3 Hz was applied to acquire the data. The χ_3 peak for i-Gd-Cd is sharper than other known spin-glass systems, for example, Tb-Mg-Zn, Ho-Mg-Zn quasicrystals[67] and an Ising spin glass system $Y_{1-x}Tb_xNi_2Ge_2$ [68], whereas superparamagnets usually exhibit a much broader feature[147]. The peak temperature in χ_3 for i-Gd-Cd, however, is 4.3 K, a value that is 0.3 K lower than the $T_{\max}$ value from the dc magnetization. This small discrepancy in temperatures possibly results from a different thermometry configuration in the QD PPMS where ac susceptibility was measured. For the current study, we follow the temperatures given by MPMS.

Whereas the data just presented for i-Gd-Cd is consistent with classic spin-glass behavior, for i-Tb-Cd and i-Dy-Cd, the canonical cusp-shaped spin-glass signature in magnetization data is replaced by a broad maximum in both ZFC and FC data with the irreversibility appearing at a significantly higher temperature than the temperature at which ZFC magnetization reaches its maximum (Fig. 4.10). Similar behavior was observed in the R -Mg-Cd quasicrystal system and explained by the presence of magnetic impurities that due to slight oxidation of the surface of the sample[98]. After annealing at 200°C for two days, the dc magnetization data for both i-Tb-Cd and i-Ho-Cd remain the same, even though a thin layer of oxidation appeared on the sample's surface. If the aforementioned argument is applied, a magnetization feature that evolves with changing degrees of oxidation would be expected. In addition, sample inhomogeneity that was

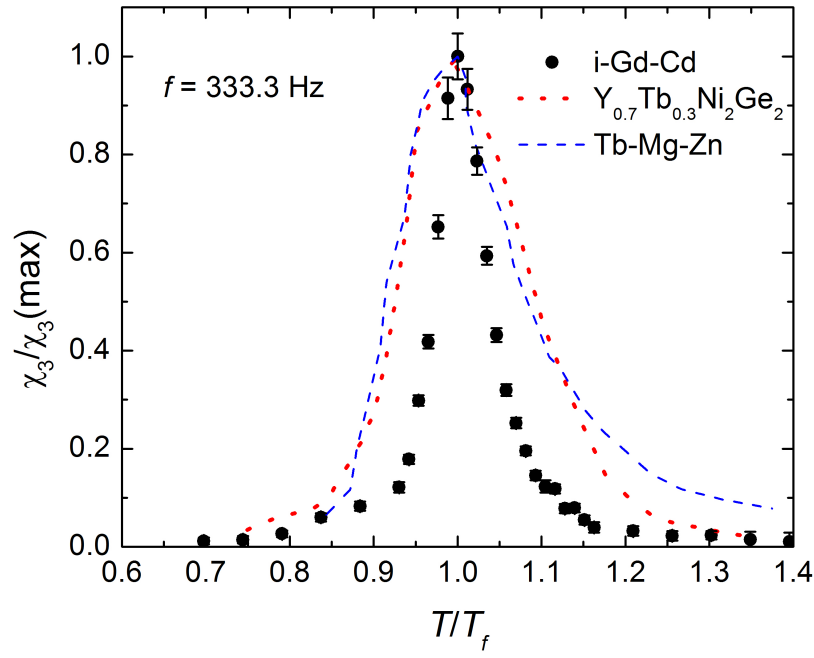


Figure 4.9 Third order magnetic susceptibility term, χ_3 , normalized in temperature and peak height. For i-Gd-Cd, χ_3 was measured at 333.3 Hz (black dots). Red and blue dashed lines present the χ_3 data, obtained from Ref. [67; 68], for Ising spin glass, $Y_{0.7}Tb_{0.3}Ni_2Ge_2$ and Tb-Mg-Zn quasicrystal.

proposed to cause non-cusp like feature in other spin glass systems[148], if exists in i-Tb-Cd and i-Dy-Cd, cannot be removed by annealing at 200°C.

In Fig. 4.10, a clear history-dependent magnetization can be observed. Comparing with i-Gd-Cd, in which different FC temperatures result in a temperature-independent magnetization from the base temperature up to T' , in the case of i-Tb-Cd and i-Dy-Cd, if T' is higher than $T_{\max}$, the temperature-independence survives only up to $T_{\max}$. This may indicate that only at temperatures that are lower than $T_{\max}$, do the magnetic moments become fully "frozen". Therefore, $T_{\max}$ might represent the spin-freezing temperature, T_f , better than T_{irr} .

The grey, solid curves shown in Fig. 4.10 are the extrapolations of the high-temperature Curie-Weiss fit to the data. Comparing with i-Gd-Cd, i-Tb-Cd and other members, the manner in which i-Dy-Cd deviates from the Curie-Weiss behavior is different, since its magnetization increases more slowly upon cooling than its high-temperature, paramagnetic state would suggest. Since i-Gd-Cd, i-Tb-Cd and i-Dy-Cd each exhibit deviation from simple Curie-Weiss behavior, it is clear that the CEF splitting is not the key factor for the formation of possible magnetic clusters. However, subtleties in the CEF splitting might alter the details of magnetic properties and make i-Dy-Cd behave differently. A similar change in the sign of the deviation was also reported in other spin-glass systems, like AuFe alloys, with different Fe concentrations[142]. However, in that case, the sign of Curie-Weiss temperature changes at the same time.

Attempts to obtain temperature-dependent χ_3 data for i-Tb-Cd were made. However, no resolvable feature was detected. Given that no clear cusp was seen in the ZFC dc magnetization measurement, it is likely that, for this compound, a possible distribution of freezing temperatures makes it difficult to experimentally see the clear feature in χ_3 . However, the experimental limitations of our instruments can not be ruled out.

The dc magnetization data measured in 50 Oe, down to 0.46 K are shown for i-Ho-Cd, i-Er-Cd and i-Tm-Cd in Fig. 4.11. In the ZFC data, clear cusps can be observed with $T_{\max} = T_{\text{irr}}$. In general, the irreversibility features for these members are much closer to what was seen in i-Gd-Cd, i.e. sharp cusps in ZFC dc magnetization. One subtle difference being that, unlike the case of i-Gd-Cd where ZFC and FC magnetization data reaches the maximum at the same temperature, for i- R -Cd ($R = \text{Ho-Tm}$), the FC maximum is located at a slightly

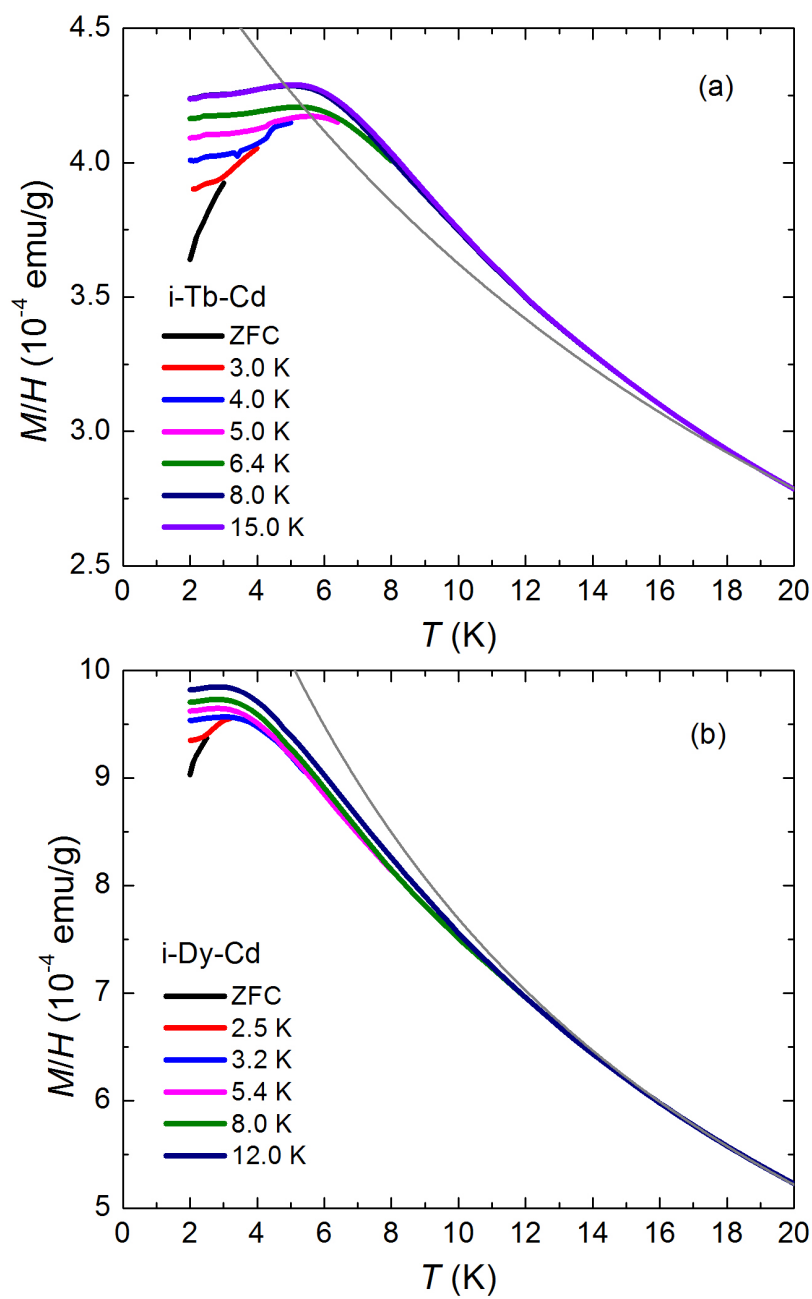


Figure 4.10 Temperature-dependent dc magnetization measured at 50 Oe for $i\text{-}R\text{-Cd}$ ($R = \text{Tb}, \text{Dy}$). Different colors indicate different FC temperatures. Gray lines represent Curie-Weiss behavior that was extrapolated from the high-temperature paramagnetic state.

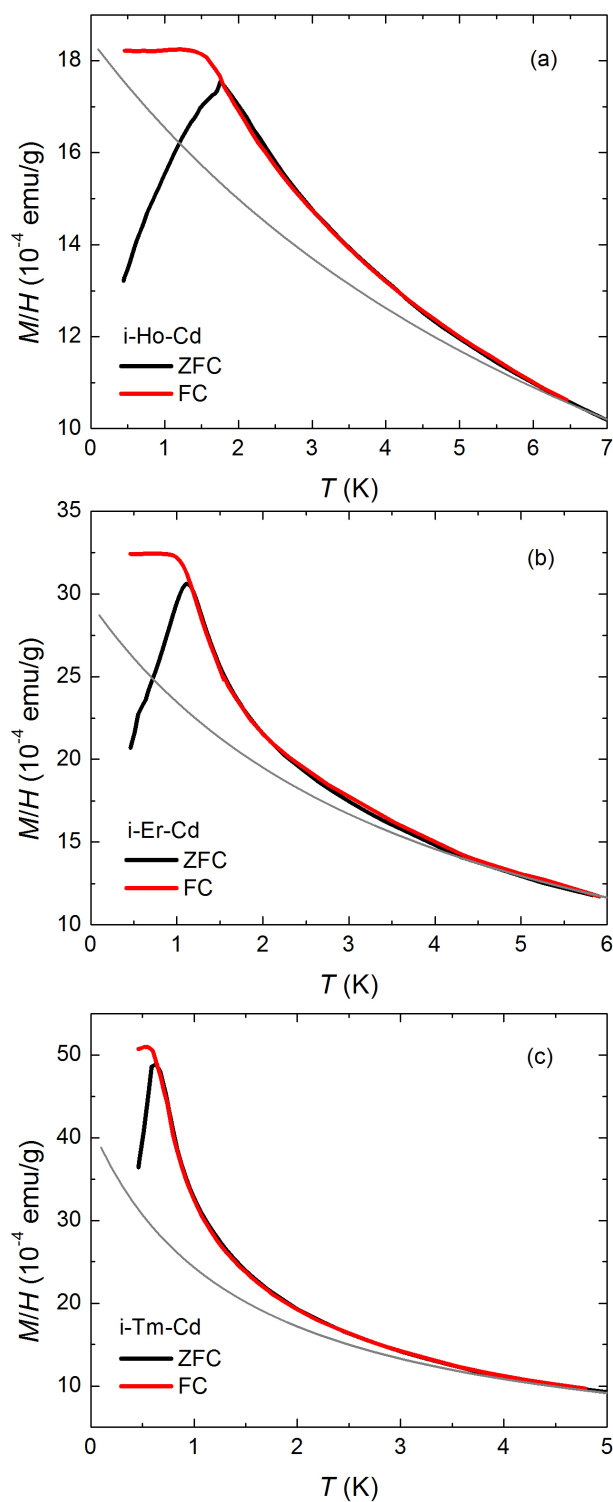


Figure 4.11 Temperature-dependent dc magnetization measured at 50 Oe for i - R -Cd ($R = \text{Ho-Tm}$). Data were acquired using a QD iHelium3 system. Gray lines represent Curie-Weiss behavior that is extrapolated from the high-temperature paramagnetic state.

lower temperature than $T_{\max}$. The deviation from the Curie-Weiss, paramagnetic state (shown in grey) occurs at higher temperature than $T_{\max}$, with a clear upward deviation. Information obtained from all of our dc magnetization measurements are summarized in Table 4.2.

Due to the limitations of our instrument, we were not able to measure ac magnetization below 1.8 K, where the dc magnetization features of i- R -Cd ($R = \text{Ho-Tm}$) emerge.

Table 4.2 $T_{\max}$ represents the temperature at which dc ZFC data reaches maximum. T_{irr} represents the temperature at which FC and ZFC data start to split by more than 0.5%. Error bars were estimated according to measurements on different samples and the data step width of each measurement.

Compound	$T_{\max}$ (K)	T_{irr} (K)
i-Gd-Cd	4.6(0.2)	4.6(0.2)
i-Tb-Cd	5.3(0.5)	8.7(0.5)
i-Dy-Cd	3.0(0.4)	10.1(0.3)
i-Ho-Cd	1.76(0.05)	1.76(0.05)
i-Er-Cd	1.11(0.05)	1.11(0.05)
i-Tm-Cd	0.63(0.05)	0.63(0.05)

4.4 Specific heat of i- R -Cd

The temperature-dependent specific heat of i-Y-Cd is shown in Fig. 4.12. The stoichiometry used for the calculation was adopted from the WDS results that were listed in Table 4.1, $\text{YCd}_{7.48}$ for i-Y-Cd in this case. Below 10 K, there is a linear region in C/T versus T^2 , which yields a Debye temperature, Θ_D , of about 140 K. The linear fit also intersects the C/T axis at roughly 4 ± 2 mJ/mol-Y K^2 (or 0.5 mJ/atom K^2). For crystalline solids, the intercept normally indicates the electronic specific heat, γ . However, it was also noticed that even for non-crystalline solids, there could still be a linear region in C/T versus T^2 plot at low temperature with a finite γ value[149], which can be explained by a distribution of two-level systems[150]. If this is the case, then the electronic specific heat contribution to C/T will be even closer to zero. If we take the measured value, 4 ± 2 mJ/mol-Y K^2 , as the γ for i-Y-Cd, both γ and Θ_D for i-Y-Cd are very close to the values obtained for YCd_6 [101].

Figs. 4.13-4.18 present the specific heat data for other i- R -Cd members. The magnetic specific heat was calculated by subtracting that of i-Y-Cd with a small molar mass correc-

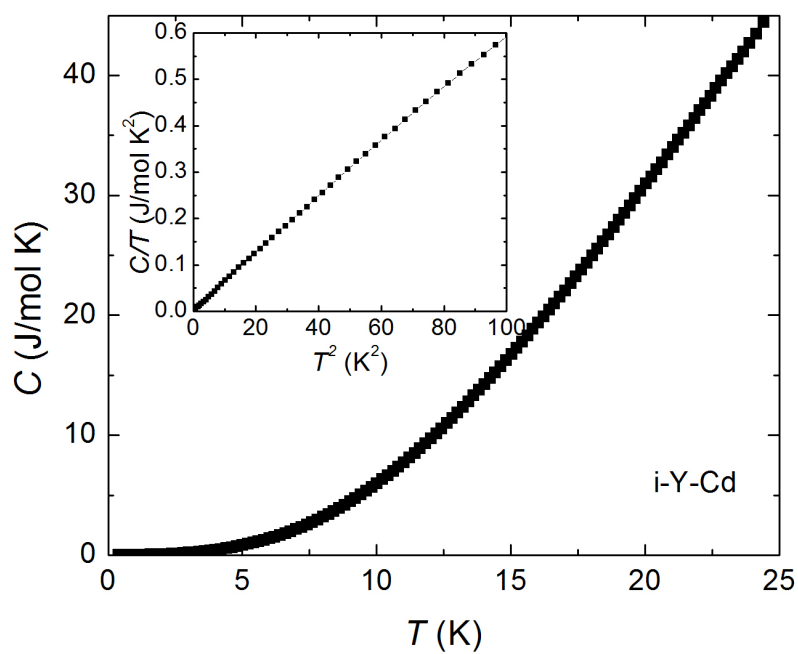


Figure 4.12 Temperature-dependent specific heat for i-Y-Cd using a stoichiometry of $\text{YCd}_{7.48}$. The inset shows C_p/T versus T^2 up to 10 K

tions according to (1) the Debye model to approximate changes due to the heavier R ions and (2) the R concentration. Although it is not well investigated if the model works for quasicrystalline compounds, the magnetic entropy thus integrated offers some information about how CEF splitting of the Hund's rule ground state multiplet J of the R^{3+} ion plays a role in the magnetism, as well as the temperatures at which the magnetic entropy starts to change. Uncertainties, shown as grey areas in Figs. 4.13-4.18, take into account the uncertainty in the WDS-determined stoichiometry and the uncertainty in the mass of the sample. Any un-physical drop in magnetic entropy at high temperature, due to this increasing error bar, can be ignored.

In Fig. 4.13, i-Gd-Cd shows a typical spin-glass behavior with a broad maximum located roughly 20% above T_f [62; 63]. Above roughly 10 K, the magnetic entropy of i-Gd-Cd tends to saturate, reaching the expected value for non-CEF-split Gd^{3+} , $\mathcal{R}\ln 8$, where $\mathcal{R}$ is the universal gas constant. The temperature where the magnetic entropy of i-Gd-Cd starts to saturate roughly corresponds to the temperature at which precursor magnetic clusters start to form as inferred from the deviation from the high-temperature Curie-Weiss tail seen in the dc magnetization measurements (see Fig. 4.7).

For the rest of the i- R -Cd members, the CEF splitting, albeit relatively small in this high symmetry structure[151], lifts the degeneracy of trivalent rare earth ground state. This results in a slower recovery of the full $\mathcal{R}\ln(2J+1)$ magnetic entropy upon warming and the thermal excitations between split levels persist to higher temperature as compared with the case of i-Gd-Cd.

The specific heat of i-Tb-Cd and i-Dy-Cd, members that exhibit non-cusp-like features in low-field magnetization data, are shown in Figs. 4.14-4.15. In the specific heat of i-Tb-Cd, the broad peak is not as clear as in i-Gd-Cd, which is possibly due to the addition of Schottky anomalies to the background. The origin of the slight low-temperature upturn observed below 1 K, however, is not yet well understood. A similar upturn is also observed in i-Ho-Cd and presented in Fig. 4.16 below. Since among all the studied i- R -Cd members, $R = Tb$ and Ho have the largest gyromagnetic ratio for the nuclear spins, it is likely that this low-temperature upturn in the specific heat originates from a nuclear Schottky anomaly. If the low-temperature specific heat upturn is included, the magnetic entropy of i-Tb-Cd is about $\mathcal{R}\ln 2$ at T_{max} and

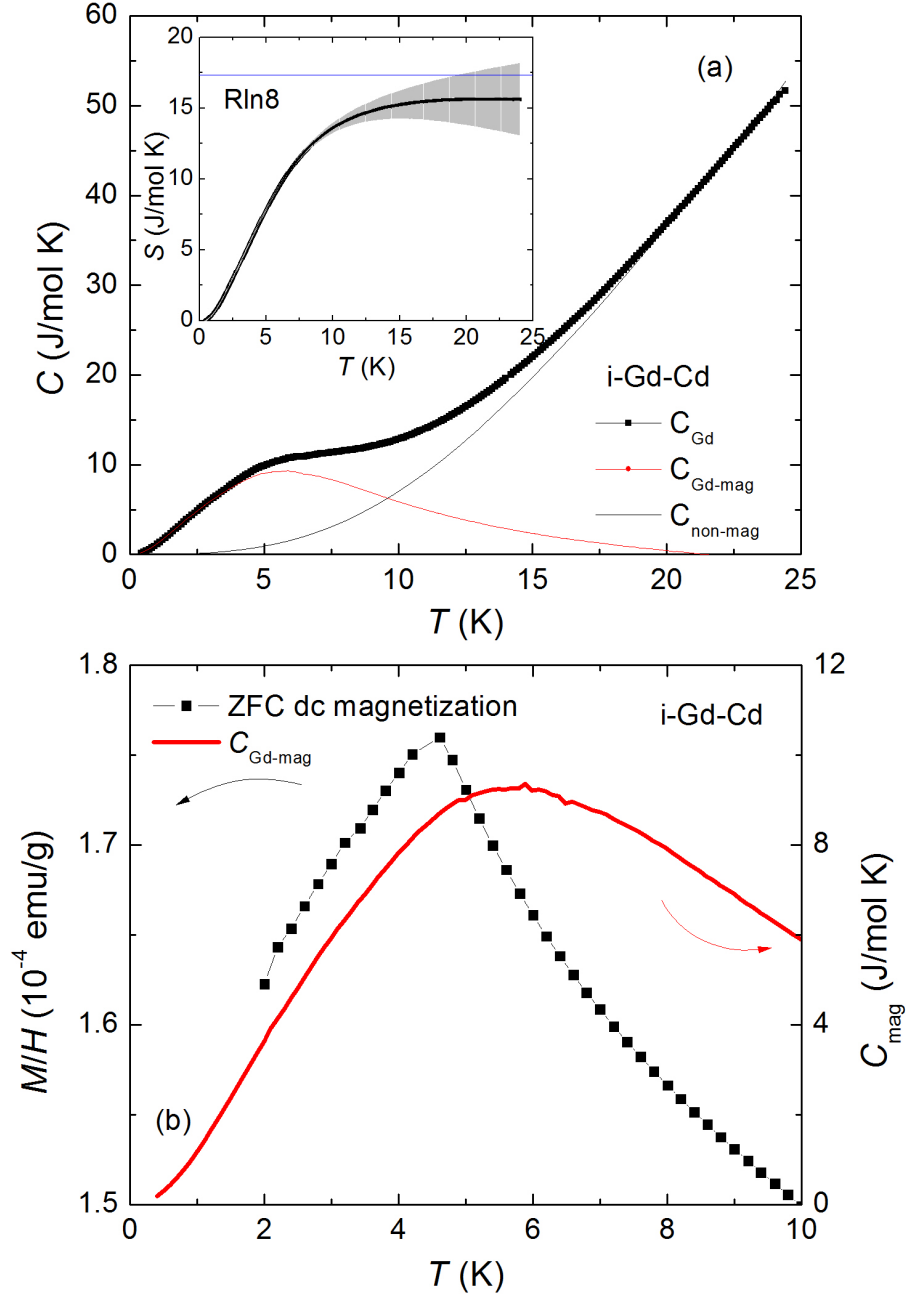


Figure 4.13 (a) Temperature-dependent specific heat of i-Gd-Cd. The grey solid line represents the non-magnetic part of the specific heat. The red solid line shows the magnetic specific heat. The inset shows the magnetic entropy with grey error bars (see text). (b) Low-temperature magnetic specific heat (red) on the right scale and low-temperature ZFC dc magnetization (black) on the left scale.

$\mathcal{R} \ln 4$ at the temperature where the dc magnetization starts to deviate from the Curie-Weiss behavior. Lacking more low-temperature data for the Schottky anomaly fit, it is difficult to offer quantitative corrections to the magnetic entropy. Qualitatively, the magnetic entropy for i-Tb-Cd may decrease by about 1 J/mol K if the upturn feature is excluded.

The specific heat of i-Dy-Cd is similar with that of i-Tb-Cd. The magnetic entropy reaches $\mathcal{R} \ln 2$ at around 5 K and approaches $\mathcal{R} \ln 4$ at 24 K. The magnetic specific heat shown in solid red line exhibits a broad maximum in the vicinity of the broad feature observed in the ZFC magnetization data. Another broad hump centered at ~ 10 K is most likely associated with Schottky anomalies due to CEF split levels.

Apart from the upturn at low temperatures, the specific heat of i-Ho-Cd (shown in Fig. 4.16) is different in a sense that it recovers the magnetic entropy much faster. After a subtraction by i-Y-Cd, a large amount of magnetic contribution in specific heat still exists below 5 K. At 24 K, the calculated magnetic entropy approaches $\mathcal{R} \ln 17$, which is the full magnetic entropy expected for Ho^{3+} . Even if the specific heat upturn below 1 K is assumed to arise from a nuclear Schottky anomaly, and is therefore excluded, an uncertainty of up to 4 J/mol K still suggests an $\mathcal{R} \ln 9$ magnetic entropy at 24 K. This large amount of entropy implies relatively small CEF splitting and is consistent with a distribution of low lying Schottky anomalies. In addition, a small, rounded, hump next to T_{max} might be consistent with a spin-glass transition.

The specific heat of i-Er-Cd and i-Tm-Cd are shown in Figs. 4.17-4.18. i-Er-Cd exhibits a hump in specific heat. At 24 K, it approaches $\mathcal{R} \ln 8$. The magnetic specific heat, in addition, shows another clear broad hump at around 12 K. This is most likely due to a Schottky anomaly associated with undetermined CEF levels. However, the current data does not allow for a more detailed analysis.

In i-Tm-Cd, only part of the specific hump was observed due to our base temperature of PPMS. It should be noted that it seems that the maximum temperature in specific heat of i-Tm-Cd is equal to, or even lower than the T_{max} in the dc magnetization data.

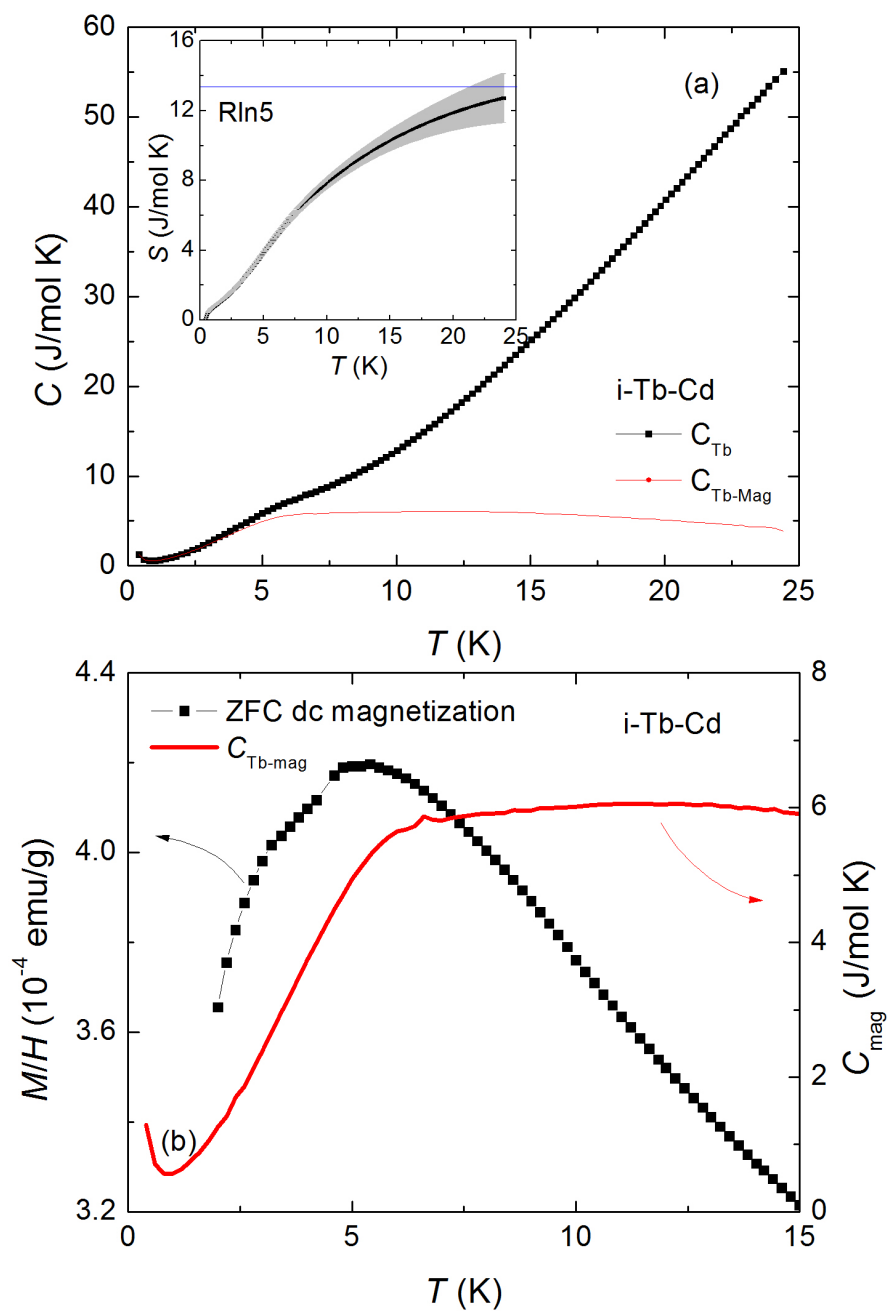


Figure 4.14 (a) Temperature-dependent specific heat of i-Tb-Cd. The red solid line shows the magnetic specific heat. The inset show the magnetic entropy with error bars. (b) Low-temperature magnetic specific heat (red) on the right scale and low-temperature ZFC dc magnetization (black) on the left scale.

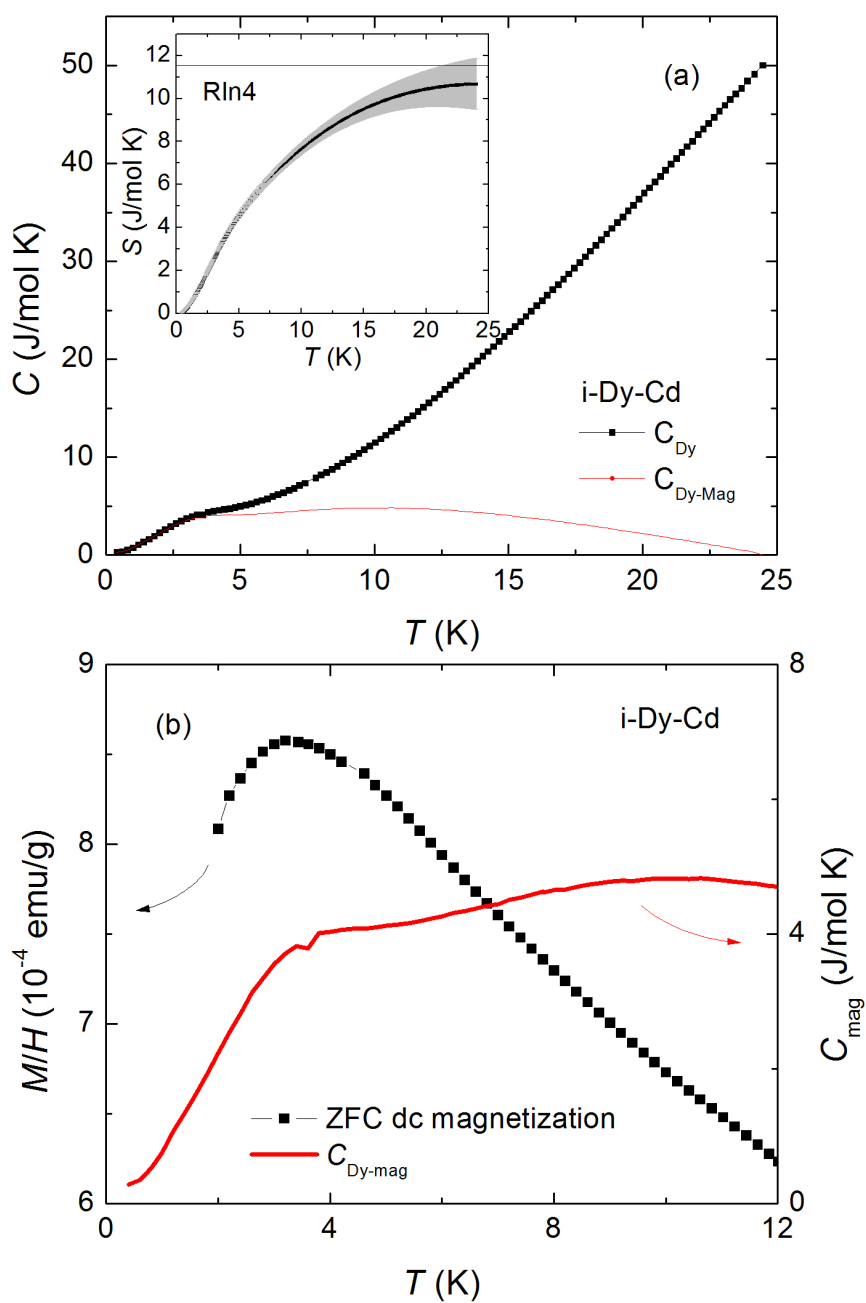


Figure 4.15 (a) Temperature-dependent specific heat of i-Dy-Cd. The red solid line shows the magnetic specific heat. The inset show the magnetic entropy with error bars. (b) Low-temperature magnetic specific heat (red) on the right scale and low-temperature ZFC dc magnetization (black) on the left scale.

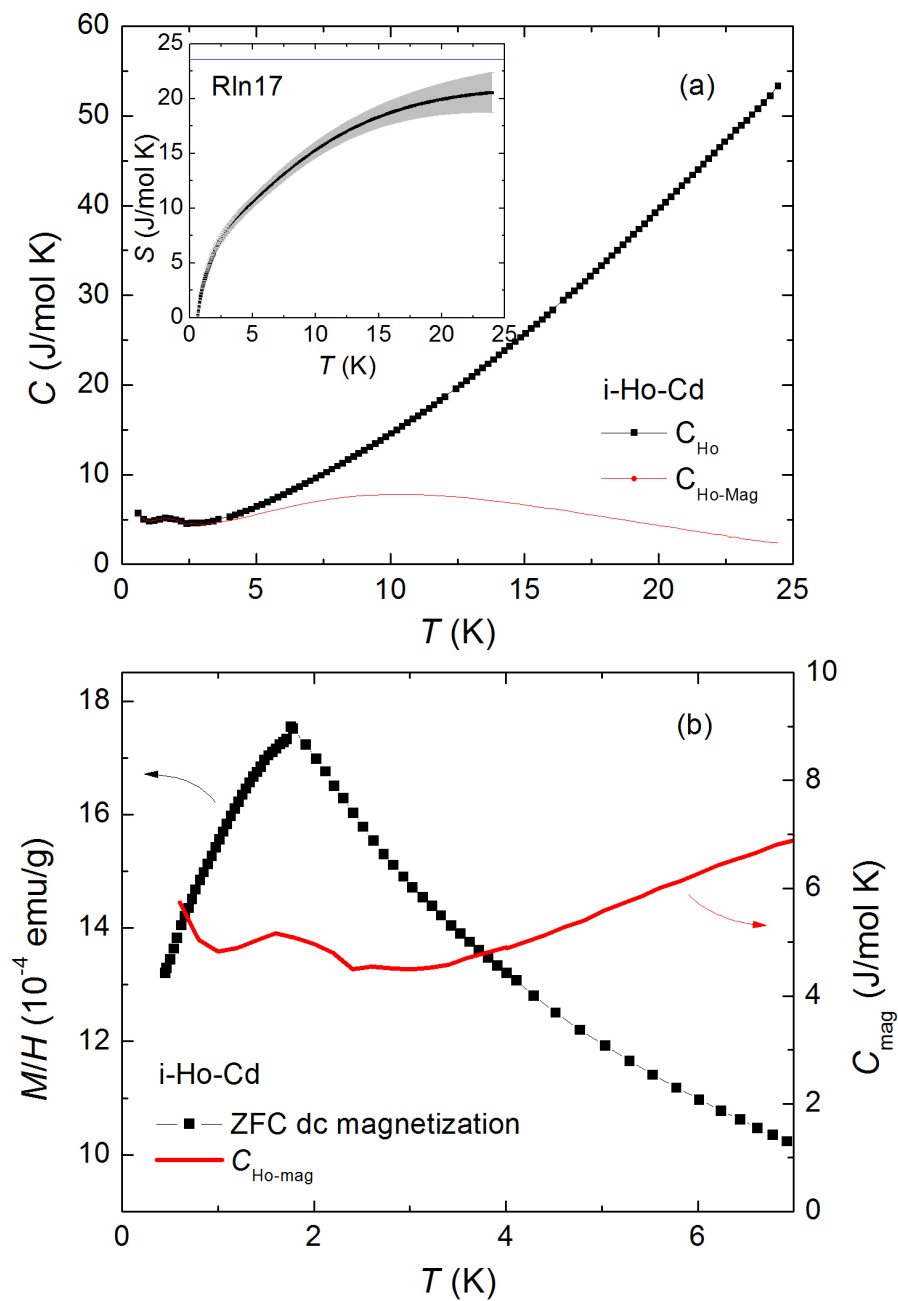


Figure 4.16 (a) Temperature-dependent specific heat of i-Ho-Cd. The red solid line shows the magnetic specific heat. The inset shows the magnetic entropy with error bars. (b) Low-temperature magnetic specific heat (red) on the right scale and low-temperature ZFC dc magnetization (black) on the left scale.

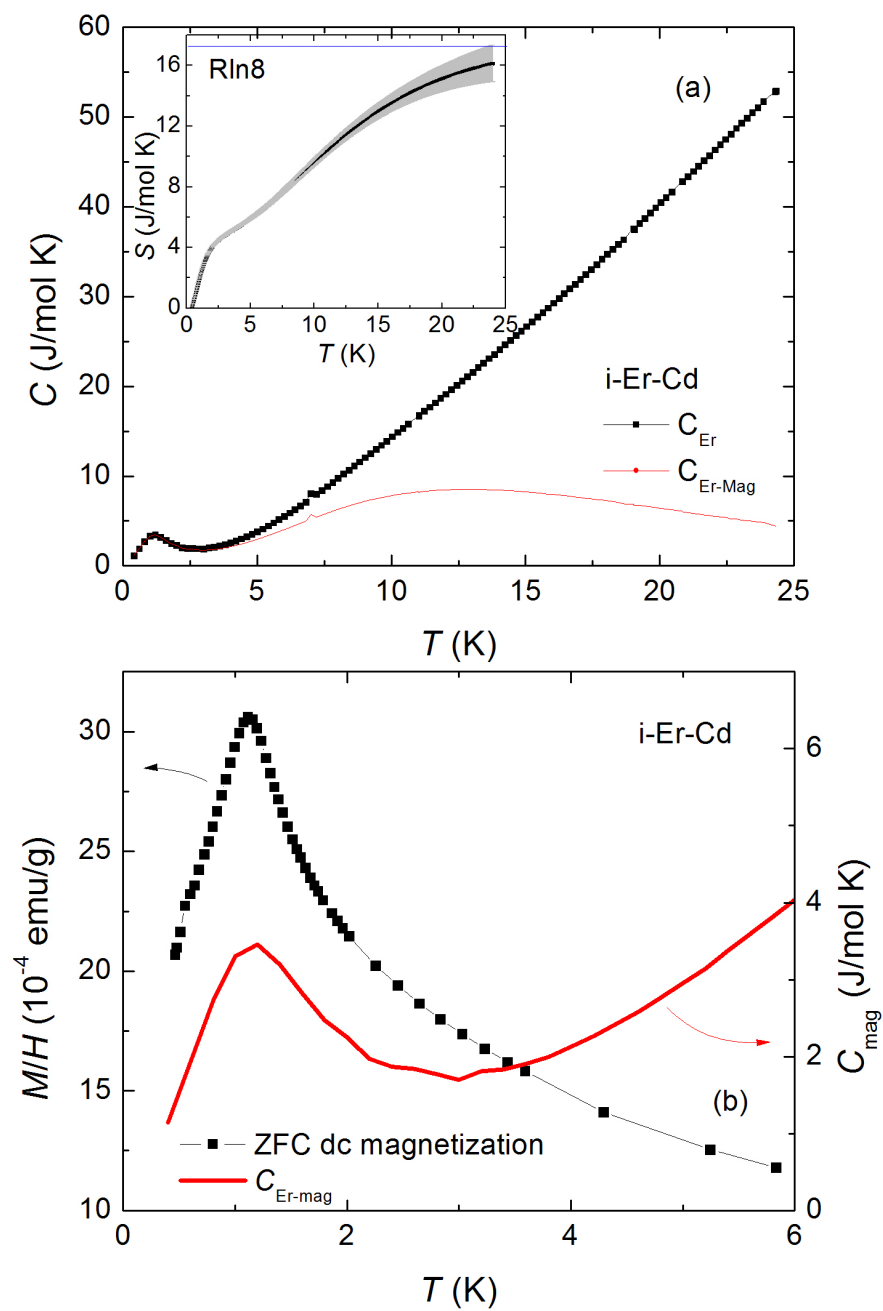


Figure 4.17 (a) Temperature-dependent specific heat of i-Er-Cd. The red solid line shows the magnetic specific heat. The inset shows the magnetic entropy with error bars. (b) Low-temperature magnetic specific heat (red) on the right scale and low-temperature ZFC dc magnetization (black) on the left scale.

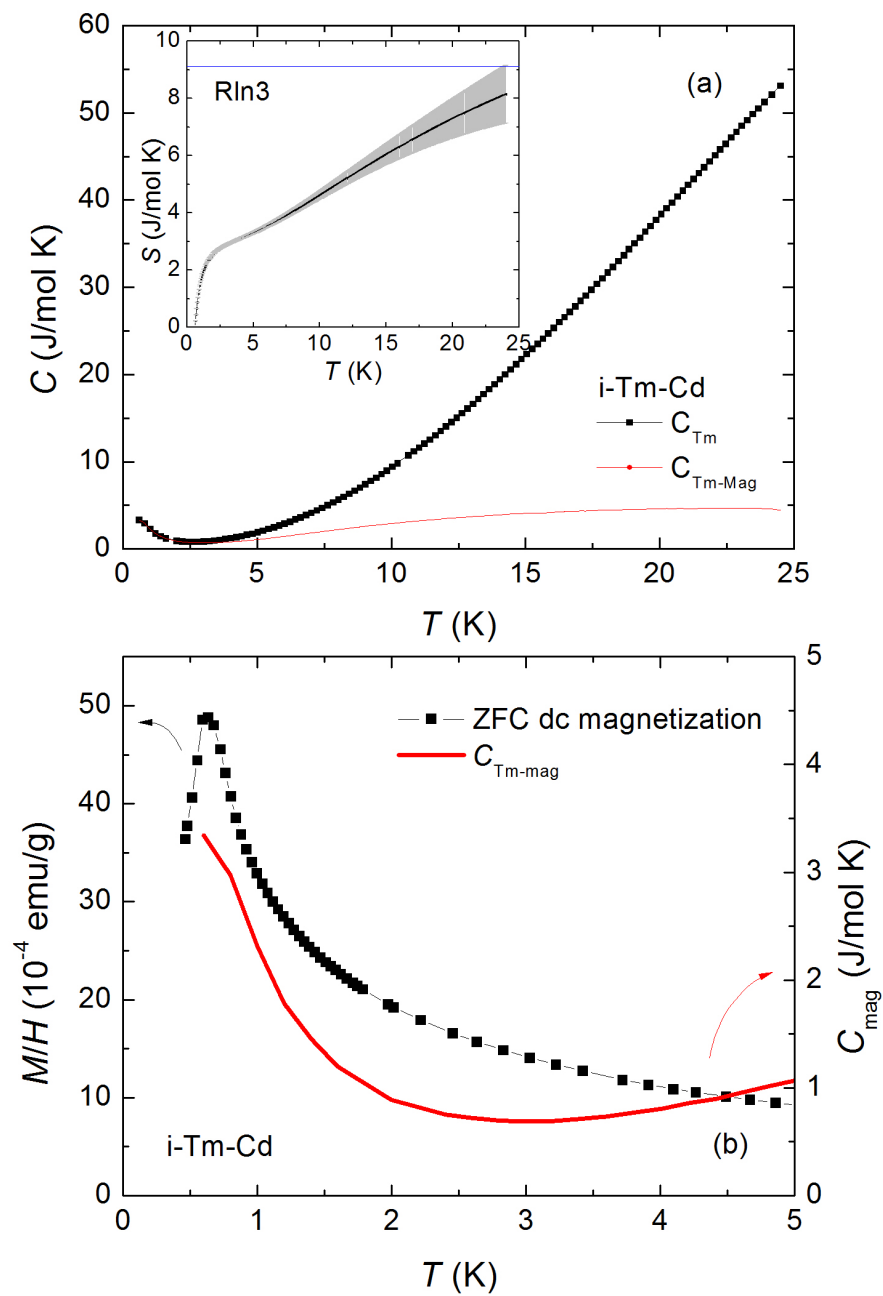


Figure 4.18 (a) Temperature-dependent specific heat of i-Tm-Cd. The red solid line shows the magnetic specific heat. The inset shows the magnetic entropy with error bars. (b) Low-temperature magnetic specific heat (red) on the right scale and low-temperature ZFC dc magnetization (black) on the left scale.

4.5 Resistivity of *i-R-Cd*

Due to a low density of states at the Fermi level, quasicrystals are generally bad metals or sometimes on the edge of a metal-insulator transition[76; 89]. The resistivity of quasicrystalline material is nearly temperature-independent, or decreases weakly with increasing temperature. Because of the high resistivity of quasicrystals, a small amount of highly conducting impurity in/on the sample is sufficient to result in significant changes in measured resistance.

In our initial attempts to measure the electric resistance of *i-R-Cd*, a standard four-probe technique was used and Pt wires were attached to an as-grown sample like shown in Fig. 4.2(b). In Fig. 4.19(a), the temperature-dependent resistance of as-grown *i-Tb-Cd* is presented (green triangles). A sizeable residual resistance ratio (RRR) of about 4.5 was obtained, which is distinct from known quasicrystal behavior[76]. However, the shape of the observed resistance can result from measuring a nearly temperature-independent resistor (the quasicrystal sample) connected in series and in parallel with a highly conducting metal, in this case, Cd.

We tried to remove the residual Cd in the following way. The sample is sealed in a long quartz tube under vacuum, in which the sample is held at 200°C whereas the other end of the tube is held at room temperature. Due to its high vapour pressure, Cd can be easily removed from the sample by this heat treatment. In preparing the sample for resistance measurements, polishing as the first step could remove residue surface Cd and the heat treatment, as the second step, could remove part of the remaining Cd that was trapped in exposed dendritic grain boundaries. After the polished sample went through the heat treatment for 3 days, a nearly temperature-independent resistance was indeed observed, as shown in Fig. 4.19(a) by black squares. However, as illustrated by the inset of Fig. 4.19(b), the resistance of *i-Tb-Cd* still decreases below about 100 K, and a clear magnetic field dependence of this low-temperature resistance emerges. For clarity, the resistance of elemental Cd was also measured. The resistance sample of Cd was prepared by pressing an elemental Cd droplet to reduce the thickness. A RRR of about 2200 was observed [Fig. 4.19(b)]. The magnetoresistance increases at low temperatures as expected in general for a simple, high purity, metal, and follows Kohler's rule[152; 153]. The resemblance of the low-temperature magnetoresistance of *i-Tb-Cd* to that

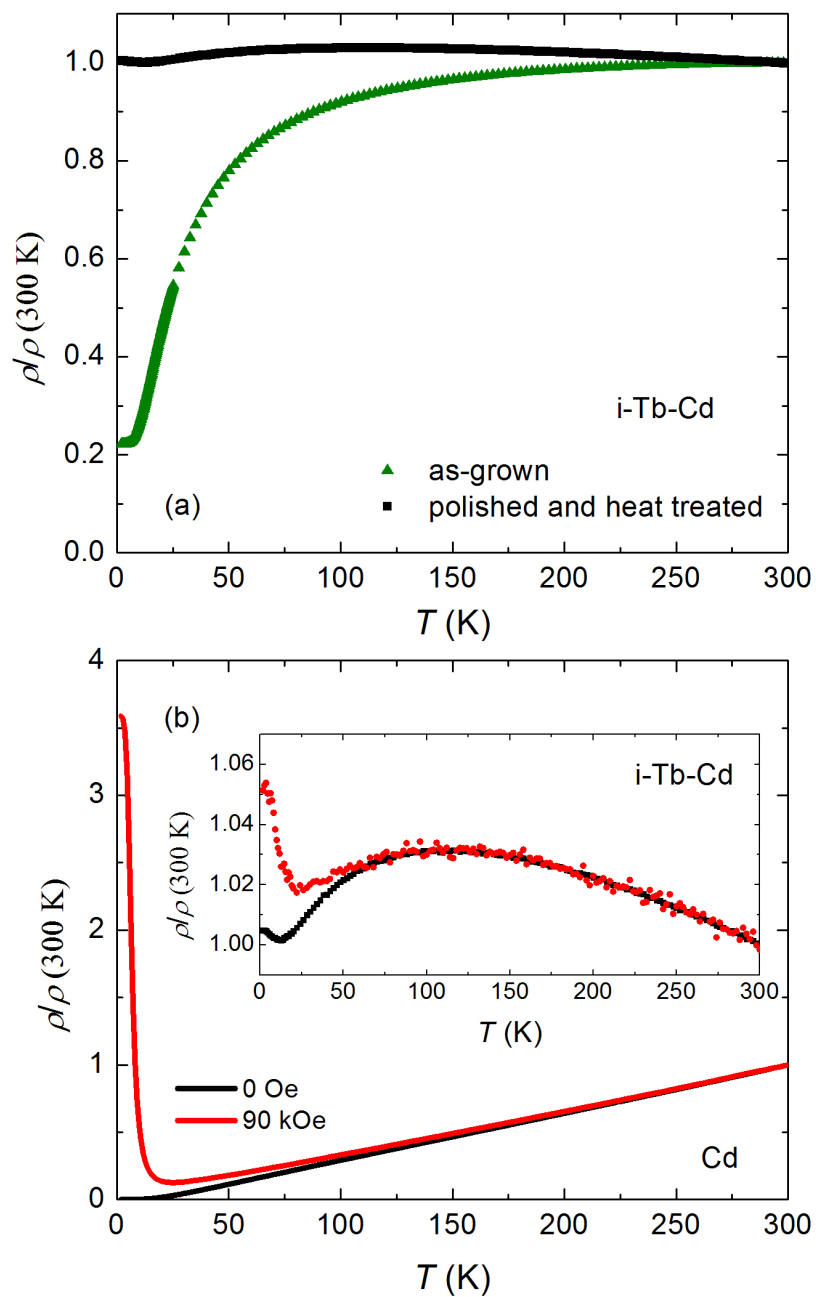


Figure 4.19 (a) Zero-field, normalized temperature-dependent resistance for i-Tb-Cd: as-grown sample (green triangle); polished and heat treated sample (black square). (b) Normalized temperature-dependent resistance of elemental Cd (polished and heat treated i-Tb-Cd sample in the inset) measured at zero field (black) and at 90 kOe (red).

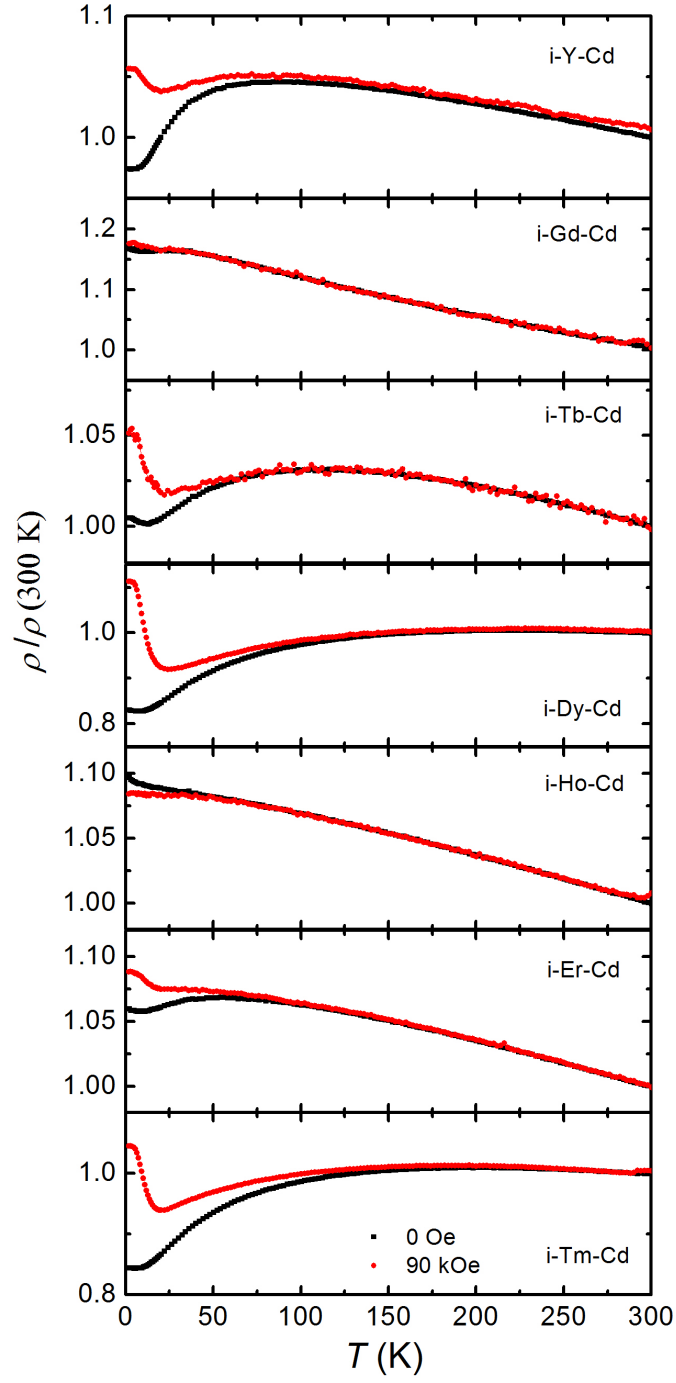


Figure 4.20 Normalized temperature-dependent resistance for i - R -Cd ($R = \text{Y, Gd-Tm}$) at zero field (black) and at 90 kOe (red). The value of resistivity is about $300\ \mu\Omega$ cm at room-temperature.

of Cd suggests that even after polishing and the heat treatment, Cd that is trapped within the quasicrystal might still affect the resistance data. Therefore, it is likely that, despite efforts to eliminate Cd, the features observed are a combination of intrinsic quasicrystal properties plus a minor amount of conducting metal.

In Fig. 4.20, the normalized resistance data are measured in zero-field and 90 kOe for all *i-R*-Cd samples shown. The room-temperature resistivity of *i-R*-Cd quasicrystals is approximately $300 \mu\Omega \text{ cm}$. Compared with other quasicrystal systems, this is close to that in *i-R*-Mg-Zn[67] and *i*-Yb-Cd[92] and is an order of magnitude smaller than in Al-Pd-Mn and Al-Cu-Fe[76; 91]. If an assumption of a low intrinsic magnetoresistance of quasicrystals is made, it seems that *i*-Gd-Cd and *i*-Ho-Cd might be the best representation for single phase quasicrystal behavior. The resistance of *i*-Gd-Cd and *i*-Ho-Cd tends to increase with decreasing temperature. At 1.8 K, the magnetoresistance is small, and negative for *i*-Ho-Cd and positive for *i*-Gd-Cd. In other quasicrystal systems, both positive and negative magnetoresistance has been observed[90]. Besides the negative slope of zero-field resistance at room temperature, the resistance of *i-R*-Cd also exhibits a broad dome at lower temperature, for example, $\sim 100 \text{ K}$ for *i*-Tb-Cd and $\sim 40 \text{ K}$ for *i*-Gd-Cd. Although this feature might be affected by metallic Cd, similar dome-shape resistances had been observed in many other quasicrystals as well and was explained by weak localization with strong spin-orbit coupling[76; 90; 91; 92; 154] and competing inelastic scattering in the presence of weak localization[155]. It worth pointing out that the existence of such a broad maxima was shown to be closely related to the sample preparation method and the sample quality[67; 156]. In addition, at low temperatures, a small upturn or saturation in resistance exists, which sometimes appears as well in other aforementioned quasicrystals that exhibit a broad dome in resistance. The temperature at which the upturn or saturation occurs does not match dc magnetization features.

It is important to point out that no sharp feature can be found in any of the data sets shown in Fig. 4.20 that can be associated with long-range magnetic ordering. This is consistent with the lack of λ -shaped features in specific heat measurements shown above. For spin-glass systems, this is usually the case. However, it should be noted that for intermetallic compounds, resistive features that are associated with long range magnetic transitions can sometimes be

obscure, even for systems with a much larger RRR than *i-R*-Cd, for example in the case of *R*Ni₂Ge₂[15].

4.6 Discussion

In terms of the magnetic ground state, for *i*-Gd-Cd, I have presented data that support the identification of $T_{\max}$ as T_f , the spin glass freezing temperature. These data include: (1) a cusp in dc magnetization; (2) a frequency-dependent freezing temperature; (3) a narrow third order magnetic susceptibility, χ_3 , at the freezing temperature; (4) a broad maximum in temperature-dependent specific heat with the temperatures of the maximum somewhat higher than the cusp temperature in dc magnetization. According to the general understanding of the experimental characteristics of spin-glasses[63; 65], *i*-Gd-Cd can be considered to be a spin-glass below $T_f = 4.6$ K. Unfortunately, we were unable to obtain as extensive sets of data for the rest of the *i-R*-Cd ($R = \text{Tb-Tm}$) series, especially χ_3 . In discussion of the magnetization features, *i*-Tb-Cd and *i*-Dy-Cd are of special interest for their non-cusp-like ZFC dc magnetization data. However, in view of the similarity in resistance and specific heat data, it is likely that neither *i*-Tb-Cd nor *i*-Dy-Cd exhibit long-range magnetic ordering. Further investigations of *i*-Tb-Cd and *i*-Dy-Cd are needed to elucidate the origin of this non-standard spin-glass-like behavior in the magnetization. The rest of the local-moment-bearing members, *i-R*-Cd ($R = \text{Ho-Tm}$), behave closer to a canonical spin-glass in terms of their dc magnetization. To obtain χ_3 for these three members, ac magnetization measurements below 2 K are needed, which is currently beyond our instrumental capability. It is worth pointing out that although broadened maxima, rather than λ -like peaks, were observed in the specific heat measurements, the maximum temperatures are close to, if not equal to, $T_{\max}$, whereas in canonical spin-glass systems, the broad maximum in specific heat often exceeds the freezing temperature, T_f , by about 20%-50%[62; 63].

The discovery of *i-R*-Cd ($R = \text{Y, Gd-Tm}$) also allows for the study of systematic trends across this binary, local-moment-bearing quasicrystal series. As shown in Fig. 4.3, there is a standard lanthanide contraction associated with changing R . Despite possible slight change in stoichiometry, there is no clear difference between *i*-Gd-Cd and *i*-Tm-Cd in terms of strain and phason strain, or in other words, sample quality.

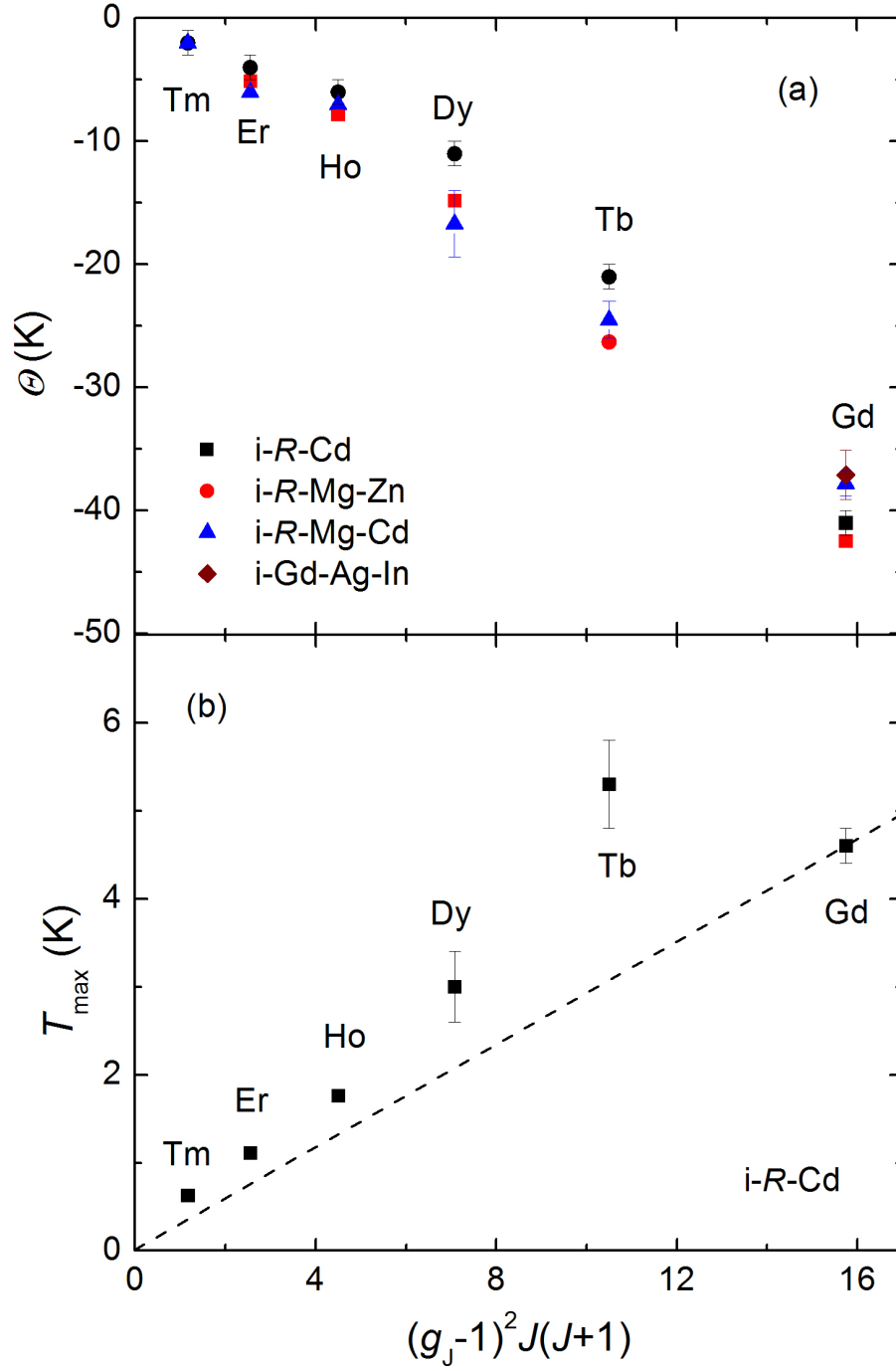


Figure 4.21 (a)/(b) Changes of $\Theta/T_{\max}$ as a function of de Gennes factor: $(g_J-1)^2 J(J+1)$. Data for i-R-Mg-Zn, i-R-Mg-Cd and i-Gd-Ag-In are obtained from Refs. [67; 98; 99; 157]. Dashed lines are guides to the eyes.

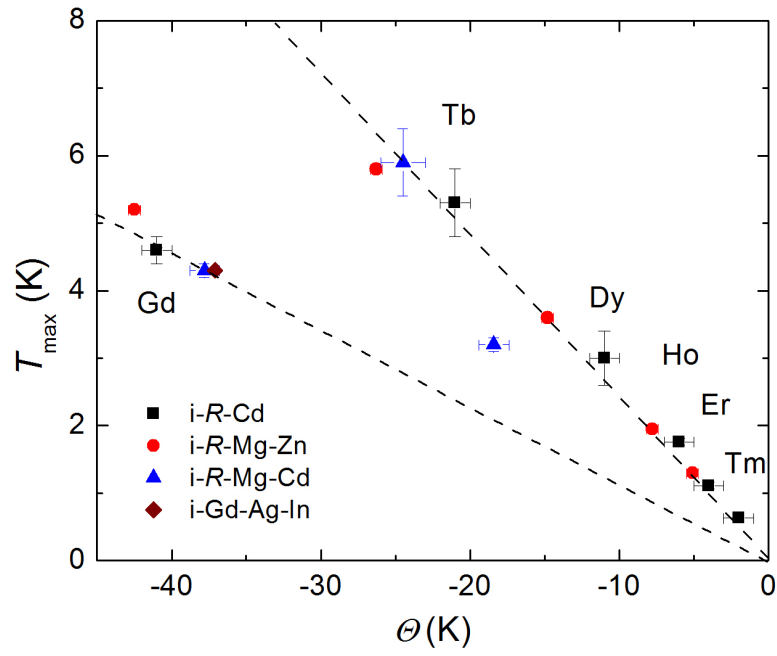


Figure 4.22 Changes of $T_{\max}$ as a function of Θ . Data for i-*R*-Mg-Zn, i-*R*-Mg-Cd and i-Gd-Ag-In are obtained from Refs. [67; 98; 99; 157]. Dashed lines are guides to the eyes.

We now return to the high-temperature $H/M(T)$ measurements shown in Fig. 4.5. In Fig. 4.21(a), the Weiss temperature, Θ , is shown together with values previously measured for other ternary rare-earth-containing quasicrystalline compounds including i-*R*-Mg-Zn[67], i-*R*-Mg-Cd[122] and i-Gd-Ag-In[125] as a function of de Gennes factors (dG). For all of these compounds, Θ is negative, denoting predominantly AFM exchange interactions, and roughly scales with the de Gennes factor, as expected. What is most striking, however, is that the values for Θ are very consistent from system to system even though these compounds manifest different compositions and structural classes. i-*R*-Mg-Zn, for example, is a ternary face-centred (F-type) icosahedral quasicrystal characterized by Bergman-type clusters, whereas it has been shown that i-*R*-Cd is a binary P-type icosahedral quasicrystal characterized by rhombic triacontahedral clusters. Nevertheless, the strength of the AFM exchange, characterized by Θ , and its monotonic dependence on the de Gennes factor, remains remarkably similar across the spectrum of structures. This may simply be a consequence of the presence, in all cases, of a similar electronic environment associated with the Hume-Rothery mechanism for the stabilization of quasicrystals[76] or from close similarities in the local environments of the *R* ions for all of these structures. Clearly, this point deserves further experimental and theoretical study.

$T_{\max}$ is plotted against dG factor in Figs. 4.21(b). It shows a non-monotonic behavior. The clear deviation from de Gennes scaling is evidenced by a higher $T_{\max}$ of i-Tb-Cd and i-Dy-Cd in Fig. 4.21(b). In magnetically ordered systems, it was argued that CEF effects can enhance the ordering temperature in materials with a strong axial anisotropy[13; 158]. In quasicrystals, although anisotropy is not well defined, the CEF effects do exist for rare earth ions that have a finite orbital angular momentum of their $4f$ electrons. It might be possible that a small CEF effect[151] helps to stabilize the freezing in this geometrically frustrated system. In Fig. 4.22, $T_{\max}$ is plotted against Θ . It shows a clear difference in $T_{\max}/\Theta$ between Gd^{3+} and the rest of the members as indicated by the dashed lines. i-Gd-Cd has a lower $T_{\max}$ for a given Θ . In Ref. [157], this phenomena was associated with the difference between Heisenberg like ion (Gd^{3+}) and non-Heisenberg like ion (Tb^{3+} - Tm^{3+}). It is worth pointing out that, in addition to the similarity in Curie-Weiss temperatures (Fig. 4.21(a)), the value for $T_{\max}/\Theta$ is also similar for different rare earth bearing quasicrystal systems[67; 98; 99; 157]. In the plot of $T_{\max}/\Theta$, the

slope is ~ 0.11 for Heisenberg-like ion and ~ 0.25 for non-Heisenberg-like ions. Both numbers indicate a moderate degree of geometrical frustration[159].

4.7 Conclusions

During this study, seven binary quasicrystals, i - R -Cd ($R = \text{Y, Gd-Tm}$), were discovered via high-temperature solution growth technique, based on the proposal that quasicrystalline phases may exist next to their corresponding approximant phases[131]. These newly discovered quasicrystals represent the world's first group of magnetic binary quasicrystals (except for non-magnetic i -Y-Cd). They were characterized by detailed elemental analysis, structural, thermodynamic and transport measurements.

Structurally, i - R -Cd has a primitive (P-type) quasilattice with Tsai-type clusters. Across the rare earth series, the lanthanide contraction is followed. The magnetic susceptibility of i -Y-Cd is essentially temperature-independent and weakly diamagnetic. The low-temperature specific heat of i -Y-Cd reveals a Debye temperature of about 140 K. Supported by the magnetization and specific heat data, i -Gd-Cd can be categorized as a spin-glass below $T_f = T_{\max} = 4.6$ K. The dc magnetization data of i -Tb-Cd and i -Dy-Cd do not show a typical cusp-like shape but rather a broad feature with a clear temperature spacing between $T_{\max}$ and T_{irr} . Further study is needed to explain this unconventional behavior. However, based on the similarity of temperature-dependent resistance and specific heat measurements, it is unlikely that i -Tb-Cd or i -Dy-Cd exhibits long-range magnetic ordering. i - R -Cd ($R = \text{Ho-Tm}$) show conventional spin-glass behavior in their magnetization, but with the maximum in the magnetic component of specific heat occurring at temperatures closer and closer to $T_{\max}$. Further investigation is needed to explain this trend. A deviation from the de Gennes scaling for the moment-bearing members was observed. It is likely this deviation is a consequence of CEF effects, which helps to stabilize the freezing state of magnetic rare earth ions with finite orbital angular momentum. Resemblance was also noted in the value of T_f/Θ between i - R -Cd and another rare earth based quasicrystal systems. Long range magnetic ordering in quasicrystals is still missing. However, further studies on antiferromagnetically ordered RCd_6 and spin glass i - R -Cd may reveal hints of how to achieve a long range magnetic order in quasicrystals, if it exists.

CHAPTER 5. PHYSICAL PROPERTIES OF SINGLE CRYSTALLINE RMg_2Cu_9 ($R = Y, Ce-Nd, Gd-Dy, Yb$) AND THE SEARCH FOR IN-PLANE MAGNETIC ANISOTROPY IN HEXAGONAL SYSTEMS

Now we move on to conventional lattices where translational symmetry exists. In this chapter, we focus on the magnetic anisotropy of rare earth local moments. This work has now been posted in Ref. [160]

Rare earth compounds are often studied for their magnetic properties when the rare earth ion is the only moment bearing element and when the rare earth fully occupies a single crystallographic site[5; 15; 161; 162; 163; 164; 165]. Magnetic anisotropies that are consistent with Heisenberg, Ising, and 4-state-clock models can be found originating from rare earth ions in the appropriate site symmetries[15; 162; 163; 164; 165; 166]. One of the interests is to look for in-plane magnetic anisotropy in a strongly planar system. Over the past decades, several studies had been carried out for systems with tetragonal symmetry, for example: $HoNi_2B_2C$ [162] and $DyAgSb_2$ [163] where a 4-state clock model was realized. Several attempts had been made to find an analogy in a hexagonal symmetry[164; 165]. However, the local symmetries of rare earth ions in Ref. [164; 165] are of orthorhombic $m2m$ symmetry, even though the crystal structures have a hexagonal space group.

The RMg_2Cu_9 series of compounds were recently systematically synthesized and structurally identified[167]. Their structure can be derived from the $CeNi_3$ type by replacing one of the two distinct rare earth sites with Mg atoms. As a consequence, there is only one rare earth site left in RMg_2Cu_9 and it has a hexagonal site symmetry of $\bar{6}m2$. The environment of R in RMg_2Cu_9 is very similar to that in RCu_5 and each layer that contains R ions is separated from another by a layer of Cu-centered Cu_6Mg_6 icosahedra (see Fig. 5.1). RMg_2Cu_9 is reported to exist for $R = Y, La-Nd, Sm-Ho, Yb$. The reported lattice parameters follow a rough lanthanide

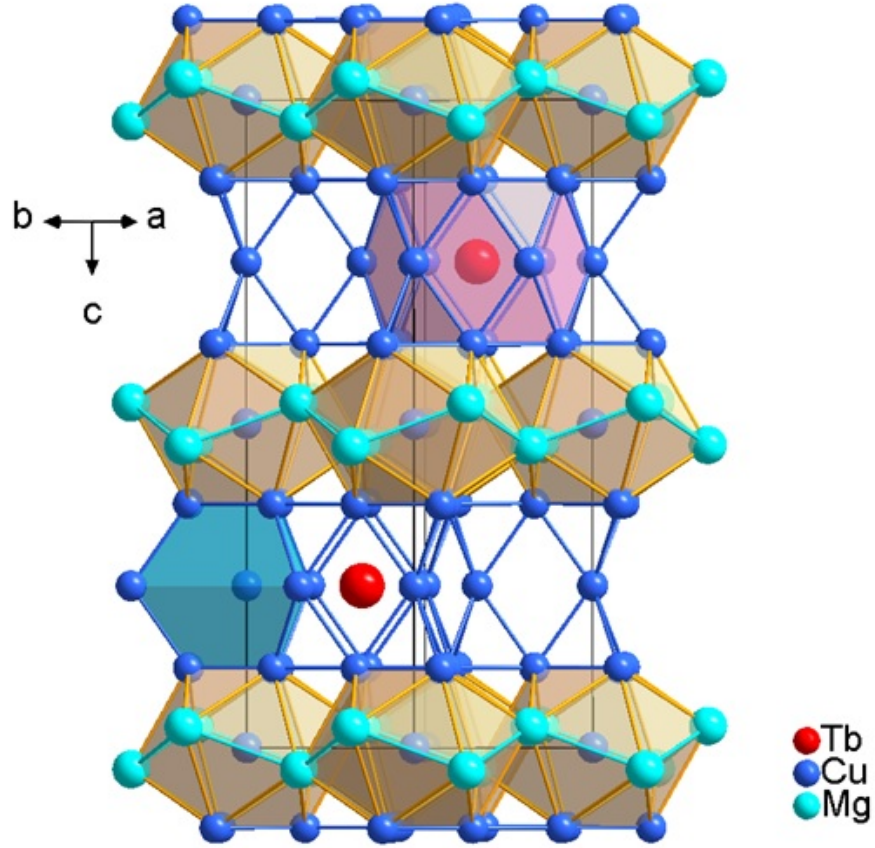


Figure 5.1 Unit cell of TbMg_2Cu_9 . Elements are represented by solid spheres: Tb(red), Cu(blue) and Mg (cyan).

contraction, except for possibly divalent Eu and Yb[167].

Little had been characterized in terms of the physical properties for these compounds. Prior to the structural study, single crystals of CeMg_2Cu_9 were grown by melting and slow cooling of a stoichiometric composition[168; 169]. It was reported to have an antiferromagnetic transition at 2.5 K. The magnetic transition temperature decreases with increasing pressure and seems to disappear at ~ 2.5 GPa[168; 169]. Polycrystalline EuMg_2Cu_9 seems to have a ferromagnetic transition at around 25 K[170]. TbMg_2Cu_9 was studied as part of a search for hydrogen storage materials and was reported to order antiferromagnetically at around 10 K[171].

In RMg_2Cu_9 , since the rare earth is the only moment-bearing element and has one unique site, these compounds could potentially be good candidates to realize a 6-state-clock model.

In this chapter, we present the results of structural measurements as well as temperature-dependent specific heat, temperature- and field-dependent electrical resistivity and temperature-, field- and angle-dependent magnetization on RMg_2Cu_9 single crystals. Motivated by these results, in-plane magnetic anisotropy measurements on Y diluted $TbMg_2Cu_9$ and $DyMg_2Cu_9$ were made and will be discussed in the context of crystal electric field splitting.

5.1 Crystal structure

Single crystals of RMg_2Cu_9 were grown using a high-temperature solution growth method[108]. Starting elements were held in a 3-cap tantalum crucible[83] and sealed in a silica jacket under vacuum. Due to the complexity of the R -Mg-Cu ternary phase space, the starting stoichiometries vary. For $R = Ce-Nd, Tb$, the starting elemental ratio was: $R:Mg:Cu=2.5:20.4:77.1$. For $R=Y, Gd, Dy, Yb$ and Y with 1% Tb/Dy, the starting elemental ratio was : $R:Mg:Cu=5:18:77$. The ampoule assemblies were gradually heated up to 1180 °C and decanted, after a 3-day slow cooling. For $R = Ce-Nd, Dy$, the growths were decanted at 730 °C; for $R = Y, Gd$, the growths were decanted at 745 °C; for $R = Tb, Yb$, the growths were decanted at 760 °C. Single crystals are pale-copper-metallic in color and plate-like with the crystallographic c -axis perpendicular to the plate. In Fig. 5.2(d), a typical sample of $PrMg_2Cu_9$ is shown on a millimeter grid paper. A clear six-fold rotational symmetry can be seen from the Laue pattern when measuring along [001] [Fig. 5.2(a)]. In-plane orientation in real space was also identified and corresponding Laue patterns are illustrated in Fig. 5.2(b-c).

Crystallographic information was obtained by both single crystal x-ray diffraction and powder x-ray diffraction. Single crystal x-ray diffraction data were collected using a Bruker SMART APEX II CCD area-detector diffractometer[172] equipped with Mo K_α ($\lambda = 0.71073\text{\AA}$) radiation. Integration of intensity data was performed by the SAINT-Plus program, absorption corrections[173] by SADABS , and least-squares refinements by SHELXL[174], in the SMART software package. Powder x-ray diffraction data were collected using a Rigaku Miniflex II diffractometer and analysed using GSAS, as described in Chapter 3. Single crystal refinement data and atomic coordination information for $TbMg_2Cu_9$ are listed in Table 5.1 and Table 5.2. A unit cell of $TbMg_2Cu_9$ is illustrated in Fig. 5.1.

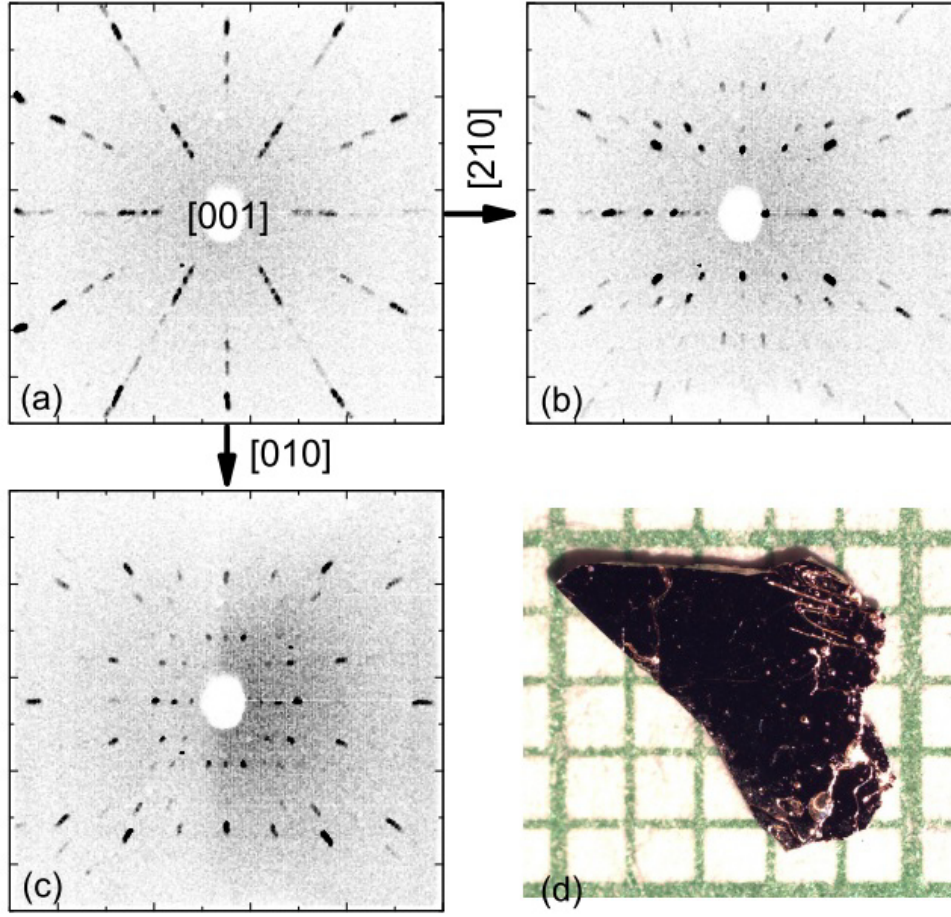


Figure 5.2 Laue pattern of RMg_2Cu_9 along (a) [001] (b) [210] and (c) [010]. (d) Single crystal of PrMg_2Cu_9 on a millimeter grid paper. [001] is perpendicular to the facet shown.

Lattice parameters and unit cell volumes obtained from powder x-ray diffraction are listed in Table 5.3 and unit cell volumes are plotted against the rare earth atomic number in Fig. 5.3. Generally, the lanthanide contraction is followed. YMg_2Cu_9 has a volume close to TbMg_2Cu_9 and DyMg_2Cu_9 . The volume of YbMg_2Cu_9 is significantly larger than what would be expected from the lanthanide contraction for Yb^{3+} . This is consistent with the larger size of divalent Yb. Results from the current study agree with previously reported values[167].

Table 5.1 Single crystal crystallographic data for TbMg₂Cu₉ at room temperature.

Chemical formula	TbMg ₂ Cu ₉
Formula weight (g/mol)	779.40
Space group	P6 ₃ /mmc
Unit cell dimensions (Å)	a = 5.0050(7) c = 16.207(3)
Volume (Å ³)	351.59(12)
Z	2
Density (g/cm ³)	7.362
Absorption coefficient (mm ⁻¹)	36.605
Reflections collected	1571 [R(int)=0.0527]
Data/restraints/parameters	213/0/8
Goodness-of-fit on F ²	1.014
Final R indices [I > 2sigma(I)]	R1=0.0385,wR2=0.0936
R indices (all data)	R1=0.0464, wR2=0.0983
Largest diff. Peak and hole (e/Å ³)	2.823 and -3.034

Table 5.2 Atomic coordinates and equivalent isotropic displacement parameters for TbMg₂Cu₉ with full occupancy.

Atoms	Wyck.	Symm.	x	y	z	U _{eq} (Å ²)
Tb	2d	-6m2	2/3	1/3	1/4	0.016(1)
Mg	4f	3m.	2/3	1/3	0.4669(5)	0.012(1)
Cu1	12k	.m.	0.1682(2)	2x	0.3768(1)	0.014(1)
Cu2	2c	-6m2	1/3	2/3	1/4	0.015(1)
Cu3	2b	-6m2	0	0	1/4	0.018(1)
Cu4	2a	-3m	0	0	1/2	0.015(1)

5.2 Physical properties of RMg₂Cu₉

5.2.1 YMg₂Cu₉

Y does not have a 4f shell and bears no local-moment. Generally, a relatively temperature-independent magnetic susceptibility is expected due to Pauli paramagnetic, Landau diamagnetic, and core diamagnetic contributions. Details in Fermi surface may result in, albeit slight, magnetic anisotropies[15; 175]. The magnetic susceptibility of YMg₂Cu₉ is weakly temperature-dependent as shown in Fig. 5.4(a). The compound is diamagnetic at room temperature with $|\chi_c| < |\chi_{ab}|$. As temperature decreases, a broad minimum develops at around 100 K, after

Table 5.3 Lattice parameters and unit cell volumes of RMg_2Cu_9 ($R = Y, Ce-Nd, Gd-Dy, Yb$) obtained from powder x-ray diffraction. The uncertainty is about 0.2% for lattice parameter values.

Compound	a (Å)	c (Å)	Volume (Å ³)
YMg ₂ Cu ₉	5.00	16.19	351.1
CeMg ₂ Cu ₉	5.05	16.29	359.5
PrMg ₂ Cu ₉	5.04	16.26	357.6
NdMg ₂ Cu ₉	5.03	16.27	357.1
GdMg ₂ Cu ₉	5.02	16.21	353.2
TbMg ₂ Cu ₉	5.00	16.21	351.4
DyMg ₂ Cu ₉	5.00	16.20	351.1
YbMg ₂ Cu ₉	5.02	16.18	353.7

which the magnetization increases. At 2 K, $\chi_c > 0$. This is consistent with field-dependent magnetization data measured at 2 K [Fig. 5.4(d)]. It is possible that some very low-level of magnetic impurities contribute to the low-temperature broad rise in magnetization as well as the non-linear, low-temperature $M(H)$ data.

The temperature-dependent specific heat data for YMg₂Cu₉ are shown in Fig. 5.4(c). From the linear fit of C/T versus T^2 , we estimated the Debye temperature to be around 320 K and the electronic specific heat, γ , to be around 15 mJ/mol-K² or ~ 1 mJ/mole-atomic-K². In order to estimate the magnetic specific heat, C_{mag} , associated with other local-moment-bearing members, the specific heat of YMg₂Cu₉ was used to estimate the non-magnetic part of the specific heat, $C_{non-mag}$, with the molar mass difference taken into account according to the Debye model[33].

The resistivity of YMg₂Cu₉ shows typical metallic behavior. The residual resistance ratio (RRR) is about 2.2. Magnetoresistance measured at 1.9 K roughly follows $H^{1.5}$ with an increase of 6% at 55 kOe.

5.2.2 CeMg₂Cu₉

The magnetic susceptibility of CeMg₂Cu₉ is anisotropic with $\chi_{ab} > \chi_c$. Fig. 5.5(a) shows a very clear Curie-Weiss behavior (especially for $\chi_{poly} = (\chi_c + 2\chi_{ab})/3$) with estimated ef-

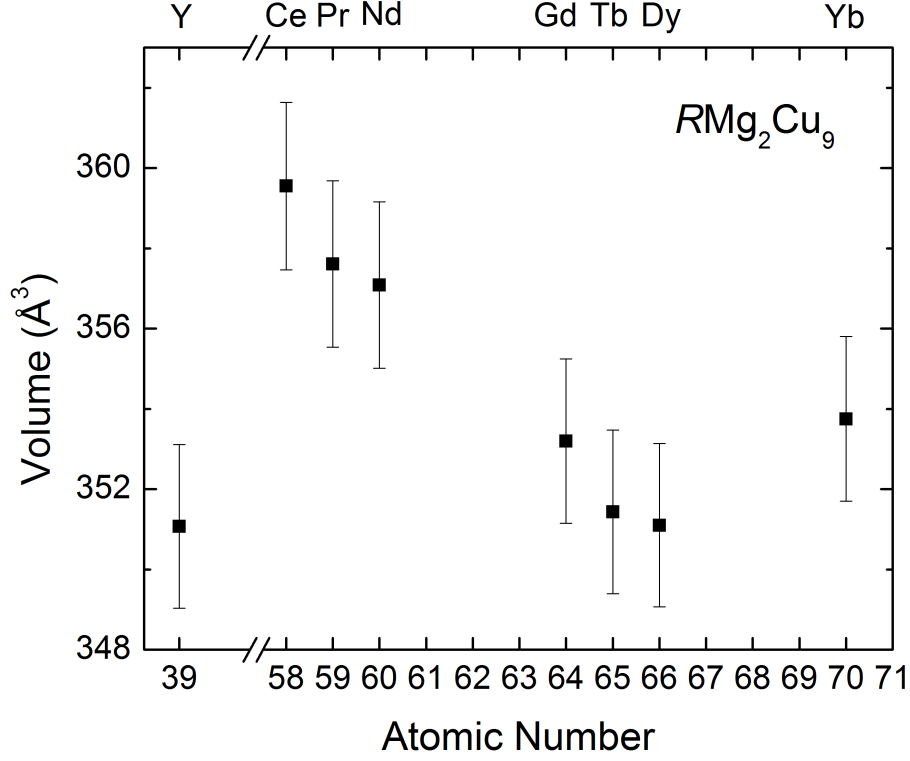


Figure 5.3 Unit cell volumes of RMg_2Cu_9 as a function of rare earth atomic number.

fective moment of Ce, $\mu_{eff} = 2.3 \mu_B$, close to the theoretical value for Ce^{3+} ($2.5 \mu_B$). The anisotropic Curie-Weiss temperatures are: $\Theta_c = -43$ K, $\Theta_{ab} = -1$ K and polycrystalline average $\Theta_{poly} = -12$ K. At around 2 K, a change in $M(T)/H$ [inset of Fig. 5.5(a)] suggests a possible antiferromagnetic transition.

In addition to the reported magnetic transition at around 2 K[168; 169], one more phase transition at around 1.5 K was observed in the present study. Features appear in resistivity [Fig. 5.5(b)] are consistent with the temperature-dependent specific heat data shown in Fig. 5.5(c). The inset to Fig. 5.5(c) shows $C_p(T)$, and $d\rho/dT$ data on and enlarged, low-temperature scale. Transitions at around 2.1 K and 1.5 K are apparent.

The electronic specific heat estimated above the transition temperature from 10 to 15 K is $\gamma \sim 58$ mJ/mol-K², which is about 4 times higher than that for YMg_2Cu_9 . It should be noted, though, that this value is smaller than previously reported values (115-160 mJ/mol-

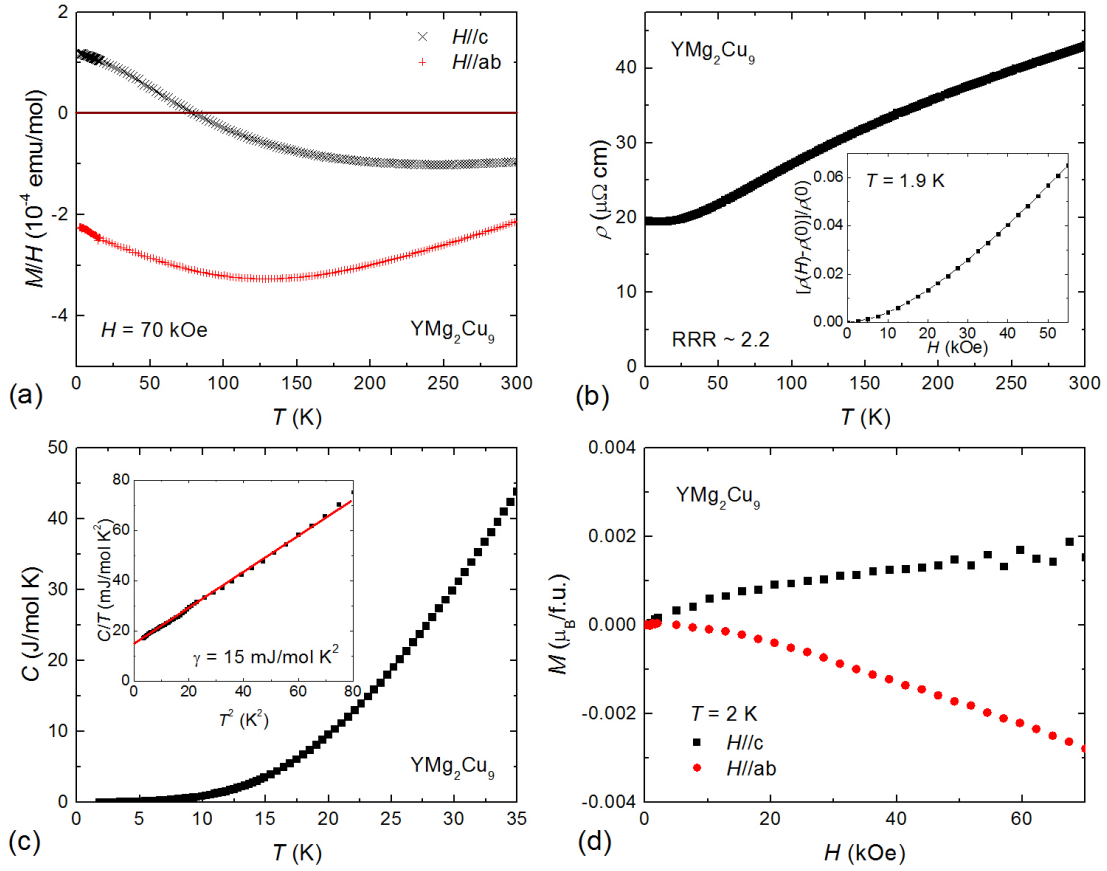


Figure 5.4 (a) Anisotropic temperature-dependent magnetization of YMg_2Cu_9 measured at 70 kOe. (b) Temperature-dependent resistivity. Inset: magnetoresistance measured at 1.9 K up to 55 kOe. (c) Temperature-dependent, zero-field specific heat (Inset: C/T as a function of T^2 . Red line shows the linear fit from base temperature to 9 K). (d) Magnetization isotherms measured at 2 K.

K²)[168; 169]. The discrepancy can be reduced by using the same temperature range of fitting; in between 8 and 10 K, the linear fit to C/T versus T^2 gives a γ value of ~ 90 mJ/mol-K². However, in that temperature range, our data already show a certain degree of non-linearity. To this extent, for this compound, it is not clear if extracting a value for γ is useful or constructive. In Fig. 5.5(c), the red dashed line represents the non-magnetic part of the specific heat, $C_{non-mag}$, estimated from the specific heat of YMg_2Cu_9 . Blue solid line represents the remaining, magnetic part of the specific heat, C_{mag} . Magnetic entropy estimated from C_{mag} is close to $R\ln 2$ by the ordering temperature.

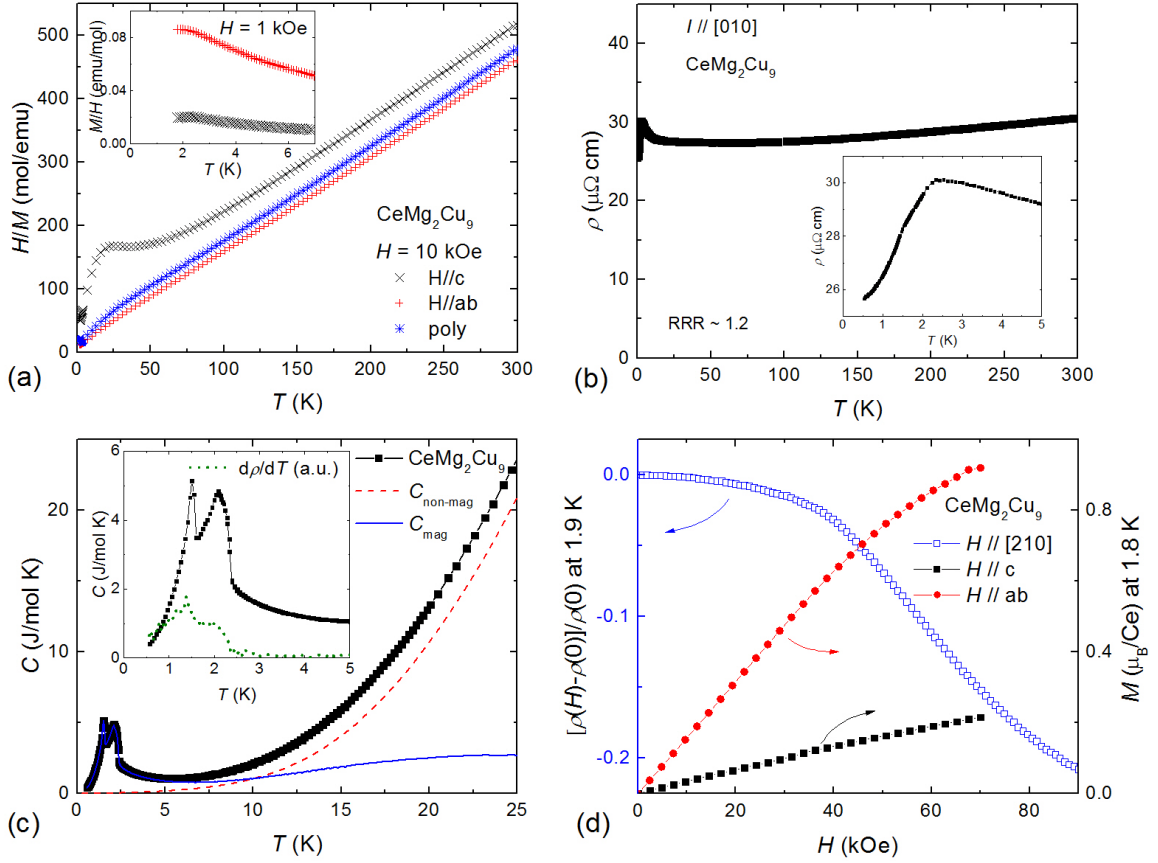


Figure 5.5 (a) Anisotropic inverse magnetic susceptibility of CeMg_2Cu_9 measured at 10 kOe (Inset: low-temperature magnetic susceptibility measured at 1 kOe). (b) Temperature-dependent resistivity (Inset: expanded view on the low temperature part of the resistivity). (c) Temperature-dependent, zero-field specific heat. Red dashed line and blue solid line represent $C_{\text{non-mag}}$ and C_{mag} respectively. Inset: low temperature specific heat. Green dotted line represents $d\rho/dT$ in arbitrary units. (d) Magnetoresistance (blue) on the left and magnetization isotherms (black and red) on the right.

The temperature-dependent resistivity has a lower RRR (~ 1.2) than YMg_2Cu_9 . It stays relatively constant down to 20 K, which could result from a distribution of local Kondo temperatures for a small number of the Ce sites affected by the disorder giving rise to the residual scattering[176]. The RRR of single crystals under study is lower than previously reported values.

The field-dependent magnetization and resistivity at ~ 1.8 K suggest a possible metamagnetic transition near 40 kOe. The metamagnetic transition is likely broadened because of the proximity of two phase transitions to the measurement temperature of 1.8 K. In the basal plane, the magnetization of $0.9 \mu_B/\text{Ce}$ at 70 kOe is nearly a half of the saturated moment of Ce^{3+} ($2.1 \mu_B$). More metamagnetic transition could exist at higher applied magnetic fields as suggested by the magnetoresistance data.

5.2.3 PrMg_2Cu_9

Data measured on PrMg_2Cu_9 single crystals are shown in Fig. 5.6. The magnetization is anisotropic with $\chi_{ab} > \chi_c$. $\Theta_c = -82$ K, $\Theta_{ab} = 19$ K and $\Theta_{poly} = 1$ K. A linear fit of the polycrystalline averaged inverse magnetic susceptibility above 100 K yielded an effective moment of $3.3 \mu_B$, close to the theoretical value of $3.6 \mu_B$ for Pr^{3+} . As temperature decreases below 25 K, the magnetization seems to roll over to a non-magnetic ground state. No magnetic ordering was observed down to 2 K in magnetization.

Specific heat of PrMg_2Cu_9 was measured down to 0.5 K and no phase transition was observed. At around 8 K, a broad dome in specific heat is consistent with a Schottky anomaly due to thermal population of excited CEF levels. The magnetic entropy increases to nearly $R \ln 5$ by 35 K. More discussions on the potential CEF level schemes will be presented in the next section.

The temperature-dependent resistivity of PrMg_2Cu_9 has a RRR of 1.8. The broad shoulder-like feature around 8 K coincides with the Schottky anomaly observed in the specific heat data. No signature of any ordering was observed down to the base temperature.

Fig. 5.6(d) shows the field-dependent magnetization measured at 2 K. When the field is applied along c-axis, the magnetization slowly increase linearly with increasing field. For field

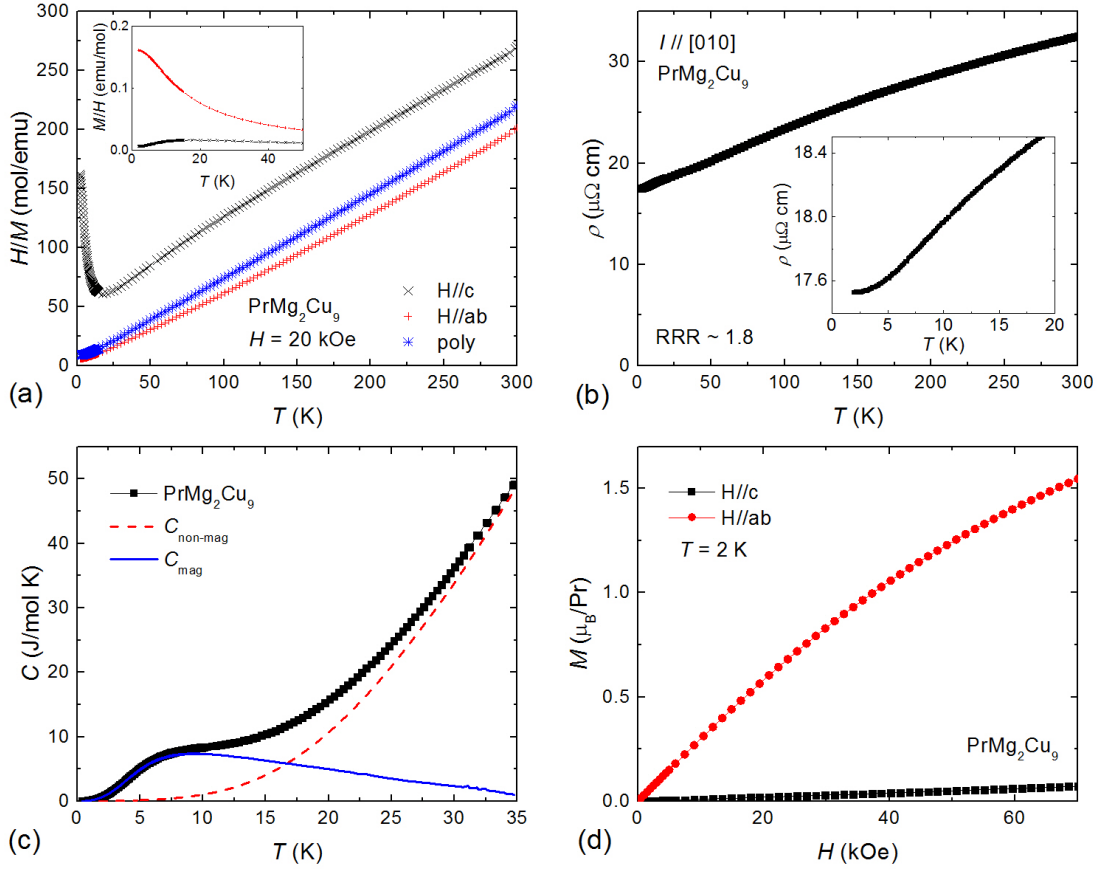


Figure 5.6 (a) Anisotropic inverse magnetic susceptibility of PrMg_2Cu_9 measured at 20 kOe. Inset shows the magnetic susceptibility at low temperature. (b) Temperature-dependent resistivity. Inset shows low temperature part of the resistivity. (c) Temperature-dependent, zero-field specific heat. Red dashed line and blue solid line represent $C_{\text{non-mag}}$ and C_{mag} respectively. (d) Magnetization isotherms measured at 2 K.

along the ab-plane, the magnetization is much larger but the in-plane magnetization is still far from the saturation value ($3.2 \mu_B$) at 70 kOe.

5.2.4 NdMg₂Cu₉

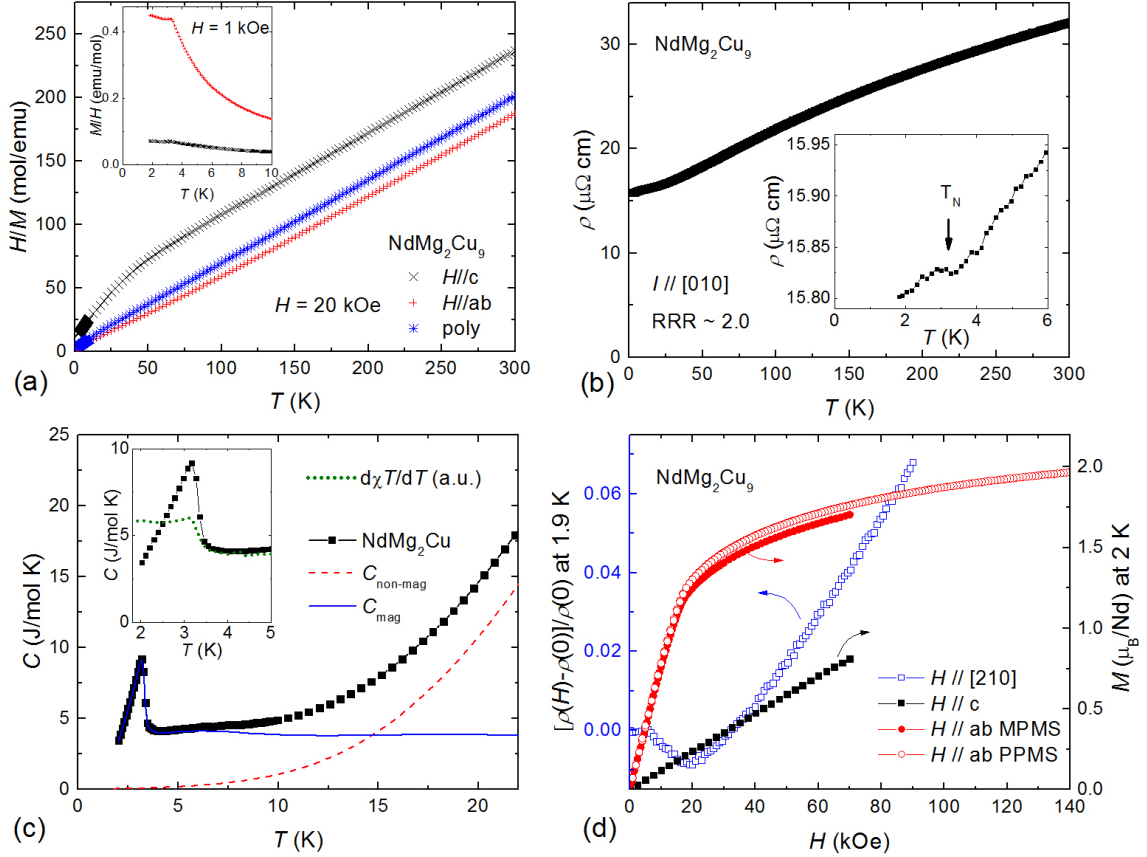


Figure 5.7 (a) Anisotropic inverse magnetic susceptibility of NdMg₂Cu₉ measured at 20 kOe (Inset: low-temperature magnetic susceptibility measured at 1 kOe). (b) Temperature-dependent resistivity (Inset: expanded view on the low temperature part of the resistivity. Arrow indicates the magnetic ordering temperature, T_N). (c) Temperature-dependent, zero-field specific heat. Red dashed line and blue solid line represent $C_{non-mag}$ and C_{mag} respectively. Inset shows an expanded view on the low-temperature specific heat. Green dotted lines represents $d(\chi_{poly}T)/dT$ in arbitrary units. (d) Magnetoresistance (blue) on the left and magnetization isotherms (black and red) on the right.

The magnetic anisotropy of NdMg₂Cu₉ in the paramagnetic state is similar to that observed in PrMg₂Cu₉ as shown in Fig. 5.7(a). From the high-temperature, linear fit of inverse magnetic

susceptibility, we obtained: $\Theta_c = -66$ K, $\Theta_{ab} = 12$ K and $\Theta_{poly} = -5$ K. The calculated effective moment is $3.5 \mu_B$ (theoretical value $3.6 \mu_B$). A magnetic transition was observed at 3.2 K as featured by a kink in magnetization and a peak in $d(\chi_{poly}T)/dT$ (Fig. 5.7(c) inset). Below the magnetic ordering temperature, the magnetization becomes roughly temperature independent.

The temperature-dependent resistivity has a RRR of 2.0. As the temperature decrease down to the magnetic ordering temperature, the resistivity first increases slightly, suggesting a possible superzone gap opening due to magnetic ordering. The transition temperature inferred from magnetization and specific heat data is indicated in the inset of Fig. 5.7(b) by a vertical arrow. The resistivity then continues decreasing at lower temperature. Clearer examples of a similar feature will be seen for $TbMg_2Cu_9$ and $DyMg_2Cu_9$ below.

Consistent with the magnetization data, the specific heat feature confirms a magnetic transition at 3.2 K. A small hump at around 7 K is most probably related to thermal population of excited CEF levels. Below the ordering temperature, an entropy of roughly $R\ln 2$ is removed.

Both field-dependent magnetization and resistivity show a metamagnetic transition at around 20 kOe. The change of slope observed in magnetoresistance at 5 kOe with field applied along [210], however could not be well resolved in the magnetization data. Field-dependent, in-plane, magnetization was measured up to 140 kOe in order to search for more, high field, metamagnetic transitions, but none were observed. The magnetization reaches $2 \mu_B/Nd$ at 140 kOe, a value that is still not reaching the saturated value for Nd^{3+} ($3.3 \mu_B$). It is possible that more metamagnetic transitions may occur at higher applied field values. For field along the c-axis, the magnetization increases linearly with increasing field up to 70 kOe.

5.2.5 $GdMg_2Cu_9$

Because Gd^{3+} has a half-filled 4f shell and thus zero angular moment, $L=0$, an essentially isotropic paramagnetic state is expected. Fig. 5.8(a) shows just this for $GdMg_2Cu_9$, with $\Theta_c=\Theta_{ab}=\Theta_{poly} = -3$ K. The effective moment is $8.1\mu_B$, consistent with the expected value for Gd^{3+} ($7.9 \mu_B$). Upon ordering near 10 K, the magnetic susceptibility for the field in-plane magnetic susceptibility keeps increasing and for field along the c-axis, magnetic susceptibility stays constant.

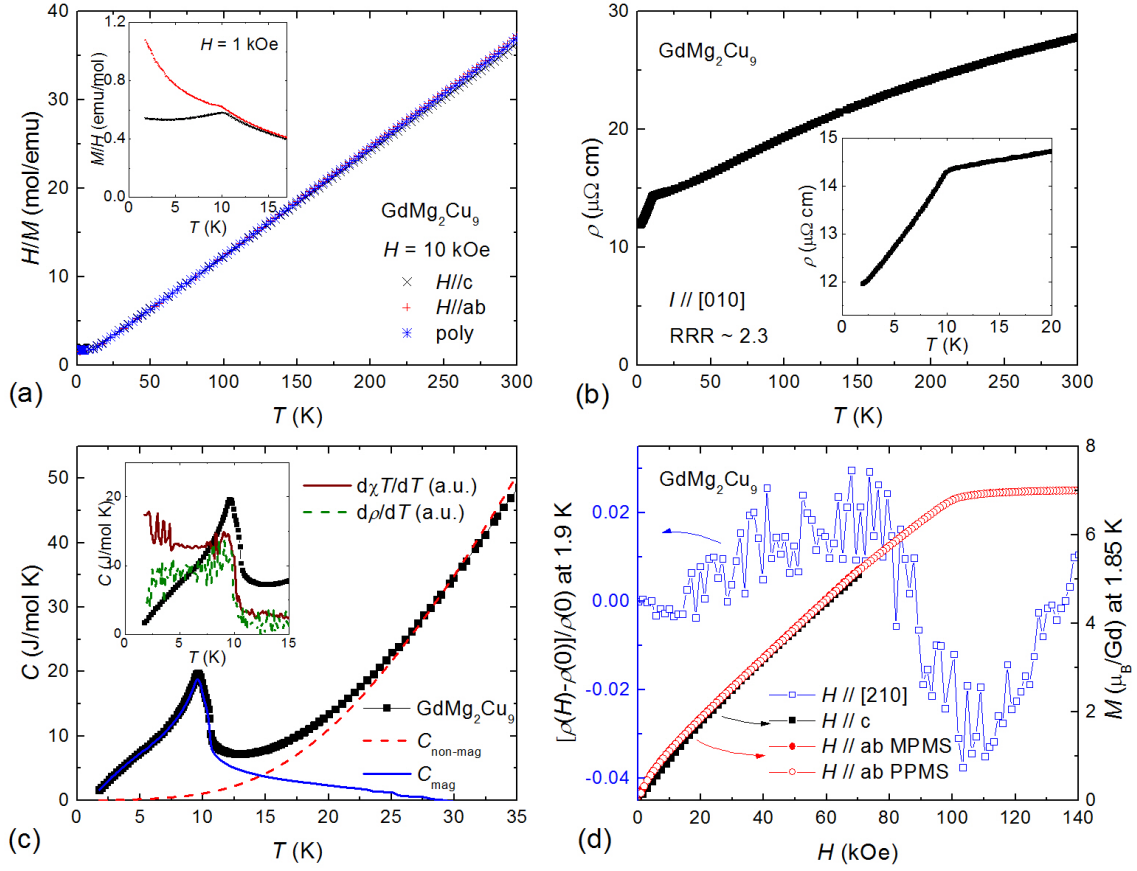


Figure 5.8 (a) Anisotropic inverse magnetic susceptibility of GdMg_2Cu_9 measured at 10 kOe (Inset: low-temperature magnetic susceptibility measured at 1 kOe. (b) Temperature-dependent resistivity (Inset: expanded view on the low temperature resistivity). (c) Temperature-dependent, zero-field specific heat. Red dashed line and blue solid line represent $C_{\text{non-mag}}$ and C_{mag} respectively. Inset shows an expanded view on the low-temperature specific heat. Green dashed line (brown solid line) represents $d\rho/dT$ ($d(\chi_{\text{poly}}T)/dT$) in arbitrary units. (d) Magnetoresistance (blue) on the left and magnetization isotherms (black and red) on the right.

The temperature-dependent resistivity [Fig. 5.8(b)] shows a clear drop at the ordering temperature due to a loss of spin-disorder scattering. Unlike what was observed for NdMg₂Cu₉, no super-zone-gap-like feature was observed. The RRR of GdMg₂Cu₉ is around 2.3.

The temperature-dependent specific heat data [Fig. 5.8(c)] does not show a clear λ -type anomaly and seem to suggest multiple transitions around 10 K. It first jumps at ~ 10.5 K and then reaches a maximum at ~ 9.6 K. Both $d(\chi_{poly}T)/dT$ and $d\rho/dT$ show similar features. If only taking the peak positions in all three types of measurements, the magnetic transition temperature is at 9.7 K. The total specific heat jump at 9.7 K, ~ 20 J/mol K, in addition, may suggest an equal-moment magnetic ordering instead of an amplitude-modulated case where moment amplitude varies from one site to another[177]. The broad shoulder near around 5 K is common for Gd based compound and arises from a (2J+1)-fold degenerate multiplet[177; 178; 175]. $R\ln 8$ magnetic entropy is recovered by ~ 17 K but since the non-magnetic part of the specific heat is not perfectly modelled by the YMg₂Cu₉ data, as evidenced by a crossing of $C_{non-mag}$ and total specific heat, the magnetic entropy inferred is only qualitative.

The field-dependent magnetization of GdMg₂Cu₉ [Fig. 5.8(d)] is close to isotropic up to 70 kOe. The in-plane magnetization is only slightly larger than the out-of-plane magnetization below 20 kOe. A single metamagnetic transition was observed at around 100 kOe, above which the magnetic moment is saturated to $7 \mu_B/\text{Gd}$, the same with theoretically predicted value. Magnetoresistance drops at the metamagnetic transition and increases with increasing field for both higher field and lower fields.

5.2.6 TbMg₂Cu₉

Data for TbMg₂Cu₉ are shown in Fig. 5.9. The magnetization anisotropy of TbMg₂Cu₉ is strongly planar. A linear fit to the inverse magnetic susceptibility yields: $\Theta_c = -214$ K, $\Theta_{ab} = 19$ K and $\Theta_{poly} = 5$ K. The inverse magnetic susceptibility of the polycrystalline averaged data remain linear down to much lower temperature even though the CEF splitting leads to much higher temperature anisotropic magnetic susceptibility[106]. The calculated effective moment is $9.8 \mu_B$, close to expected value for Tb³⁺ ($9.7 \mu_B$).

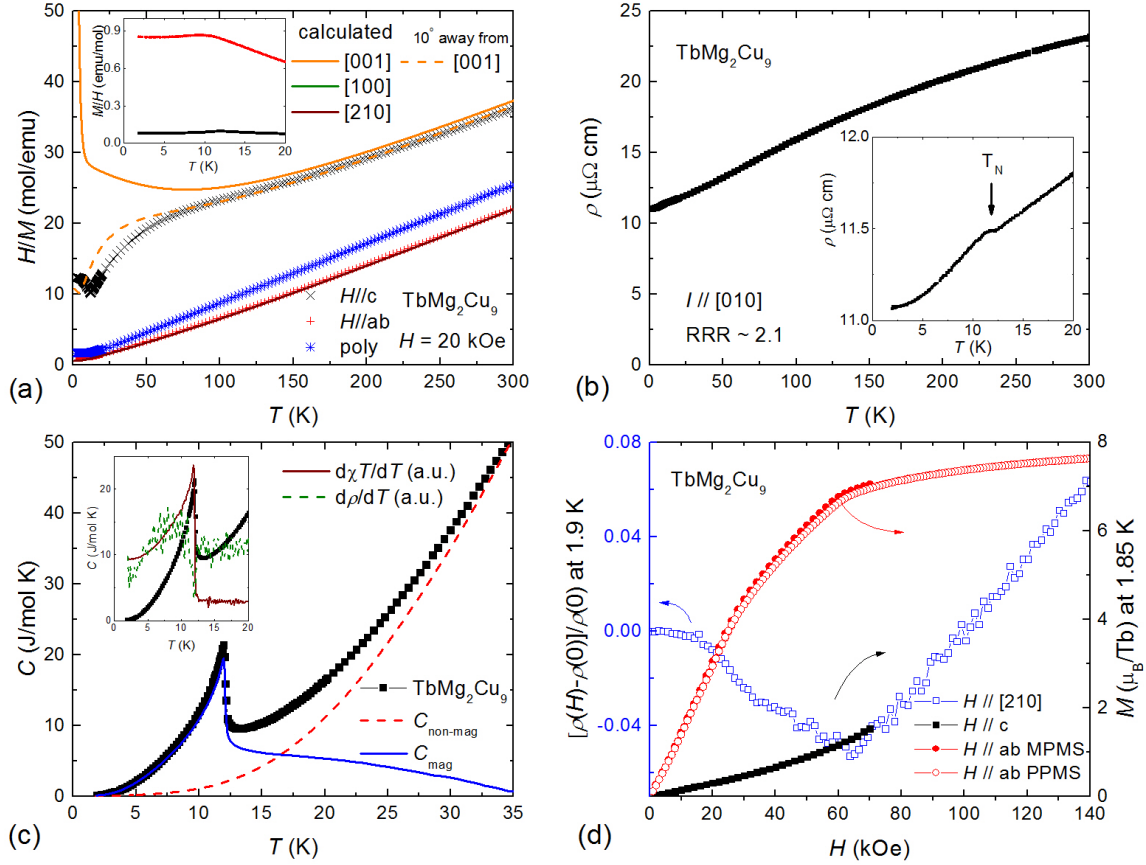


Figure 5.9 (a) Anisotropic inverse magnetic susceptibility of TbMg_2Cu_9 measured at 20 kOe (Inset: magnetic susceptibility at low temperature). Solid lines are calculated from proposed CEF levels (see text). (b) Temperature-dependent resistivity (Inset: low temperature part of the resistivity. Arrow indicates the magnetic ordering temperature, T_N). (c) Temperature-dependent, zero-field specific heat. Red dashed line and blue solid line represent $C_{\text{non-mag}}$ and C_{mag} respectively. Inset shows an expanded view on the low-temperature specific heat. Green dashed line (brown solid line) represents $d\rho/dT$ ($d(\chi_{\text{poly}}T)/dT$) in arbitrary units. (d) Magnetoresistance (blue) on the left and magnetization isotherms (black and red) on the right.

The temperature-dependent resistivity of TbMg₂Cu₉ [Fig. 5.9(b)] has a RRR of 2.1. Upon magnetic ordering, the resistivity shows behavior similar to NdMg₂Cu₉, suggesting the opening of a superzone gap.

The specific heat, resistivity and magnetic susceptibility data all show consistent transition temperature values of $T_N=11.9$ K [Fig. 5.9(c)]. The magnetic entropy was estimated to be close to $R\ln 2$ by the ordering temperature. Similar to GdMg₂Cu₉, magnetic entropy for TbMg₂Cu₉ upon ordering might be slightly different from that estimated here due to the imperfect nature of the YMg₂Cu₉ background subtraction, even after the mass correction for Tb instead of Y (see experimental methods).

Metamagnetic transitions were observed in both electrical transport and magnetization measurements at ~ 20 kOe and ~ 60 kOe [Fig. 5.9(d)]. For $H \perp c$, the magnetoresistance decreases below 60 kOe with a change in slope at 20 kOe. Above 60 kOe, the magnetoresistance increases linearly in field. The out-of-plane magnetization shows a weak up-curvature up to 70 kOe. The in-plane magnetization of TbMg₂Cu₉ is close to, but not yet reached the saturated moment of Tb³⁺ ($9 \mu_B$) by 140 kOe.

5.2.7 DyMg₂Cu₉

The anisotropy of the temperature-dependent magnetization of DyMg₂Cu₉ [Fig. 5.10(a)] is similar to that of TbMg₂Cu₉. χ_{ab} is much larger than χ_c . At temperatures just above the magnetic ordering, $\chi_{ab}/\chi_c \sim 20$. The Curie-Weiss temperatures extracted from inverse magnetic susceptibility are: $\Theta_c = -245$ K, $\Theta_{ab} = 25$ K and $\Theta_{poly} = -4$ K. The effective moment is $10.9 \mu_B$ (theoretical value: $10.6 \mu_B$). Below ~ 9 K, DyMg₂Cu₉ orders antiferromagnetically as suggested by the drop in magnetic susceptibility.

As shown in Fig. 5.10(b), the RRR of DyMg₂Cu₉ is about 1.6. A very clear increase of resistivity was observed at the magnetic transition temperature, similar to TbMg₂Cu₉.

Features for the magnetic transition in DyMg₂Cu₉ as seen from magnetic susceptibility and resistivity are consistent with λ -like anomaly in specific heat [Fig. 5.10(c)]. The magnetic transition temperature T_N is inferred to be 9.0 K. There is roughly $R\ln 4$ magnetic entropy removed below the ordering temperature.

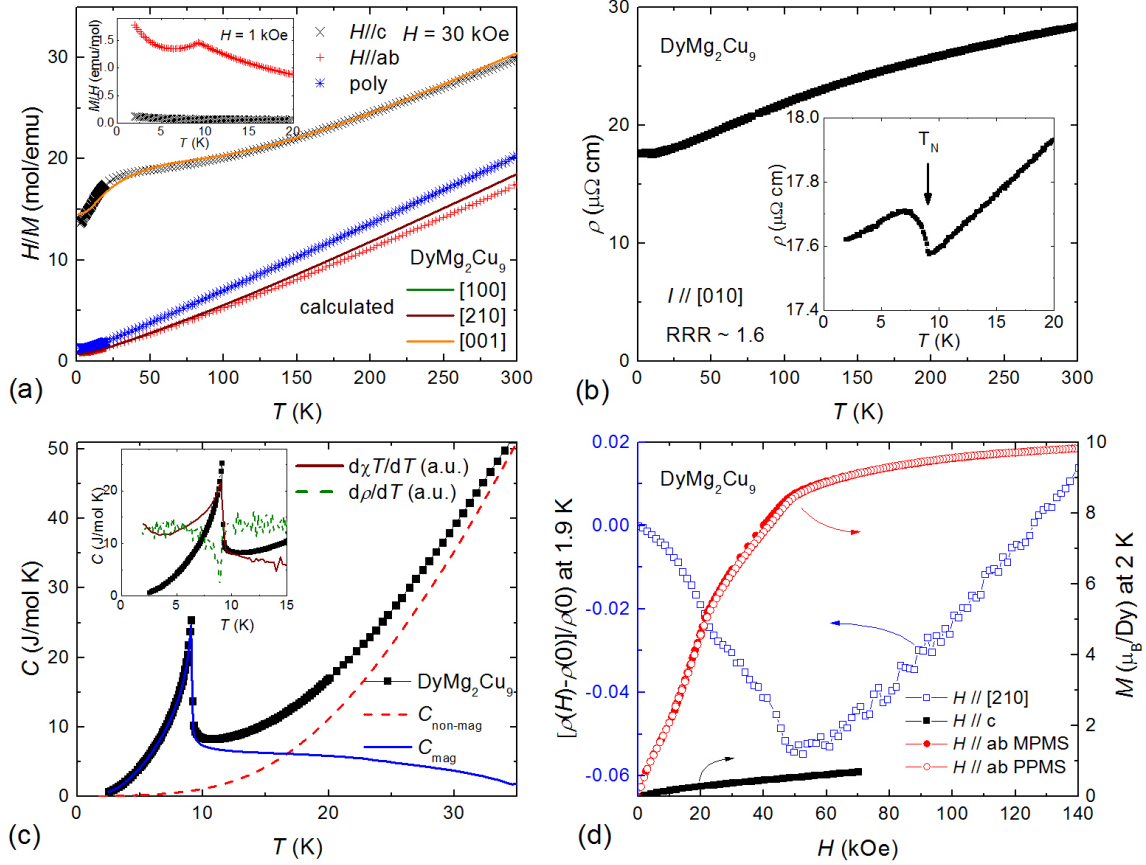


Figure 5.10 (a) Anisotropic inverse magnetic susceptibility of DyMg_2Cu_9 measured at 30 kOe (Inset: low-temperature magnetic susceptibility measured at 1 kOe). Solid lines are calculated from proposed CEF levels (see text). (b) Temperature-dependent resistivity (Inset: low temperature part of the resistivity. Arrow indicates the magnetic ordering temperature, T_N). (c) Temperature-dependent, zero-field specific heat. Red dashed line and blue solid line represent $C_{\text{non-mag}}$ and C_{mag} respectively. Inset shows an expanded view of low-temperature specific heat. Green dashed line (brown solid line) represents $d\rho/dT$ ($d(\chi_{\text{poly}}T)/dT$) in arbitrary units. (d) Magnetoresistance (blue) on the left and magnetization isotherms (black and red) on the right.

There are two metamagnetic transitions observed at ~ 20 kOe and ~ 50 kOe [Fig. 5.10(d)], above which the in-plane magnetization approaches the theoretical saturation value of $10 \mu_B$. Overall, the field-dependent magnetization, specific heat and resistance are similar with what were observed in TbMg₂Cu₉. Magnetoresistance decreases with increasing field below 50 kOe and then increases linearly afterwards. The metamagnetic transition is marked by a change of slope. Magnetization along the c-axis increases monotonically up to 70 kOe.

5.2.8 YbMg₂Cu₉

Given that the lattice parameters and unit cell volume of YbMg₂Cu₉ strongly deviate from the lanthanide contraction of R^{3+} ions (Fig. 5.3), it is not surprising that the Yb ions appears to be Yb²⁺. The temperature-dependent magnetization of YbMg₂Cu₉ is shown in Fig. 5.11(a). The low-temperature Curie-tail and the cusp in magnetic susceptibility at around 2.5 K can be accounted for by about 0.5% molar contamination of Yb₂O₃ on or in the sample[179]. The intrinsic magnetic susceptibility of YbMg₂Cu₉ can be inferred to be paramagnetic and temperature-independent with a magnitude of $\sim 5 \times 10^{-4}$ emu/mol. This is comparable in magnitude to what was found for the non-magnetic YMg₂Cu₉. However, the difference in the core diamagnetism of Yb²⁺ and Y³⁺ is not sufficient to explain the exact change of the magnetic susceptibility[180]. The Fermi surfaces of the two are likely different due to an extra electron provided to the conduction band by Y³⁺.

Fig. 5.11(b) shows the resistivity of YbMg₂Cu₉. It has a RRR value of 1.6. There is no indication of a phase transition down to 2 K. Magnetoresistance measured at 1.9 K increases by 1% 55 kOe.

5.3 Trends across the RMg₂Cu₉ series

Anisotropic Curie-Weiss temperatures, effective moment in the paramagnetic state and the ordering temperatures for compounds under study are summarized in Table 5.3. Apart from isotropic GdMg₂Cu₉, the other local-moment-bearing compounds exhibit magnetic anisotropy with greater in-plane magnetization. The most extreme examples, TbMg₂Cu₉ and DyMg₂Cu₉, have χ_{ab} an order of magnitude larger than χ_c for $T \geq T_N$

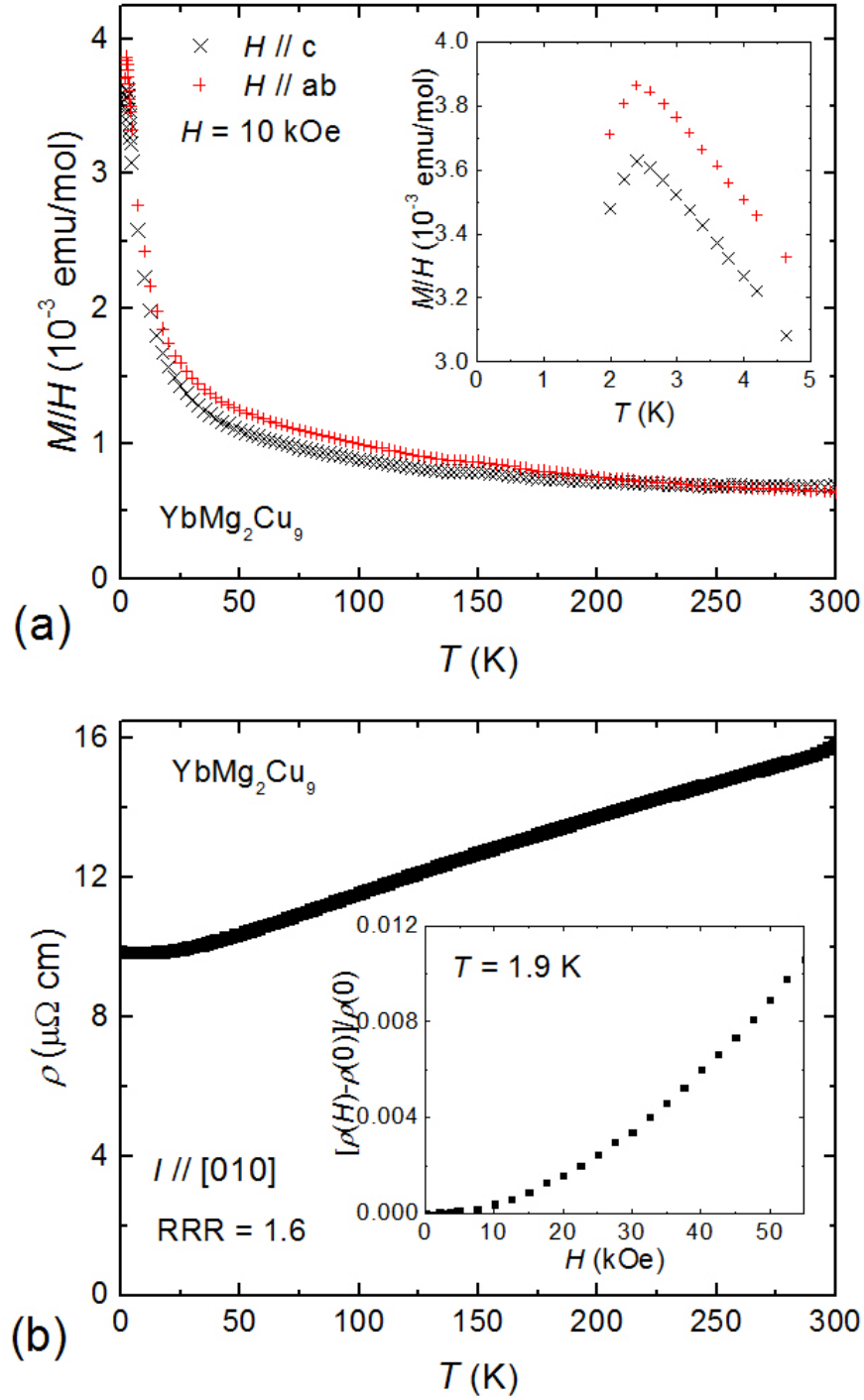


Figure 5.11 (a) Anisotropic magnetic susceptibility of YbMg_2Cu_9 measured at 10 kOe (inset: low-temperature magnetic susceptibility). (b) Temperature-dependent resistivity (inset: magnetoresistance measured at 1.9 K).

Table 5.4 Anisotropic Curie-Weiss temperatures (Θ_c , Θ_{ab} and Θ_{poly}), effective magnetic moment in paramagnetic state (μ_{eff}) and magnetic transition temperatures (T_N) of RMg_2Cu_9 ($R = Y, Ce-Nd, Gd-Dy, Yb$). Magnetic transition temperatures are inferred from the peak temperatures of $d(\chi_{poly}T)/dT$ [181], $d\rho/dT$ [182] and specific heat. *: There could be multiple transitions around this temperature up to 10.5 K.

R	Θ_c (K)	Θ_{ab} (K)	Θ_{poly} (K)	μ_{eff} (μ_B)	T_N (K)
Y	-	-	-	-	-
Ce	-43	-1	-12	2.3	2.1, 1.5
Pr	-82	19	1	3.3	-
Nd	-66	12	-5	3.5	3.2
Gd	-3	-3	-3	8.1	9.7*
Tb	-214	19	5	9.8	11.9
Dy	-245	25	-4	10.9	9.0
Yb	-	-	-	-	-

Ignoring the CEF effect and anisotropic exchange interaction, de Gennes argued that the Curie-Weiss temperatures and therefore, the magnetic ordering temperatures, in mean field theory, will be scaled with de Gennes factor[11]: $dG = (g_J - 1)^2 J(J+1)$. The magnetic transition temperatures listed in Table. 5.3 are plotted as a function of de Gennes factor in Fig. 5.12. As can be seen, such simple de Gennes scaling is not followed with $TbMg_2Cu_9$ and $DyMg_2Cu_9$ having higher transition temperatures than expected. In practice, both anisotropy in exchange interaction and CEF effect can, arguably, modify this scaling[12; 13]. In addition, since the magnetic anisotropy is mainly due to CEF effect, the strength of the exchange interaction that is responsible for low-temperature magnetic ordering may not be completely captured in the polycrystalline averaged Curie-Weiss temperatures (see Table 5.3). This may account for the inconsistency of Θ_{poly} values with de Gennes scaling. Experimentally, deviation from de Gennes scaling is not uncommon and has been observed in a variety of systems[158; 175; 183].

In the presence of the CEF effect, the ground state degeneracy will be lifted. In the case of $PrMg_2Cu_9$, both temperature-dependent magnetization and specific heat data are consistent with a singlet ground state. From temperature-dependent C_{mag} data, $PrMg_2Cu_9$ likely has a singlet excited state at ~ 12 K and a doublet at ~ 25 K. As temperature drops below 10 K there is a gradual depopulation of the excited CEF levels that results in a rounded feature

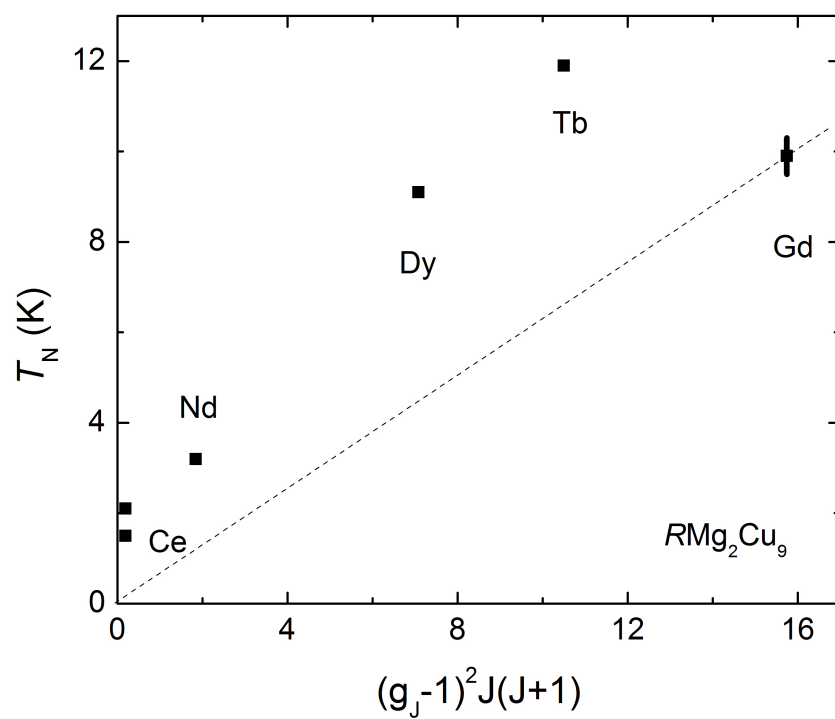


Figure 5.12 Magnetic ordering temperatures of RMg_2Cu_9 as a function of de Gennes factor $dG = (g_J - 1)^2 J(J + 1)$. Potential multiple transitions for $GdMg_2Cu_9$ are represented by an error bar. Dotted line is a guide for the eyes.

in temperature-dependent magnetization and a broad dome in C_{mag} . PrMg_2Cu_9 , therefore, may be another example of a Pr-based intermetallic compound with a non-moment bearing, singlet CEF ground state[16; 184]. The lift of degeneracy due to the CEF effect is also the dominating factor for the magnetic anisotropy that is observed in RMg_2Cu_9 . Quantitatively, the CEF Hamiltonian for the hexagonal rare earth site in this series can be written as[21]:

$$H_{CEF} = B_2^0 O_2^0 + B_4^0 O_4^0 + B_6^0 O_6^0 + B_6^6 O_6^6 \quad (5.1)$$

where B_n^m are CEF parameters, O_n^m are Steven operators[19; 21]. In the point charge model, the CEF parameters can be expressed as $B_n^m = A_n^m \langle r^n \rangle \theta_n$, where $\theta_2 = \alpha_j$; $\theta_4 = \beta_j$; $\theta_6 = \gamma_j$ are Steven's factors. $\langle r^n \rangle$ is the expectation value of the 4f radial function to the nth power. A_n^m can often be viewed as a constant given the same crystalline neighboring environment. For uniaxial systems, B_2^0 is the leading term in determining the anisotropic Curie-Weiss temperatures, or in another word, being more planar or more axial[25]. Since A_2^0 does not change much from one rare earth to another in the same series of compounds and $\langle r^2 \rangle$ is always positive, the sign change of α_j will alter the axial/planar magnetic anisotropy. From theoretically calculated values for α_j [19; 22; 21], one can predict that the axial/planar magnetic anisotropy will be the same for $R = \text{Ce-Nd}$, Tb-Ho trivalent ions. This is consistent with the data observed in RMg_2Cu_9 series of compounds. In the following section, more detailed discussion on the CEF effect with respect to in-plane magnetic anisotropy will be presented.

5.4 Angular dependent magnetization

In rare earth compounds, the interplay between strong magnetic anisotropy and exchange interaction can often result in complex phase diagrams. For example, in strong axial systems, the Ising model with competing interactions was proposed to exhibit an infinite number of commensurate phases, also know as the devil's staircase[185]. Experimentally, many rare-earth-based systems, such as TbNi_2Ge_2 [15], CeSb [186; 187], TbNi_2Si_2 [188] have been studied as possible candidates. In the same manner, in strong planar systems, the 4-state-clock model was proposed in which moments in a tetragonal site symmetry are not only confined in-plane

but also along a specific direction (an easy-axis)[162; 189]. Deviating from the easy-axis, the longitudinal magnetization decreases as a function of $\cos(\theta)$ where θ is the angle between the direction of measurement and the nearest easy-axis. Such a model was motivated by and then used to understand complex phase diagrams and angular-dependent magnetization in tetragonal systems such as $\text{HoNi}_2\text{B}_2\text{C}$ [162] and DyAgSb_2 [163]. Similarly, the complex phase diagrams of hexagonal compounds TbPtIn and TmAgGe have been interpreted in a modified 6-state-clock model based on three, crossed, in-plane Ising-like moments, caused by the orthorhombic site symmetry of the rare earth ions[165]. A model system of a strongly planar, rare-earth-based compound with a hexagonal site symmetry has been, up to now, missing. In RMg_2Cu_9 , most of the investigated members in this study manifest promising features for such a study. There is a single rare earth site in a hexagonal site symmetry with a strong planar magnetization. Additionally, field-induced metamagnetic transitions were observed in all ordered members, even though not being very sharp compared to aforementioned 4-state-clock systems. Therefore, extremely planar members, DyMg_2Cu_9 and TbMg_2Cu_9 , were examined more in detail with angular-dependent magnetization measurements.

The confinement of the local-moments in plane is a critical requirement for the clock-type model. The CEF effect was considered as the primary contributor of such anisotropy for $\text{HoNi}_2\text{B}_2\text{C}$ [162] and DyAgSb_2 [163]. Since CEF splitting is fundamentally a single ion effect, in order to better investigate the single ion magnetic anisotropy due to CEF splitting, 1% Dy or Tb was substituted into non-magnetic YMg_2Cu_9 in order to minimize the influence of magnetic interaction between local moments. In Fig. 5.13, both in-plane to out-of-plane, as well as purely in-plane, angular-dependent magnetization measurements are shown for $\text{Y}_{0.99}\text{Dy}_{0.01}\text{Mg}_2\text{Cu}_9$.

Fig. 5.13(a) shows a large axial-to-planar anisotropy. The in-plane magnetization is nearly two orders of magnitude larger than the out-of-plane magnetization. This is consistent with the magnetic anisotropy observed in pure DyMg_2Cu_9 (Fig. 5.10). It also suggests that most of the magnetic anisotropy observed in the paramagnetic state comes from the single ion CEF effect. The in-plane anisotropy [Fig. 5.13(b)], on the other hand, is field-dependent and, even at $H=50$ kOe, only weakly angular-dependent. The magnetization measured at 10 kOe shows little indication of any 6-fold magnetic anisotropy. Under 50 kOe, the 6-fold modulation is only

$\sim 3\%$ of the total magnetization [inset in Fig. 5.13(b)]. A closer look at the data measured at both 10 kOe and 50 kOe reveals an additional 2-fold angular-dependence. This is likely due to an angular-dependent radial displacement of the sample from the centerline of the SQUID pick-up coil[118] associated with the sample mounting. Similar 2-fold modulation was observed for other systems when this rotating sample stage was utilized[67].

Given that our experience has been that when a system has enough CEF splitting to manifest extreme planar anisotropy, it also manifests clear in-plane anisotropy in magnetic field[162; 163; 165], these results require some study. One possible, extrinsic cause of the co-existent of a strong planar and a weak in-plane magnetic anisotropy is a random twinning or crystalline domain formation such that the in-plane crystalline orientation is close to polycrystalline. This scenario was ruled out by conducting Laue measurements on different locations of the same crystal of sample at different depths (achieved by polishing).

CEF splitting, without any extrinsic disorder, was then considered in order to explain the phenomena. In the presence of magnetic field, an additional Zeeman term, $-\vec{\mu} \cdot \vec{B}$, needs to be added into Equation (5.1). Magnetization under applied field can then be calculated based the derivative of free energy with field. Whereas B_2^0 determines axial/planar magnetic anisotropy, the mixture of different J_z states is essential to the existence of in-plane magnetic anisotropy. In the current case, only applied magnetic field and $B_6^6 O_6^6$ will mix different states. Worth noting, $B_6^6 O_6^6$ by itself, or in a more general statement, pure CEF effect will not produce an in-plane magnetic anisotropy without the presence of magnetic field, be it externally applied or internal[190]. More detailed example will be illustrated and discussed below.

The temperature-dependent magnetic susceptibility of pure DyMg_2Cu_9 , rather than the diluted, $\text{Y}_{0.99}\text{Dy}_{0.01}\text{Mg}_2\text{Cu}_9$, was used to compare with calculated values. This avoid problems caused by the weak temperature-dependence of YMg_2Cu_9 's magnetic susceptibility. And since the magnetic exchange interaction responsible for the low-temperature magnetic ordering of DyMg_2Cu_9 probably does not influence the magnetic anisotropy in its paramagnetic state by much (e.g. as can be seen in Table 5.3, $\Theta_{poly} \ll \Theta_{ab} \ll \Theta_c$), the magnetic susceptibility of pure DyMg_2Cu_9 is a good approximation. In Fig. 5.10(a), solid lines show the calculated inverse magnetic susceptibility at 30 kOe with constraints of temperature-dependent magnetic entropy

above the transition temperature, estimated from specific heat measurements. CEF parameters used are: $B_2^0 = 1.99$ K, $B_4^0 = -1.00 \times 10^{-4}$ K, $B_6^0 = -1.70 \times 10^{-5}$ K and $B_6^6 = -7.50 \times 10^{-4}$ K. The angular-dependent magnetization was then calculated based on this set of CEF parameters. In Fig. 5.13, solid lines show results of the calculated angular-dependent magnetization at various applied magnetic fields. For the in-plane to out-of-plane magnetization, the calculated values matches with measured values quite well. The calculated magnetization value for $H \parallel [001]$ does not go to zero because the ground state doublet, $\Gamma_{8,c}$, which is a mixture of $|\mp \frac{7}{2}\rangle$ and $|\pm \frac{5}{2}\rangle$, has a finite, but small, magnetization along c-axis. The calculated in-plane anisotropy is very small at 10 kOe, consistent with what was observed even though the value of magnetization is smaller than the actual measured value. Taking into account a $|\cos\theta|$ -dependent radial displacement of the sample from the centerline of the pick-up coil during rotation with a maximum value of 2 mm, the calculated in-plane magnetic anisotropy at 50 kOe seems to qualitatively agree with experimentally observed results. The calculated magnetization at 300 kOe, as shown by green solid line, has a much clearer in-plane anisotropy. And the angular dependence is close to what would be expected if the moment can be simplified as a dipole with a preferred in-plane orientation (i.e. what would be called a 6-state-clock model). However, such a high magnetic field could not be accessed due to instrumental limitations.

The origin of the in-plane magnetization can be better understood by looking at evolution of the CEF levels with applied field. In Fig. 5.14, the field-dependent CEF levels for DyMg_2Cu_9 are plotted up to 70 kOe with applied field along three characteristic orientations for a hexagonal structure. In zero-field, the total CEF splitting is close to 350 K with the first excited and second excited states lying about 20 and 40 K above the ground state. Each CEF level of the Kramer's ion, Dy^{3+} , is a doublet. The label of each state follows the nomenclature used in Ref. [24]. At low-temperatures, only the low-lying states contribute to the single ion magnetization. When field is applied along the c-axis, the energies of the three low-lying doublets only change slightly with field indicating a very small moment. All the levels with large c-axis magnetization values are high in energy and therefore not populated at any significant level at 1.85 K. When field is applied in-plane, the CEF splitting only becomes markedly different above around 20 kOe where the first excited state $\Gamma_{9,b}$ evolves differently for the $[100]$ and $[210]$ directions. The

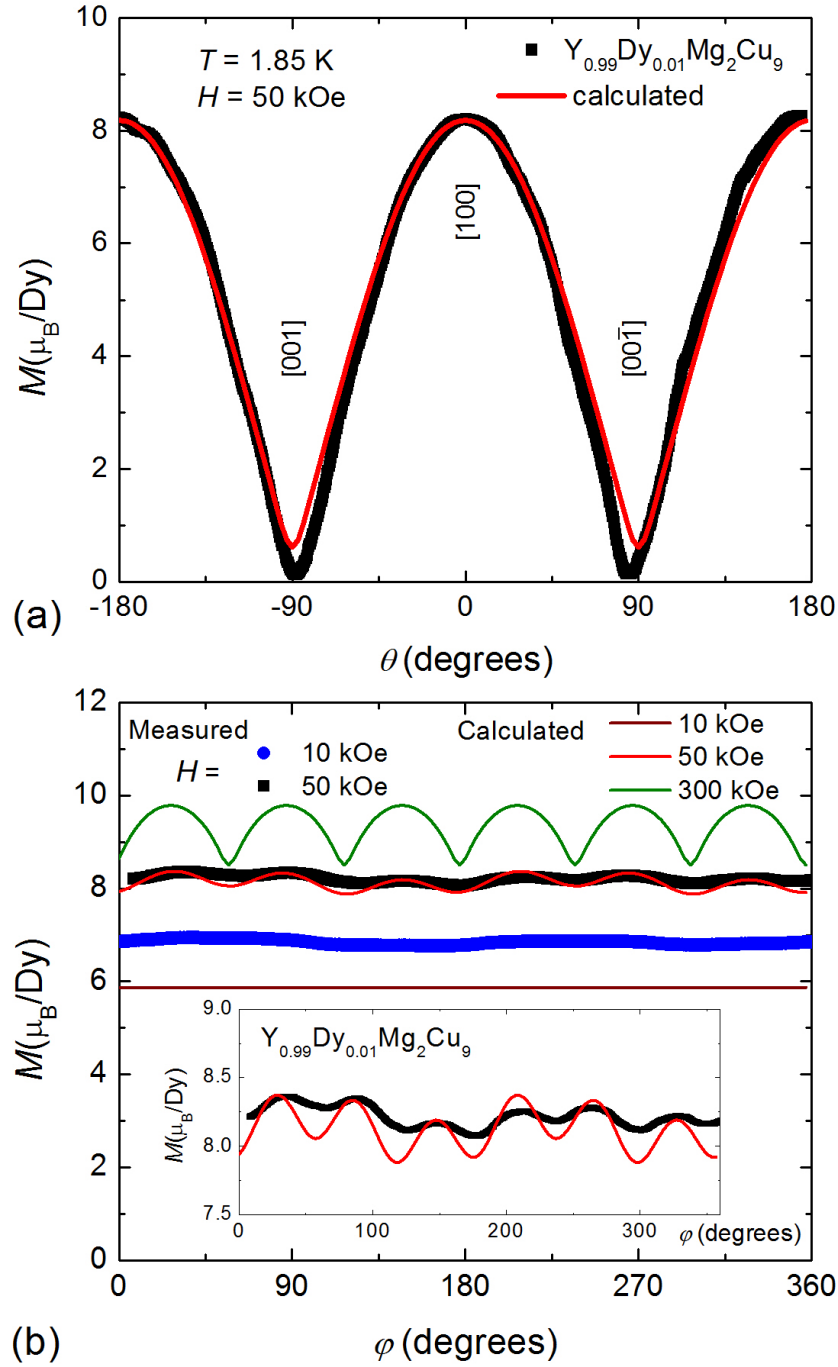


Figure 5.13 (a) In-plane to out-of-plane magnetization measured at 1.85 K with 50 kOe. Red solid line represents results of CEF calculations. Field orientations are indicated by Miller indices. (b) In-plane magnetization measured at 1.85 K with 10 kOe, 50 kOe as a function of angle starting from $[210]$. Solid lines are calculated based on proposed single ion anisotropy of Dy due to CEF for $H=10$ kOe, 50 kOe and for comparison a hypothetical 300 kOe. Inset: expanded view of $H=50$ kOe data and results of CEF calculations.

mixing between $\Gamma_{9,b}$ and the ground state, $\Gamma_{8,c}$, plays an important role in the in-plane magnetic anisotropy. As a consequence, the variation of in-plane magnetization is small at 10 kOe. With increasing field, the difference in mixing among the low-lying states becomes more and more pronounced. This leads to a stronger in-plane anisotropy. The calculated in-plane magnetic anisotropy of the ground state ($\Gamma_{8,c}$) at 50 kOe is around 4% which is similar to the measured results.

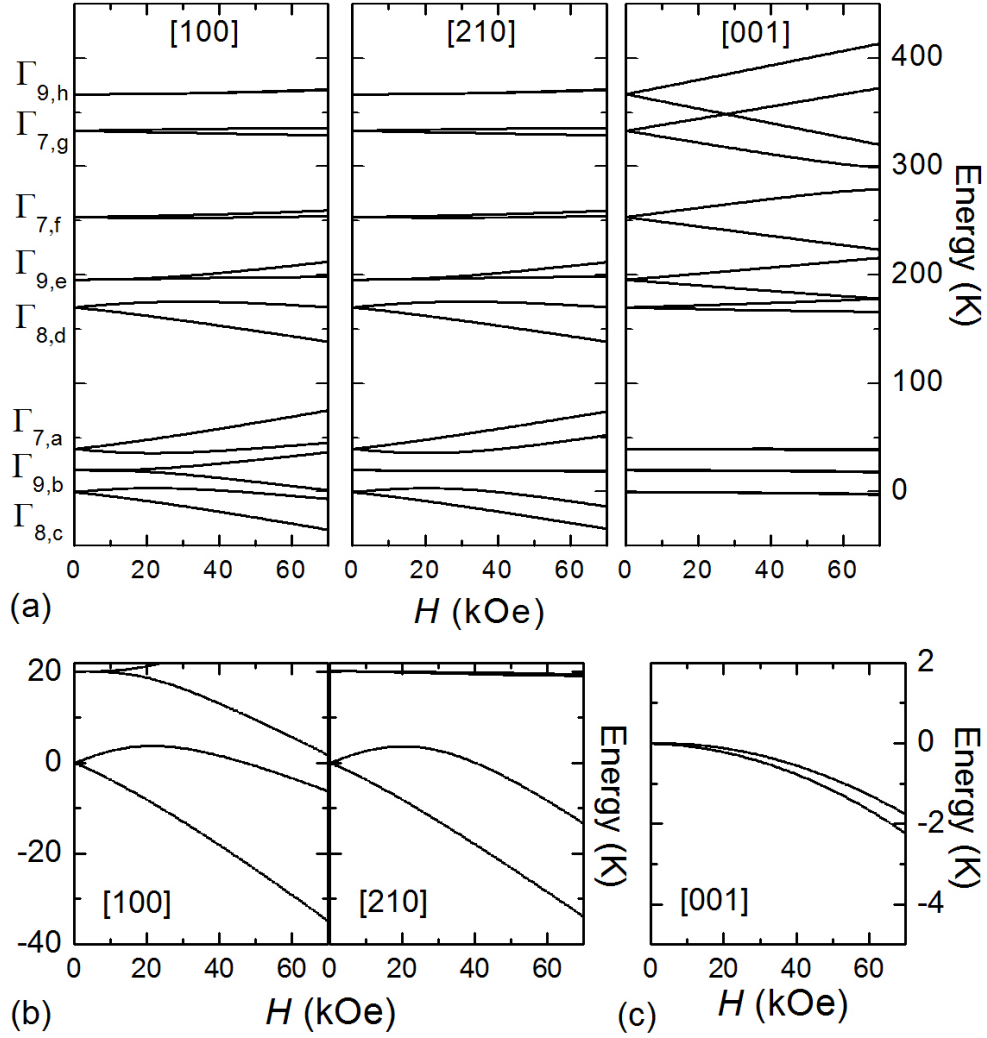


Figure 5.14 Field-dependent CEF level energies for DyMg₂Cu₉ with H along (a) [100], (b) [210] and (c) [001]. The label on the left side was adapted from Ref. [24].

A similar fit can be done to TbMg₂Cu₉ which gives $B_2^0 = 3.38$ K, $B_4^0 = 4.12 \times 10^{-4}$ K, $B_6^0 = 1.88 \times 10^{-5}$ K and $B_6^6 = 8.48 \times 10^{-4}$ K. In Fig. 5.9(a), the modelled temperature-dependent

magnetic susceptibility data at 20 kOe are shown together with the measured values. It qualitatively well matches experimentally obtained values above 150 K. Below 100 K, the calculated out-of-plane magnetization is smaller than measured data. This lower-temperature range can suffer from magnetic ordering and/or large, in-plane magnetization contribution from slightly misalignment of the sample. By a small, 10° , misalignment from the c-axis as shown by the dashed line in Fig. 5.9, the modelled magnetic susceptibility agrees much better with the experimentally measured data.

Using the CEF parameters for Tb^{3+} , the angular-dependent magnetization can be calculated and compared to the experimental data. As shown in Fig. 5.16, the ground state of TbMg_2Cu_9 , $\Gamma_{1,o}$, is a singlet. In addition, higher order terms such as Van Vleck contribution can only come from the mixture of $\Gamma_{1,o}$ and Γ_2 . But as can be seen in Fig. 5.16, these levels are very far apart in energy. As a consequence, the magnetization along c-axis is nearly zero. Only a very small c-axis magnetization can arise from the mixing of the lowest lying states $\Gamma_{1,o}$ and $\Gamma_{6,a}$. That would give rise to a big in-plane to out-of-plane magnetic anisotropy. At 1.85 K, the measured in-plane to out-of-plane magnetization of $\text{Y}_{0.99}\text{Tb}_{0.01}\text{Mg}_2\text{Cu}_9$ resembles what was observed in $\text{Y}_{0.99}\text{Dy}_{0.01}\text{Mg}_2\text{Cu}_9$. The red solid line, representing the calculated value matches the experimental data very well. Note that the experimental magnetization value along [001] indeed goes toward zero for the systematically rotated sample, further suggesting that the low-temperature disagreement between data and CEF modelling in Fig. 5.9(a) is due to slight misalignment.

In-plane angular-dependent magnetization measured at both 10 kOe and 50 kOe show little angular-dependence. This behavior is also well reproduced by the calculations and can be understood by considering the similar evolution of the low lying CEF levels with field in the [100] and [210] as shown in Fig. 5.16. Even above 20 kOe, the majority of the ground state mixing is very similar between [100] and [210] that does not show a strong in-plane magnetic anisotropy.

Based on theoretically calculated values for $\langle r^n \rangle$ and θ_n in the point charge model listed in Fig. 1.2[19; 22; 21], the CEF parameters for Tb^{3+} can also be directly predicted from the values obtained for Dy^{3+} , which would be: $B_2^0 = 3.33 \text{ K}$, $B_4^0 = 2.27 \times 10^{-4} \text{ K}$, $B_6^0 = 2.09 \times 10^{-5}$

K and $B_6^6 = 9.21 \times 10^{-4}$ K. These theoretically predicted parameters are close to the parameters that are directly obtained from experimental fitting shown above. Both sets of parameters give almost identical CEF level schemes as well as their field-dependences. The agreement between the point charge model prediction and the experimental fitted results in this case also partly validate our previous model used to understand the CEF effect in DyMg_2Cu_9 . In general, angular-dependent magnetization observed here can be well modelled with CEF.

Comparing these results with $\text{HoNi}_2\text{B}_2\text{C}$ and DyAgSb_2 , where the 4-state-clock model is robust, TbMg_2Cu_9 and DyMg_2Cu_9 do not show comparable in-plane magnetic anisotropy under 50 kOe, even though the condition of a strong planar magnetization is satisfied. As described above, within the single ion picture, the CEF ground state will always have an isotropic, or XY-like, in-plane magnetization. It is only by mixing excited CEF levels in magnetic field that in-plane anisotropy can be realized. Of course, once the magnetic field becomes sufficiently strong, it will swamp the CEF splitting and remove any anisotropy, but that generally is at very large fields. Therefore there will be a "sweet spot", where the magnetic field can maximize the in-plane anisotropy. In TbMg_2Cu_9 and DyMg_2Cu_9 , 50 kOe is very likely below that sweet spot. However, as shown in Fig. 5.13(b), the ideal $\max[\cos(\theta - n\pi/3)]$ modulation of in-plane magnetization could potentially still be realized in DyMg_2Cu_9 for larger fields (300 kOe).

On one hand, in this single ion situation, we can adjust the external applied magnetic field to find that sweet spot. On the other hand, in realizing a clock model in magnetically ordered compounds, the internal magnetic field due to exchange interaction, as a mean-field that originates from neighboring magnetic ions, can also induce the anisotropy. Essentially, the anisotropy of the moments ($\vec{S}_i$) depends on the effective magnetic field they feel ($\vec{H}_i$). Once the mean-field on each site, $\vec{H}_i = \sum_j J_{ij} \vec{S}_j$ ($\vec{H}_j$) becomes non-zero, below magnetic transition, they will develop an in-plane anisotropy, similar to $\vec{S}_i(\vec{H}_i)$ shown in the single-ion magnetization. This dependence leads to a slightly more complicated non-linear mean-field theory, where the energy from $H = \sum_{ij} J_{ij} \vec{S}_i(\vec{H}_i) \cdot \vec{S}_j(\vec{H}_j)$ need to be minimized self-consistently with $\vec{H}_i = \sum_j J_{ij} \vec{S}_j(\vec{H}_j)$.

In searching for an in-plane state-clock model system, one needs a mixture of low-lying CEF states, which are well separated from higher-lying CEF states. In addition, in-plane magnetic

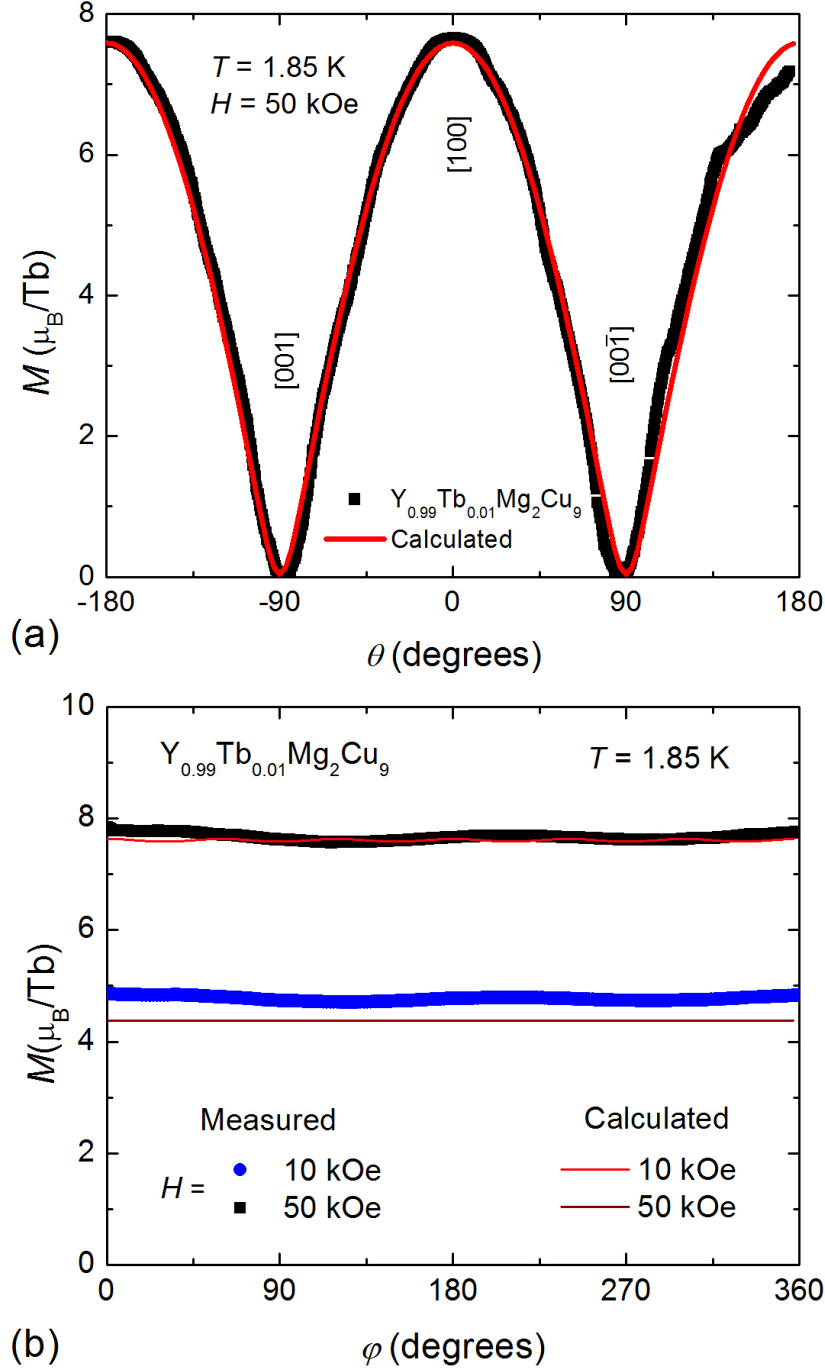


Figure 5.15 (a) In-plane to out-of-plane magnetization measured at 1.85 K with 50 kOe. Red solid line represents results of CEF calculations. Field orientations are indicated by Miller indices. (b) In-plane magnetization measured at 1.85 K with 10 kOe, 50 kOe as a function of angle starting from [210]. Solid lines are calculated based on proposed single ion anisotropy of Tb due to CEF effect.

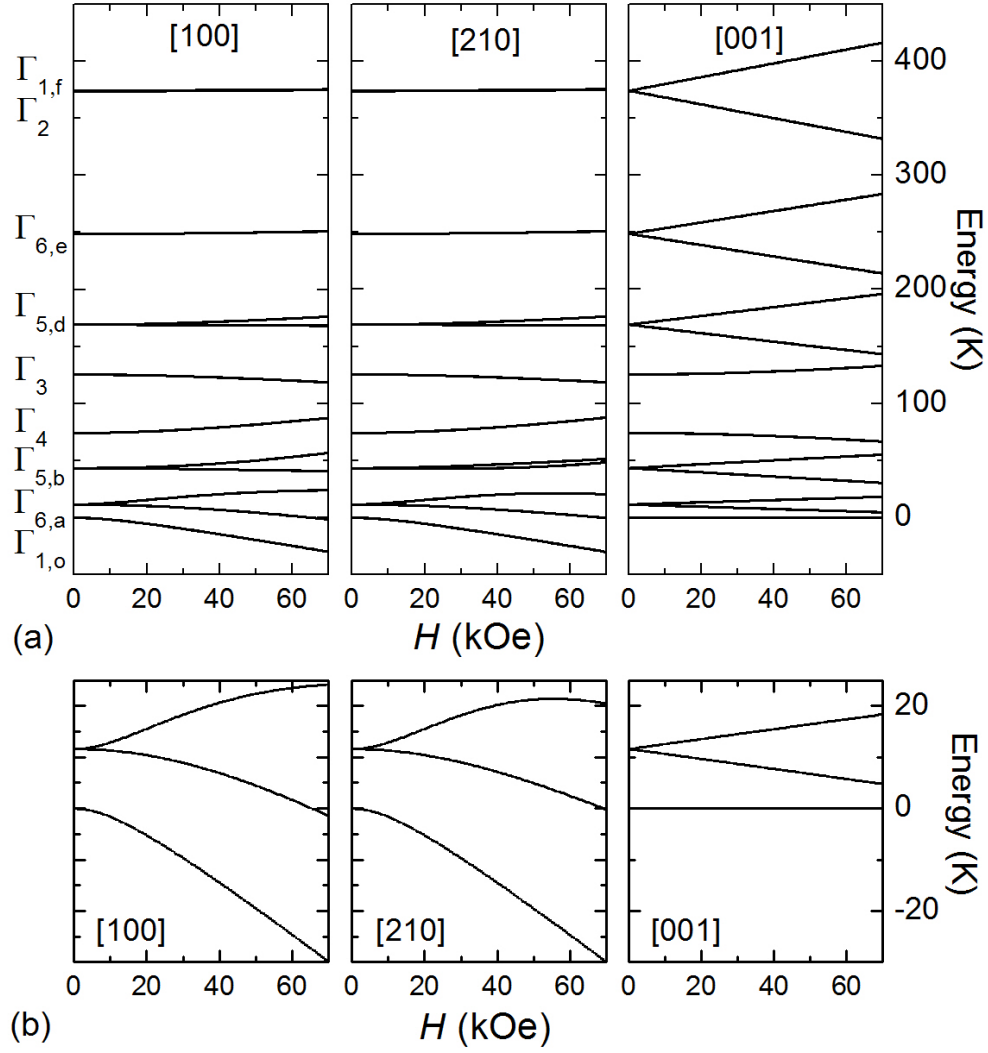


Figure 5.16 Field-dependent CEF level energies for TbMg_2Cu_9 with H along (a) $[100]$, (b) $[210]$ and (c) $[001]$. The label on the left side was adapted from Ref. [24].

anisotropy requires a very subtle balance between CEF effect, internal magnetic field and applied magnetic field. For example, decreasing the energy difference between low-lying states will increase the relative strength of a given applied magnetic field. In the case of DyMg_2Cu_9 , by reducing the splitting between of the three lower-lying doublets ($\Gamma_{8,c}$, $\Gamma_{9,b}$, $\Gamma_{7,a}$) from 40 K to 10 K, a nearly ideal 6-state-clock state like that shown by green solid line in Fig. 5.13(b) can be realized at 50 kOe (as opposed to 300 kOe for the real compound). In the proposed CEF schemes for $\text{HoNi}_2\text{B}_2\text{C}$ [191], the 3 lowest-lying CEF levels in fact only have a span of ~ 10 K and nearly 90 K away from higher CEF levels. This condition favors a clock-state-model at a moderate, reachable applied magnetic field as observed[162]. However, angular-dependent magnetization data at different magnetic fields have not been measured on $\text{HoNi}_2\text{B}_2\text{C}$, nor on other 4-state-clock model systems[162; 163], which would be helpful to investigate the effect of this interplay between CEF and magnetic field on in-plane magnetic anisotropy.

5.5 Conclusion

Single crystals of RMg_2Cu_9 ($R = \text{Y, Ce-Nd, Gd-Dy, Yb}$) have been synthesized using a high-temperature solution growth technique and characterized by magnetization, resistivity and specific heat measurements. YMg_2Cu_9 is non-magnetic. Ce is trivalent in CeMg_2Cu_9 . It undergoes two magnetic transitions at 2.1 and 1.5 K respectively. PrMg_2Cu_9 does not order down to 0.5 K and appears to have a non-magnetic singlet ground state based on temperature-dependent magnetization and specific heat data. Yb is divalent, and therefore non-moment-bearing, in YbMg_2Cu_9 . All the other local-moment-bearing members order antiferromagnetically at low-temperature. The ordering temperature of TbMg_2Cu_9 (11.9 K) is higher than that found in GdMg_2Cu_9 (9.7 K), indicating a deviation from de Gennes' scaling. Magnetic anisotropies were observed for RMg_2Cu_9 ($R = \text{Ce-Nd, Tb, Dy}$) with all of them showing a $\chi_{ab} > \chi_c$ in their paramagnetic states. Angular-dependent magnetization was studied in more detail for TbMg_2Cu_9 and DyMg_2Cu_9 . Even though they have a strong planar magnetization, their in-plane magnetic anisotropy is small and field-dependent. This phenomena can be explained by single ion CEF effect where the laboratory magnetic field is not large enough to observe a clear clock-state given the CEF splitting. To observe an in-plane state-clock-model at low applied

magnetic fields, the lower-lying CEF levels that can give rise to a large in-plane magnetization, as compared to out-of-plane magnetization, need to be relatively closely spaced in temperature and well separated from the higher-lying levels. Such a condition was met in the case of $\text{HoNi}_2\text{B}_2\text{C}$. However, a model system for a 6-clock-state is yet to be found.

CHAPTER 6. TUNING THE KONDO EFFECT IN $\text{Yb}(\text{Fe}_{1-x}\text{Co}_x)_2\text{Zn}_{20}$

The $RTM_2\text{Zn}_{20}$ (R = rare earth elements. TM = transition metals) series of compounds were discovered two decades ago, in 1997[192]. They crystallize in a cubic, $\text{CeCr}_2\text{Al}_{20}$ type structure (space group $\text{Fd}\bar{3}\text{m}$) where R ions occupy a single crystallographic site. The nearest, and next-nearest neighbors of R ions are all Zn and thus varying the transition metal does not significantly alter the local environment of the R^{3+} . Even though more than 85% of the atomic constituents are zinc, these compounds exhibit myriad physical properties depending on the rare earth and transition metal that are involved[193; 194; 195; 196; 197]. When the rare earth element is Yb, there are six closely related $\text{Yb}TM_2\text{Zn}_{20}$ heavy fermion compounds for $TM = \text{Fe, Ru, Os, Co, Rh, Ir}$ [197; 198]. Among these six compounds, $\text{YbCo}_2\text{Zn}_{20}$ has the largest Sommerfeld coefficient, $\gamma \sim 7900 \text{ mJ/mol-K}^2$. This value is comparable to the record holding YbBiPt [199], and is more than an order of magnitude larger than the other members in this family, which have γ values ranging from 520 mJ/mol K^2 for $\text{YbFe}_2\text{Zn}_{20}$ to 740 mJ/mol K^2 for $\text{YbRh}_2\text{Zn}_{20}$ [197]. The reason behind the dramatic difference between $\text{YbCo}_2\text{Zn}_{20}$ and the other five $\text{Yb}TM_2\text{Zn}_{20}$ compounds is still not clear, although band structure calculations reveal that the 4f level is closer to the Fermi level in $\text{YbCo}_2\text{Zn}_{20}$ than in $\text{YbFe}_2\text{Zn}_{20}$. Upon Co substitution, the d band is gradually filled, which is accompanied by a drop in d band energy[200].

Being the heaviest of the $\text{Yb}TM_2\text{Zn}_{20}$ compounds, $\text{YbCo}_2\text{Zn}_{20}$ has been studied intensively ever since its discovery[197]. Upon application of pressure, there is an indication that the heavy Fermi liquid regime can be suppressed, followed by the appearance of an antiferromagnetic ordering for $P > 1 \text{ GPa}$ [201]. It has, therefore, been argued that $\text{YbCo}_2\text{Zn}_{20}$ is close to a quantum critical point (QCP)[201; 202]. Similar suppressions of Fermi liquid regime under pressure were also observed for $TM = \text{Fe/Rh/Ir}$ [203; 204; 205]. In the case of $\text{YbFe}_2\text{Zn}_{20}$,

$\gamma = 520$ mJ/mol K², and is thus likely to be further away from a QCP in terms of the Doniach diagram, indeed, a much higher critical pressure, around 10 GPa was proposed in order to reach a QCP[203]. With an effective negative pressure induced by Cd substitution, the hybridization between Yb³⁺ 4f electrons in YbFe₂Zn₂₀ and the conduction electrons becomes weaker[206]. Apart from pressure induced ordering, metamagnetic transitions were reported for YbCo₂Zn₂₀ at high magnetic fields[207; 208; 209; 210]. Crystalline electric field (CEF) schemes for YbCo₂Zn₂₀ have been proposed based on specific heat and anisotropic magnetization measurements. The first and the second excited CEF levels are around 10 K and 25 K above the ground state doublet[211; 53]. Inelastic neutron scattering measurements show some excitations that might be related to these proposed CEF schemes[212]. Experimentally, band structure had only been reported for YbCo₂Zn₂₀ via quantum oscillations[213], with heavy ground state being strongly suppressed by increasing field. In a zero field limit, the mass of the quasiparticles was extrapolated to be 100-500 times the free electron mass.

Given that (i) the first and second nearest neighbors of Yb³⁺ in Yb*TM*₂Zn₂₀ do not have *TM* and (ii) as *TM* changes from Fe to Co the values of T_K and γ change by an order of magnitude, it is of interest to see how the strongly correlated electron state evolves in Yb(Fe_{1-x}Co_x)₂Zn₂₀ for 0 ≤ x ≤ 1. In this paper, we report the temperature-dependent resistivity and specific heat data on 19 members of the Yb(Fe_{1-x}Co_x)₂Zn₂₀ series and track the effects of band filling and disorder on the coherence and Kondo temperatures as well as amounts of entropy removed by thermal depopulation of CEF levels versus Kondo state. This work has now been posted in Ref. [115]

6.1 Experimental Results

Single crystals were grown using a high temperature solution growth technique[193; 197]. The starting molar stoichiometry was Yb:*TM*:Zn = 2:4:94. Bulk elemental material (Yb from Ames Laboratory Material Preparation Center (99.9% absolute purity); Fe (99.98%), Co (99.9+%) and Zn (99.999%) from Alfa Aesar) were packed in a frit-disc crucible set[111] and sealed in a silica tube under ~0.25 bar of Ar atmosphere. The ampoule assembly was then heated up to 900 °C over three hours; dwelt at 900 °C for 10 hours and then cooled to 600 °C

over 100 hours. At 600 °C, the remaining Zn rich solution was decanted from the crystals that formed on cooling.

Fig. 6.1 shows the WDS determined Co concentration as a function of nominal Co concentration. Although the average value of the WDS determined concentration changes close to linearly with the nominal concentration, in the middle of the substitution range, the variation of the substitution level is large. The variation is based on WDS results measured at different spots on the sample as well as different samples in the same batch. Near the two ends of the series, the variation in substitution level is significantly smaller.

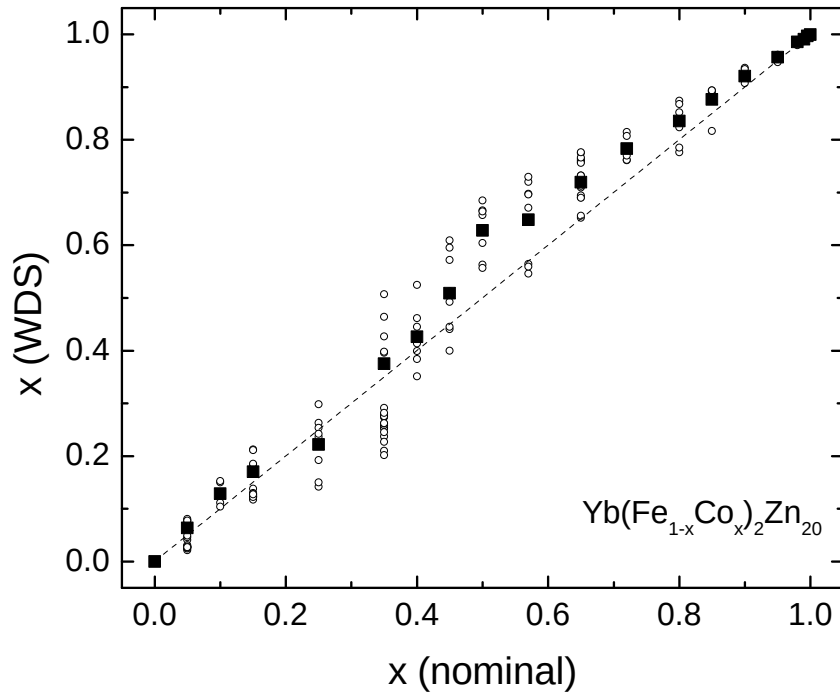


Figure 6.1 Co concentrations determined by WDS as a function of nominal Co concentration values. Solid squares represent averaged WDS values. Hollow circle data points show measured values at different spots of samples. Dashed line is a guide for the eyes with a slope of 1.

Fig. 6.2 shows the temperature-dependent resistivity data of $\text{Yb}(\text{Fe}_{1-x}\text{Co}_x)_2\text{Zn}_{20}$ on semi-log plots. Fig. 6.2(a) shows data closer to the pure $\text{YbFe}_2\text{Zn}_{20}$ side. At $x = 0$, the resistivity of $\text{YbFe}_2\text{Zn}_{20}$ shows a broad shoulder at ~ 40 K, after which it goes into a Kondo coherence. At

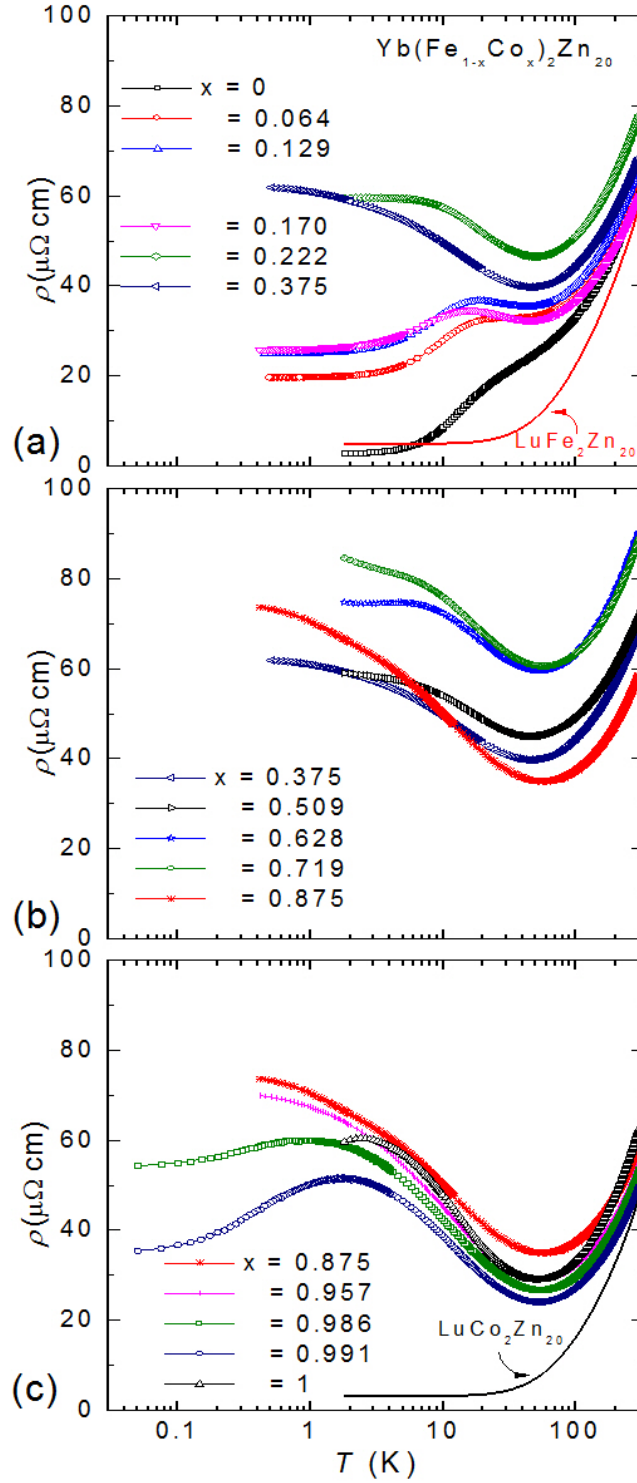


Figure 6.2 Zero-field temperature-dependent resistivity of $\text{Yb}(\text{Fe}_{1-x}\text{Co}_x)_2\text{Zn}_{20}$ for a selective of Co concentrations on semi-log plots. Resistivity of non-magnetic $\text{LuFe}_2\text{Zn}_{20}$ and $\text{LuCo}_2\text{Zn}_{20}$ are also shown for comparison.

low-temperature, $\text{YbFe}_2\text{Zn}_{20}$ manifests a T^2 temperature-dependence with the coefficient of T^2 resistivity, $A = 0.054 \mu\Omega \text{ cm/K}^2$ [[197]]. As the Co concentration increases, the resistivity value at 300 K increases, most likely as a result of increasing amount of scattering due to chemical disorder (i.e. Fe/Co). In addition, the temperature at which resistivity starts to decrease, after the low temperature shoulder or local maximum, gradually shifts to lower temperatures, indicating a lowering of the Kondo coherence temperature. At $x = 0.064$, the low-temperature resistivity still follow a T^2 behavior with $A = 0.113 \mu\Omega \text{ cm/K}^2$. This value doubles the value for $\text{YbFe}_2\text{Zn}_{20}$ ($x = 0$). The A coefficient keeps increasing with Co concentration: $\sim 0.173 \mu\Omega \text{ cm/K}^2$ for $x = 0.129$ and $\sim 0.197 \mu\Omega \text{ cm/K}^2$ for $x = 0.170$. At $x = 0.375$, the low-temperature resistivity does not show a decrease and seems to saturate down to 500 mK. As x increases from 0 to 0.375, $\text{Yb}(\text{Fe}_{1-x}\text{Co}_x)_2\text{Zn}_{20}$ evolves from a system with a clear Fermi liquid signature in transport to one that does not.

Fig. 6.2(b) shows resistivity data in the middle of the substitution range ($0.375 \leq x \leq 0.875$). None of the data shown have a clear signature of a resistivity drop that would be associated with a Kondo coherence. For $x = 0.628$ (blue star) and 0.719 (green dotted circle), the low-temperature resistivity data show a minor decrease which is followed by an secondary increase at a lower temperature. This is reminiscent of what one would expect from a CEF feature when lowering the temperature depopulates the CEF levels and thus change the degeneracy participating in the Kondo effect[48]. However, it is unclear at this point if a coherence might be reached for these substitution levels for temperatures below 500 mK.

Fig. 6.2(c) presents data close to the pure $\text{YbCo}_2\text{Zn}_{20}$ side ($0.875 \leq x \leq 1$). Black hollow triangles show the resistivity data for pure $\text{YbCo}_2\text{Zn}_{20}$ which are consistent with the previously reported results[197]. The resistivity increases with decreasing temperature below ~ 50 K, indicative of a Kondo effect. The drop of resistivity below 2 K is an indication of Kondo coherence. With a small amount of substitution of Fe for Co, shown by the blue hollow circles ($x = 0.991$) and green hollow squares ($x = 0.986$), the temperature at which resistivity starts to drop decreases. With further Fe substitution, the Kondo coherence signature in resistivity could not be observed down to 500 mK as illustrated by purple bar ($x = 0.957$) and red star data ($x = 0.875$). Since the coherence temperature of $\text{YbCo}_2\text{Zn}_{20}$ is much lower than that for

$\text{YbFe}_2\text{Zn}_{20}$, it takes less Fe substitution to suppress the coherence temperature of $\text{YbCo}_2\text{Zn}_{20}$ to below 500 mK.

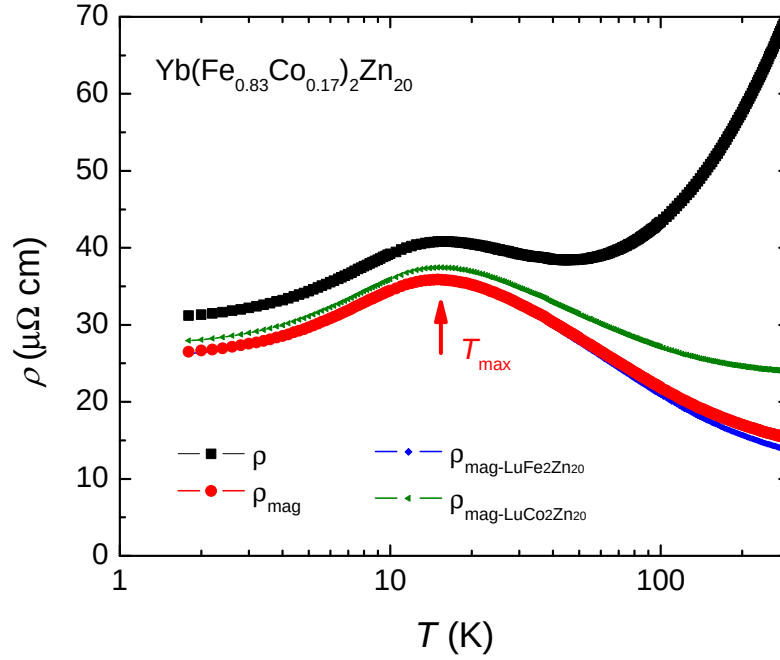


Figure 6.3 Temperature-dependent resistivity for $\text{Yb}(\text{Fe}_{0.83}\text{Co}_{0.17})_2\text{Zn}_{20}$ on a semi-log plot. Black squares show the total resistivity. Red circles show the magnetic part of the resistivity. Blue diamonds and green triangles represent magnetic part of resistivity by subtracting the resistivity of pure $\text{LuFe}_2\text{Zn}_{20}$ or $\text{LuCo}_2\text{Zn}_{20}$ (see text). Arrows indicate criteria for determining T_{max} from the ρ_{mag} data.

Fig. 6.3 illustrates the criteria that were used to infer characteristic temperatures for the $\text{Yb}(\text{Fe}_{1-x}\text{Co}_x)_2\text{Zn}_{20}$ compounds from the resistivity data. The magnetic part of resistivity was estimated by subtracting a combination of the resistivity for the non-magnetic $\text{LuFe}_2\text{Zn}_{20}$ and $\text{LuCo}_2\text{Zn}_{20}$ with the same Fe/Co ratio. For example, in Fig. 6.3, the non-magnetic part of the resistivity data for $\text{Yb}(\text{Fe}_{0.83}\text{Co}_{0.17})_2\text{Zn}_{20}$ were estimated as $0.83\rho_{\text{LuFe}_2\text{Zn}_{20}} + 0.17\rho_{\text{LuCo}_2\text{Zn}_{20}}$. Note, however, such subtraction does not take into account the disorder scattering introduced by Fe/Co substitution. The temperature of the maximum in ρ_{mag} was tracked as T_{max} . For comparison, the magnetic part of the resistivity estimated by subtracting the resistivity of pure $\text{LuFe}_2\text{Zn}_{20}$ (blue diamonds) and $\text{LuCo}_2\text{Zn}_{20}$ (green triangles) as well as the resistivity

of $\text{Yb}(\text{Fe}_{0.83}\text{Co}_{0.17})_2\text{Zn}_{20}$ (black squares) are also shown in Fig. 6.3. The temperatures of the maximum in all these data sets are similar and consistent. In the absence of low-temperature data for non-magnetic subtraction below 1.8 K, the total resistivity data were then used to extract characteristic temperatures.

The temperature-dependent magnetic specific heat data for $\text{Yb}(\text{Fe}_{1-x}\text{Co}_x)_2\text{Zn}_{20}$ are shown in Fig. 6.4. Similar to the magnetic part of the resistivity, the specific heat of $\text{LuCo}_2\text{Zn}_{20}$ and $\text{LuFe}_2\text{Zn}_{20}$ were used to perform non-magnetic background subtraction. Quantitatively, subtracting $\text{LuFe}_2\text{Zn}_{20}$ or $\text{LuCo}_2\text{Zn}_{20}$ only results in a $\lesssim 2\%$ difference in the magnetic specific heat value and a $\lesssim 5\%$ change in characteristic temperature values. Therefore, for all the doped samples, a consistent non-magnetic background specific heat of $\text{LuCo}_2\text{Zn}_{20}$ was subtracted.

The magnetic specific heat of $\text{YbFe}_2\text{Zn}_{20}$ (black squares in Fig. 6.4(a)) can be well explained by a $N = 8$ Kondo resonance as shown by the brown solid line[47]. With Co substitution, the Kondo resonance peak moves towards lower temperature accompanied by a decrease in maximum value. At $x = 0.064$, the electronic specific heat, γ , increases from 520 mJ/mol K^2 for $\text{YbFe}_2\text{Zn}_{20}$ [197] to 690 mJ/mol K^2 . With more Co substitution, γ increases to ~ 790 mJ/mol K^2 for $x = 0.129$ and ~ 890 mJ/mol K^2 for $x = 0.170$. Together with the increase in the coefficient of T^2 resistivity, the positions of $\text{Yb}(\text{Fe}_{1-x}\text{Co}_x)_2\text{Zn}_{20}$ ($x = 0.064, 0.129$ and 0.170) on the generalized Kadowaki-Woods plot gradually move toward the $\text{YbCo}_2\text{Zn}_{20}$ side[197] as shown in the inset of Fig. 6.4(c). As Co substitution increases further, the single peak in $\text{YbFe}_2\text{Zn}_{20}$ gradually evolves to two maxima, as a result of competing energy scale of CEF splitting and the Kondo effect[52].

In between $0.375 \lesssim x \lesssim 0.719$, the magnetic specific heat data show very similar behavior. We keep track of the two maxima temperatures as C_{high} (maxima that locates at a higher temperature) and C_{low} (maxima that locates at a lower temperature) [Fig. 6.4(b)]. For $x = 0.628$, the specific heat was measured down to 50 mK. An upturn at below 100 mK was observed and will be discussed later. With more Co substitution, C_{high} starts to move towards lower temperature.

Fig. 6.4(c) shows magnetic specific heat data close to the pure $\text{YbCo}_2\text{Zn}_{20}$ side. From a generalized Kadowaki-Woods plot, the degeneracy that is responsible for Kondo coherence for

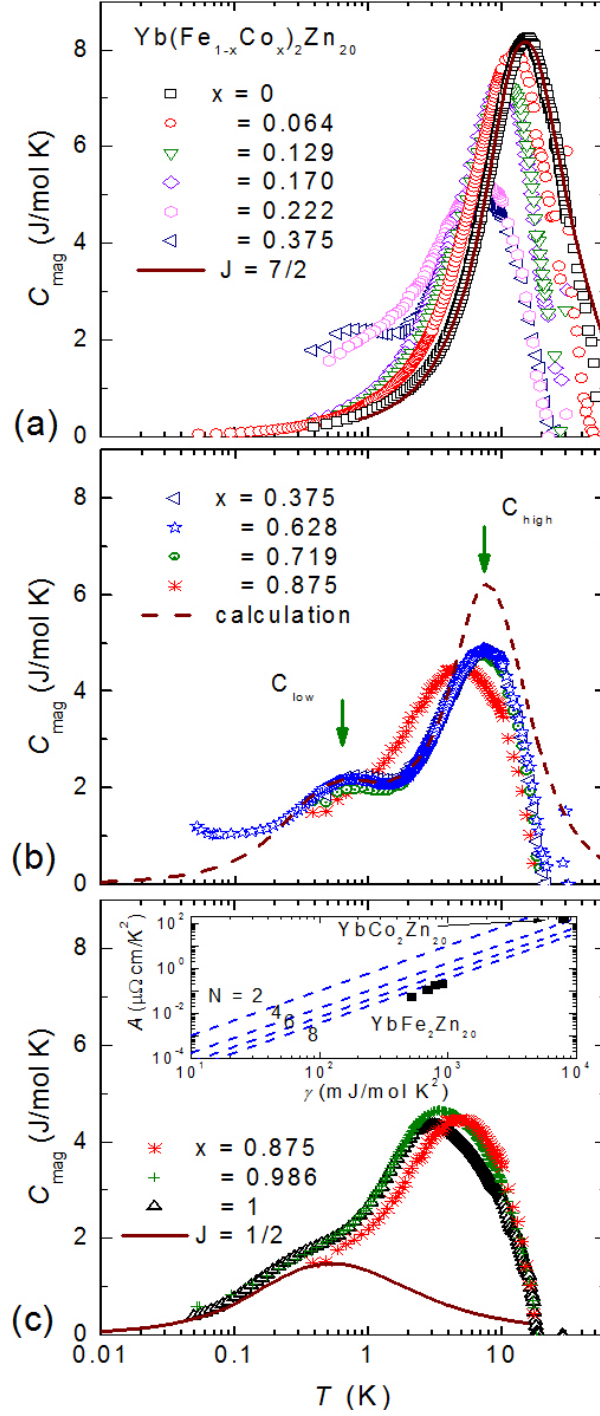


Figure 6.4 Temperature-dependent magnetic specific heat of $\text{Yb}(\text{Fe}_{1-x}\text{Co}_x)_2\text{Zn}_{20}$ for a various of Co concentrations. Solid lines in (a) and (c) represent magnetic specific heat of the Coqblin-Schrieffer model for $J = 7/2$ and $1/2$ [46; 47]. The brown dashed line in (b) represents calculated magnetic specific heat based on a model proposed in Ref. [53] (see text). Green arrows indicate the criteria for determining C_{high} and C_{low} . Inset in (c) is a generalized Kadowaki-Woods plot with N denoting the degeneracy that is responsible for the Kondo effect[59] and data points representing $\text{Yb}(\text{Fe}_{1-x}\text{Co}_x)_2\text{Zn}_{20}$ ($x = 0, 0.064, 0.129, 0.170$ and 1).

$\text{YbCo}_2\text{Zn}_{20}$ is in between 2 and 4. The specific heat can be tentatively understood with a spin 1/2 Kondo resonance with additional contribution from higher temperature Schottky peak-features due to CEF splitting[211; 53]. The brown solid line presents the magnetic specific heat due to a spin 1/2 Kondo resonance[47]. It captures, for the most part, the low-temperature part of the measured data (black triangles), with differences at higher temperatures coming from CEF effects, suggesting a doublet CEF ground state. With addition of Fe, the high-temperature maximum moves towards higher temperature, indicating a small increase of CEF splitting. In the mean time, the low-temperature part of the specific heat sees a slight increase (green squares) at the base temperature. This feature may eventually evolve to an upturn seen for $x = 0.628$.

6.2 Discussion

Summarizing resistive and specific heat features presented above, we can plot characteristic temperatures of $\text{Yb}(\text{Fe}_{1-x}\text{Co}_x)_2\text{Zn}_{20}$ as a function of Co concentration, x . In Fig. 6.5, the green diamonds and cyan triangles represent characteristic temperatures inferred from specific heat data and black circles were inferred from resistivity measurements. At a gross level, the phase diagram can be divided into three regions. Two regions are on the pure $\text{YbFe}_2\text{Zn}_{20}$ or $\text{YbCo}_2\text{Zn}_{20}$ sides where the original Kondo lattice characteristic temperatures gradually evolve with Fe/Co substitution. The third region is in the middle where all feature temperatures are relatively similar and do not significantly change or evolve with x .

We first look at the two regions close to the pure $\text{YbFe}_2\text{Zn}_{20}$ and $\text{YbCo}_2\text{Zn}_{20}$ sides. The crossover from a high-temperature, single ion regime to a low-temperature coherent regime can usually be seen and inferred from temperature-dependent resistivity measurements[214; 215]. In the coherent regime, the resistivity drops at low-temperature, becoming a heavy Fermi-liquid state. Both $\text{YbFe}_2\text{Zn}_{20}$ and $\text{YbCo}_2\text{Zn}_{20}$ have a heavy Fermi liquid ground state down to 50 mK as evidenced by linear specific heat and a T^2 dependence in resistivity[197; 196]. On the $\text{YbFe}_2\text{Zn}_{20}$ side, Co substitution suppresses T_{max} at roughly 1.8 K/%Co. At $x = 0.222$, the T_{max} is suppressed to 3 K. With more Co substitution, T_{max} was suppressed below the base temperature of measurements. A similar situation happens on the $\text{YbCo}_2\text{Zn}_{20}$ side. T_{max} is

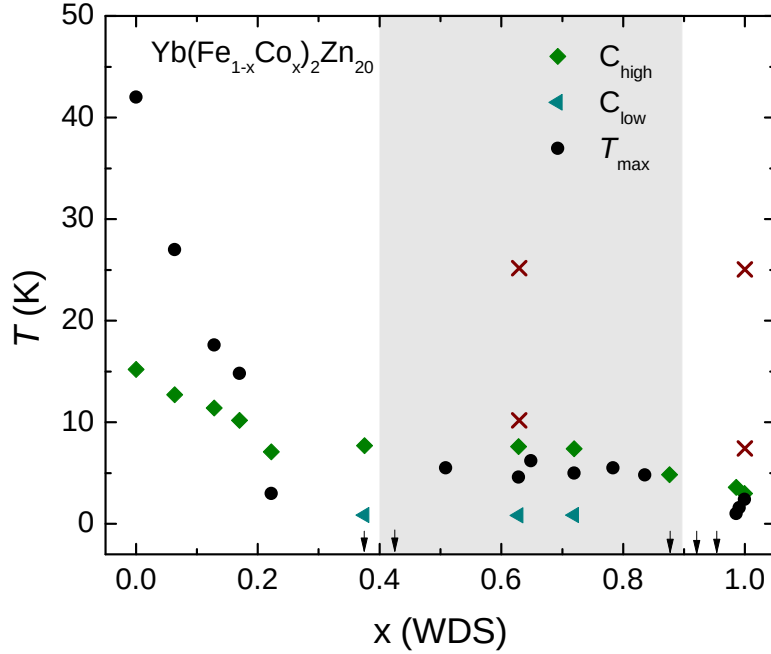


Figure 6.5 Characteristic temperatures as a function of Co concentration in $\text{Yb}(\text{Fe}_{1-x}\text{Co}_x)_2\text{Zn}_{20}$. Green solid diamond and cyan triangle represent specific heat maxima temperatures at high temperature and low temperature respectively. Black circles represent $T_{\max}$ values extracted from resistivity data as illustrated in Fig. 6.3. Arrows at the bottom indicate samples that were measured resistively but showed no $T_{\max}$ down to 2 K ($x = 0.426, 0.921$) or 500 mK ($x = 0.375, 0.875, 0.957$). Brown crosses indicate the estimated energy of excited CEF levels for $x = 0.628$ and 1. The grey shaded area separates the phase diagram into three regions as described in the text.

suppressed upon Fe substitution at roughly 1 K/%Fe. Given a much smaller, initial $T_{\max}$ value to start with, the trackable features quickly disappears to below 50 mK.

Magnetoresistance is sometimes used to probe the Kondo state at low temperature as well[216]. The single ion Kondo regime has been theoretically calculated to show a negative magnetoresistance[217]. In the coherent regime, the compound is essentially a heavy Pauli-paramagnetic metal. Magnetoresistance therefore is most commonly positive. The magnetoresistance for $\text{YbFe}_2\text{Zn}_{20}$ is positive at 1.8 K, which is consistent with a coherent state (Fig. 6.6). For $\text{YbCo}_2\text{Zn}_{20}$, prior to the metamagnetic transition, the magnetoresistance is also positive below 0.1 K whereas shows negative magnetoresistance above 3 K[218; 210].

Magnetoresistance data are shown for various Co concentrations at 1.8 K in Fig. 6.6. Samples were cut and polished so that magnetic field is applied along the [111] crystallographic direction. Positive magnetoresistances for Co concentrations $x \lesssim 0.170$ suggest a coherence at 1.8 K. Other members ($x \geq 0.222$) show negative magnetoresistances that suggest a single ion state. Assuming that the T_{max} is commensurate with coherence temperature, together with the magnetoresistance data, the coherence is suppressed on both ends of the phase diagram (Fig. 6.5). In the middle of the substitution range, however, no clear indication of coherence could be determined at 1.8 K.

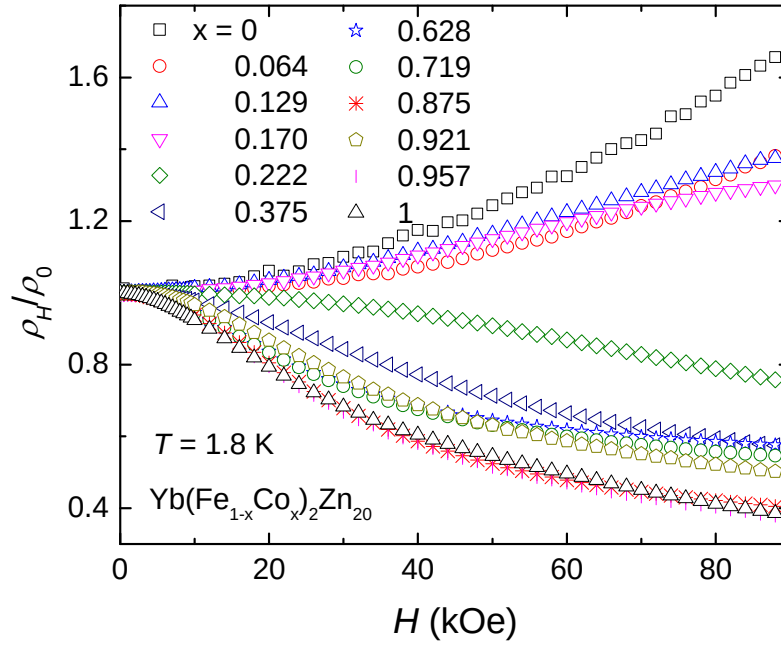


Figure 6.6 Magnetoresistance of $\text{Yb}(\text{Fe}_{1-x}\text{Co}_x)_2\text{Zn}_{20}$ measured at 1.8 K up to 90 kOe.

Specific heat features close to the pure $\text{YbFe}_2\text{Zn}_{20}$ and $\text{YbCo}_2\text{Zn}_{20}$ sides evolve gradually with chemical substitution. On the $\text{YbFe}_2\text{Zn}_{20}$ side, with Co substitution, C_{high} moves to lower temperature, indicating a lowering of Kondo temperature[47]. On the pure $\text{YbCo}_2\text{Zn}_{20}$ side, where the Kondo temperature is smaller than the CEF splitting, with Fe substitution, C_{high} moves towards higher temperature, indicating a slight increase of CEF splitting.

The Kondo coherence feature in specific heat is much more subtle and under debate. Various models have proposed a decrease of density of states at the Fermi energy due the formation of coherence[219; 220; 34; 35]. Experimentally, this decrease of density of states was used to explain the low-temperature drop in C/T (or γ) in different systems, for example, in CeAl_3 [221; 222], CuCu_6 [223], CeNi_2Ge_2 [224] and CeCu_2Si_2 [222]. However, a feature associated with coherence in specific heat is not always so apparent and is commonly missing, for example in $\text{YbNi}_2\text{B}_2\text{C}$ [225], YbCuAl [226], CeCoGe_2 [227], YbAgCu_4 [228; 229] and CeNi_9Si_4 [230]. A single ion model based on a Coqblin-Schrieffer analysis[46; 47] seems to describe these Kondo lattice systems very well, even in the coherent regime. For $\text{Yb}TM_2\text{Zn}_{20}$, despite the fact that coherence emerges in resistivity at low-temperature, specific heat can be well captured by single ion Kondo effect[197].

Close to pure $\text{YbFe}_2\text{Zn}_{20}$ and $\text{YbCo}_2\text{Zn}_{20}$, it is shown above that upon Fe/Co substitution, the coherence temperatures on both sides are suppressed. The suppression of coherence is commonly achieved by substituting the moment bearing ions with non-moment bearing ions[44]. In the case of $\text{Yb}(\text{Fe}_{1-x}\text{Co}_x)_2\text{Zn}_{20}$, moment bearing Yb-sites are always fully occupied and ordered. Substituting Fe/Co, however, will inevitably bring in chemical disorder as well as a change in band filling. As a consequence of chemical disorder, the decrease in mean free path of the conduction electrons, as can be represented by the increase of residual resistivity, may lead to a suppression of Kondo coherence temperature[231]. This is sometimes also seen in systems with artificially created defects with irradiation[232]. Theoretically, it is proposed that disorder on the moment-bearing site (f-site) affects Kondo coherence more efficiently than disorder on the conduction-electron sites. To produce the same suppression of Kondo coherence temperature, energetically, f-sites disorder need to be equivalent to T_K whereas conduction-electron sites need to be comparable to the band width of the conduction band, which is more difficult[233]. However, with a change of band filling due to Fe/Co substitution, disorder in the conduction electron sites could affect Kondo coherence in these $\text{Yb}(\text{Fe}_{1-x}\text{Co}_x)_2\text{Zn}_{20}$ compounds.

The change in band filling due to Fe/Co substitution, on one hand, could be part of the disorder in conduction electrons in aforementioned theoretical model. On the other hand, it may lead to a change in the ratio of Kondo coherence temperature over Kondo temperature,

T_{coh}/T_K [37]. At half-filling, it is proposed that T_{coh} is larger than T_K . Away from half-filling, T_{coh} drops quickly below T_K [37]. It is possible that with changing band filling, T_{coh} decreases from both the $\text{YbFe}_2\text{Zn}_{20}$ and $\text{YbCo}_2\text{Zn}_{20}$ sides, which leaves a clear single ion Kondo effect with features associated with CEF population whereas showing no coherence or a very low coherence temperature. Such an extended range of low T_{coh} is observed in the middle region of the phase diagram. A change in band filling may be inferred from the density of states at Fermi energy. It worth noting that the density of states for $\text{YFe}_2\text{Zn}_{20}$ experiences a quick drop upon adding Co and stays relatively constant above 20% Co substitution[193]. This is very similar to the suppression of T_{max} close to the $\text{YbFe}_2\text{Zn}_{20}$ side. Close to the $\text{YCo}_2\text{Zn}_{20}$ side, though, there are not enough data density to make similar comparison to $\text{YbCo}_2\text{Zn}_{20}$.

We now move onto the middle region of the phase diagram shown in Fig. 6.5. Whereas there are clear changes of characteristic temperatures as the sample departs from perfect chemical order, in the middle region, for $0.4 \lesssim x \lesssim 0.9$, characteristic temperatures stay fairly constant. It worth noting though, as shown in Fig. 6.1, the variation in concentration across a sample in this middle region may make the data blurred and offer only more qualitative information rather than quantitative.

In a single ion Kondo picture, different local moment degeneracy can give rise to unique features in thermodynamic and transport properties[46; 48; 49]. In the presence of crystalline electric field, features can be observed in temperature-dependent transport measurements, exhibited as broad maxima in resistivity, for example in CeAl_2 [234], CeCu_2Si_2 [235], CePdIn [236], CeZn_{11} [237]. This was observed for several members of $\text{Yb}(\text{Fe}_{1-x}\text{Co}_x)_2\text{Zn}_{20}$ series, in the middle substitution range, for example, $x = 0.628$ and 0.719 . However, the CEF feature is not as clear as systems mentioned above. If the CEF levels are not well separated, given a certain combination of density of states and Kondo coupling, these broad maxima can be hard to observe[48]. In the case of $\text{YbTM}_2\text{Zn}_{20}$, the CEF splitting is indeed small and may cause the CEF feature to be difficult to observe. Impurity scattering can also lead to a smear of Kondo CEF features. In $\text{YbNi}_2\text{B}_2\text{C}$, the improved sample quality after annealing dramatically changed the temperature-dependent transport properties. This can be attributed to a distribution of Kondo temperature in a non-ideal lattice with local defects and strain[238]. In

$\text{Yb}(\text{Fe}_{1-x}\text{Co}_x)_2\text{Zn}_{20}$, the substitution variation in the sample may cause such disorders even though transition metal is not in the direct neighborhood of the Yb ions.

To understand what happens in the middle of the substitution range in $\text{Yb}(\text{Fe}_{1-x}\text{Co}_x)_2\text{Zn}_{20}$, more insights can be obtained from the specific heat data. In the presence of crystal fields, the temperature-dependence of magnetic specific heat in Kondo systems is complicated. An arbitrary CEF splitting has only been recently studied numerically for Ce-based compounds[52]. For Yb, more degeneracy, and levels, are involved. A quantitative interpretation of the temperature-dependent specific heat can be approached by combining a resonance model solution together with a, CEF, Schottky-like contribution[53]. In a cubic symmetry, Yb will be split into two doublets and a quartet. Assuming the quartet is at higher temperature, the temperature-dependent specific heat can be written as[53]:

$$C_{mag} = C_{2d} - \frac{1}{k_B T^2} \left[\frac{\Delta^2 e^{-\Delta/k_B T}}{(1 + e^{-\Delta/k_B T})^2} \right] + C_s \quad (6.1)$$

in which,

$$C_{2d} = -\frac{k_B}{2(\pi k_B T)^2} \text{Re} \sum_{j=0}^1 \left\{ (\Gamma_j + i\Delta_j)^2 \left[4\psi' \left(\frac{\Gamma_j + i\Delta_j}{\pi k_B T} \right) - \psi' \left(\frac{\Gamma_j + i\Delta_j}{2\pi k_B T} \right) \right] \right\} + \frac{\Gamma_0 + \Gamma_1}{\pi T} \quad (6.2)$$

$$C_s = \frac{1}{k_B T^2} [(\Delta_1)^2 e^{-\Delta_1/k_B T} + 2(\Delta_2)^2 e^{-\Delta_2/k_B T} + 2(\Delta_2 - \Delta_1)^2 e^{-(\Delta_1 + \Delta_2)/k_B T}] (1 + e^{-\Delta_1/k_B T} + 2e^{-\Delta_2/k_B T})^{-2} \quad (6.3)$$

Here, C_{2d} is the Kondo resonance contribution from the lower lying two doublets. Γ_j represents the half-width at half-maximum of the spectral density for each crystal field level. ψ' is the derivative of the digamma function and C_s is the Schottky expression for a three level system. Δ_j represents the excited CEF energies. The second term in Eq.(1) accounts for the double counting of the Schottky contribution. Δ equals to Δ_1 ignoring complications of the

ground state doublet[53]. Δ_0 for the ground state doublet is introduced to account for the resonance that is displaced away from the Fermi energy[53].

In Fig. 6.4(b), data for $\text{Yb}(\text{Fe}_{0.372}\text{Co}_{0.628})_2\text{Zn}_{20}$ could be best fitted by the brown dashed line with parameters: $\Delta_0 = 1$ K, $\Delta_1 = 10$ K, $\Delta_2 = 25$ K, $\Gamma_0 = 0.87$ K, $\Gamma_1 = 4$ K. The low-temperature rise is omitted in the fit and will be discussed below. C_{low} mainly comes from the Kondo effect for the ground state doublet and C_{high} largely comes from Schottky contribution due to CEF population. Therefore, the temperature of C_{high} also reflects an upper limit of the total CEF splitting.

The calculated value qualitatively agrees with experimental data. Higher calculated values around 10 K might due to an error caused by non-magnetic background subtraction as illustrated by a negative value of C_{mag} for $T > 20$ K. It could also due to a lack of bandwidth information for the highest lying quartet in the theoretical model[53]. In general, the best fit indicates that the two CEF levels are at around 10 K and 25 K, which is similar to what had been proposed for $\text{YbCo}_2\text{Zn}_{20}$ [211; 53]. Thus at least to this level of Co substitution, as shown in Fig. 6.5 for Co-rich side of the phase diagram, the CEF splitting does not change significantly from the pure $\text{YbCo}_2\text{Zn}_{20}$. In addition, since the temperature of C_{high} sets an upper limit of the total CEF splitting, the total CEF splitting does not change much across the whole substitution range and may have increased slightly when approaching the $\text{YbFe}_2\text{Zn}_{20}$ side. In contrast, the CEF effect is more apparent for $\text{YbCo}_2\text{Zn}_{20}$. The difference in Kondo physics between $\text{YbFe}_2\text{Zn}_{20}$ and $\text{YbCo}_2\text{Zn}_{20}$ most likely originate from the difference in density of states as well as Kondo coupling strength.

Going back to the generalized Kadowaki-Woods plot shown in Fig. 6.4(c), upon Co substitution up to $x = 0.170$, the degeneracy that is responsible for the Kondo effect is still very close to the full degeneracy: $N = 8$. However, the temperatures at which Kondo coherence is developed have become comparable or even smaller than the estimated CEF splitting. This trend can be clearly represented by T_{max} shown in Fig. 6.5. It may be possible that, for $x = 0.170$ as an example, the Kondo temperature is still at a relatively higher temperature than the CEF splitting, which quenches the local moment with a degeneracy close to 8[52]. On the other hand, Kondo coherence, as tracked by T_{max} , does not significantly affect the way

magnetic entropy is removed. With an even lower Kondo energy scale, the CEF feature would have enough room to be more apparent, like in the case for $x = 0.222$.

Finally, as for the low-temperature rise in the specific heat of $\text{Yb}(\text{Fe}_{0.372}\text{Co}_{0.628})_2\text{Zn}_{20}$, since there is no magnetic ordering or applied magnetic field, there should not be a nuclear Schottky anomaly due to Zeeman splitting of nuclear levels in specific heat measurement. However, the low-temperature upturn in the specific heat data observed below 100 mK could still come from a nuclear quadrupolar splitting of the ^{173}Yb nuclear moment[239]. Such quadrupole splitting for Yb in a cubic point symmetry may arise from the electric field gradient caused by chemical substitution induced distortion. Even though transition metal is not the first, nor the second nearest neighbors of Yb, as substitution increases, the distortion to the original cubic symmetry increase. This is consistent with our observation that the low-temperature rise only emerges with chemical substitution and becomes more pronounced in the middle of the doping range. An alternative scenario is that the upturn is of a Kondo origin. However, that requires a decreasing CEF split energies upon substitution and a very small first excited CEF energy which was not observed in specific heat data. Instead, the C_{low} feature stays unchanged for the majority of the substitution range which otherwise should also evolve and split.

We would also like to mention a similar doping series: CeNi_9X_4 ($X = \text{Si}, \text{Ge}$)[240]. Changing from CeNi_9Ge_4 to CeNi_9Si_4 , the Kondo temperature increases from ~ 4 K to ~ 70 K with ground state CEF degeneracy changing from 4 for $X = \text{Ge}$ to 6 for $X = \text{Si}$ [240]. Upon doping, the coherence temperature drops quickly from both sides. In the middle of the doping, specific heat shows continuous evolution from high γ , Ge side, to the low γ , Si side. Understanding the suppression of Kondo coherence in these two systems might offer useful insights into the formation of Kondo coherence.

6.3 Conclusions

In conclusion, we studied the evolution of Kondo effect in $\text{Yb}(\text{Fe}_{1-x}\text{Co}_x)_2\text{Zn}_{20}$ via resistivity and specific heat measurements. With Co substitution, the Kondo coherence temperature of $\text{YbFe}_2\text{Zn}_{20}$ decreases gradually with emerging features in specific heat that can be associated with CEF effect. On the $\text{YbCo}_2\text{Zn}_{20}$ side, the coherence temperature is also suppressed at

the beginning of Fe substitution. In between, $0.4 \lesssim x \lesssim 0.9$, CEF features can be observed in both resistivity and specific heat data whereas showing no clear feature of coherence down to 500 mK. However, only qualitative information can be obtained in this middle substitution region due to a large substitution level variation. Comparing all the experimental results, the CEF splitting stays roughly unchanged across the substitution series. The ground state of the compound evolves from a $N = 8$ coherent state for $\text{YbFe}_2\text{Zn}_{20}$ to a $N = 2$ coherent state in $\text{YbCo}_2\text{Zn}_{20}$. More measurements are needed to reveal the mechanism behind the suppression of coherence on the $\text{YbFe}_2\text{Zn}_{20}$ and $\text{YbCo}_2\text{Zn}_{20}$ side.

APPENDIX. SUMMARY OF OTHER RESEARCH AND PUBLICATIONS

During my graduate school years, I was also heavily involved in the following projects.

$R\text{Co}_2\text{Ge}_2$ ($R = \text{Y, La-Nd, Sm-Tm}$)

In this project, single crystals of $R\text{Co}_2\text{Ge}_2$ ($R = \text{Y, La-Nd, Sm-Tm}$) were grown using a self-flux method and were characterized by room-temperature powder x-ray diffraction; anisotropic, temperature and field dependent magnetization; temperature and field dependent, in-plane resistivity; and specific heat measurements. In this series, the majority of the moment-bearing members order antiferromagnetically; YCo_2Ge_2 and LaCo_2Ge_2 are non-moment-bearing. Ce is trivalent in CeCo_2Ge_2 at high temperatures, and exhibits an enhanced electronic specific heat coefficient due to Kondo effect at low temperatures. In addition, CeCo_2Ge_2 shows two low-temperature anomalies in temperature-dependent magnetization and specific heat measurements. Three members ($R = \text{Tb-Ho}$) have multiple phase transitions above 1.8 K. Eu appears to be divalent with total angular momentum $L = 0$. Both EuCo_2Ge_2 and GdCo_2Ge_2 manifest essentially isotropic paramagnetic properties consistent with $J = S = 7/2$. Clear magnetic anisotropy for rare-earth members with finite L was observed, with ErCo_2Ge_2 and TmCo_2Ge_2 manifesting planar anisotropy and the rest members manifesting axial anisotropy. The experimentally estimated crystal electric field (CEF) parameters B_2^0 were calculated from the anisotropic paramagnetic θ_{ab} and θ_c values and follow a trend that agrees well with theoretical predictions. The ordering temperatures, T_N , as well as the polycrystalline averaged paramagnetic Curie-Weiss temperature, Θ_{avg} , for the heavy rare-earth members deviate from the de Gennes scaling, as the magnitude of both are the highest for Tb, which is sometimes seen

for extremely axial systems. Except for SmCo_2Ge_2 , metamagnetic transitions were observed at 1.8 K for all members that ordered antiferromagnetically.

This was the first project I participated. Before my existence, most of the single crystals had been synthesized by previous group members. I regrew some LaCo_2Ge_2 single crystals with the help of Mandi Buffon. Physical properties were measured with many helps from Dr. Lin and Dr. Bud'ko. This work was published in Ref. [175].

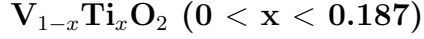
$\text{K}_2\text{Cr}_3\text{As}_3$ superconductor

$\text{K}_2\text{Cr}_3\text{As}_3$ is a newly discovered superconductor with a superconducting temperature, $T_c = 6.1$ K[241]. It was proposed to be a rare example of unconventional, quasi-one-dimensional, superconductor. In this project, single crystalline $\text{K}_2\text{Cr}_3\text{As}_3$ was synthesized and characterized. In zero-field, the temperature-dependent resistivity is metallic. Deviation from a linear temperature-dependence is evident below 100 K and a T^3 -dependence is roughly followed from just above T_c (~ 10 K) to ~ 40 K. The electronic specific heat coefficient, γ , just above T_c , is 73 mJ/mol K^2 ; the Debye temperature, Θ_D , is 220 K. The specific heat jump at the superconducting transition $\Delta C \sim 2.2 \gamma T_c$. For hydrostatic pressures up to ~ 7 kbar, T_c decreases under pressure linearly at a rate of -0.034 K/kbar .

Anisotropic $H_{c2}(T)$ data were measured up to 600 kOe and $T > 0.6$ K with field applied along ($H_{c2}^{\parallel}(T)$) and perpendicular ($H_{c2}^{\perp}(T)$) to the rod-like crystals. Close to T_c , the initial slope of $H_{c2}(T)$ is $\sim 70 \text{ kOe/K}$ for the applied field perpendicular to the rod, and $\sim 120 \text{ kOe/K}$ for field applied along the rod. With increasing field, $H_{c2}^{\parallel}(T)$ exhibits a paramagnetically-limited behavior, whereas the shape of the $H_{c2}^{\perp}(T)$ curve has no evidence of paramagnetic effects. As a result, the curves $H_{c2}^{\perp}(T)$ and $H_{c2}^{\parallel}(T)$ cross at $T \approx 4$ K, so that the anisotropy parameter $\gamma_H(T) = H_{c2}^{\perp}/H_{c2}^{\parallel}(T)$ increases from $\gamma_H(T_c) \approx 0.35$ near T_c to $\gamma_H(0) \approx 1.7$ at 0.6 K. This behavior of $H_{c2}^{\parallel}(T)$ is inconsistent with triplet superconductivity but suggests a form of singlet superconductivity with the electron spins locked onto c-axis.

In this project, I grew the samples and performed the basic physical property characterization. Measurements under pressure was performed by Dr. Bud'ko. High magnetic field measurements were performed by Dr. Balakirev et al. at Los Alamos National High Magnetic

Field Laboratory. Theoretical explanation was put forward by Dr. Gurevich. This work was published in Refs. [113; 242].



Free standing, low strain, single crystals of pure and titanium doped VO_2 were grown out of an excess of V_2O_5 using high temperature solution growth techniques. At $T_{MI} \sim 340$ K, pure VO_2 exhibits a clear first-order phase transition from a high-temperature paramagnetic tetragonal phase (R) to a low-temperature non-magnetic monoclinic phase (M1). With Ti doping, another monoclinic phase (M2) emerges between the R and M1 phases. The phase transition temperature between R and M2 increases with increasing Ti doping while the transition temperature between M2 and M1 decreases. The size of the magnetic susceptibility change at each transition was studied. The fact that the magnetic susceptibility change at R-M2 and M1-M2 are not equivalent suggests that there may be a preference for pairing V^{4+} ions (rather than Ti^{4+} - V^{4+} ions) in the M2 phase.

In this project, crystals were grown by Dr. Canfield and M. Masters. I performed the measurements and analysed the data. It was published in Ref. [243]. These samples were later studied by infrared spectroscopy and imaging to reveal more details of the phase transitions in nanoscale[244].

frit-disc crucible sets

Solution growth of single crystals from high temperature solutions often involves the separation of residual solution from the grown crystals. For many growths of intermetallic compounds, this separation has historically been achieved with the use of plugs of silica wool. Whereas this is generally efficient in a mechanical sense, it leads to a significant contamination of the decanted liquid with silica fibers. Dr. Canfield developed a simple design for frit-disc alumina crucible sets that has made their use in the growth single crystals from high temperature solutions both simple and affordable. An alumina frit-disc allows for the clean separation of the residual liquid from the solid phase. This allows for the reuse of the decanted liquid, either

for further growth of the same phase, or for subsequent growth of other, related phases. I was partly involved in the calibrating and testing of this new design. A detailed description can be found in Ref. [111]

CaKFe₄As₄ superconductor

CaKFe₄As₄ is a newly recognized, Fe-based, superconductor with a T_c of 35 K[245]. During this project, we provided basic physical property information of this new compound. Single crystalline, single phase CaKFe₄As₄ has been grown out of a high temperature, quaternary melt. Temperature dependent measurements of x-ray diffraction, anisotropic electrical resistivity, elastoresistivity, thermoelectric power, Hall effect, magnetization and specific heat, combined with field dependent measurements of electrical resistivity and field and pressure dependent measurements of magnetization indicate that CaKFe₄As₄ is an ordered, stoichiometric, Fe-based superconductor with a superconducting critical temperature, $T_c = 35.0 \pm 0.2$ K. Other than superconductivity, there is no indication of any other phase transition for $1.8 \text{ K} \leq T \leq 300 \text{ K}$. All of these thermodynamic and transport data reveal striking similarities to that found for optimally- or slightly over-doped $(\text{Ba}_{1-x}\text{K}_x)\text{Fe}_2\text{As}_2$, suggesting that stoichiometric CaKFe₄As₄ is intrinsically close to what is referred to as "optimal-doped" on a generalized, Fe-based superconductor, phase diagram. The anisotropic superconducting upper critical field, $H_{c2}(T)$, of CaKFe₄As₄ was determined up to 630 kOe. The anisotropy parameter $\gamma(T) = H_{c2}^\perp/H_{c2}^\parallel$, for H applied perpendicular and parallel to the c-axis, decreases from $\simeq 2.5$ at T_c to $\simeq 1.5$ at 25 K which can be explained by interplay of paramagnetic pairbreaking and orbital effects. The slopes of $dH_{c2}^\parallel/dT \simeq -44 \text{ kOe/K}$ and $dH_{c2}^\perp/dT \simeq -109 \text{ kOe/K}$ at T_c yield an electron mass anisotropy of $m_\perp/m_\parallel \simeq 1/6$ and short Ginzburg-Landau coherence lengths $\xi_\parallel(0) \simeq 5.8 \text{ \AA}$ and $\xi_\perp(0) \simeq 14.3 \text{ \AA}$. The value of $H_{c2}^\perp(0)$ can be extrapolated to $\simeq 920 \text{ kOe}$, well above the BCS paramagnetic limit.

I proposed the initial project and was heavily involved in the single crystal synthesis, anisotropic magnetization and transport measurements, and H_{c2} determination. This work has been published in Ref. [246]. I was also involved in several other projects, which study the Fermi surface, penetration depth and vortex lattice of CaKFe₄As₄[247; 248; 249].

Miscellaneous

As a part of research collaboration, I provided samples to many groups around the world. For i - R -Cd quasicrystals, I synthesized samples for optical conductivity measurements[250] and also for structural refinement[139]. In addition, isotopic Cd was used to prepare samples for neutron scattering experiments (results will be published later). I synthesized TmB_4 samples for the study of the magnetism in geometrically frustrated Shastry-Sutherland lattice[251; 252]. For the semimetals, I synthesized samples for the study of Cd_3As_2 [253] and LaBi [254]. $R\text{Fe}_2\text{Zn}_{20}$ ($R = \text{Lu}, \text{Yb}$ and Gd) samples were synthesized for the study of Mössbauer effect[255].

BIBLIOGRAPHY

- [1] G. B. Haxel, J. B. Hedrick, and G. J. Orris. Rare earth elements-critical resources for high technology. *US Geol. Surv*, Fact sheet 087-02, 2005.
- [2] A. J. Freeman and R. E. Watson. Theoretical investigation of some magnetic and spectroscopic properties of rare-earth ions. *Phys. Rev.*, 127:2058–2075, Sep 1962.
- [3] A. J. Freeman. *Magnetic properties of rare earth metals*, chapter 6, pages 245–333. Springer US, Boston, MA, 1972.
- [4] Patrick Fazekas. *Lecture notes on electron correlation and magnetism*. World Scientific, Singapore, 1999.
- [5] K. N. R. Taylor and M. I. Darby. *Physics of Rare Earth Solids*. Chapman and Hall Ltd, London, 1972.
- [6] M. A. Ruderman and C. Kittel. Indirect exchange coupling of nuclear magnetic moments by conduction electrons. *Phys. Rev.*, 96:99–102, Oct 1954.
- [7] Tadao Kasuya. A Theory of Metallic Ferro- and Antiferromagnetism on Zener’s Model. *Progr. Theoret. Phys.*, 16(1):45–57, 1956.
- [8] Kei Yosida. Magnetic Properties of Cu-Mn Alloys. *Phys. Rev.*, 106:893–898, Jun 1957.
- [9] N. W. Ashcroft and N. D. Mermin. *Solid State Physics*. Cengage Learning, Belmont, 1976.
- [10] S. H. Liu. Exchange interaction between conduction electrons and magnetic shell electrons in rare-earth metals. *Phys. Rev.*, 121:451–455, Jan 1961.

- [11] P-G de Gennes. Interactions indirectes entre couches 4f dans les métaux de terres rares. *J. Phys. Radium*, 23(8-9):510–521, 1962.
- [12] L. L. Hirst. Theory of the coupling between conduction electrons and moments of 3d and 4f ions in metals. *Adv. Phys.*, 27(2):231–285, 1978.
- [13] D. R. Noakes and G. K. Shenoy. The effect of a crystalline electric field on the magnetic transition temperatures of rare-earth rhodium borides. *Phys. Lett. A*, 91(1):35 – 36, 1982.
- [14] Jean Etourneau, Jean-Pierre Mercurio, Roger Naslain, and Paul Hagenmuller. Structure électronique de quelques hexaborures de type CaB_6 . *J. Solid State Chem.*, 2(3):332 – 342, 1970.
- [15] S. L. Bud’ko, Z. Islam, T. A. Wiener, I. R. Fisher, A. H. Lacerda, and P. C. Canfield. Anisotropy and metamagnetism in the RNi_2Ge_2 ($\text{R}=\text{Y}$, LaNd , SmLu) series. *J. Magn. Magn. Mater.*, 205(1):53 – 78, 1999.
- [16] K. D. Myers, S. L. Bud’ko, I. R. Fisher, Z. Islam, H. Kleinke, A. H. Lacerda, and P. C. Canfield. Systematic study of anisotropic transport and magnetic properties of RAgSb_2 ($\text{R}=\text{Y}$, LaNd , Sm , GdTm). *J. Magn. Magn. Mater.*, 205(1):27 – 52, 1999.
- [17] K. W. H. Stevens. Matrix elements and operator equivalents connected with the magnetic properties of rare earth ions. *Proc. Phys. Soc. A*, 65(3):209, 1952.
- [18] R. J. Elliott and K. W. H. Stevens. The theory of magnetic resonance experiments on salts of the rare earths. *Proc. R. Soc. Lond. A*, 218(1135):pp. 553–566, 1953.
- [19] M. T. Hutchings. Point-Charge Calculations of Energy Levels of Magnetic Ions in Crystalline Electric Fields. *Solid State Physics*, 16:227, 1964.
- [20] H-G. Purwins, E. Walker, B. Barbara, M. F. Rossignol, and P. Bak. Magnetization, magnetocrystalline anisotropy and the crystalline electric field in (rare earth) Al_2 compounds. *J. Phys. C: Solid State Phys.*, 7(19):3573, 1974.
- [21] E. Bauer and M. Rotter. *Properties and Applications of Complex Intermetallics*, volume 2, chapter 5, pages 183–248. World Scientific, Singapore, 2009.

- [22] Peter Fulde and Michael Loewenhaupt. Magnetic excitations in crystal-field split 4f systems. *Adv. Phys.*, 34(5):589–661, 1985.
- [23] K. R. Lea, M. J. M. Leask, and W. P. Wolf. The raising of angular momentum degeneracy of f-electron terms by cubic crystal fields. *J. Phys. Chem. Solids*, 23(10):1381 – 1405, 1962.
- [24] E. Segal and W. E. Wallace. Rare-earth ions in a hexagonal field I. *J. Solid State Chem.*, 2(3):347 – 365, 1970.
- [25] Yung-Li Wang. Crystal-field effects of paramagnetic Curie temperature. *Phys. Lett. A*, 35(5):383 – 384, 1971.
- [26] W. J. de Haas, J. de Boer, and G. J. van den Berg. The electrical resistance of gold, copper and lead at low temperatures. *Physica*, 1(7):1115 – 1124, 1934.
- [27] Jun Kondo. Resistance minimum in dilute magnetic alloys. *Progr. Theoret. Phys.*, 32(1):37–49, 1964.
- [28] Andriy H. Nevidomskyy and P. Coleman. Kondo Resonance Narrowing in *d*- and *f*-Electron Systems. *Phys. Rev. Lett.*, 103:147205, Oct 2009.
- [29] P. W. Anderson. Localized magnetic states in metals. *Phys. Rev.*, 124:41–53, Oct 1961.
- [30] Kenneth G. Wilson. The renormalization group: Critical phenomena and the Kondo problem. *Rev. Mod. Phys.*, 47:773–840, Oct 1975.
- [31] Alexander C. Hewson. *The Kondo problem to heavy fermions*. Cambridge University Press, Cambridge, 1997.
- [32] K. Andres, J. E. Graebner, and H. R. Ott. 4f-Virtual-Bound-State Formation in CeAl₃ at Low Temperatures. *Phys. Rev. Lett.*, 35:1779–1782, Dec 1975.
- [33] Charles Kittel. *Introduction to Solid State Physics*. John Wiley & Sons, Hoboken, 2005.
- [34] C. Lacroix. Coherence effects in the Kondo lattice. *J. Magn. Magn. Mater.*, 60(2):145 – 152, 1986.

- [35] H. Kaga, H. Kubo, and T. Fujiwara. Coherent Kondo-lattice state and the crossover transitions in the Anderson-lattice model. *Phys. Rev. B*, 37:341–355, Jan 1988.
- [36] S. Burdin, A. Georges, and D. R. Grempel. Coherence Scale of the Kondo Lattice. *Phys. Rev. Lett.*, 85:1048–1051, Jul 2000.
- [37] Th. Pruschke, R. Bulla, and M. Jarrell. Low-energy scale of the periodic Anderson model. *Phys. Rev. B*, 61:12799–12809, May 2000.
- [38] Satoru Nakatsuji, David Pines, and Zachary Fisk. Two Fluid Description of the Kondo Lattice. *Phys. Rev. Lett.*, 92:016401, Jan 2004.
- [39] Yi-Feng Yang, Zachary Fisk, Han-Oh Lee, J. D. Thompson, and David. Pines. Scaling the Kondo lattice. *Nature*, 454:611–613, 2008.
- [40] S. Doniach. The Kondo lattice and weak antiferromagnetism. *Physica B+C*, 91(0):231 – 234, 1977.
- [41] J. R. Iglesias, C. Lacroix, and B. Coqblin. Revisited Doniach diagram: Influence of short-range antiferromagnetic correlations in the Kondo lattice. *Phys. Rev. B*, 56:11820–11826, Nov 1997.
- [42] N. Andrei, K. Furuya, and J. H. Lowenstein. Solution of the Kondo problem. *Rev. Mod. Phys.*, 55:331–402, Apr 1983.
- [43] G. R. Stewart. Heavy-fermion systems. *Rev. Mod. Phys.*, 56:755–787, Oct 1984.
- [44] G. R. Stewart. Non-Fermi-liquid behavior in d- and f-electron metals. *Rev. Mod. Phys.*, 73:797–855, Oct 2001.
- [45] Hilbert v. Löhneysen, Achim Rosch, Matthias Vojta, and Peter Wölfle. Fermi-liquid instabilities at magnetic quantum phase transitions. *Rev. Mod. Phys.*, 79:1015–1075, Aug 2007.
- [46] B. Coqblin and J. R. Schrieffer. Exchange Interaction in Alloys with Cerium Impurities. *Phys. Rev.*, 185:847–853, Sep 1969.

- [47] V. T. Rajan. Magnetic Susceptibility and Specific Heat of the Coqblin-Schrieffer Model. *Phys. Rev. Lett.*, 51:308–311, Jul 1983.
- [48] B. Cornut and B. Coqblin. Influence of the Crystalline Field on the Kondo Effect of Alloys and Compounds with Cerium Impurities. *Phys. Rev. B*, 5:4541–4561, Jun 1972.
- [49] A. K. Bhattacharjee and B. Coqblin. Thermoelectric power of compounds with cerium: Influence of the crystalline field on the Kondo effect. *Phys. Rev. B*, 13:3441–3451, Apr 1976.
- [50] H.-U. Desgranges and K.D. Schotte. Specific heat of the Kondo model. *Phys. Lett. A*, 91(5):240 – 242, 1982.
- [51] K. D. Schotte and U. Schotte. Interpretation of Kondo experiments in a magnetic field. *Phys. Lett. A*, 55(1):38 – 40, 1975.
- [52] H.-U. Desgranges. Crystal fields and Kondo effect: Specific heat for Cerium compounds. *Physica B Condens. Matter*, 454:135 – 140, 2014.
- [53] M. A. Romero, A. A. Aligia, J. G. Sereni, and G. Nieva. Interpretation of experimental results on Kondo systems with crystal field. *J. Phys. Condens. Matter*, 26(2):025602, 2014.
- [54] C. L. Yang, X. Wang, X. Zhang, D. S. Wu, M. Liu, P. Zheng, J. Y. Yao, Z. Z. Li, Y.-F. Yang, Y. G. Shi, J. L. Luo, and N. L. Wang. Kondo effect in the quasiskutterudite $\text{Yb}_3\text{Os}_4\text{Ge}_{13}$. *Phys. Rev. B*, 91:075120, Feb 2015.
- [55] Shin-ichi Kashiba, Sadamichi Maekawa, Saburo Takahashi, and Masashi Tachiki. Effect of Crystal Field on Kondo Resistivity in Ce Compounds. *J. Phys. Soc. Jpn.*, 55(4):1341–1349, 1986.
- [56] B. Coqblin, A. K. Bhattacharjee, and S. M. M. Evans. Anisotropy effects in Cerium Kondo compounds. *J. Magn. Magn. Mater.*, 90-91:393 – 397, 1990.
- [57] S. Evans, A. Bhattacharjee, and B. Coqblin. Anisotropic transport properties of Cerium Kondo compounds. *Phys. Rev. B*, 45:7244–7257, Apr 1992.

- [58] K. Kadowaki and S. B. Woods. Universal relationship of the resistivity and specific heat in heavy-fermion compounds. *Solid State Commun.*, 58(8):507 – 509, 1986.
- [59] N. Tsujii, H. Kontani, and K. Yoshimura. Universality in Heavy Fermion Systems with General Degeneracy. *Phys. Rev. Lett.*, 94:057201, Feb 2005.
- [60] A. C. Jacko, J. O. Fjaerestad, and B. J. Powell. A unified explanation of the Kadowaki-Woods ratio in strongly correlated metals. *Nature Phys.*, 5(6):422–425, JUN 2009.
- [61] D. C. Cavanagh, A. C. Jacko, and B. J. Powell. Breakdown of the universality of the Kadowaki-Woods Ratio in multi-band metals. *Phys. Rev. B*, 92:195138, Nov 2015.
- [62] K. Binder and A. P. Young. Spin glasses: Experimental facts, theoretical concepts, and open questions. *Rev. Mod. Phys.*, 58:801–976, Oct 1986.
- [63] J. A. Mydosh. *Spin Glasses: An Experimental Introduction*. Taylor & Francis Group, London, 1993.
- [64] V. Cannella and J. A. Mydosh. Magnetic ordering in gold-iron alloys. *Phys. Rev. B*, 6:4220–4237, Dec 1972.
- [65] J. A. Mydosh. Spin glasses: redux: an updated experimental/materials survey. *Rep. Prog. Phys.*, 78(5):052501, 2015.
- [66] Sumiyoshi Fujiki and Shigetoshi Katsura. Nonlinear susceptibility in the spin glass. *Progr. Theoret. Phys.*, 65(4):1130–1144, 1981.
- [67] I. R. Fisher, K. O. Cheon, A. F. Panchula, P. C. Canfield, M. Chernikov, H. R. Ott, and K. Dennis. Magnetic and transport properties of single-grain R-Mg-Zn icosahedral quasicrystals [R=Y,(Y_{1-x}Gd_x),(Y_{1-x}Tb_x), Tb, Dy, Ho, and Er]. *Phys. Rev. B*, 59:308–321, Jan 1999.
- [68] T. A. Wiener, I. R. Fisher, S. L. Bud’ko, A. Kracher, and P. C. Canfield. Design of a metallic Ising spin glass in the Y_{1-x}Tb_xNi₂Ge₂ system. *Phys. Rev. B*, 62:15056–15066, Dec 2000.

- [69] G. E. Brodale, R. A. Fisher, W. E. Fogle, N. E. Phillips, and J. van Curen. The effect of spin-glass ordering on the specific heat of CuMn. *J. Magn. Magn. Mater.*, 31:1331 – 1333, 1983.
- [70] D. Shechtman, I. Blech, D. Gratias, and J. W. Cahn. Metallic Phase with Long-Range Orientational Order and No Translational Symmetry. *Phys. Rev. Lett.*, 53:1951–1953, Nov 1984.
- [71] N. Wang, H. Chen, and K. H. Kuo. Two-dimensional quasicrystal with eightfold rotational symmetry. *Phys. Rev. Lett.*, 59:1010–1013, Aug 1987.
- [72] An-Pang Tsai, Akihisa Inoue, and Tsuyoshi Masumoto. Stable decagonal Al-Co-Ni and Al-Co-Cu quasicrystals. *Mater. T. JIM*, 30(7):463–473, 1989.
- [73] K. K. Fung, C. Y. Yang, Y. Q. Zhou, J. G. Zhao, W. S. Zhan, and B. G. Shen. Icosahedrally Related Decagonal Quasicrystal in Rapidly Cooled Al-14-at.%-Fe Alloy. *Phys. Rev. Lett.*, 56:2060–2063, May 1986.
- [74] H. Chen, D. X. Li, and K. H. Kuo. New type of two-dimensional quasicrystal with twelvefold rotational symmetry. *Phys. Rev. Lett.*, 60:1645–1648, Apr 1988.
- [75] Alan L. Mackay. Crystallography and the Penrose pattern. *Physica A*, 114(13):609 – 613, 1982.
- [76] C. Janot. *Quasicrystals. A Primer, 2nd edition*. Clarendon Press, New York, 1997.
- [77] Dov Levine and Paul J. Steinhardt. Quasicrystals. I. Definition and structure. *Phys. Rev. B*, 34:596–616, Jul 1986.
- [78] A. I. Goldman and R. F. Kelton. Quasicrystals and crystalline approximants. *Rev. Mod. Phys.*, 65:213–230, Jan 1993.
- [79] G. Bergman, J. L. T. Waugh, and L. Pauling. The crystal structure of the metallic phase $\text{Mg}_{32}(\text{Al}, \text{Zn})_{49}$. *Acta Cryst.*, 10(4):254–259, Apr 1957.

- [80] Hiroyuki Takakura, Cesar Pay Gomez, Akiji Yamamoto, Marc De Boissieu, and An Pang Tsai. Atomic structure of the binary icosahedral Yb-Cd quasicrystal. *Nature Mater.*, 6(1):58–63, January 2007.
- [81] Keisuke Nagao, Tomoaki Inuzuka, Kazue Nishimoto, and Keiichi Edagawa. Experimental observation of quasicrystal growth. *Phys. Rev. Lett.*, 115:075501, Aug 2015.
- [82] I. R. Fisher, M. J. Kramer, Z. Islam, A. R. Ross, A. Kracher, T. Wiener, M. J. Sailer, A. I. Goldman, and P. C. Canfield. On the growth of decagonal Al-Ni-Co quasicrystals from the ternary melt. *Philos. Mag. B*, 79(3):425–434, 1999.
- [83] Paul C. Canfield and Ian R. Fisher. High-temperature solution growth of intermetallic single crystals and quasicrystals. *J. Cryst. Growth*, 225(24):155 – 161, 2001.
- [84] Takeo Fujiwara and Takeshi Yokokawa. Universal pseudogap at fermi energy in quasicrystals. *Phys. Rev. Lett.*, 66:333–336, Jan 1991.
- [85] J. Hafner and M. Krajčí. Electronic structure and stability of quasicrystals: Quasiperiodic dispersion relations and pseudogaps. *Phys. Rev. Lett.*, 68:2321–2324, Apr 1992.
- [86] M. Krajčí, M. Windisch, J. Hafner, G. Kresse, and M. Mihalkovič. Atomic and electronic structure of icosahedral Al-Pd-Mn alloys and approximant phases. *Phys. Rev. B*, 51:17355–17378, Jun 1995.
- [87] X. Wu, S. W. Kycia, C. G. Olson, P. J. Benning, A. I. Goldman, and D. W. Lynch. Electronic Band Dispersion and Pseudogap in Quasicrystals: Angular-Resolved Photoemission Studies on Icosahedral $\text{Al}_{70}\text{Pd}_{21.5}\text{Mn}_{8.5}$. *Phys. Rev. Lett.*, 75:4540–4543, Dec 1995.
- [88] Z. M. Stadnik, D. Purdie, M. Garnier, Y. Baer, A.-P. Tsai, A. Inoue, K. Edagawa, S. Takeuchi, and K. H. J. Buschow. Electronic structure of quasicrystals studied by ultrahigh-energy-resolution photoemission spectroscopy. *Phys. Rev. B*, 55:10938–10951, Apr 1997.

- [89] J. Nayak, M. Maniraj, Abhishek Rai, Sanjay Singh, Parasmani Rajput, A. Gloskovskii, J. Zegenhagen, D. L. Schlagel, T. A. Lograsso, K. Horn, and S. R. Barman. Bulk Electronic Structure of Quasicrystals. *Phys. Rev. Lett.*, 109:216403, Nov 2012.
- [90] Hirofumi Akiyama, Tatsuo Hashimoto, Tadaharu Shibuya, Keiichi Edagawa, and Shin Takeuchi. Electrical Resistivities of Al-Pd-Mn Icosahedral Quasicrystals. *J. Phys. Soc. Jpn.*, 62(2):639–646, 1993.
- [91] C. A. Swenson, I. R. Fisher, N. E. Anderson, P. C. Canfield, and A. Migliori. Icosahedral quasicrystal $\text{Al}_{71}\text{Pd}_{21}\text{Mn}_{08}$ and its ξ' approximant: Linear expansivity, specific heat, magnetic susceptibility, electrical resistivity, and elastic constants. *Phys. Rev. B*, 65:184206, May 2002.
- [92] A. L. Pope, T. M. Tritt, R. Gagnon, and J. Strom-Olsen. Electronic transport in Cd-Yb and Y-Mg-Zn quasicrystals. *Appl. Phys. Lett.*, 79(15):2345–2347, 2001.
- [93] Ron Lifshitz. Symmetry of Magnetically Ordered Quasicrystals. *Phys. Rev. Lett.*, 80:2717–2720, Mar 1998.
- [94] Stefan Wessel, Anuradha Jagannathan, and Stephan Haas. Quantum Antiferromagnetism in Quasicrystals. *Phys. Rev. Lett.*, 90:177205, May 2003.
- [95] E. Y. Vedmedenko, U. Grimm, and R. Wiesendanger. Noncollinear Magnetic Order in Quasicrystals. *Phys. Rev. Lett.*, 93:076407, Aug 2004.
- [96] Stefanie Thiem and J. T. Chalker. Long-range magnetic order in models for rare-earth quasicrystals. *Phys. Rev. B*, 92:224409, Dec 2015.
- [97] Alan I Goldman. Magnetism in icosahedral quasicrystals: current status and open questions. *Sci. Technol. Adv. Mater.*, 15(4):044801, 2014.
- [98] S. E. Sebastian, T. Huie, I. R. Fisher, K. W. Dennis, and M. J. Kramer. Magnetic properties of single grain R-Mg-Cd primitive icosahedral quasicrystals (R=Y, Gd, Tb or Dy). *Philos. Mag.*, 84(10):1029–1037, 2004.

- [99] Zbigniew M. Stadnik, Khalid Al-Qadi, and Pu Wang. Magnetic properties and ^{155}Gd Mossbauer spectroscopy of the icosahedral quasicrystal $\text{Ag}_{50}\text{In}_{36}\text{Gd}_{14}$. *J. Phys.: Condens. Matter*, 19(32):326208, 2007.
- [100] Tai Kong, Sergey L. Bud'ko, Anton Jesche, John McArthur, Andreas Kreyssig, Alan I. Goldman, and Paul C. Canfield. Magnetic and transport properties of i- R -Cd icosahedral quasicrystals ($R=\text{Y}$, Gd-Tm). *Phys. Rev. B*, 90:014424, Jul 2014.
- [101] Akinobu Mori, Hisashi Ota, Shingo Yoshiuchi, Ken Iwakawa, Yuki Taga, Yusuke Hirose, Tetsuya Takeuchi, Etsuji Yamamoto, Yoshinori Haga, Fuminori Honda, Rikio Settai, and Yoshichika Ōnuki. Electrical and Magnetic Properties of Quasicrystal Approximants RCd_6 (R : Rare Earth). *J. Phys. Soc. Jpn.*, 81(2):024720, 2012.
- [102] M. G. Kim, G. Beutier, A. Kreyssig, T. Hiroto, T. Yamada, J. W. Kim, M. de Boissieu, R. Tamura, and A. I. Goldman. Antiferromagnetic order in the quasicrystal approximant Cd_6Tb studied by x-ray resonant magnetic scattering. *Phys. Rev. B*, 85:134442, Apr 2012.
- [103] Andreas Kreyssig, Guillaume Beutier, Takanobu Hiroto, Min Gyu Kim, Gregory S. Tucker, Marc de Boissieu, Ryuji Tamura, and Alan I. Goldman. Antiferromagnetic order and the structural order-disorder transition in the Cd_6Ho quasicrystal approximant. *Phil. Mag. Lett.*, 93(9):512–520, 2013.
- [104] T. Hiroto, G. H. Gebresenbut, C. Pay Gómez, Y. Muro, M. Isobe, Y. Ueda, K. Tokiwa, and R. Tamura. Ferromagnetism and re-entrant spin-glass transition in quasicrystal approximants Au-SM-Gd ($\text{SM} = \text{Si}, \text{Ge}$). *J. Phys.: Condens. Matter*, 25(42):426004, 2013.
- [105] A. Ishikawa, T. Hiroto, K. Tokiwa, T. Fujii, and R. Tamura. Composition-driven spin glass to ferromagnetic transition in the quasicrystal approximant Au-Al-Gd . *Phys. Rev. B*, 93:024416, Jan 2016.
- [106] B. D. Dunlap. Crystalline electric field effects on the paramagnetic susceptibility of polycrystalline materials. *J. Magn. Magn. Mater.*, 37(2):211 – 214, 1983.

- [107] Thaddeus B. Massalski, Hiroaki Okamoto, P. R. Subramanian, and Linda Kacprzak, editors. *Binary Alloy Phase Diagrams*. ASM International, 1990.
- [108] P. C. Canfield and Z. Fisk. Growth of single crystals from metallic fluxes. *Phil. Mag. B*, 65(6):1117–1123, 1992.
- [109] Paul C Canfield. *Book Series on Complex Metallic Alloys*, volume 2, chapter 2, pages 93–111. World Scientific, Singapore, 2010.
- [110] William F. Smith and Javad Hashemi. *Foundations of materials science and engineering*. McGraw-Hill Education, 2011.
- [111] Paul C. Canfield, Tai Kong, Udhara S. Kaluarachchi, and Na Hyun Jo. Use of frit-disc crucibles for routine and exploratory solution growth of single crystalline samples. *Philos. Mag.*, 96(1):84–92, 2016.
- [112] Kunihiro Kihou, Taku Saito, Shigeyuki Ishida, Masamichi Nakajima, Yasuhide Tomioka, Hideto Fukazawa, Yoh Kohori, Toshimitsu Ito, Shin-ichi Uchida, Akira Iyo, Chul-Ho Lee, and Hiroshi Eisaki. Single Crystal Growth and Characterization of the Iron-Based Superconductor KFe_2As_2 Synthesized by KAs Flux Method. *J. Phys. Soc. Jpn.*, 79(12):124713, 2010.
- [113] Tai Kong, Sergey L. Bud’ko, and Paul C. Canfield. Anisotropic H_{c2} , thermodynamic and transport measurements, and pressure dependence of T_c in $\text{K}_2\text{Cr}_3\text{As}_3$ single crystals. *Phys. Rev. B*, 91:020507, Jan 2015.
- [114] N. Ni, M. E. Tillman, J.-Q. Yan, A. Kracher, S. T. Hannahs, S. L. Bud’ko, and P. C. Canfield. Effects of Co substitution on thermodynamic and transport properties and anisotropic H_{c2} in $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$ single crystals. *Phys. Rev. B*, 78:214515, Dec 2008.
- [115] Tai Kong, Valentin Taufour, Sergey L. Bud’ko, and Paul C. Canfield. Tuning the Kondo effect in $\text{Yb}(\text{Fe}_{1-x}\text{Co}_x)_2\text{Zn}_{20}$. *arXiv: 1609.06233*, 2016.
- [116] A. C. Larson and R. B. Von Dreele. General Structure Analysis System (GSAS). Technical report, Los Alamos National Laboratory Report LAUR 86-748, 2000.

- [117] Brian H. Toby. EXPGUI, a graphical user interface for GSAS. *J. Appl. Crystallogr.*, 34(2):210–213, Apr 2001.
- [118] Mike McElfresh, Shi Li, and Ron Sager. Effects of magnetic field uniformity on the measurement of superconducting samples. Technical report, Quantum Design, Inc.
- [119] Jih Shang Hwang, Kai Jan Lin, and Cheng Tien. Measurement of heat capacity by fitting the whole temperature response of a heat-pulse calorimeter. *Rev. Sci. Instrum.*, 68(1):94–101, 1997.
- [120] Kazuaki Fukamichi. *Magnetic Properties of Quasicrystals*, pages 295–326. Springer, Berlin, Heidelberg, 1999.
- [121] F. Hippert and J. J. Préjean. Magnetism in quasicrystals. *Philos. Mag.*, 88(13-15):2175–2190, 2008.
- [122] Taku J Sato, Junqing Guo, and An Pang Tsai. Magnetic properties of the icosahedral Cd-Mg-rare-earth quasicrystals. *J. Phys.: Condens. Matter*, 13(4):L105, 2001.
- [123] Taku J. Sato. Short-range order and spin-glass-like freezing in A-Mg-R (A = Zn or Cd; R = rare-earth elements) magnetic quasicrystals. *Acta Cryst.*, A61(1):39–50, Jan 2005.
- [124] M. Heggen, M. Feuerbacher, J. Ivkov, P. Popčević, I. Batistić, A. Smontara, M. Jagodič, Z. Jagličić, J. Janovec, M. Wencka, and J. Dolinšek. Anisotropic physical properties of the Taylor-phase T-Al_{72.5}Mn_{21.5}Fe_{6.0} complex intermetallic. *Phys. Rev. B*, 81:184204, May 2010.
- [125] P. Wang, Z. M. Stadnik, K. Al-Qadi, and J. Przewoźnik. A comparative study of the magnetic properties of the 1/1 approximant Ag₅₀In₃₆Gd₁₄ and the icosahedral quasicrystal Ag₅₀In₃₆Gd₁₄. *J. Phys. : Condens. Matter*, 21(43):436007, 2009.
- [126] S. Jazbec, Z. Jagličić, S. Vrtnik, M. Wencka, M. Feuerbacher, M. Heggen, S. Roitsch, and J. Dolinšek. Geometric origin of magnetic frustration in the μ -Al₄Mn giant-unit-cell complex intermetallic. *J. Phys. : Condens. Matter*, 23(4):045702, 2011.

- [127] Soshi Ibuka, Kazuki Iida, and Taku J Sato. Magnetic properties of the Ag-In-rare-earth 1/1 approximants. *J. Phys.: Condens. Matter*, 23(5):056001, 2011.
- [128] R. Tamura, Y. Muro, T. Hiroto, K. Nishimoto, and T. Takabatake. Long-range magnetic order in the quasicrystalline approximant Cd_6Tb . *Phys. Rev. B*, 82:220201, Dec 2010.
- [129] Kazue Nishimoto, Takeru Sato, and Ryuji Tamura. Low-temperature superstructures of a series of Cd_6M ($\text{M} = \text{Ca}, \text{Y}, \text{Sr}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Gd}, \text{Tb}, \text{Dy}, \text{Ho}, \text{Er}, \text{Tm}, \text{Yb}$ and Lu) crystalline approximants. *J. Phys.: Condens. Matter*, 25(23):235403, 2013.
- [130] Alan I. Goldman, Tai Kong, Andreas Kreyssig, Anton Jesche, Mehmet Ramazanoglu, Kevin W. Dennis, Sergey L. Bud'ko, and Paul C. Canfield. A family of binary magnetic icosahedral quasicrystals based on rare earths and cadmium. *Nat Mater*, 12(8):714–718, August 2013.
- [131] P. C. Canfield, M. L. Caudle, C.-S. Ho, A. Kreyssig, S. Nandi, M. G. Kim, X. Lin, A. Kracher, K. W. Dennis, R. W. McCallum, and A. I. Goldman. Solution growth of a binary icosahedral quasicrystal of $\text{Sc}_{12}\text{Zn}_{88}$. *Phys. Rev. B*, 81:020201, Jan 2010.
- [132] Thomas L. Reichmann and Herbert Ipser. Reinvestigation of the Cd-Gd phase diagram. *J. Alloys Comp.*, 617:292 – 301, Aug 2014.
- [133] Perhaps Nature journals are not often read in Vienna.
- [134] A. Kreyssig, S. Chang, Y. Janssen, J. W. Kim, S. Nandi, J. Q. Yan, L. Tan, R. J. McQueeney, P. C. Canfield, and A. I. Goldman. Crystallographic phase transition within the magnetically ordered state of $\text{Ce}_2\text{Fe}_{17}$. *Phys. Rev. B*, 76:054421, Aug 2007.
- [135] R. D. Shannon. Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Cryst.*, A32(5):751–767, Sep 1976.
- [136] A. P. Tsai, J. Q. Guo, E. Abe, H. Takakura, and T. J. Sato. Alloys - A stable binary quasicrystal. *Nature*, 408(6812):537–538, Nov 2000.
- [137] Cesar Pay Gómez and Sven Lidin. Comparative structural study of the disordered MCd_6 quasicrystal approximants. *Phys. Rev. B*, 68:024203, Jul 2003.

- [138] Daichi Kawana, Tetsu Watanuki, Akihiko Machida, Takahisa Shobu, Katsutoshi Aoki, and AnPang Tsai. Intermediate-valence quasicrystal of a Cd-Yb alloy under pressure. *Phys. Rev. B*, 81:220202, Jun 2010.
- [139] T. Yamada, H. Takakura, T. Kong, P. Das, W. T. Jayasekara, A. Kreyssig, G. Beutier, P. C. Canfield, M. de Boissieu, and A. I. Goldman. Atomic structure of the i-R-Cd quasicrystals and consequences for magnetism. *Phys. Rev. B*, 94:060103, Aug 2016.
- [140] T. Mitani and T. Ishimasa. A metastable icosahedral quasicrystal in the Zn-Mg-Yb alloy system. *Philos. Mag.*, 86(3-5):361–366, 2006.
- [141] A. F. J. Morgownik, J. A. Mydosh, and L. E. Wenger. High-temperature susceptibility of cobalt and manganese aluminosilicate glasses. *J. Appl. Phys.*, 53(3):2211–2213, 1982.
- [142] A. F. J. Morgownik and J. A. Mydosh. Analysis of the high-temperature spin-glass susceptibility: Determination of the local magnetic exchange. *Solid State Commun.*, 47(5):321 – 324, 1983.
- [143] A. F. J. Morgownik and J. A. Mydosh. Atomic short-range order and its relation to the magnetic behavior of noble-metal based spin-glass alloys. *Solid State Commun.*, 47(5):325 – 328, 1983.
- [144] J. R. L. de Almeida and D. J. Thouless. Stability of the Sherrington-Kirkpatrick solution of a spin glass model. *J. Phys. A*, 11(5):983, 1978.
- [145] Marc Gabay and Gérard Toulouse. Coexistence of Spin-Glass and Ferromagnetic Orderings. *Phys. Rev. Lett.*, 47:201–204, Jul 1981.
- [146] Sergey L. Bud’ko and Paul C. Canfield. Frequency dependence of the spin glass freezing temperatures in icosahedral R-Mg-Zn (R=rare earth) quasicrystals. *Philos. Mag.*, 92(35):4492–4497, 2012.
- [147] T. Bitoh, K. Ohba, M. Takamatsu, T. Shirane, and S. Chikazawa. Comparative study of linear and nonlinear susceptibilities of fine-particle and spin-glass systems: quantita-

- tive analysis based on the superparamagnetic blocking model. *J. Magn. Magn. Mater.*, 154(1):59 – 65, 1996.
- [148] R. V. Chamberlin, M. Hardiman, and R. Orbach. Reversibility and time dependence of the magnetization in Ag:Mn and Cu:Mn spin glasses. *J. Appl. Phys.*, 52(3):1771–1772, 1981.
- [149] C. Talón, M. A. Ramos, and S. Vieira. Low-temperature specific heat of amorphous, orientational glass, and crystal phases of ethanol. *Phys. Rev. B*, 66:012201, Jun 2002.
- [150] W. A. Phillips. Two-level states in glasses. *Rep. Prog. Phys.*, 50(12):1657, 1987.
- [151] U. Walter. Crystal-field splitting in icosahedral symmetry. *Phys. Rev. B*, 36:2504–2512, Aug 1987.
- [152] Aleksej Alekseevič Abrikosov. *Fundamentals of the Theory of Metals*, volume 1. North-Holland, Amsterdam, 1988.
- [153] S. L. Bud'ko, P. C. Canfield, C. H. Mielke, and A. H. Lacerda. Anisotropic magnetic properties of light rare-earth dantimonides. *Phys. Rev. B*, 57:13624–13638, Jun 1998.
- [154] H. Fukuyama and K. Hoshino. Effect of Spin-Orbit Interaction on Magnetoresistance in the Weakly Localized Regime of Three-Dimensional Disordered Systems. *J. Phys. Soc. Jpn.*, 50(7):2131–2132, 1981.
- [155] Archna Jaiswal, R. Rawat, and N.P. Lalla. Dominance of magnetic scattering in the electrical-transport of $\text{Al}_{70.5}\text{Pd}_{22}\text{Mn}_{7.5}$ icosahedral quasicrystal. *J. Non-Cryst. Solids*, 352(2122):2129 – 2136, 2006.
- [156] S. Kashimoto, S. Matsuo, H. Nakano, T. Shimizu, and T. Ishimasa. Magnetic and electrical properties of a stable Zn-Mg-Ho icosahedral quasicrystal. *Solid State Commun.*, 109(1):63–67, 1998.
- [157] P. C. Canfield and I. R. Fisher. $\text{R}_9\text{Mg}_{34}\text{Zn}_{57}$ icosahedral quasicrystals: The tuning of a model spin glass. *J. Alloys Comp.*, 317-318(0):443 – 447, 2001.

- [158] B. D. Dunlap, L. N. Hall, F. Behroozi, G. W. Crabtree, and D. G. Niarchos. Crystal-field effects and the magnetic properties of rare-earth rhodium borides. *Phys. Rev. B*, 29:6244–6251, Jun 1984.
- [159] A. P. Ramirez. Strongly geometrically frustrated magnets. *Annu. Rev. Mater. Sci.*, 24(1):453–480, 1994.
- [160] Tai Kong, William R. Meier, Qisheng Lin, Scott M. Saunders, Sergey L. Bud’ko, Rebecca Flint, and Paul C. Canfield. Physical properties of single crystalline RMg_2Cu_9 ($R = Y, Ce-Nd, Gd-Dy, Yb$) and the search for in-plane magnetic anisotropy in hexagonal systems. *arXiv:1608.04310*, 2016.
- [161] Andrej Szytula and Janusz Leciejewicz. *Handbook of Crystal Structures and Magnetic Properties of Rare Earth Intermetallics*. CRC press, 1994.
- [162] P. C. Canfield, S. L. Bud’ko, B. K. Cho, A. Lacerda, D. Farrell, E. Johnston-Halperin, V. A. Kalatsky, and V. L. Pokrovsky. Angular dependence of metamagnetic transitions in $HoNi_2B_2C$. *Phys. Rev. B*, 55:970–976, Jan 1997.
- [163] K. D. Myers, P. C. Canfield, V. A. Kalatsky, and V. L. Pokrovsky. Angular dependence of metamagnetic transitions in $DyAgSb_2$. *Phys. Rev. B*, 59:1121–1128, Jan 1999.
- [164] E. Morosan, S.L. Budko, P.C. Canfield, M.S. Torikachvili, and A.H. Lacerda. Thermodynamic and transport properties of $RAgGe$ ($R=TbLu$) single crystals. *J. Magn. Magn. Mater.*, 277(3):298 – 321, 2004.
- [165] E. Morosan, S. L. Bud’ko, and P. C. Canfield. Angular-dependent planar metamagnetism in the hexagonal compounds $TbPtIn$ and $TmAgGe$. *Phys. Rev. B*, 71:014445, Jan 2005.
- [166] P. C. Canfield and S. L. Bud’ko. Angular dependence of metamagnetic transitions in RNi_2B_2C ($R = Er, Ho, Dy, \text{ and } Tb$). *J. Alloys Comp.*, 262:169 – 174, 1997.
- [167] P. Solokha, V. Pavlyuk, A. Saccone, S. De Negri, W. Prochwicz, B. Marciniak, and E. Różycka-Sokołowska. Rare earth-copper-magnesium compounds $RECu_9Mg_2$

- (RE=Y, La-Nd, Sm-Ho, Yb) with ordered CeNi₃-type structure. *J. Solid State Chem.*, 179(10):3073 – 3081, 2006.
- [168] H. Nakawaki, Y. Inada, R. Asai, M. Yamada, T. Okubo, S. Ikeda, A. Thamizhavel, T. C. Kobayashi, R. Settai, E. Yamamoto, and Y. Ōnuki. Pressure study of an antiferromagnet, CeMg₂Cu₉. *J. Phys. : Condens. Matter*, 14(14):L305, 2002.
- [169] Masakazu Ito, Koji Asada, Yuko Nakamori, Jyun'ya Hori, Hironobu Fujii, Fumihiko Nakamura, Toshizo Fujita, and Takashi Suzuki. Thermodynamic and Transport Properties of CeMg₂Cu₉ under Pressure. *J. Phys. Soc. Jpn.*, 73(8):2252–2256, 2004.
- [170] A. Mauger, D. Ravot, P. Bonville, P. Solokha, S. De Negri, V. Pavlyuk, A. Saccone, and J.-C. Tedenac. Ferromagnetic spin fluctuations in quasi-2D-EuCu₉Mg₂. *J. Alloys Comp.*, 508(1):28 – 36, 2010.
- [171] Volodymyr Pavlyuk, Ewa Rozycka-Sokolowska, Bernard Marciniak, Valerie Paul-Boncour, and Maria Dorogova. The structural, magnetic, hydrogenation and electrode properties of REMg₂Cu_{9-x}Ni_x alloys (RE= La, Pr, Tb). *Cent. Eur. J. Chem.*, 9(6):1133–1142, 2011.
- [172] Bruker AXS, Madison WI. *SMART APEX, Version 5.0*, 2001.
- [173] R. H. Blessing. An empirical correction for absorption anisotropy. *Acta Cryst.*, A51(1):33–38, Jan 1995.
- [174] G. M. Sheldrick. Shelx16. 1; crystallographic software package. *Bruker AXS Inc.: Madison, WI*, 2000.
- [175] Tai Kong, Charles E. Cunningham, Valentin Taufour, Sergey L. Bud'ko, Malinda L.C. Buffon, Xiao Lin, Heather Emmons, and Paul C. Canfield. Thermodynamic and transport properties of single crystalline RCo₂Ge₂ (R=Y, La-Nd, Sm-Tm). *J. Magn. Magn. Mater.*, 358-359(0):212 – 227, 2014.

- [176] M. A. Avila, S. L. Bud'ko, and P. C. Canfield. Drastic annealing effects in transport properties of single crystals of the $\text{YbNi}_2\text{B}_2\text{C}$ heavy fermion system. *Phys. Rev. B*, 66:132504, Oct 2002.
- [177] J. A. Blanco, D. Gignoux, and D. Schmitt. Specific heat in some gadolinium compounds. II. Theoretical model. *Phys. Rev. B*, 43:13145–13151, Jun 1991.
- [178] M. Bouvier, P. Lethuillier, and D. Schmitt. Specific heat in some gadolinium compounds. I. Experimental. *Phys. Rev. B*, 43:13137–13144, Jun 1991.
- [179] H. Li, C. Y. Wu, and J. C. Ho. Calorimetric study of the antiferromagnetic transition in ytterbium sesquioxide. *Phys. Rev. B*, 49:1447–1449, Jan 1994.
- [180] Gordon A. Bain and John F. Berry. Diamagnetic Corrections and Pascal's Constants. *J. Chem. Educ.*, 85(4):532, 2008.
- [181] Michael E. Fisher. Relation between the specific heat and susceptibility of an antiferromagnet. *Philos. Mag.*, 7(82):1731–1743, 1962.
- [182] Michael E. Fisher and J. S. Langer. Resistive Anomalies at Magnetic Critical Points. *Phys. Rev. Lett.*, 20:665–668, Mar 1968.
- [183] Xiao Lin, Warren E. Straszheim, Sergey L. Bud'ko, and Paul C. Canfield. Anisotropic magnetization and resistivity of single crystalline $\text{RNi}_{1-x}\text{Bi}_{2y}$ ($\text{R}=\text{La-Nd, Sm, Gd-Dy}$) . *J. Alloys Comp.*, 554(0):304 – 311, 2013.
- [184] Marie Méasson, Hiroshi Muranaka, Tomoya Kawai, Yuuki Ota, Kiyohiro Sugiyama, Masayuki Hagiwara, Koichi Kindo, Tetsuya Takeuchi, Katsuya Shimizu, Fuminori Honda, Rikio Settai, and Yoshichika Ōnuki. Magnetic Properties of RCoGe_3 (R: Ce, Pr, and Nd) and Strong Anisotropy of the Upper Critical Field in Non-centrosymmetric Compound CeCoGe_3 . *J. Phys. Soc. Jpn.*, 78(12):124713, 2009.
- [185] Per Bak and J. von Boehm. Ising model with solitons, phasons, and "the devil's staircase". *Phys. Rev. B*, 21:5297–5308, Jun 1980.

- [186] J. Rossat-Mignod, P. Burlet, S. Quezel, J.M. Effantin, D. Delacôte, H. Bartholin, O. Vogt, and D. Ravot. Magnetic properties of cerium monopnictides. *J. Magn. Magn. Mater.*, 31-34:398 – 404, 1983.
- [187] T. A. Wiener and P. C. Canfield. Magnetic phase diagram of flux-grown single crystals of CeSb. *J. Alloys Comp.*, 303-304:505–508, 2000.
- [188] J. A. Blanco, D. Gignoux, D. Schmitt, and C. Vettier. Field induced magnetic structures in TbNi₂Si₂. *J. Magn. Magn. Mater.*, 97(1-3):4–14, 1991.
- [189] V. A. Kalatsky and V. L. Pokrovsky. Microscopic model for the magnetic subsystem in HoNi₂B₂C. *Phys. Rev. B*, 57:5485–5488, Mar 1998.
- [190] Jens Jensen and Allan R. Machintosh. *Rare Earth Magnetism*. Clarendon Press-Oxford, 1991.
- [191] B. K. Cho, B. N. Harmon, D. C. Johnston, and P. C. Canfield. Crystalline electric-field effects in single-crystal HoNi₂B₂C. *Phys. Rev. B*, 53:2217–2220, Feb 1996.
- [192] T. Nasch, W. Jeitschko, and U. Ch. Rodewald. Ternary Rare Earth Transition Metal Zinc Compounds RT₂Zn₂₀ with T = Fe, Ru, Co, Rh and Ni. *Z. Naturforsch.*, 52b(9):1023–1030, 1997.
- [193] S. Jia, S. L. Bud'ko, G. D. Samolyuk, and P. C. Canfield. Nearly ferromagnetic Fermi-liquid behaviour in YFe₂Zn₂₀ and high-temperature ferromagnetism of GdFe₂Zn₂₀. *Nature Phys.*, 3(5):334–338, May 2007.
- [194] Shuang Jia, Ni Ni, S. L. Bud'ko, and P. C. Canfield. Magnetic properties of Gd_xY_{1-x}Fe₂Zn₂₀: Dilute, large-**S** moments in a nearly ferromagnetic Fermi liquid. *Phys. Rev. B*, 76:184410, Nov 2007.
- [195] Shuang Jia, Ni Ni, S. L. Bud'ko, and P. C. Canfield. Magnetic properties of RFe₂Zn₂₀ and RCo₂Zn₂₀ (R = Y, Nd, Sm, Gd~Lu). *Phys. Rev. B*, 80:104403, Sep 2009.

- [196] P. C. Canfield, S. Jia, E.D. Mun, S. L. Bud'ko, G. D. Samolyuk, and M. S. Torikachvili. Myriad of correlated electron effects found in the family . *Physica B Condens. Matter*, 403(5-9):844 – 846, 2008.
- [197] M. S. Torikachvili, S. Jia, E. D. Mun, S. T. Hannahs, R. C. Black, W. K. Neils, Dinesh Martien, S. L. Bud'ko, and P. C. Canfield. Six closely related $\text{YbT}_2\text{Zn}_{20}$ ($\text{T} = \text{Fe}, \text{Co}, \text{Ru}, \text{Rh}, \text{Os}, \text{Ir}$) heavy fermion compounds with large local moment degeneracy. *Proc. Natl. Acad. Sci.*, 104(24):9960–9963, JUN 12 2007.
- [198] E. D. Mun, S. Jia, S. L. Bud'ko, and P. C. Canfield. Thermoelectric power of the $\text{YbT}_2\text{Zn}_{20}$ ($\text{T} = \text{Fe}, \text{Ru}, \text{Os}, \text{Ir}, \text{Rh}, \text{and Co}$) heavy fermions. *Phys. Rev. B*, 86:115110, Sep 2012.
- [199] Z. Fisk, P. C. Canfield, W. P. Beyermann, J. D. Thompson, M. F. Hundley, H. R. Ott, E. Felder, M. B. Maple, M. A. Lopez de la Torre, P. Visani, and C. L. Seaman. Massive electron state in YbBiPt . *Phys. Rev. Lett.*, 67:3310–3313, Dec 1991.
- [200] Toshiaki Tanaka and Yasunori Kubo. Electronic Structure of Heavy-Fermion Systems $\text{YbT}_2\text{Zn}_{20}$ ($\text{T} = \text{Fe}, \text{Co}, \text{Ru}, \text{Rh}, \text{Os}, \text{Ir}$). *J. Phys. Soc. Jpn.*, 79(12):124710, 2010.
- [201] Yuta Saiga, Kazuyuki Matsubayashi, Tetsuya Fujiwara, Masashi Kosaka, Susumu Katano, Masato Hedo, Takehiko Matsumoto, and Yoshiya Uwatoko. Pressure-induced Magnetic Transition in a Single Crystal of $\text{YbCo}_2\text{Zn}_{20}$. *J. Phys. Soc. Jpn.*, 77(5):053710, 2008.
- [202] Y. Nakanishi, T. Kamiyama, K. Ito, M. Nakamura, Y. Saiga, M. Kosaka, Y. Uwatoko, and M. Yoshizawa. Ultrasonic investigation close to quantum critical point in $\text{YbTr}_2\text{Zn}_{20}$ ($\text{Tr}: \text{Co}, \text{Rh}, \text{and Ir}$). *J. Phys. Conf. Ser.*, 200(1):012142, 2010.
- [203] S. K. Kim, M. S. Torikachvili, S. L. Bud'ko, and P. C. Canfield. Search for pressure-induced quantum criticality in $\text{YbFe}_2\text{Zn}_{20}$. *Phys. Rev. B*, 88:045116, Jul 2013.
- [204] K. Matsubayashi, Y. Saiga, T. Matsumoto, and Y. Uwatoko. Fermi-liquid properties of

- the heavy fermion systems $\text{YbT}_2\text{Zn}_{20}$ ($T = \text{Ir, Rh and Co}$) under pressure. *J. Phys. Conf. Ser.*, 150(4):042117, 2009.
- [205] Kazuyuki Matsubayashi, Yuta Saiga, Takehiko Matsumoto, and Yoshiya Uwatoko. Pressure-induced variation of Kondo behavior on the heavy fermion compounds $\text{YbT}_2\text{Zn}_{20}$ ($T = \text{Co, Rh, Ir}$). *J. Phys. Conf. Ser.*, 200(1):012112, 2010.
- [206] M. Cabrera-Baez, R. A. Ribeiro, and M. A. Avila. Tuning the electronic hybridization in the heavy fermion cage compound $\text{YbFe}_2\text{Zn}_{20}$ with Cd doping. *J. Phys. : Condens. Matter*, 28(37):375601, 2016.
- [207] Yasuyuki Shimura, Toshiro Sakakibara, Shingo Yoshiuchi, Fuminori Honda, Rikio Settai, and Yoshichika Ōnuki. Evidence of a Field-Induced Ordering in $\text{YbCo}_2\text{Zn}_{20}$ in a [111] Magnetic Field. *J. Phys. Soc. Jpn.*, 80(7):073707, 2011.
- [208] Tetsuya Takeuchi, Masahiro Ohya, Shingo Yoshiuchi, Masaki Matsushita, Fuminori Honda, Rikio Settai, and Yoshichika Ōnuki. Metamagnetic behavior in a heavy fermion compound $\text{YbCo}_2\text{Zn}_{20}$. *J. Phys. Conf. Ser.*, 273(1):012059, 2011.
- [209] Yasuyuki Shimura, Toshiro Sakakibara, Shingo Yoshiuchi, Fuminori Honda, Rikio Settai, and Yoshichika Ōnuki. Field-Induced Ordering in the Heavy Fermion Compound $\text{YbCo}_2\text{Zn}_{20}$. *J. Phys. Conf. Ser.*, 391(1):012066, 2012.
- [210] Fuminori Honda, Yuki Taga, Yusuke Hirose, Shingo Yoshiuchi, Yoshiharu Tomooka, Masahiro Ohya, Jyunya Sakaguchi, Tetsuya Takeuchi, Rikio Settai, Yasuyuki Shimura, Toshiro Sakakibara, Ilya Sheikin, Toshiki Tanaka, Yasunori Kubo, and Yoshichika Ōnuki. Novel Electronic States of Heavy Fermion Compound $\text{YbCo}_2\text{Zn}_{20}$. *J. Phys. Soc. Jpn.*, 83(4):044703, 2014.
- [211] Tetsuya Takeuchi, Shingo Yoshiuchi, Masahiro Ohya, Yuki Taga, Yusuke Hirose, Kiyohiro Sugiyama, Fuminori Honda, Masayuki Hagiwara, Koichi Kindo, Rikio Settai, and Yoshichika Ōnuki. Field-Induced Quadrupolar Ordered Phase for $H // < 111 >$ in Heavy-Fermion Compound $\text{YbCo}_2\text{Zn}_{20}$. *J. Phys. Soc. Jpn.*, 80(11):114703, 2011.

- [212] Koji Kaneko, Shingo Yoshiuchi, Tetsuya Takeuchi, Fuminori Honda, Rikio Settai, and Yoshichika Ōnuki. Effect of magnetic field in heavy-fermion compound $\text{YbCo}_2\text{Zn}_{20}$. *J. Phys. Conf. Ser.*, 391(1):012026, 2012.
- [213] Masahiro Ohya, Masaki Matsushita, Shingo Yoshiuchi, Tetsuya Takeuchi, Fuminori Honda, Rikio Settai, Toshiki Tanaka, Yasunori Kubo, and Yoshichika Ōnuki. Strong Field Quenching of the Quasiparticle Effective Mass in Heavy Fermion Compound $\text{YbCo}_2\text{Zn}_{20}$. *J. Phys. Soc. Jpn.*, 79(8):083601, 2010.
- [214] D. L. Cox and N. Grewe. Transport-properties of the Anderson Lattice. *Z. Phys. B*, 71(3):321–340, 1988.
- [215] Ernst Bauer. Anomalous properties of Ce-Cu- and Yb-Cu-based compounds. *Adv. Phys.*, 40(4):417–534, 1991.
- [216] M. C. Aronson, J. D. Thompson, J. L. Smith, Z. Fisk, and M. W. McElfresh. Kondo coherence in UBe_{13} : Magnetoresistance at high pressure. *Phys. Rev. Lett.*, 63:2311–2314, Nov 1989.
- [217] P. Schlottmann. Bethe-Ansatz solution of the ground-state of the SU (2j+1) Kondo (Coqblin-Schrieffer) model: Magnetization, magnetoresistance and universality. *Z. Phys. B*, 51(3):223–235, 1983.
- [218] Yuta Saiga, Kazuyuki Matsubayashi, Tetsuya Fujiwara, Takehiko Matsumoto, Masashi Kosaka, Susumu Katano, and Yoshiya Uwatoko. Magnetoresistivity of $\text{YbCo}_2\text{Zn}_{20}$ at low temperature. *J. Phys. Conf. Ser.*, 150(4):042168, 2009.
- [219] Richard M. Martin. Fermi-Surface Sum Rule and its Consequences for Periodic Kondo and Mixed-Valence Systems. *Phys. Rev. Lett.*, 48:362–365, Feb 1982.
- [220] N. Grewe. One particle excitation spectrum of the Kondo-lattice. *Solid State Commun.*, 50(1):19 – 23, 1984.

- [221] G. E. Brodale, R. A. Fisher, C. M. Lisse, N. E. Phillips, and A. S. Edelstein. Specific heat of CeAl_3 below 20 K in fields to 8 T: Effect of CeAl_2 and/or $\text{Ce}_3\text{Al}_{11}$ phases. *J. Magn. Magn. Mater.*, 54:416 – 418, 1986.
- [222] C. D. Bredl, S. Horn, F. Steglich, B. Lüthi, and Richard M. Martin. Low-Temperature Specific Heat of CeCu_2Si_2 and CeAl_3 : Coherence Effects in Kondo Lattice Systems. *Phys. Rev. Lett.*, 52:1982–1985, May 1984.
- [223] T. Fujita, K. Satoh, Y. nuki, and T. Komatsubara. Specific heat of the dense Kondo compound CeCu_6 . *J. Magn. Magn. Mater.*, 47:66 – 68, 1985.
- [224] G. Knopp, A. Loidl, R. Caspary, U. Gottwick, C.D. Bredl, H. Spille, F. Steglich, and A.P. Murani. Specific heat, resistivity and neutron scattering studies in the Kondo lattice CeNi_2Ge_2 . *J. Magn. Magn. Mater.*, 74(3):341 – 346, 1988.
- [225] A. Yatskar, N. K. Budraa, W. P. Beyermann, P. C. Canfield, and S. L. Bud’ko. Heavy-electron behavior in single-crystal $\text{YbNi}_2\text{B}_2\text{C}$. *Phys. Rev. B*, 54:R3772–R3775, Aug 1996.
- [226] P. Schlottmann. Some exact results for dilute mixed-valent and heavy-fermion systems. *Phys. Rep.*, 181(1-2):1 – 119, 1989.
- [227] E. D. Mun, B. K. Lee, Y. S. Kwon, and M. H. Jung. Kondo ground state of CeCoGe_2 with $j = \frac{5}{2}$. *Phys. Rev. B*, 69:085113, Feb 2004.
- [228] C. Rossel, K. N. Yang, M. B. Maple, Z. Fisk, E. Zirngiebl, and J. D. Thompson. Strong electronic correlations in a new class of Yb-based compounds: YbXCu_4 ($\text{X}=\text{Ag}, \text{Au}, \text{Pd}$). *Phys. Rev. B*, 35:1914–1918, Feb 1987.
- [229] M. J. Besnus, P. Haen, N. Hamdaoui, A. Herr, and A. Meyer. Kondo behavior of YbAgCu_4 . *Physica B Condens. Matter*, 163(1-3):571 – 573, 1990.
- [230] H. Michor, St. Berger, M. El-Hagary, C. Paul, E. Bauer, G. Hilscher, P. Rogl, and G. Giester. Crystal structure and Kondo lattice behavior of CeNi_9Si_4 . *Phys. Rev. B*, 67:224428, Jun 2003.

- [231] Johnpierre Paglione, T. A. Sayles, P.-C. Ho, J. R. Jeffries, and M. B. Maple. Incoherent non-Fermi-liquid scattering in a Kondo lattice. *Nature Phys.*, 3(10):703–706, October 2007.
- [232] G. E. Adrian and H. G. Adrian. Influence of lattice disorder on superconductivity and normal state transport properties of heavy fermion systems. *J. Less-Common Met.*, 149:313 – 317, 1989.
- [233] Zlatko Tešanović. Disorder and coherence in heavy-fermion systems. *Phys. Rev. B*, 34:5212–5216, Oct 1986.
- [234] M. Nicolas-Francillon, A. Percheron, J. C. Achard, O. Gorochoy, B. Cornut, D. Jerome, and B. Coqblin. Measurements of the CeAl_2 and LaAl_2 resistivities under pressure: Variations of the Kondo effect and of the crystalline field of cerium. *Solid State Commun.*, 11(6):845 – 849, 1972.
- [235] H. Schneider, Z. Kletowski, F. Oster, and D. Wohlleben. Transport properties of single crystals of CeCu_2Si_2 and CeNi_2Ge_2 . *Solid State Commun.*, 48(12):1093 – 1097, 1983.
- [236] H. Fujii, T. Takabatake, and Y. Andoh. Anisotropic hybridization in some cerium and uranium compounds with hexagonal ZrNiAl -type structure. *J. Alloys Comp.*, 181(1-2):111 – 121, 1992.
- [237] Valentin Taufour, Halyna Hodovanets, Stella K. Kim, Sergey L. Bud’ko, and Paul C. Canfield. Electrical resistivity study of CeZn_{11} : Magnetic field and pressure phase diagram up to 5 GPa. *Phys. Rev. B*, 88:195114, Nov 2013.
- [238] M. A. Avila, Y. Q. Wu, C. L. Condon, S. L. Bud’ko, M. Kramer, G. J. Miller, and P. C. Canfield. Anomalous temperature-dependent transport in $\text{YbNi}_2\text{B}_2\text{C}$ and its correlation to microstructural features. *Phys. Rev. B*, 69:205107, May 2004.
- [239] Alexander Steppke, Manuel Brando, Niels Oeschler, Cornelius Krellner, Christoph Geibel, and Frank Steglich. Nuclear contribution to the specific heat of $\text{Yb}(\text{Rh}_{0.93}\text{Co}_{0.07})_2\text{Si}_2$. *Phys. Status Solidi B*, 247(3):737–739, 2010.

- [240] C. Gold, P. Gross, L. Peyker, G. Eickerling, G. G. Simeoni, O. Stockert, E. Kampert, F. Wolff-Fabris, H. Michor, and E-W. Scheidt. Interplay between crystal field splitting and Kondo effect in $\text{CeNi}_9\text{Ge}_{4-x}\text{Si}_x$. *J. Phys. Condens. Matter*, 24(35):355601, 2012.
- [241] Jin-Ke Bao, Ji-Yong Liu, Cong-Wei Ma, Zhi-Hao Meng, Zhang-Tu Tang, Yun-Lei Sun, Hui-Fei Zhai, Hao Jiang, Hua Bai, Chun-Mu Feng, Zhu-An Xu, and Guang-Han Cao. Superconductivity in Quasi-One-Dimensional $\text{K}_2\text{Cr}_3\text{As}_3$ with Significant Electron Correlations. *Phys. Rev. X*, 5:011013, Feb 2015.
- [242] F. F. Balakirev, T. Kong, M. Jaime, R. D. McDonald, C. H. Mielke, A. Gurevich, P. C. Canfield, and S. L. Bud'ko. Anisotropy reversal of the upper critical field at low temperatures and spin-locked superconductivity in $\text{K}_2\text{Cr}_3\text{As}_3$. *Phys. Rev. B*, 91:220505, Jun 2015.
- [243] Tai Kong, Morgan W. Masters, Sergey L. Bud'ko, and Paul C. Canfield. Physical properties of $\text{V}_{1-x}\text{Ti}_x\text{O}_2$ ($0 < x < 0.187$) single crystals. *APL Materials*, 3(4):–, 2015.
- [244] Mengkun Liu, Aaron J. Sternbach, Martin Wagner, Tetiana V. Slusar, Tai Kong, Sergey L. Bud'ko, Salinporn Kittiwatanakul, M. M. Qazilbash, Alexander McLeod, Zhe Fei, Elsa Abreu, Jingdi Zhang, Michael Goldflam, Siyuan Dai, Guang-Xin Ni, Jiwei Lu, Hans A. Bechtel, Michael C. Martin, Markus B. Raschke, Richard D. Averitt, Stuart A. Wolf, Hyun-Tak Kim, Paul C. Canfield, and D. N. Basov. Phase transition in bulk single crystals and thin films of VO_2 by nanoscale infrared spectroscopy and imaging. *Phys. Rev. B*, 91:245155, Jun 2015.
- [245] Akira Iyo, Kenji Kawashima, Tatsuya Kinjo, Taichiro Nishio, Shigeyuki Ishida, Hiroshi Fujihisa, Yoshito Gotoh, Kunihiro Kihou, Hiroshi Eisaki, and Yoshiyuki Yoshida. New-Structure-Type Fe-Based Superconductors: $\text{CaAFe}_4\text{As}_4$ ($A = \text{K}, \text{Rb}, \text{Cs}$) and $\text{SrAFe}_4\text{As}_4$ ($A = \text{Rb}, \text{Cs}$). *J. Am. Chem. Soc.*, 138(10):3410–3415, 2016.
- [246] W. R. Meier, T. Kong, U. S. Kaluarachchi, V. Taufour, N. H. Jo, G. Drachuck, A. E. Böhmer, S. M. Saunders, A. Sapkota, A. Kreyssig, M. A. Tanatar, R. Prozorov, A. I. Goldman, Fedor F. Balakirev, Alex Gurevich, S. L. Bud'ko, and P. C. Canfield. Anisotropic

- thermodynamic and transport properties of single-crystalline $\text{CaKFe}_4\text{As}_4$. *Phys. Rev. B*, 94:064501, Aug 2016.
- [247] Daixiang Mou, Tai Kong, William R Meier, Felix Lochner, Lin-Lin Wang, Qisheng Lin, Yun Wu, SL Bud'ko, Ilya Eremin, DD Johnson, P C Canfield, and Adam Kaminski. Enhancement of the superconducting gap by nesting in $\text{CaKFe}_4\text{As}_4$ -a new high temperature superconductor. *arXiv:1606.05643*, 2016.
- [248] Kyuil Cho, A Fente, S Teknowijoyo, MA Tanatar, T Kong, W Meier, U Kaluarachchi, I Guillaumon, H Suderow, SL Bud'ko, et al. Nodeless multiband superconductivity in stoichiometric single crystalline $\text{CaKFe}_4\text{As}_4$. *arXiv:1606.06245*, 2016.
- [249] A. Fente, W. R. Meier, T. Kong, V. G. Kogan, S. L. Bud'ko, P. C. Canfield, I. Guillaumon, and H. Suderow. Vortices in two-effective-band, stoichiometric high T_c $\text{CaKFe}_4\text{As}_4$ superconductor. *arXiv:1608.00605*, 2016.
- [250] N. M. R. Armstrong, K. D. Mortimer, T. Kong, S. L. Bud'ko, P. C. Canfield, D. N. Basov, and T. Timusk. Quantum diffusion of electrons in quasiperiodic and periodic approximant lattices in the rare earth-cadmium system. *Philos. Mag.*, 96(11):1122–1130, 2016.
- [251] Keola Wierschem, Sai Swaroop Sunku, Tai Kong, Toshimitsu Ito, Paul C. Canfield, Christos Panagopoulos, and Pinaki Sengupta. Origin of modulated phases and magnetic hysteresis in TmB_4 . *Phys. Rev. B*, 92:214433, Dec 2015.
- [252] Sai Swaroop Sunku, Tai Kong, Toshimitsu Ito, Paul C. Canfield, B. Sriram Shastry, Pinaki Sengupta, and Christos Panagopoulos. Hysteretic magnetoresistance and unconventional anomalous Hall effect in the frustrated magnet TmB_4 . *Phys. Rev. B*, 93:174408, May 2016.
- [253] A. Narayanan, M. D. Watson, S. F. Blake, N. Bruyant, L. Drigo, Y. L. Chen, D. Prabhakaran, B. Yan, C. Felser, T. Kong, P. C. Canfield, and A. I. Coldea. Linear Magnetoresistance Caused by Mobility Fluctuations in n -Doped Cd_3As_2 . *Phys. Rev. Lett.*, 114:117201, Mar 2015.

- [254] Yun Wu, Tai Kong, Lin-Lin Wang, D. D. Johnson, Daixiang Mou, Lunan Huang, Benjamin Schrunck, S. L. Bud'ko, P. C. Canfield, and Adam Kaminski. Asymmetric mass acquisition in LaBi: Topological semimetal candidate. *Phys. Rev. B*, 94:081108, Aug 2016.
- [255] Sergey L Bud'ko, Tai Kong, Xiaoming Ma, and Paul C Canfield. Study of ^{57}Fe Mössbauer effect in $\text{RFe}_2\text{Zn}_{20}$ (R = Lu, Yb, Gd). *J. Phys. Condens. Matter*, 27(33):336003, 2015.