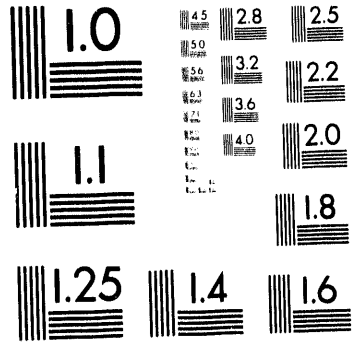
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Muon Spin Relaxation Studies of the Interplay between Magnetism and Superconductivity in Heavy Fermion Systems

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Abstract

The interplay between magnetism and superconductivity in heavy fermion systems is discussed and the role of muon spin relaxation in elucidating these properties is emphasized. Relevant properties of all six heavy fermion superconductors are briefly surveyed and instances where superconductivity and magnetism compete, coexist and couple with one another are pointed out. Current theoretical concepts underlying these phenomena are highlighted.

Key Words: heavy fermions, magnetism, muon spin relaxation, superconductivity

I. Introduction

Because new classes of superconducting materials have been discovered in recent years, the study of superconductivity, only ten years ago thought to be passé, remains a most fascinating challenge for material's researchers. For example, the collection of new superconducting materials now includes the high-temperature oxide superconductors, with transition temperatures T_c as high as 130 K, doped C_{60} Fullerines ($T_c \approx 30K$), low-dimensional organic superconductors ($T_c \approx 10K$), and heavy fermion (HF) superconductors ($T_c \approx 1K$). All of these materials exhibit very interesting magnetic phenomena as well. This paper concerns a brief discussion of the interplay between magnetism and superconductivity in the HF materials and the role muon spin rotation (μSR) experiments have played in elucidating their properties. Heavy fermion materials involve rare-earth (Ce and Yb, usually) and uranium-based compounds in which the f-electrons are strongly hybridized with the conduction electrons at low temperatures [1,2]. In order to understand the superconducting properties of HF, it is first necessary to have a framework to describe the normal state produced by this strong hybridization.

One of the key normal-state properties of HF materials is that at low temperatures the f-electron moments are reduced to a fraction of their high-temperature values, which are close to the full f-shell moment ($\approx 3\mu_B$). This moment compensation occurs through an antiferromagnetic exchange interaction which produces a virtual bound state between the conduction electrons and the f-moments. For dilute magnetic ions in metals this is

the well known single-ion Kondo interaction. Although this crossover from full-moment to reduced-moment behavior does not occur through a sharp phase transition, it can still be characterized by a scaling temperature T^*, the coherence temperature. "Coherence" is implied because below T^* the resistivity drops significantly, indicating the loss of inelastic scattering and the formation of the HF state, consisting of renormalized (heavy mass) quasiparticles describable in a Fermi liquid theory. For HF materials $T^* \approx$ 10-100K. Although this general picture is now well accepted, no complete microscopic theory of this many-body state has yet been formulated [2]. The evolution of such a theory is a major challenge for the theory of electrons in materials.

A variety of different low-temperature ground states emerges from this background of moment compensation: paramagnetism (PM), antiferromagnetism (AFM) and superconductivity. Where magnetic or superconducting phase transitions are found it is clear from the entropy balance that the heavy quasiparticles themselves form the ordered state. In the case of AFM the ordered moments are typically very small (0.001-0.1μ_B), as expected from screening by the conduction electrons. Whether the system will exhibit an AFM or PM state depends upon a competition between the local on-site exchange interaction, which compensates the local f-moment, and the non-local long-range f-f interaction, which gives rise to magnetic order through the RKKY interaction. The intra- and inter-site interactions are related through a common conduction-electron local-moment exchange coupling.

Superconductivity in HF systems is interesting and important because most evidence indicates that both the symmetry of the superconducting order parameter and the pairing interaction itself are different from more conventional superconductors like Al or Pb. In conventional superconductors the superconducting gap exists over the entire Fermi surface, and the electrons pair in a zero angular momentum, spin-singlet state which is produced by the electron-phonon interaction. A non-vanishing gap gives rise to exponential temperature dependences for all measurements involving the thermal excitation of quasiparticles across the gap: specific heat, magnetic-field penetration depth and nuclear spin lattice relaxation rate, as examples. However, measurements of these quantities in heavy fermion superconductors all exhibit power-law temperature dependences, usually considered as evidence for nodes in the energy gap [1].

Power-law temperature dependencies do not provide definitive evidence for an unconventional gap structure, however [3]. (A conventional gap-less superconductor can also exhibit power-law behavior, for example.) More decisive conclusions can only be

drawn from tests of the symmetry-breaking nature of the order parameter $\Delta(k)$. In conventional superconductors $\Delta(k)$ obeys the symmetry of the Hamiltonian, which includes rotational, reflection (parity) and time-reversal symmetry. An unconventional superconductor has a lower symmetry in at least one of these respects. Experimental tests of this property include a transition from one superconducting state to another, observation of magnetism associated with the superconducting order parameter, or anisotropy in the temperature dependence of the penetration depth or the critical fields.

II. Experiments

The known HF superconductors are listed in Table I, together with some properties which are relevant to this discussion. A thorough survey can be found in Ref [2]. The manifestations of the interplay between magnetism and superconductivity display much variety in HF systems. This is doubtless because the f-electrons themselves are involved in both phenomena and, as discussed below, there is growing evidence that magnetic spin fluctuations (paramagnons) may also be the dominant superconducting pairing mechanism. This is in contradistinction to an earlier class of "magnetic-superconductors," the rare-earth rhodium-borides and moly-sulfides [4], where the magnetism is localized on the rare-earths but the superconductivity is carried by separate conduction electrons which interact weakly with the local moments. In this sense the Cr-Re systems [5] may be more analogous to HF superconductors.

It is clear from Table I that antiferromagnetism occurs both above and below the superconducting transition temperature. Below examples are given where these two phases can compete, coexist and/or couple with one another.

A. Competition: $CeCu_2Si_2$

This was the first HF superconductor to be discovered and remains the only rare-earth based system. Extensive studies have shown that the existence of superconductivity and/or magnetism in this system is very sensitive to subtle changes in unit-cell volume, which can be induced by La doping and Cu deficit ($\Delta V/V > 0$) or Cu excess and hydrostatic pressure ($\Delta V/V < 0$) [2]. Samples with large unit-cell volume tend to be magnetic and non-superconducting, reflecting a reduction in T^*; when the volume is reduced superconductivity appears and T^* is raised. Antiferromagnetism can also be induced by the application of fields in superconducting samples; the field-temperature phase diagram continues to be investigated [6]. In addition, spontaneous magnetism, possibly of spin-glass-like origin, exists along with superconductivity in zero field [7].

Experiments [7,8] using μSR provide incite into this appearance of both magnetism and superconductivity. In zero field the μSR relaxation function for $CeCu_{2.05}Si_2$ exhibits two components below about 1.35 K, one of which is attributable to paramagnetic domains, with volume fraction A_1, and the other to magnetic domains, with volume fraction A_2 ($A_1 + A_2 = 1$). The temperature dependence of these amplitudes is shown in Fig. 1. The magnetic volume fraction grows below 1.3K, reaching a maximum at T_c and then decreasing as the superconductivity develops. Furthermore, experiments in an applied field show a change in the muon precession frequency below T_c (due to the diamagnetism) only in the paramagnetic fraction. Thus superconductivity and magnetism do not appear to coexist in the same sample volume, but instead compete for volume with one another. This competition between magnetism and superconductivity is different from the HF behavior found in the materials discussed below.

B. Coexistence: UNi_2Al_3, UPd_2Al_3, URu_2Si_2

These three actinide superconductors all exhibit magnetic order above T_c which coexists with superconductivity below T_c. A plot of the muon precession frequency versus temperature in UNi_2Al_3 is shown in Fig. 2 for zero applied field [9]. The muon frequency spectrum shows four components: three precession signals (Fig. 2) and one non-precession signal, corresponding to different interstitial muon stopping sites. The dipole field at each muon site depends upon the AFM structure and the magnitude of the local moment μ. The data are constistent with $\mu \approx 0.1\mu_B$. Recent neutron scattering data [10] confirm this value. A most important point for this discussion is that the muon precession frequencies and their amplitudes are unaltered by the onset of superconductivity, indicating not only a coexistence but also a weak interaction between the two types of ground states.

A similar situation is found in UPd_2Al_3 [11]. Neutron scattering experiments [12] reveal a moment $\mu \approx 0.85\mu_B$, ordered ferromagnetically in the basal plane and antiferromagnetically along the c-axis below 14.5 K. Several different magnetic phases have been found in the field-temperature phase diagram [11]. The μSR data [13] are similar to UNi_2Al_3, however only one relaxation component is observed. This component corresponds to a single occupancy site for the muon, that of highest symmetry where the dipole fields from the AFM order cancel, and so no precession signals are seen.

The temperature dependence of the transverse-field μSR rate in polycrystalline UPd_2Al_3 is shown in Fig. 3 [13]. This rate increases at T_N and again at T_c, below

which the local-field distribution increases due to the flux lattice produced in the mixed state of the superconductor. Note that the line broadening from the antiferromagnetic state persists below T_c, again indicating coexistence with superconductivity. Recent results on a single crystal of UPd_2Al_3 are qualitatively the same [8].

A similar situation is seen in a single crystal of URu_2Si_2, another HF superconductor with T_c = 1.3 K and T_N = 17 K. Here the much-reduced moments ($\mu \approx 0.04\mu_B$) are ordered antiferromagnetically along the c-axis [14]. The μSR rate [15] for a field applied parallel to the c-axis shows an increasing linewidth as the temperature is decreased below T_N. Below T_c the relaxation rate increases and the precession frequency changes, both reflections of entering the superconducting state, similar to the case of UPd_2Al_3. Again only a single relaxation component is seen.

It is important to note that in these three HF superconductors the muon data show that the magnetism and superconductivity coexist on a microscopic scale; that is, there is not one relaxation component which shows magnetic behavior and another which responds to superconductivity, as in $CeCu_2Si_2$. This microscopic coexistence of AFM and superconductivity in these three materials has been verified with neutron and, in the case of URu_2Si_2, with light scattering. The μSR data also show that, although the magnetism and superconductivity in UNi_2Al_3, UPd_2Al_3 and URu_2Si_2 coexist throughout the entire sample volume, they do not appear to strongly interact, despite the fact the the f-electrons are involved in both ground states. This is also different from $CeCu_2Si_2$ discussed above.

C. Coupling: UPt_3 and $(U,Th)Be_{13}$

The examples given above all have antiferromagnetic transition temperatures greater than T_c. This also occurs in UPt_3, where an AFM transition at 5K was first discovered by μSR [16]. Comprehensive neutron scattering experiments [17] then delineated the AFM, which consists of small moments ($\mu \approx 0.03\mu_B$) antiferromagnetically ordered in the basal plane. Most important, however, is that in zero applied field the growth of the magnetic Bragg intensity for decreasing temperatures below T_N is reversed and falls again below T_c. The specifics of this behavior are both field and temperature dependent. This reflects a clear interaction between the superconducting and magnetic order parameters not found in the superconductors mentioned above.

Subsequent studies using a variety of probes have revealed a rich phase diagram in the field-temperature-pressure planes for UPt_3, in which at least three different superconducting phases have been discovered [18]. In zero field and ambient pressure

there are two superconducting transitions near T = 0.55K, separated by only about 60 mK. There is evidence [19] that this splitting is produced by the coupling between the AFM order parameter (setting in at 5K) and the superconducting order parameter. Remarkably, recent zero-field μSR experiments show the onset of very weak spontaneous magnetism below the lower of the two superconduction transition temperatures [20]. These issues will be discussed again below.

UBe_{13} itself shows no magnetic order down to 10mK, only a superconducting transition at T_{c1} = 0.9K. However, when UBe_{13} is doped with Th the superconducting transition temperature exhibits a non-monotonic suppression [21], as shown in Fig. 4. Furthermore, for $0.019 < x < 0.043$ in $U_{1-x}Th_xBe_{13}$, a second phase transition [22] occurs at T_{c2} below T_{c1}. μSR experiments [23] reveal the onset of magnetism below T_{c2}, again with very small moments ($\mu \leq 0.01\mu_B$). The large specific heat jump at T_{c2} indicates a change in the superconducting state below this temperature. What is remarkable is that the magnetic phase boundary at T_{c2} begins and terminates on the superconducting phase boundary [23] at T_{c1}. This is similar to the case of UPt_3, and again suggests possible coupling of the magnetic and superconducting order parameters. Finally, we note that the normal state of UBe_{13} has a resistance peak [24] at about T_{max} = 2.2K which moves lower in temperatyure as Th is added, so that it intersects the superconducting phase boundary T_{c1} at $x \approx 0.019$, just where the suppression of T_{c1} is reversed (see Fig. 4). Recent magnetoresistance and specific heat studies [25] of $(U,Th)Be_{13}$ are consistent with an association of the resistance anomaly with correlated spin fluctuations in the heavy electron system. These spin fluctuations may be freezing out below T_{c2} giving rise to a small-moment AFM state which couples to the superconducting order parameter as in UPt_3.

III. Concluding Discussion

The above examples show that the interplay of magnetism and superconductivity has great variety in HF materials. At this point there is no detailed microscopic theory which can uniquely explain all of these phenomena [2]. Nevertheless, there is a line of reasoning which explains some of the phenomena and provides a framework for thinking about HF superconductors. An important point is that the strongly-hybridized f-electron quasiparticles are involved in the magnetic and superconducting phase transitions in these systems. Second, because these quasiparticles exhibit strong AFM correlations even in the paramagnetic state, it is tempting to consider that AFM spin fluctuations may also provide the dominant superconducting pairing force in HF materials. This assumption is

strengthened by theoretical studies [26] which show that AFM paramagnons can give rise to both a spin-density-wave (SDW) instability and an even-parity, anisotropic pairing state (d-wave) for strong on-site Coulomb repulsion. Likewise ferromagnetic paramagnons favor triplet p-wave pairing. A conventional isotropic pairing state is not indicated; indeed, spin fluctuations are pairbreaking for s-wave pairing [27]. The fact that all HF superconductors exhibit power-law temperature dependencies for low-temperature transport and thermodynamic measurements and that some materials show multiple superconducting phases and anisotropic critical fields rules out conventional superconductivity for most HF superconductors. This means that the f-electron Fermi surface can be divided between superconductivity and AFM, where the nesting which gives rise to the SDW occupies that region of the Fermi surface where there are nodes in the anisotropic superconducting order parameter [28]. This seems to be the case in URu_2Si_2, for example, where the specific heat jumps at T_N and T_c indicate that neither phase transition occupies the full Fermi surface. Such a picture provides a natural way of understanding how superconductivity and AFM can coexist in these systems.

Interactions between superconductivity and magnetism are described through explicit terms in the free energy which couple the tensors representing the magnetization and the superconductivity, while preserving the overall symmetry. In UPt_3, for example, the magnetization below 5K, as measured by neutron scattering [17], lies in the basal plane. One recent model [29] for the superconducting order parameter in UPt_3 assumes a complex two-dimensional vector with basal-plane components (η_x,η_y), which can therefore couple through a vector product to the magnetization. In the model this coupling causes the zero-field splitting of the superconducting phase transitions near 0.55K. If a superconducting order parameter of similar symmetry were present in URu_2Si_2, however, no coupling with the magnetization in that system would occur because the moments are polarized along the c-axis. This could account for the observed lack of change in magnetization below T_c.

These ideas, only briefly mentioned here, have been discussed in detail in the recent literature [2]. While such concepts are useful, they are not definitive. Although HF superconductors exhibit many common properties which these models encompass, the distinguishing normal- and superconducting- state characteristics of each material--band properties, and coherence and scattering lengths, for example--must be examined before the interplay between magnetism and superconductivity in that material can be understood. For example, the absence of microscopic coexistence in $CeCu_2Si_2$ may reflect a fundamental difference between 4f and 5f systems (such as the degree of

hybridization), as may the fact that only one Ce-based HF superconductor has been discovered.

One final point must be mentioned regarding the very weak magnetism which sets in below T_c in UPt_3 and $(U,Th)Be_{13}$. The above discussion implies that these magnetic correlations are induced by a paramagnetic exchange interaction. It is also possible that the superconducting phase itself may possess orbital [30] or spin [31] magnetism. Such a phase violates time-reversal symmetry and can be expected for an unconventional superconductor (3He is a good example). This picture would explain why the magnetism occurs right at T_c and is confined to the superconducting phase boundaries. So far there is no definitive evidence which can distinguish between purely magnetic or superconducting origins for these small moments.

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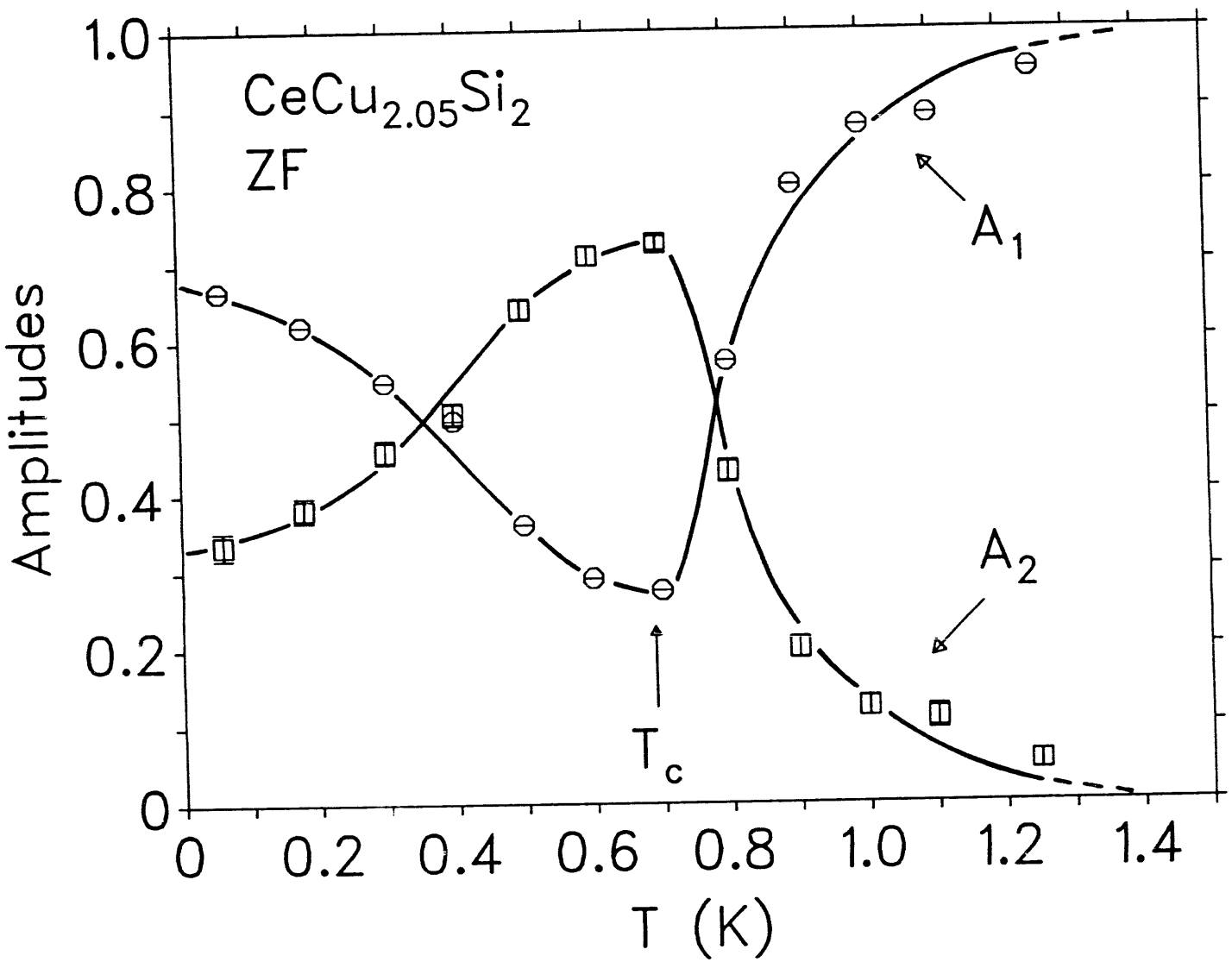
Table I

Material	Structure	γ(J/mol-K^2)	T_c(K)	T_N(K)	Moment(μ_B)
$CeCu_2Si_2$	Tetragonal	1.100	0.70	0.8-1.3	0.2
URu_2Si_2	Tetragonal	0.065	1.20	17.5	0.04
UPd_2Al_3	Hexagonal	0.150	2.00	14.5	0.85
UNi_2Al_3	Hexagonal	0.120	1.00	4.4	0.12
UPt_3 [a]	Hexagonal	0.450	0.55	5.0	0.03
UBe_{13} [b]	Cubic	1.100	0.90	-	-

a) transition at about 0.50K with very small moment ($\approx 0.001\mu_B$)

b) $(U,Th)Be_{13}$ exhibits transition below 0.4K with small moment ($\approx 0.01\mu_B$)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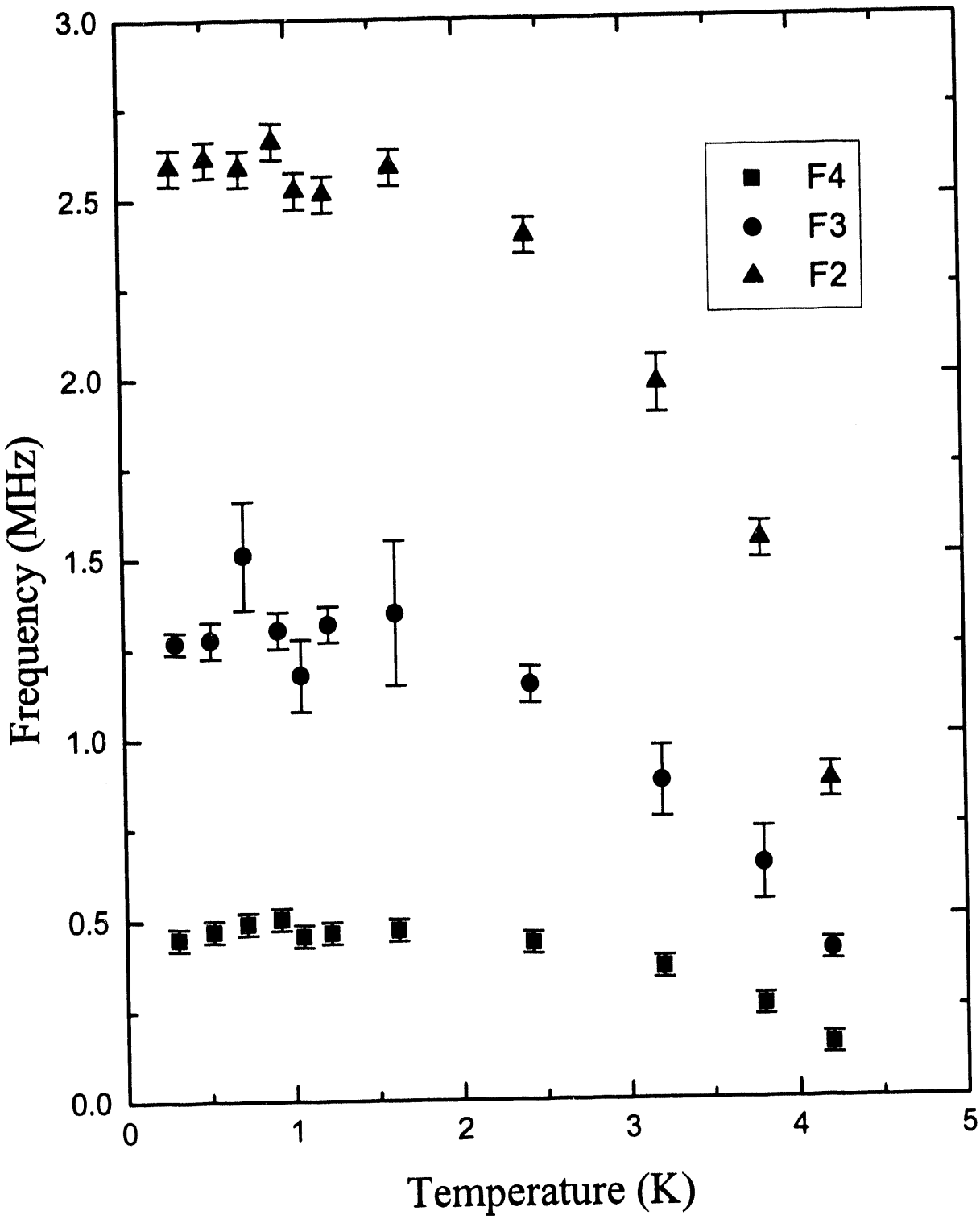
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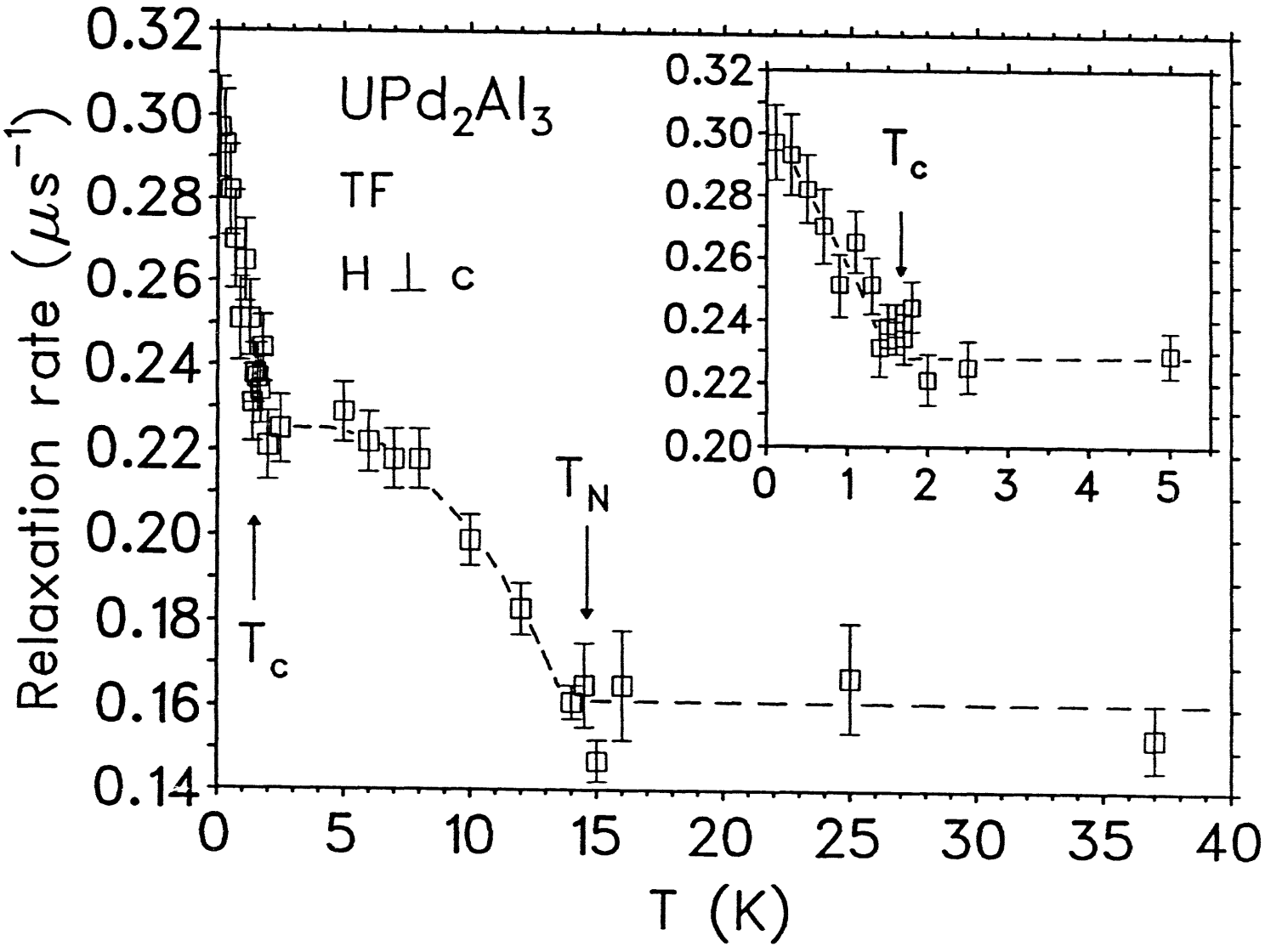
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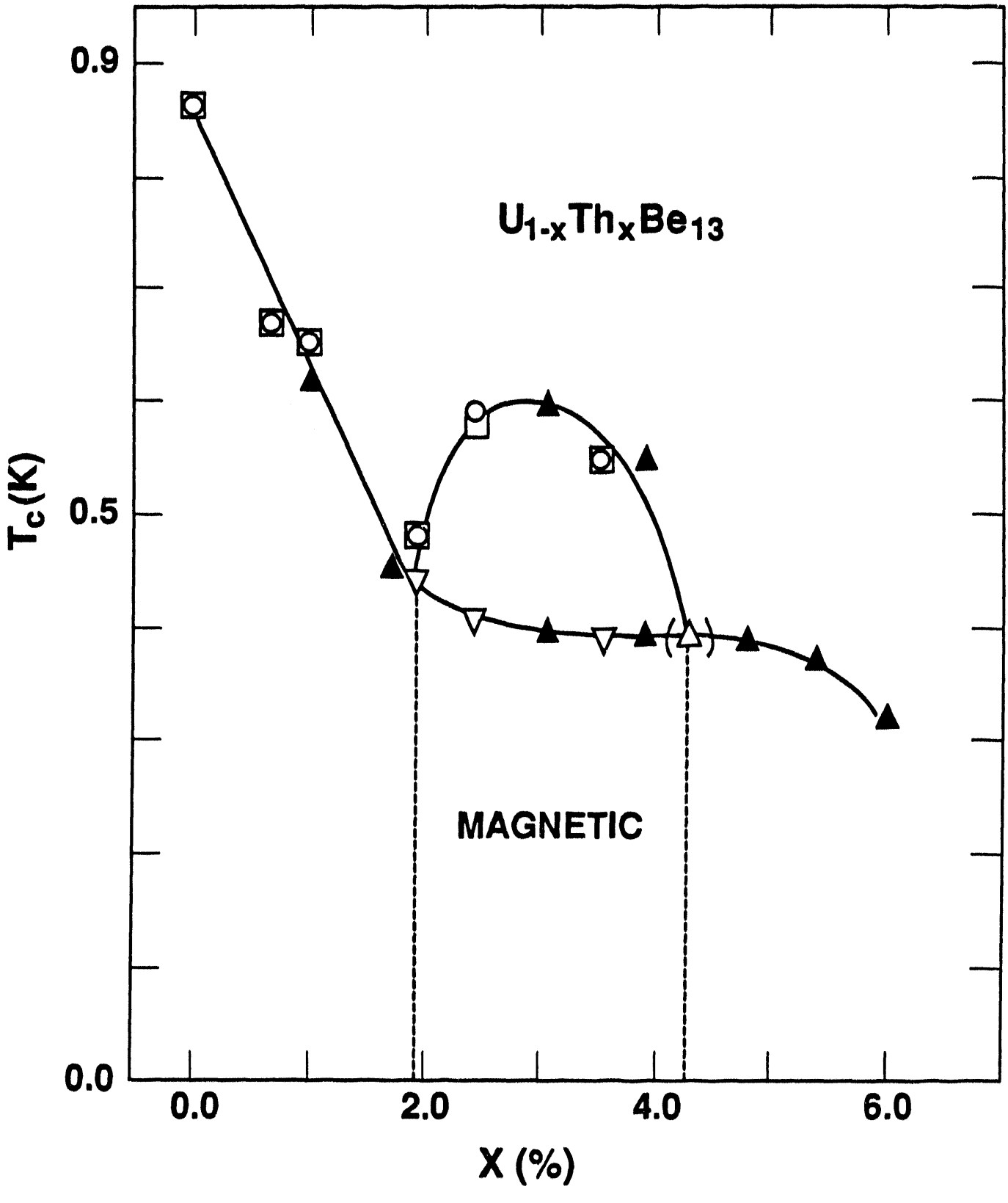

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