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^{29}Si-NMR study of magnetic anisotropy and hyperfine interactions in the uranium-based ferromagnet $UNiSi_2$

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Abstract. $UNiSi_2$ orders ferromagnetically below T_{Curie} = 95 K. This material crystallizes in the orthorhombic $CeNiSi_2$-type structure. The uranium atoms form double-layers, which are stacked along the crystallographic *b* axis (the longest axis). From magnetization measurement the easy (hard) magnetization axis is found to be the *c* axis (*b* axis). ^{29}Si-NMR measurements have been performed in the paramagnetic state. In $UNiSi_2$, two crystallographic Si sites exist with orthorhombic local symmetry. The Knight shifts on each Si site have been estimated from the spectra of random and oriented powders. The transferred hyperfine couplings have been also derived. It is found that the transferred hyperfine coupling constants on each Si site are nearly isotropic, and that their Knight shift anisotropy comes from that of the bulk susceptibility. The nuclear-spin lattice relaxation rate $1/T_1$ shows temperature-independent behaviour, which indicates the existence of localized 5*f* electron.

1. Introduction

Uranium-based ferromagnets are attractive materials to be explored extensively in condensed-matter physics, since recently, superconductivity on the background of ferromagnetism has been discovered in UGe_2 [1], URhGe [2], UCoGe [3], and UIr [4]. To understand the mechanism by which superconductivity coexists with ferromagnetism, it is also important to characterize the background 5*f* ferromagnetism. As a common feature among these U-based ferromagnets, the U atoms seem to be arranged with low-dimensionality in their orthogonal (or monoclinic) crystal structure. The ferromagnet $UNiSi_2$ with a Curie temperature of T_{Curie}=95 K [5] is a candidate to study the 5*f* ferromagnetism with such a crystallographic feature. This material crystallizes in the orthorhombic $CeNiSi_2$-type structure, and the U atoms form double-layers, which are stacked along the crystallographic *b* axis (the longest axis), as shown in figure 1. Previous powder neutron diffraction measurements have revealed collinear ferromagnetic ordering with the U-moments directed along *c* (parallel to U-double-layers). [6] The specific heat Sommerfeld coefficient was estimated to be 27 mJ mol^{-1} K^{-2} using polycrystalline sample. [6] Since the temperature dependence of resistivity shows the ln*T*-like behavior above T_{Curie}, $UNiSi_2$ was proposed to be ferromagnetic Kondo lattice system. [5] For a more detailed examination of potential magnetic anisotropies, measurements on single crystals are desired.

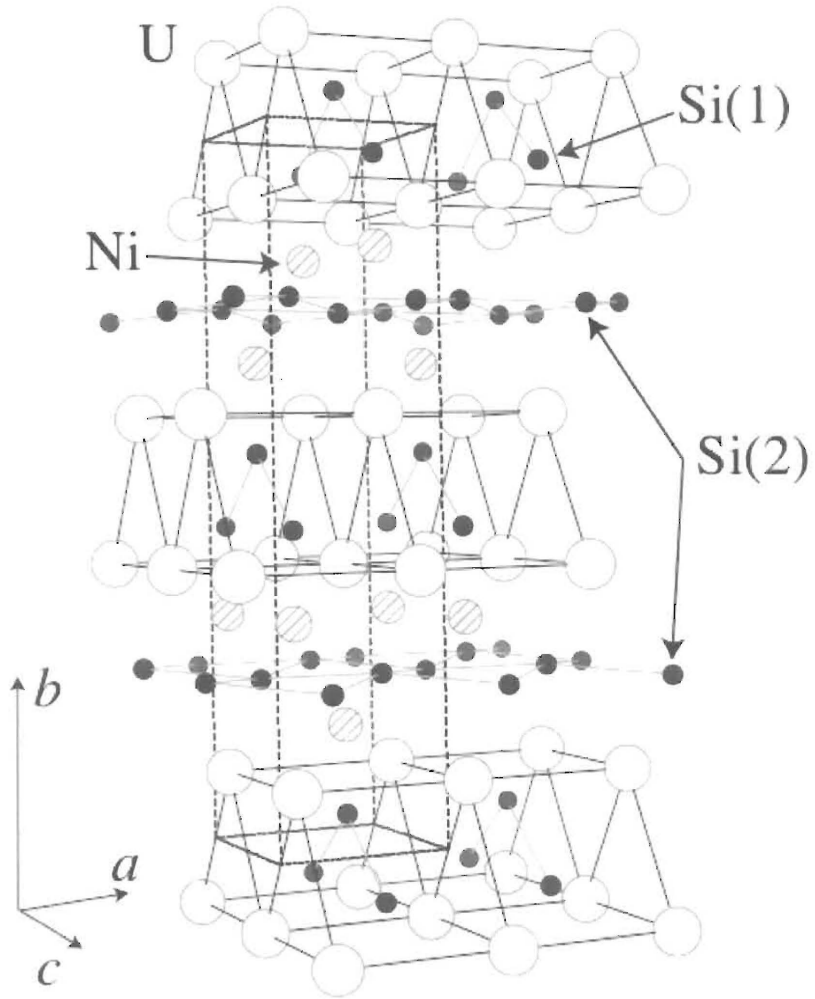


Figure 1. Crystal structure of $UNiSi_2$

We have measured resistivity and magnetization using a single crystal of $UNiSi_2$ in order to characterize the ferromagnetism of $UNiSi_2$. Moreover, in order to investigate 5*f* electronic state microscopically, we have also performed ^{29}Si-nuclear magnetic resonance (NMR) measurements for $UNiSi_2$.

2. Experiment

Single crystals of $UNiSi_2$ were grown by Ga-flux method and characterized by x-ray diffraction. The obtained single crystals have thin rectangular forms with large *b* surface. The determined lattice parameters were a=4.008 Å, b=16.07 Å, and c=4.009 Å, respectively. Resistivity was measured by four probe method using a low-frequency ac resistance bridge. DC magnetization measurements of a single crystal with the dimensions of ~2 × 3 × 0.5 mm^3 were carried out using a superconducting quantum interference device magnetometer with applied field of 1 kOe. Magnetization data were taken under field cooled condition. In this paper, magnetic susceptibility (χ) below T_{Curie} was defined as the magnetization (M) divided by the applied field (H_0), i.e., $\chi=M/H_0$.

^{29}Si-NMR measurements were performed using a phase-coherent pulsed spectrometer. Field-swept NMR spectra were obtained at constant frequency (ν_L) by accumulation of spin-echo signals at each step of applied field. In order to increase the surface penetration of rf fields, powder $UNiSi_2$ samples were prepared by crushing the single crystals carefully. The powder was mixed with varnish to

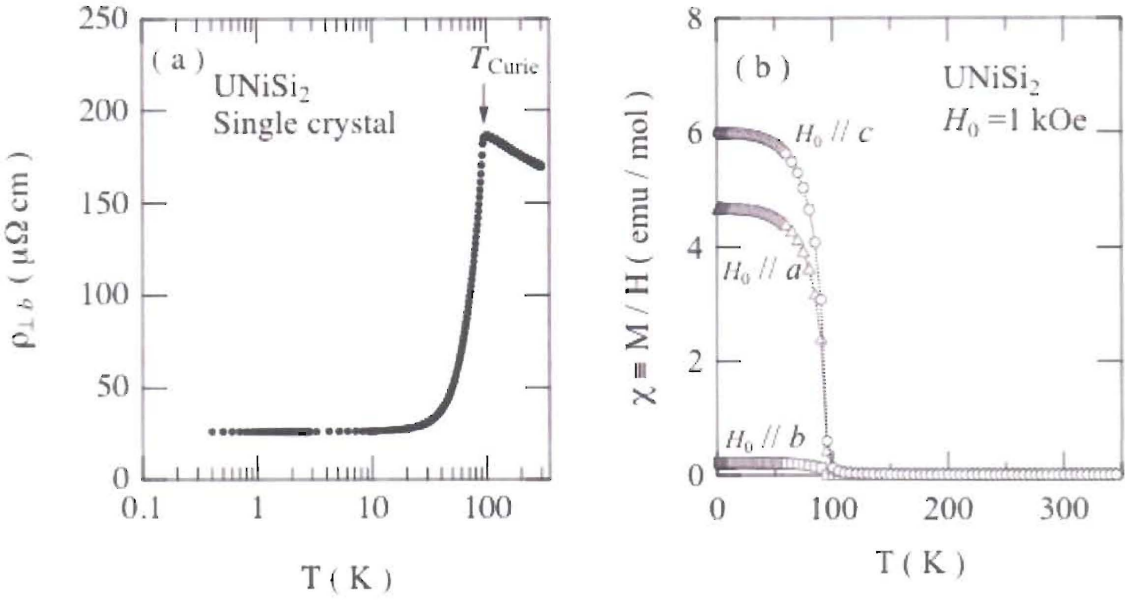


Figure 2. (a) Temperature dependence of resistivity in ac plane of $UNiSi_2$. (b) Temperature dependence of magnetization (M) divided by applied field (H_0) for single crystal of $UNiSi_2$.

insulate the surface of each particle and to fix their orientation randomly. Moreover, the oriented powder sample embedded in epoxy was also prepared. The crystallographic c-axis in this oriented powder sample was parallel to H_0.

3. Results and discussions

3.1. Resistivity and magnetization

As shown in figure 2(a), the resistivity in the ac plane (perpendicular to b axis) for a single crystal of $UNiSi_2$ shows a sharp drop below T_{Curie}=95 K. The resistivity shows Kondo-like behavior above T_{Curie}, as reported previously in polycrystalline samples [5], that is, $\rho = \rho_0 + \rho_0^{\infty} - c_K \ln T$, where ρ_0 is the residual resistivity determined at low temperatures, ρ_0^{∞} the temperature independent spin disorder term and c_K the Kondo coefficient. Here, the obtained values are $\rho_0 = 26$ $\mu\Omega$ cm, $\rho_0^{\infty} = 234$ $\mu\Omega$ cm, and $c_K = 15.9$ $\mu\Omega$ cm, respectively.

Figure 2(b) shows temperature dependence of magnetic susceptibility measured with the applied field of H_0=1 kOe along a, b, and c-axis. The onset of ferromagnetism in $UNiSi_2$ is seen clearly at T_{Curie}=95 K. The magnetization below T_{Curie} shows a huge magnetic anisotropy with easy (hard) magnetization axis of c (b) axis. Since the neutron scattering experiment has revealed that uniaxial magnetic anisotropy along c axis, the rather small anisotropy between a and c axes than between b and c may suggest the existence of magnetic and/or structural domains in the ac plane. Above T_{Curie}, the susceptibility follows the Curie-Weiss law. The effective moments (and paramagnetic Curie temperatures Θ) for a, b, and c axes are estimated to be 2.37 μ_B (89 K), 2.88 μ_B (-250 K), and 2.37 μ_B (86 K), respectively. These effective moments are smaller than the free ion values of 3.62 μ_B for U^{3+} or 3.58 μ_B for U^{4+}. This reduction of effective moments may result from c-f hybridization indicated by the Kondo-like behavior of resistivity, while the anisotropy of the paramagnetic Curie temperatures may suggest anisotropy of the exchange interactions.

3.2. Knight shifts in the paramagnetic state of $UNiSi_2$

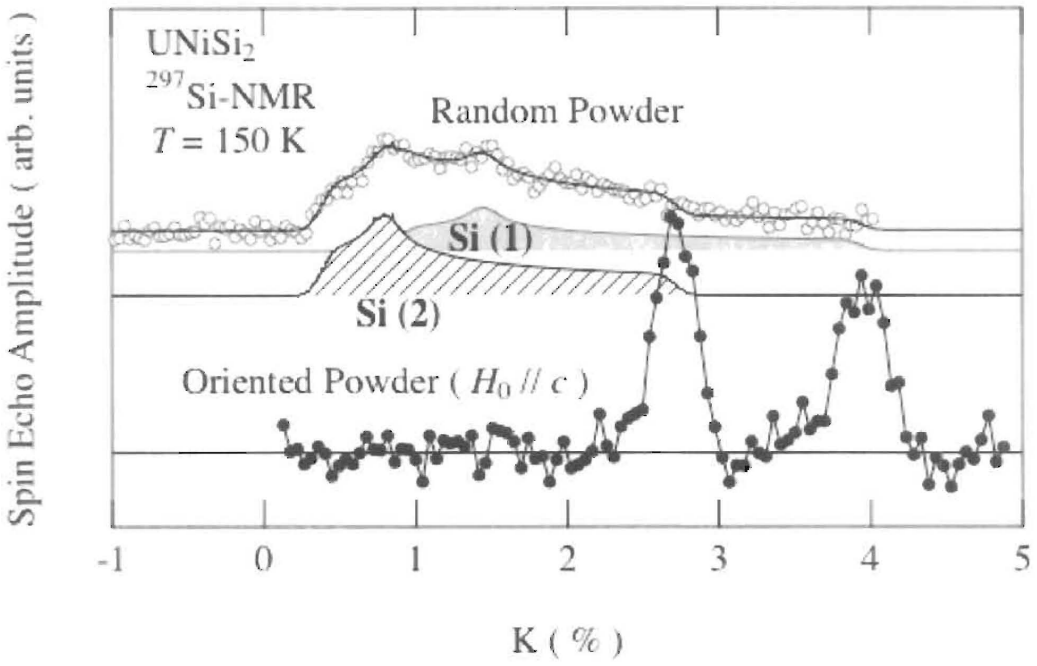
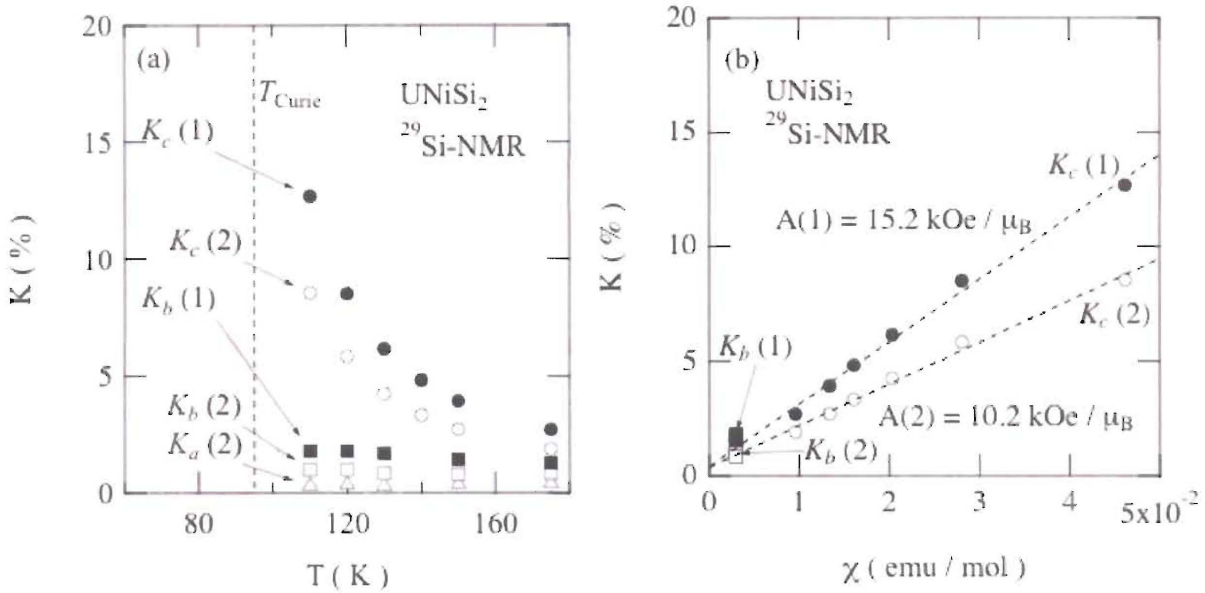


Figure 3. ^{29}Si-NMR spectra of $UNiSi_2$ for the random (open circles) and the oriented (closed circles) powder samples at 150 K. The solid curve for the random powder represents a fitting result of two decomposed orthogonal powder patterns.

There are two crystallographic Si sites of Si(1) and Si(2), as denoted in figure 1, both of which have orthogonal local symmetry. The Si(1) sites, which form zig-zag chains along the *c*-axis, are located inside the U-double-layers, and the Si(2) sites, which form a distorted Si(2)-plane between U-double-layers. It is noted that the nearest neighbor distance of U-Si(1) is shorter than that of U-Si(2). Since the nuclear spin of ^{29}Si is 1/2 (nuclear gyromagnetic ratio γ_N= 0.84578 MHz/kOe), the orthogonal powder pattern due to anisotropic Knight shift should appear for the each Si sites if the sample is randomly oriented. Such an orthogonal powder pattern is well known to have a sharp singularity at the position of H_0 // *b'* axis, where the *b'* axis is defined in the frame of local symmetry on each site. In this case, the coordinates of each Si site are identical to the crystallographic axes.

Figure 3 shows ^{29}Si-NMR spectrum obtained at 150 K with Knight shift (K) equal to $((\nu_L/\gamma_N)-H_0)/H_0$ using a constant frequency of ν_L=38.7 MHz for the random powder sample and 52.15 MHz for the oriented powder sample. This NMR spectrum for the random powder can be fit to the sum of two orthogonal powder patterns, as shown in figure 3. For the confirmation of this spectral assignment, the NMR spectrum for the oriented powder sample is also shown, for which the resonance positions are according to the K_c-edges of the each orthogonal powder pattern. Because of the shorter distance from the magnetic U atom, the powder pattern with larger K_c value can be assigned to Si(1) sites. In addition, the two broad peaks in the random powder spectrum correspond to the respective K_b positions for the Si(1) and Si(2) sites. In this way, the K_b and K_c for Si(1) and Si(2) sites are determined. The K_a for Si(2) sites is estimated from the lower K-edge of the random powder spectrum. However, the spectral edge of K_a for Si(1) cannot be determined precisely since this edge is submerged in the spectrum.

As shown in figure 4(a), the temperature dependence of $K_b(1)$, $K_c(1)$, $K_a(2)$, $K_b(2)$, and $K_c(2)$ is quite anisotropic, similar to that of the susceptibility. For both Si sites, K_c shows strong temperature-dependence. In order to obtain the transferred hyperfine coupling constants $A(1)$ and $A(2)$ for each Si site, the so-called K-χ plots are shown in figure 4(b) with temperature as an implicit parameter (here, $K_a(1)$ and $K_a(2)$ are not shown since these values seem to contain large uncertainty). The linear K-χ



behaviors are clearly obtained for both Si sites along the *c* axis. From these *K*-χ slopes, A(1) and A(2) are estimated to be 15.2 and 10.2 kOe/μ_B, respectively.

Moreover, these *K*-χ lines are found to intercept near the origin. This means that the Van Vleck susceptibility and the orbital shifts are negligibly small in this system. On the other hand, as for the transferred hyperfine coupling constant along the *b* axis, these *K*-χ points are on the same K_c-χ lines, although the susceptibility and the Knight shifts along the *b* axis are nearly temperature-independent. It strongly suggests that the transferred hyperfine couplings have no anisotropy between *b* and *c* axes. These isotropic transferred hyperfine couplings reflect *s* character of the conduction electrons.

3.3. Nuclear spin-lattice relaxation rate $1/T_1$ in the paramagnetic state

The nuclear spin-lattice relaxation rate $1/T_1$ has been measured for Si(1) and Si(2) sites using the oriented powder sample. The $1/T_1$ for both Si sites is nearly temperature-independent in the paramagnetic state, as shown in figure 5. Such a constant behavior of $1/T_1$ suggests the existence of well-defined localized moment. In general, assuming the hyperfine coupling is isotropic, $1/T_1$ can be expressed as

$$\frac{1}{T_1} \propto A^2 \sum_{\mathbf{q}} \frac{\mathrm{Im}\,\chi_{\perp}(\mathbf{q}, \omega_0)}{\omega_0},$$

where A is the isotropic hyperfine coupling constant, $\mathrm{Im}\,\chi_{\perp}(\mathbf{q}, \omega_0)$ is the imaginary part of the dynamical susceptibility perpendicular to the quantization axis, and ω_0 is the NMR frequency. Since the ratio of $1/T_1$ between Si(1) and Si(2) sites is close to that of the square of hyperfine coupling constants, the $1/T_1$ for both sites is found to be determined only by the spin fluctuation of U moments. If the spin fluctuations are governed by the exchange interaction between localized U moments, such a fluctuation rate ω_{ex} can be estimated from the T_{Curie} as [8]

$$(\hbar\omega_{ex})^2 = (k_B T_{Curie})^2 \frac{3g_J}{z|g_J - 1|^3 J(J+1)},$$

where g_J is the Landé g factor, and z is the number of nearest neighbor magnetic ions. Then, $1/T_1$ can be estimated from ω_{ex} and the following formula

$$\left(\frac{1}{T_1}\right) = \sqrt{2\pi}\left(\frac{\gamma_N g_J \mu_B A}{z'}\right)^2 \frac{z' J(J+1)}{3\omega_{ex}},$$

where z' is the number of magnetic ions coupling to the ligand nucleus. Using these formulae, assuming the free ionic values of U^{3+} or U^{4+}, the exchange narrowing limit is estimated to be 3×10^3 sec^{-1} or 5×10^2 sec^{-1}, respectively. These estimations are much larger than the experimental value of ~75 sec^{-1}. This discrepancy may admit two interpretations. One interpretation is due to the reduction of local moments due to *c-f* hybridization and/or CEF effect. Another interpretation originates from possible anisotropy of exchange interactions which are ignored in this estimation. In order to examine these two possible interpretations, further experiments to measure the anisotropy of $1/T_1$ are required.

4. Summary

The magnetization data for a single crystal of $UNiSi_2$ show a huge magnetic anisotropy between the easy *c* axis and the hard *b* axis. Moreover, the resistivity and magnetization measurements for a single crystal of $UNiSi_2$ indicate the reduction of effective moment due to *c-f* hybridization.

We have also performed ^{29}Si-NMR measurements in the paramagnetic state, using the random and oriented powder samples which are prepared by crushing single crystals. We have succeeded to deduce the Knight shifts on both Si sites from the spectral analyses of NMR powder patterns. The Knight shifts on each Si site exhibit similar anisotropy to the static susceptibility. From the K-χ

Figure 4. (a) Temperature dependence of ^{29}Si-NMR Knight shifts (K_i) in $UNiSi_2$. The subscript i indicates the direction of H_0. The closed and open symbols represent Si(1) and Si(2) sites, respectively. (b) K-χ plot for Si(1) and Si(2) sites with temperature as an implicit parameter.

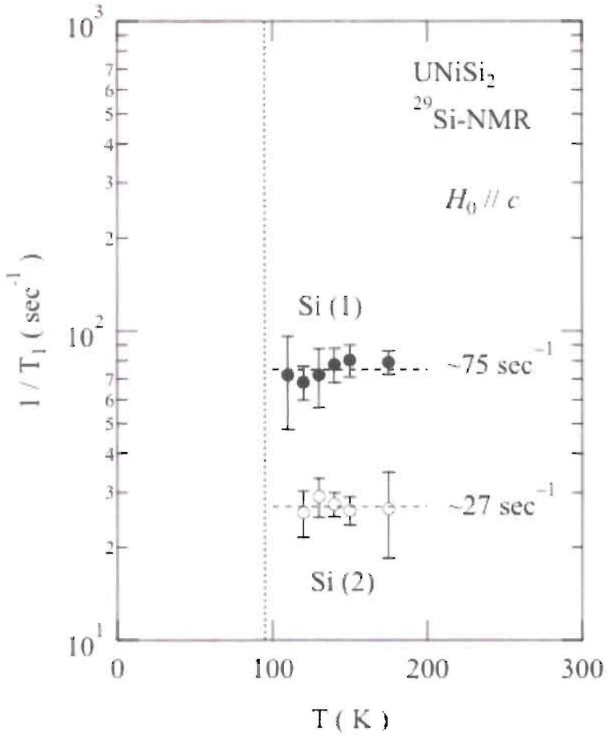


Figure 5. Temperature dependence of $1/T_1$ for Si(1) and Si(2) sites in the paramagnetic state of $UNiSi_2$, which have been measured using the oriented powder sample.

analysis, the transferred hyperfine coupling is found to be nearly isotropic, which suggests the s –wave character of conduction electrons. The relaxation rates $1/T_1$ are nearly constant in the paramagnetic state, which strongly suggests localized $5f$ character. However, the experimental $1/T_1$ value is much smaller than the exchange narrowing limit assuming the free ionic values of U and isotropic exchange interaction. This discrepancy may result from the reduction of effective moment and/or anisotropic exchange interactions.

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