

First-order transition to a noncollinear antiferromagnetic structure in $U_2Rh_3Si_5$

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We have determined the antiferromagnetic structure of monoclinic $U_2Rh_3Si_5$ and the temperature dependence of the magnetically ordered moment μ via single-crystal neutron diffraction. The value of μ exhibits a sharp discontinuity at the ordering temperature $T_N=25.5$ K, jumping from $1.6\mu_B$ to zero within a narrow temperature interval [$\Delta T_N=0.2$ K, $\mu(9\text{ K})=2.35\mu_B$]. This demonstrates the first-order nature of the transition. The magnetically ordered structure is a noncollinear arrangement of the eight uranium magnetic moments within the crystallographic unit cell. The moments are oriented parallel to nearest-neighbor U-Rh bonds, creating uniaxial (Ising-type) magnetic behavior, with canted local easy axes. The temperature dependence of the lattice parameters, as determined via high-resolution x-ray diffraction, exhibit pronounced discontinuities at T_N . These data demonstrate a strong magnetoelastic coupling. [S0163-1829(97)06446-1]

Uranium intermetallic compounds are attracting great interest due to their variety of unusual magnetic (and sometimes coexisting superconducting) ground states. An understanding of these ground-states involves investigation of the delicate balance between different and partly competing interactions, like inter-U magnetic exchange and quadrupolar interactions, the crystal-electric field, as well as electron-electron correlation and hybridization effects, touching some fundamental questions of present day research on intermetallics.¹⁻³

Previously, particular interest has been devoted to first-order antiferromagnetic transitions observed in insulating and metallic uranium compounds like UO_2 and several uranium monopnictides.⁴ In these compounds quadrupolar interactions appear to play a major role. However, first-order antiferromagnetic transitions are rare in *intermetallic* uranium compounds. The only examples we are aware of are UPd_3 , where the lower of the two successive antiferroquadrupolar transitions is also magnetic in character,⁵ and the extraordinary antiferromagnetic metal to paramagnetic semiconductor transition in $UNiSn$.⁶

In this paper we present results of neutron diffraction and high-resolution x-ray diffraction studies on single-crystal $U_2Rh_3Si_5$. This intermetallic compound has been synthesized recently,^{7,8} and has been suggested to exhibit a first-order antiferromagnetic transition at $T_N=25.6$ K.^{9,10} At the transition, an unusually large anomaly of the specific heat, and dramatic jumps of the magnetic susceptibility and the electrical resistivity at T_N have been observed. These results were interpreted in terms of a combined magnetic-quadrupolar transition in $U_2Rh_3Si_5$. The relatively small linear specific-heat term, $\gamma=22\text{mJ/K}^2\text{mol}$,¹⁰ suggests that the magnetic moments are well localized in $U_2Rh_3Si_5$.

Our neutron-diffraction results show that the transition to the magnetically ordered state is associated with a jump of the sublattice magnetization from zero to 2/3 of its maximum value within $\Delta T_N=0.2$ K which clearly demonstrates the first-order nature of the transition. In the ordered state, we

observe a noncollinear antiferromagnetic arrangement of the eight uranium magnetic moments within the unit cell of $U_2Rh_3Si_5$. This magnetic structure appears to be a natural result of a uniaxial (Ising-type) magnetic anisotropy at each uranium ion and a relative canting of the local magnetic easy axes which we find to be oriented along nearest-neighbor U-Rh bonds. In qualitative agreement with thermal expansion data,¹¹ our x-ray-diffraction data reveal pronounced discontinuities of the lattice constants and an expansion of the unit-cell volume on ordering, demonstrating the presence of a strong magnetoelastic coupling in $U_2Rh_3Si_5$. With its distinctive magnetic behavior, $U_2Rh_3Si_5$ adds a new flavor to the variety of magnetic ground states observed in uranium intermetallic compounds.

A single crystal (30 mm in length, 4.5 mm in diameter) was grown in a triarc furnace¹² using the Czochralski method (starting material: U 3N, Rh 4N, and Si 5N). The crystal was annealed for one week at 900 °C under high vacuum. Electron-probe microanalysis (EPMA) established it to be single-phase material with a maximum limit of $\approx 1\%$ for impurity phases. Our neutron-diffraction data show a mosaic spread smaller than 0.3° . The small annealed single crystal of mass 8 mg used in the x-ray study is a piece of the crystal employed for the previous investigations of the bulk properties.^{10,11}

The neutron-diffraction studies have been carried out at the Chalk River Laboratories, Canada, in the temperature range 9–35 K, using a closed-cycle refrigerator. The neutron wavelength was $\lambda=2.3705$ Å. The analysis of the Bragg scattering intensities was carried out using GSAS.¹³ High-resolution x-ray diffraction has been carried out using Cu $K_{\alpha 1}$ radiation which was further monochromated via the (111) reflection of a perfect Ge single crystal.

The crystal structure of $U_2Rh_3Si_5$ at $T=40$ K has been determined recently by neutron powder diffraction.¹⁴ We find the structural parameters as listed in Table I. The compound $U_2Rh_3Si_5$ crystallizes in the monoclinic $Lu_2Co_3Si_5$ -type structure, spacegroup $C2/c$. The actual distortion from

TABLE I. Atom positions in $U_2Rh_3Si_5$, in the quasiorthorhombic representation of the lattice structure, cell-choice $I12/c1$, as determined at $T=40$ K [$\beta'=90.045(10)^\circ$].

Lattice parameters	a' (Å)	b (Å)	c (Å)
	9.8096(7)	11.3857(8)	5.8415(4)
Atom (site)	x	y	z
U (8 <i>f</i>)	0.2678(3)	0.1323(3)	0.5021(22)
Rh1 (8 <i>f</i>)	0.1103(4)	0.3607(4)	0.5012(25)
Rh2 (4 <i>e</i>)	0	0.0030(8)	1/4
Si1 (8 <i>f</i>)	0.1526(7)	0.1066(6)	0.0125(28)
Si2 (4 <i>e</i>)	0	0.2149(15)	1/4
Si3 (4 <i>e</i>)	0	0.5074(22)	1/4
Si4 (4 <i>e</i>)	0	0.7695(15)	1/4

the orthorhombic $U_2Co_3Si_5$ structure (space group $Ibam$) is so small that we represent the lattice structure in the quasiorthorhombic cell choice $I12/c1$, as suggested in Ref. 15.

In the neutron-diffraction studies we have measured Bragg reflections of type $(h0l)$ and $(0kl)$. In systematic scans of the reciprocal space at $T=9$ K nonzero scattering intensity has been observed only for integer h , k , and l , indicating that the magnetic and the crystallographic unit cells are identical. Peaks of type $(h0l)$ obey the rule $h+l$ even. By comparing their intensities with those at $T=28$ K $> T_N$ we find that for all magnetic $(h0l)$ Bragg reflections h and l are both odd. In the second scattering plane only reflections $(0kl)$ with $k+l$ even have been observed, some of which carry significant magnetic contribution. This suggests the rule $h+k+l=2n$ to hold for both nuclear (as expected from the lattice symmetry) and magnetic Bragg reflections in $U_2Rh_3Si_5$.

We have measured the temperature dependence of several Bragg reflections. As an example, Fig. 1 shows the square root of the integrated intensity for the (301) reflection. This directly monitors the temperature dependence of the magnetically ordered moment. The antiferromagnetic transition, observed at $T_N=25.5$ K in this sample, is associated with a

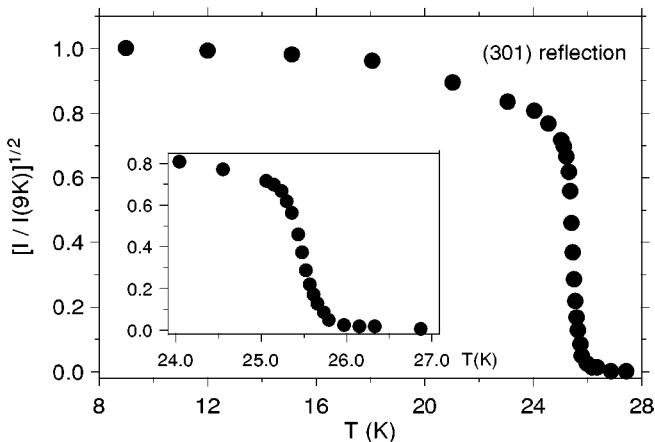


FIG. 1. The temperature dependence of the square root of the integrated intensity of the (301) Bragg reflection, normalized to its value at $T=9$ K, which directly reflects the temperature dependence of the magnetically ordered moment. The inset shows a blowup of the same data close to T_N .

TABLE II. Observed magnetic integrated intensities $I(9\text{ K})-I(28\text{ K})$ after absorption and extinction corrections described in the text, and calculated intensities I_{cal} from the best fit of the magnetic structure described in the text, all normalized to the (101) calculated intensity. The magnetic intensities have been calculated using the U^{4+} form factor (Ref. 18).

hkl	$2\theta(^\circ)$	$I(9\text{ K})-I(28\text{ K})$	I_{cal}
101	27.33	99.70	100
200	27.97	0.26 ^a	0
301	49.11	46.28	45.89
103	76.73	27.09	27.19
501	79.20	15.44	18.65
303	90.26	15.21	19.28
020	24.03	2.10 ^a	0
011	26.36	31.86	26.89
031	43.73	11.34	10.06
022	54.27	38.21	34.24
051	67.92	10.11	11.14
013	76.27	5.69	7.13
033	88.34	3.48	3.93
062	96.29	6.71	5.37
071	98.30	1.63	1.78
053	106.43	3.98	5.68

^aThe weak observed intensity is assigned to multiple scattering effects; the (200) reflection sets an upper limit of $0.4\mu_B$ for a component μ_c of the ordered moment; the (020) magnetic intensity vanishes in the scattering plane $(hk0)$.

sharp drop of the ordered moment μ from $1.6\mu_B$, i.e., $2/3$ of its value at $T=9$ K [$\mu(9\text{ K})=2.35\mu_B$, as determined below], to zero within a narrow temperature interval of half-width $\Delta T=0.2$ K around T_N . The minor broadening of the transition is presumably due to imperfections and impurities. From the thermodynamic properties there is no evidence for any other phase transition down to 1.5 K.¹⁰

In order to determine the magnetic structure a detailed analysis of the Bragg intensities has been performed. First, the measured intensities I were corrected for ^{103}Rh absorption of neutrons. A comparison of the relative nuclear Bragg intensities calculated from the crystal structure with the absorption-corrected values yielded good agreement for all reflections of low intensity. However, for a few high-intensity reflections, the measured intensities were markedly smaller than calculated. This is expected from (secondary) extinction. Because the crystal structure is known, the extinction effects can be accounted for by adding to the ^{103}Rh absorption coefficient a contribution cI_0 , where I_0 is the unperturbed Bragg intensity and c the same for all reflections. Including this correction brought our calculated nuclear intensities into good agreement with the experimental results [residual value $R=0.09$ for 13 independent (21 in total) nuclear reflections]. The magnetic intensities are only weakly affected by this correction.

The refinements for the relative intensities of the magnetic reflections are listed in Table II (residual value for this fit: $R=0.08$). The agreement between calculated and observed values is better for the $(h0l)$ subset than for the $(0kl)$ reflections, presumably because in the latter the average mag-

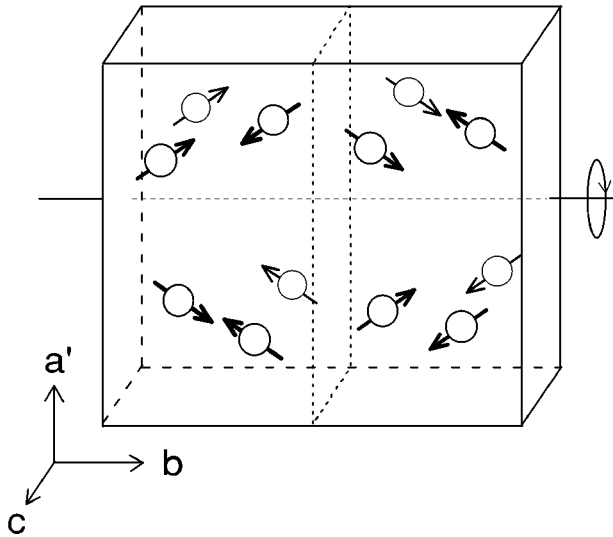


FIG. 2. The magnetic structure of single crystal $\text{U}_2\text{Rh}_3\text{Si}_5$. The magnetic moments are confined to the $a'b$ plane. Two symmetry elements of the lattice are marked by dashed lines: the glide plane $c[x, 1/2, z]$ (glide vector $[0, 0, 1/2]$) and the twofold axis $2[1/2, y, 3/4]$. A third symmetry element is the body-centering translation $I=[1/2, 1/2, 1/2]$.

netic intensities are weaker and therefore more sensitive to (unaccounted) multiple-scattering effects.

From these data, we arrive at the magnetic structure depicted in Fig. 2. It is characterized by the following properties: (i) Two U atoms related by the body-centering translation are of equal size and direction (no time reversal). This is consistent with the rule $h+k+l=2n$; (ii) the reflection of a magnetic moment at the glide plane, see Fig. 2, involves a time-reversal (note that the magnetic moment is an axial vector); (iii) the 180° rotation about the twofold symmetry axis, see Fig. 2, involves no time reversal. This, together with (ii), is consistent with the rule $h, l=2n+1$ for magnetic reflections ($h0l$). A component of the magnetic moments parallel to b also explains the presence of magnetic reflections of type $(0kl)$, $k, l=2n$. However, the observed $(0kl)$ reflections with $k, l=2n+1$ require a magnetic moment component perpendicular to b ; (iv) The magnetic moments appear to be confined to the $a'b$ plane, being oriented at angles $\alpha = \pm 34(3)^\circ$ with respect to the b axis. We find the relative intensities of the (011) and (022) reflections, produced by the a' and the b components of the magnetic moment, respectively, to scale linearly between 9 K and T_N . This sets an upper limit for a temperature-dependent change of α of $\pm 2^\circ$.

A comparison of magnetic and nuclear intensities results in the absolute value of the ordered moment $\mu = 2.35(10)\mu_B$ at $T=9$ K, with components $\mu_{a'} = 1.34(8)\mu_B$ and $\mu_b = 1.95(5)\mu_B$ (the upper limit for the component μ_c is $0.4\mu_B$). In the resulting magnetic structure the moments are oriented parallel to the nearest-neighbor U-Rh bonds which are at angles $\pm 30.7^\circ$ with respect to the b axis. We presume that the local easy axis is determined by the crystal electric field. With respect to the dominant b component of the magnetic moment, the magnetic structure can be described as an up-down stacking of “ferromagnetic” $a'c$ layers along b .

The magnetic structure observed in the present high-

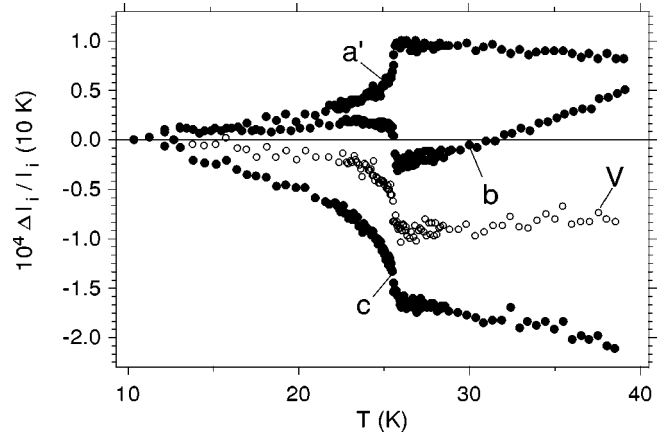


FIG. 3. The temperature dependence of the lattice parameters and the unit-cell volume in single crystal $\text{U}_2\text{Rh}_3\text{Si}_5$, normalized to their values at $T=10$ K, using a quasiorthorhombic cell (cell-choice $I12/c1$ of space group $C2/c$). Every second data point was taken on cooling, with the points in between on heating, in order to check for thermal hysteresis.

quality single crystal is related to but *different* from the magnetic structure reported previously for a polycrystalline sample.¹⁴ In the latter, the magnetic moments are also oriented along the U-Rh bonds, however, a two-up-two-down stacking of “ferromagnetic” $a'c$ layers along b was observed, resulting in the presence of magnetic Bragg reflections of the kind $h+k+l=2n+1$, only. The origin of the different magnetic structures is unclear. A thorough check of the composition of the two samples by EPMA showed a significantly higher Si concentration relative to the Rh content for the polycrystalline sample (actual composition 2.10:2.80:5.10). The single crystal proved to be closer to the ideal composition (actual composition 2.07:2.96:4.97, homogeneous over its whole length). This observation demonstrates the superior quality of the single crystal. The sample dependence will be the subject of further investigation.

The temperature dependence of the lattice parameters of single crystal $\text{U}_2\text{Rh}_3\text{Si}_5$, as determined by x-ray diffraction, is shown in Fig. 3. The lattice parameters observed at 40 K, $a' = 9.816(1)$ Å, $b = 11.399(1)$ Å, $c = 5.8311(5)$ Å, compare well to the results of the neutron powder-diffraction measurements. At $T_N = 25.6$ K, all three lattice parameters exhibit pronounced relative jumps of $\delta_{a'} = +0.4 \times 10^{-4}$, $\delta_b = -0.45 \times 10^{-4}$, and $\delta_c = -0.35 \times 10^{-4}$, resulting in a relative discontinuity of the unit-cell volume of $\delta_V = -0.4 \times 10^{-4}$. Notably, the unit-cell volume expands on cooling below T_N . No thermal hysteresis was observed, within ± 0.05 K, in agreement with previous investigations.¹⁰ Hysteresis should be present at a first-order phase transition but it might be too small to be observable. The present results are in qualitative agreement with the macroscopic length changes observed in the thermal expansion,¹¹ although our data show significantly larger jumps of a' and c .

Since the sublattice magnetization is a thermodynamic variable, the present results clearly demonstrate the first-order magnetic nature of the phase transition in $\text{U}_2\text{Rh}_3\text{Si}_5$. The behavior of $\text{U}_2\text{Rh}_3\text{Si}_5$ is reminiscent of that of UO_2 ,¹⁶ in which the magnetic transition is coupled with a distortion of the

the oxygen sublattice.¹⁷ However, in our neutron powder-diffraction study,¹⁴ no indication for a change of atom positions has been observed. In addition, since UO_2 is an insulator, the magnetic exchange mechanism is certainly different from that in $\text{U}_2\text{Rh}_3\text{Si}_5$, where the conduction-electron-mediated Ruderman-Kittel-Kasuya-Yosida interaction is expected to be dominant. Several different models have been employed to explain first-order transitions in uranium compounds,⁴ some of them assuming the presence of quadrupole-quadrupole as well as magnetic exchange interactions. The common element of all those theories is a kind of “bootstrap” mechanism, in which an initial reduction of the order parameter self-amplifies via a change in the splitting—and thus of the population—of associated crystal electric field levels. Such a mechanism is certainly active in $\text{U}_2\text{Rh}_3\text{Si}_5$, as demonstrated by the pronounced magnetoelastic coupling. However, due to the low symmetry of the system and the resulting lack of detailed information on the crystal electric field, at present no microscopic model for the phase transition in $\text{U}_2\text{Rh}_3\text{Si}_5$ can be offered.

To conclude, we have demonstrated the first-order magnetic nature of the phase transition in $\text{U}_2\text{Rh}_3\text{Si}_5$. It is associated with a pronounced magnetoelastic coupling. $\text{U}_2\text{Rh}_3\text{Si}_5$ appears to be an Ising-type antiferromagnet with canted local easy axes in the direction of the nearest-neighbor U-Rh bonds, where the local easy axis is presumably determined by the crystal electric field. A microscopic model of the phase transition in terms of a CEF level scheme, the hybridization, magnetic exchange, and possible quadrupolar interactions would be highly desirable to understand the unusual properties of $\text{U}_2\text{Rh}_3\text{Si}_5$.

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