Magnetism in URhSi


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Magnetism in URhSi

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Our neutron-powder-diffraction experiment revealed that URhSi crystallizes in the orthorhombic TiNiSi (space group Pnma) structure and orders ferromagnetically at low temperatures with the U magnetic moments of 0.11 μμμμ aligned along the c axis. Anomalies in the temperature dependence of the magnetic susceptibility, specific heat and electrical resistivity indicate that URhSi orders below 9.5 K. The enhanced C_p/T value (extrapolated to 0 K) of 186 mJ/mol K^2 can be partially reduced in magnetic fields, which indicates a considerable magnetic contribution even at very low temperatures. The ferromagnetic ground state is documented also by magnetization measurements at low temperatures. The high-field magnetization data obtained on oriented powder reveal a strong magnetocrystalline anisotropy. All the results obtained on polycrystalline samples classify URhSi as an itinerant 5f ferromagnet with very reduced U magnetic moments. © 1996 American Institute of Physics.

I. INTRODUCTION

The literature reports for URhSi either the CeCu_2 type structure^{1,2} (space group Imma) or its ordered version of the TiNiSi type^{3} (Pnma) similar to a number of other equiatomic ternary UTX (T=transition metal, X=Si or Ge) compounds. The differences between the x-ray or neutron-diffraction patterns for the two types of structures can be sometimes easily overlooked because the extra reflections, which appear for the ordered ternary version, are usually very weak. In both structures, the U atoms are coordinated in zigzag U chains within which each U atom has two nearest U neighbors at a distance of d_{U-U}~350 pm. In Hill’s classification,^{5} such a value of d_{U-U} means that these compounds are situated in a critical region between localized and itinerant 5f electron behavior. The present contribution involves the determination of the type of the crystal structure and the magnetic ground state in the context of magnetic, transport and thermal properties.

II. EXPERIMENT

A polycrystalline sample of URhSi has been prepared by arc-melting stoichiometric amounts of the constituting elements of at least 99.9% purity under an argon atmosphere and subsequently annealed for four weeks at 900 °C under vacuum. The purity and the composition homogeneity were checked by x-ray diffraction and by electron-microprobe analysis. The average composition of the major phase in the sample is deviating from the stoichiometric composition by less than 0.9 at. %. Nevertheless, a slight amount of URh_2Si_2 could be traced by the electron-microprobe analysis.

The magnetic susceptibility (M/H) in the temperature region 10–300 K and the low-temperature (down to 2 K) magnetization curves were measured in a Quantum Design SQUID magnetometer in magnetic fields up to 5 T on a fine-powder sample with grains fixed in random orientation by diamagnetic glue.

The specific heat was measured by a standard semiadiabatic method in the temperature region 1.6–250 K and compared with the previous results^{3} from the temperature region 1.3–40 K.

The electrical resistivity was measured on a small bar-shaped sample by standard ac four-point method. Assuming large errors in the geometrical factor (in addition to the expected influence of internal microcracks) only the normalized electrical resistivity ρ/ρ_{900 K} is presented.

Neutron-diffraction data at 2.8, 24, and 80 K were obtained using the neutron powder diffractometer E6 installed at the Hahn–Meitner Institute using an incident neutron wavelength of 2.386 Å. For these measurements URhSi was powdered and encapsulated into a vanadium container under He atmosphere. The recorded spectra were analyzed by means of the Rietveld profile procedure^{6} using the program FULLPROF. The neutron-scattering lengths were taken from Sears^{7} and uranium magnetic form factor from Delapalme.^{8}

III. BULK MEASUREMENTS

The susceptibility (Fig. 1) is nearly field independent above 30 K. Below this temperature, the magnetization curves (Fig. 2) become progressively curved reflecting increasing ferromagnetic correlations.

The 1/χ vs T dependence above 150 K is nearly linear and satisfies Curie–Weiss (CW) law

χ=C/(T−Θ_p)

with C=(1.268±0.008)×10^{-5} m^3/mol K \ (μ_{eff}=2.84±.01 μB/U atom) and Θ_p=−164.3±0.9 K.
The strongly nonlinear part between 20 and 150 K can be roughly approximated by a modified CW law including a temperature independent term $\chi_0$

$$\chi = C/(T - \Theta_p) + \chi_0$$

with significantly lower value of Curie constant, a positive paramagnetic Curie temperature of 9.7 K and $\chi_0\sim10^{-8}$ m$^3$/mol. Although, the applicability of both approaches for polycrystalline data of an anisotropic material is rather questionable some tentative conclusions can be made. The value of the effective moment from the high temperature fit, which can be taken as the upper limit in this material is much lower compared to free ion $U^{3+}$ or $U^{4+}$ expectation values in localized systems. We can take it as a good evidence of delocalization of 5$f$ moments in the present system. The drastically different $\Theta_p$ values from the high- and low-temperature region point to very strong magnetocrystalline anisotropy in the paramagnetic range.

The magnetic ordering at $T_C=9.5$ K is reflected by a relatively broad peak in the $C_p/T$ vs $T$ curve [Fig. 1(b)]. No other anomalies are seen between 1.6 and 250 K. The linear extrapolation of $C_p/T$ vs $T^2$ from the region 1.6–8 K to $T=0$ K gives a tentative $\gamma$ value of 185.6±1.3 mJ/mol K$^2$. A much better fit can, however, be obtained by the formula

$$C/T = \gamma + \beta T^2 + \delta T^2 \ln(T)$$

which involves the contribution of spin fluctuations through the additional logarithmic term. For the temperature region 1.6–9 K, the fitting parameters: $\gamma=180.9±0.6$ mJ/mol K$^2$, $\beta=-2.4±0.1$ mJ/mol K$^4$, and $\delta=0.5±0.05$ mJ/mol K$^4$. In K were obtained. To estimate the magnetic entropy we tried to subtract the Debye function with a probable value of Debye temperature $\Theta_D$. This task turns out to be very difficult. It seems impossible to assign one single value of $\Theta_p$. The best agreement in the high-temperature part can be obtained for $\Theta_D=290$ K together with the assumption of $\gamma=20$ mJ/mol K$^2$. In this way, we obtained by integrating $(C/T-C_{Debye}/T)$ in the temperature region 0–100 K, a value of 9.1 J mol$^{-1}$ K$^{-1}$ for the magnetic entropy. This means a value of 1.58 $R \ln 2$ or, through the expression $R \ln(2j+1)$, a value for $J$ of 1.0. In fact, this value represents the estimated upper limit. The magnetic entropy connected with the magnetic transition is only a very small fraction of this value, the rest originates most probably from magnetic fluctuations.

The onset of magnetic ordering at $T_C=9.5$ K is reflected also by the maximum in the temperature derivative of the electrical resistivity [Fig. 1(c)] near this temperature. The resistivity in the paramagnetic range is slightly decreasing with lowering temperature. It drops significantly below $T_C$, where also a quadratic temperature dependence with normalized parameters $\rho_0=0.4088±0.0004$ and the quadratic coefficient $A=3.292±0.009\times10^{-3}$ K$^{-2}$ is observed.

The high-field magnetization measured at 4.2 K up to 35 T on a field-aligned powder sample saturates slowly and at 35 T it reaches 0.67 $\mu_B$ f.u. ($M_{\text{free}}$). A value of 0.3 $\mu_B$ f.u. is obtained by extrapolation to zero magnetic field. For a powdered sample with randomly oriented grains, somewhat smaller values of 0.52 $\mu_B$ f.u. ($M_{\text{fix}}$) and 0.23 $\mu_B$ f.u., respectively, are recorded. Although the magnetization is by far not yet saturated in 35 T the ratio $M_{\text{free}}/M_{\text{fix}}=0.78$ can be taken as a supporting indication for an easy-plane anisotropy.

The low-field magnetization measured at different temperatures on a fixed-powder sample are shown in Fig. 2, where also some points from the previous high-field magnetization measurements (big open points) are displayed. It is clear that both data sets compare well and that hysteresis effects set in at low temperatures, as can be seen from the inset in Fig. 2 yielding a value of the remanent magnetization of 0.10 $\mu_B$ f.u.
IV. NEUTRON DIFFRACTION RESULTS

Two possible crystallographic structures were considered: the CeCu$_2$ type of structure (space group Imma) and its ordered version TiNiSi (space group Pnma). The neutron-diffraction patterns obtained above the transition temperature, namely at 80 K (Fig. 3) and 24 K, can be indexed using the orthorhombic TiNiSi type of structure. Note that the lines indexed as 102, 111, 200, 201, and 210 would not be present for the CeCu$_2$ type. The structural parameters determined at 80 K are summarized in Table I. The absence of any unindexed reflection proofs the very low content of the URh$_2$Si$_2$ secondary phase indicated by the electron microprobe. A considerable improvement of fit is achieved by introducing a secondary phase indicated by the electron microprobe. A considerable improvement of fit is achieved by introducing a slightly higher fraction of Rh ($\sim 0.8\%$). This is in a good agreement with the electron-microprobe analysis.

The spectrum recorded at 2.8 K (well below $T_C$ inferred from bulk experiments) contains no additional reflections, but only additional magnetic contributions to the 101, 011, 200, 112, 202, and 211 nuclear Bragg reflections. This is consistent with identical magnetic and crystallographic unit cells. The magnetic structure was determined by fitting to the models possible within the experimental constrain. The best agreement was obtained for the model with all $U$ moment parallel to the $c$ axis, i.e., for the ferromagnetic model with the size of magnetic moments $0.11 \pm 0.02 \mu_B$ per atom.

V. CONCLUSIONS

URhSi crystallizes in the orthorhombic TiNiSi-type of structure (space group Pnma) and orders ferromagnetically below 9.5 K with ordered $U$ moments of about 0.11 $\mu_B$. This rather small value in comparison with most $UTX$ compounds together with magnetization, susceptibility, specific-heat, and resistivity behavior suggests that the magnetism in URhSi is governed by strongly delocalized uranium $5f$ electron states. The origin of this itinerant behavior can be found mainly in the strong $5f$-ligand hybridization.

The ordered $U$ moment determined by the neutron-diffraction is much smaller than the value obtained from the field-induced moments in the latter experiment. The presence of magnetic fluctuations which play an important role at zero field even well above the transition temperature can be inferred from the bulk measurements. Studies on single-crystalline URhSi are highly desirable to get more specific information on substantial issues of magnetism in URhSi as are the magnetocrystalline anisotropy, orbital and spin moments, etc.

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**TABLE I.** The refined structural parameters of URhSi at 80 K.

<table>
<thead>
<tr>
<th>Space group</th>
<th>Pnma</th>
<th>$T=80$ K</th>
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<tbody>
<tr>
<td>$U$</td>
<td>4c</td>
<td>$X_U$ 1/4</td>
</tr>
<tr>
<td>$Rh$</td>
<td>4c</td>
<td>$X_{Rh}$ 1/4</td>
</tr>
<tr>
<td>$Si$</td>
<td>4c</td>
<td>$X_{Si}$ 1/4</td>
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</table>

<table>
<thead>
<tr>
<th>Lattice parameters</th>
<th>$R$ factors</th>
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<tbody>
<tr>
<td>$a=702.256 \pm 0.103$ pm</td>
<td>$R_p=3.63%$</td>
</tr>
<tr>
<td>$b=412.104 \pm 0.076$ pm</td>
<td>$R_p=5.04%$</td>
</tr>
<tr>
<td>$c=745.842 \pm 0.079$ pm</td>
<td>$R_p=2.35%$</td>
</tr>
</tbody>
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$\chi^2=0.954$