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Magnetic structure of the heavy-fermion compound U_2Zn_{17}

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The phase transition of U_2Zn_{17} at 9.7 K has been investigated by neutron powder diffraction. The transition corresponds to the onset of antiferromagnetic order where the U moments are oriented antiparallel to their nearest neighbors within the basal planes and the near neighbor along the $\hat{c}$ axis of this rhombohedral compound. At 5 K, the ordered moments lie within the basal planes and are of magnitude $(0.8 \pm 0.1)\mu_B$, which is substantially below the paramagnetic moment of $2.25\mu_B$/U atom given by high-temperature susceptibility data.

The list of "heavy-fermion" systems, which display extraordinarily large ($\gtrsim 400m_e$) effective conduction electron masses as deduced from the low-temperature specific heat, now includes both superconductors and metals remaining paramagnetic to the lowest temperatures.[1] Recent magnetic susceptibility and specific-heat measurements suggest that there are also heavy-fermion systems which undergo transitions to magnetically ordered ground states.[2] In this paper, we present the first neutron-scattering determination of magnetic order in a heavy-fermion system, U_2Zn_{17}. The essential results are as follows. First, the ordering, which sets in at $T_N \simeq 10$ K, is exceedingly simple, with the magnetic unit cell identical to the nuclear unit cell, and the moments associated with the two U atoms in the primitive unit cell oriented in opposite directions. Second, the ordered moment is $(0.8 \pm 0.1)\mu_B$/U atom which is well below the moment of $2.25\mu_B$/U atom deduced from the high-temperature (bulk) susceptibility.

U_2Zn_{17} was made by heating the appropriate amounts of U and Zn to 1050 °C in an evacuated BeO crucible. Approximately 20 g of material were crushed into a coarse powder and loaded into a cylindrical aluminum sample holder in an atmosphere of helium. Data were collected at the Brookhaven High Flux Beam Reactor with 2.353-Å neutrons from a pyrolytic-graphite monochromator in the (002) setting. A pyrolytic-graphite filter suppressed higher-order wavelengths. For the structure determination at 15 K ($> T_N$), a pyrolytic-graphite analyzer in the (004) setting was used in order to optimize the resolution at higher scattering angles. The collimations were 20′-open-40′-20′ for in-pile, monochromator-sample, sample-analyzer, and analyzer-detector, respectively. The resulting diffraction pattern showed a number of weak impurity peaks in addition to those characteristic of U_2Zn_{17}. The major impurity was identified as Zn, estimated to be about 5% by weight. The remaining peaks were an order of magnitude weaker (with intensities $\leq 1\%$ of the strong U_2Zn_{17} peaks) and could not be identified. The d spacings are listed in the caption to Fig. 1, and do not correspond to those of UZn_{12} or α-U.

At room temperature, U_2Zn_{17} (Ref. 3) has the Th_2Zn_{17}-type structure, which is one of a series of ordered structures [e.g., Pu_3Zn_{22},[4] UZn_{12} (Ref. 5)] which can be derived from that of $CaCu_5$.[6] In U_2Zn_{17}, Zn occupies the Cu sites and U is ordered on two-thirds of the Ca sites, the remaining one-third being replaced by pairs of Zn atoms about 2.6 Å apart.[7] The ordered structure has rhombohedral symmetry, space group $R\bar{3}m$, with hexagonal lattice constants $\sqrt{3}a$ and $3c$ with respect to those of the parent $CaCu_5$-type cell. Because the structural parameters for U_2Zn_{17} near its 10-K transition were unknown, we carried out a Rietveld analysis[8] of the data shown in Fig. 1. Regions around the impurity peaks and Al reflections from the sample holder were excluded from the refinement, and background contributions were estimated by interpolation between values obtained by averaging over regions where no Bragg peaks were present. Table I displays the lattice parameters and atomic coordinates given by the profile refinement. In the upper frame of Fig. 1, the solid line represents the calculated profile which best fits the data, while in the lower frame, the difference between the calculated and observed profiles is shown. The results are in excellent agreement with a room-temperature x-ray scattering determination of the structure.[3]

Below 10 K some very weak additional scattering at some of the low-angle nuclear peak positions was observed. To gain more intensity and thus allow adequate counting statistics to be obtained in a reasonable period of time, the

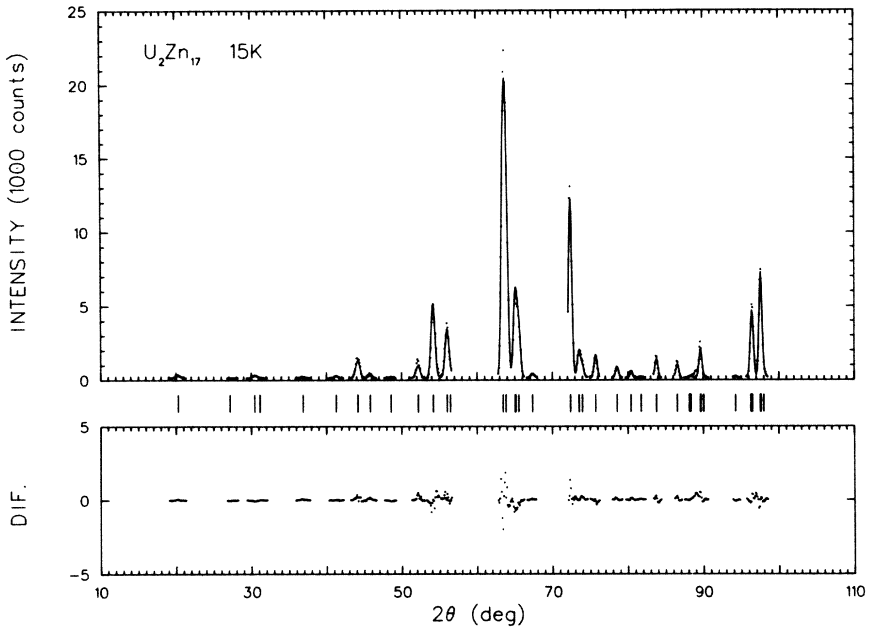

FIG. 1. Profile fit and difference plot for U_2Zn_{17} at 15 K. Short vertical markers represent calculated peak positions. Background is included in the upper plot. Peaks from the Al sample holder, and from impurities of Zn and an unidentified phase (d spacings 5.19, 2.77, 2.27, 1.89, 1.78, 1.74, and 1.62 Å) were excluded from the refinement. The neutron wavelength was 2.353 Å.

analyzer setting was changed to (002) and the collimation relaxed to 40′-80′-40′-40′. Figure 2 shows the low-angle diffraction data for temperatures well above (15 K) and well below (5 K) the peak observed at 10 K in the specific heat for U_2Zn_{17}.[2] The allowed nuclear reflections are labeled by hexagonal indices, with arrows indicating their positions. The important features of the data are (1) that no superlattice peaks appear at low temperature, and (2) that the intensity at some of the nuclear Bragg peak positions increases upon lowering T through T_N. We note that the (012) nuclear reflection is allowed by symmetry, but is accidentally weak. Polarized neutron-scattering measurements on a single crystal of U_2Zn_{17} also demonstrate the magnetic origin of the enhanced Bragg scattering at low temperatures. The inset to Fig. 1 shows the temperature dependence of the magnetic contribution to the peak heights of the (101) and (012) reflections, from which the transition temperature is seen to be about 10 K.

TABLE I. Results of Rietveld refinement of neutron powder data from U_2Zn_{17} at 15 K, space group $R\bar{3}m$ (hexagonal setting), with standard deviations referred to the least significant figure(s) in parentheses. Scattering amplitudes taken as 0.842 and 0.568×10^{-12} cm for U and Zn, respectively (Ref. 9), G is the preferred orientation parameter and R_I, R_{wp}, and R_E are indicators of the goodness of fit (for definitions, see Ref. 8). $a=8.955(9)$ Å, $c=13.124(2)$ Å, $G=0.198(11)$. $R_I=5.38\%$, $R_{wp}=14.82\%$, $R_E=3.08\%$.

	Site	x	y	z	$B(A^2)$
U	6(c)	0	0	0.3338(7)	0.1(3)
Zn(1)	6(c)	0	0	0.1007(8)	1.6(5)
Zn(2)	9(d)	$\frac{1}{2}$	0	$\frac{1}{2}$	0.7(3)
Zn(3)	18(f)	0.2986(6)	0	0	0.2(3)
Zn(4)	18(h)	0.1643(3)	−0.1643	0.4823(4)	−2.2(3)

Because the magnetic scattering occurs only at nuclear peak positions, the magnetic unit cell is the same size as the chemical cell and contains two U atoms in the primitive unit cell at $\pm 00z$, where z is very close to $\frac{1}{3}$ (see Table I). Since ferromagnetism is precluded by the susceptibility data,[2] the two moments must be antiferromagnetically coupled, which leaves only their direction and magnitude to be determined. The latter requires knowledge of the scale factor relating Bragg intensities measured in counts per minute to scattering cross sections expressed in barns; this factor was determined from a refinement of the high-intensity nuclear reflections obtained for $43° < 2\theta < 66°$ performed by using the known scattering lengths of U and Zn, and the structural parameters obtained from the Rietveld analysis of the higher-resolution, 15-K data described above. The subsequent intensity calculations (see Table II) show that the moments have a magnitude of $0.8\pm0.1\mu_B$/U atom and lie in the basal planes. From power diffraction data alone, it is not possible to specify the direction in the planes. The magnetic structure is illustrated in Fig. 3. In addition to antiferromagnetic coupling between near-neighbor c-axis pairs of moments 4.36 Å apart, a given moment is coupled antiferromagnetically to three near neighbors in the basal planes at a distance of 5.16 Å.

While there are many other U compounds which order magnetically,[11] U_2Zn_{17} is unusual because of its low U density (one U atom per 151 Å^3), low T_N, low ordered moment, and large linear term in the specific heat, even as $T\rightarrow 0$. Furthermore, the isostructural diluted alloys $U_2(Zn_{1-x}M_x)_{17}$ do not order magnetically above 1.5 K (Ref. 12) even for the smallest x probed (0.018 for $M=$Cu, 0.01 for $M=$Mn). For comparison, a uranium pnictide with a large lattice constant is USb,[11] where the volume per U atom is 59 Å^3 and each U atom has 12 nearest neighbors at a distance of 4.38 Å. The Néel temperature is 213 K, and the ordered moment is $2.85\mu_B$/U atom, while the effective

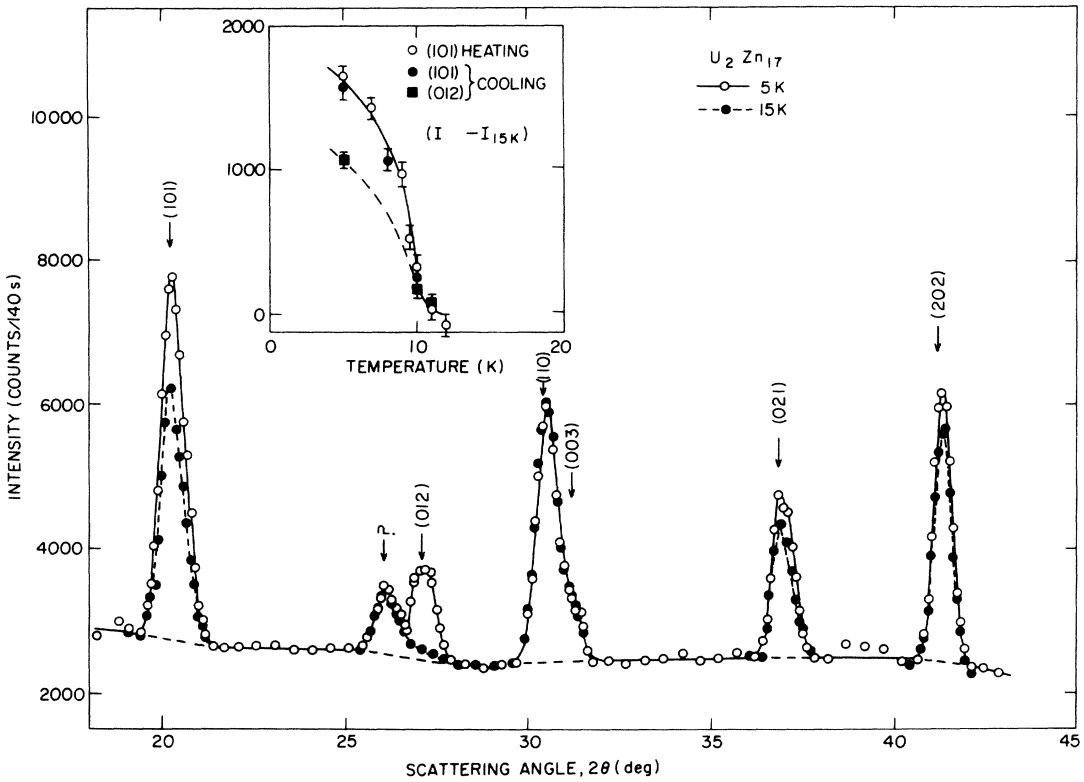

FIG. 2. Intensity data for U_2Zn_{17} at 5 K (open circles) and 15 K (filled circles) in the low-angle region showing the magnetic contribution to the scattering. The small peak at about 26.2° is due to an unidentified impurity. The inset shows the temperature dependence of the magnetic scattering from (101) and (012). The lines are a guide to the eye.

moment from high-temperature susceptibility data is $3.75\mu_B$. Dilution of USb with Te or Th hardly affects the magnetism for $x \lesssim 0.1$ ($USb_{1-x}Te_x$) and $y \lesssim 0.07$ ($U_{1-y}Th_ySb$); indeed, the low-temperature states remain magnetic for all x and for $y \lesssim 0.8$.

For U_2Zn_{17}, the ordered moment $\mu_0 = 0.8\mu_B$ is considerably less than the effective moment $\mu_{\text{eff}} = 2.25\mu_B$ derived from the high-temperature, Curie-type susceptibility, a result which is consistent with the earlier (bulk) observation that large magnetic fluctuations persist at $T \to 0$. In particular, even below T_N, there is a large "electronic" contribution γT to the specific heat, as well as a large Pauli-type susceptibility $\chi_0 = 0.9$ emu/mole U atom. It is amusing to note that $[(\mu_{\text{eff}} - \mu_0)/\mu_{\text{eff}}]^2 = 0.4$, which is the mean square fluctuating moment μ_f^2 normalized to μ_{eff}^2, has the same value as $\gamma(T=0)/\gamma(T=T_N)$. Thus, U_2Zn_{17} behaves as an itinerant antiferromagnet where a gap develops only over a fraction $1-\gamma(T=0)/\gamma(T=T_N)$ of the Fermi surface.[13] It may also be appropriate to compare U_2Zn_{17} to singlet ground-state magnets, where the ordered moment μ_0 is also suppressed relative to μ_{eff}.[14] Such an analogy is particularly attractive because U_2Zn_{17} is suspected to be a dense Kondo system, where the interactions between the conduction electrons and moments localized near the U atoms yield singlet

TABLE II. Observed and calculated nuclear and magnetic integrated intensities from U_2Zn_{17} at 15 and 5 K. Nuclear intensities are based upon the parameters listed in Table I, and magnetic intensities are calculated for the antiferromagnetic structure illustrated in Fig. 3 with moments of $0.79\mu_B$ per U atom lying in the (001) planes. The calculated intensities contain the preferred orientation correction $\exp(G\alpha^2)$ as described in Ref. 8. The magnetic form factor was taken from Ref. 10.

			15 K			5 K	
hkl	$\sin\theta/\lambda$	$\exp(G\alpha^2)$	I_N (obs)	I_N (calc)	I_{N+M} (obs)	I_M (obs)	I_M (calc)
101	0.075	1.24	18.6(2)	14.2	27.7(3)	9.1(4)	9.4
012	0.100	1.10	0.8(3)	2.4	6.8(3)	6.0(4)	5.8
110	0.112	1.63	20.7(3)	21.6	20.7(3)	0.0(4)	0.0
003	0.114	1.00		1.1			0.0
021	0.135	1.39	9.1(2)	2.9	11.4(2)	2.3(3)	2.5
202	0.150	1.24	14.3(2)	11.9	16.9(2)	2.6(3)	2.0

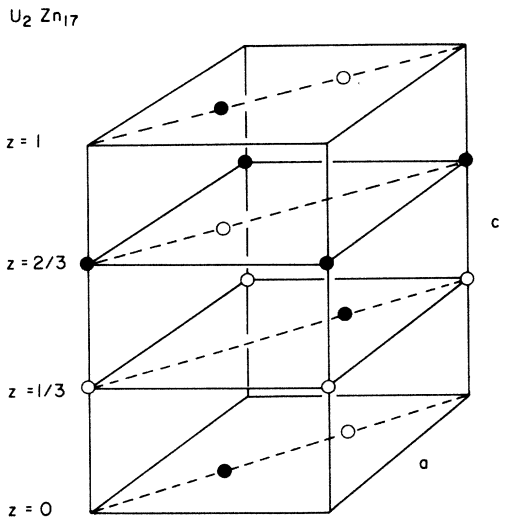

FIG. 3. Magnetic structure of U_2Zn_{17}. Open and filled circles represent oppositely directed moments lying within the basal planes.

ground states for the latter.[15] Both the Kondo singlet-triplet splitting Δ (Ref. 15) and the interaction J between neighboring ions can be large, while if Δ/J is close to unity, T_N is much less than both J and Δ. Similarly, if $\Delta/J \approx 1$, magnetic fields of order Δ and J, rather than of order T_N, are needed to influence T_N.

As far as the high-temperature ($T > T_N$) specific heat[2] is concerned, conventional Schottky anomalies need not be found because Δ is generated dynamically, via interactions with the conduction electrons, rather than being due to fixed crystal-field levels. In conclusion, we caution that while it seems useful to consider U_2Zn_{17} as a collection of single Kondo impurities, there is no doubt that a solution of the lattice problem[16] is required to understand several important properties, notably the sensitivity to impurities and temperature dependence of the resistivity.

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