Magnetic ordering of Ce in the heavy-fermion compound Ce_3Al

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Neutron diffraction and specific heat measurements have been performed to study the magnetic ordering of the Ce ions in the heavy-fermion compound Ce_3Al. Detailed crystal structure analysis, determined using high resolution neutron diffraction patterns and Rietveld method, shows that the Ce ions may be grouped into two types: one in the Ce–Al chain, the other in the Ce–Ce chain. The specific-heat data reveal an anomaly at $T \approx 2.2$ K, but the calculated magnetic entropy is much smaller than the expected $R \ln 2$ if all Ce spins ordered. Low temperature neutron diffraction measurements confirm that the transition at 2.2 K is magnetic and is associated with the ordering of the Ce spins. The magnetic unit cell is double the nuclear one along the a and c axes, and contains 48 Ce ions. Only the Ce ions in the Ce–Al chains participate in the ordering at 2.2 K, and they are coupled antiferromagnetically. © *1998 American Institute of Physics.* [S0021-8979(98)21011-5]

The unusual properties found in heavy-fermion systems continue to generate renewed interest in the f-electron materials. Their physical origin is believed to effectively arise from the strong coupling between the conduction electrons and the fluctuating f-electron moments.[1,2] Among the Ce-based compounds, the family Ce_xAl_y has attracted considerable attention. On the magnetic side, antiferromagnetic order has been observed in CeAl and $CeAl_2$, whereas no ordering was found down to 0.6 K in $CeAl_3$. Previous studies[3,4] have shown that the thermodynamic, magnetic, and transport properties of intermetallic Ce_3Al behaves as a heavy-fermion system. Above 520 K, Ce_3Al crystallizes into the cubic Cu_3Au type of structure (β-Ce_3Al), below which it transforms into the hexagonal Ni_3Sn type of structure (α-Ce_3Al). Another structural transition occurs at 115 K, below which monoclinic (but very close to orthorhombic) symmetry was found (γ-Ce_3Al).[5] A Kondo effect develops below 20 K, and antiferromagnetic ordering is expected at ~ 2.5 K. In this article, we report studies made on the ordering of the Ce spins in γ-Ce_3Al, by using specific heat and neutron diffraction measured at low temperatures. A relatively small value for the magnetic entropy was observed, and only a portion of the Ce spins orders in a simple antiferromagnetic arrangement at $T_N \approx 2.2$ K.

A polycrystalline sample of Ce_3Al was prepared by arc melting high-purity cerium (99.99%) and aluminum (99.9999%) in a helium atmosphere. The arc-melting process was repeated 20 times to obtain a more homogeneous sample. After arc melting, the ingot was sealed in vacuum, followed by annealing at 500 °C for 3 days and then 200 °C for another three weeks to relieve strains and promote conversion from the cubic to hexagonal phase. Ce_3Al is highly ductile, and is quite stable against oxidation. The fabricated sample was characterized using high resolution neutron diffraction and Rietveld analysis,[6] covering a range in temperature from 300 to 12 K. At 300 K, α-Ce_3Al was found with essentially no unexpected peaks present. We estimated the impurity levels to be less than 1%. Below 110 K, both α-Ce_3Al and γ-Ce_3Al were present, with the γ phase gradually becoming dominate with reducing temperature. At 12 K, it shows 92% γ-Ce_3Al phase and 8% α-Ce_3Al phase, with monoclinic lattice parameters $a = 6.8212(6)$ Å, $b = 12.458(1)$ Å, $c = 5.3587(4)$ Å, and the angle between the a and b axes $\gamma = 89.96(1)°$.

The specific heat data were taken on a 9 mg thin specimen employing the time constant technique.[7] Shown in Fig. 1 is the temperature dependence of the specific heat below 25 K. The main feature seen is the peak at $T = 2.2$ K, which is associated with the ordering of the Ce spins (see below).

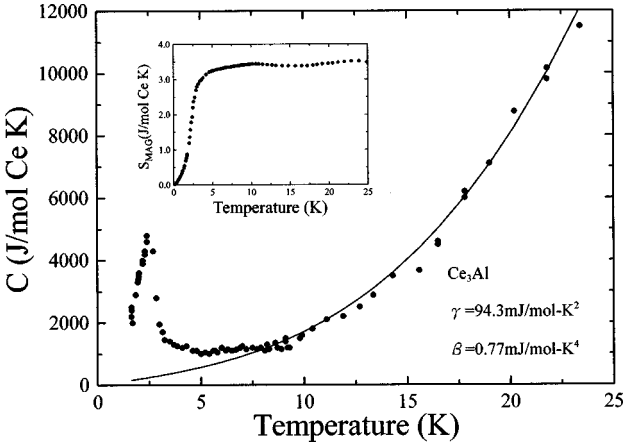

FIG. 1. Temperature dependence of the specific heat. The peak at 2.2 K is associated with the ordering of the Ce spins. The solid curve shows the contributions from phonons and conduction electrons. Shown in the inset is the magnetic entropy calculated from the magnetic specific heat data.

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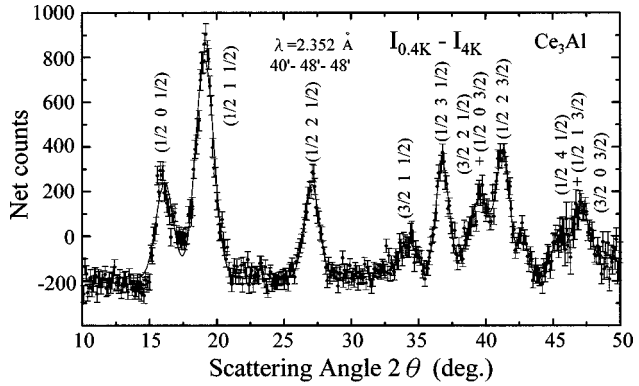

FIG. 2. Magnetic diffraction pattern obtained at $T=0.4$ K, where the indices shown are based on the nuclear unit cell. The solid curves are fits of the peaks to the Gaussian instrumental resolution function.

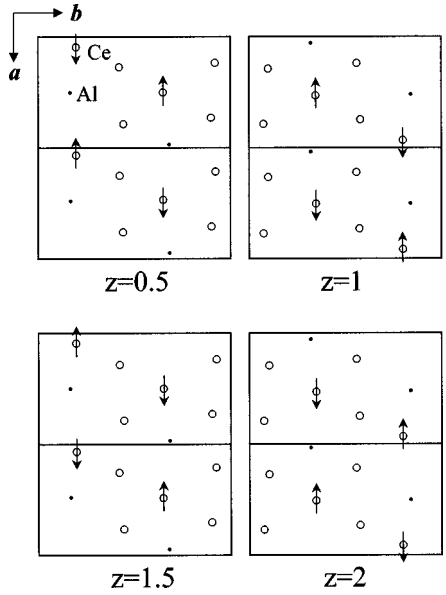

FIG. 3. The proposed spin configuration. Only the Ce in the Ce–Al chains order, with $T_N \approx 2.2$ K.

Above 10 K, the contribution from phonons becomes dominate. The solid curve shown is a fit of the data obtained between $15\,\mathrm{K} \leqslant T \leqslant 40\,\mathrm{K}$ (not shown) to the expression $C(T)=\gamma T+\beta T^3$, with $\gamma=95$ mJ/mol-Ce–K^2 for the contribution from electrons and $\beta=0.77$ mJ/mol-Ce–K^4 from phonons. The value obtained for the linear coefficient γ is about two orders of magnitude larger than that for ordinary metals. It is, however, still smaller than what is usually obtained for heavy-fermion compounds.

The magnetic contribution to the specific heat C_m may be isolated by subtracting the phonon and electron terms discussed above from the observed data. Shown as an inset in Fig. 1 is the magnetic contribution to the entropy, determined by calculating the area beneath the C_m/T versus T curve. We may expect that the low crystal symmetry of monoclinic γ-Ce_3Al should split the $J=5/2$ line for Ce into three doublets. An integrated entropy of $R \ln 2 = 5.76$ J/mol K is then anticipated for the ground state. The observed value, however, is substantially smaller at all temperatures shown. This may indicate only a fraction of the entropy of a doublets is liberated at the magnetic phase transition.

Neutron diffraction experiments were conducted at the US NIST Research Reactor. Data were collected on the BT-9 triple-axis spectrometer operated in double-axis mode without using an analyzer crystal. The incoming neutrons had a wavelength of 2.352 Å defined by a pyrolytic graphite (PG) (002) monochromator, with a PG filter placed in front of the monochromator to suppress higher-order wavelength contaminations. Collimators with horizontal divergences of 40′, 48′, and 48′ full width at half maximum acceptance were used for the in-pile, monochromatic, and diffracted beams, respectively. The samples were mounted in an aluminum can filled with helium exchange gas to facilitate thermal conduction at low temperatures. A pumped ^{3}He cryostat was used to cool the sample, and the lowest temperature achieved was 0.4 K.

Figure 2 shows the magnetic diffraction peaks that develop as the temperature is reduced from 4 to 0.4 K. These data are obtained by subtracting the diffraction pattern taken at 4 K from the one taken at 0.4 K. This magnetic diffraction pattern originates from the Ce spin ordering. The solid curves shown are fits of the data to the Gaussian instrumental resolution function, and the peaks may all be indexed (as shown) based on the monoclinic nuclear unit cell. A half-integer value for the Miller's index means that the length of the magnetic unit cell along the corresponding axis is double that of the nuclear one. The magnetic unit cell is then double the nuclear one along both the *a* and *b* axis directions. It contains 48 Ce ions, since there are 12 in each nuclear unit cell.

The arrangement of the Ce spins can be determined from the relative intensities of the magnetic peaks.[8] Although the structure of the γ phase is complicated, it, however, can be viewed as consisting of slightly tilted Ce–Al and Ce–Ce chains (hence Ce_3Al) along the *a* axis alternately stacked along both the *b* and *c* axis directions, as shown in Fig. 3. Finding the spin arrangement is not a simple matter in the present case, since there are 48 Ce ions in the magnetic unit cell. We tried over 80 models, each with a different spin arrangement, considering essentially all possible arrangements including collinear and noncollinear structures. Starting with the assumption that all Ce spins are ordered, we found two models that could describe the correct *d* spacings for the observed magnetic pattern. However, the spin direction was found to be arbitrary, leading us to believe that the models were not physical. We next tried models assuming either only the Ce in the Ce–Ce chains or those in the Ce–Al chains order. No satisfactory models were found in the former case, while the model in which the Ce spins in the Ce–Al chains are aligned antiparallel with no moments on the Ce in the Ce–Ce chains, was found to describe the observed pattern fairly well. The spin structure of this proposed model is shown in Fig. 3, and comparisons between the observed and calculated intensities are listed in Table I. We note that the goodness of the fit of this proposed model is the best among all models studied. This result of only a portion of the Ce spins participates in the magnetic order at this

TABLE I. Observed and calculated magnetic integrated intensities at 0.4 K. The intensities are normalized with respect to the {1/2 2 1/2} intensity.

Miller index (h k l)	Scattering angle (deg.)		Integrated intensity	
	Observed	Calculated	Observed	Calculated
(1/2 0 1/2)	16.1	15.9	1.18	1.29
(1/2 1 1/2)	19.1	19.3	2.81	2.98
(1/2 2 1/2)	27.1	27.1	1	1
(3/2 1 1/2)	34.1	34.4	0.30	0.27
(1/2 3 1/2)	36.8	36.8	0.96	0.90
(3/2 2 1/2)+(1/2 0 3/2)	39.2	39.5	1.04	0.76
(1/2 2 3/2)	45.4	45.7	1.05	1.19
(3/2 3 1/2)	47.0	46.9	0.19	0.26
(1/2 4 1/2)+(1/2 1 3/2)	47.5	47.5	0.23	0.58

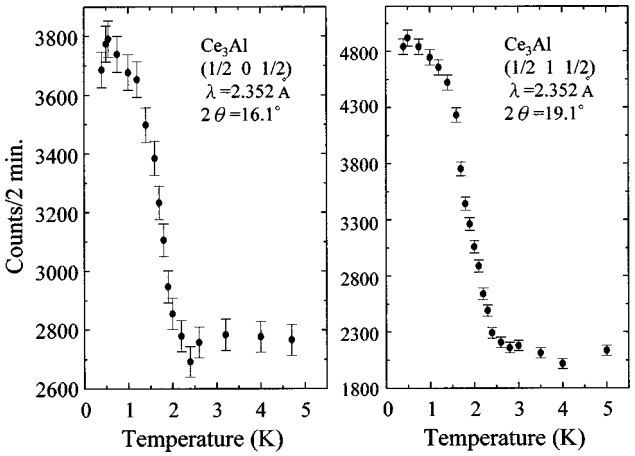

FIG. 4. Temperature dependence of the $\{\frac{1}{2}0\,\frac{1}{2}\}$ and $\{\frac{1}{2}1\,\frac{1}{2}\}$ peak intensities, showing the variation of the square of the staggered magnetization with temperature.

transition is consistent with the conclusion made in a separate study[4] based on specific heat and resistivity measurements. Dividing the rare-earth ions into two sublattices has been suggested for the Ce in CeAl as well, where different magnetizations (magnitude and direction) were proposed for the two sublattices.[9]

The variations of the $\{\frac{1}{2}0\,\frac{1}{2}\}$ and $\{\frac{1}{2}1\,\frac{1}{2}\}$ peak intensities with temperature are shown in Figs. 4(a) and 4(b), respectively. Both plots reveal basically the same temperature dependence, and a typical order-parameter curve for polycrystalline samples. On cooling, the intensity starts to grow around 2.5 K, increasing in the usual way, and reaching saturation around 1 K. The ordering temperature for the Ce spins, as determined by the inflection point of the $\{\frac{1}{2}1\,\frac{1}{2}\}$ curve, is $T_N \approx 2.2$ K. This ordering temperature matches the temperature at which the peak in $C(T)$ occurs. By comparing the $\{\frac{1}{2}2\,\frac{1}{2}\}$ integrated intensity to the {110} nuclear one, we obtained the low temperature saturated moment of $\langle \mu_z \rangle = 1.24(3)\ \mu_B$ for each Ce ions.

In summary, we have performed specific heat and neutron diffraction measurements to study the ordering of the Ce spins in a polycrystalline Ce_3Al. Intermetallic Ce_3Al may be classified as a heavy-fermion system, as its electronic specific heat is much larger than that of ordinary metals. However, the electrons in Ce_3Al are not as heavy as those in other heavy-fermion systems like $CeAl_3$ and UPt_{13}. Below 110 K, Ce_3Al transforms gradually from hexagonal α phase into monoclinic γ phase with reducing temperature. A magnetic transition associated with the ordering of the Ce spins was observed to occur at $T_N \approx 2.2$ K. Only those Ce ions located on the Ce–Al chains participate in this ordering. The coupling is antiferromagnetic in nature, and a simple collinear antiferromagnetic spin arrangement was found. However, the calculated entropy is about 40% smaller than the observed value. We believe that crystalline electric field effect plays an important role in this issue, and inelastic neutron scattering measurements are needed to resolve this point.

ACKNOWLEDGMENT

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[1] G. R. Stewart, Rev. Mod. Phys. **56**, 755 (1984).
[2] P. Fulde, J. Keller, and G. Zwicknagl, *Solid State Physics*, edited by H. Ehrenreich and D. Turnbull (Academic, New York, 1988), Vol. 41, p. 1.
[3] Y. Y. Chen, J. M. Lawrence, J. D. Thompson, and J. O. Willis, Phys. Rev. B **40**, 10 766 (1989).
[4] Y. Y. Chen, Y. D. Yao, B. C. Hu, C. H. Jamg, J. M. Lawrence, H. Huang, and W.-H. Li, Phys. Rev. B **55**, 5937 (1997).
[5] A. C. Lawson, J. M. Lawrence, J. D. Thompson, and A. Williams, Physica B **163**, 587 (1990).
[6] H. M. Rietveld, J. Appl. Crystallogr. **2**, 65 (1969).
[7] G. R. Stewart, Rev. Sci. Instrum. **54**, 1 (1983).
[8] G. E. Bacon, *Neutron Diffraction*, 3rd ed. (Clarendon, Oxford, 1975).
[9] J. M. Lawrence, K. Parvin, and S. M. Shapiro, J. Phys. C **19**, 2021 (1986).