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Coexistence of magnetic order and heavy-fermion paramagnetism in Ce_5Sn_3

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We report resistivity, magnetic, thermodynamic, and neutron-diffraction data for the heavy-fermion compound Ce_5Sn_3. These data indicate an antiferromagnetic phase transition at $T_N = 17.5$ K, but at lower temperatures the linear coefficient of specific heat $\gamma(T) = C(T)/T$ rises to 1.6 J/f.u. mol K^2, characteristic of a moderately-heavy-fermion compound. Only a small amount of entropy is liberated by the phase transition ($\ll R$ ln2), whereas most of the entropy [$(3-4)R$ ln2] is liberated by heavy-fermion processes. This implies a small ordered moment. Further, neutron diffraction implies a rather complicated magnetic order. We discuss two alternatives: (a) that ordering occurs on the Ce site of higher symmetry, while heavy-fermion behavior occurs on the lower-symmetry Ce site; and (b) that itinerant-fermion antiferromagnetism occurs. Due to the overall low site symmetries, crystal-field effects are strong; in particular, the susceptibility is highly anisotropic (by a factor of at least 20 at low temperatures) and enhanced by the presence of strong ferromagnetic correlations in the heavy-fermion state.

INTRODUCTION

In heavy-fermion systems, the low-temperature heavy-mass state develops because of strong electronic correlations that are dominated by the Kondo effect. The ground state of these systems may be paramagnetic, superconducting, or magnetically ordered; but even in the first two cases, experiments suggest proximity to a magnetic instability.[1] Here we present structural, transport, magnetic, and thermodynamic results for Ce_5Sn_3, in which magnetic order and a paramagnetic heavy-mass state coexist. This compound crystallizes in the tetragonal W_5Si_3 [$I4/mcm$ (D_{4h}^{18})] structure,[2] which has two inequivalent cerium sites, Ce(2) (Wyckoff 16k) with C_s (m) symmetry and Ce (1) (Wyckoff 4b) with D_{2d} ($\bar{4}2m$) symmetry. Ce_5Sn_3 is not unique in this regard. For example, the compounds[3] Ce_2Sn_5 and Ce_3Sn_7, which are vacancy-ordered variants of $CeSn_3$, have two inequivalent cerium sites: Ce(1), with the same local environment as Ce in $CeSn_3$, and Ce(2), with very low symmetry. In both cases, the Ce(1) $4f$ electron is nonmagnetic as in $CeSn_3$, whereas antiferromagnetic order occurs on the Ce(2) site and considerable anisotropy is observed in the magnetization. An even more relevant example is Ce_5Si_3, where there are two sites (Wyckoff 4c and 16 l) in the Cr_5B_3 (also $I4/mcm$) structure.[4] In that compound the magnetic behavior is believed to be different on the two sites, with magnetic ordering occurring on the high-symmetry (Wychoff 4c) site and nonmagnetic heavy-fermion behavior on the low-symmetry (Wychoff 16 l) site. We show that the same thing may happen in Ce_5Sn_3, namely, ordering on the higher-symmetry (4b) site and nonmagnetic behavior on the lower-symmetry (16k) site. An alternative possibility is that the ground state is that of an itinerant-heavy-fermion antiferromagnet. Due to the overall low site symmetries, crystal fields play a very strong role; in particular, the susceptibility is extremely anisotropic at low temperatures. Specific-heat data indicate that $4f$ electrons are moderately heavy, and, when compared with the susceptibility, indicate that ferromagnetic correlations are very strong at low temperature. Although we have not solved the low-temperature magnetic structure, preliminary neutron-diffraction data provide some indication about the nature of the order.

EXPERIMENTAL DETAILS

Electrical-resistivity, magnetic-susceptibility, and specific-heat measurements were performed on single crystals grown from a cobalt flux. Because of sample-size requirements, neutron-diffraction data were collected on polycrystalline samples prepared by arc melting and annealing at 500 °C for one week. Neutron diffraction was performed on the high-intensity powder diffractometer (HIPD) at the Manuel Lujan, Jr., Neutron Scattering Center (LANSCE), which has additional forward detector banks that allow diffraction data to be collected to d spacings of 50 Å. No indication of the high-temperature hexagonal Mn_5Si_3 phase[2] was found in x-ray or neutron-diffraction spectra for either the single-crystal or polycrystalline samples. Resistivity was measured using a standard four-probe lock-in technique and the magnetic susceptibility was determined using a SQUID magnetometer with an applied field of 1 T. A thermal-relaxation technique was used in measuring the specific heat.

RESULTS

Structural information obtained from Rietveld refinement with the neutron data is summarized in Table

TABLE I. Lattice constants, site parameters, thermal parameters, and agreement factors for structural refinement of Ce_5Sn_3. Numbers in parentheses following refine parameters represent standard deviations in the last digit(s).

Atom	Wyckoff	Crystal structure: W_5Si_3 ($I4/mcm$; No. 140) Point symmetry	Lattice position $+\frac{1}{2},\frac{1}{2},\frac{1}{2}$
Ce(2)	16k	m	$x,y,0;\bar{x},\bar{y},0;\bar{y},x,0;y,\bar{x},0;x,\bar{y},\frac{1}{2};$ $\bar{x},y,\frac{1}{2};y,x,\frac{1}{2};\bar{y},\bar{x},\frac{1}{2}$
Sn(2)	8h	$mm2$	$z,z+\frac{1}{2},0;\bar{z},\frac{1}{2}-z,0;z+\frac{1}{2},\bar{z},0;$ $\frac{1}{2}-z,z,0;$
Ce(1)	4b	$\bar{4}2m$	$0,\frac{1}{2},\frac{1}{4};\frac{1}{2},0,\frac{1}{4}$
Sn(1)	4a	42	$0,0,\frac{1}{4};0,0,\frac{3}{4}$

T (K)	a_0 (Å)	c_0 (Å)	Ce(2) x	y	Sn(2) z	R_{WP}/R_{exp}
10[a]	12.431(13)	6.1434(6)	0.08550(7)	0.22004(6)	0.15972(5)	0.0324/0.0221
30	12.5349(13)	6.1398(6)	0.08537(6)	0.22017(6)	0.15976(5)	0.0321/0.0221
300	12.5668(20)	6.1676(10)	0.08448(9)	0.219545(8)	0.15991(7)	0.0338/0.0231

Isotropic thermal parameters (10^{-2} Å)

T (K)	Ce(2)	Sn(2)	Ce(1)	Sn(1)
10	0.337(15)	0.229(16)	0.319(27)	0.209(21)
30	0.360(15)	0.292(16)	0.361(27)	0.252(21)
300	0.942(26)	0.735(28)	0.66(4)	0.53(3)

[a]At 10 K additional lines that could not be indexed on the crystallographic cell were observed at $d_1=21.87$ Å and $d_2=8.16$ Å.

I. The good quality of fit to the W_5Si_3-structure type is attested to by the low value of the weighted profile agreement factors R_{WP} and the expected agreement factor R_{exp} $(=\langle\chi^2\rangle^{1/2}R_{WP})$. Although the thermal expansion is small (a few parts in a thousand), the large change in thermal parameters with temperature suggests that the Debye temperature is small. The powder patterns at 10 and 30 K are nearly identical for d spacings less than 5 Å; but, at 10 K, two additional lines, which do not index on the crystallographic cell, are observed at $d_1=21.87$ Å and $d_2=8.16$ Å. Evidence for their origin comes from the resistivity for Ce_5Sn_3, as shown in Fig. 1. The most

FIG. 1. Normalized resistivity of Ce_5Sn_3 and La_5Sn_3 vs temperature for current along the c axis. Note the anomaly near 17 K in the Ce_5Sn_3 resistivity. The resistivity of both samples are comparable ($\sim 125 \mu\Omega$ cm) at 300 K.

notable feature is a kink at 17.5 K in the Ce_5Sn_3 data, which is absent in the resistivity of La_5Sn_3 and indicates that a phase transition is responsible for the extra diffraction lines observed at 10 K.

The susceptibility is shown in Fig. 2. The most striking feature is the strong anisotropy; the susceptibility is small for the magnetic field H parallel the c axis, and large for H perpendicular to the c axis (i.e., in the basal plane). This effect is substantial even at elevated temperature, but becomes even larger at low temperature, where the ratio of susceptibilities in the two directions is nearly 20. The susceptibility χ_c for H parallel to the c axis is sufficiently small at low temperature that it might be dominated by extrinsic effects. Small quantities of impurities could give a susceptibility of this magnitude; and, if there were a slight misalignment of the sample relative to the applied magnetic field, the measured susceptibility would include a contribution from the large basal-plane susceptibility χ_{ab}. If this is so, then the measured anisotropy is a lower bound. Indeed, it is possible that the intrinsic susceptibility has no rise at all at low temperature but is essentially of Van Vleck form.

At high temperatures the perpendicular susceptibility χ_{ab} is Curie-Weiss-like, with $\chi_{ab}(T)=C/(T+\Theta)$, where C is the $J=\frac{5}{2}$ free-ion value 0.807 emu K mol-Ce and $\Theta=-7$ K. At low temperatures χ_{ab} rises to a very large value, but then saturates, taking the form $\chi_{ab}(T)=\chi_{ab}(0)-AT^2$ below 10 K. There is an enhancement of the "effective moment" $T\chi_{ab}(T)$ over its free-ion value C; this enhancement peaks at 10 K, below which $T\chi_{ab}$ approaches zero. Finally, no anomaly in $\chi(T)$ is observed at 17.5 K, where the resistivity indicates the presence of a phase transition.
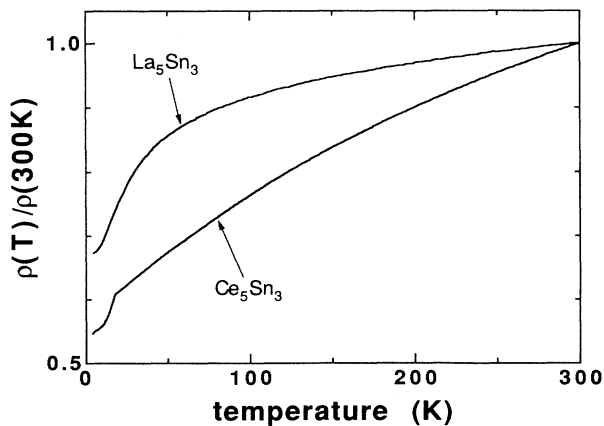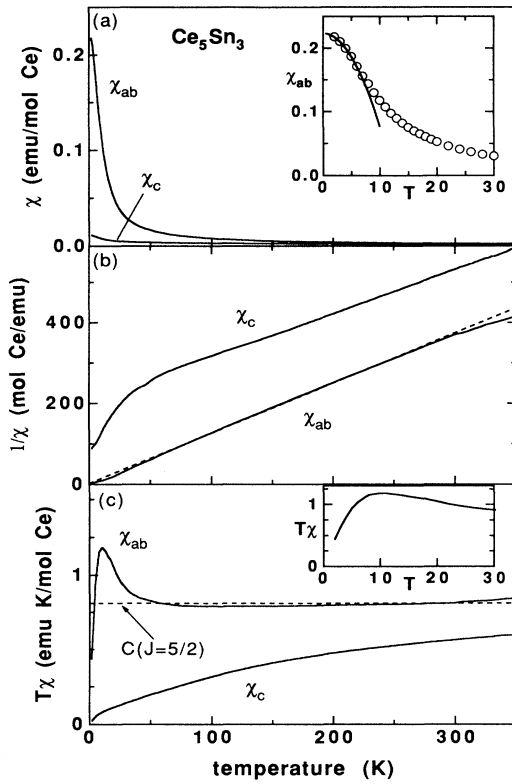
FIG. 2. (a) The susceptibility of Ce_5Sn_3 vs temperature for a magnetic field of 1 T along the c axis (χ_c) and in the basal plane (χ_{ab}). The inset shows the basal-plane susceptibility at low temperature; the solid line is a fit with the form $\chi_{ab} = \chi_{ab}(0)[1-(T/T_*)^2]$, with $T_* = 12.4$ K. (b) Inverse susceptibility for the field applied parallel and perpendicular to the c axis. The dashed line is a fit to $\chi_{ab}(T) = C/(T+\Theta)$, where C is the free-ion Curie constant for $J = \frac{5}{2}$ and $\Theta = -7$ K. (c) The "effective moment" $T\chi(T)$ for the two field directions. The dashed line is the free-ion value for $J = \frac{5}{2}$. The inset shows $T\chi_{ab}$ at low temperatures.
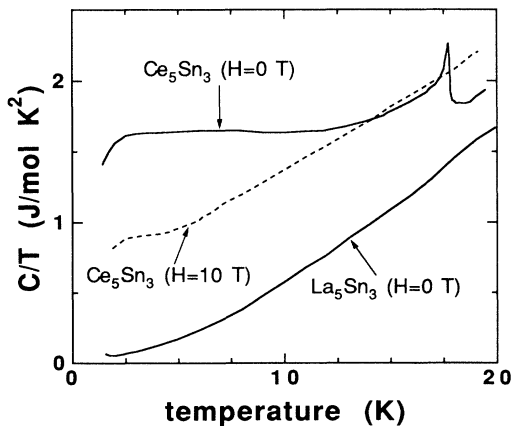

FIG. 3. The specific heat C divided by temperature T vs T for Ce_5Sn_3 in zero magnetic field and a 10-T field, and for La_5Sn_3 in zero field.
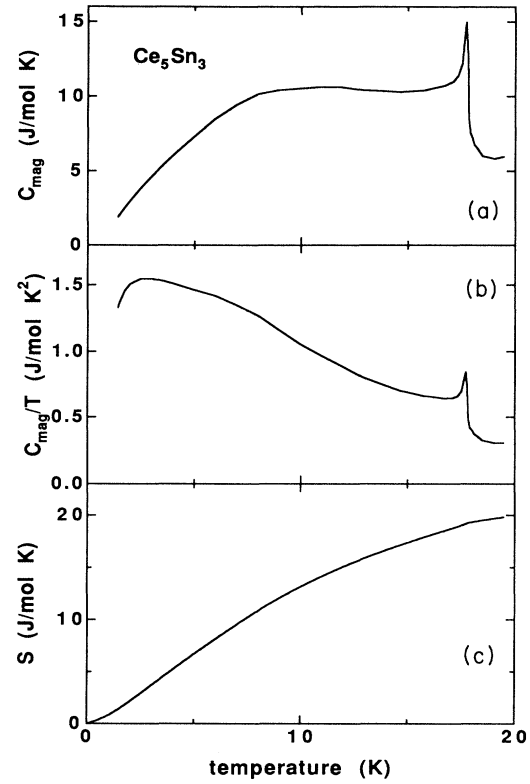

FIG. 4. (a) The magnetic specific heat C_{mag} of Ce_5Sn_3, obtained by subtracting $C(T)$ for La_5Sn_3 from the as-measured $C(T)$ for Ce_5Sn_3. (b) The linear coefficient of the magnetic specific heat as a function of temperature. (c) Temperature evolution of magnetic entropy in Ce_5Sn_3.

In Fig. 3 we show the linear coefficient of the specific heat $[\gamma(T) = C(T)/T]$ of Ce_5Sn_3 in zero and an applied magnetic field of 10 T and compare it to $\gamma(T)$ for La_5Sn_3. The phase transition at 17.5 K is apparent in the zero-field data; the magnetic field strongly suppresses the transition. Below the phase transition, the specific heat saturates to a large value (1.6 J/f.u. mol K^2), indicating heavy-fermion behavior. The magnetic specific heat C_{mag} (obtained by subtracting the specific heat of the nonmagnetic analogue La_5Sn_3) is plotted in Fig. 4. Note that C_{mag} has a broad peak near 10 K, whereas C_{mag}/T peaks near 3 K. Finally, the Debye temperature obtained for La_5Sn_3 is only 142 K, consistent with the large temperature dependence of the neutron thermal parameters mentioned above.

DISCUSSION

We first discuss the phase transition that occurs at 17.5 K. The fact that a magnetic field of 10 T suppresses the specific-heat peak suggests that this is an antiferromagnetic transition. The observation in neutron diffraction of two additional reflections at $d_1 = 21.87$ Å and $d_2 = 8.16$ Å supports this interpretation. Though additional work is needed to determine the spin ordering, we note that

these reflections can be indexed approximately as $d_1 \rightarrow (0,0,\frac{2}{7})$ and $d_2 \rightarrow (1,1\frac{2}{7})$, suggesting a rather complicated ordering; for example, a modulated moment structure, as observed in $CeAl_2$.[5]

One possibility is that the ordering occurs on the high-symmetry Ce(1) site, while the low-symmetry Ce(2) site remains paramagnetic. Support for this comes from the specific-heat data. Under the assumption (discussed further below) that the crystal-field ground state will be a doublet at each site, the total magnetic entropy per formula unit available at low temperature is $5R \ln 2 = 28.8$ J/mol K. The peak in the specific heat at the transition is quite small, and only a small fraction of this entropy is liberated at the phase transition. Estimating this fraction depends on the choice of the background specific heat at the phase transition. A lower limit is given by the area above a smooth extrapolation of C_{mag}/T from above T_N to ~ 12 K, which gives an entropy of 0.53 J/f.u. mol K, less than $0.1R\ln2$. At least 80% of the magnetic entropy $[(3-4)R\ln2]$ is associated with the heavy-fermion contribution, which is generated over the interval 0–20 K. Because the ratio of Ce(2) atoms to Ce(1) atoms is 4:1, it is plausible that ordering occurs on the Ce(1) sites.

The absence of an antiferromagnetic anomaly in the susceptibility can be explained on this basis. Four fifths of the sites do not order, and the susceptibility due to these atoms is (for reasons explained below) anomalously large and rapidly increasing with decreasing temperature. When a small antiferromagnetic peak due to one-fifth of the sites is added to this susceptibility, no net peak is observed. A similar effect is observed[4] in the compound Ce_5Si_3, in which there is only a change in slope in $\chi(T)$ at the antiferromagnetic transition.

The small amount of entropy liberated at T_N, less than the $R\ln2$ expected for the Ce(1) site, suggests that the ordered moment is small. If, contrary to the interpretation given above, the ordering occurs simultaneously on both Ce sites, the ordered moment would have to be even smaller. It is surprising that such a small ordered moment structure has such a high Néel temperature, particularly since there are only a small number of Ce compounds having a Néel temperature greater than 10 K.

An alternative interpretation is that the ground state of Ce_5Sn_3 is an itinerant antiferromagnet. This is consistent with a small ordered moment and with the fact that the specific-heat anomaly [Fig. 4(a)] at T_N has the appearance of a BCS discontinuity. Using values for the specific-heat jump at T_N, $\Delta C = 9$ J/f.u. mol K, and γ $(T \geq T_N) = 0.3$ J/f.u. mol K^2 leads to the ratio $\Delta C/\gamma T_N = 1.7$, close to the BCS (mean-field) value. In this interpretation only a fraction of the heavy-fermion entropy would be removed by the spin-density wave, the remainder by the onset of degeneracy.

We turn next to the heavy-fermion behavior. If we assume that this arises from the four out of five Ce atoms per formula unit residing on the Ce(2) sites, and scale the maximum value of the linear coefficient of specific heat to account for this, we obtain a value of $\gamma = 400$ mJ/K^2 mol-Ce(2)-atom. Assuming a crystal-field doublet on each site, we can use single-ion Kondo theory[6] to estimate the Kondo temperature, $T_K = \pi R/6\gamma$, where R is

the gas constant. This gives $T_K = 10.9$ K. A further prediction is that for a ground-state doublet, a peak in $C(T)$ is expected at $0.9T_K$, i.e., at 9.8 K. A broad peak in $C_{mag}(T)$ centered at 10 K is indeed observed in Fig. 4.

Single-ion Kondo theory predicts that $C(T)/T$ should decrease monotonically with increasing temperature; but in many heavy-fermion compounds, including Ce_5Si_3, a peak is observed in C/T at temperatures small compared to T_K. This is attributed typically to coherence effects.[7] Such a peak is also observed in Ce_5Sn_3 at 3 K (Fig. 4). Another phenomenon observed in other Ce-based heavy-fermion compounds is the sensitivity of the specific heat to applied fields.[8] Application of a 10-T magnetic field decreases C/T by nearly a factor of 2 at low temperatures. In large measure this can be attributed to single-ion effects: when μH becomes comparable to kT_K, as is the case here, the Kondo effect is suppressed. It is interesting that the specific heat is enhanced by the field above the phase transition: In large enough field, the temperature scale for generating entropy is the Zeeman splitting, which is larger than kT_K.

Recently we reported[9] the existence of a large Wilson ratio ($\mathscr{R} \approx 11$) in the compound Ce_3In; we attributed this to ferromagnetic correlations. For Ce_5Sn_3, the point symmetries are too low to allow prediction of the moment of the ground-state doublet; hence, we cannot determine $\mathscr{R}$. Nevertheless, the value of γ for Ce_5Sn_3 is smaller than in Ce_3In (400 mJ/mol K^2 compared with 700), whereas the susceptibility is four times larger (0.22 emu/mol-Ce compared with 0.057). This suggests an even larger Wilson ratio. The importance of ferromagnetic correlations can be observed directly in the plot (Fig. 2) of $T\chi(T)$. The Kondo effect, crystal fields, and antiferromagnetism all work to decrease $T\chi$ from its free-ion value. The large peak observed in $T\chi$ can only arise from ferromagnetic interactions. (It is worth pointing out that as long as the heavy-fermion ground state is nonmagnetic, $T\chi$ must vanish at $T=0$; this holds even in the presence of ferromagnetic correlations. Hence the peak.) A very interesting feature is that the peak occurs at 10 K, i.e., it coincides with the single-ion Kondo temperature. In a sense there is no simple single-ion regime; magnetic correlations, here ferromagnetic, are important at all temperatures.

The low-temperature susceptibility [Fig. 1(a) inset] can be fitted with the form $\chi_{ab} = \chi_{ab}(0)[1-(T/T_*)^2]$, with $T_* = 12.4$ K $\approx T_K$. Such Fermi-liquid behavior is observed in other cerium compounds.[5] For Ce_5Sn_3, it is observed in the temperature range where the susceptibility is strongly enhanced by ferromagnetic correlations, and hence is not simply a single-ion effect.

Finally, we comment on the role of crystal fields. We have already indicated their effect on the specific heat, i.e., they give rise to ground-state doublets in which the heavy-fermion behavior on the Ce(2) sites and ordering on the Ce(1) sites occur. They also give rise to the strong anisotropy in the susceptibility, i.e., the observed easy axis is in the basal plane. Such anisotropy can arise when matrix elements of J_z or $J_{\pm}$ (where the z axis is taken as the local symmetry axis) vanish in the ground-state doublet. For example, when the splitting is $|\pm\frac{5}{2}\rangle$, $|\pm\frac{3}{2}\rangle$, and

$[\pm\frac{1}{2}\rangle$, with $[\pm\frac{5}{2}\rangle$ lowest, then χ_z will be of Zeeman form but χ_x or χ_y will be of Van Vleck form.[10] For the case of Ce_5Sn_3, where the local axis is along the c axis and the easy axis is in the basal plane for both Ce sites, the Zeeman (diagonal) terms for χ_z must be suppressed relative to those for χ_x or χ_y.

The symmetry on the Ce(1) site is D_{2d} ($\bar{4}2m$). This splits the $J=\frac{5}{2}$ sextet into three doublets ($2\Gamma_6+\Gamma_7$).[11] The Stevens operators[12] are O_2^0, O_4^0, and O_4^4; these and the corresponding wave functions $\psi_{1\pm}=|\pm\frac{1}{2}\rangle$, $\psi_{2\pm}=a|\pm\frac{5}{2}\rangle+b|\mp\frac{3}{2}\rangle$, $\psi_{3\pm}=c|\pm\frac{5}{2}\rangle+d|\mp\frac{3}{2}\rangle$ are similar to the cubic case, but group theory places no restrictions on the coefficients. Large anisotropy can arise for special values of the coefficients (e.g., if $\psi_{2\pm}$ is lowest, then the Zeeman matrix elements are $\langle\psi_{2\pm}|J_+|\psi_{2-}\rangle=2\sqrt{5}ab$ and $\langle\psi_{2+}|J_z|\psi_{2+}\rangle=\frac{5}{2}a^2-\frac{3}{2}b^2$). The (16k) site, with four-fifths of the Ce atoms, has C_s (m) symmetry. This is the lowest possible symmetry. The sextet splits into three doublets (each of form $\Gamma_3+\Gamma_4$). A large number of Stevens operators, including odd orders such as O_1^1, are allowed. Each doublet can have components from all m values. Again, group theory places no restrictions on the coefficients, and we can only say that anisotropy will arise for special values of the coefficients.

CONCLUSIONS

The ground state of Ce_5Sn_3 is very unusual: Heavy-fermion behavior develops in the presence of antiferromagnetic order as well as strong ferromagnetic correlations. The ordered state is also not typical of Ce-based Kondo-lattice compounds. The Néel temperature is high relative to most Ce-based antiferromagnets; yet the or-

dered moment is small. Further, the ordering is complex; either small moment ordering occurs only on high-symmetry Ce(1) sites or even smaller moment ordering on all the Ce sites in the form of a possibly modulated structure, such as that found in $CeAl_2$, or as itinerant-fermion antiferromagnetism. The first possibility is analogous to that inferred for Ce_5Si_3, whereas the latter is supported most strongly by the shape and magnitude of the specific-heat anomaly at T_N. None of these interpretations can be ruled out a priori from the data available. It is possible that the crystallographic inequivalence of Ce sites conspires to produce this unconventional behavior. Such speculation might be tested by substituting a nonmagnetic atom that preferentially occupies either all the Ce(1) or all the Ce(2) sites. Certainly, determining the ordered magnetic structure through single-crystal neutron diffraction would be extremely helpful in resolving the questions raised here. Further, the large anisotropy in the magnetic susceptibility implicates the importance of resolving the crystal-field scheme in Ce_5Sn_3, as might be done by inelastic neutron scattering.

ACKNOWLEDGMENTS

[1] Z. Fisk, D. W. Hess, C. J. Pethick, D. Pines, J. L. Smith, J. D. Thompson, and J. O. Willis, Science **239**, 33 (1988).

[2] E. Franchesci, J. Less-Common Met. **66**, 175 (1979).

[3] F. Givord, P. Lejay, E. Ressouche, J. Schweizer, and A. Stunalat, Physica B **156&157**, 805 (1989).

[4] M. Kontani, M. Senda, M. Nakano, J. M. Lawrence, and K. Adachi, J. Magn. Magn. Mater. **70**, 378 (1987).

[5] J. M. Lawrence, P. S. Riseborough, and R. D. Parks, Rep. Prog. Phys. **44**, 1 (1981).

[6] V. T. Rajan, Phys. Rev. Lett. **51**, 308 (1983).

[7] C. D. Bredl, S. Horn, F. Steglich, B. Luthi, and R. M. Martin, Phys. Rev. Lett. **54**, 2537 (1985).

[8] G. R. Stewart, Rev. Mod. Phys. **56**, 755 (1984).

[9] Y.-Y. Chen, J. M. Lawrence, J. D. Thompson, and J. O. Willis, Phys. Rev. B **40**, 10 766 (1989); J. M. Lawrence, Y.-Y. Chen, J. D. Thompson, and J. O. Willis, in *Proceedings of the International Conference on the Physics of Highly Correlated Electron Systems*, edited by J. O. Willis, J. D. Thompson, R. P. Guertin, and J. E. Crow (North-Holland, Amsterdam, 1990), p. 56.

[10] J. W. Rasul and P. Schlottmann, Phys. Rev. B **39**, 3065 (1989).

[11] G. F. Koster, J. O. Dimmock, R. J. Wheeler, and H. Statz, *Properties of the Thirty-Two Point Groups*, (MIT, Cambridge, MA 1963).

[12] M. T. Hutchings, in *Solid State Physics: Advances in Research and Applications*, edited by F. Seitz and D. Turnbull (Academic, New York, 1965), Vol. 17, p. 227.