

Itinerant f -Electron Antiferromagnetism in NpSn_3 †

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We report measurements of the specific heat, Mössbauer effect, and electrical resistivity of NpSn_3 , which identify its weak antiferromagnetism ($T_N=9.5$ K) as arising from itinerant $5f$ electrons. This is the first known verification of itinerant f -electron antiferromagnetism in any system.

The origin of the rich variety of magnetic behavior found in light actinide compounds lies in the rather large spatial extent of the $5f$ wave function relative to that of the $4f$ wave function of rare-earth systems.¹ Thus, depending on the interatomic separation of actinide atoms and their site symmetry, the $5f$ states may either remain localized or broaden into bands by means of direct f - f overlap and/or mixing with states of other angular-momentum character. Considerable evidence exists for local-moment magnetism in many actinide compounds,^{2,3} whereas many actinide paramagnets⁴ and a few ferromagnets^{5,6} exhibit itinerant f -electron character.

In this Letter, we report the identification of itinerant-electron antiferromagnetism (IAF) in NpSn_3 , the first such observation for any f -electron system. In fact, only a few itinerant antiferromagnets, notably Cr and some Cr compounds, are known to exist in d -electron systems. One unique feature of the antiferromagnetism in NpSn_3 is that it is extremely weak, with a Néel temperature T_N of only 9.5 K, whereas all other known IAF systems exhibit Néel temperatures near room temperature and above. The low T_N found for NpSn_3 thus permits examination with unprecedented resolution of the effects of IAF on a number of physical properties. The work reported here consists of measurements of polycrystalline samples of the specific heat (between 2.5 and 30 K), Mössbauer effect (on both the ^{237}Np and ^{119}Sn nuclei), and electrical resistivity (2–300 K).

NpSn_3 crystallizes into the ordered cubic AuCu_3 structure (type Ll_2).⁷ Samples used in this study were prepared both by arc-melting and by isothermal reaction at approximately 600°C for periods up to two weeks. High-purity electrorefined ^{237}Np was used in the sample preparation.⁸ X-ray diffraction patterns showed only the presence of NpSn_3 , although subsequent magnetic susceptibility measurements indicated the possible existence of a small amount of second phase in the arc-melted sample. Physical property meas-

urements made on samples prepared by both techniques indicate, however, that the small second phase does not measurably affect the low-temperature properties of NpSn_3 . The experimental procedures have been discussed elsewhere.⁹

The Mössbauer spectra of NpSn_3 using the 59.5-keV resonance in ^{237}Np were measured at 77 and 4.2 K on a sample prepared by the isothermal reaction method. The data at 4.2 K showed a magnetically split spectrum characteristic of magnetic ordering, with a low hyperfine field $H_{\text{hf}}=0.53$ MOe, in excellent agreement with the $T=0$ value of 0.55 MOe obtained by Gal *et al.*¹⁰ Those authors also measured the temperature dependence of H_{hf} for an arc-melted sample and found an ordering temperature of 9 K. Using the correlation of Dunlap and Lander² between the hyperfine field and the ordered moment, we obtain a very small moment $\mu=0.28\mu_B$ for NpSn_3 . Although the correlation between H_{hf} and μ is rigorously valid only for localized systems, and so may be suspect for the present case, such a small value is nonetheless indicative of the itinerant nature of NpSn_3 .

A weakly temperature-dependent susceptibility indicates that the ordered state is antiferromagnetic.¹¹ This is confirmed by the Mössbauer spectra obtained using the ^{119}Sn resonance in NpSn_3 . Figure 1(b) shows the spectrum at room temperature characterized by a simple electric-quadrupole splitting due to the noncubic site symmetry of the Sn atoms. Figure 1(a) shows the spectrum at 4.2 K. The solid line is the result of an analysis assuming two nonequivalent sites, with magnetic splitting in one and no magnetic splitting in the other. This is typical of what happens in antiferromagnets where some sites may be surrounded by magnetic moments all oriented in the same direction, whereas other sites are surrounded by equal numbers of oppositely directed spins. Such a case has been discussed, for example, in PrSn_3 .¹² In principle, a measurement of the relative areas of the two sites can be used to elucidate the detailed spin structure of

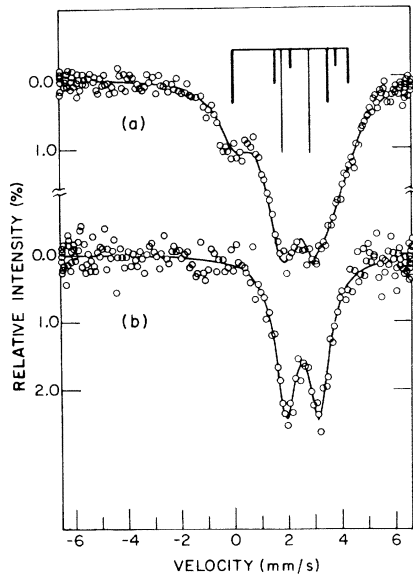


FIG. 1. ^{119}Sn Mössbauer spectra in NpSn_3 at (a) 4.2 K and (b) room temperature. The bar diagram shows the decomposition of the 4.2-K spectrum into two sites, one having magnetic splitting (heavy lines) and one having only quadrupole splitting (light lines).

the system. In this case, however, the small H_{hf} and difficulties related to absorber thickness make such a determination inaccurate.

The specific heat C of NpSn_3 between 2.5 and 30 K is shown in Fig. 2, plotted as C/T vs T . A peak is observed at 9.5 ± 0.1 K, near the value of T_N determined from the temperature dependence of H_{hf} .¹⁰ We have assumed that the phonon specific heat of NpSn_3 , shown as the solid curve in Fig. 2, is equal to that found for isostructural USn_3 .¹³ Molecular weights differing by 0.2% and lattice constants differing by $\approx 0.01\%$ between the two compounds validate this assumption. The difference C_E between C and the phonon contribution is shown in Fig. 3 as C_E/T vs T .

Figure 3 shows that above T_N , $C_E = \gamma_p T$, where γ_p is an unusually large 242 ± 5 mJ/mole $^\circ\text{K}$. This is the largest electronic specific heat coefficient yet observed in an actinide compound and, even acknowledging that γ_p contains enhancements due to electron-phonon and electron-spin-fluctuation interactions, indicates an extremely high density of electronic states at the Fermi level $N(\epsilon_F)$. It is interesting to note that USn_3 , which does not order magnetically, also exhibits a very large low-temperature electronic specific heat coefficient of 170 mJ/mole $^\circ\text{K}^2$.^{13,14}

Below 5 K, C_E is described to within 2% or better by $\gamma_0 T + \alpha T^3$. In this representation, γ_0 is the

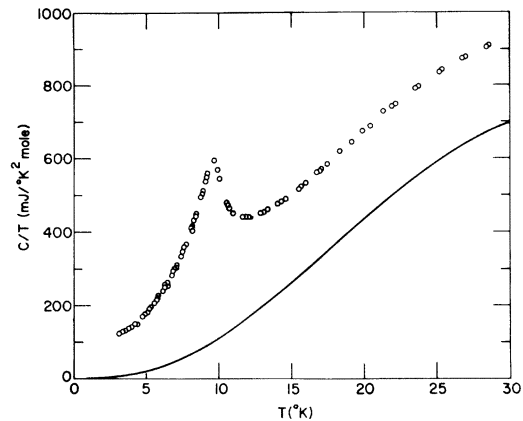


FIG. 2. C/T vs T for NpSn_3 . The solid line represents the phonon contribution, determined from data for isostructural USn_3 .

electronic specific heat coefficient of the magnetically ordered phase and αT^3 is a magnetic contribution, presumably dominated by antiferromagnetic spin waves, which give the T^3 dependence. The low-temperature magnetic part cannot be described by $\exp(-\Delta/T)$ as would be predicted by a mean-field model. The T^3 representation of the magnetic contribution might be a fortuitous consequence of fitting the data over such a small temperature interval (2.5–5.0 K), since a purely spin-wave specific heat is usually observed only at somewhat lower values of T/T_N than could be attained in this experiment. However, this procedure does provide a reliable

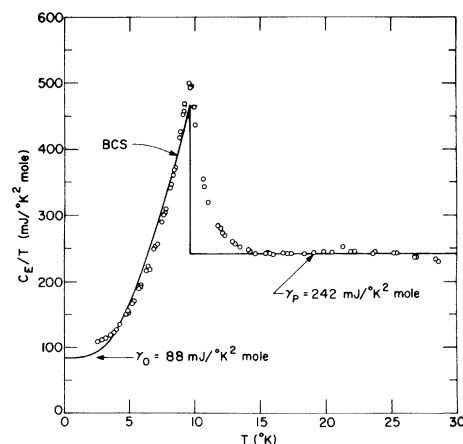


FIG. 3. C_E/T vs T for NpSn_3 where C_E is the electronic specific heat. The solid curve is the mean-field theoretical prediction. The electronic specific heat coefficients of the paramagnetic and ordered states are designated by $\gamma_p = 242$ and $\gamma_0 = 88$ mJ/mole $^\circ\text{K}^2$, respectively.

means of determining γ_0 since $\gamma_0 T \gg \alpha T^3$ at the lowest temperatures. We find $\gamma_0 = 88 \pm 5$ mJ/mole $^\circ\text{K}^2$ and $\alpha = 5.2 \pm 0.3$ mJ/mole $^\circ\text{K}^4$.

The large reduction $\gamma_p - \gamma_0$ in the electronic coefficient at T_N indicates the formation of a gap in the density of states at the Fermi level. This is a requirement of any theory of IAF,¹⁵ but has been difficult to characterize precisely in the specific heats of systems like Cr because of their relatively high T_N and low values of γ_p and γ_0 . The mean-field treatment of the IAF transition in systems for which there is perfect nesting of electron and hole sheets of Fermi surface is mathematically similar to the BCS theory of superconductivity.¹⁶ Within the framework of this model, similar thermodynamic properties are expected for superconductors and itinerant antiferromagnetics.¹⁶ In Fig. 3, the specific heat predicted by the mean-field model is shown. Above T_N we set $C_E = \gamma_p T$; below T_N , C_E is assumed to be composed of a BCS function (determined only by T_N and $\gamma_p - \gamma_0$ with no adjustable parameters) and the $\gamma_0 T$ contribution. The remarkable agreement between experiment and this most simplified theory is strong evidence that the magnetic transition is second-order and itinerant. We note that the comparison between experiment and mean-field theory fails (see Fig. 3) in those temperature regimes where it is expected to fail: at the very lowest temperatures where collective modes are important and just above T_N where C_E exhibits a considerable tail (although some of the tail may be due to sample inhomogeneity). The jump in C_E at T_N is $\Delta C_E(T_N)/(\gamma_p - \gamma_0)T_N = 1.63$, which is quite close to the BCS prediction of 1.43.

Although the above analysis provides a useful physical picture of the magnetism in NpSn₃, it is an oversimplification of the problem. This is illustrated by the relatively large value for γ_0 , which indicates that below T_N there is still appreciable f character at the Fermi level. Thus, only a portion of the Fermi surface is responsible for the antiferromagnetism in NpSn₃. A proper analysis, which considers the complicated nature of the Fermi surface and the importance of hybridization between electrons in f states and in s , p , and d states, requires more knowledge of the NpSn₃ band structure.

The excess entropy associated with the magnetic transition, $\Delta S = \int (C_E - \gamma_p T)(dT/T)$, may be determined graphically from Fig. 3. Using the value of γ_p determined above and assuming that C_E goes to $T=0$ as $\gamma_0 T + \alpha T^3$, we find $\Delta S = -0.047$ J/

mole $^\circ\text{K} = -0.007R \ln 2$. This value differs from zero by an amount equivalent to shifting γ_p by less than 1%; thus, $\Delta S = 0$ to within the accuracy of this measurement. Since a transition involving the ordering of local moments requires $\Delta S \geq R \ln 2$, whereas a second-order itinerant-electron transition must yield $\Delta S \approx 0$, this result confirms the absence of ordered local moments below T_N in NpSn₃.

The electrical resistivity ρ of NpSn₃ was measured on a small slab, electrolytically machined from the arc-melted button used for the specific heat measurements. A maximum is observed in $d\rho/dT$ near T_N , but no evidence of a maximum in $\rho - T$ is observed below T_N as for Cr.¹⁷ However, due to the likelihood of small amounts of second phase being present, these results must be regarded as preliminary. Above 100 K, ρ exhibits strong negative curvature, indicative of sharp structure in the density of states.¹⁸ This results in a saturation of ρ near 175 K and a slow decrease above 175 K. The incremental resistivity, $\Delta\rho = \rho - \rho_0$, where $\rho_0 = 3 \mu\Omega \text{ cm}$ is the residual resistivity, has values of 125 and 115 $\mu\Omega \text{ cm}$ at 175 and 300 K, respectively.

Aldred and Lam have measured the magnetic susceptibility χ , at applied fields from 1–14 KOe, and between 2 and 300 K of a NpSn₃ sample prepared by the isothermal reaction method.¹¹ We have measured χ at applied fields of 3–14.5 KOe on a sample cut from our specific-heat button, and our data corroborate the temperature dependence observed in the earlier investigation, except for a bump we observe near 80–100 K. This bump, which is not reproducible in different arc-melted samples, is attributed to the aforementioned possible second phase.

The susceptibility rises from its value of 2 K to a rounded maximum near 18 K and then decreases slowly with increasing T . There is a maximum in $d\chi/dT$ near T_N , which we associate with the appearance of the gap in $N(\epsilon_F)$. At all temperatures, the magnitude of χ is a factor of 4–5 smaller than that found for exchange-enhanced USn₃.¹⁹ The temperature dependence of χ above T_N is interpreted as arising predominantly from the narrow f -band contribution to the Pauli susceptibility, although a detailed assessment must await more information about the NpSn₃ band structure.

The magnitude of χ just above T_N provides an upper-limit estimate of $N(\epsilon_F)$, since we have no way of accounting for an orbital contribution (expected to be larger than any anticipated negative

diamagnetic term) or other magnetic enhancements. Since $\gamma_p = \frac{2}{3}\pi^2 k_B^2 (1 + \lambda) N(\epsilon_F)$, where λ is a many-body enhancement containing electron-phonon and presumably spin-fluctuation contributions, a comparison of χ and γ_p gives a lower-limit estimate of λ . We find $\lambda \geq 0.6$.

It is unlikely that NpSn₃ is the only IAF system among light actinide intermetallics. Magnetic measurements on the cubic Laves-phase compound^{16,20} NpIr₂ indicate a very small ordered moment below the Néel temperature of ≈ 6 K; and our preliminary specific heat measurements on NpIr₂ suggest a number of properties similar to those of NpSn₃. More direct investigations of the nature of the spin densities in these systems, by methods such as neutron scattering, require the preparation of good single crystals. Such efforts are presently underway.

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