Localized Properties of the Itinerant 5f-Electron Antiferromagnet NpSn$_3$

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Electronic properties of the itinerant-electron antiferromagnet NpSn$_3$ were studied by ^{237}Np Mössbauer spectroscopy under pressures up to ~6.2 GPa. These measurements revealed totally unexpected results: With reduced volume the hyperfine field changes very slightly, but the Néel temperature increases strongly. Such a behavior is typical for localized 5f electrons. We propose that NpSn$_3$ should be viewed as a concentrated Kondo system, similar to CeAl$_2$.

The large variety of magnetic and structural properties of the actinides (A) and their intermetallic compounds is a consequence of the unique characteristics of the 5f electrons. Because of their relatively wide radial extent delocalization processes may occur which produce itinerant (bandlike) character, as is typical for many 3d magnets, rather than the localized behavior which one would expect if they were rare-earth-like (i.e., 4f).[1,2]

Recently, it has been argued[3,4] that the anisotropic character of f-electron hybridization found in some actinide and Ce materials may contribute significantly to their anisotropic magnetic properties observed in resistivity and susceptibility measurements.[4]

Most puzzling are the cubic AX_3 intermetallic compounds which crystallize in the cubic AuCu$_3$ structure. Their A-A separations are over 4 Å and by Hill criterion[5] all of these intermetallics should order magnetically at low temperatures. Experimentally this is found not to be true in most of the cases. This explicitly indicates the importance of 5f-electron hybridization with ligand electrons. Of special interest are the NpX$_3$ (X =Al, Ge, Rh, Pd, and Sn) intermetallics, for which Mössbauer data indicate drastic changes of the s-electron density at the Np nucleus via the broad variation of their isomer shifts and their magnetic properties as well.[6]

The present Letter focuses on NpSn$_3$ which, on the basis of specific-heat data[7] and Mössbauer spectroscopy at low temperatures,[8] has been assigned as a model itinerant-electron antiferromagnet.[9-11] The paramagnetic electronic specific-heat coefficient was determined to be γ =242 mJ/mol K^2.[8] The high sensitivity of 5f-electron hybridization to the interatomic separation makes the Mössbauer high-pressure technique a unique tool to investigate details of the electronic structure properties.[12,13] The present contribution reports on high-pressure Mössbauer-effect and x-ray compressibility measurements. Surprisingly, despite the arguments mentioned above for itinerant properties in this compound, our high-pressure data indicate localized behavior, which will be discussed in terms of a Kondo mechanism,[14] together with orbitally driven anisotropic hybridization.[4]

The Mössbauer experiments on NpSn$_3$ under pressures up to 6.2 GPa in the temperature range between 1.5 and 100 K were carried out by using the 60-keV resonance in ^{237}Np. Details of the high-pressure, variable-temperature Mössbauer spectrometer are described elsewhere.[15] The system uses a clamp device which allows the application of quasihydrostatic pressures up to 10 GPa. The pressure-dependent Néel temperature was determined via the Mössbauer thermal-scan method.[15] The absorber thickness was 75 mg/cm^2 of ^{237}Np, and the source 250 mCi of ^{241}Am in metallic form. Compressibility data were obtained by x rays using the high-pressure Guinier-type diffractometer described in Ref. 16.

The NpSn$_3$ sample was prepared by the arc-melting in dry argon atmosphere of stoichiometric amounts of the desired composition. The sample was checked by x-ray and zero-pressure Mössbauer spectroscopy. We found that some additional impurities were always present which most probably consist of Np$_3$Sn together with some free β-Sn. A similar observation of precipitation of β-Sn was previously reported for the isostructural rare-earth systems RSn$_3$.[17] Also, the earlier studies of NpSn$_3$ (Refs. 7 and 8) showed a second phase. These impurity phases were taken into account in the analysis of our Mössbauer hyperfine spectra, but do not directly affect the results reported.

Figure 1 displays Mössbauer spectra of NpSn$_3$ for a complete pressure cycle. The data were fitted with a

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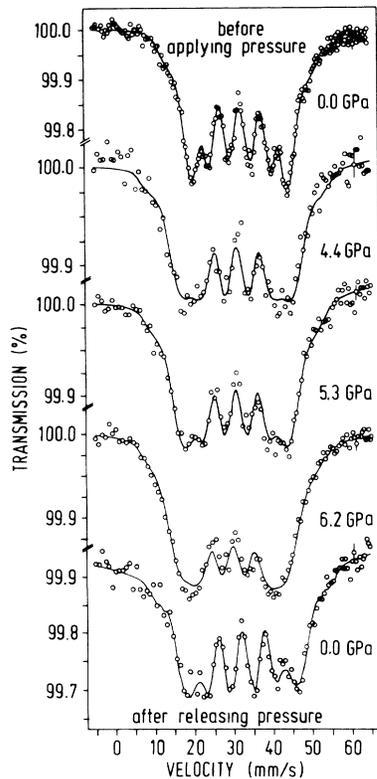
FIG. 1. ^{237}Np Mössbauer absorption spectra of NpSn$_3$ recorded at 4.2 K and various pressures.

FIG. 2. Pressure dependence of the magnetic hyperfine field B_{hf}, of the isomer shift S, and of the Néel temperature T_N.

pure magnetic hyperfine interaction (solid lines in Fig. 1). At zero pressure we find $B_{hf} \sim 70$ T corresponding to an ordered moment at Np of $\sim 0.3\mu_B$. This is in agreement with earlier data.[8] Raising the temperature above T_N gives a single resonance line.

The following behavior is observed.

(a) The magnetic hyperfine field B_{hf} changes only slightly when the volume of the unit cell is reduced [Fig. 2(a)].

(b) The resonance lines broadened out under pressure (see Fig. 1). This broadening does not vanish altogether when pressure is released. If the resulting spectrum (Fig. 1, bottom) is analyzed as a pure magnetic interaction, a slightly different value of B_{hf} results compared to that before applying pressure. A similar line broadening is observed for the single-line resonance above T_N. This shows that the effect is not truly of magnetic nature, but rather due to additional unresolved quadrupole interactions, and the change of B_{hf} is an artifact of the fitting procedure.

(c) The pressure dependence of the isomer shift S [Fig. 2(b)] was derived from the Mössbauer spectra above T_N. The observed isomer-shift difference between ambient pressure and 6.2 GPa corresponds to an increase of the s-electron density at the Np nucleus. The change of S is completely reversible. This allows the conclusion that the irreversible effects mentioned above do not prin-

cipally affect the electronic structure of NpSn$_3$ and hence need not be considered in the later discussion.

(d) A drastic increase of the Néel temperature T_N by about 9 K is seen when pressure is increased to 6.2 GPa [Fig. 2(c)]. The magnetic transition is very sharply defined at all pressures. After releasing the pressure, T_N remains slightly higher ($T_N = 11 \pm 1$ K).

(e) Mössbauer spectra obtained earlier with the 23-keV resonance in ^{119}Sn at 4.2 K and ambient pressure reveal the presence of magnetic and nonmagnetic Sn sites as expected for a type-I antiferromagnet of the AuCu$_3$ structure.[8] Preliminary experiments at 4.4 GPa and 4.2 and 70 K show that the Sn spectra remain practically unchanged; i.e., the magnetic structure is unaffected by external pressure.

The volume coefficients of the ^{237}Np hyperfine parameters found in the present study are summarized in Table I and compared to similar data found in other Np intermetallics.[12,13] The volume changes are deduced from the x-ray compressibility data. As can be seen from Table I the volume coefficients show trends like those of DyAl$_2$ and NpCo$_2$Si$_2$ which are highly localized f-electron magnets. They certainly differ considerably from those of NpOs$_2$ which is a typical itinerant-electron ferromagnet. This localized-electron behavior of NpSn$_3$ is further corroborated when calculating $L = |\partial \ln B_{hf}/ \partial \ln T_{ord}|$. For localized magnets this ratio should be

TABLE I. Volume coefficients of the magnetic transition temperature (T_{ord}), the ordered magnetic moment μ at Np (or Dy), and the electronic charge density at the Np (or Dy) nucleus $[\rho(0)]$. The Np-Np separation d_{Np-Np} is also given.

Compound	$10^4\dfrac{d\ln T_{ord}}{-d\ln V}$	$10^4\dfrac{d\ln\mu}{-d\ln V}$	$10^4\dfrac{d\ln\rho(0)}{-d\ln V}$	d_{Np-Np} (Å)
DyAl$_2$	+5.3	+0.1	+5.6	$\cdots$
NpCo$_2$Si$_2$	+7.0	+0.2	$\sim +5$	3.90
NpAs	−1.3	−0.8	+4.2	4.07
NpAl$_2$	−16.0	−4.0	+5.0	3.37
NpOs$_2$	−80.0	−46.0	+12.5	3.28
NpSn$_3$	+8.0	$\le +1.0$	+2.0	4.62

$\ll 1$.[18] For NpSn$_3$ we get $L \sim 0.2$. Although this value is considerably larger than those for NpCo$_2$Si$_2$ $(L \sim 0.02)$ and DyAl$_2$ $(L \sim 0.07)$, it still is well below unity. Another characteristic feature is the correlation between the increase of T_N and the change in S. In terms of the rigid-spin model of Ruderman, Kittel, and Arrott[19] a linear correlation $\Delta(\sqrt{T_N}) = C\Delta S$ is predicted for highly localized f systems (e.g., rare earths). Such a correlation, which has previously been observed for NpCo$_2$Si$_2$ with $C = 0.25$,[20] is found again for NpSn$_3$ (Fig. 3) with a similar value of $C \sim 0.4$. In summary, we are forced on the basis of our high-pressure data to conclude that NpSn$_3$ behaves like a localized $5f$ magnet. In contrast, as stated earlier, specific-heat data reveal a very small change in entropy $(\Delta S_M \approx 0)$,[7,8] which strongly points to highly itinerant $5f$ electrons. Also band-structure calculations[11] characterize NpSn$_3$ as an itinerant-electron magnet, due to the formation of a (although narrow) $5f$ band.

The problem is to reconcile the rather low magnetic moment and the tiny entropy change with the localized response under high pressure. The first two properties closely resemble those of CeAl$_2$.[14] There, the explanation was based on invoking the Kondo effect. We suggest that the same mechanism is responsible for the small moment in NpSn$_3$. In addition, for concentrated Kondo systems like CeAl$_2$ a recent paper[4] discusses the effect of orbitally driven anisotropic hybridization of the f electrons with conduction electrons.[3,4] The anisotropic part of the mixing interaction causes a substructure within the rather narrow f band,[4] which leads to crystal-field effects even in highly itinerant-electron systems, and rather localized moments may develop. On account of this crystal-field dressing[3] the $5f$ electrons in NpSn$_3$ behave as localized.

We first discuss the value of the magnetic moment in terms of a conventional crystalline-electric-field (CEF) picture. Within the systematics of the Mössbauer isomer shifts of Np intermetallics, NpSn$_3$ is shifted by $+20$ mm/sec relative to NpAl$_2$. This would suggest a
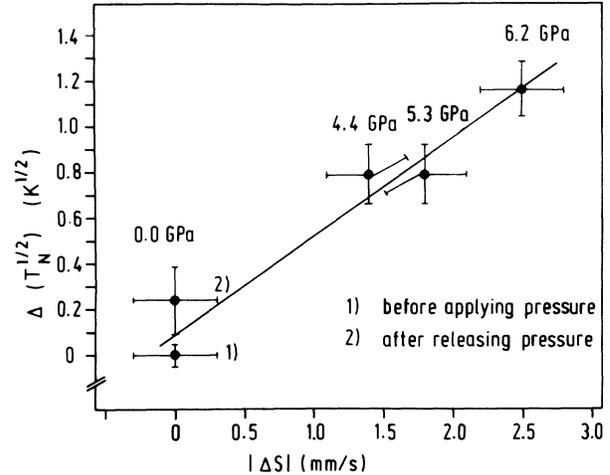
FIG. 3. Change of $\sqrt{T_N}$ vs the change in isomer shift at various pressures. The solid line is a fit according to the rigid-spin model.

$Np^{3+}(5f^4)$ non-Kramers ion with a $^5I_4$ Hund's rule ground state. In a cubic CEF the $^5I_4$ state splits into a singlet Γ_1, a non-Kramers doublet Γ_3, and two triplets Γ_4 and Γ_5.[9] The calculated ordered moments for these levels are $0.8\mu_B$ and $1.5\mu_B$ for Γ_4 and Γ_5, respectively. Smaller ordered moments may arise for a singlet ground state (Γ_1) with an exchange-induced moment caused by off-diagonal matrix elements between Γ_1 and Γ_4 CEF levels.[21,22] Within a molecular-field approximation and using an appropriate exchange field we find that a stable minimum in the free energy can only be obtained for induced moments larger than $\sim 0.8\mu_B$. Whether these ordered moments can still be reduced in a realistic crystal-field-dressing model remains an open question. We conclude that the ordered moments calculated by conventional CEF interactions are much too large when compared to $0.3\mu_B$ observed in NpSn$_3$.

For explaining our experimental results we therefore invoke the Kondo effect. This implies that the moment originating from Γ_4 and Γ_5 CEF levels is partially quenched by the conduction electrons in the whole pressure range investigated. A similar explanation has been proposed by Barbara et al.[14] for CeAl$_2$ at ambient pressure. CeAl$_2$ is a well established concentrated Kondo system and a reduction of the ordered moment was recorded in a neutron-diffraction experiment.[14]

Our interpretation is further supported by preliminary dc-magnetization studies. The temperature-dependent susceptibility of NpSn$_3$ above T_N closely resembles that predicted by an oversimplified theoretical model of a Kondo lattice, as, e.g., shown in Fig. 2 of Ref. 23.

In summary, our study reveals a substantial increase of T_N under reduced volume while the moment remains fairly constant, a behavior typical for localized f systems. The moment on the Np ion in the ordered state of

NpSn₃ is very small. We view the compound as a partially magnetic concentrated Kondo-lattice system with medium heavy-fermion properties. Our Letter shows that $NpSn_3$ possesses novel, hitherto unknown properties which call for careful studies by other methods, in particular by neutron scattering.

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