Local and Bulk Susceptibilities of Np Intermetallics in Their Paramagnetic State

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Mössbauer-effect investigations under applied magnetic field and magnetization studies of neptunium intermetallics in their paramagnetic state are reported. It is shown that the bulk and local susceptibilities at 4.2 K (χ_B and χ_L, respectively) agree even for highly hybridized $5f$-electron systems. The results indicate dominant orbital contributions to the magnetic moment also for paramagnetic neptunium heavy-fermion compounds. For these Np systems proportionalities between χ_L, χ_B, density of states at the Fermi energy, and the isomer shift are pointed out.

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Because of the large spatial distribution of the electrons in the open $5f$ shell, hybridization with nearest-neighbor ligand orbitals may lead in certain actinide intermetallics to a suppression of the ordered moments and a decrease of the ordering temperatures, as observed by applying high pressures.[1,2] Delocalization of the $5f$ electrons together with narrow-band formation close to the Fermi surface introduces a complex situation in which enhanced electronic and magnetic properties may develop.

Enhanced electronic specific heats $\tau(T)$ and enhanced susceptibilities $\chi(T)$ is some Np intermetallics have recently been reported,[3] leading to their classification as heavy-fermion systems (HFS).

Superconductivity and the coexistence of magnetic and superconducting states have been observed for uranium HFS.[3] Up to now, evidence for superconductivity in Np HFS has not been reported. In turn, some of the Np HFS may be stabilized in either a magnetically ordered state or a paramagnetic state, depending on the specific stoichiometry and on the annealing history.[4] The paramagnetic state seems to be less stable than the magnetic one. This instability recalls the instability of the superconducting state in some uranium heavy-fermion systems.[5] Of special interest are those Np intermetallics whose Mössbauer absorption spectra indicate fast spin fluctuations (fast-relaxation limit). In this case, in the paramagnetic state a single absorption line is observed, whereas a magnetically split Zeeman pattern is associated with the presence of magnetic order.[6] In the magnetically ordered state, the splitting is proportional to the value of the ordered moment of the Mössbauer atom. As shown by Lander and Dunlap (LD) there exists a relation between the ordered moment as determined from the neutron data and the magnetic hyperfine splitting.[7] Within the experimental accuracy no exceptions are known to date. However, the LD relation deserves a theoretical explanation. We have applied this empirical relation to magnetic hyperfine fields measured under external magnetic fields for Np compounds in their paramagnetic state, at liquid-He temperature. This external field causes polarization of the electronic spin distribution. Using the LD relation a local susceptibility $\chi_L(T)$ can be derived.

In the present paper we report on measurements of the local and bulk magnetic susceptibilities of all those Np intermetallic compounds known to remain paramagnetic down to 1.8 K, including some Np HFS stabilized in their paramagnetic state. Our results show that the local and bulk susceptibilities are the same. In addition, for the Np heavy-electron compounds in their paramagnetic state, new proportionalities between thermodynamical and hyperfine parameters are demonstrated.

Mössbauer experiments utilizing the 60-keV ($E1$) transition of ^{237}Np were performed in fields up to 6 T parallel to the direction of observation of the γ rays. As a source we used ^{241}Am metal. The bulk-susceptibility measurements were carried out in a balance and a vibrating-sample magnetometers.

The intermetallic compounds were prepared by arc melting of the stoichiometric amounts of the desired composition. The samples were checked by x-ray (Guinier transmission technique) and Mössbauer analysis, confirming a single phase. Some of the crystallographic and magnetic properties of the presently reported compounds were discussed in recent publications.[4,8] We were able to stabilize $NpIr_2$ and $NpBe_{13}$ in their paramagnetic states down to 1.8 K by variation of the Ir and Be contents of the compounds. They should be assigned as $NpIr_{2\pm x}$ and $NpBe_{13\pm x}$. These compounds are normally ordered magnetically below $T_N = 6.5$ and 4.9 K, respectively. Mössbauer-effect investigations of these stable paramagnetic samples confirmed either a single absorption line or a purely quadrupole-split spec-

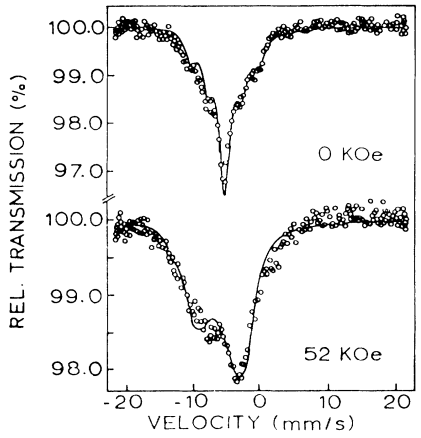

FIG. 1. Mössbauer studies with and without external magnetic field of $NpRu_{2.0}$ at 4.2 K. The solid lines represent theoretical least-squares fits taking into account the direction of observation of the γ rays, which was parallel to the magnetic field.

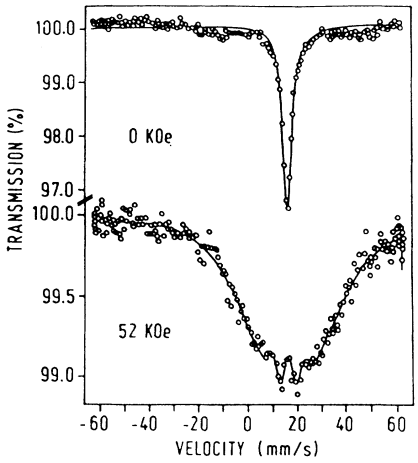

FIG. 2. Mössbauer absorption spectra with and without external magnetic field, at 4.2 K, of $NpBe_{13+x}$ ($x \simeq 2$) stabilized in the paramagnetic state.

trum at low temperatures (Figs. 1 and 2, top).

Typical Mössbauer spectra are depicted in Fig. 1 ($NpRu_{2.0}$) and Fig. 2 ($NpBe_{13+x}$). The main results are summarized in Table I. All the compounds given in Table I show an unbroadened single absorption Mössbauer resonance down to 1.8 K. By application of external magnetic fields significant broadening is observed. In $NpRu_{2.0}$ quadrupole splitting is dominant. For $NpIr_{2.0}$ and $NpBe_{13\pm x}$ Zeeman patterns together with a distribution of hyperfine fields can be recognized. This is demonstrated, for example, in Fig. 2. The derived values of $B_{hf}/B = (B_{eff} - B)/B$ (see discussion) for an external field of $B = 5.2$ T are summarized in Table I.

The paramagnetic state was also confirmed by the behavior of the magnetization: The reciprocal susceptibilities indicate Curie-Weiss behavior with no sign of magnetic transitions down to 4.2 K. The presently derived effective paramagnetic moments μ_{eff} and the values of the bulk susceptibilities χ_B(4.2 K) are also given in Table I. An exception is $NpGe_3$ which shows temperature-independent paramagnetism (TIP) with an almost constant $\chi(T)$ of 1×10^{-3} emu/mole from RT down to 4.2 K. The results of the bulk measurements confirm our conclusions from the Mössbauer studies, namely that all the investigated compounds were definitely in the paramagnetic state.

Generally, in paramagnetic metallic materials the application of an external magnetic field produces polarization of the electronic spin distribution which induces an effective magnetic field at the nucleus. In the actinide intermetallic compounds the $5f$ electrons often have itinerant character where hybridization of the wave functions takes place. This has been confirmed by the general systematics of the Mössbauer isomer shifts (IS) and

TABLE I. Magnetic bulk and hyperfine properties of the paramagnetic Np compounds. The full width at half maximum (FWHM), the local susceptibility χ_L, and the bulk susceptibility χ_B are given at 4.2 K. The errors for χ_L and χ_B are given in Fig. 3. P denotes Weiss-Curie paramagnetic behavior and TIP the temperature-independent paramagnetism.

Paramagnetic Np compounds	Γ_0 FWHM (mm/s)	B_{hf}/B	χ_L (10^{-3} emu/mole)	χ_B (10^{-3} emu/mole)	μ_{eff} (μ_B)	Type
$NpGe_3$	2.5(1)	0.26	0.7	1.0		TIP
NpH_2	4.4(1)	0.47	1.2	?	?	?
$NpRh_3$	2.1(1)	1.27	3.3	3.4	3.56	P
$NpRu_2$	2.6(1)	3.0	7.8	8.0	2.6	P
NpO_2[a]	3.0	3.4	8.8	8.5	2.6	P
$NpIr_2$	2.1(1)	6.73	17.4	16.0	3.1	P
$NpBe_{15}$	3.3(1)	13.8	36.0	42.0	2.7	P

[a]Derived from Friedt, Litterst, and Rebizant (Ref. 9).

the Mössbauer studies of IS and magnetic hyperfine fields under applied high pressure.[1,2] The angular momentum J is thus not a good quantum number, and the validity of the effective-field approximation has always been questionable. For highly localized (rigid) spins mean-field theory predicts a linear correlation between the Weiss sublattice magnetization $M(T)$ and $\langle J_z\rangle$, leading to $\langle J_z\rangle \propto M(T)$. Since in the effective-field approximation $\langle J_z\rangle \propto B_{\rm hf}$, one would expect $B_{\rm hf} \propto M(T)$. Within a localized picture, mean-field theory predicts the same temperature behavior of $B_{\rm hf}$ and $M(T)$, and the proportionalities $\mu_{\rm ord}(T) \propto M(T) \propto B_{\rm hf}(T)$ should hold. By applying an external field B an effective hyperfine field $B_{\rm eff} = B_{\rm hf} + B$ is generated at the ^{237}Np nucleus.[10] Similar to the definition of the bulk susceptibility we define χ_L to be the local susceptibility,

$$\chi_L(T) = CB_{\rm hf}/B\,. \tag{1}$$

Using the LD relation $B_{\rm hf} = [(215\ {\rm T})/\mu_B]\mu_{\rm ord}$,[7] the local susceptibility can be expressed in electromagnetic units:

$$\chi_L = (2.59\times 10^{-3} B_{\rm hf}/B)\ {\rm emu/mole}\,. \tag{2}$$

The low-temperature susceptibilities $\chi_L(4.2\ {\rm K})$ and $\chi_B(4.2\ {\rm K})$ are shown in Fig. 3. A close agreement between χ_B and χ_L is observed. Such an agreement has already been found previously for the nonmetallic paramagnet NpO_2.[8] Our data on the intermetallics confirm, within the experimental accuracy, the validity of the LD relation for small induced hyperfine fields. By assuming that the LD relation originates from localized $5f$ electrons, our results point to the presence of a strong orbital component also in highly hybridized $5f$-electron systems.

$NpBe_{13\pm x}$ and $NpIr_{2\pm x}$ in their paramagnetic state have been previously assigned as heavy-fermion systems.[4,5] At high temperatures the HFS exhibit Curie-Weiss susceptibility, which flattens out at low temperatures and is severely enhanced towards a value $\chi(0)$ as $T \to 0$ [like $\tau(T)$]. Enhanced $\tau(0)$ and $\chi(0)$ indicate a high density of states at the Fermi level resulting from narrow $5f$ bands and from $5f$-d,p hybridization.[11] According to some theoretical models the orbital moment in HFS is quenched at low temperatures.[12,13] Our present results, however, indicate the presence of a $5f$ orbital component in these Np heavy-electron systems. In addition, our results reveal interesting proportionalities: If we assume that $\chi(4.2\ {\rm K})$ is already close enough to $\chi(0\ {\rm K})$, the use of χ_L in the Wilson ratio R (Refs. 11 and 13) suggests a proportionality between χ_L and $\tau(0)$, where R is different from unity for a Fermi liquid. Previously a linear correlation between the isomer shift S and $\tau(0)$ has been derived.[4] Therefore the following relations should hold for the Np HFS at low temperatures:

$$\chi_L \approx \chi_B \propto \tau(0) \propto S\,.$$

We expect these proportionalities to be characteristic for a Fermi-liquid state and thus to hold for other HFS as well.

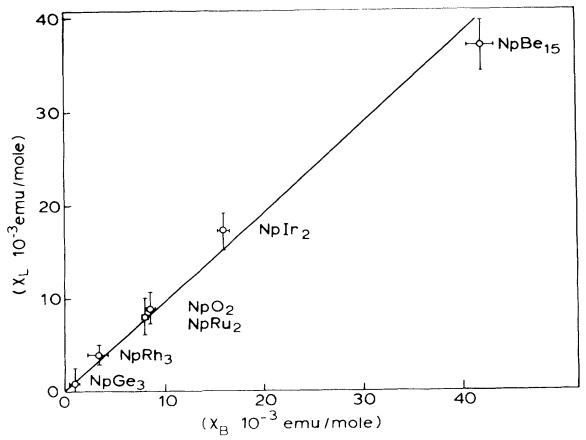

FIG. 3. Correlation between the local and bulk susceptibilities at 4.2 K of Np intermetallics in their paramagnetic state.

In summary, the presence of a strong orbital moment also in highly hybridized $5f$-electron systems is surprising. We expect, however, that the present systems could be described by the theoretical approach of Cooper *et al.*[14,15] In this model orbitally driven, hybridization-mediated anisotropic interactions of the actinide ions coupled to the band sea are claimed. A similar theory has been recently proposed by Levy and Zhang.[16,17] They take into account that hybridization (mixing interaction) depends on the orbital index m of the local electrons and show that anisotropic hybridization between electrons in local f states and conduction bands is the primary origin of the crystal-field splitting observed in Kondo systems, heavy fermions, and mixed-valence compounds. These novel theoretical models may provide a more quantitative explanation of our experimental observations. Unfortunately, until now no calculations using these models are available for Np systems.

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