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Magnetic and electronic properties of cubic NpX_3 intermetallics

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We report on the magnetic and electronic properties of $NpSi_3$, $NpGa_3$, and $NpIn_3$, which crystallize in the cubic $AuCu_3$ crystallographic structure (space group $Pm3m$). Studies by Mössbauer as well as ac and dc magnetization techniques are presented. From the Mössbauer isomer-shift data we argue that the Np ion in NpX_3 is close to the formal 3+ ($^5I_4$) charge state. The magnetic moment of the Np in $NpSi_3$ is totally suppressed, whereas in $NpGa_3$ a localized (narrow band) moment ($1.5\mu_B$) is established. However, in $NpIn_3$ at 4 K, a modulated magnetic moment $[(0-1.5)\mu_B]$ is observed. Comparing the magnetic behavior of the NpX_3 family (X=Si, Al, Ga, Ge, Sn, and In), we find an impressive variation of the magnetic properties, from temperature-independent paramagnetism, localized and modulated ordered moments, to the formation of a concentrated Kondo lattice. Hybridization of $5f$ electrons with ligand electrons appears to play a crucial role in establishing these magnetic properties. However, a consistent theoretical picture cannot be drawn at present.

I. INTRODUCTION

It has recently been shown that the electronic properties of the model itinerant antiferromagnet $NpSn_3$ (Ref. 1) also exhibits localized behavior. This outstanding magnetic property was attributed to the sensitivity of the spatial distribution of the $5f$-electron wave functions to anisotropic hybridization with nearest-neighbor orbitals in a cubic environment.[2] Hybridization dressing of the local Np $5f$ levels[3] causes a fine structure in the $5f$ bands. Thus orbitally driven anisotropic hybridization leads to splitting of the local crystalline electric-field (CEF) levels, and a localized moment can develop.[2-4] For this reason orbital moments are observed even in highly itinerant electron systems and $NpSn_3$ was an example of this phenomenon. $NpSn_3$ belongs to the NpX_3 (X=s,p-electron ligand) intermetallic family, which crystallizes in the cubic $AuCu_3$ ($Pm3m$) phase.

In the present paper we report on three members of this family, $NpSi_3$, $NpGa_3$, and $NpIn_3$. From Mössbauer isomer-shift (IS) data, we argue that the Np ion in the NpX_3 (X=s- and p-electron ligands) is close to the formal 3+ ($^5I_4$) charge state. We compare and discuss their electronic and magnetic properties, which vary from temperature-independent paramagnetism- (TIP) modulated magnetic structures to Kondo-lattice behavior. We show that $5f$-electron hybridization plays a crucial role in establishing the magnetic properties. However, similar to the NpX_2 system,[5] at present a consistent theoretical picture cannot be drawn.

II. EXPERIMENTAL DETAILS

$NpSi_3$ and $NpGa_3$ were prepared by arc melting stoichiometric amounts of neptunium and gallium or silicon in a dry argon atmosphere. X-ray- (Guinier-) diffraction patterns showed that the samples consisted of a cubic $AuCu_3$ phase (space group $Pm3m$) with lattice parameters a=4.035 and 4.227(3) Å, respectively. The compound $NpSi_3$ also consisted of impurities of $NpSi_2$ (≈5%) and about 3% of an unknown phase which could be observed only by the Mössbauer technique. No other phases could be identified in the x-ray diffractogram of $NpGa_3$. However, a second phase (Np_3Ga?) of ≈10% is clearly observed in the Mössbauer spectrum at 70 K.

$NpIn_3$ was prepared in an alumina crucible in a resistance furnace at 800 °C. $NpIn_3$ crystallizes in the cubic $AuCu_3$ structure with a lattice parameter of a=4.619(10) Å. An extra phase of about 8% of NpO_{2-x} was also observed and was taken into account in our Mössbauer fitting procedures. The samples were powdered and sealed in aluminum containers for the Mössbauer experiments and in highly pure plastic holds[6] for the magnetization measurements.

^{237}Np 60-keV Mössbauer transmission experiments were carried out between 4.2 and 120 K in a conventional variable-temperature cryostat.[7] The source used was ≈5% ^{241}Am (60 mCi) in Th metal. The dc magnetization measurements were performed with a vibrating-sample magnetometer. The ac susceptibility results were obtained with our low-field (≈8 G) triple-coil susceptometer, which is described elsewhere.[8]

III. RESULTS

A. $NpSi_3$

The Mössbauer absorption spectrum of $NpSi_3$ is depicted in Fig. 1. It shows a single absorption line of full width at half maximum of only 2.3(1) mm/sec at 4.2 K.

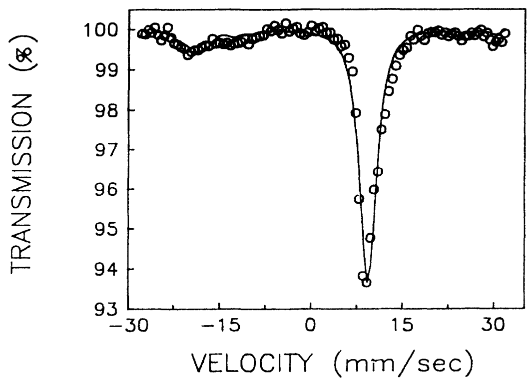

FIG. 1. ^{237}Np Mössbauer absorption spectrum of $NpSi_3$ at 4 K. The sample contains about 8% of a second phase, which was identified as $NpSi_2$ and was taken into account in our fitting procedure (see text). The Mössbauer source was ^{241}Am(Th).

This behavior suggests that magnetic order will not occur until far below 4 K. Other phases were always present in our samples, among which magnetically ordered $NpSi_2$ ($T_c = 55$ K) (Ref. 5) was identified; thus bulk magnetization measurements have to be postponed until we will be able to produce a pure single-phase sample.

B. $NpGa_3$

Typical ^{237}Np Mössbauer absorption spectra of $NpGa_3$ in the temperature region between 4.2 and 70 K are shown in Fig. 2. Magnetically split patterns are observed below 60 K, indicating magnetic order of the Np moments. The hyperfine field at 4.2 K is $B_{\mathrm{hf}} = 340(20)$ T, which corresponds to a Np ordered moment of $\mu_{\mathrm{ord}} = 1.6(1)\mu_B$.[9]

The dc susceptibility of $NpGa_3$ between 4.2 and 140 K is shown in Fig. 3. The dc magnetization is typical for ferromagnetic behavior with a transition temperature at 55(5) K. However, the magnetization under applied magnetic fields gives a saturation moment of only $\approx 0.8\mu_B$, in clear discrepancy with μ_{ord} obtained from the Mössbauer data. This rather suggests a ferrimagnetic structure. In addition, within the sensitivity of our ac susceptometer, we are not able to detect a cusp at the vicinity of the expected transition temperature. A sharp cusp is usually indicative of a ferromagnetic transition.[5]

The reciprocal susceptibility at elevated temperatures (inset in Fig. 3) shows a Curie-Weiss behavior in the temperature range of 150–265 K with a paramagnetic effective moment of $\mu_{\mathrm{eff}} = 2.6(2)\mu_B$ and a paramagnetic Curie-Weiss temperature $\Theta \approx 80$ K. We have no explanation for the non-Curie-Weiss behavior below 140 K. However, the Brillouin-like susceptibility below the ordering temperature of $NpGa_3$ may be caused by ferrimagnetic order in the powder sample.

C. $NpIn_3$

^{237}Np Mössbauer absorption spectra of $NpIn_3$ in the temperature range between 4.2 and 120 K are shown in Fig. 4. The Mössbauer absorption spectra at temperatures above 16 K show a single absorption line. In addition, an impurity phase of about 8%, with a different IS (probably NpO_2) is observed in the Mössbauer spectra above the ordering temperature and was taken into account in our fitting procedures. Magnetically split patterns are observed below 17(2) K, indicating magnetic ordering of the Np moments below this temperature. However, the magnetic structure seems to be rather complicated. At 4 K a superposition of several unusually well-defined magnetic patterns can be identified (see Fig. 4). In order to fit the magnetic spectrum at 4.2 K, we had to

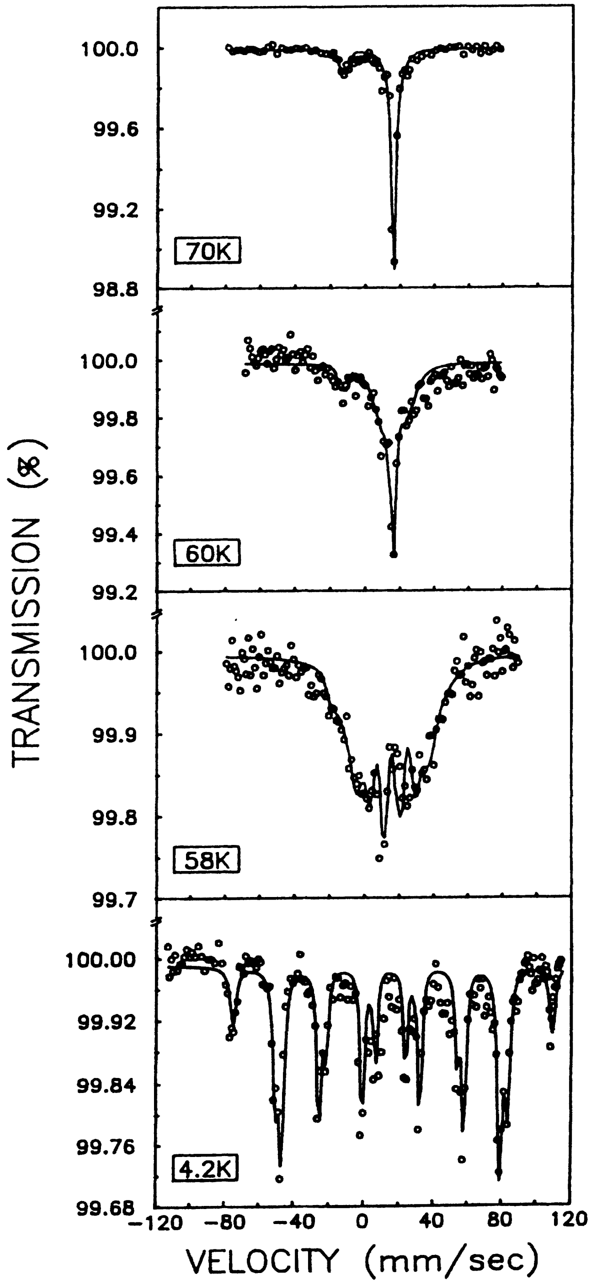

FIG. 2. ^{237}Np Mössbauer absorption spectra of $NpGa_3$ at various temperatures. The Mössbauer source was ^{241}Am(Th) at 4 K.

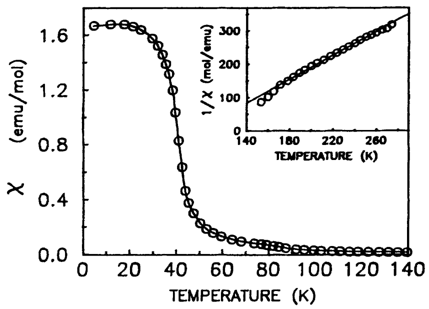

FIG. 3. dc magnetization of $NpGa_3$ (powder sample) as function of temperature in an applied magnetic field of 0.3 T. The reciprocal susceptibility at elevated temperatures is depicted in the inset.

assume a modulated spin structure with at least nine different values of hyperfine fields, varying from 0 to 325 T. No line broadening or change in the IS was detected. The maximum value obtained for the hyperfine field, $B_{\mathrm{hf}}^{\max}=325(20)$ T, corresponds to an ordered Np moment of $\mu_{\mathrm{ord}}=1.5(1)\mu_B$.[9] The modulation of the ordered moment is depicted in Fig. 5.

The low-field (0.018 T) dc susceptibility of $NpIn_3$ between 4.2 and 180 K is shown in Fig. 6. The dc magnetization indicates a possible antiferromagnetic transition at ≈ 17 K, in agreement with our present Mössbauer thermal scan measurement, which gave $T_{\mathrm{ord}}=17(2)$ K, shown in Fig. 7. The reciprocal susceptibility at elevated temperatures (inset in Fig. 6) exhibits a Curie-Weiss behavior with a paramagnetic effective moment of $\mu_{\mathrm{eff}}=2.1(2)\mu_B$. Below 150 K irregularities in the magnetic susceptibility are observed. The similarity between the temperature behavior of the susceptibility of $NpIn_3$ and $NpSn_3$ (Refs. 1 and 2) is striking and is depicted in Fig. 6.

In Table I we summarize our experimental results on the three compounds reported here and compare them with other intermetallics of the NpX_3 family.

IV. DISCUSSION

The electronic and magnetic properties of the NpX_3 (X = Si,Al,Ga,Ge,Sn,In) intermetallics sequenced according to their isomers shifts relative to $NpAl_2$ are compared in Table I. Within the systematics of the Mössbauer IS, these compounds are close to the formal $Np^{3+}(5f^4)$ charge state.[5,10] In a simple localized model of crystalline electric fields, according to Hund's rule, the ground term of $Np^{3+}(5f^4)$ is $^5I_4$. In such an ionic model, the $^5I_4$ state in a cubic CEF generally splits into a singlet Γ_1, a non-Kramers doublet Γ_3, and two triplets Γ_4 and Γ_5.[11] When lowering the symmetry, the degeneracies of the Γ_4 and Γ_5 are lifted. Using free-ion Russell-Saunders (RS) coupling, reasonable values for the ordered moments of a Np^{3+} ion in a large number of compounds can be derived: At low temperatures exchange splitting removes the degeneracy of the Γ_5, leading to a calculated ordered moment of $1.5\mu_B$ and an effective moment of $2.1\mu_B$.[12,13] These calculated values ($1.5\mu_B$) are surprisingly close to the experimental results for $NpAl_3$, $NpGa_3$, and $NpIn_3$ as given in Table I and would point to a localized (narrow band) $5f$-electron system. Intermediate coupling usually improves this approximation even further, leading to correct values of the calculated ordered moments in many $5f$ systems,[13] especially in the case of $NpAl_3$.[14]

However, the large variation of the observed IS and the absence of induced quadrupole interaction is not explained by the simple CEF approach (Table I). Therefore

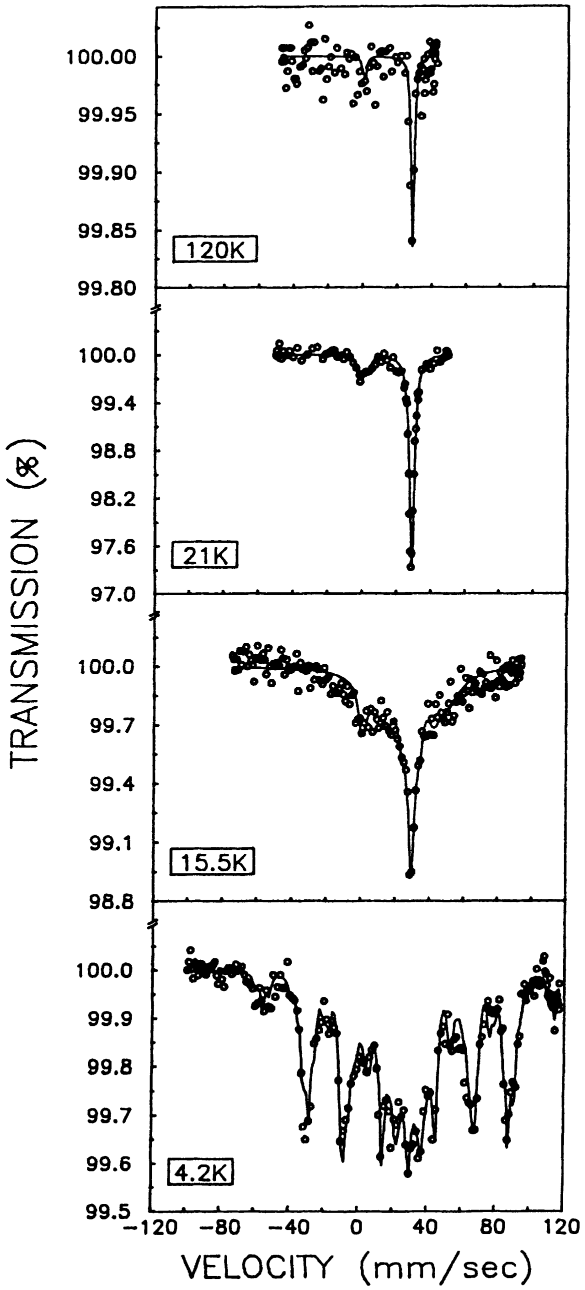

FIG. 4. ^{237}Np Mössbauer absorption spectra of $NpIn_3$ at various temperatures. The Mössbauer source was $^{241}Am(Th)$ at 4 K. The sample contains $\approx 5\%$ of a second phase, which was identified as NpO_2. The solid line at the 4.2 K spectrum represents the theoretical best fit assuming a superposition of nine well-defined magnetic patterns indicating spin modulation.

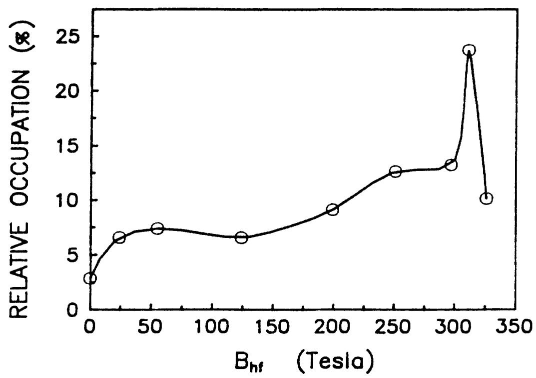

FIG. 5. Modulation of the Np ion ordered moment in $NpIn_3$ at 4 K.

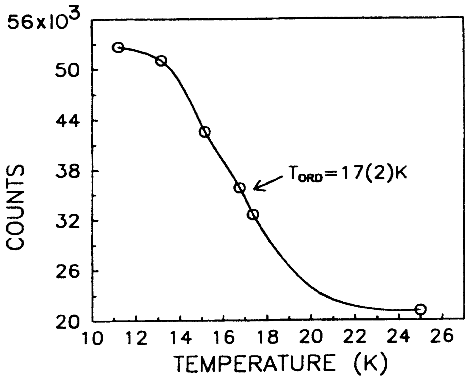

FIG. 7. Mössbauer thermal scan of $NpIn_3$. The derived ordering temperature is $T_{\text{ord}}=17(2)$ K.

we believe that hybridization of the $5f$ electrons plays an important role in the $NpX_3(AuCu_3)$ system [similar to UX_3 (Ref. 15)] and will be the main aspect of the following discussion.

Recently, we described the shielding effect of the $5f$ electrons and the similarity between covalent electrons in insulators and hybridization of $5f$ electrons with band electrons in metallic compounds.[5] It was pointed out that in metallic systems having a Np ion close to a formal 3+ charge state the conduction s electrons are highly shielded and thus contribute negligible density $\rho(0)$ at the ^{237}Np nucleus. Therefore, in order to observe a significant IS in the metallic 3+ region, the $5f$-electron density must be strongly affected. This is possible by hybridization, e.g., by application of external hydrostatic pressure on metallic Np compounds. Hybridization can be increased decisively, and the degree of hybridization can be correlated to the volume dependencies of μ_{ord}, T_{ord}, and $\rho(0)$.[2] In addition, under pressure, the change in the Mössbauer IS is always negative [$\rho(0)$ increases] because $5f$ delocalization decreases the shielding of s electrons. We conclude that increasing hybridization in the Np^{3+} region *must be associated with a more negative IS*. This, again, is confirmed in the NpX_3 systems as their IS's increase with the Np-Np distances, shown in Fig. 8, thus providing a measure of $5f$ hybridization with conduction electrons. For example, the IS of $NpSi_3$ (-0.2 mm/sec) lies close to $NpAl_2$. As the IS is -38.2 mm/sec relative to NpF_3 ($5f^4$ configuration), a severe $5f$ hybridization of the $5f^4$ core has to be present.

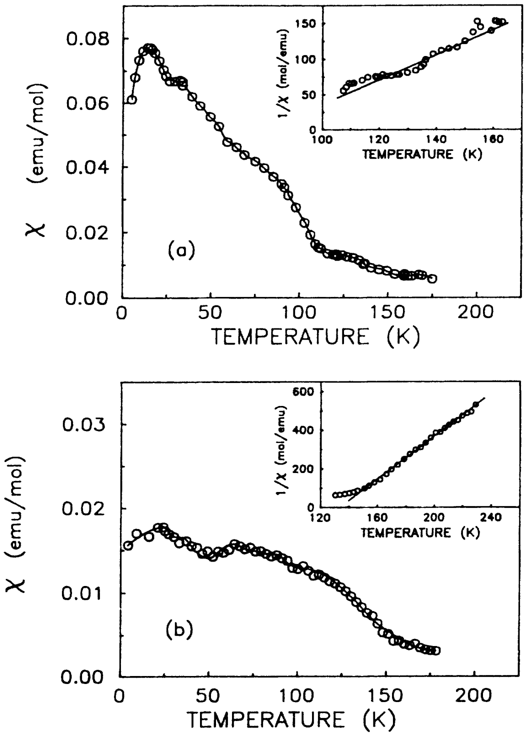

FIG. 6. (a) dc magnetization of $NpIn_3$ (powder sample) as function of temperature in an applied magnetic field of 0.018 T. The reciprocal susceptibility at elevated temperatures is shown in the inset. (b) dc magnetization of $NpSn_3$ (powder sample) as function of temperature in an applied magnetic field of 0.3 T. The reciprocal susceptibility at elevated temperature is shown in the inset.

As discussed in Refs. 1–4, anisotropic hybridization may give rise to coupling between orbital moments, establishing magnetic order and an effective crystal-field splitting. This results in a fine structure in the $5f$ bands. Such a mechanism could occur, for example, via unfilled s and p bands of the appropriate symmetry near the Fermi energy which mix with $5f$ crystal-field levels of the same symmetry, causing hybridization dressing of the local Np $5f$ levels. In $NpSn_3$,[2] such a process takes place. It finally results in a concentrated Kondo system similar to $CeAl_2$.[4,16]

On the other hand, anisotropic hybridization may, in addition, lead to a shift of the effective CEF levels and thus cause a total suppression of the magnetic moment, as observed in CeTe, PuTe, and $NpTe_2$.[3,5] It is likely that the same mechanism can be applied to $NpSi_3$ and $NpGe_3$, where again a total suppression of the moments is observed. From the Mössbauer single-line spectrum at 4 K, we conclude that $NpSi_3$ does not order magnetically even below 4 K. The same result is found for $NpGe_3$, where the width of the single absorption line even at 1.8 K is only 1.8(1) mm/sec. The absorption line is isomeri-

TABLE I. Properties of NpX_3 ($AuCu_3$) intermetallics. The isomer shifts are given with respect to $NpAl_2$.[a]

Compound	$NpSi_3$	$NpAl_3$	$NpGa_3$	$NpGe_3$	$NpSn_3$	$NpIn_3$
Isomer shift (mm/sec)	−0.2	2	6	7.6	18.2	19.5
Hyperfine field B_{hf} (T)	0	288	340	0	60	0–325
Quadrupole interaction e^2qQ (mm/sec)	≈ 0	≈ 0	≈ 0	≈ 0	≈ 0	≈ 0
T_{ord} (K)	?	62.5	60		9.5	17
Magnetic structure	TIP?	ferri?	ferri?	TIP	AF[b]	AF-MS[c]
Ordered moment at 4.2 K (units of μ_B)	0	1.3	1.6	0	0.3	0–1.5
Saturation moment (units of μ_B)		0.47	0.8		0.5??	???
Paramagnetic moment (units of μ_B)		2.5	2.15		1.2	2.1
Np-Np spacing (Å)	4.035	4.266	4.243	4.212	4.627	4.619
References	this paper	14	this paper	22	1	this paper

[a] NpF_3 is shifted +32 mm/sec relative to $NpAl_2$.
[b] AF, antiferromagnet.
[c] MS, modulated structure.

cally shifted by 30.8 mm/sec versus NpF_3. In both systems dressing of the CEF levels may push the Γ_1 singlet state down to be lowest in energy with negligible mixing from higher magnetic levels.

In magnetically ordered systems with cubic crystallographic symmetry, the principal component of the electric-field-gradient (EFG) tensor eq_z evaluated at the nucleus originates mainly from $5f$ electrons.[17] Therefore a noticeable magnetically induced quadrupole interaction is expected in the ordered state, as actually found for the semimetallic NpAs compound.[18] Experimentally, however, as shown in Table I, in the ordered state of $NpAl_3$, $NpGa_3$, $NpSn_3$, and $NpIn_3$ systems, no (or at most a very small) induced quadrupole interaction is observed. This strongly indicates that hybridization also "washes out" the induced eq_z, although a magnetic moment still exists.[5,19]

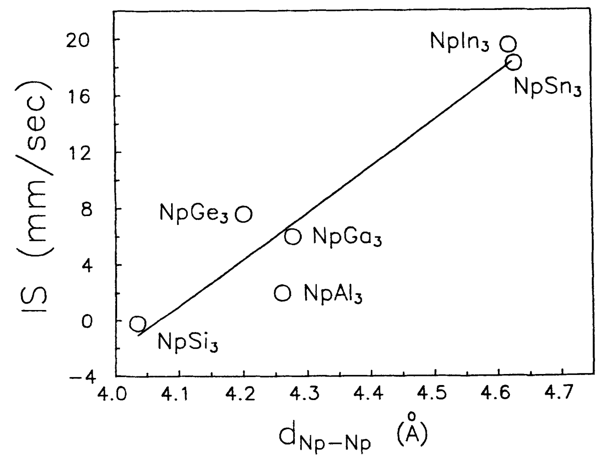

FIG. 8. Isomer shifts relative to $NpAl_2$ vs Np-Np distance for NpX_3 ($AuCu_3$) systems. The solid line is a guide to the eye.

The large discrepancy between μ_{ord} and μ_{sat}, which is present in all the magnetically ordered NpX_3 compounds investigated, as shown in Table I, is probably an indication that these compounds are not ferromagnetically ordered (in contradiction to Ref. 13 for $NpAl_3$), but rather a ferrimagnetic ordering is established. Nevertheless, this discrepancy could also be due to the delocalization of $5f$ electrons, as expected from the IS. Recent relativistic calculations for $NpAl_2$ and $NpOs_2$ by Eriksson, Johansson, and Brooks utilizing a local-spin-density (LSD) formalism[20] showed that by taking into account the conduction-electron polarization, in part (correction of about 30%), this discrepancy can be resolved. At present, LSD calculations for NpX_3 compounds are not available. Still, as the discrepancy is large indeed, we rather attribute this to the ferrimagnetic ordering and not to conduction-electron polarization. Neutron-diffraction studies of these compounds are needed to clarify this problem.

The localized properties of the itinerant $5f$-electron $NpSn_3$ has recently been discussed in Ref. 1. For explaining the Mössbauer high-pressure data, the Kondo effect had to be invoked by assuming that the moment originating from the Γ_4 and Γ_5 CEF levels is partially quenched $(0.3\mu_B)$ by the conduction electrons. This compound should be viewed as a partially magnetic concentrated Kondo-lattice system.[2]

Recent resistivity measurements have confirmed this prediction.[21] For these reasons it is interesting to investigate the magnetic and electronic properties of $NpIn_3$, which differs just by one $5p$ electron from $NpSn_3$. As expected, one $5p$ electron will hardly affect the s-electron density $\rho(0)$ at the nucleus; thus the IS's of the two compounds, relative to NpF_3, are about the same (see Table I). However, their Mössbauer spectra differ markedly. For $NpIn_3$ below T_{ord} (17 K), a modulated magnetic hyperfine field (B_{hf}) was needed to fit the experimental spectra (see Fig. 5). The IS is well defined and the same for all the magnetic subspectra. No line broadening was observed. Again, the induced quadrupole interaction is negligible.

Because of the close similarity of the electronic structures of $NpSn_3$ and $NpIn_3$, we expect $NpIn_3$ also to be a Kondo-lattice system. Indeed, a hint for Kondo behavior is given by recent resistivity data[21] and by the similarity of these two compounds (see Fig. 6). It is interesting to check whether the moment modulation could be caused by a Kondo-lattice mechanism. To clarify this question, neutron-diffraction measurements would be of great help. In addition, Mössbauer high-pressure experiments on $NpIn_3$, similar to $NpSn_3$,[2] are planned in the near future.

V. CONCLUSIONS

Anisotropic $5f$-electron hybridization plays a decisive role in the $NpX_3(AuCu_3)$ system, similar to the NpX_2 family.[5] This hybridization affects all Mössbauer hyperfine parameters, namely, the magnetic hyperfine field (and accordingly μ_{ord}), the quadrupole interaction and, the isomer shift. Although CEF dressing turns out to be important, at present there exists no theoretical model which explains consistently, the ordered magnetic moments, the quadrupole interaction, and the isomer shifts in the NpX_3 family.

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