ELSEVIER

Journal of Alloys and Compounds 223 (1995) 242–250

Journal of ALLOYS AND COMPOUNDS

Mössbauer studies on the volume stability of f-electron configurations

G.M. Kalvius

Physik-Department, Technische Universität München, D-85747 Garching, Germany

Abstract

The behaviour of 4f and 5f electron structure under reduced volume was investigated by high-pressure Mössbauer spectroscopy in compounds of europium, dysprosium, and neptunium. The study of 4f systems is limited for technical reasons to the heavy elements. There the main case of instability is valence fluctuations between well localized neighbouring $4f^n$ configurations. In the light 5f systems, for which neptunium is taken as an example, the central question is the delocalization of 5f electrons via 5f–5f overlap or 5f–ligand electron hybridization. Characteristic features of the high-pressure Mössbauer spectra which give insight into these problems are presented. The most challenging cases in Np intermetallics are those with the $AuCu_3$ structure. Recent data on several such systems are discussed.

Keywords: Electron structure; Europium; Dysprosium; Neptunium; Mössbauer studies; Volume stability

1. Introduction

Mössbauer spectroscopy is based on nuclear resonance absorption. An element to be studied by the Mössbauer technique must possess a stable (or at least metastable) isotope whose nuclear properties fulfil certain conditions. The most basic one is a γ-ray transition of low energy (typically $\leqslant 100$ keV) into the ground state. This limits the cases available for Mössbauer studies. The situation is favourable, however, in the lanthanides and actinides, as demonstrated in Fig. 1. With the notorious exception of Ce, all rare earth elements can in principle be studied. In the actinides one is at present limited to the first half of the series on account of the stability and availability of the heavier transuranium elements. For broader solid-state physics applications additional practical and technical requirements must also be met. For example, sources for the resonant γ radiation should be readily available, the resonant isotope should not be scarce and the resolution of the resonance with respect to hyperfine interactions must be sufficient. These conditions seriously restrict the number of good cases in the 4f and 5f series to the elements underlined in Fig. 1. For elements marked with asterisks high-pressure data are also available, most numerous for europium and neptunium.

Ce	Pr	Nd	Pm	Sm	Eu*	Gd*	Tb	Dy*	Ho	Er	Tm	Yb*	Lu
Th	Pa	U	Np*	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

Fig. 1. Mössbauer elements in the lanthanide and actinide series. Shaded boxes, Mössbauer studies cannot be carried out; underlined elements, more commonly used for Mössbauer spectroscopy; elements marked with asterisks, high-pressure data are available.

Information on electronic structure by Mössbauer spectroscopy is gained via the hyperfine interactions, that is, the coupling of nuclear electromagnetic moments to the surrounding electronic charges and currents. It is customary to use a multipole expansion of the interaction Hamiltonian and to consider separately the three relevant terms: electric monopole, magnetic dipole and electric quadrupole couplings. The monopole term causes a shift in position of the resonance, usually referred to as the isomer shift. The relevant electronic parameter is the electron density at the nucleus ρ_0, often also called the contact density. It relates to the charge state of the resonant ion. The magnetic dipole interaction causes a Zeeman splitting of the nuclear levels engaged in the resonant transition. This leads to a characteristic multi-line resonance pattern. From the separation of lines one deduces the magnetic field at the nucleus, usually referred to as the hyperfine field B_{hf}. In most cases, a Zeeman splitting is only observable in an ordered magnet (ferro-, antiferro- or ferrimagnet) and vanishes at the magnetic transition temperature. This allows the determination of the Curie or Néel point, respectively. The hyperfine field for $T \to 0$ can

SSDI 0925-8388(94)09007-6

be related to the ordered magnetic moment present on the Mössbauer ion. The electric quadrupole interaction also leads to a multi-line pattern but with different line positions to those of a magnetic spectrum. One extracts the electric field gradient at the nucleus, which gives information on the spatial symmetry of electronic charges. More details can be found in the literature, e.g. Ref. [1].

The 'standard rare earth' electron configuration is the highly localized trivalent ionic state. Next to a half-filled or a full 4f shell, the neighbouring charge states are also stable, i.e. Eu^{2+}. However, they are not necessarily found in their pure form. One observes the phenomenon of intermediate valence or valence fluctuations [2].

In the actinides, the presence of intermediate valence is not definitely established. Here, the common deviation from standard $5f^n$ electron structure arises from the wide radial extent of the 5f electrons which is comparable to that of 3d electrons in transition metals. This allows the 5f electrons to participate in the bond and to form via f–f overlap of f–d, f–s and perhaps f–p hybridization more or less wide bands in metallic solids.

The localized picture for the 4f electron configuration need not generally be true. Well known cases of strong 4f electron hybridization are cerium compounds exhibiting heavy fermion or Kondo lattice properties [3]. Analogous behaviour is seen in many uranium intermetallics. However, cerium has no Mössbauer transition and uranium is a technically difficult to handle resonance which, in addition, suffers from poor resolution. Hence these very modern aspects of f electron structure are largely outside the reach of Mössbauer spectroscopy. There are, however, possible candidates for heavy fermion behaviour in neptunium. We shall come back to this point later.

With a few exceptions we shall only consider compounds which exhibit long-range magnetic order. The behaviour of the hyperfine field and the magnetic transition temperature are most sensitive indicators of f-electron instability.

The Mössbauer high-pressure systems used are based on high-pressure cells with opposed anvils made either of B_4C or diamonds. The pressure limit for the B_4C cells is 15 GPa; the diamond cell reaches 50 GPa. In the Mössbauer studies of Np the limit of 10 GPa has not been exceeded for safety reasons. All pressures are measured in situ under experimental conditions. A temperature range from 300 to ca. 2 K is available in principle, but for Np the Mössbauer effect is observable only at low temperatures ($\leq$150 K).

To convert pressure dependences into volume dependences one has to have information on the bulk moduli of the materials under investigation. We use for this purpose a Guinier-type X-ray diffractometer also equipped with either B_4C or diamond anvil cells. The design of the diffractometer has recently been extended to allow measurements at cryogenic temperatures. Details were described by Potzel [4].

2. Stable f-electron configurations

Especially in the middle of the second half of the lanthanide series (Eu and beyond), on expects fully developed trivalent $4f^n$ configurations. These lead to highly localized magnetic properties. A pertinent example is Dy. In Fig. 2 results of a high-pressure Mössbauer study on ferromagnetic $DyAl_2$ are presented, and the following conclusions can be drawn. (a) The isomer shift changes strongly with pressure. This reflects the compression of conduction electrons by volume reduction, which leads to an increase in s-electron density at the nucleus. We shall return to this point later. (b) The Curie temperature rises sharply. (c) The hyperfine field at 4.2 K (which approximates $T \to 0$) remains virtually constant, or perhaps decreases minutely. The

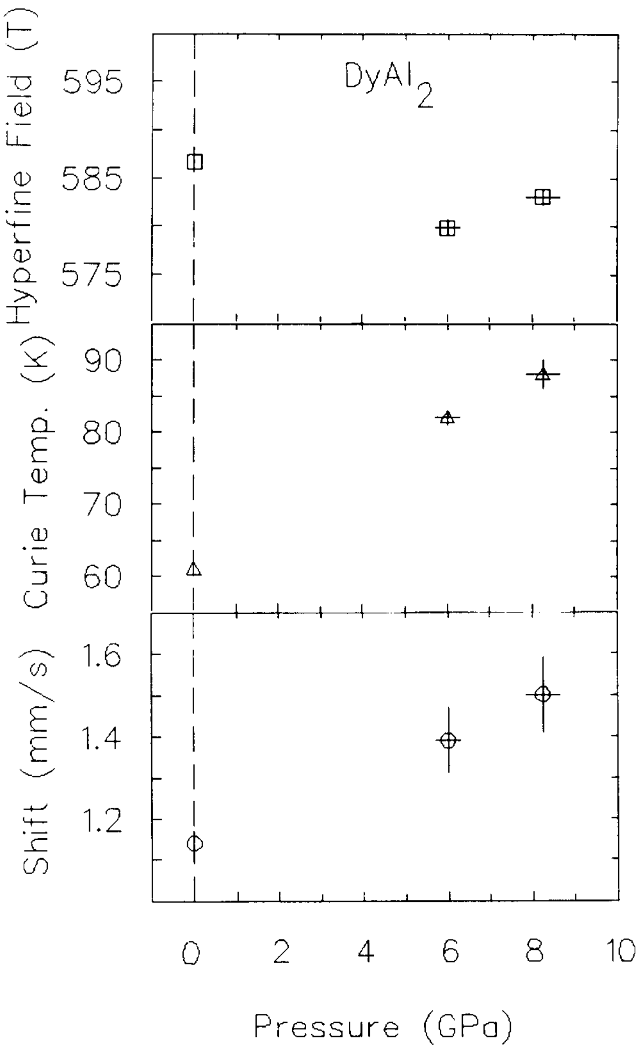

Fig. 2. Variation of hyperfine field, Curie temperature and isomer shift with pressure for $DyAl_2$ at 4.2 K. The 25.6 keV resonance in ^{161}Dy was used.

constancy of B_{hf} reflects the constancy of the ordered magnetic moment of Dy^{3+} in $DyAl_2$. The absolute value of B_{hf} is very close to the trivalent free ion value. Since μ_{Dy} or B_{hf} originates mainly from the orbital motion of the 4f electrons located well within the electronic core, one does not expect an influence of reduced volume. It should be kept in mind that the pressure range discussed here leads to a volume reduction of only a few per cent. Magnetic exchange is expected to be due to the RKKY mechanism. However, the RKKY model based on a free electron gas for conduction electrons and a point-like exchange interaction will not lead to an increase in magnetic transition temperature with reduced volume. The problem has been solved by a modification of the RKKY exchange mechanism [5] which involves d/r_i as a sensitive parameter, where d is the rare earth separation and r_i the radial extent of the 4f orbitals. For $DyAl_2$ the authors calculated $dT_c/dP \approx 0.2$ K kbar^{-1}, which roughly agrees with our data ($dT_c/dP \approx 0.3$ K kbar^{-1}). The model is based on the assumption that r_i independent of volume, which is the essential point here. It still contains, however, some simplifications such as free electron gas conduction electrons.

In summary, the signature of a well localized f-electron configuration giving rise to orbital magnetism is a nearly constant hyperfine field (magnetic moment) coupled to a substantial rise in magnetic transition temperature with reduced volume. Such a relationship had also been proposed by Fourier et al. [6]. In addition, there exists an increase in contact density.

In Fig. 3, high-pressure data are presented for $EuAl_2$ [7]. Here, the diamond anvil technique allowed pressures up to 40 GPa, which led to substantial volume reductions of 30%. $EuAl_2$ had been suspected as a candidate for intermediate valence. Our data proved differently. As will be discussed in the next section, the essential signature for valence fluctuations is the combined appearance of a temperature and pressure dependence of isomer shift. Fig. 4 demonstrates this not to be the case in $EuAl_2$ [8]. Returning to Fig. 3, we observe a strong increase in magnetic ordering temperature under reduced volume, one of our indicators for a localized f configuration. The second rule, namely a constant hyperfine field, seems to be violated. This, however, is easily explained. The configuration of Eu^{2+} is $4f^7{:}{}^8S_{7/2}$ and hence the orbital contribution to B_{hf} is lacking. This leaves for the intra-atomic sources of B_{hf} the Fermi contact fields from the core electrons (B_c) and the polarization of conduction electrons (B_{cp}) by the magnetic moment on the resonant atom. An additional dipolar field (B_{dp}) contribution is small and can be neglected. A major component of B_{hf} here is the inter-atomic contribution, which is called the transferred hyperfine field, B_{tr}. It represents the field arising from the moments on neighbouring atoms. In metals

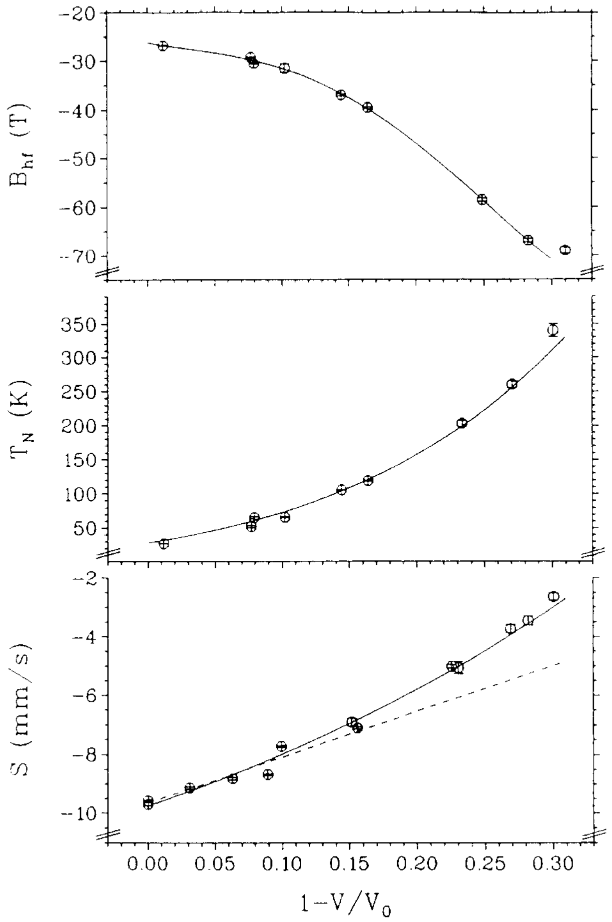

Fig. 3. Volume dependences of hyperfine field (B_{hf} for $T \rightarrow 0$), the Néel temperature (T_N) and the isomer shift S (at 300 K) in $EuAl_2$. The solid lines for $B_{hf}(V)$ and $T_N(V)$ are power expansion fits. For $S(V)$ it represents the parabolic dependence discussed in text. For comparison a linear fit to the data for the region $\Delta V/V_0 \leqslant 10\%$ is shown as a dashed line. The data were obtained with the 21.6 keV resonance in ^{151}Eu.

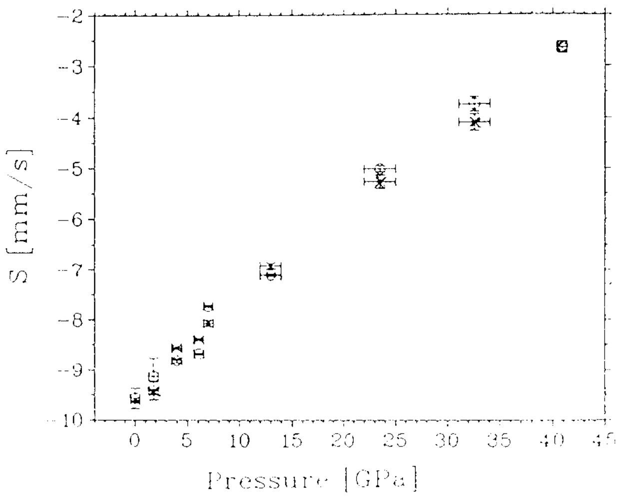

Fig. 4. Comparison of the pressure dependence of the isomer shift of $EuAl_2$ at 300 K (circles) and 4.2 K (crosses). No systematic difference between the two sets of data is noticeable.

this is transmitted mainly via the conduction electrons. B_{tf} is, of course, present in all magnetic materials. However, in cases where B_{hf} contains the large contribution by the orbital motion, it is only a minor addition which can be neglected. As can be seen from a comparison between Figs. 2 and 3, the hyperfine field in $EuAl_2$ is about an order of magnitude smaller than in $DyAl_2$ although the ionic moments are not so much different ($7.9\mu_B$ vs. $9.7\mu_B$). It has been shown that B_c and B_{cp} (which relate to the Eu^{2+} ionic moment) are largely independent of volume [9]. Clearly, B_{tf} depends on the Eu–Eu separation and this is what we observe in the case of $EuAl_2$.

As stated, the isomer shift mainly reflects the increase in contact density caused by the compression of conduction electrons. Of importance is that for larger volume changes the usually assumed linear dependence (on volume reduction, not on pressure!) does not hold. The data can be fitted with a hyperbolic dependence analogous to the ideal gas law: $V\rho_0 = \text{constant}$. Care has to be exercised when discussing the presence of an apparent 'break' in the slope of isomer shift vs. volume as an indicator for change in electron configuration.

The combination of changes in isomer shift and magnetic transition temperature, however, leads us to another signature of a localized 4f electron configuration. Applying the RKKY model to localized f spins results in the prediction: $\Delta(\sqrt{T_N}) \propto \Delta S$ [7]. As can be seen from Fig. 5, this relationship is perfectly fulfilled for $EuAl_2$.

Hence, to detect a localized f configuration by high-pressure Mössbauer spectroscopy, we look for cases where

$$-\mathrm{d}\ln\mu/\mathrm{d}\ln V \approx 0 \text{ and } -\mathrm{d}\ln T_{mag}/\mathrm{d}\ln V = \text{large, positive}$$

and the relationship

$$\Delta(\sqrt{T_N}) \propto \Delta S$$

is fulfilled. The salient question is: do such cases exist for Np? The answer is 'yes', as the data for $NpCo_2Si_2$ in Fig. 6 demonstrate. It appears that in the tetragonal series NpT_2X_2 (T = d transition element, X = Ge, Si), the Np configuration is a fairly pure $5f^4{:}{}^5I_4$ (Np^{3+}) state. The observed magnetic moments in this series

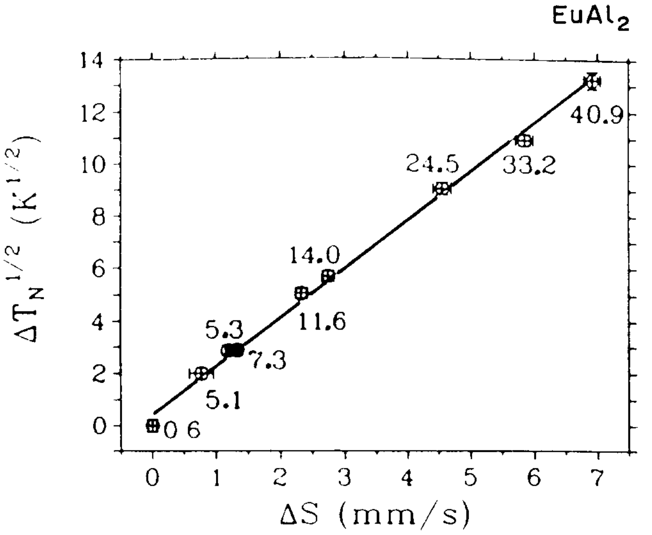

Fig. 5. Plot of change in $\sqrt{T_N}$ with change in isomer shift in $EuAl_2$. The pressure (in GPa) for each data point is indicated. A perfect linear relationship exists.

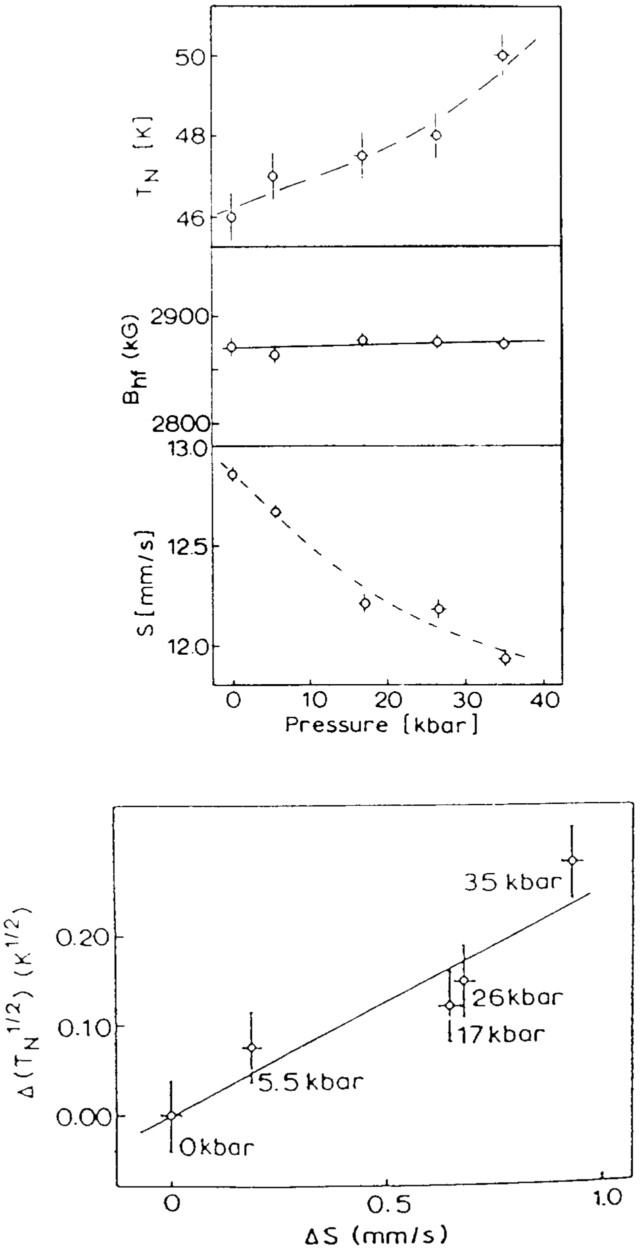

Fig. 6. Results of high-pressure Mössbauer studies (using the 60 keV resonance in ^{237}Np) in $NpCo_2Si_2$. Top: variations of Néel temperature, hyperfine field and isomer shift with pressure (compare with Fig. 2). Bottom: change in $\sqrt{T_N}$ with change in isomer shift (compare with Fig. 5). 10 kbar = 1 GPa.

can well be explained by crystalline electric field (CEF) interactions [1].

3. Unstable f configurations

The best known deviation of rare earth ions from a pure $4f^n$ configuration is intermediate valence. In Eu the Eu^{3+} and Eu^{2+} states are mixed. For the ^{151}Eu resonance the difference in isomer shift between corresponding compounds containing the Eu^{2+} and the Eu^{3+} ions is large (ca. 10 mm s^{-1}) compared with the linewidth (ca. 1.5 mm s^{-1}) and hence easily detected. The standard model describing Mössbauer data on valence fluctuating materials [10] assumes rapid charge fluctuations between the two f states involved. They are separated by the excitation energy E_{ex} which is considered to be independent of temperature. Boltzmann statistics gives the relative occupancy of the two states, which in turn determines the temperature dependence of the intermediate valence ν. The main effect of reduced volume is to decrease E_{ex} and, in consequence, the temperature dependence of ν is altered with pressure. The rapid charge fluctuations determined a mean ν even on the time-scale of hyperfine interactions. A concomitant mean isomer shift is observed:

$$S=S(4f^n)P(4f^n)+S(4f^{n-1})P(4f^{n-1})$$

where $P(4f)$ are the relevant occupation numbers.

A typical example is $EuCu_2Si_2$ [11]. Fig. 7 (top) shows the isomer shift to be strongly dependent on temperature. At 4.2 K the shift corresponds to a charge state $Eu^{+\nu}$ with $\nu \approx 2.8$, whereas at 673 K the valence had dropped to $\nu \approx 2.35$. The change of S with applied pressure at 300 K is equally dramatic (Fig. 7, bottom). The valence has increased to $\nu \approx 2.9$ at 4.5 GPa compared with $\nu \approx 2.6$ at ambient pressure. At 4.2 K the valence has reached its closest limit to the Eu^{3+} state independent of pressure. The remaining weak pressure dependence of isomer shift reflects, as usual, the compression of conduction electrons. It has not been subtracted in the 300 K data.

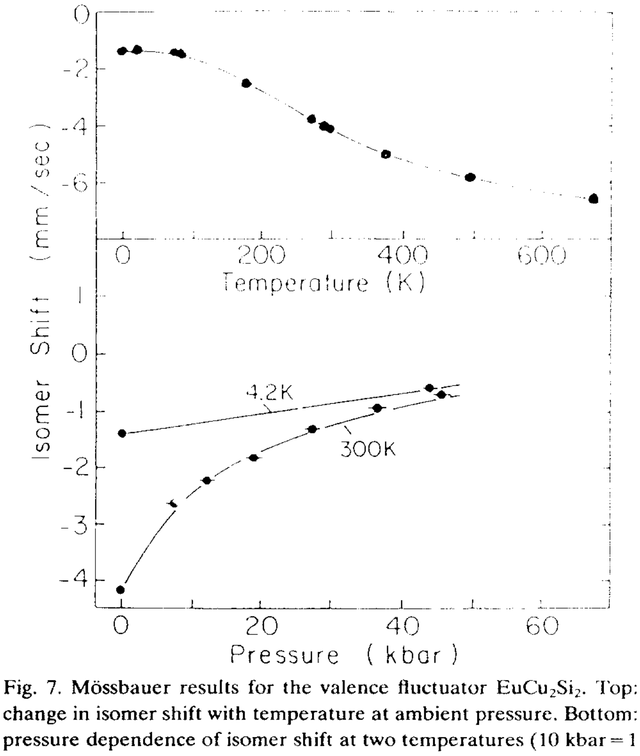

Fig. 7. Mössbauer results for the valence fluctuator $EuCu_2Si_2$. Top: change in isomer shift with temperature at ambient pressure. Bottom: pressure dependence of isomer shift at two temperatures (10 kbar = 1 GPa).

In summary, the presence of intermediate valence can be established safely only if the pressure dependence of isomer shift changes significantly with temperature. As mentioned, this is not the case in $EuAl_2$.

Again we ask the question: has such a behaviour been seen in Np intermetallics. The answer at present is 'no'. In other words, no case of intermediate valence has been established in Np intermetallics despite the fact that Np can and does exist in various formal charge states [1]. The Np analogue $NpCu_2Si_2$ in particular exhibits magnetic properties which are satisfactorily explained with a fully ionic Np^{3+} state under the influence of CEF interaction. A suspicious candidate had been $NpAl_2$. The theoretical explanation of the pressure dependence of the $NpAl_2$ hyperfine spectra required the presence of rapid electronic fluctuations between (at least) two states with different magnetic properties. The absence of a marked temperature dependence of isomer shift at any pressure largely ruled out valence fluctuations, however. Recently, the situation was explained quantitatively in a CEF model, showing that the ratio of the CEF parameters A_4/A_6 is volume dependent [13]. Candidates for intermediate valence in the light actinides can more likely be found in Pa and Am materials. Corresponding data are not available at present. The occurrence of intermediate valence has been suggested [14] in Pu compounds.

In 5f systems, the commonly found deviation from a localized $5f^n$ state is the formation of 5f bands. The underlying reason is the wide radial extent of the 5f wavefunction which allows overlap with the wavefunctions of outer electrons of neighbouring ions. This effect is considered to be most pronounced for U and to vanish for Am. Clearly, Np is an intermediate case and the answer as to the degree of 5f delocalization can be sought well by high-pressure Mössbauer studies. What one looks for are deviations from the rules on the volume coefficients for the magnetic moment (detected via the hyperfine field) and the transition temperatures. Our findings in this realm are summarized in Fig. 8. We had already commented on the localized behaviour of $NpCo_2Si_2$. The rock salt monopnictide NpAs is no longer fully localized. Its placement in Fig. 8 leads to the classification as a narrow band system. Since the Np–Np separation is large, 5f–5f overlap is not expected to occur and band formation must be due to hybridization with ligand electrons. The degree of hybridization is weakly volume sensitive. More

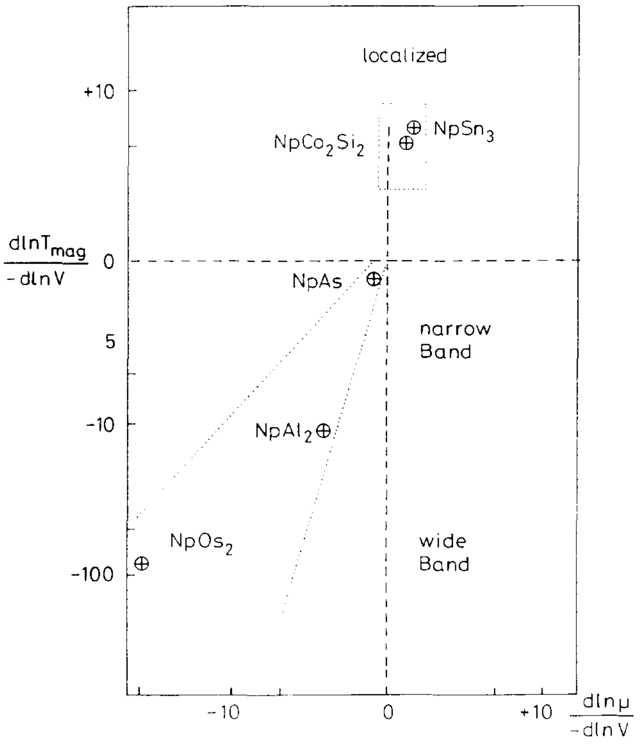

Fig. 8. Plot of the volume coefficient of magnetic ordering temperature (vertical scale) against the volume coefficient of Np magnetic moment as derived from the saturation hyperfine field (horizontal scale) for various Np intermetallics. Different regions are indicated as 'localized', 'narrow band' and 'wide band' f-electron configurations. The logarithmic scales are for convenience only and have no theoretical background.

dramatic effects are seen in the cubic Laves phases $NpAl_2$ and $NpOs_2$. The former is a case having moderately wide 5f bands. The relatively small Np–Np separation and the strong volume dependence suggest 5f–5f overlap to be the main mechanism, as discussed originally by Hill [15]. This is further borne out by $NpOs_2$, which has an even smaller atomic volume at ambient pressure and consequently forms wide 5f bands. Here the volume dependence of delocalization is extreme, as is expected when the 'Hill limit' of Np–Np separation is approached. Below this limit the 5f bands become too wide to support magnetism. Although $NpAl_2$ must be considered a moderately delocalized system, the application of CEF interactions works well, as mentioned earlier. This means that that 5f bandwidth is still small when compared with the average CEF splitting. Finally, the $AuCu_3$ intermetallic $NpSn_3$ also occupies a 'localized position' in Fig. 8. This is an unexpected result, which will be discussed in the next section.

4. Np intermetallics with the $AuCu_3$ structure

Large-scale solid-state physics and chemistry research has only recently turned towards this class of intermetallics, although the number of AnX_3 compounds is about as large as those of the AnX_2 Laves phases. A composition of type AnX_3, however, does not guarantee that the material crystallizes in the cubic $AuCu_3$ structure. Other crystallographic structures are formed. A prominent example is the important heavy fermion compound UPt_3. In some cases (e.g. $NpPd_3$) either a cubic or a non-cubic (hexagonal) structure can be formed depending on details of the production process. We shall limit ourselves to NpX_3 materials which crystallize in the cubic $AuCu_3$ phase. They defy a simple classification in the terms just discussed for the NpX_2 and NpX materials. Their interactinide distance is large and consequently one would expect that all members of the series are highly localized magnets when evoking the Hill model. This is by no means the case, however. About half of the known members are non-magnetic and notably $NpSn_3$ possesses only a very small (ca. $0.3\mu_B$) moment in its antiferromagnetic state which is formed at a low temperature ($T_N = 9.5$ K at ambient pressure). This, together with specific heat data, lead to the assignment of $NpSn_3$ as a model itinerant antiferromagnet [16]. On the basis of ambient pressure data, such a classification is fully justified. In contradiction stand the Mössbauer high-pressure data [17], which showed the behaviour typical of a localized magnet as discussed above (see Fig. 8). As Fig. 9 demonstrates, $NpSn_3$ also passes the other test of localized magnetic behaviour, that is, it displays a linear relationship between changes in $\sqrt{T_N}$ and the isomer shift S. The other materials studied to date are $NpGa_3$, $NpIn_3$ and (in a preliminary fashion) $NpAl_3$ [18]. Results are displayed in Fig. 10 for the first two compounds together with the earlier data on $NpSn_3$. The behaviour of $NpAl_3$ appears to be similar to that of $NpIn_3$, i.e. a weak rise in B_{hf} and a strong rise in the ordering temperature.

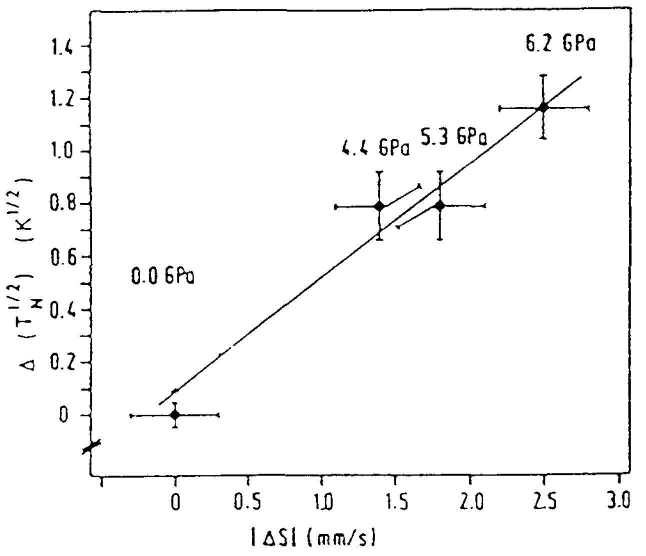

Fig. 9. Change in $\sqrt{T_N}$ with change in isomer shift for $NpSn_3$ (compare with Figs. 5 and 6).

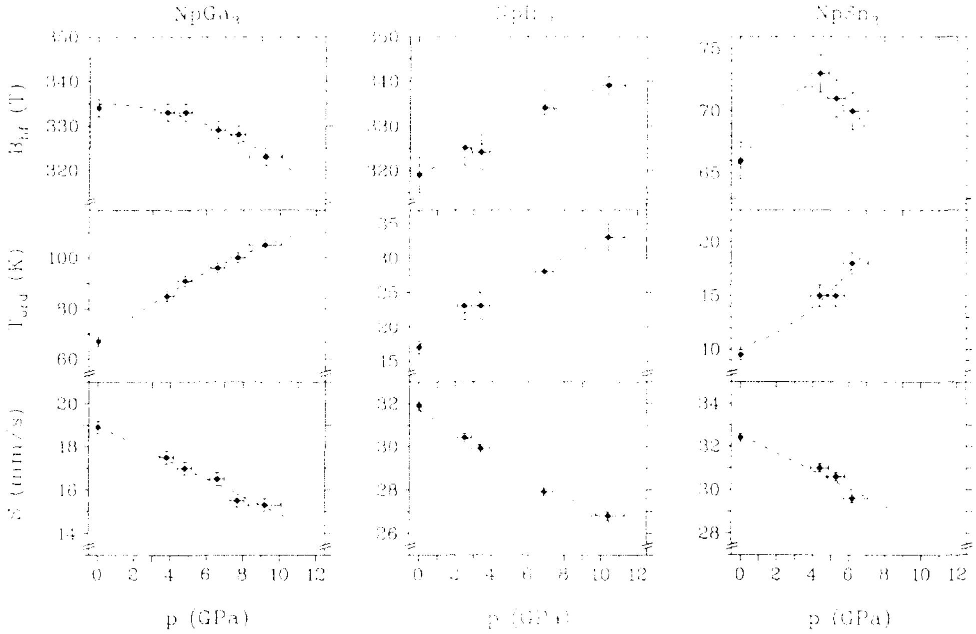

Fig. 10. Pressure dependences of hyperfine field, magnetic ordering temperature and isomer shift for three AuCu$_3$ intermetallics of Np.

The three compounds NpGa$_3$, NpIn$_3$ and NpAl$_3$ show the 'normal' saturation hyperfine fields of about 300 T (corresponding to an ordered moment of roughly 1.4 μ_B), in contrast to the very low moment case NpSn$_3$. The pressure dependence of the hyperfine field is not uniform. Although the variations in $B_{hf}(P)$ are small in all cases, there is a weak reduction visible for NpGa$_3$ and a more pronounced increase in NpIn$_3$. It is possible that NpSn$_3$ shows a 'combined' behaviour, that is, first an increase and then a decrease in hyperfine field, but to establish this safely one would need data of higher precision (which is difficult in view of the small and only partially resolved splitting).

Especially NpSn$_3$ is nowadays described more in terms of a highly correlated electron system. The strong reduction in moment would be the result of Kondo screening. For the other members such a classification is under discussion (for example, on account of resistivity data), but is in part controversial. Clearly, Kondo screening has to be very weak. On the other hand, the Np ordered moments in NpIn$_3$ and NpGa$_3$ could well be explained by crystal field interactions alone. This need not be a contradiction; it would place the materials only at the limit of correlated systems. In any case, the picture of a correlated electron system requires a certain amount of 5f conduction electron hybridization which needs to be strongest in NpSn$_3$. To gain more insight, the series Np(Sn$_x$Ge$_{1-x}$)$_3$ was studied [18] at ambient pressure. The replacement of Sn by Ge leads to a substantial reduction in volume which can be compared with the high-pressure data on NpSn$_3$. Such a comparison between volume changes by external pressure to volume change by chemical means gives consistent results in case of the NpX$_2$ Laves phases (see the next section). In the AuCu$_3$ case, Fig. 11 shows that the situation is different. The isomer shift shows a smooth volume dependence and indicates that the

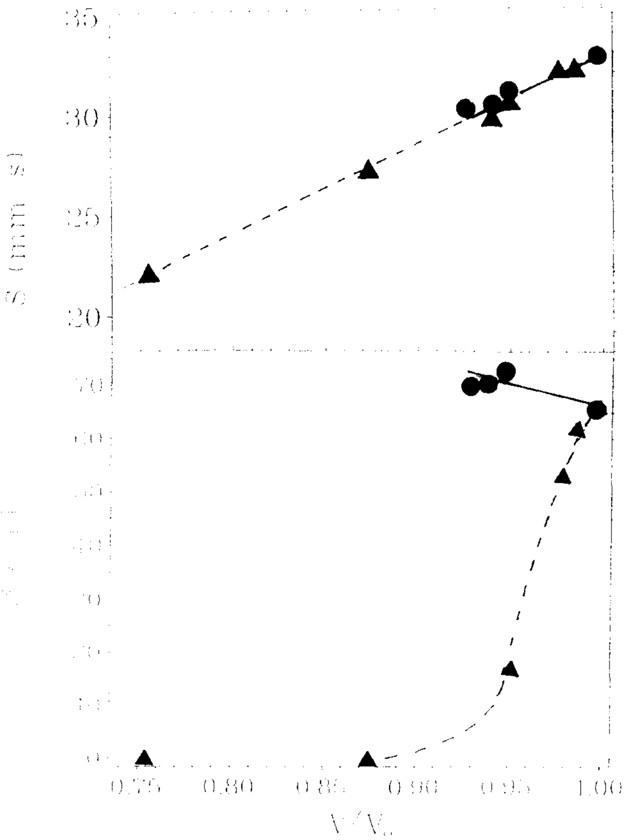

Fig. 11. Variation with volume of isomer shift and hyperfine field as a function of pressure for NpSn$_3$ (circles) and as function of x for the alloy system Np(Sn$_x$Ge$_{1-x}$)$_3$ (triangles).

conduction electrons are merely compressed but that a substantial change in electronic structure does not take place. The value of the shift indicates a trivalent charge state. The hybridization behaviour of the 5f electrons is more clearly reflected in the hyperfine field. Here the difference between a chemical- and a pressure-induced volume change is apparent. If the change in B_{hf} reflects a change in 5f electron hybridization, then the chemical influence on the difference in electron structure between the ligands Sn and Ge is dominant and the pure volume dependence is minor.

At this stage we are left with two conclusions. First, 5f hybridization is clearly present and it is dominated by chemical properties of the ligand. Second, the existing hybridization is insensitive to volume changes (at least up to $\Delta V/V_0 \approx 10\%$). It is likely that we are still not too far away from a localized configuration. The moments found on $NpGa_3$ and $NpIn_3$ (which are less than the free ion value) can be explained satisfactorily by CEF interactions. This does not hold, however, for $NpSn_3$. On the whole, the systematics of electronic structure in $AuCu_3$ intermetallics remain a challenge calling for more data and theoretical studies.

5. Summary and outlook

The high-pressure Mössbauer results presented show that in the heavier lanthanides a delocalization of 4f configurations cannot be induced by the volume changes covered ($\Delta V/V_0 \leqslant 30\%$). This, of course, does not rule out such effects in the lighter lanthanides, especially Ce, or at considerably higher pressures. The configurational instability observed in some Eu compounds is due to valence fluctuations between two (energetically) closely spaced, localized $4f^n$ configurations. This energetic separation is volume dependent. In Np and its compounds (our representative light actinide), valence fluctuations have not been observed. Stable, localized 5f electron behaviour can be seen in the tetragonal NpT_2X_2 compounds. However, the majority of intermetallics studied rather show the formation of more or less wide 5f bands via 5f–5f overlap or 5f–ligand electron hybridization. The following basic picture emerges:

In the NpX_2 cubic Laves phases (excluding 3d transition elements as ligands [1]) the delocalization of 5f electrons is dominated by atomic volume. This is expected for 5f–5f overlap as the major contributor (Hill mechanism). The NpX rock salt compounds are not as localized as one expects from the Hill systematics. Hybridization with ligand electrons leads to the formation of narrow bands. Their width is clearly dependent on volume. In the $AuCu_3$-type intermetallics 5f delocalization is dominated by the chemical nature of the ligand but is nearly independent of volume. We would classify those materials also as narrow band cases.

This general (and surely oversimplified) picture of 5f delocalization in Np is supported by looking (see Fig. 12) for the different series of intermetallics at the variation in hyperfine field (magnetic moment) for various ligands plotted against the atomic volume (or Np–Np separation) at ambient pressure. We have already pointed out that B_{hf} is the sensitive parameter and that the isomer shift will exhibit a smooth behaviour

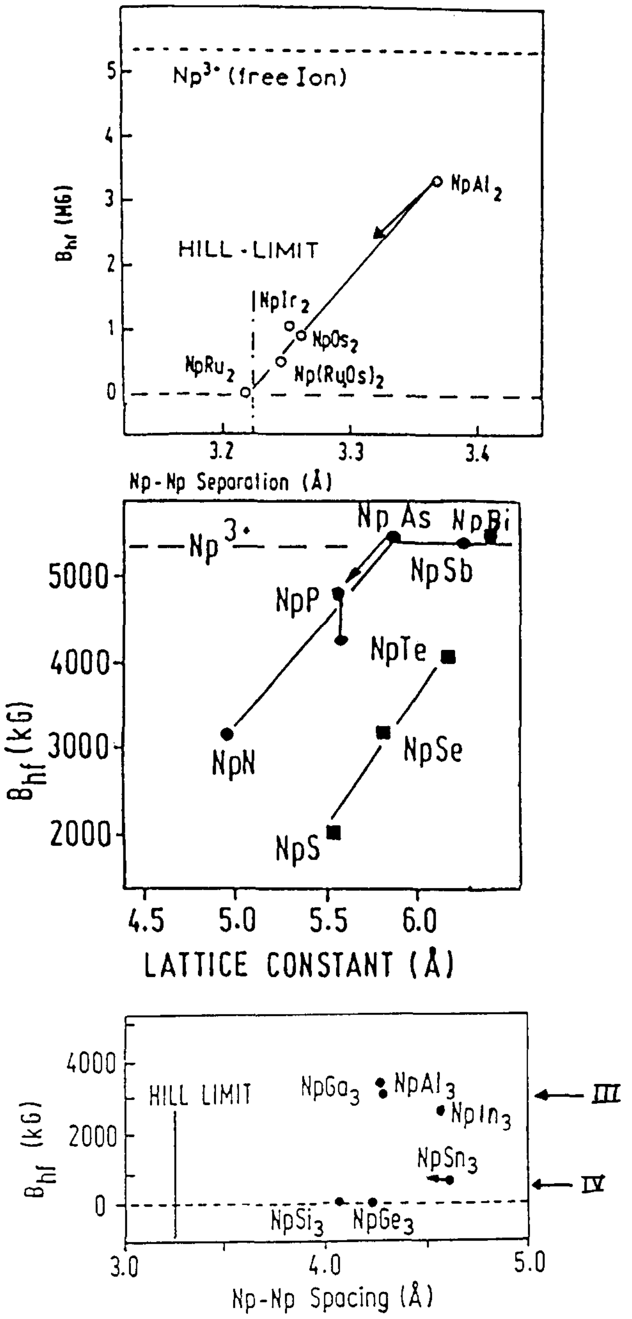

Fig. 12. Dependence of hyperfine field on lattice constant (or Np–Np separation) for various ligands in the cubic Laves phases NpX_2 (top), the rock salt compounds NpX (centre) and the $AuCu_3$ intermetallics NpX_3 (bottom). The roman numbers refer to the chemical group of ligands in the Periodic Table. The pressure dependences for $NpAl_2$, NpAs and $NpSn_3$ are indicated by arrows.

as long as no sudden change in Np charge state occurs. Within the NpX_2 series the total variation is covered by the change in volume. This holds in particular for the quasi-binary alloys $Np(Os_{1-x}Ru_x)_2$. Also, the induction of volume change by external pressure or by a variation of ligand produces practically the same volume coefficient $d\ln B_{hf}/d\ln V$. The Hill limit is crossed smoothly. Creating a similar plot for the NpX materials shows a clear distinction between the pnictide and the chalcogenide ligands. The shift to smaller hyperfine fields is in keeping with the more pronounced covalent character of the chalcogenides. Within the pnictides, however, the variation of B_{hf} is still dominated by volume up to NpAs with $a \approx 5.8$ Å. Then the Np^{3+} free ion value is reached and the hyperfine field cannot increase further. Chemical substitution and applied pressure produce the same result below a lattice parameter of ca. 5.8 Å. Unfortunately, data on a chalcogenide are not available. In the $AuCu_3$ intermetallics one finds a difference in hyperfine field between Group III and Group IV elements but at the same time an independence of volume.

Another subject of interest in this connection is the stability of magnetic phases. The limited Mössbauer results available [13,18] can be summarized as follows. In the NpX_2 Laves phases $NpAl_2$ and $NpOs_2$, we see no changes in magnetic structure with reduced volume. This is expected for the ferromagnetic state as long as the crystal structure is not altered. In the antiferromagnetic Np rock salt compound NpAs a change of magnetic structure is clearly seen to set in at 2 GPa. It is preliminarily interpreted as the transition from the 3*k* up–down structure to the 1*k* four up–four down arrangement which is stable under reduced volume. Recent resistivity data (which cover a wider pressure and temperature range) hint at the presence of a multitude of magnetic transitions in NpAs [19]. Turning to the $AuCu_3$ intermetallics, we find the simple antiferromagnetic structure of $NpSn_3$ to be stable. In $NpIn_3$ and $NpGa_3$ a complex magnetic phase diagram seems to exist. High pressure stabilizes the ferromagnetic spin arrangement. The understanding of volume dependences of exchange and anisotropy in the actinides is a major challenge for the future and without doubt an important one.

Finally, let us look briefly at the situation concerning heavy fermion behaviour in Np intermetallics. The only well established case is $NpBe_{13}$, a magnetic ($T_N \approx 3.5$ K) heavy fermion compound [20]. Mössbauer data at ambient pressure [1] showed a strong dependence of magnetic properties on sample preparation. High-pressure data are not available, mainly owing to the lack of a good sample. In general, the 5f electrons are less hybridized in Np intermetallics than in their U analogues. This becomes apparent when comparing an Np compound with the related (isostructural) U heavy fermion material. Examples are $NpPd_2Al_3 \leftrightarrow UPd_2Al_2$ and $NpNi_2Al_3 \leftrightarrow UNi_2Al_3$ [18,21]. The Np material are antiferromagnets with large (i.e. 'normal') moments and higher ordering temperatures. Perhaps the better search for Np heavy fermion materials is to compare U compounds which have just lost magnetic order with their Np analogues (if they exist at all). The comparison between $NpSn_3 \leftrightarrow USn_3$ points in that direction. Again, this is work for the future.

To conclude, the main problem when discussing differences in volume instabilities of electronic configurations is the lack of systematic magnetic data in the actinides. We surely have not reached the end of the road (which is rather stony); we have just begun to travel.

References

[1] W. Potzel, G.M. Kalvius and J. Gal, in K.A. Gschneidner, Jr., L. Eyring, G.H. Lander and G.R. Chopin (eds.), *Handbook on the Physics and Chemistry of Rare Earths*, Vol. 17, Elsevier, Amsterdam, 1993, p. 539.

[2] C.M. Varma, *Rev. Mod. Phys., 48* (1976) 219.

[3] N. Grewe and F. Steglich, in K.A. Gschneidner Jr., and L. Eyring (eds.), *Handbook on the Physics and Chemistry of Rare Earths*, Vol. 14, Elsevier, Amsterdam, 1991, p. 343.

[4] W. Potzel, *High-Press. Res., 2* (1990) 367.

[5] L.B. Robinson, L.F. Ferguson, Jr., and F. Melstein, *Phys. Rev. B, 3* (1971) 1025.

[6] J.M. Fournier, J. Beille, A. Boeuf, C. Veltier and A. Wedgewood, *Physica B, 102* (1980) 282.

[7] A. Gleissner, W.Potzel, J. Moser and G.M. Kalvius, *Phys. Rev. Lett., 70* (1993) 2032.

[8] A. Gleissner, *Ph.D. Thesis*, Technical University, Munich, 1992.

[9] M.M. Abd-Elmeguid, H. Micklitz, G. Kaindl and D. Wagner, *Phys. Rev. B, 25* (1982) 7055.

[10] I. Nowik, *Hyperfine Interact., 13* (1983) 89.

[11] J. Röhler, D. Wohlleben, G. Kaindl and H. Balster, *Phys. Rev. Lett., 49* (1982) 65.

[12] G.M. Kalvius, W. Potzel, J. Moser, F.J. Litterst, L. Asch, J. Zankert, U. Potzel, A. Kratzer, M. Wunsch, J. Gal, S. Fredo, D. Dayan, M.P. Dariel, M. Bogé, J. Chappert, J.C. Spirlet, U. Benedict and B.D. Dunlap, *Physica B, 130* (1985) 393.

[13] G.M. Kalvius, W. Potzel, S. Zwirner, J. Gal and I. Nowik, *J. Alloys Comp., 213/214* (1994) 138.

[14] P. Wachter, F. Marabelli and B. Bucher, *Phys. Rev. B, 43* (1991) 11136.

[15] H.H. Hill, in W. Miner (ed.), *Plutonium 1970 and Other Actinides*, Metallurgical Society of America, New York, 1970, p. 2.

[16] M.B. Brodsky and R.J. Trainor, *Physica B, 91* 271.

[17] G.M. Kalvius, S. Zwirner, U. Potzel, J. Moser, W. Potzel, F.J. Litterst, J. Gal, S. Fredo, I. Yaar and J.C. Spirlet, *Phys. Rev. Lett., 65* (1990) 2290.

[18] S. Zwirner, *Ph.D. Thesis*, Technical University, Munich, 1994.

[19] V. Ichas, Transuranium Institute, Karlsruhe, personal communication.

[20] G.R. Stewart, Z. Fisk, J.L. Smith, J.O. Willis and M.S. Wire, *Phys. Rev. B, 30* (1984) 1249.

[21] S. Zwirner, J.C. Spirlet, J. Rebizant, W. Potzel, G.M. Kalvius, Ch. Geibel and F. Steglich, *Physica B, 186–188* (1993) 681.