4f Spin Dynamics of Isolated Nd, Pr, and Ce Ions in Simple Metals

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The $4f$ spin dynamics of extremely dilute Nd, Pr, and Ce ions in liquid metals are microscopically observed by the time-differential perturbed γ-ray distribution method. The $4f$ spin rates are dominated by strong mixing exchange interaction in all systems investigated, which is, e.g., reflected by a Kondo-like behavior for Nd systems. The pressure-driven valence transition in dilute *La*Pr alloys is probably of the $4f^2 \rightarrow 4f^1$ type. One has to expect that $4f$ instabilities might occur for all light rare-earth ions in appropriate systems.

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At present, there exists deep theoretical uncertainty in the description of intermediate valence (IV) phenomena (for a review, see Lawrence, Riseborough, and Parks[1]) and their relation to less pronounced $4f$ configurational instabilities which usually are described in terms of Kondo theories (for a review, see Maple, DeLong, and Sales[2]). Hitherto, configurational instabilities (IV and/or Kondo effect) have been found for metallic systems containing Ce, Pr, Sm, Eu, Tm, and Yb ions. In the center of current interest is the behavior of light rare-earth (RE) ions in metals, as reflected by a large number of studies[1,2] in Ce, Sm, and Eu systems and some investigations[2,3] in Pr systems. The interpretation of previous results on Nd systems (e.g., Barberis *et al.*,[4] DeLong *et al.*,[5] and Schmid and Umlauf[5]) has remained in an unsatisfying stage.

Since the $4f$ linewidth is perhaps the most fundamental parameter for both IV and Kondo-like instabilities in dilute and concentrated rare-earth systems, the present work aimed to study the $4f$ spin dynamics of isolated Nd, Pr, and Ce ions in simple metals. Accurate measurements of this elusive quantity are possible by the time-differential perturbed angular γ-ray distribution method (TDPAD)[6-8] following nuclear reactions. The choice of *liquid hosts* allows for a direct extraction of the $4f$ spin relaxation rate τ_J^{-1} from the nuclear relaxation times τ_N observed. Furthermore, the influence of crystal electric field (CEF) effects on the magnetic response of the liquid systems seems to be negligible, which can be formulated as $k_B T$ large compared with the CEF splitting Δ. For solid metallic Nd, Pr, and Ce systems Δ/k_B is ~100 K.[2-8] Additionally, the liquid state permits measurements in alloys over a wide range of concentration. Of particular importance is the possibility to compare the $4f$ spin dynamics for isolated Nd and Ce ions in the same liquid hosts.

The Nd, Pr, and Ce systems were produced by the heavy-ion reactions ^{122}Sn(^{20}Ne, $4n$)^{138}Nd, ^{139}La(α, $4n$)^{139}Pr, and ^{124}Sn(^{16}O, $4n$)^{136}Ce (see Barth *et al.*[7]), respectively. Liquid natural La, liquid Sn, and liquid SnAu and SnBi alloys were used as targets which were enriched in ^{122}Sn for the Nd systems and in ^{124}Sn for the *SnBi*Ce systems. The concentration of the RE ions produced was smaller than 1 ppm. Pulsed ^{20}Ne, ^{16}O, and α beams were provided by the VICKSI accelerator at the Hahn-Meitner-Institut, Berlin. By these reactions the 10^+, $T_{1/2}$ = 350-ns isomer in ^{138}Nd, the 10^+, 2000-ns isomer in ^{136}Ce, and the $\frac{11}{2}^-$, 40-ns isomer in ^{139}Pr were excited and oriented. Spin rotation patterns $R(t)$ (Refs. 6–8) of the decaying nuclear isomers were observed at various γ lines by NaI(Tl) detectors in an external field B_{ext} around 20 kG.

All $R(t)$ spectra yield $k = 2$ for the tensor degree of the nuclear alignment. Figure 1 shows an example of $R(t)$ for *Sn*^{138}Nd (compare Ref. 7 for *Sn*^{136}Ce) and the T dependence of the Larmor frequencies $\omega_L(T) = \hbar^{-1} g_N \mu_N \beta(T) B_{ext}$ for Nd and Ce systems. As shown in Fig. 1(b) by the dashed lines, the paramagnetic enhancement factor $\beta(T)$ (Ref. 7) can be well fitted by the Curie law $\beta - 1 = g_J \mu_B (J+1) B(0)/k_B T$, with $g_J = \frac{8}{11}$ for Nd^{3+} and $\frac{6}{7}$ for Ce^{3+} and $B(0)$ the field at 0 K. The fits yield the nuclear g_N factor $g_N = -0.174(4)$ and $B(0) = 3.51(10)$ MG for the ^{138}Nd systems and $g_N = -0.180(3)$ and $B(0) = 1.79$ MG for the ^{136}Ce systems (compare Ref. 7). If one includes the small contribution to $\beta(T)$ of the first excited $J = \frac{11}{2}$ state of Nd^{3+}, $B(0)$ changes to 3.69(15) MG. For *La*^{139}Pr $g_N = +1.3(1)$ and $B(0) \sim 3$ MG can be estimated, and the τ_N value results as 17(5) ns in liquid La at 1250 K.

The Curie-like behavior of $\beta(T)$ and the $B(0)$ values extracted, which all are smaller but close to the estimated free-ion values,[4,7] support the picture of nearly stable Nd^{3+}, Pr^{3+}, and Ce^{3+} in

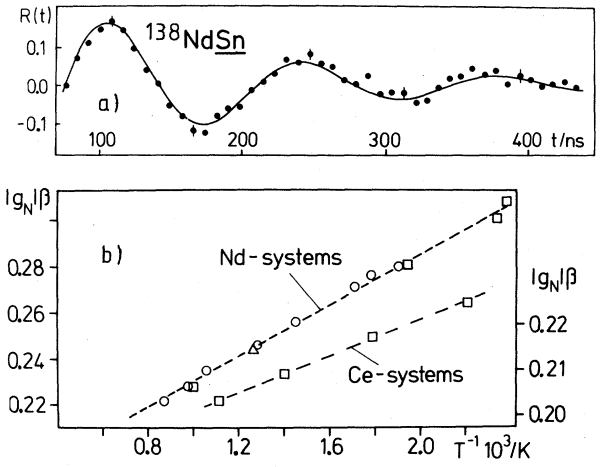

FIG. 1. (a) Spin rotation pattern $R(t)$ of the 884- and 972-keV γ lines of ^{138}Nd in liquid Sn at 1025 K and B_{ext} = 21.30 kG. (b) T dependence of $|g_N|\beta$ of ^{138}Nd (left-hand scale) and ^{136}Ce (right-hand scale) in the liquid hosts Sn (circles), $Sn_{57}Bi_{43}$ (squares), and $Sn_{30}Au_{70}$ (triangles). The dashed lines are explained in the text.

all systems investigated and further validate the assumption that CEF influences are negligible for $T \gtrsim 300$ K.

A more detailed discussion of the various experiments and of the g_N and $B(0)$ values will be given in a forthcoming paper; I now turn to the analyses and discussions of the $4f$ spin dynamics. In liquid metals τ_J^{-1} can be directly extracted from the observed τ_N values, which are derived from the exponential damping of $R(t)$ [see Fig. 1(a)] by[6,7]

$$\tau_N^{-1} = 2(\mu_N/\hbar)^2 J^{-1}(J+1) g_N^2 B^2(0) \tau_J. \quad (1)$$

By the given values above for g_N, $B(0)$, and τ_N, the $4f$ spin rate for LaPr at 1250 K is calculated to be $\tau_J^{-1} = 13(6) \times 10^{12}$ s^{-1}. The τ_N and τ_J^{-1} values for the Nd and Ce systems are given in Figs. 2 and 3.

The results exhibit the following exciting features: (a) The magnitudes of τ_J^{-1} are anomalously high for all systems. The τ_J^{-1} rate for SnNd is about 15 times larger than $\tau_J^{-1} = 0.21 \times 10^{12}$ s^{-1} for SnGd at 700 K.[6] (b) $\tau_J^{-1}(T)$ for SnNd increases much more slowly than predicted by the Korringa relation $\tau_J^{-1} = \text{const} \times T$. (c) The concentration (x) dependencies of τ_J^{-1} turn out to be surprisingly weak. (d) Magnitude, T dependencies, and x dependencies of τ_J^{-1} scale very similarly for Nd and Ce ions in the corresponding systems.

This one-to-one correspondence of the single-ion behavior of Nd and Ce in all these systems

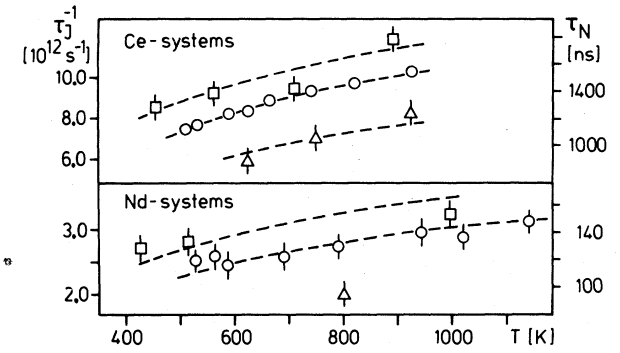

FIG. 2. Temperature dependence of τ_N and τ_J^{-1} for ^{136}Ce (upper part) and ^{138}Nd (lower part) in the liquids $Sn_{57}Bi_{43}$ (squares), Sn (circles), and $Sn_{30}Au_{70}$ (triangles). The data for SnCe and $SnAu$Ce are taken from Ref. 7. The dashed lines represent fits by Eq. (2).

strongly indicates the same relaxation mechanism for the Nd and Ce systems. For many Ce systems, Kondo anomalies and large $4f$ spin rates have been explained by the mixing exchange interaction with large negative couplings. This seems to be established in the low- (e.g., Refs. 2 and 10) and high-temperature regions (e.g., Refs. 10–12) and for Ce in liquid metals[7,12] also. In the following points (i)–(iii) I want to discuss that in fact the $4f$ spin dynamics in all systems under consideration are consistent with the dominance of mixing exchange interaction.

(i) *Magnitude of the τ_J^{-1} rates.*—Starting for simplicity from $\tau_J^{-1} = 4\pi\hbar^{-1}(NJ_C)^2 k_B T$ (for Gd, J_C has to be replaced by J_{sf}), where N is the density of states at the Fermi energy and J_C is the effective mixing exchange integral, the

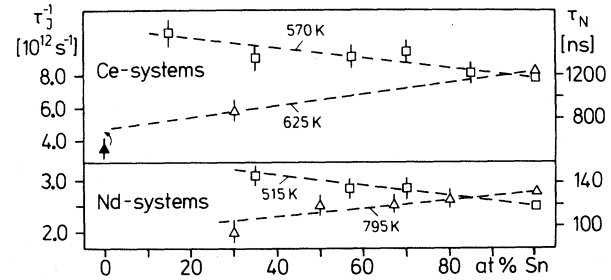

FIG. 3. Concentration dependence of τ_N and τ_J^{-1} for ^{136}Ce (upper part) and ^{138}Nd (lower part) in liquid SnBi (squares) and liquid SnAu (triangles) alloys. Measurement temperatures are given in the figure; the lines serve to guide the eye. The solid triangle represents τ_J^{-1} for Ce in Au at 400 K taken from Ref. 9 and the arrow indicates the extrapolation to 625 K of this value by Eq. (2).

exchange couplings $|NJ_C|$ are found to be 0.082, 0.044, and 0.013 for Ce, Nd (Fig. 2), and Gd (Ref. 6) in liquid Sn at 900 K, respectively. If one analyzes these τ_J^{-1} rates in terms of the classical J_{sf} exchange, $\tau_J^{-1} = 4\pi\hbar^{-1}[(g_J - 1)NJ_{sf}]^2 \times k_B T$, the coupling $|NJ_{sf}|$ is found to be 0.57, 0.16, and 0.013 for Ce, Nd, and Gd in liquid Sn, respectively. An analogous comparison of τ_J^{-1} for Pr in liquid La with the ESR rate for *La*Gd (see Ref. 6) yields $|NJ_C| = 0.08$ and $|NJ_{sf}| = 0.4$ for *La*Pr and $|NJ_{sf}| = 0.028$ for *La*Gd. The analysis in terms of the J_{sf} exchange is shown to be highly unreasonable for the Nd, Pr, and Ce systems, since J_{sf} is expected to be nearly constant throughout the RE series. Instead, these results and the one-to-one correspondence for the Nd and Ce systems indicate the dominance of mixing exchange for the Nd, Pr, and Ce systems. In view of these analyses, the ESR rates observed in Nd systems[4] at low T seem to be dominated by the mixing exchange also.

(ii) *T dependence of τ_J^{-1}.*—Since for the Nd case tractable Kondo theories are not available,[13] I use as a rough extrapolation the high-temperature rate (T_K, $\Delta/k_B \ll T$) calculated for Ce systems,[7,10]

$$\tau_J^{-1} = \frac{4\pi}{\hbar}(NJ_C)^2 k_B T\left[1 + 2(2J+1)NJ_C \ln\left(\frac{k_B T}{D'}\right)\right], \quad (2)$$

for Nd systems also. As shown by the dashed line in Fig. 2, all $\tau_J^{-1}(T)$ data can be well parametrized by Eq. (2), yielding negative NJ_C values of −0.040 for *Sn*Nd, −0.043 for Nd in $Sn_{57}Bi_{43}$, −0.062 for Ce in $Sn_{30}Au_{70}$, −0.070 for *Sn*Ce (Ref. 7), and −0.074 for Ce in $Sn_{57}Bi_{43}$. The cutoff parameter D' (Refs. 7 and 10) is found to be 104 meV for the Nd systems and 120 meV for the Ce systems. Within the approximation Eq. (2), *the degeneracy factor $2J+1$ causes a more pronounced Kondo effect* on $\tau_J^{-1}(T)$. Since this factor is 10 for Nd and 6 for Ce the slightly weaker T dependence for *Sn*Nd compared with *Sn*Ce can be reproduced in spite of the smaller $|NJ_C|$ value for *Sn*Nd.

(iii) *Concentration dependence of τ_J^{-1}.*—To discuss the *trends* of $\tau_J^{-1}(x)$ (Fig. 3), we start from the concept (compare Ref. 14) that the mixing exchange coupling $|NJ_C|$ (a) increases with N of the liquid hosts, which are 0.15 (liquid and solid Au), 0.33 (Sn), and 0.42 (Bi) states/(eV at.-spin) and (b) increases with the lattice pressure acting on the isolated Nd and Ce ions. The lattice pressure might be scaled by the differences of metallic radii between the RE metals ($r = 1.82$ Å for Ce, Pr, and Nd) and the liquid hosts, these being $\Delta r = 0.38$ (liquid and solid Au), 0.20 (Sn), and 0.12 (Bi) Å. Considering, e.g., the $Sn_{100-x}Au_x$ alloys, which are known to behave as nearly free-electron metals for all x, $N(x)$ decreases and the lattice pressure and $|J_C(x)|$ increase with increasing Au content. Thus the influences of these two effects on $\tau_J^{-1}(x)$ partly cancel. For Nd and Ce in SnBi the trends of the two contributions are revised. The "slopes" of the $\tau_J^{-1}(x)$ dependencies for SnBi (positive) and SnAu (negative) suggest that the influence of $N(x)$ on $\tau_J^{-1}(x)$ is slightly larger in all systems shown in Fig. 3. The connection of $\tau_J^{-1} = 3.4(4) \times 10^{12}$ s^{-1} for isolated Ce ions in *solid* Au (Ref. 9) at 400 K to the data in the liquid systems is highly satisfying (Fig. 3).

This work seems to include the first observation of Kondo-like behavior in any Nd system. Studies of the Kondo effect are possible at high T, partly because of the large degeneracy factors of the $4f$ levels. The various τ_J^{-1} data are all dominated by hybridization, yielding estimates of the mixing exchange couplings not only in d metals, in which the bulk of investigations have been performed hitherto, but in simple s and p metals also. Also exciting are the findings (a) that the τ_J^{-1} rates are anomalously high in all systems and (b) that the exchange couplings for Nd ions are only moderately smaller compared with Ce ions in the same hosts. With use of $\tau_J \Delta E = \hbar$, the τ_J^{-1} rates correspond to $4f$ linewidths $\Delta E/k_B$ ranging from 22 K (*Sn*Nd) to about 100 K (*La*Pr).

One is led to argue that the $4f$ levels, not only for Ce ions but also for Pr and Nd (and perhaps for all light RE) ions, are close to the Fermi level. This speculation seems to be consistent with the atomic double-well model, discussed for Ce by Bauchspiess *et al.*[15] The picture, if correct, proposes that a part of the $4f$ electrons of Ce (and Pr and Nd) are located at a large radius near the $5d$ distribution. This part gives rise to strong hybridization, consistent with the results of this work.

In view of the large $4f$ linewidths (compare Refs. 1, 8, and 11) one might suspect that the present systems are not far away from more pronounced $4f$ instabilities described in terms of IV. In fact, dilute *La*Pr alloys[3] reflect pressure-driven IV phenomena at low T.

Wittig[3] posed the fundamental problem of whether the transition in *La*Pr around 230 kbar can be described by a delocalization of both $4f^2$ electrons

($Pr^{3+} \rightarrow Pr^{5+}$) or if alternatively this transition is of the $Pr^{3+} \rightarrow Pr^{4+}$ type. Using the concept of point (iii) and the result[16] that the magnetic response of 1% Pr in Pd is consistent with the $4f^1$ configuration of Pr^{4+}, I suggest that most probably the transitions in *Pd*Pr and *La*Pr are both of the $4f^2 \rightarrow 4f^1$ type.[17] The (high) N values of Pd and La are nearly equal, so that one has to compare the pressure acting on the Pr ions. Since $r = 1.37$ Å for Pd is smaller than $r \sim 1.53$ Å for La at 400 kbar, the lattice pressure for *Pd*Pr seems to be considerably larger than the highest external pressures applied for *La*Pr.[3]

In order to test the possibility of valence transitions in dilute Nd and Pm systems (Pm isotopes are unstable) I plan to study the fate of Nd and Pm ions which are implanted into hosts with small r and high N by the TDPAD method.

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