Observation of Magnetic Instabilities in Dilute Pr, Nd, and Pm Systems

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By application of the perturbed γ-ray distribution method in connection with heavy-ion reactions and recoil-implantation techniques, magnetic single-ion instabilities of Pr, Nd, and Pm ions in small-volume hosts like Ta, W, Os, and Ir have been found. The local susceptibilities observed in the unstable Pr, Nd, and Pm systems are strongly reduced compared to both the stable 3^+ and 4^+ ion behaviors. The data indicate a strong $4f$– conduction-electron hybridization as the common basic mechanism for the instabilities in Ce, Pr, Nd, and Pm systems.

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Hitherto, $4f$ instabilities have been attributed to certain metallic systems containing Ce, Pr, Sm, Eu, Tm, and Yb ions.[1] The $4f$ instabilities in Sm, Eu, Tm, and Yb systems have been usually interpreted in terms of ionic models by consideration of transitions between localized 3^+ and 2^+ states.[2] In contrast to this situation there exists deep uncertainty about the nature of $4f$ instabilities in systems containing Ce ions[1-3] as attested by a wide spectrum of theories ranging from Kondo-type models,[3,4] mixed-valence models,[5] to models emphasizing the itinerant behavior of the $4f$ electrons.[6] Besides spins and degeneracy factors the positions of the $4f$ levels and the strength of the $4f$–conduction-electron hybridization are decisive parameters within these models.[1-6] Unstable Ce systems are often believed to contain essential parts of the more general problems in the region between localized and itinerant f- and d-electron behavior in metallic systems.

In view of the importance of the so-called Ce problem, which might be reflected in the very many experimental and theoretical works on Ce systems, it is highly attractive to try to investigate unstable Pr, Nd, and Pm systems. In principle, the basic parameters which are believed to control the Ce instabilities can be varied most effectively by a change of the $4f$ ion species. However, such experiments are difficult to realize since the trends of the location of the $4f$ levels and the decreasing hybridization (see below) are both directed against the occurrence of $4f$ instabilities in Pr and especially in Nd and Pm systems. This is reflected in the experimental results known hitherto: The number of unstable Ce systems is legion while only a few Pr systems have been driven into anomalous behavior under high external pressure.[7] Weak instabilities have been indicated for Nd ions in Sn by anomalously large $4f$ spin rates[8] and studies of Pm systems are hampered because of the lack of a stable Pm isotope. In this paper we describe attempts to drive Pr, Nd, and Pm ions toward more unstable behavior by implantation of the large $4f$ ions into tightly bound hosts with small atomic volumes, e.g., into Ta, W, Re, Os, Ir, and Pt. Such nonalloying systems can be produced by heavy-ion reactions and the implantation technique, and the magnetic response of the dilute $4f$ ions can be measured by the time-differential perturbed angular γ-ray distribution method.[9] These techniques allow us to probe the magnetic behavior of transition-metal ions under extreme conditions, e.g., in hosts where extremely high positive lattice pressures are acting on the $4f$ ion. Magnetic instabilities have been observed for Pr, Nd, and Pm ions in certain hosts. The various data yield systematic trends of the magnetic behavior as a function of the matrix, temperature, and the $4f$ ion species. Also important is the possibility of comparison of the local susceptibility $\beta-1$ for isolated Pr, Nd, and Pm ions with β for Ce ions[9] in the same hosts. Details of the many implantation experiments and their analyses will be given in a forthcoming paper.[10]

The extremely dilute Pr, Nd, and Pm systems were produced by the heavy-ion reactions ^{124}Sn(^{19}F, $4n$)^{139}Pr, ^{122}Sn(^{20}Ne,$4n$)^{138}Nd, and ^{128}Te(^{19}F, $4n$)^{143}Pm, respectively. Pulsed ^{19}F and ^{20}Ne beams in an energy range 75–100 MeV were provided by the VICKSI accelerator at the Hahn-Meitner-Institut, Berlin. The rare-earth ions were recoil implanted out of thin ^{122,124}Sn and ^{128}Te layers into metallic elements. Simultaneously by these reactions the $I^\pi=\frac{11}{2}^-$, $T_{1/2}=40$-ns isomer in ^{139}Pr, the 10^+, 350-ns isomer in ^{138}Nd, and the $\frac{15}{2}^+$, 10-ns isomer in ^{143}Pm were excited and oriented. They serve as nuclear probes to detect the magnetic hyperfine interaction of the system produced. Spin-rotation patterns $R(t)$ (see Ref. 9) of the decaying isomers were measured at various γ lines in an external field $B_{\rm ext}$ around 2 T, as a function of host and temperature. Figure 1 shows a few examples of $R(t)$ patterns, from which the nuclear Larmor frequency $\omega_{\rm L}$ and spin-relaxation times can be extracted. From the frequencies observed $\omega_{\rm L}(T)=\hbar^{-1}\mu_N \times g_N B_{\rm ext}\beta(T)$, the local susceptibilities[9] $\beta-1$ can be deduced (Figs. 2–4). The dashed lines in Figs. 2–4 indicate the Curie behavior $\beta-1=g_J\mu_{\rm B}(J+1)B(0)/3k_{\rm B}T$ calculated by use of spins J, Landé factors g_J, and magnetic hyperfine fields[9] $B(0)$ for free 3^+ and 4^+ Pr, Nd, and Pm ions,[10] respectively. With use of

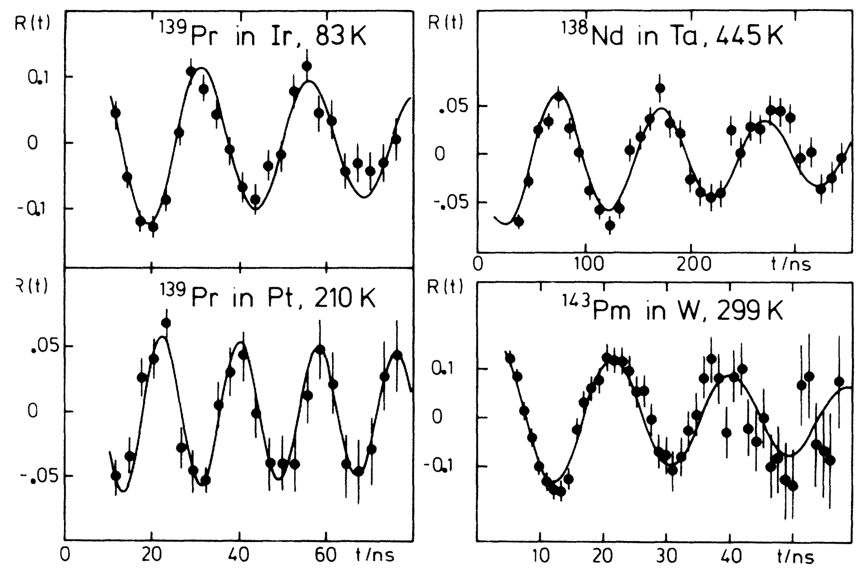

FIG. 1. Spin-rotation patterns of ^{139}Pr, ^{138}Nd, and ^{143}Pm in various hosts at B_{ext} around 2 T. The different Larmor precessions for Pr in Ir and Pt reflect the different β values as shown in Fig. 2.

extrapolated $\langle r^{-3}\rangle$ values,[10] $B(0)$ was estimated to be 435 T for Pm^{3+} and 526 T for Pm^{4+}. Fortuitously, $\beta(T)$ for Nd^{3+} and Nd^{4+} comes out to be almost equal (Fig. 3). The local susceptibilities for, e.g., Pr in Th and Pd, Nd in Sn and Pt, and Pm in Th and Ir are consistent with nearly stable 3^+ systems. An anomalous behavior of $\beta(T)$ is found for Pr in Pt, W, Ta, and Ir, for Nd in Ta, Ir, and W, and for Pm in Ta, W, Re, and Os (Figs. 2–4). Very strongly reduced susceptibilities are found for Pr in W, Ta, and Ir; the remaining susceptibilities are independent of temperature (Fig. 2). As a function of the host matrix, the single ion varies from nearly stable 3^+ to drastically unstable magnetic behavior correlated with very different temperature dependences of β ranging from Curie type to constant.

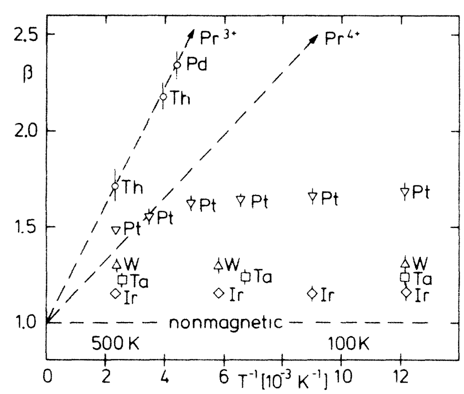

FIG. 2. Local susceptibilities of ^{139}Pr ions as a function of the host matrix and temperature. The dashed lines represent $\beta(T)$ calculated for free 3^+ and 4^+ ions (see text).

As will be discussed in more detail in Ref. 10, such drastic reductions of the susceptibility cannot be explained by crystal electric field effects on β. One essential argument for this is that the $4f$ spin linewidths in the unstable Pr, Nd, and Pm systems exceed some 10^2 K,[10] so that—similar to the situation in strongly unstable Ce systems[1,5-10]—the linewidths seem to be larger than a possible crystal electric field splitting. Thus the data include the first observation of magnetic $4f$ instabilities in Pr, Nd, and Pm systems.

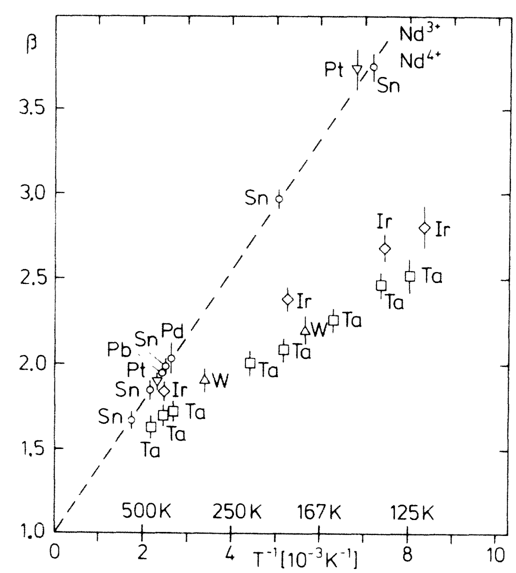

FIG. 3. Nearly stable and unstable systems of dilute Nd ions in various hosts. The dashed line is explained in the text.

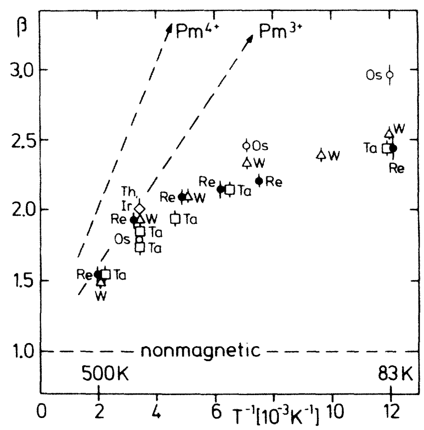

FIG. 4. Local susceptibilities of isolated ^{143}Pm ions in various hosts as a function of temperature.

Of special importance is the finding that the local susceptibilities for all the unstable Pr, Nd, and Pm systems do not fit within the range between neighboring ionic configurations (Figs. 2–4). Even at high temperatures the susceptibilities remain reduced compared to both the stable 3^+ and 4^+ behavior. These results cannot be explained by changes of valence, which are induced by $4f$ core-level shifts alone. This conclusion is inferred from the presence of two magnetic states in the Pr, Nd, and Pm systems, in contrast to Ce systems where the interpretations of magnetic instabilities are severely hampered by the presence of one magnetic state only (see, e.g., Ref. 9).

According to photoemission data in the pure rare-earth metals[11] the energy differences, E_f, between the stable 3^+ configurations and the Fermi level E_F increase drastically from ~ 2 eV for Ce, 3.3 eV for Pr, to 4.7 eV for Nd metal.[11] For Pm metal E_f is estimated to be 5 eV.[12] Within the concept of a Born-Haber cycle[12] a 3^+ to 4^+ transition would occur if E_f is compensated by matrix-dependent $4f$ core-level shifts, which can be estimated by the difference of the heats of solution of the 3^+ and 4^+ states in the various hosts.[9] Such ΔH_s values for Ce in hosts are < 2 eV; the largest shifts occur for Ce in W and in Ta.[9] Since ΔH_s values for Ce, Pr, Nd, and Pm ions in the same hosts are nearly equal,[10] the shifts of the $4f^2$, $4f^3$, and $4f^4$ levels toward E_F are considerably smaller than E_f for Pr and especially for Nd and Pm systems. Thus the experimental results shown in Figs. 2–4 and this analysis within a Born-Haber cycle are both directed against a simple promotional-like picture for the unstable Pr, Nd, and Pm systems.

The various experimental data allow a detailed comparison of the magnetic $4f$ instabilities observed in Pr, Nd, Pm (Figs. 2–4), and Ce systems (see Fig. 2 in Ref. 9). Instabilities for Pr, Nd, and Pm ions have been found in hosts where the Ce ion exhibits nonmagnetic behavior. The degree of demagnetization decreases from Ce, Pr, Nd to Pm in the same host. Besides these trends as a function of the $4f$ ion species in the same host, the data in Ce, Pr, Nd, and Pm systems reflect clear systematic trends of β as a function of the host matrix and of temperature. Basically similar trends are also observed in the $4f$ spin rates of the nearly stable and unstable Ce, Pr, Nd, and Pm systems. Details of this complex comparison will be given in Ref. 10. All these systematic trends and similarities strongly suggest a common basic mechanism for the instabilities in Ce systems and in Pr, Nd, and Pm systems.

As the dominant mechanism, a strong hybridization of $4f$ electrons with conduction electrons and/or ligands is suggested. The implantation of the large $4f$ ions into the tightly bound hosts with small volumes and low compressibility like Ta, W, Os, and Ir might cause a drastic volume reduction of the substitutional[13] $4f$ ion. The volume reduction of the $4f$ cell in these hosts seems to be considerably larger than in any alloying systems. As a consequence, one should expect a drastic increase of hybridization. The effective coupling of the $4f$ mixing is assumed to follow the volume reduction with a power coefficient of about 3–6 (e.g., Refs. 4–6). On this basis one might try to parametrize the Ce, Pr, Nd, and Pm instabilities by high T_K values within Kondo-type theories[3–5] and/or by more delocalized $4f$ shells within bandlike approaches.[6]

Besides a drastic volume reduction, other quantities, e.g., character and band structure of the conduction electrons, might also be essential for the understanding of the degree of stability of a certain $4f$ ion as a function of the host matrix. In contrast to d-metal hosts we have not found any instability in β by implanting Pr, Nd, and Pm ions in s and p host metals. Even Ce in the small Cu host reflects stable behavior.[9] Concerning a possible influence of the host band structure on β, we refer to the more stable behavior of Pr in Pd and Pt relative to β observed in Ta, W, and Ir (Fig. 2) and of Nd in Pt relative to Nd in Ta and Ir (Fig. 3). In these systems the volume reductions of the $4f$ cells are nearly equal. The higher stability observed in the Pd and Pt systems is consistent with an almost filled d band, which thus decreases the density of d states at E_F and/or weakens the f-d hybridization. Basically similar trends for the behavior of UPt_3 and UPd_3 relative to other UX_3 compounds have been discussed by Koelling *et al.*[6]

In conclusion, magnetic $4f$ instabilities of single Pr, Nd, and Pm ions can be produced and investigated in nonalloying systems, where extremely high lattice pressures are acting on the implanted $4f$ ions. Clear systematic trends indicate a common basic mechanism for Ce, Pr, Nd, and Pm instabilities. Strong $4f$ electron mixing is suggested as the dominant mechanism, whereas $4f$ core-level shifts seem to be relatively unimportant. These results provide an improved basis for the testing of the many controversial theories on Ce instabilities.[1-6] The drastic variations of the f count, spin, and degeneracy factor, of the strength of hybridization as a function of the matrix and the $4f$ ion species, and in particular of the locations of the $4f$ levels all might be essential reasons to extend theory from Ce to Pr, Nd, and Pm systems.

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