Formation of Local Magnetic Moments of Ce in Metallic Elements

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The local susceptibility of extremely dilute Ce ions recoil implanted into more than thirty metallic elements is microscopically observed by perturbed angular γ-ray distribution techniques. Many elements in which the single Ce ion reflects intermediate or even nonmagnetic behavior have been found. These results allow correlation of the magnetic Ce-ion behavior with matrix-dependent quantities.

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The formation of local moments in metals is one of the central problems in the field of magnetism. At present there exists deep uncertainty about the matrix (and pressure and temperature) dependence of magnetic instabilities of 4*f*, 3*d*, and 5*f* ions in metallic systems. Large parts of the general problems are reflected in the important example of 4*f* instabilities in dilute and concentrated Ce systems, as attested by several recent papers.[1-5]

In this Letter we try to concentrate on the most essential and general results concerning the formation of local Ce moments in metals, which are implied by microscopic studies of the magnetic single-Ce-ion behavior of extremely dilute Ce ions (concentration <10 ppm) in more than thirty metallic elements. Details of the many implantation experiments and their analyses will be given elsewhere.[6]

^{138}Ce and ^{139}Ce ions were recoil implanted[6-8] out of a thin ^{130}Te layer into metallic elements by the heavy-ion reactions ^{130}Te(^{13}C, 5*n*) and ^{130}Te(^{13}C, 4*n*) using the VICKSI accelerator at the Hahn-Meitner-Institut, Berlin. Spin rotation patterns[7-9] $R(t)$ of the two decaying nuclear isomers[7] in ^{138}Ce ($I^\pi = 10^+$; $g_N = -0.179$) and ^{139}Ce ($\frac{19}{2}^-$; $+0.425$) were simultaneously observed at various γ lines in an external field, B_{ext}, by the time-differential perturbed angular γ-ray distribution (TDPAD) method. Examples for ^{139}Ce in some hosts are shown in Fig. 1, including the concentrated system γ-Ce.

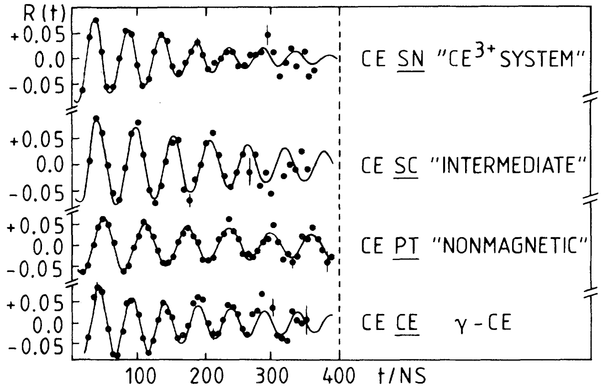

FIG. 1. Spin rotation of the 270-keV γ line of ^{139}Ce in several hosts at ~ 370 K and $B_{\text{ext}} = 24.39$ kG. The different Larmor precessions reflect the different β values as shown in Fig. 2.

From the Larmor frequencies observed (Fig. 1) $\omega_L(T) = \hbar^{-1}\mu_N g_N B_{\text{ext}}\beta(T)$, the local susceptibility[7-9] $\beta - 1$ can be extracted. To suppress crystal-field effects[6-9] on β, we have measured mainly in the high-temperature range around 400 K. The majority of the experimental results are collected in Fig. 2.

According to the β values observed, we classify the Ce systems into three groups: (i) Ce^{3+} systems: Many systems reflect nearly stable Ce^{3+} behavior described by the Curie law $\beta - 1 = g_J \mu_B (J$

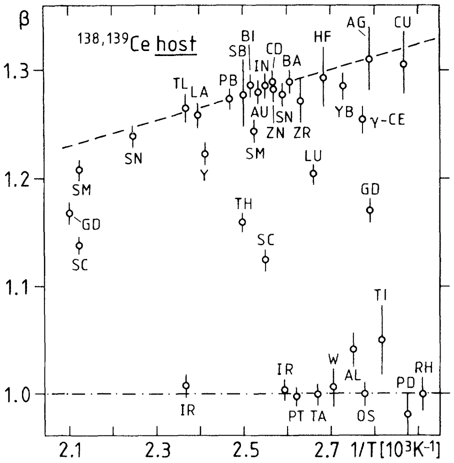

FIG. 2. Local susceptibility of ^{138,139}Ce ions in elements around 400 K. The β values are uncorrected for normal Knight and diamagnetic shifts. For most cases such corrections are smaller than the error bars. Lines are explained in the text.

$+1)B(0)/3k_BT$ with $g_J = \frac{6}{7}$ and with the hyperfine field produced by the $4f^1$ electron at the Ce nucleus at $T=0$, $B(0)$, close to 1.8 MG (dashed line in Fig. 2).[7,9] (ii) Nonmagnetic Ce systems: As an important feature we have found for several systems β equal to 1 (dot-dashed line in Fig. 2) which corresponds to a vanishing $B(0)$. (iii) Intermediate Ce systems: We also have found several new elements in which isolated Ce ions reflect intermediate magnetic behavior between Ce^{3+} and $\beta=1$ (Fig. 2). All $R(t)$ spectra reflect a single ω_L, which proves the dynamic nature of the intermediate systems.[8] The special case Th^{136}Ce is described in more detail in Ref. 8; we note that even at low T, $\beta=1.12$ for *Th*Ce remains far away from $\beta=1$.

The central problem can now be formulated: What kind of matrix dependence causes the very different magnetic single-Ce-ion behavior observed in all these elements? As presented in Fig. 3 we have found two correlations, which reasonably relate the magnetic behavior to matrix-dependent quantities. An empirical two-parameter correlation is shown in Fig. 3(a), where the elements are characterized by the inverse of the metallic radius, $1/r$, and by the density of conduction-electron states at the Fermi level, $N(E_F)$; both quantities are taken for the pure hosts.

Secondly we have tested in Fig. 3(b) the relation of the magnetic behavior to the difference of the heats of solution, ΔH_s, of metallic Ce^{3+} $\{4f^1(ds)^3\}$ and Ce^{4+} $\{4f^0(ds)^4\}$ cells[11] [defined as $3+(M)$ and $4+(M)$ in the inset in Fig. 3(b)] in the various hosts. An extension of the Born-Haber cycle[11,12] to the present case of dilute Ce impurities yields the energy difference between $4f^1$ and $4f^0$ as $\Delta H(\text{Ce metal}) - \Delta H_s$. As discussed in Refs. 11 and 12 the term ΔH(Ce metal) refers to the $4f^1 \rightarrow 4f^0$ transition in pure Ce metal. Thus $\Delta H_s = H_s^{3+} - H_s^{4+}$ [see Fig. 3(b)] might scale the matrix dependence of the relative shifts of the $4f^1$ and $4f^0$ levels. If one places $4f^0$ at E_F, ΔH_s approximately scales the $4f^1$ core-level shifts relative to E_F of the hosts (see Ref. 11). The ΔH_s values were calculated by the semiempirical theory of Miedema, de Châtel, and de Boer.[13,14]

Combining the experimental basis (Figs. 1 and 2) with the correlations in Fig. 3, we would like to infer the following major results.

(a) *Magnetic behavior versus* $1/r$ *and* $N(E_F)$.

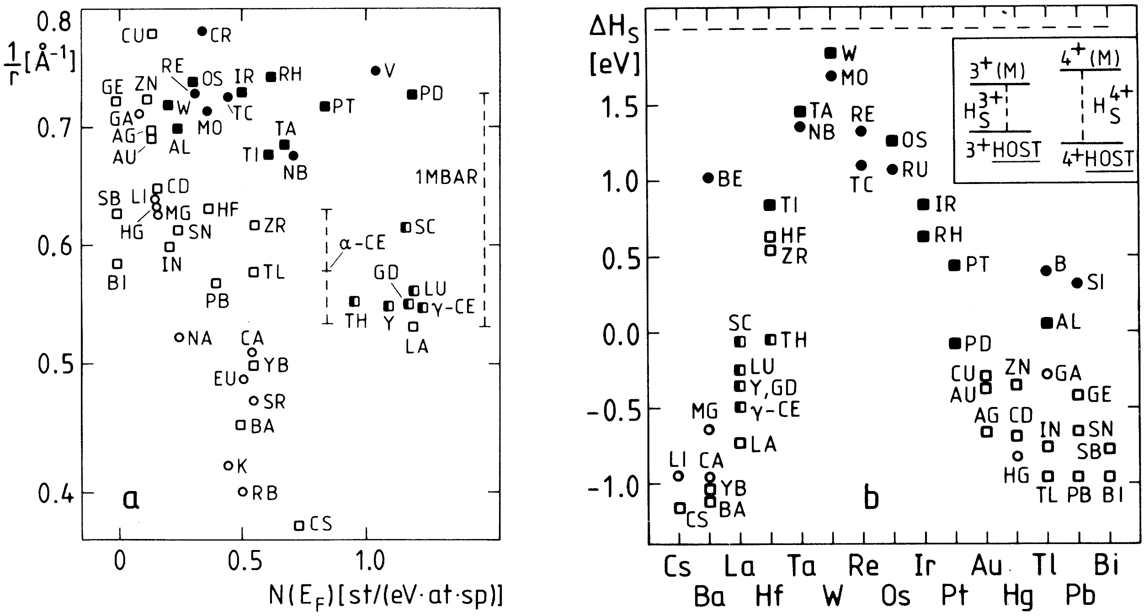

FIG. 3. Correlation of the Ce-ion behavior (a) with $1/r$ and $N(E_F)$, and (b) with ΔH_s (see text). (b) The hosts are arranged according to the groups of the periodic table. The magnetic Ce-ion behavior is indicated by the symbols: open squares, Ce^{3+}; half-filled squares, intermediate; and filled squares, nonmagnetic. For the basis of these assignments and borderline cases see Fig. 2. The circles present predictions for 3^+ (open circles) and nonmagnetic (filled circles) Ce behavior in some hosts. The right-hand dashed line in (a) indicates that an external pressure as high as 1 Mbar is needed to compress La to r of Pd (see also Ref. 9). The other dashed line in (a) roughly scales the $1/r$ variation at the Ce place in metallic concentrated Ce systems (Ref. 10) without specifying $N(E_F)$ values. Inset and dashed line in (b) are explained in the text.

—The data in Fig. 3 are consistent with the rule that the degree of the $4f$ instability (within an ionic two-configurational picture this is the effective valence[1]) increases with both increasing $1/r$ and $N(E_F)$. The nonmagnetic Ce systems are located in the upper right part of Fig. 3(a), the 3^+ systems in the lower and left parts, and the intermediate systems in the borderline region (roughly about a line through Cu-Al-Lu). If one roughly scales the lattice pressure by the variation of $1/r$ relative to $1/r$ of γ-Ce as a reference, Fig. 3(a) contains systems with extremely large positive and negative lattice pressures acting on the isolated Ce ion. The widely used interpretation (e.g., Refs. 1–3) that the degree of the $4f$ instability is mainly governed by the lattice pressure is only applicable if one compares systems with nearly equal $N(E_F)$ values.

(b) *Magnetic behavior versus* ΔH_s.—As shown in Fig. 3(b), nearly all Ce^{3+} systems are located in the lower part of the figure, all nonmagnetic systems in the upper part, and the intermediate systems in the region between the Ce^{3+} and nonmagnetic systems. With respect to the uncertainties[6,13,14] in calculating ΔH_s values, Hf and Zr cannot be regarded as severe exceptions. The data imply that the formation of local Ce moments in elements is strongly correlated with the one parameter ΔH_s. Also exciting is the feature that the transition from magnetic to nonmagnetic systems occurs around $\Delta H_s = +0.4 \pm 0.4$ eV [Fig. 3(b)]. This value is almost independent of the particular choice of parameters used for the calculations of ΔH_s (see Ref. 14). If one relates the occurrence of the magnetic instabilities to core-level shifts alone [see point (d) below for a discussion of this critical assumption], this finding is not consistent with the estimated ΔH(Ce metal) ~ 2 eV,[11,12] which would shift the transition to about the dashed line in Fig. 3(b) at $\Delta H_s \sim 2$ eV. On this basis the correlation Fig. 3(b) is consistent with the interpretation of photoemission data by Hüfner and Steiner,[15] who suggest that the $4f^1$ level in Ce metal is located close to E_F.

(c) *Intermediate Ce systems.*—The intermediate Ce-ion behavior found in Sc, Y, γ-Ce, Gd, Lu, and Th and perhaps found in the borderline cases Al, Ti, and Sm (see Fig. 2) fits reasonably the trends given in both Figs. 3(a) and 3(b). Especially for the rare-earth-like hosts [nearly equal values of $N(E_F)$], we have found intermediate single-Ce-ion behavior in just the $1/r$ range where many concentrated Ce systems reflect $4f$ instabilities also [Fig. 3(a)]. These findings indicate that the occurrence of $4f$ instabilities in concentrated Ce systems is mainly induced by the single-Ce behavior (see also Refs. 1 and 8). Furthermore the data imply a clear concept for searching for new intermediate Ce systems. In alloys of a "black" with a "white" host (see Fig. 3, e.g., CuAl, SnAl, AuPt alloys) the magnetic single-Ce-ion behavior must change drastically as a function of concentration.

(d) *Nonmagnetic Ce systems.*—For the first time we have found nonmagnetic dilute Ce systems within high accuracy (Fig. 2) which have to be compared with controversially interpreted nonmagnetic concentrated Ce systems,[1,2,10,16] where, as far as we know, the macroscopic susceptibility remains considerably enhanced[16] relative to diamagnetic reference systems. This aspect and the successful relation to the picture of core-level shifts [Fig. 3(b), point (b)] might favor the interpretation that Ce^{4+} (unoccupied $4f^1$ level above E_F) exists in dilute systems. However, such an interpretation remains uncertain, since the $4f$–conduction-electron hybridization is disregarded within the concept of the Born-Haber cycle.

In fact, the experimental data are also consistent with the idea that the degree of the Ce instability is mainly governed by the strength of the $4f$–conduction-electron hybridization. For the matrix dependence[9] one might assume as rough trends that hybridization increases with increasing $1/r$ and $N(E_F)$ which leads to one possible interpretation[17] of the correlation Fig. 3(a). Within this interpretation nonmagnetic Ce systems might have extremely large Kondo temperature[3,5] ($T_K \gg 500$ K) or extremely large $4f$ linewidths, so that the $4f^1$ electron is completely delocalized.[4]

(e) *Methodological implications.*—On the basis of the experimental ingredients—heavy-ion reactions, TDPAD method, and especially the implantation technique—we have realized that the magnetic behavior of isolated Ce ions can be studied microscopically in simple hosts across large parts of the periodic table [Fig. 3(b)]. Of special importance is the possibility of investigating the fate of Ce ions under extreme conditions, including a number of nonalloying systems. This exciting feature is reflected in Fig. 3(a) in the large $1/r$ variation of the hosts which considerably exceeds the $1/r$ variation of Ce ions in concentrated systems and the $1/r$ variation induced by external pressure. It is also reflected in the large variation of the ΔH_s scale in Fig. 3(b). Essential parts of the major results (a) to (d) depend on just the experiments where Ce ions are probed under extreme conditions.

It seems possible that recoil implantation and TDPAD can be applied more generally for aimed studies of the formation of, e.g., local Pr, Nd, Sm, Eu, Tm, and Yb moments as a function of the matrix. In fact, very recently we have found a matrix in which isolated Nd ions reflect drastic 4*f* instabilities; details will be published elsewhere.

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