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Spin fluctuations of trivalent Sm ions in γ-Ce, α-Ce, and La

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Strong reduction in the local susceptibility was found for Sm impurities in metallic hosts. This was achieved by implanting Sm ions in an extremely dilute concentration into cerium and lanthanum. In the γ and α phases of cerium, the Ce and Sm ions show essentially the same behavior, although their ionic properties differ considerably. The observed demagnetization in these hosts can be described by assuming the Sm ion to be in the Kondo regime of the Anderson model.

Sm belongs to those few rare earths which are energetically susceptible to valence fluctuations,[1] and many valence-fluctuating Sm compounds have been discovered. Several attempts were made to find systems in which Sm ions are controlled by spin fluctuations; however, only a few compounds of this nature are known today. Kondo-like behavior for Sm in (La,Sm)Sn_3 was established by resistivity measurements and an anomalous initial depression of the superconducting transition temperature was found.[2] Recently, it was suggested that $SmYbB_6$ compounds may exhibit the Kondo effect.[3] Extremely dilute concentrations of Sm ions in many metals were investigated by the perturbed angular distribution (PAD) method,[4] but no Kondo system was found.

Studying the magnetic behavior of extremely diluted Sm ions in Ce and La by PAD, we found strong reductions in the local susceptibility compared to the local susceptibility for a stable Sm^{3+} configuration. The demagnetization effect increases going from the γ phase to the α phase of the Ce host, quite similar to the magnetic behavior of the host itself.[5] In La the demagnetization effect for Sm ions is even larger than in Ce, although there is no indication for an anomalous depression of the superconducting transition temperature in dilute Sm-La alloys.[2] The Ce impurity in La is known to exhibit only a weak deviation.[6] We argue in the following that Sm in Ce and La metals have to be treated as Kondo systems.

A distinction between the Kondo regime and the valence-fluctuation regime may be deduced within the framework of the Anderson model:[1] The competing quantities are the transition energies E between neighboring ground-state multiplets of different $4f$-electron occupancy and the strength of hybridization Γ between $4f$ electrons and the conduction electrons which act as a reservoir. Now the regime

$$\Gamma/E \ll 1 \tag{1}$$

is regarded as the Kondo regime. The energy scale for the thermodynamic properties is set by the Kondo temperature[1,7]

$$k_B T_K \approx D \exp[-\pi E/(2J+1)\Gamma] , \tag{2}$$

with an appropriate width D of the occupied part of the conduction electron band. Valence fluctuations are possible as soon as $\Gamma/E \approx 1$ is reached, and the energy scale is set by the fluctuation temperature $k_B T_f \approx (2J+1)\Gamma$.[8]

The $4f$ transitions are observable in x-ray photoemission spectroscopy (XPS) and Bremsstrahlung isochromat spectroscopy (BIS) and differ in Sm and Ce ions considerably concerning their energetics. For Ce, the $4f^1 \rightarrow 4f^0$ transition below the Fermi energy E_F is relevant for its properties. For Sm it is the $4f^5 \rightarrow 4f^6$ transition above E_F from which a $4f$ instability may arise as well. In the limit of large $4f$-electron Coulomb interaction the positions of the transitions relative to the Fermi level determine the energies E.[9] When going from γ- to α-Ce, i.e., with decreasing volume, the hybridization width Γ increases for Ce, whereas E was found to be nearly constant,[9] thus the Kondo temperature according to Eq. (2) is varied by the variation of Γ. For the essentially trivalent Sm ions, we expect the decreasing host volume to stabilize the trivalent configuration by driving the $4f^6$ configuration further away. However, the increasing hybridization strength counteracts by increasing a possible Kondo temperature. Experiment has to reveal whether hybridization can gain superiority.

For our measurement we have used the 7^- isomer of ^{142}Sm($T_{1/2}=170$ ns, $g=0.06$) (Ref. 4) produced in the ^{126}Te(^{20}Ne,$4n$) reaction. The ^{20}Ne beam of 90 MeV from the VICKSI heavy-ion accelerator facility at the Hahn-Meitner-Institut was pulsed at a repetition time of 2 μs. The excited ^{142}Sm nuclei were implanted by their recoil energy out of the 1.2 mg/cm^2 thick isotopically enriched Te foil, into Ce samples up to a depth of 2 μm, ensuring that only bulk properties were measured. The samples were mounted on a cold plate, that was temperature controlled by a continuous He-flow cryostat between 50 and 300 K. Pure α-Ce was prepared from material with 99.999% nominal purity by applying 13 kbar pressure at 300 K, cooling down to 78 K, releasing the pressure, and mounting on the precooled cold plate using an air lock held at 78 K. In order to achieve a sufficiently high precision a large external magnetic field $B_{\text{ext}} = 9.64(1)$ T from the superconducting split pair magnet SULEIMA was applied. The local susceptibility was derived from the local magnetic field, $B_{\text{loc}}(T) = [1 + X_{\text{loc}} \times (T)] B_{\text{ext}}$, where $(1+X) = \beta$ is also called the paramagnetic enhancement factor.[10] The values of β were extracted from the Larmor precession frequency of the nuclear magnetic moment in the local field. The probability of creating lattice defects in the near neighborhood of the probe ion is very small and radiation damage may influence the damping of the Larmor precession spectra only slightly.[4] Larmor precession spectra and parts of the data were presented as a conference contribution,[11] the complete results are plotted in Fig. 1.

A calculation[10,12] of the paramagnetic enhancement factor of free Sm ions has to take into account the low-lying first excited states of Sm^{3+}, $\Delta E/k_B = 1600$ K, and of Sm^{2+}, $\Delta E/k_B = 400$ K. These results for the whole temperature range are shown in Fig. 1 as solid lines. Accompanying the lines are our data for ^{142}Sm implanted into Pt and Yb. They fit well the free ion behavior of Sm^{3+} and Sm^{2+}, respectively. For the measurements at lower temperatures, where $\Delta E \gg k_B T$, the general expression for β as presented in Ref. 10 can be simplified to

$$\beta(T) = 1 + \tfrac{2}{3}\mu_B^2\langle r_f^{-3}\rangle\{[g_J J(J+1)\langle J\|N\|J\rangle]/k_B T + (2J+2)(2J+3)\langle J+1\|\Lambda\|J\rangle\langle J+1\|N\|J\rangle/\Delta E + \dots\}\,. \tag{3}$$

Here, g_J is the atomic g factor and $\langle J+1\|\Lambda\|J\rangle$, $\langle J\|N\|J\rangle$, and $\langle J+1\|N\|J\rangle$ are the reduced matrix elements of the magnetic moment and the angular part of the magnetic hyperfine operator. In Eq. (3) the second term reflects a Curie-like behavior of the ground-state multiplet and the third term describes the temperature-independent Van Vleck paramagnetism. For trivalent Sm ions, we have a $^6H_{7/2}$ ground-state multiplet with $g_J = \frac{2}{7}$. Taking $\langle r_f^{-3}\rangle = 6.796$ a.u. (Ref. 13) and including a core polarization field B_{core} of 18 T,[14] we expect the hyperfine field

$$B(0) = 2\mu_B\langle r_f^{-3}\rangle\langle J\|N\|J\rangle J + B_{\text{core}}$$

of the ground state to be 347 T.

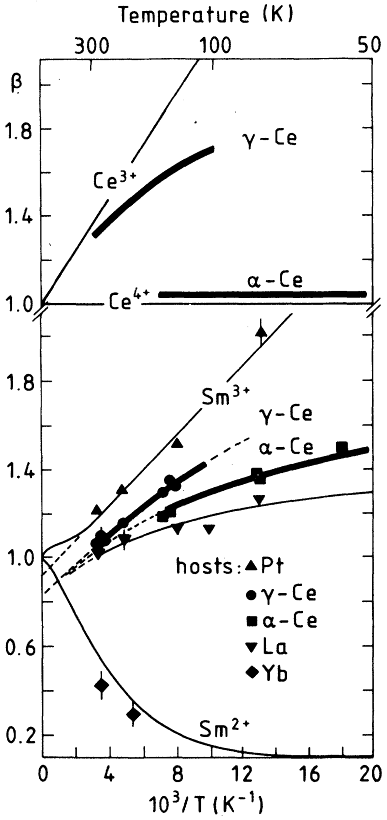

FIG. 1. Lower part: Temperature dependence of the paramagnetic enhancement factor β for Sm implanted into Pt, γ-, α-Ce, La, Yb. The solid lines Sm^{2+} and Sm^{3+} indicate the calculations according to Ref. 10. The measured values for ^{142}Sm in γ-, α-Ce, and La are fitted to Eq. (3), where T is replaced by $(T+\theta)$. Upper part: For comparison, the β values for pure Ce are plotted taken from Ref. 5. Ce ions behave qualitatively equal to Sm ions although quantitatively a difference is obvious, attributable to the different number of $4f$ electrons.

The measured values for γ-Ce and α-Ce, inserted in Fig. 1, resemble essentially trivalent behavior. The observed reductions of the local susceptibility are moderate for γ-Ce, stronger for α-Ce, and even stronger for La. Only poor fits to the data are obtained assuming crystal electric fields (CEF) as a source for the demagnetization. Unreasonably high CEF splittings of 400, 700, and 2000 K are required for γ-Ce, α-Ce, and La, respectively.[11] In addition, there is no indication of even weak CEF effects for trivalent Sm impurities in a large variety of metallic host.[4,12] Our measurement in Pt serves as an example. Equation (3) can be fitted to the data, if a Weiss temperature is introduced to account for the demagnetization effect, thus T is replaced by $(T+\theta)$. Best fits for Sm in Pt, γ, α-Ce, and La are obtained, when in all cases the magnetic hyperfine field $B(0) \approx 347$ T, but the excitation energy to the first excited state $^6H_{7/2}$ changes from (1600 K) k_B for Pt to about (900 K) k_B in all cases, where demagnetization is observed. Thus the demagnetization seems to be accompanied by a reduction of the $4f$-electron exchange and spin-orbit coupling. A discussion of a similar variation in multiplet splitting found in Ce compounds is given in Ref. 15. The Weiss temperatures are listed in Table I.

The deciding result of our experiment is the fact that in the smaller lattice of α-Ce, Sm shows stronger demagnetization effects than in γ-Ce. This cannot simply be attributed to increasing charge fluctuations involving the nonmagnetic divalent Sm, since Sm^{2+} ions are of larger size. Squeezing an initially divalent Sm ion, either by externally applied or "chemical" pressure, we expect a relocalization of the f-electrons in the trivalent configuration. At a borderline, where both configurations become degenerate, valence fluctuations occur. Such a valence transition was observed for example in SmS.[20] Biedermann and coworkers[12] have implanted Sm ions in many different metals and found divalent behavior in metals with large lattice parameters like Yb and trivalent behavior for metals with small lattice parameters like Pt. Our results for γ- and α-Ce do not match these volume systematics. In addition, estimates of the transition energy E, we will give below, place Sm in these hosts well beyond that borderline and the effect of hybridization on the trivalent Sm ion has

TABLE I. Measured Kondo-temperatures T_K and calculated widths Γ and transition energies E.

Probe	Host	V_0 (Å^3/atom)[a]	T_K (K)	Γ (eV)	E (eV)[b]
Sm (r_f = 0.524 Å)[c]	α-Ce	28.1	67(6)	0.09	1.1
	γ-Ce	34.4	28(7)	0.06	0.8
	La	37.4	115(15)	0.05	0.5
Ce (r_f = 0.607 Å)[c]	α-Ce	28.1	≈2500[d]	0.40	2[e]
	γ-Ce	34.4	87[f]	0.17	2[e]
	La	37.4	27[g]	0.15	2.1

[a] Reference 16.

[b] Calculated according to Eq. (2), where $D = 3$ eV was taken (Ref. 17).

[c] Reference 13.

[d] References 18 and 19.

[e] From spectroscopic data Ref. 9.

[f] Reference 5.

[g] Reference 6.

to be considered.

These qualitative considerations emphasizing the importance of spin fluctuations can be based on more quantitative criteria, comparing the Sm and Ce behavior (Fig. 1). Therefore, we take the measured Weiss temperatures as rough estimates of the Kondo temperature.[21]

The relation between T_K, E, and Γ, as given in Eq. (2), is strictly valid only for the Ce ion[7] (transition between $4f^1\,{}^2F_{5/2}$ and $4f^0\,{}^1S_0$). However, for our estimate of Sm ($4f^5\,{}^6H_{5/2}$ and $4f^6\,{}^7F_0$), we neglect a possible dependence of the hybridization matrix element on the momentum projection and proceed with Eq. (2). Using the parametrization in the Kondo-lattice-volume-collapse model,[18] we assume E to be 2 eV for γ-Ce from spectroscopic data.[9] With the measured Kondo temperature $T_K = 87$ K (Ref. 5) we obtain the hybridization width Γ to be Γ(γ-Ce) = 0.17 eV. From the value of Γ for γ-Ce we estimate the hybridization width for other systems by scaling the d-f-hybridization matrix elements $V \sim r_f^4/r_0^6$ obtained from muffin-tin orbital theory.[22] Here, r_f is the radius of the $4f$ shell and r_0 is the atomic radius related to the atomic volume $V_0 = (4\pi/3)r_0^3$. With the assumption of the same ($5d6s$) conduction electron density of states for these rare earths Γ of element A is obtained from Γ of element B: $\Gamma(A) = \Gamma(B)V_0^4(B)r_f^8(A)/V_0^4(A)r_f^8(B)$ and for the impurity A in the host B we scale with geometrically averaged volumes: $\Gamma(A\underline{B}) = \Gamma(A)[V_0^2(A)/V_0^2(B)]$. The results for the widths derived from the fixed value Γ(γ-Ce) are tabulated in Table I. In the next step we calculate E from these values of Γ according to Eq. (2).

We may now test the reliability of the obtained values for E by comparing with values obtained from a completely different method. We estimate E using the Born-Haber-cycle explained in detail in Ref. 23. Within this cycle the energy differences between different valence states of $4f$ ions in metals are estimated comparing differences in the energies of the free ion states, their cohesion energies[24] and heat of formations for the alloys.[25] For Sm in γ-Ce we obtain: $E = 1$ eV, for Sm in La: $E = 0.8$ eV, and for Ce in La: $E = 2.2$ eV, in reasonable agreement with the values in Table I.

Considering the uncertainties in the above estimates, the values of Table I have to be taken with care. However, they underline the possible mechanism for the observed demagnetization effects: It is the decrease in E with increasing volume, typical for the Sm ion, which competes with the decrease of Γ and leads to demagnetization effects larger in La than in γ-Ce, whereas in the smaller α-Ce the hybridization strength overcomes the increase of E and dominates the magnetic behavior. Thus, the magnetic behavior of the pure as well as of the substituted systems discussed are described consistently within the spin fluctuation picture.

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[1] A. M. Tsvelick and P. B. Weigmann, Adv. Phys. **32**, 453 (1983).

[2] S. Bakanowski, J. E. Crow, and T. Mihalisin, Solid State Commun. **22**, 241 (1977); L. E. DeLong, R. W. McCallum, W. A. Fertig, and M. B. Maple, Solid State Commun. **22**, 245 (1977); L. E. DeLong, M. B. Maple, R. W. McCallum, L. D. Woolf, R. N. Shelton, and D. C. Johnston, J. Low Temp. Phys. **34**, 445 (1979).

[3] B. Liu, M. Kasaya, F. Iga, and T. Kasuya, J. Magn. Magn. Mater. **47/48**, 472 (1985).

[4] D. Riegel and K. D. Gross, in *Nuclear Physics Applications on Material Science*, edited by E. Recknagel and J. C. Soares, Nato Advanced Study Institute Series E (Kluwer Academic Publishers, Dordrecht, 1988), p. 327.

[5] H. H. Bertschat, C. Broude, E. Dafni, F. D. Davidovsky, M. Hass, and P. M. S. Lesser, Solid State Commun. **47**, 525 (1983); H. H. Bertschat, H.-E. Mahnke, E. Dafni, F. D. Davidovsky, and M. Hass, Phys. Lett. **101A**, 507 (1984).

[6] A. S. Edelstein, L. R. Windmiller, J. B. Ketterson, G. W. Crabtree, and S. P. Bowen, Phys. Rev. Lett. **26**, 516 (1971); T. A.

Thiel, M. Böttcher, and E. Gerdau, Hyperfine Interact. **36**, 65 (1987).

[7] B. Coqblin and J. R. Schrieffer, Phys. Rev. **185**, 847 (1969).

[8] N. Grewe, J. Magn. Magn. Mater. **47/48**, 20 (1985).

[9] J. W. Allen, S. J. Oh, O. Gunnarsson, K. Schönhammer, M. B. Maple, and M. S. Torikachvili, Adv. Phys. **35**, 275 (1986).

[10] C. Günther and I. Lindgren, in *Perturbed Angular Correlations,* edited by E. Karlsson, E. Matthias, and K. Siegbahn (North-Holland, Amsterdam, 1964), p. 357.

[11] W. Müller, H. H. Bertschat, H. Haas, H.-E. Mahnke, and B. Perscheid, in *Theoretical and Experimental Aspects of Valence Fluctuations and Heavy Fermions,* edited by L. C. Gupta and S. K. Malik (Plenum, New York, 1987), p. 441.

[12] K. Biedermann, Ph.D. thesis, Freie Universität, Berlin, 1987; K. Biedermann, L. Büermann, M. Luszik-Bhadra, G. Netz, and D. Riegel, Wissenschaftlicher Ergebnisbericht, Hahn-Meitner-Institut, Berlin, Report No. HMI-B-Nr. 420, 1984, p. 170.

[13] A. J. Freeman and J. P. Desclaux, J. Magn. Magn. Mater. **12**, 11 (1979).

[14] R. E. Watson and A. J. Freeman, in *Hyperfine Interactions,* edited by A. J. Freeman and R. B. Frankel (Academic, New York, 1967), p. 53.

[15] C. Laubschat, W. Grentz, and G. Kaindl, Phys. Rev. B **36**, 8233 (1987).

[16] K. A. Gschneidner, Jr., in *Physical Properties and Interrelationships of Metallic and Semimetallic Elements,* edited by F. Seitz and D. Turnbell, Solid State Physics, Vol. 16 (Academic, New York, 1964), p. 275.

[17] We have taken a width of 3 eV for the occupied part of the conduction electron band. Values between 2 and 3 eV are given in the literature, e.g., W. E. Pickett, A. J. Freeman, and D. D. Koelling, Phys. Rev. B **23**, 1266 (1981); in Ref. 18.

[18] J. W. Allen and R. M. Martin, Phys. Rev. Lett. **49**, 1106 (1982); R. M. Martin and J. W. Allen, J. Magn. Magn. Mater. **47/48**, 257 (1985).

[19] J. Röhler, D. Wohlleben, J. P. Kappler, and G. Krill, Phys. Lett. **103A**, 220 (1984).

[20] V. A. Shaburov, A. E. Sovestnov, and O. I. Sumbaev, Phys. Lett. **49A**, 83 (1974).

[21] J. Lawrence, Phys. Rev. B **20**, 3770 (1979).

[22] W. A. Harrison, *Electronic Structure and the Properties of Solids* (Freeman, San Francisco, 1980), p. 504; O. K. Anderson, Phys. Rev. B **12**, 3060 (1975).

[23] P. F. de Châtel and F. R. de Boer, in *Valence Fluctuations in Solids,* edited by L. M. Falicov, W. Hanke, and M. B. Maple (North-Holland, Amsterdam, 1981), p. 337.

[24] B. Johansson, Phys. Rev. B **20**, 1315 (1979).

[25] A. K. Niessen and A. R. Miedema, CALPHAD: Int. Res. J. Calc. Phase Diagrams **7**, 51 (1983).