Observation of Magnetism and Kondo Effect for Sc Ions in Metallic Hosts

J. Kapoor, J. Andres, Yi Li, A. Metz, C. Polaczyk, and D. Riegel
Hahn-Meitner-Institut Berlin GmbH, 14109 Berlin, Germany

W. D. Brewer
Fachbereich Physik, Freie Universität Berlin, 14195 Berlin, Germany
(Received 17 October 1995)

By applying perturbed angular γ-ray distribution methods we have explored the possible occurrence of magnetism for Sc ions implanted into metallic hosts. Strongly host-dependent magnetic behavior was found for Sc in alkali metals. The local susceptibility reflects predominantly orbital contributions and shows a maximum as a function of temperature, both of which are consistent with a nearly localized, ionic $3d^1$ one-electron configuration. These features are similar to certain $4f^1$ Ce systems. We compare to theory within the framework of Kondo models and local spin density calculations.

PACS numbers: 75.20.Hr, 75.30.Cr, 76.30.Fc, 76.80.+y

The formation of local magnetic moments and the problem of d electron localization has been intensively studied for $3d$ impurities in solid hosts [1]. Up to now, the occurrence of local magnetic $3d$ moments in metallic systems was restricted to certain $3d$ ions, i.e., essentially to Cr, Mn, Fe, Co, and Ni. Hitherto, local magnetic moments for Sc ions have not been observed in any metallic host. Even in semiconductors, the finding of magnetic Sc ions is a rare event [2]. To some extent, these trends in the occurrence of magnetism seem to be related to variations in the $3d$ linewidth. Compared to ions from the middle and end of the $3d$ series, the hybridization of d electrons with conduction electrons and/or ligands is much stronger for Sc, due to the larger ratio of $3d$ shell volume to the impurities' Wigner-Seitz cell volume. Large $3d$ linewidths are one essential reason why atomic correlations and local magnetism are hard to detect for Sc ions in metallic systems. The weak itinerant magnetism observed in the compound $ScIn_3$ [3] is presumably caused by rather coincidental band structure effects.

We have explored the possible occurrence of local magnetism of Sc ions in metallic hosts using recoil implantation techniques combined with the microscopic sensitivity of a nuclear probe measurement. In particular, we have studied nonalloying systems with extreme differences between the properties of the probe and host atoms. In the large-volume alkali metal hosts, e.g., Cs, a reduced Sc $3d$ shell interaction with the host conduction electrons can be expected because of the increased interatomic distances. This favors the survival of the Sc $3d$ spin correlations and could possibly lead to the occurrence of magnetism.

Magnetic behavior with strong orbital contributions is observed for Sc ions implanted into the heavier alkali metal hosts. The results can be analyzed in terms of an ionic type model with nearly localized, ionic $3d^1$ configuration of Sc^{2+}. This one-electron configuration and also the observed maximum in the local susceptibility as a function of temperature parallel to the behavior of $4f^1$ Ce ions in metals. Special effort was applied to the study of the host dependence of Sc magnetism in alkali metal hosts, which yield rather unique and illustrative examples of Kondo effects in $3d$ magnetism. We also investigated the magnetism of Sc in Ba, Yb, Au, and Pd hosts.

The systems were studied by means of the time-differential perturbed γ-ray distribution (TDPAD) method at the ISL accelerator of the Hahn-Meitner, Institut, Berlin, using a pulsed 136 MeV ^{36}Ar beam to produce ^{43}Sc ions by the heavy ion reaction $^{12}C(^{36}Ar,\alpha n)^{43}Sc$ in a thin carbon foil followed by recoil implantation into the various host metals. This technique produces extremely dilute ^{43}Sc nuclear probes with spin $I^\pi = 19/2^-$, nuclear g factor $g_N = 0.3286(7)$, and a half-life of 473(5) ns [4], which allows the measurement of the magnetic response via the observation of spin rotation spectra in an external magnetic field. Details of methodical aspects of the TDPAD technique can be found in Ref. [5]. The $19/2^-$ isomer in ^{43}Sc proved to be an excellent probe for solid state applications, because of its long half-life and high γ-ray anisotropy, combined with the large cross section and high recoil energy of the selected nuclear reaction.

Spin rotation patterns $R(t)$ for ^{43}Sc implanted into the hosts Sc, Pd, Ba, Yb, Au, Na, K, Rb, Cs, and some RbCs alloys were observed in an external field near 2 T. Selected examples of $R(t)$ spectra are shown in Fig. 1. From the Larmor frequencies $\omega_L = \hbar^{-1}\mu_N g_N \beta B_{\text{ext}}$, the local susceptibilities $\beta - 1 = B_{\text{int}}/B_{\text{ext}}$ (see Ref. [5]) can be deduced. Some results are shown in Fig. 2. High precision was achieved due to an exact determination of B_{ext} using a calibration measurement on ^{43}Sc implanted into Sc metal, with its known Knight shift [6].

The most essential features of the experimental results (Figs. 1–3) can be summarized as follows: (i) The major changes in ω_L and β as a function of temperature and host are evidence for the existence of local Sc moments in the alkali metal hosts, particularly in Cs, Rb, and RbCs alloys. In the magnetic Sc systems, the $\beta(T)$ values are seen to be larger than 1, which indicates positive magnetic hyperfine fields and predominantly orbital contributions

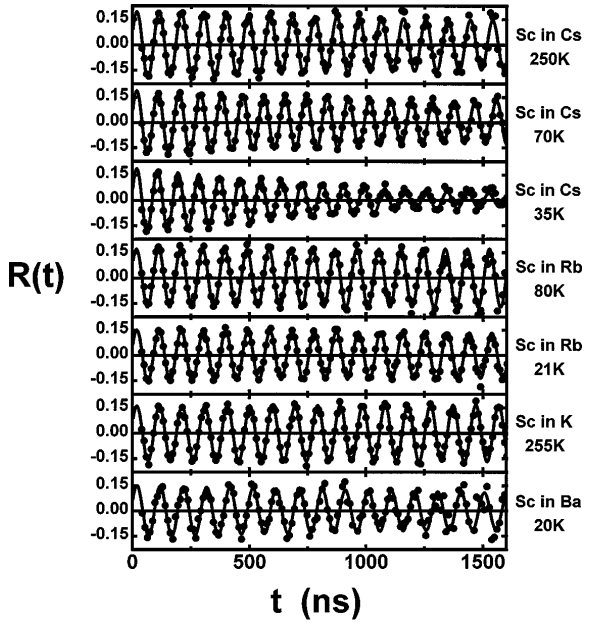

FIG. 1. Examples of spin rotation spectra for ^{43}Sc in Cs, Rb, K, and Ba, recorded at $B_{\mathrm{ext}} \approx 2$ T.

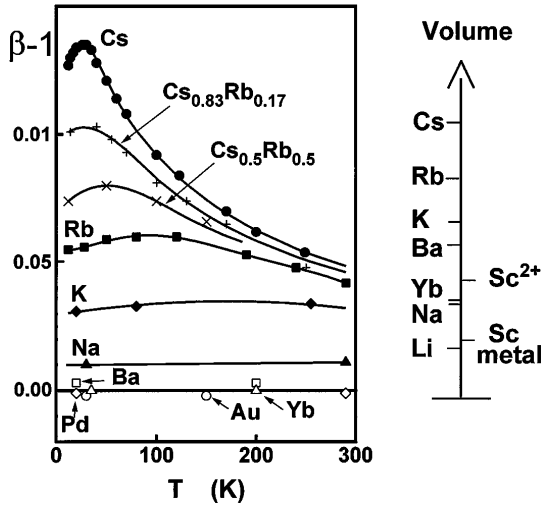

FIG. 2. Host and temperature-dependent local susceptibility $\beta - 1$ of ^{43}Sc implanted into various hosts (lines are a guide to the eye), and plot of atomic volumes for coordination number 12.

to $\beta(T)$ (Figs. 1 and 2). (ii) Concerning the host dependence, the local susceptibilities systematically decrease in the alkali host series Cs, Rb, K, and Na (Fig. 2). (iii) For the magnetic systems, $\beta(T)$ exhibits a maximum as a function of temperature (Fig. 2), which to our knowledge has not been observed for $3d$ impurity systems before. (iv) The fact that only one frequency is observed for the magnetic Sc systems, along with the clear systematic trends for the host dependence of the Sc magnetism, shows that Sc ions occupy only one and the same lattice site in the alkali metal hosts, probably a substitutional site (see Ref. [7]). (v) Sc ions in the hosts Sc, Pd, Ba, Yb, and Au are found to be nonmagnetic as indicated by $\beta(T) = 1$ (Fig. 2).

We start our discussion with the question of which electronic Sc $3d$ configuration is responsible for the magnetic response observed in the alkali metals. For temperatures above their maximum, the susceptibility data for Sc in Cs (and in RbCs alloys) can be fit well to a Curie-Weiss law, $\beta(T) - 1 = C/(T + T_K)$, which yields for Sc in Cs a Curie constant C of $+20(1)$ K and a Kondo temperature T_K of 120(10) K. Such large positive Curie constants point to predominantly positive hyperfine field contributions originating from unquenched orbital momentum and motivate an analysis in terms of ionic-type electron configurations, i.e., in terms of the energetically more favorable $3d^1(L = 2, S = 1/2)$ or $3d^2(L = 3, S = 1)$ configurations corresponding to Sc^{2+} or Sc^{1+}, respectively. Assuming intact LS coupling and negligible crystal fields (compare Ref. [8]), the ionic-based Curie constant is given by $C_J = g_J \mu_B (J + 1) B(0)/3k_B$, where g_J is the Landé factor. Generally, the magnetic hyperfine field at 0 K, $B(0)$, is composed of an essentially orbital, and hence positive, direct $3d$ shell contribution B_J, and a generally negative spin contact term B_S, due to spin-polarized s core and conduction electrons. For a rough estimate of the relatively small B_S contribution, we use -7 T per spin as found for Fe in metals, whereas B_J can be calculated to be $+48$ and $+43$ T for the d^1, $J = 3/2$ and d^2, $J = 2$ states, respectively. Fortuitously, the C_J values obtained for the d^1 and d^2 configurations turn out to be almost equal ($\approx$23 K), and both agree satisfactorily with the experimental value $C = 20$ K (see Ref. [9] for values for LS decoupled states). In order to find out whether $3d^1$ or $3d^2$ is the ground state, we have applied a Born-Haber cycle to estimate the energy

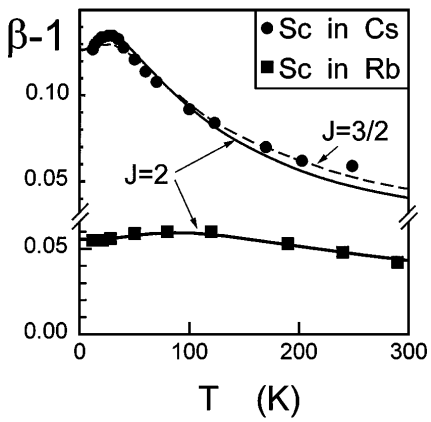

FIG. 3. Fits of the susceptibility data for ^{43}Sc in Cs and Rb using Rajan's solutions of the Coqblin-Schrieffer model (Ref. [14]) with total angular momentum $J = 3/2$ and 2, respectively (see text).

difference $\Delta E = \Delta E(\text{atom}) + \Delta E(\text{coh}) + \Delta E(\text{sol})$ [10] between the d^1 and d^2 state of Sc ions in Cs and Rb. The analysis is performed under the premise of localized nonbonding $3d$ states, which is supported by the observed strong orbital contributions, i.e., ionic magnetism. From optical spectroscopy of the Sc atom [11], the separation between the $3d^14s^2$ ground state and the $3d^24s^1$ state is known to be $\Delta E(\text{atom}) = +1.64$ eV, after averaging over the two spin configurations of the $3d^24s^1$ state. As discussed in more detail in Ref. [10], the cohesive energies $\Delta E(\text{coh})$ and the heats of solution $\Delta E(\text{sol})$ of these novel ions $Sc^{2+/1+}$ ($3d^1/3d^2$) in alkali metals can be reasonably approximated by values given for alkaline earth ions Mg^{2+} and Ca^{2+}, and alkali ions Na^{1+} and K^{1+}, respectively. This interpolation results in $\Delta E(\text{coh}) = +0.8$ eV and $\Delta E(\text{sol}) = -0.6$ eV for Sc in Cs metal. Thus this cycle shows that the ground state of the system Sc in Cs is the $3d^1$ state of Sc^{2+}, separated by 1.8 eV from the next excited $3d^2$ state of Sc^{1+}. Even larger ΔE values can be estimated for the other alkali metal hosts, being 1.9 eV for Sc in Rb, 2 eV for Sc in K, and 2.4 eV for Sc in Na. These considerations provide strong arguments that the magnetic response of Sc ions in the alkali metal hosts under consideration is governed by the one-electron configuration $3d^1$ of Sc^{2+} ions, with $L = 2$ and $S = 1/2$.

We now turn to the interpretation of the striking host and temperature dependence of the susceptibility in the alkali metal-based systems in terms of Kondo effects, originating from a weak hybridization-induced antiferromagnetic coupling of the Sc $3d$ shell to the host s conduction electrons.

Using as a first approximation $\beta - 1 \propto C/T + T_K$ for $T \gg T_K$ and $\beta - 1 \propto C/T_K$ for $T \ll T_K$, and the experimentally determined Curie constant $C = 20$ K, the essential trends of the host dependence of the susceptibility, including the crossover from strongly temperature-dependent behavior in Cs and CsRb alloy to nearly constant β values in the lighter alkali metals, can be reproduced by the variation of a single parameter—the Kondo temperature T_K—ranging from about 120 K for Sc in Cs to values as high as 2000 K for Sc in Na. We attribute this increase of T_K to a much stronger hybridization of the Sc $3d$ shell in the smaller-volume hosts due to an increasing spatial overlap of the Sc $3d$ and the host electronic states. Following Harrison and Froyen [12], the host dependence of the hybridization matrix element can be estimated by $|V_{\text{mix}}|^2 \propto 1/V_{\text{host}}^2$. In view of the large volume changes within the alkali metal series (Fig. 2), and since the coupling constant J which exponentially determines the Kondo temperature $T_K = T_F \exp(1/\rho J)$ is proportional to $|V_{\text{mix}}|^2$, dramatic variations of T_K can be expected, in qualitative agreement with the experiments. The influence of the host density of states at the Fermi level, ρ, or the Fermi temperature T_F, seems to be of minor significance.

The maximum in $\beta(T)$ (see Fig. 2) can be interpreted in terms of a more sophisticated Kondo model. In contrast to more conventional $3d$ systems, Sc develops an ionic $3d^1$ one-electron configuration in alkali metal hosts, thus forming a $3d$ analog to stable-valent $4f^1$ Ce^{3+} systems; this allows an interesting comparison. Susceptibility maxima are known to be present in certain Ce $4f^1$ and corresponding one-electron-hole Yb $4f^{13}$ systems [13]. Based on theoretical studies of the Coqblin-Schrieffer-Kondo model [13,14], such maxima have been attributed to the thermal population of the Kondo resonance, which is located above the Fermi level due to the high total angular momentum values ($J = 5/2$ and $7/2$, respectively) of these $4f$ states. According to Rajan [14], such maxima can be expected more generally for states with $J \geq 3/2$. We have applied the theory given by Rajan to fit the Sc $3d^1$ susceptibility data; some results are shown in Fig. 3. We considered $J = 3/2$ for the *LS*-coupled Sc $3d^1$ configuration and an effective $J \approx 2$ for a decoupled $3d^1$ state, the latter because the Kondo temperatures for the present systems are of the order of the free ion *LS* multiplet separation of about 250 K [11], so that spin fluctuations can wash out the *LS* coupling (for details see Ref. [9]). Within the model, the height of the maxima and also their shift to higher temperatures with increasing T_K can be well reproduced. Residual deviations from the experimental data may result from the neglect of excited spin-orbit states in Rajan's calculation, which could destroy the universality of his curves (compare Ref. [15]).

We now return to magnetic moment formation at Sc ions in metals, which has attracted considerable theoretical interest within the framework of *ab initio* local spin density (LSD) calculations. Such calculations do not take into account spin fluctuations or the Kondo effect, but yield a detailed insight into the local electronic structure and magnetic moments. Since usually LSD approximations include only spin exchange interactions and neglect orbital correlations, a reproduction of orbital moments and ionic configurations with integral d occupation numbers cannot be expected. In remarkable agreement with experiment, sizable magnetic moments have been predicted by LSD theory for substitutional Sc ions in the alkali metal hosts, ranging from $1.54\mu_B$ for Sc in Cs to $0.69\mu_B$ for Sc in Na [16]. In addition, the unusually small d linewidths calculated for $3d$ impurities in alkali metal hosts and their systematic increase in the host series Cs to Li are consistent with our analysis given above. Concerning the d occupation numbers, we refer to the result of 1.24 d electrons obtained for Y in Rb from a so-called LDA + U calculation especially designed to describe the ionic limit more appropriately [17]. Y in Rb is isoelectronic to the Sc systems discussed here, and the calculated d count is compatible with the proposed Sc $3d^1$ configuration.

In order to test more generally the host-dependent trends in local moment formation, we have also studied Sc in the large-volume divalent sp band metal hosts Ba

and Yb (see Fig. 2 for the volumes), in the monovalent host Au, and in Pd, the latter because of its unusual band structure and high density of states at the Fermi level. Sc in all these systems has been found to be nonmagnetic, characterized by $\beta = 1$ (see Fig. 2) [18]. The nonmagnetic responses observed in the Ba and Yb hosts are in agreement with recent local spin density calculations for substitutional Sc in Ba [19] and in Yb [20], which yield no moments for both cases.

In summary, we have studied the magnetic behavior of Sc ions in metallic hosts by means of recoil implantation and PAD techniques. Sc in alkali metal hosts was found to develop an ionic type of magnetism with a strongly localized $3d^1$ one-electron configuration, showing strong orbital contributions to the local susceptibility. In agreement with the one-electron picture, a successful analysis of the Sc susceptibility maximum and its host dependent shifts was carried out in terms of Rajan's calculations extrapolated to the case of a $3d^1$ state. Essential features of the magnetism of Sc in alkali metals deviate significantly from the $3d$ magnetism usually seen in alloying systems, but parallel to the behavior of certain Ce systems. Furthermore, the host dependence of Sc magnetism has been explored in Ba, Yb, Au, and Pd hosts, all of which show nonmagnetic Sc. Concerning the existence or nonexistence of local Sc moments in various hosts (Cs, Rb, K, Na, Ba, and Yb), the results of the local spin density calculations agree (almost surprisingly) well with the experimental findings.

We are grateful for the support of Professor F. Mezei and for valuable discussions and/or the assistance of E. Beck, P. H. Dederichs, S. Frota-Pessôa, P. Szymkowiak, and R. Zeller. This work was supported by the Bundesminister für Bildung und Wissenschaft.

[1] For a data compilation for dilute $3d$ impurities in metals see: K. H. Fisher, in *Numerical Data and Functional Relationships in Science and Technology*, edited by K.-H. Hellwege, Landolt-Börnstein, New Series, Group III, Vol. 15a (Springer-Verlag, Berlin, 1982), p. 289.

[2] A. O. Barksdale and T. L. Estle, Phys. Lett. **42A**, 426 (1973).

[3] B. T. Matthias *et al.*, Phys. Rev. Lett. **7**, 7 (1961).

[4] O. Häusser *et al.*, Phys. Lett. **73B**, 127 (1978).

[5] D. Riegel and K. D. Gross, in *Nuclear Physics Applications on Material Science*, edited by E. Recknagel and J. C. Soares NATO ASI, Ser. E. Vol. 144 (Kluwer Academic, Norwell, MA, 1988), p. 327.

[6] G. C. Carter, L. H. Bennett, and D. J. Kahan, in *Metallic Shifts in NMR*, Progress in Material Science (Pergamon Press, Oxford, 1977), Pt. 1, Vol. 20.

[7] Except for Sc in Cs at temperatures below 25 K, where the data yield a superposition of two frequencies. A detailed discussion of lattice sites for Sc (and other $3d$ ions in alkali metal hosts) will be given in a forthcoming paper. See also K. D. Gross, D. Riegel, and R. Zeller, Phys. Rev. Lett. **63**, 1176 (1989).

[8] D. Riegel *et al.*, Phys. Rev. Lett. **57**, 388 (1986); R. Kowallik *et al.*, Phys. Rev. Lett. **63**, 434 (1989).

[9] J. Kapoor, Ph.D. Thesis, FU Berlin, 1993 (unpublished).

[10] K. D. Gross and D. Riegel, Phys. Rev. Lett. **61**, 1249 (1988).

[11] C. E. Moore, in *Atomic Energy Levels*, (Natl. Bur. Stand. (U.S.) Circular No. 467 (U.S. GPO, Washington, DC, 1952/58), Vols. II and III.

[12] W. A. Harrison and S. Froyen, Phys. Rev. B **21**, 3214 (1980).

[13] P. Schlottmann, Phys. Rep. **181**, 1 (1989).

[14] V. T. Rajan, Phys. Rev. Lett. **51**, 308 (1983). Identifying the experimental Curie constant C with $\mu^2(\nu^2 - 1)/12k_B$ (in Rajan's notation), we derived from $\mu^2\nu(\nu^2 - 1)/24\pi k_B$ the low temperature susceptibility $\beta - 1_{T=0} = C(2J + 1)/2\pi T_0$, where $T_0 \approx 4T_{\max}$ serves as a fit and scaling parameter determined by the location of the maximum. The susceptibility data for Sc in Rb can be reproduced well using $T_0 = 300$ K and $J = 2$; for the Cs host, the scaling relations are not so strictly fulfilled.

[15] J. Bonca and J. E. Gubernatis, Phys. Rev. B **50**, 10 427 (1994). As an interesting difference, the free ion LS multiplet splitting for Sc is about an order of magnitude smaller than that in rare earth systems.

[16] N. Papanikolaou, N. Stefanou, R. Zeller, and P. H. Dederichs, Phys. Rev. B **46**, 10 858 (1992).

[17] V. I. Anisimov and P. H. Dederichs, Solid State Commun. **84**, 241 (1992).

[18] Based on our experience with Fe and Mo ions implanted into Ba and Yb (to be published), we expect that Sc ions in these hosts (in contrast to the alkali metal hosts) occupy both substitutional and interstitial lattice sites. From experiment we can conclude that all Sc recoils in Ba and Yb show a nonmagnetic response.

[19] N. Papanikolaou, N. Stefanou, R. Zeller, and P. H. Dederichs, Phys. Rev. B **51**, 11 473 (1995).

[20] S. Frota-Pessôa (private communication); (to be published).