Fully Localized 3d-Shell Behavior of Fe Ions in Alkali-Metal Hosts

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The local susceptibility and 3d-spin dynamics of isolated Fe ions recoil implanted into alkali-metal hosts is measured by the perturbed-γ-ray-distribution method. The observations of extremely large values for the hyperfine fields and magnetic moments and of an extremely small spin linewidth are quantitatively consistent with a stable $3d^6$ configuration of Fe^{2+} ions in spin-orbit coupling along with a negligible crystal-field splitting. Fe in Li strongly deviates from the magnetic behavior of a purely ionic configuration. The results permit a comparison of local-moment formation of 3d with 4f systems.

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The question of local magnetic-moment formation of a transition-metal atom in a host metal continues to attract considerable experimental and theoretical attention. The problem of electronic structure and magnetism in 3d systems and unstable 4f systems is particularly interesting in the region between localized and itinerant d- and f-electron behavior in metallic systems. The results obtained from extensive experimental investigations of dilute magnetic 3d systems are discussed in a wide spectrum of different models such as the Friedel-Anderson model,[1] Kondo-type models,[2] ionic models,[3] and in a variety of more recent treatments of electronic properties of 3d atoms in dilute alloys,[4] surfaces, and interfaces.[5] In spite of some recent progress, the relationship of the models to real systems remains uncertain.

The main problem in the interpretation of local 3d magnetism seems to be the strong 3d–conduction-electron (CE) hybridization, so that 3d electrons are often regarded as itinerant or partially delocalized. Because of these large 3d linewidths, atomic correlations are hard to detect unambiguously. Many questions are discussed in a controversial way: How large is the 3d-CE hybridization? How effective are atomic correlations between the 3d electrons? Which atomiclike configuration (if any) is the ground state, and why are orbital contributions to the magnetism of 3d systems generally small? What is the reason that spin-orbit (*LS*) interactions are hard to measure in metallic 3d systems, in contrast to the usual behavior of 4f systems? Is it really an unobservably large crystal-field (CF) splitting, by which orbital moments in metallic 3d systems are quenched? These problems are illustrated by the example Co in Au, which has been interpreted in terms of an ionic configuration,[6] while Fe in Cu[7] or Fe in Ca[8] have been analyzed in terms of the Anderson model.

In view of this situation it is highly desirable to find an experimental way to decrease the strength of the interaction of 3d electrons with conduction electrons and/or ligands. At first sight this appears very hard to realize, since negative pressures are not available, and since a sufficiently large reduction of the 3d mixing by changing the host metal has not been observed in spite of the very many 3d ion-host combinations investigated so far.[1-8]

In this Letter we describe the implantation of Fe ions into alkali-metal hosts to produce 3d-ion–host combinations in which the 3d mixing is small compared to atomic configurational interactions. We report the observation of localized 3d-shell behavior in LS coupling for an isolated 3d atom in a metal host. The occurrence of this phenomenon is correlated with extremely large values for the positive hyperfine fields and the magnetic moments and with very small values for the 3d-spin linewidths and CF splittings. These unique features have been found for Fe in K, Rb, and Cs, whereas Fe in Li shows unstable magnetic behavior. The results permit a comparison of nearly stable and unstable 3d systems with 4f systems.

The idea of studying 3d ions in alkali-metal host systems was stimulated by the sharp contrast in atomic volume, electronegativity, and electronic character and density of states. Because of these contrasts such systems do not alloy. On the other hand, just these contrasts may be the source for anomalous behavior of local electronic properties. The first dedicated investigation of the behavior of a d ion in an alkali-metal host has been performed for Y ions in Rb, which demonstrates a vanishing local s-electron density at the Fermi surface.[9]

Such nonalloying systems can be produced by

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heavy-ion reactions and the implantation technique. The static and dynamic magnetic response of the transition-metal ions can be measured by the time-differential perturbed angular γ-ray–distribution (TDPAD) method. These techniques allow microscopic studies of the local susceptibilities and spin dynamics of isolated transition-metal ions in many simple hosts over wide temperatures ranges.[8–10] Roughly speaking, one might say that the magnetic behavior of Fe in, e.g., Cs is probed under extremely high negative lattice pressures due to the factor-of-ten difference in atomic volume of Fe compared to Cs.

The systems Fe in K and Fe in Sc were produced by the reactions, ^{39}K(^{18}O,$p2n$)^{54}Fe and ^{45}Sc(^{12}C, $p2n$)^{54}Fe, respectively, with natural targets. The remaining systems were produced by recoil implantation of the ^{54}Fe ions out of a thin Sc foil into the high-purity ($< 99.9\%$) Li, Rb, and Cs hosts following the reaction ^{45}Sc(^{12}C,$p2n$). Pulsed ^{12}C and ^{18}O beams in an energy range of 40–55 MeV were provided by the VICKSI accelerator at the Hahn-Meitner-Institut in Berlin. The concentration of the Fe ions thus produced is smaller than 1 ppm. The target assembly was mounted on a Cu finger attached to cooling devices, and the temperature could be varied from 20 to 350 K. By these reactions the $I^{\pi}=10^{+}$, $T_{1/2}=360$ ns isomer[8] in ^{54}Fe was excited and oriented, and served as a very well suited nuclear probe to detect the magnetic hyperfine interaction of the systems produced. Spin rotation patterns $R(t)$ (see Refs. 8–10) of the decaying isomer were measured at various γ lines in an external field $B_{\rm ext}$ as a function of host and temperature.

Figure 1 shows some $R(t)$ patterns, from which the nuclear Larmor frequency $\omega_{\rm L}$ and spin-relaxation time τ_N can be extracted. The system Fe in Sc can be used for normalization, since it is close to being nonmagnetic. The very large differences in frequency and damping with changing temperature reflect the large local moment for Fe in the alkali-metal hosts.

From the observed frequencies $\omega_{\rm L}(T)=\hbar^{-1}\mu_N g_N \times B_{\rm ext}\beta(T)$, the local susceptibilities $\beta-1$ can be deduced.[10] The β values thus obtained are displayed in Fig. 2. $\beta(T)\equiv 1$ indicates nonmagnetic behavior. The values for Fe in Li, K, Rb, and Cs are all much larger than $\beta=1$, which indicates that the orbital component is the dominant contribution to the magnetic hyperfine field $B(0)$. Usually $B(0)$ values for $3d$ systems are negative ($\beta<1$), because of the dominance of spin magnetism. For Fe in Ca, where a positive $B(0)$ has been found, $\beta(T)$ increases only by 10% from 300 to 80 K,[8] which has to be compared to the 300% change of β found for Fe in K, Rb, and Cs. For Fe in K, Rb, and Cs, $\beta(T)$ follows nicely a Curie-type behavior in its most simple form: $\beta-1\propto \text{const}/T$ (Fig. 2).

An analysis of such large orbital contributions necessarily requires the inclusion of LS coupling.

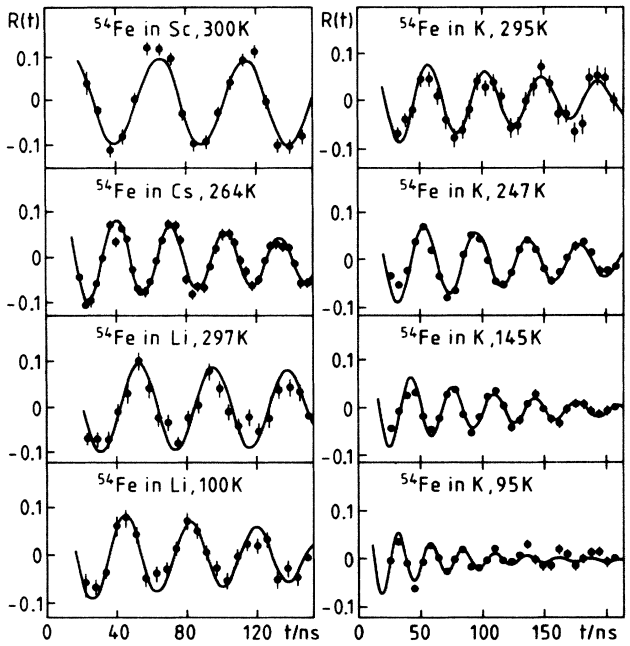

FIG. 1. Spin rotation patterns of ^{54}Fe in several hosts at various temperatures and $B_{\rm ext}$ around 2 T. The different frequencies reflect the β values as shown in Fig. 2. The damping reflects the τ_N values as plotted in Fig. 3.

Thus models based on itinerant $3d$ electrons or based on one-particle approaches cannot be used for the system in question. This holds also for an analysis in terms of the Friedel-Anderson model, as applied, e.g., for the system Fe in Ca.[8] Even if one assumes an unquenched orbital moment of $L=2$, the maximum value of $\beta-1$ can be estimated to be 0.4 at 100 K, much smaller than the values observed for Fe in K, Rb, and Cs (Fig. 2).

Considering now ionic models, one is forced by the magnitude of the orbital contributions to give up the premise that CF splittings are large compared to the LS coupling (e.g., Refs. 3, 6, and 8). For an analysis of $\beta(T)$ we assume CF effects to be negligible and start from the free-ion-like *Ansatz:* $\beta-1=g_J\mu_{\rm B}(J+1) \times B(0)/3k_{\rm B}T$, which has often been used to fit $\beta(T)$ data in stable $4f$ systems.[10]

First of all, we can disregard the $3d^5$ configuration of Fe^{3+} since $L=0$ and $\beta<1$. The dashed lines in Fig. 2 are calculated for the ionic $3d^6$ configuration of Fe^{2+} by use of the total spin $J=4$, the Landé factor $g_J=\frac{3}{2}$, and $B(0)=+97$ T, and for the $3d^7$ configuration of Fe^{1+} by use of $J=\frac{9}{2}$, $g_J=\frac{4}{3}$, and $B(0)=+134$ T.[11] $B(0)$ can be regarded as the sum of the direct $3d$-shell contribution B_J (essentially orbital), and a term B_s which includes contributions from spin-polarized core s electrons and conduction electrons. With experimentally derived values for the matrix elements

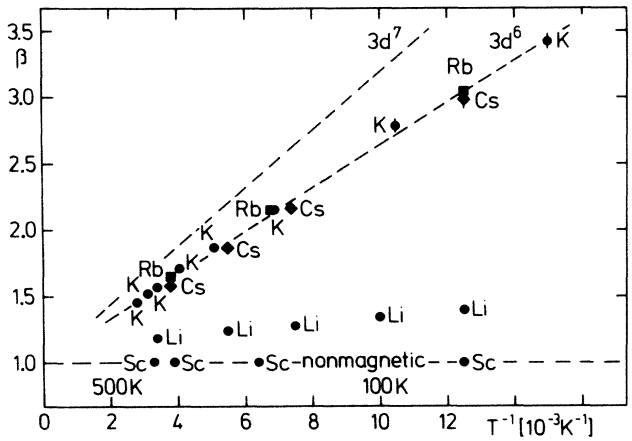

FIG. 2. Local susceptibilities of Fe ions as a function of the host matrix and temperature. The dashed lines represent $\beta(T)$ calculated for the ionic $3d^6$ and $3d^7$ configurations (see text).

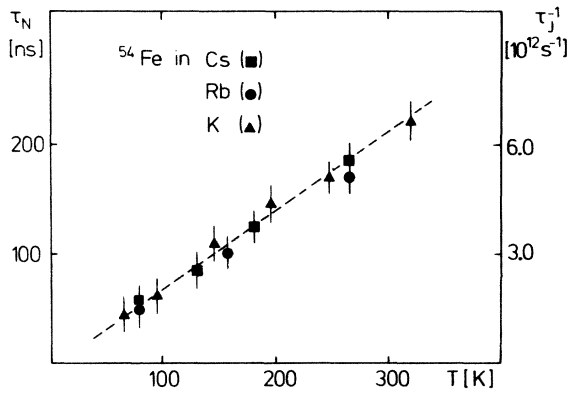

FIG. 3. Temperature dependence of the magnetic nuclear relaxation times τ_N and the $3d$-spin rates τ_J^{-1} for Fe in K, Rb, and Cs. The dashed line corresponds to the Korringa law $\tau_J^{-1} \propto T$.

$\langle r_{3d}^{-3} \rangle$,[12] B_J is calculated to be $+125$ T and $+155$ T for the $3d^6$ and $3d^7$ configurations, respectively. For an estimate of B_s we use $(-7\ \text{T}) \times 2S$ (Refs. 3, 8, and 11) yielding $B_s = -28$ T for $3d^6$ and -21 T for $3d^7$. The $B(0)$ thus calculated for $3d^6$ compares reasonably with $B(0) = +110$ T, $B_J = +125$ T, and $B_s = -15$ T known for the free $3d^6 4s^2$ Fe atom.[12] A smaller $|B_s|$ value for the free atom compared to Fe in a metal host might be expected because of the significant positive contribution of polarized $4s^2$ core electrons in the atom. The nice agreement between experiment and this simple analysis strongly supports a $3d^6$ configuration in LS coupling with the ground state $J = 4$ for Fe in K, Rb, and Cs (see Fig. 2).

As discussed in the introduction, large parts of the theoretical uncertainties in the description of magnetic $3d$ systems are directly correlated with our poor knowledge of the $3d$ mixing. Information about this elusive quantity can be obtained from measurements of the $3d$-spin dynamics. Because of this mixing a $3d$ spin fluctuates, which produces a fluctuation of $B(0)$ at the site of the nucleus, which in turn causes a relaxation of the nuclear alignment. Under certain conditions, discussed by Riegel[13] for the case of $4f$ systems, the magnetic nuclear spin rate is given by

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

where τ_J^{-1} is the $3d$-spin–relaxation rate, and $g_N = 0.728$ (Ref. 8) is the nuclear g factor of the 10^+ isomer. In this form, Eq. (1) holds for stable systems with well-defined J and $B(0)$, as is the case for Fe in K, Rb, and Cs. Usually the τ_J^{-1} values in $3d$ systems are large, so that the nuclear magnetic rates are too small for the experimental sensitivity of the TDPAD method. It is just the anomalously small $3d$ mixing which permits a measurement of τ_N as reflected in the host- and temperature-dependent damping in Fig. 1.

Since a quadrupolar damping is unimportant, τ_J^{-1} can be extracted directly from τ_N by use of Eq. (1). The results, shown in Fig. 3, exhibit the following exciting features: (a) The τ_J^{-1} rates for Fe in K, Rb, and Cs are very similar and follow nicely a Korringa-type behavior $\tau_J^{-1} \propto T$. (b) The τ_J^{-1} are anomalously small. By use of the uncertainty principle the rates can be converted to the spin linewidth yielding 1 meV at the measuring temperature of 100 K. To the best of our knowledge this is by far the smallest value known in any Fe, Co, and Ni system. The relation between $\tau_J^{-1}(T)$ and the strength of the mixing can be found in Ref. 13 within Kondo-type models.

The Curie-type $\beta(T)$, the sign and magnitude of $B(0)$, the Korringa-type behavior of $\tau_J^{-1}(T)$, and the narrow spin linewidth—all these properties are quantitatively consistent with a fully localized $3d^6$ configuration of isolated Fe^{2+} ions with $L = 2$, $S = 2$, $J = 4$ in LS coupling. This result includes the largest local moment of $6.7\mu_B$ reported for a $3d$ ion in a metal host. An interpretation of the data in terms of a stable $3d^7$ configuration would require the assumptions of rather unrealistically large fields $|B_s|$ along with a crystal field comparable to the LS coupling.[11]

Also important is the finding that there are no indications of CF effects. As a consequence of the small linewidth for Fe in K, Rb, and Cs, both the $\beta(T)$ and the $\tau_J^{-1}(T)$ data can be expected to be sensitive to CF splittings comparable to the measuring temperatures. An estimate—based on calculations of CF-induced changes of $\beta(T)$ alone—yields an upper limit of 0.025 eV for the total splitting. This finding suggests a more critical view of assumptions that CF splittings are large compared to measuring temperatures for $3d$ ions in metal hosts. We are not aware of an unambiguously

obtained experimental proof of such an assumption.

As the crucial mechanism for the strongly enhanced local magnetism of Fe in alkali-metal hosts a drastic decrease of the d-s hybridization is suggested. Hybridization might be reduced mainly because of the large differences in volume between the Fe and the alkali-metal cells and because of the s-like character of the host conduction electrons.[9]

The observation of fully localized $3d$-electron behavior allows a comparison of $3d$ with $4f$ systems on a more reliable basis than before. The spin linewidths for Fe in K, Rb, and Cs are smaller than those obtained in many nearly stable Ce systems, e.g., Ce in Sn.[13] In selected metallic systems the $3d$ mixing might be comparable to or smaller than the $4f$ mixing. On the other hand, the linewidth of Fe in K, Rb, and Cs is large compared to Gd systems, so that one can characterize Fe in K, Rb, and Cs as Kondo systems with Kondo temperatures of the order of 1 K.

A comparison to unstable $4f$ systems can yield valuable information for the mechanism of $3d$ instabilities, particularly for Fe in Li (Fig. 2) and in Ca (Ref. 8), and perhaps also for $3d$ ions in noble metals.[3-7] The strongly reduced magnetism of, e.g., Fe in Li (Fig. 2) might be dominated by basically the same mechanism—strong hybridization—as suggested for unstable Ce, Pr, Nd, and Pm systems.[14] As a specific example we want to compare $\beta(T)$ data of Fe in Li with Pr in Pt (see Fig. 2 in Ref. 14). Both cases show strongly reduced β values compared to the stable ionic behaviors. In both systems the orbital component is dominant and $\beta(T)$ differs from Curie-type behavior. Following the interpretation line for Pr in Pt (Ref. 14), one might speculate that the $3d$ linewidth is larger than a possible CF splitting for unstable $3d$ systems, also. Compared to the stable behavior of Fe in, e.g., Cs a drastic increase of $3d$-CE hybridization can be expected in Li, Ca, and noble-metal hosts due to the increasing lattice pressure. On this basis one can parametrize the $3d$ instabilities by high T_K values within Kondo-type theories and/or by more delocalized $3d$ shells within bandlike approaches without introducing CF effects. If correct, these considerations are of obvious importance for local magnetism in general.

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