Magnetic Behavior of Fe Impurities in Tc and Re, and Its Relevance to the General Problem of the Magnetism of Fe in *d*-Band Metal Hosts

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We have observed implanted Fe ions to be nonmagnetic in the group VIIb hosts Tc and Re, by applying the in-beam perturbed angular γ-ray distribution method. This result is in agreement with local spin density calculations for Fe in Tc using both supercell and single impurity approaches. The results are of key importance for a reasonable and consistent understanding of the basic, general features of local magnetic moment formation on Fe ions in transition metal hosts. [S0031-9007(96)01284-7]

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An important and fundamental question is whether or not a transition metal atom dissolved in a metal host forms a local magnetic moment. Qualitatively, the existence of magnetic moments depends on the subtle competition between the *intra*-atomic Coulomb interactions responsible for Hund's rules, and *inter*-atomic interactions with the host band electrons. Extremely dilute systems and the problem of local moment formation of 3*d* impurities in nonmagnetic hosts have been the object of intense interest because the interactions of impurity *d* states with the host *s*, *p*, and *d* bands can be studied rigorously.

Early systematic work was due to Clogston *et al.* [1], who addressed the local moment formation of Fe impurities dissolved in the 4*d* transition metal hosts. The observed complicated host dependence of local moment formation could not be satisfactorily reproduced by simple theories based on the Friedel-Anderson [2] or Wolff [3] models, and the mechanism governing local moment formation remained insufficiently understood.

Recently, both the experimental and the theoretical basis for studying local moment formation on magnetic impurities (in particular, for Fe) in metallic hosts have been improved considerably. Experimentally, many more systems have been investigated in a reliable manner, partly by the application of the time differential perturbed γ-ray angular distribution method (TDPAD), which has made even nonalloying impurity-host combinations accessible. Such studies have yielded qualitatively different features for the behavior of Fe in *sp* metal hosts as compared to *d*-band metal hosts [4]. On the theoretical side, progress in understanding local magnetic moment formation has been due mainly to sophisticated calculations within the framework of local spin density (LSD) approximation theories [5], which for the case of Fe ions have been applied in various forms to *d* metal hosts [6] and also to *sp* metal hosts [7].

It is the aim of this work to study central open questions concerning the host dependence of Fe magnetism in transition metals. Experiments and theory focus on the most relevant and puzzling cases (as will be argued below): Fe in Tc and Fe in Re. We apply the TDPAD method to answer the question of whether Fe impurities are really magnetic in Tc and nonmagnetic in Re. Theoretically, we carry out LSD calculations using supercell as well as *single-impurity* approaches for Fe in hcp and bcc Tc, based on the flexible real-space linear muffin tin atomic sphere approximation (RS-LMTO-ASA) method [8]. The theoretical results can be compared to experiment and to the supercell approach of Beuerle *et al.* [6].

In contradiction to theory [6], Fe in Tc has been claimed to develop a magnetic moment with a saturation hyperfine field of 7.3 kG [9]. This conclusion was based on Mössbauer spectroscopy using samples of coelectrodeposited ^{57}Co and ^{99}Tc which were subsequently annealed. In addition to the difficulties of handling the radioactive Tc host, this procedure, like any other attempt to produce isolated Fe impurities in a metal by conventional alloying, may be dubious when the alloy preparation is handicapped by a low solubility and an often concomitant high impurity diffusion rate, which can lead to uncontrolled Fe clustering or defect association, e.g., with dissolved O atoms. These difficulties can be avoided by the application of the TDPAD method (see below). For the system Fe in Re, a new investigation is necessary, since the hitherto available information on the magnetism of Fe in Re essentially relied on one spectrum measured at 80 K [4].

A disk of Tc metal was prepared by arc melting commercial Tc powder with a nominal purity of 99.8 at.%

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(no nonmetallic contaminants quoted) supplied by the Oak Ridge National Laboratory. X-ray diffraction patterns showed a clean hcp structure with lattice constants $c = 3D4.400(4)$ and $a = 3D2.745(2)$ Å, which agree well with values reported in the literature. A special effort was made to determine the C and O content by performing an in-beam activation analysis of the same Tc sample used for the Fe implantation measurements. By bombarding the Tc sample (and carbon and oxygen compounds for range-corrected calibration) with ^{12}C beams in the range of 30 to 40 MeV, we monitored the yield of specific γ rays following various fusion reactions, e.g., $^{12}\mathrm{C}(^{12}\mathrm{C}, pn)^{22}\mathrm{Na}$ or $^{16}\mathrm{O}(^{12}\mathrm{C}, pn)^{26}\mathrm{Al}$, and determined the C and O contaminations in our Tc to be less than 0.5 and 0.1 at. %, respectively.

The TDPAD experiments were performed at the ISL accelerator of the Hahn-Meitner-Institut in Berlin, using a pulsed ^{12}C beam of 42 MeV energy to populate the 10^+, 360 ns isomeric state in ^{54}Fe by the heavy ion reaction $^{45}\mathrm{Sc}(^{12}\mathrm{C}, p2n)^{54}\mathrm{Fe}$ and to implant the Fe probe atoms $1-2$ μm deep into the Tc and Re (99.99%) hosts. From the spin rotation spectra, hyperfine interactions at the site of the implanted Fe probe can be detected. For details of the method we refer to Ref. [10]. We point out that the low concentration ($\ll$1 ppm) of Fe implants combined with the short time scale of the measurements (20 ns to 2 μs; see Fig. 1) ensures the study of truly isolated Fe ions, which are unable to form impurity or defect-associated clusters. The observed low concentrations of nonmetallic impurities in our Tc sample also reinforce this conclusion.

Figure 1 shows spin rotation spectra recorded for ^{54}Fe in Tc and in Re at several temperatures in an external magnetic field of 2 T. From the observed (nearly maximal) anisotropy amplitudes we can deduce that nearly all Fe implants contribute to the spin rotation pattern. From the Larmor frequency $\omega_L = 3D\hbar^{-1}\mu_N B_{\mathrm{ext}}\beta$, local susceptibilities $\beta - 1$ can be calculated, leading to very small and completely temperature independent $\beta - 1$ (or Knight shift) values of 0.007(1) for Fe in both Tc and in Re. The observed temperature-independent damping (see Fig. 1) is of quadrupolar origin. All these features consistently indicate that implanted Fe impurities do not develop a local magnetic moment either in Tc or in Re.

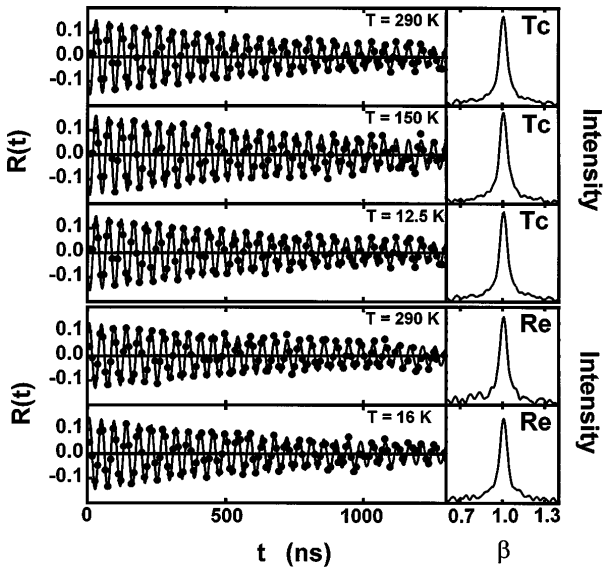

FIG. 1. Examples of spin rotation spectra and corresponding Fourier transforms for ^{54}Fe in Tc and Re metal hosts, recorded in an external field of 2 T.

We first comment on the lattice location of the Fe ions. Based on recent elaborate studies by TDPAD [11] and in-beam Mössbauer effect [12], the following systematic trends have emerged for the lattice site occupations of Fe ions recoil implanted into metallic elements: When Fe ions are implanted into metallic hosts with a clearly measurable Fe solubility (e.g., Fe in Au), only substitutional Fe lattice sites can be observed, whereas in hosts with low or vanishing Fe solubility, the implantation process usually leads to the occupation of interstitial as well as substitutional Fe lattice sites. The solubility of Fe in Tc and in Re can be estimated as being on the borderline between alloying and nonalloying systems [13]. In transition metal hosts with lower or comparable Fe solubility, implantation experiments by TDPAD and/or Mössbauer effect have yielded readily detectable fractions for both the substitutional and the interstitial Fe lattice sites, for example, in Ti, Zr, and Hf, in Sc, Y, Nb, Mo [4,11], and even in completely nonalloying systems such as Fe in Ba and Pb [11]. These considerations provide a strong argument that the observed nonmagnetic response corresponds mainly to substitutional and (with less confidence) also to interstitial Fe in Tc and Re. For the purpose of this paper, only the substitutional Fe sites are relevant [14].

The theoretical part of this Letter concentrates on the system Fe in Tc, since the nonrelativistic approaches used are expected to yield more appropriate results for Tc as compared to Re host. In order to elucidate band structure and lattice symmetry effects on the magnetism of the Fe impurities, we consider both hcp and (hypothetical) bcc Tc hosts. The LSD calculations were performed using supercell as well as *single-impurity* approaches within the framework of the RS-LMTO-ASA method (for details of the scheme, see Ref. [8]). This scheme is similar to the reciprocal space method used by Beuerle *et al.* [6], but, when solving the eigenvalue problem, it substitutes a real space recursion procedure for the *k*-space diagonalization, with the consequence that the real space scheme can be applied to both isolated impurities and periodic (e.g., supercell) systems. In all calculations presented here, large clusters of 1600 atoms or more have been used to simulate the solid. The supercell calculations allow a consistency check with the supercell results of Ref. [6]. The single-impurity approach is closer to the real physical situation and additionally provides a sensitive test for

possible shortcomings of the supercell method, which actually represents calculations for an alloy with a rather high effective Fe concentration.

The real space supercell results show no Fe moment on Fe in hcp Tc, while a rather high Fe moment of $2.36\mu_B$ is found in bcc Tc ($a_0 = 3D3.058$ Å, as in Ref. [6]). Both results and also the local density of states $N(E)$ are comparable with the predictions of Ref. [6], which yielded no moment in the hcp and $\mu_{\mathrm{Fe}} = 3D2.03\mu_B$ in the bcc structure of Tc.

The results for $N(E)$ of Fe in hcp and bcc Tc obtained in the single-impurity calculations are plotted in Fig. 2. The gross features of $N(E)$ for the two crystal symmetries obtained by the single-impurity and supercell approaches are found to be similar (Fig. 2). The single-impurity calculations yield no Fe moment in hcp Tc and a moment of $2.75\mu_B$ in bcc Tc, the latter somewhat larger compared to both the supercell results under consideration. The reasonable agreement between the results obtained from the supercell and the single-impurity calculations is by no means trivial since, e.g., the charge transfers and corresponding electrostatic potentials are quite different in the two situations. But in a self-consistent calculation, the charge transfers and potentials adjust themselves to prevent large, unphysical charge accumulation at any particular region in the metal. Since both the calculations are self-consistent, they place the bands (in particular, the *d* bands, with their large densities of states near the Fermi energy) at similar positions. This, and the fact that in transition metals $N(E)$ is dominated by the *d* contribution, helps to explain the similar shapes of $N(E)$ obtained from the supercell and single-impurity calculations (see Fig. 2).

The main reason for the existence of Fe moments in bcc Tc and for the nonmagnetic behavior of Fe in hcp Tc is the different shape and location of the local Fe 3*d* states in the two lattices, arising mainly from two major influences, as can be seen from a comparison of the results shown in Fig. 2. Basically, $N(E)$ at the Fe impurity adopts the shape of the characteristic host bands for the given symmetry, but there is also a certain redistribution within $N(E)$. Compared to the larger-volume host, the less extended Fe 3*d* states are hybridized more weakly with the Tc 4*d* states, leading to narrower Fe 3*d* bands with a suppressed $N(E)$ at the lower band edges and higher peak densities near the Fermi level. As a consequence, the local $N(E)$ for Fe in a bcc Tc lattice shows two pronounced peaks with the Fermi level E_F located at the upper E_g peak. In the hcp Tc lattice, in contrast, the Fermi level is positioned well above a dominant peak, in a region of low $N(E)$. These large differences in the values of $N(E_F)$ are decisive for the occurrence of Fe moments according to the Stoner criterion $IN(E_F) \geq 1$; I is the host independent exchange integral $I = 3D0.068$ Ry (the same value used in Ref. [6]). They are the main reason why all calculations suggest magnetic Fe in the bcc structure, but not in the hcp structure. Our supercell calculations give $IN(E) = 3D0.60$ and 1.3 for the hcp and bcc Tc hosts, respectively. From the isolated-impurity approach, we find $IN(E) = 3D0.52$ for Fe in hcp and 1.9 for Fe in bcc Tc.

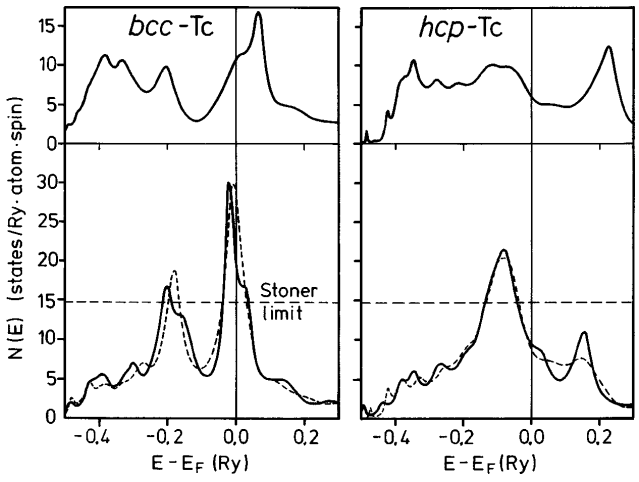

FIG. 2. Calculated local DOS curves for Fe in bcc Tc (left) and in hcp Tc host (right). The upper plots show the DOS of the pure host, the lower plots the DOS for Fe in Tc. Full curves represent supercell calculations for $FeTc_7$; dashed curves represent single-impurity results.

Thus all LSD predictions for Fe in hcp Tc consistently yield a rather small value for the Stoner criterion, which in turn predicts nonmagnetic Fe behavior. Our experimental finding of nonmagnetic Fe ions in hcp Tc removes the previously existing serious discrepancy between experiment and theory. Almost certainly, the earlier discrepancies for Fe in Tc and also for Fe in Zr [11] were due to erroneous experimental results using inadequate sample preparation techniques. LSD methods seem to be well suited for calculating the electronic structure and the magnetic properties of these extremely dilute transition metal alloys, where the tendency of the localized Fe 3*d* states to form a magnetic, i.e., spin split, electronic structure can be explained along the lines of itinerant band magnetism using a local Stoner criterion. Combining the results of this work with those of Ref. [6], complete consistency between experimental and theoretical results for Fe moment formation throughout the 4*d* metal host series is established, thus confirming convincingly that the occurrence of Fe moments in these hosts strongly depends on the real host lattice structure and host *d*-band symmetry.

Encouraged by this basic understanding of Fe moments in 4*d* metal hosts, we now wish to generalize our discussion to Fe magnetism in 5*d* and in nonmagnetic 3*d* metal hosts. As far as we know, no theoretical predictions are available for Fe in 5*d* metals, while Fe in Ti and Cu has been calculated to be magnetic [5], in agreement with experiment. As can be seen by inspection of Fig. 3, without exception the existence or nonexistence of Fe moments in 3*d*, 4*d*, and 5*d* elements occurs groupwise,

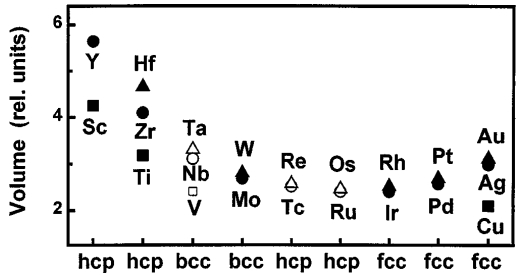

FIG. 3. Occurrence of local Fe moments in 3*d* (squares), 4*d* (triangles), and 5*d* (circles) transition metal hosts, as a function of host volumes and lattice symmetries. The solid symbols indicate magnetic Fe impurities, open symbols indicate nonmagnetic impurities.

i.e., Fe is magnetic in hcp Sc and Y [11], in hcp Ti, Zr, and Hf, in bcc Mo and W, in fcc Rh and Ir, in fcc Pd and Pt, and in fcc Cu, Ag, and Au; and nonmagnetic in bcc V, Nb, and Ta, in hcp Tc and Re, and in hcp Ru and Os. These clear systematic trends indicate that the basic features of Fe local moment formation in 3*d* and 5*d* metal hosts are dominated by the same leading interactions as found for the 4*d* metal hosts. Most probably the interaction of the Fe 3*d* electrons with the structure- and symmetry-dependent host *d* bands governs, via the shape of $N(E)$, the intricate host dependence of Fe impurity moment formation in transition metals in a rather general manner. Furthermore, this interpretation provides a good explanation of the lack of a correlation of Fe magnetism to the host lattice volume in *d* metal hosts (see Fig. 3); such a correlation is found for Fe in *sp* metal hosts [4]. Apparently, Fe magnetism in *d* metal hosts is more decisively governed by the host *d*-band structure than by the changes in host volume, which can be rather large (Fig. 3). One might also extrapolate that the magnetism of thin 3*d* films is determined more by symmetry effects than by changes in lattice volume (cf. Ref. [15]). Moreover, in light of the present results, one is led to conclude that Fe magnetism in *d* metal hosts is not dominated by spin fluctuation or Kondo effects as speculated in, e.g., Ref. [4], which are not included in LSD approaches. (At the present level of knowledge this statement cannot be extended to Fe in *sp* metal hosts or to, e.g., Ce in metals.)

The results of this work yield a consistent and convincing picture for the basic features of local moment formation on substitutional Fe ions in transition metal hosts. Further experimental and theoretical work is necessary for studying finer but important details of the relevant interactions, e.g., the influence of host lattice volume and the Kondo effect on Fe magnetism. LSD theory can be applied to study Fe moments and magnetic hyperfine fields in 5*d* metal hosts and to test the importance of relativistic effects.

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