Substitutional and Interstitial Fe in hcp Zr, Ti, and Hf: Theory and Experiments

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Implanted Fe atoms in hcp Zr, Ti, and Hf occupy both substitutional and interstitial lattice sites. In all three systems, substitutional Fe is found to be strongly magnetic, while interstitial Fe is nonmagnetic. First principles calculations for the magnetic properties and the isomer shift have been carried out for substitutional sites (by two independent methods) and for the interstitial sites. The theoretical predictions for both lattice sites are in excellent agreement with the experimental results.

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Considerable effort has been expended in the past in the investigation of Fe atoms as dilute impurities in the Group IV metals Ti, Zr, and Hf, in order to determine their solubility, lattice location, diffusion, magnetism, and electronic properties. Such systems have attracted attention because of their extremely fast diffusivities [1], up to 6 orders of magnitude faster than self-diffusion, which have generally been attributed to interstitial Fe diffusion. A major effort has also been invested in the study of local magnetic moment formation in these systems. Based on the pioneering work of Clogston *et al.* [2] and on later studies [3], it has been suggested that (substitutional) Fe ions in Ti and Zr carry no local magnetic moments. This could be understood qualitatively in terms of the Anderson model [4], but was in contradiction to more quantitative calculations, which suggest local moments for, e.g., Fe in Zr [5]. Additional attempts to investigate the magnetic state of Fe in Ti and Zr by Mössbauer spectroscopy, using thermally prepared alloys [6] or conventional implantation methods [7], now raise the question of whether it is even possible to produce isolated, substitutional Fe ions in these hosts, given the conditions of nearly vanishing solubility and very rapid diffusion. In general, this seems to be extremely difficult, as will be discussed below. At the same time, advances in theoretical methods [8–10] have permitted quantitative predictions of magnetic moments, isomer shifts, and magnetic hyperfine fields at substitutional, and, as reported in this Letter, also at interstitial Fe sites, making an accurate determination of lattice site and a comparison with experiments on nonthermally prepared samples most interesting.

One applicable experimental method, useful for nonalloying systems, is the time-differential perturbed angular distribution technique (TDPAD) combined with heavy ion reactions and recoil implantation of the (Fe) impurities. Comparison of this method and the related in-beam Mössbauer spectroscopy (IBMS) [11] with modern theoretical calculations offers the opportunity to study a number of interesting physical questions: Can Fe impurities in Group IV hosts occupy both substitutional and interstitial sites? Are truly substitutional Fe impurities magnetic after all? What can be learned about the local properties of interstitial Fe impurities? In the following, we present new theoretical results using two different *ab initio* methods [8,9] to investigate the local properties of substitutional Fe and, for the first time, interstitial Fe impurities in Group IV host metals, and compare them to data from TDPAD experiments (as well as to published IBMS data). We concentrate the presentation on the most thoroughly investigated case of Fe in Zr, giving in addition some data for Ti and Hf hosts; more detailed experimental and theoretical [12] results will be published in forthcoming papers.

Two theoretical methods were used to calculate properties of substitutional Fe impurity sites, and one of them was also applied to Fe ions at interstitial sites; we will discuss the latter calculation first, since it represents an important new development. The method used is the real-space linear muffin-tin orbital atomic sphere approximation (RS-LMTO-ASA), a first principles, self-consistent local spin density approach described in detail in Ref. [9]. It is based on the tight-binding representation of the LMTO-ASA formalism [10] and makes use of the recursion method [13] to solve the eigenvalue problem in real space. The real space formulation has the interesting advantage that lattices with a complex nonperiodic structure can be treated without putting severe limits on the size of the cluster. In Fig. 1(a) we show results for the local density of states (LDOS) at an Fe impurity on the interstitial site in α-Zr. The interstitial impurity was placed at the center of an octahedral site in a cluster of 1200 atoms having the hcp structure. The six nearest neighbors were relaxed radially by 0.23 Å, in such a way as to distribute the overlap evenly among close neighbors.

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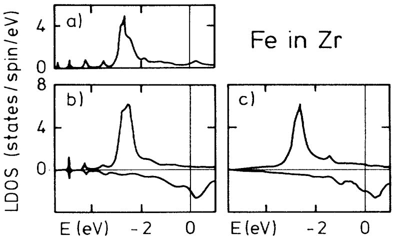

FIG. 1. The calculated local density of states of (a) interstitial Fe in hcp Zr and substitutional Fe in (b) hcp Zr and (c) fcc Zr (see text). In all cases the energies are given relative to the Fermi level of the host. The two calculations for substitutional Fe yield almost the same values for the local spin density.

The potentials at the impurity and the first three Zr neighbor shells (of six atoms each) were determined self-consistently. Interstitial Fe is predicted to be nonmagnetic, in agreement with the analyses of the experimental results given below. Furthermore, the isomer shift (IS) is calculated to be -0.59 mm/s, taking the s electron density of Fe in α-Fe, calculated by the same method, as a reference. The calibration constant to convert calculated electronic-density differences to isomer shifts was taken from Akai *et al.* [14]. The IS at the interstitial site is considerably lower than for the substitutional site (see Table I). It corresponds to a higher electron density at the interstitial site, as is systematically observed for interstitial impurities [11]. The calculated IS is in excellent agreement with that reported in Ref. [15] for interstitial Fe lattice sites in Zr.

For Fe on the substitutional site, the RS-LMTO-ASA calculations indicate a magnetic moment of $2.71\mu_B$, corresponding to an effective spin $S_{\mathrm{eff}}=1.35$ [Fig. 1(b)]. For the contact hyperfine field, neglecting orbital, and dipolar contributions, we find a total field $B_{hf}=-10.9$ T, consisting of a core contribution of -27.0 T and a valence contribution of $+16.1$ T. The calculated product $B_{hf}(S_{\mathrm{eff}}+1)$ and the IS are shown in Table I and compared there to the experiments; again, excellent agreement is found.

TABLE I. Summary of results for isolated Fe impurities in Group IVa hosts: s and i denote substitutional and interstitial sites, respectively, and n.m. means "nonmagnetic."

		$B_{hf}(S_{\mathrm{eff}}+1)$ (T)		δ (mm/s)	
Host	T_K (K)	Expt.	Theory	Expt.[d]	Theory
s-Zr	< 5	−26.1(6)	−25.7[a] −27.8[b]	0.17(1)	0.16[a] 0.27[b]
i-Zr		n.m.	n.m.	−0.58(2)	−0.59[a]
s-Ti	30(5)	−19.9(5)	−20.3[c] −19.7[b]	0.06(2)	0.04[c]
i-Ti				−0.78(2)	−0.74[c]
s-Hf	5(5)	−19.7(5)			

[a] Calculated using the RS-LMTO-ASA method.
[b] Calculated with the KKR method.
[c] Preliminary results (Ref. [12]).
[d] From Refs. [11] and [15].

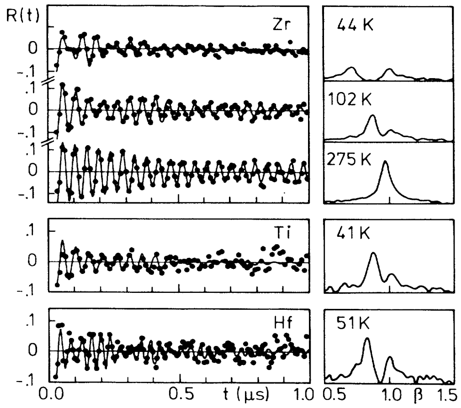

FIG. 2. Spin rotation patterns of ^{54}Fe in Zr, Ti, and Hf (left panel) and their Fourier transforms (right panel) as a function of β (see text).

Using the Kohn-Korringa-Rostoker Green's function (KKR) method, parallel calculations of the electronic properties of substitutional Fe impurities surrounded by an infinite lattice of Ti and Zr atoms in the fcc structure have been carried out, neglecting lattice relaxation around the Fe cell. This approach, based on local spin density calculations using the Green's function method, has been extensively described in the literature [8], so that we restrict ourselves here to noting that an angular momentum cutoff at $l=4$ was used in the present calculations and that potential perturbations on the Fe atom and twelve near neighbors were determined self-consistently. The correct embedding of this cluster of thirteen atoms is given by the Green's function of the host. The calculations show stable local moments for substitutional Fe in both Ti and Zr hosts, having S_{eff} of 1.07 and 1.36, respectively. The calculated hyperfine fields are -9.5 T in Ti and -11.8 T in Zr host; the calculated LDOS for substitutional Fe in fcc Zr is shown in Fig. 1(c).

TDPAD experiments were performed at the VICKSI accelerator of the Hahn-Meitner-Institut in Berlin, using a pulsed ^{12}C beam of 42 MeV energy to produce excited ^{54}Fe nuclei by the fusion reaction $^{45}\mathrm{Sc}(^{12}\mathrm{C},2pn)^{54}\mathrm{Fe}$ and implant the recoiling Fe ions into the host material. Under these implantation conditions, the ^{12}C beam penetrates to a depth of about 20 μm, while the Fe ions are implanted at a mean depth of about 2 μm. The maximum impurity concentration at a typical dose of 10^{10} at/cm^2 is well below 1 ppm. This low impurity concentration, combined with the short time scale of the measurement (a few hundred ns), ensures that the Fe ions remain isolated during the experiment and are unable to form impurity or associated defect clusters. Experimental conditions are similar in the IBMS experiments on ^{57}Fe in α-Zr, but differ from those in conventional implantation studies, mainly due to the much longer time scale of the latter measurements.

The 10^+, 360 ns isomer in ^{54}Fe serves as a probe to detect hyperfine interactions, in particular the local magnetic environment of the probe nuclei. For a general description of this experimental method, we refer the reader to Ref. [16]. Figure 2 shows typical spin rotation patterns $R(t)$ and their Fourier transforms, recorded in an applied magnetic field of 2 T. The spectra clearly show a superposition of two components. For each component the amplitude of the anisotropy A, the Larmor frequency ω_L, and the nuclear damping time τ_N can be extracted from the time spectra. Using $\omega_L = h^{-1}\mu_N g_N \times\beta(T)$, the local susceptibility $\beta - 1$ can be deduced. In all three systems studied, a minority component of the implanted Fe impurities gives a nonmagnetic response, characterized by $\beta = 1.00(1)$. The inverse local susceptibility χ^{-1} of the magnetic components is shown in Fig. 3(a). The data exhibit a linear dependence on T, characteristic of a Curie-Weiss law: $\chi^{-1} \propto T + T_K$. The Kondo temperature T_K for Fe in Zr is zero within experimental error, while for Hf and Ti hosts we find T_K equal to 5(5) and 30(5) K, respectively (Table I). From the experimental Curie constant C, the product of the (0 K) hyperfine field B_{hf} and the effective spin S_{eff} can be extracted using the relation $C = 2\mu_B(S_{\text{eff}}+1)B_{hf}/3k_B$ (see Table I). The nuclear relaxation time τ_N shows a linear dependence on T, corresponding to a Korringa relaxation process [6] as shown in Fig. 3(b).

The two components observed in all three systems correspond to Fe impurities on different lattice sites. For the assignment of the lattice sites in α-Zr, we compare these results to the IBMS data given in Yoshida *et al.* [15]. These authors have identified interstitial Fe in Zr, by the isomer shift, the quadrupole splitting, and most importantly, by the temperature dependence of these parameters, which gives convincing indications of localized interstitial motion at low temperatures. As indicated by the relative amplitudes of the $R(t)$ data in Fig. 2, the ratio of magnetic to nonmagnetic components found in the TDPAD experiments is 1.8(3), in good agreement with the ratio 2.2(3) of the areas of the two Mössbauer lines attributed to substitutional and interstitial lattice sites [15]. This suggests that the magnetic component corresponds to Fe on substitutional sites; further support for this assumption is given by the nuclear damping time of the nonmagnetic component, which shows essentially no temperature dependence and is caused predominantly by the static electric quadrupolar interaction (cf. Ref. [17]). The site assignment as deduced from both the IBMS and TDPAD experiments is in addition strongly supported by the good agreement of the measured and calculated values for the isomer shifts and magnetic properties on substitutional and interstitial sites: compare Table I.

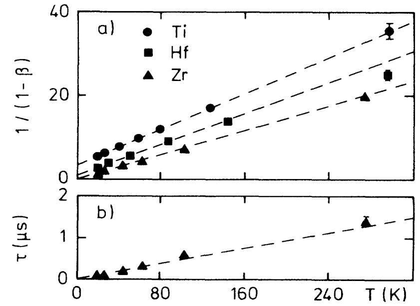

FIG. 3. (a) The inverse local susceptibilities of the magnetic components of Fe in Ti, Zr, and Hf can be well fitted by Curie-Weiss functions, which also yield the Kondo temperatures (see text). (b) The nuclear relaxation time of Fe in Zr follows a Korringa law: $\tau_N \propto T$.

To conclude, we summarize the important new results of this work: We have successfully explored *ab initio* calculations for an interstitial site in a metal, using the RS-LMTO-ASA method. Calculations for the substitutional sites using this method and the well-established KKR-Green's function technique agree with each other and both show excellent agreement with the experimental results of TDPAD and IBMS measurements on recoil-implanted Fe in Group IV metal hosts. This type of experiment, with sample preparation by deep implantation followed by a measurement within a short time (< 1 μs), seems to be the only reliable way of investigating truly isolated impurities in metals under conditions of almost negligible solubility and fast diffusion. Substitutional Fe atoms in all three Group IV hosts are found to be strongly magnetic with large local moments, and, especially for Fe in α-Zr, low Kondo temperatures. Interstitial Fe atoms are observed to be nonmagnetic, in agreement with the calculations.

We emphasize here the mutual benefits that theory and experiment receive from the combined investigation of microscopic properties in nonalloying systems, since they offer new and unusual applications and also provide critical tests of theoretical concepts under extreme conditions which cannot be found in alloying systems.

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