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Magnetic Behaviour of Implanted Transition Metal Probes at Different Lattice Sites in Metals*

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Abstract

Usually, the occurrence of magnetism on isolated, substitutional $3d$, $4d$ and $5d$ impurity ions in metals is restricted to certain $3d$ ions (mainly Cr, Mn, Fe, Co, Ni) in alloying metallic systems. The application of the perturbed γ-ray distribution method following heavy ion reactions and recoil implantation has offered an experimental technique for producing and investigating new magnetic systems. Of special importance are nonalloying systems, which can exhibit extreme variations of e.g. density of states and atomic volume in the probe–host combinations produced by recoil implantation. Recent developments in this field include the following: Magnetism and the Kondo effect observed for ^{43}Sc ions in alkali metal hosts are found to be consistent with a nearly localised, ionic $3d^1$ single-electron configuration, and parallel the behaviour observed in certain Ce systems. More generally, essential features of the magnetism of $3d$ and $4d$ ions in sp metal hosts are similar to those of $4f$ systems. Recent experimental and theoretical studies of ^{54}Fe in d-band metal hosts are of key importance for an understanding of the basic features of local moment formation on substitutional Fe ions in transition metal hosts in general.

In many nonalloying ^{54}Fe probe–host combinations, (at least) two different magnetic responses have been detected. These components correspond to substitutional and interstitial sites of the implanted probes, as has been verified by in-beam Mössbauer spectroscopy of ^{57}Fe in a series of host metals. This provides new insight into lattice site occupation as a function of host properties and allows directed investigations of the magnetic behaviour of Fe (and Mo) ions on interstitial lattice sites. Depending on the host metal, interstitial Fe is found to be nonmagnetic, e.g. in Zr, or magnetic, e.g. in Yb. Surprisingly, even the $4d$ ion Mo can be magnetic on interstitial sites. The experimental results for the substitutional as well as the interstitial sites can be compared to extensive theoretical work within the framework of local spin density calculations.

1. Introduction

Before discussing new magnetic systems, we would like to review some of the basic trends in magnetism of the $3d$ and $4f$ ions in metals. The magnetic behaviour and electronic structure of a dilute transition metal ion in a host metal is the result of a competition between the tendency towards localisation of partially-filled (d or f) shells, and charge and spin delocalisation due to hybridisation. The study of dilute systems is necessary to improve our knowledge about the basic interactions between the d or f orbitals with conduction electrons and/or ligands.

It is also important for an understanding of narrow-band phenomena in concentrated systems. During the past decades, extensive experimental investigations have been carried out using f and d ions placed into a variety of host metals with different electronic and lattice structures (Moriya 1985; Landolt-Börnstein 1989). Usually, f ions in metals reflect f linewidths small in comparison to Coulomb correlation energies, which allows a treatment within a localised picture. The bulk of metallic $4f$ systems has been described in terms of ionic-type models using configurations with intact intra-atomic correlations including spin–orbit (LS) coupling. In contrast, the d electrons in metallic $3d$ systems are often assumed to be itinerant. Usually local magnetic moments of $3d$ ions in metals are parametrised by an effective spin S_{eff}, as exhibited e.g. for Fe in noble metals and in certain d-band metal hosts. From the theoretical viewpoint, important quantities of $3d$ moment formation are not sufficiently well understood, e.g. the interactions of impurity $3d$ with s, p and d electrons of the hosts, the atomic spin and orbital correlations between the $3d$ electrons, and the role of crystal field effects.

In this review, we want to concentrate on new and recent developments in the field of electronic structure and magnetism of d ions in metals. Many of the systems studied are nonalloying and have been made accessible by applying perturbed γ-ray distribution techniques following heavy-ion reactions and recoil implantation (the time-differential perturbed angular distribution method—TDPAD). An extensive description of the TDPAD method, nuclear probes and measured quantities has been given in reviews (Riegel *et al.* 1982; Riegel and Gross 1988), which also include a discussion of basic aspects of local magnetism of $4f$, $3d$ and $4d$ ions in metals. Heavy-ion reactions combined with perturbed γ-ray techniques allow microscopic studies of the local susceptibility, spin dynamics and damping effects for $3d$, $4d$ and $4f$ ions in metals, in alloying and non-alloying systems. Many methodical aspects are governed by the heavy-ion reactions which, along with the production of the systems studied, also excite and align nuclear isomeric states. These then serve as nuclear probes for the measurement of the magnetic response via the magnetic hyperfine interaction. The magnetic response is observed by applying perturbed γ-ray distribution techniques. In the context of this paper we would like to note the following features of the method:

(i) Many appropriate nuclear probes of $3d$, $4d$ and $4f$ elements can be produced by heavy-ion reactions (Riegel and Gross 1988), exceeding by far the number of nuclear probes accessible to perturbed γ–γ angular correlations (PAC) and the Mössbauer effect.

(ii) One can observe the magnetic single-ion behaviour since the concentration of the d ions produced in the host metal is less than 1 ppm. Interactions between implanted magnetic ions can be excluded.

(iii) In many systems, the spin dynamics of the magnetic ion can also be observed.

(iv) The method is very sensitive to orbital effects in magnetism, due to the fact that magnetic hyperfine fields depend strongly on orbital contributions.

(v) Of special value is the possibility of observing the magnetic response in a large number of different probe–host combinations. The great variety of hosts permitted by recoil implantation allows a wide variation of the chemical surroundings of the magnetic ion, as reflected by the possibility of producing

both alloying and nonalloying systems. In particular, the extreme conditions in nonalloying systems, characterised e.g. by large differences in the cell volumes of the magnetic ions and hosts and by different electron densities at the Wigner–Seitz boundaries, can lead to new and extreme cases of local magnetism. In nonalloying systems it is even possible to explore the magnetic behaviour at *interstitial* lattice sites.

According to the results obtained so far, the magnetism and electronic structure of substitutional $3d$ and $4d$ ions in sp-metal hosts exhibit qualitative differences when compared to hosts with d-band electrons. In the following section we briefly review the basic results for d ions in sp-metal hosts with special emphasis on the illustrative example of Sc in alkali metals. Next, we wish to summarise recent progress in understanding the host dependence of local moment formation on substitutional Fe ions in transition metal hosts. This will be followed by a discussion of the production, lattice site characterisation, and magnetic behaviour of interstitial Fe impurities in metallic hosts. Nearly all results can be compared to extensive theoretical work within the framework of local spin density calculations.

2. Observation of Magnetism and Kondo Effect for Sc Ions in Alkali Metal Hosts

We have explored the possible occurrence of local magnetism on Sc ions in metallic hosts. In particular, we have investigated non-alloying systems with extreme differences between the properties of impurity and host atoms, which might favour the occurrence of magnetism. In large-volume 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 favours the survival of Sc $3d$ spin correlations and could possibly lead to the occurrence of magnetism.

The systems were investigated by means of the 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, αn)^{43}Sc in a thin carbon foil, followed by a recoil implantation into the various host metals. This technique produces extremely dilute ^{43}Sc nuclear probes with spin $I\ \pi = \frac{19}{2}^-$, nuclear g-factor $g_{\mathrm{N}} = 0 \cdot 3286(7)$, and a half-life of 473(5) ns (Häusser *et al.* 1978). The $\frac{19}{2}^-$ 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 have been observed in an external field near 2 T. Some selected examples of $R(t)$ spectra are shown in Fig. 1. From the Larmor frequencies ($\omega_{\mathrm{L}} = 2\pi h^{-1}\mu_{\mathrm{N}}\ g_{\mathrm{N}} B_{\mathrm{ext}}$), the local susceptibilities $\beta - 1 = B_{\mathrm{int}}/B_{\mathrm{ext}}$ (Riegel and Gross 1988) can be deduced. Some results are shown in Fig. 2. The large 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 predominant orbital contributions to $\beta(T)$ (Figs 1 and 2).

The fact that only one frequency is observed for the magnetic Sc systems, along with the clear systematic trends in the host dependence of Sc magnetism, indicates that Sc ions occupy only one and the same lattice site in the alkali
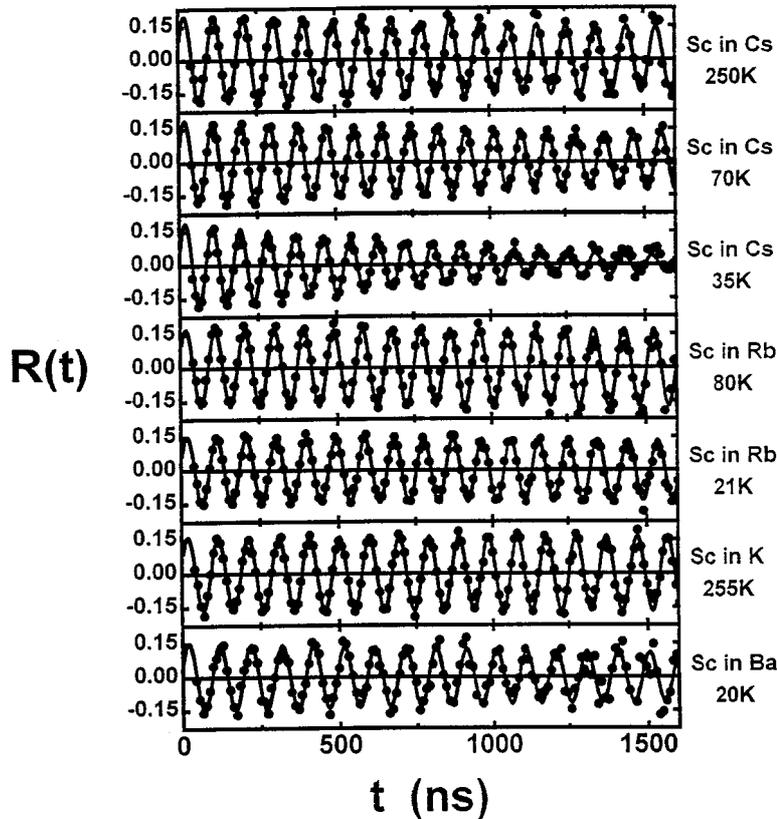
Fig. 1. 'Spin rotation' patterns: time spectra from ^{43}Sc implanted into Cs, Rb, K and Ba hosts; the normalised γ-ray counting rate is plotted as a function of time following implantation (beam pulse). The oscillation frequency $2\omega_{\mathrm{L}}$ gives information about the local magnetic field B_{int}, the amplitude about site occupation, and the damping times about relaxation rates and/or a possible distribution in values of B_{int}. [From Kapoor *et al.* (1996*a*).]

metal hosts, probably a substitutional site. [A single site is observed 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 of Sc (and other $3d$ and $4d$ ions) in alkali metal hosts will be given in a forthcoming paper. See also Gross *et al.* (1989).] As described in detail in Kapoor *et al.* (1996*a*), the results can be consistently analysed in terms of an ionic model with Sc^{2+} in a nearly localised, ionic $3d^1$ ($L = 2$, $S = \frac{1}{2}$) configuration. This one-electron configuration and the observed maximum in the local susceptibility as a function of temperature parallel the behaviour of $4f^1$ (Ce) ions in metals. We have given special attention to the study of the host dependence of the observed local magnetism of Sc in alkali metals, which represents a rather unique and illustrative example of the Kondo effect in $3d$ magnetism, originating from a weak hybridisation-induced antiferromagnetic coupling of the Sc $3d$ shell to the host s conduction electrons. Using the approximations $\beta - 1 \propto C/(T + T_{\mathrm{K}})$ for $T \gg T_{\mathrm{K}}$ and $\beta - 1 \propto C/T_{\mathrm{K}}$ for $T \ll T_{\mathrm{K}}$, and the experimentally determined Curie constant $C = 20$ K, the

essential trends of the host-dependent susceptibility, including the crossover from a strongly temperature dependent behaviour in Cs and the CsRb alloys 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 an increasing hybridisation of the Sc $3d$ shell in the smaller-volume hosts due to an increasing spatial overlap of the Sc $3d$ states with the host electronic states. Also, the maxima in $\beta(T)$ and their shift to higher temperatures with increasing T_K (see Fig. 2) can be reasonably well reproduced in terms of a Kondo model developed for localised one-electron states (cf. Kapoor *et al.* 1996a).
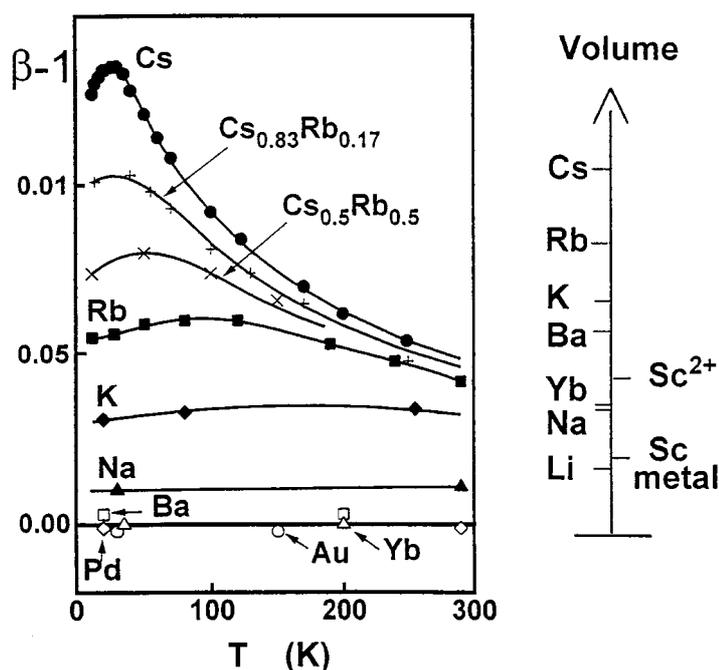

Fig. 2. Local susceptibility $\beta - 1$ as a function of temperature for Sc implanted into a variety of alkali-metal and alloy hosts. For comparison, results for Pd, Ba, Au and Yb hosts, where Sc is found to be nonmagnetic, are also shown. The relative atomic volumes for coordination number 12 are indicated at the right. [From Kapoor *et al.* (1996a).]

The formation of a magnetic moment on Sc ions in metals has attracted considerable theoretical interest in applying *ab initio* local spin density approximation (LSDA) calculations. Such calculations do not take into account spin fluctuations or the Kondo effect, but do yield a detailed insight into local electronic structure and magnetic moments. Since LSDA theories generally include only spin exchange interactions and neglect orbital correlations, the reproduction of orbital moments and ionic configurations with integral d occupation numbers cannot be expected. In remarkable agreement with experiment, sizeable magnetic moments have been predicted by LSDA theory for substitutional Sc ions in the alkali metal hosts, ranging from $1\cdot54\,\mu_B$ for Sc in Cs to $0\cdot69\,\mu_B$ for Sc in Na (Papanikolaou *et al.* 1992). Furthermore, the calculated unusually small d linewidths for $3d$ ions in

alkali metal hosts and their systematic increase in the host series Cs to Li are consistent with our analysis as given above.

In order to test more generally the host-dependent trends of 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, characterised by $\beta = 1$ (see Fig. 2). [Based on our experience with Fe and Mo ions implanted into Ba and Yb (Andres 1996; Andres et $al.$ 1998), we expect that Sc ions in these hosts (in contrast to the alkali metal hosts) will occupy both substitutional and interstitial lattice sites. From experiment we can conclude that all Sc recoils in Ba and Yb show a nonmagnetic response; see Section 5.] The lack of a magnetic response observed in the Ba and Yb hosts is in agreement with recent local spin density calculations for substitutional Sc in Ba (Papanikolaou et $al.$ 1995) and in Yb (Frota-Pessôa 1997), which yield no moments for either case.

3. General Features of the Magnetic Behaviour of $3d$ and $4d$ Ions in sp Metals

The behaviour of Sc ions in metallic hosts exhibits basic features common to the magnetism of other $3d$ and of $4d$ ions in alkali metal hosts and more generally in sp-metal hosts. It was shown some time ago by TDPAD experiments that Fe (Riegel et $al.$ 1986), Ni (Kowallik et $al.$ 1989), Mo (Riegel et $al.$ 1987; Gross et $al.$ 1989), Ru, and Tc (Gross and Riegel 1988) ions implanted into alkali metal hosts also develop ionic-type magnetism with strongly localised d-shell configurations. In many cases the ionic ground-state configuration can be determined with some certainty by applying a Born–Haber cycle, making use of experimental data for cohesive energies and heats of solubility (Riegel 1989). For a review of work on $4d$ impurities, see the article by Riegel (1994).

Special emphasis was put on studying the host dependence of local moment formation and the spin dynamics of Fe ions in sp metals in a systematic way (Riegel et $al.$ 1986, 1988). If magnetic, Fe ions in sp-metal hosts exhibit positive magnetic hyperfine fields and dominant orbital contributions to the local susceptibility (cf. Fig 3). In the extremely large-volume alkali metal hosts K, Rb and Cs, analyses of the magnetic properties are consistent with a fully localised $3d^6$ configuration for isolated Fe^{2+} ions with $L = 2$, $S = 2$, $J = 4$ in LS coupling. These results include the largest local moment of $6 \cdot 7 \, \mu_B$ yet observed for a $3d$ ion in a metal host. Also important is the finding that there are no indications of crystal field (CF) effects. The large lattice volumes and lack of $d–d$ hybridisation in these hosts allow the Fe impurities to retain their free-ion configurations to a large extent. The local susceptibilities of the Fe impurities systematically decrease with decreasing host lattice volumes (Riegel and Gross 1990), mainly due to increasing hybridisation of local Fe d electrons with host sp electrons. In hosts with small lattice volumes, e.g. Al and Ga, Fe ions are found to be nonmagnetic. Essential features of the magnetism of $3d$ and $4d$ ions in sp-metal hosts parallel the behaviour of $4f$ systems.

Starting with the work of R. Zeller for Mo in Na (Gross et $al.$ 1989), a rapidly increasing number of local spin density and cluster calculations have been performed for the magnetism and electronic structure of $3d$ and $4d$ ions in alkali and other sp-metal hosts. The systems are attractive for theory, because

of the many unexpected experimental results, the transition from itinerant to localised ionic-type behaviour, the simple electronic host structure, the possibility of testing theory over a wide range of host volumes, and that of investigating the d-impurity response in a given host as a function of the d-ion species. The interplay between experiment and theory is also important to improve theoretical concepts. Cluster calculations have been performed for d ions in alkali metals (McHenry *et al.* 1989) and for Fe in Al and alkaline-earth metals (Guenzburger and Ellis 1991; Papanikolaou *et al.* 1995). The magnetic behaviour of $3d$ and $4d$ ions in alkali metals has been calculated within a jellium model (Stefanou and Papanikolaou 1991), and extensive studies of $3d$ and $4d$ ions in monovalent metals were performed using the jellium model and Green function calculations (Papanikolaou *et al.* 1992). Furthermore, the magnetism of $4d$ ions in noble metals (Willenborg *et al.* 1992) and in Rb (Anisimov and Dederichs 1992) has been studied using the local spin density approximation theory. Recently, theoretical developments in this field have been reviewed by P. H. Dederichs (Dederichs *et al.* 1992). As in the Sc systems, the overall qualitative agreement of theory with experiment is satisfying. A quantitative agreement cannot be expected, since the LSDA calculations do not include intra-ionic orbital correlations or spin fluctuations. Furthermore, the calculations can be improved by taking into account lattice relaxation, in particular for systems such as Fe in alkali metal hosts, in which considerable lattice relaxation around the Fe impurity is to be expected (see e.g. Gonzales *et al.* 1998).

Fig. 3. Overview of TDPAD results for the local magnetism of substitutional Fe in metallic elements. The light grey shading indicates positive hyperfine fields and predominant orbital magnetism; dark grey shading indicates negative hyperfine fields and thus predominant spin magnetism. In host elements shown on a black field, Fe is nonmagnetic. Elements shown on a white field have not been studied or exhibit more complex behaviour as hosts for Fe (e.g. possible induced moments in the case of magnetically ordered hosts). [For references see Kapoor *et al.* (1996*b*) and Andres (1996).]

4. Magnetism of Substitutional Fe Impurities in d-band Metals

In contrast to the magnetism and electronic structure of Fe ions in sp-metal hosts, a qualitatively different behaviour has been observed for Fe ions in hosts with d-band electrons. As can be seen in the overview (Fig. 3), the hyperfine field of magnetic Fe impurities on substitutional lattice sites in d-band metals is found to be negative, including the systems Fe in Cu, Ag, Au, and even Fe in Hg (Riegel *et al.* 1989; Mishra *et al.* 1989). In d-band host metals, Fe, like other transition-element impurities, exhibits *effective-spin magnetism*: its orbital moment is effectively quenched and the effective spin S_{eff} is in general smaller than the ionic (Hund's rule) value. On a phenomenological basis it has been proposed that the magnetism in these systems is generally governed by interatomic interactions between impurity $3d$ and host d-band electrons. This interatomic d–d interaction is assumed to produce the more itinerant, spin dominated magnetism with negative hyperfine fields at the Fe site (Riegel and Gross 1990). However, the decisive problem of the appearance or disappearance of a local magnetic Fe moment as a function of the d-band host metal remained basically unsolved. As can be seen by inspection of Figs 3 and 4, Fe moment formation is not clearly correlated to straightforward host properties such as volume or electronegativity.
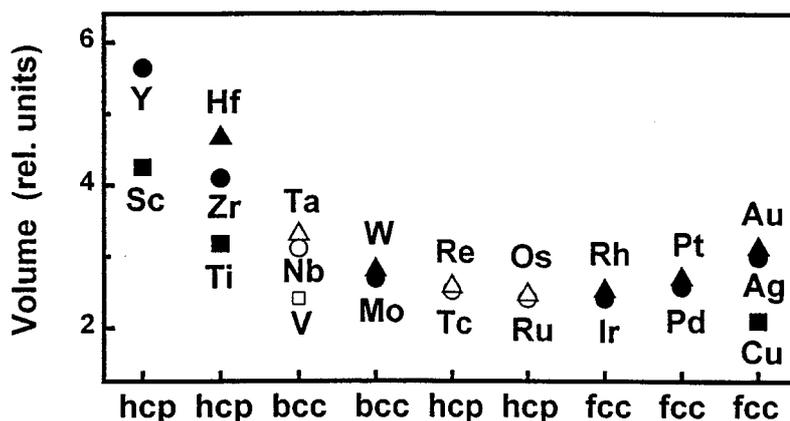

Fig. 4. Systematics of local moment formation on substitutional Fe in d-band hosts: squares indicate $3d$ hosts, circles are for $4d$ hosts, and triangles for $5d$ hosts. Filled symbols indicate the formation of local magnetic moments on Fe impurities, open symbols indicate nonmagnetic Fe impurities; note the groupwise occurrence of magnetism. The ordinate shows the relative host atomic volume for coordination number 12, and the lattice structure is indicated on the abscissa. [From Kapoor *et al.* (1996*b*).]

Only recently has this seemingly random behaviour been understood in terms of a simple physical picture (Kapoor *et al.* 1996*b*). The key to its explanation was a reliable study of the magnetic behaviour of Fe in certain d-band metal hosts by TDPAD, accompanied by *ab initio* theoretical calculations which offered insight into the mechanisms determining whether the Fe impurity will form a magnetic moment or not. The LSDA calculations for Fe in d-band metal hosts can be expected to be more reliable than those in sp-metal hosts because of the quenched orbital contributions and the smaller volume mismatch between

impurity and host atoms, and the resulting smaller lattice relaxation around the Fe impurities.

Using the TDPAD method, in part combined with in-beam Mössbauer spectroscopy (IBMS) data, and thus avoiding the cluster and compound formation which probably accompanied previous attempts to study these systems, it could be clearly shown that substitutional Fe impurities in Zr, Ti and Hf (Metz *et al.* 1993), and in Sc and Y (Kapoor *et al.* 1993) are magnetic, in agreement with theoretical predictions. Other important systems proved to be Fe in hosts from the seventh column of the Periodic Table. Earlier experiments had indicated the Fe impurity to be nonmagnetic in Re host, but magnetic in Tc (Riegel and Gross 1990; Tabatake *et al.* 1978) (the first member of this series, Mn, is magnetically ordered and has a *bcc* lattice structure, in contrast to the *hcp* structures of Re and Tc, and is therefore not directly comparable). Recent TDPAD results for Fe in Tc and Re (Kapoor *et al.* 1996*b*) confirm that it is nonmagnetic in both these hosts, completing the systematics for the $4d$ series of host metals (Fig. 4), and removing previous discrepancies.

If we combine the results of Kapoor *et al.* (1996*b*) with those of Beuerle *et al.* (1994), complete consistency between experimental and theoretical results for moment formation on Fe throughout the whole series of $4d$ metal hosts is established. The formation of local moments on Fe is clarified in terms of the local density of states at the impurity site, which results from the competition between *intra*-atomic and *inter*-atomic d–d-correlations. According to LSDA calculations (Frota-Pessôa 1992; Frota-Pessôa *et al.* 1993; Beuerle *et al.* 1994; Kapoor *et al.* 1996*b*), the essential factor in answering the question of moment formation is the hybridisation between the Fe $3d$ electrons and the d-band electrons of the host, causing the local density of states (LDOS) at the Fe site to adjust to the shape of the host band. Whether or not the local Stoner criterion is fulfilled, and thus the Fe impurity is magnetic, depends sensitively on the details of the host d-band shape, in particular near the Fermi energy, and on the strength of the d–d hybridisation. Furthermore, while the LDOS around the impurity site adjusts to the density of states $N(E)$ of the host, there remain important differences which are related to detailed properties of the host and the impurity, e.g. to their different lattice volumes. If the host offers a larger lattice volume than would be occupied by the impurity (Fe) in its own lattice, hybridisation between impurity and host d-electrons will in general be weaker than in the host itself, leading to narrower features in the LDOS, which typically is dominated by the d-electron density. This is illustrated in Fig. 5, which shows calculated LDOS curves for Fe as a substitutional impurity in *hcp* Tc and in a (hypothetical) *bcc* Tc host lattice (Kapoor *et al.* 1996*b*). Compared to the large-volume host, the less extended Fe $3d$ states are hybridised more weakly with the Tc $4d$ states, leading to narrower Fe $3d$ bands with a suppressed $N(E)$ at the lower band edges and higher peak densities near the Fermi level. As a consequence, the LDOS for Fe in a *bcc* Tc lattice shows two pronounced peaks near the Fermi level E_{F}, which is located near 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 $N(E_{\mathrm{F}})$ are decisive for the occurrence of Fe moments according to the Stoner criterion $I.N(E_{\mathrm{F}}) \geq 1$, where I is the host independent exchange integral $I = 0 \cdot 068$ Ry. In the hexagonal Tc

host lattice, Fe is calculated to be nonmagnetic, as found by experiment. The *bcc* Tc host, which is not experimentally accessible, would contain magnetic Fe impurities with a (spin) moment near $2 \cdot 4\,\mu_\mathrm{B}$.
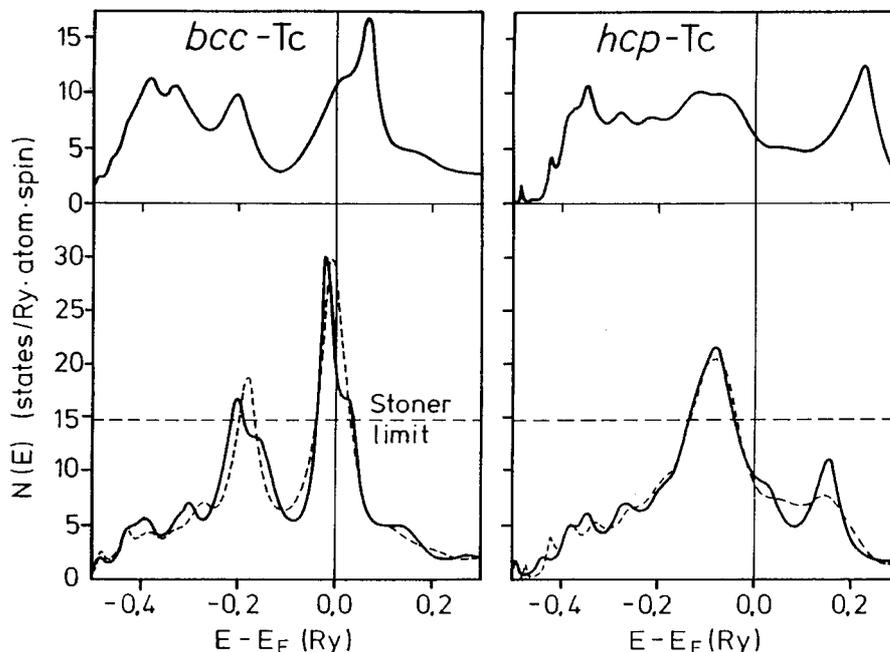

Fig. 5.   Calculated local densities of states at Fe impurities in *bcc* and *hcp* Tc hosts; for comparison, the pure host densities of states are shown above. The solid lines in the lower curves are results of a supercell calculation for FeTc$_7$, the dashed curves indicate an impurity calculation (cluster of 1600 atoms). The horizontal dashed lines show the local Stoner criterion for the occurrence of magnetism. [From Kapoor *et al.* (1996*b*).]

Most probably, the basic features now known for Fe moment formation in the $4d$ metal hosts can be generalised to Fe magnetism in $5d$ and in nonmagnetic $3d$ hosts. As can be seen from Fig. 4, without exception the existence or nonexistence of Fe moments in $3d$, $4d$ and $5d$ elements occurs groupwise, i.e. Fe is magnetic in *hcp* Sc, Y, in *hcp* Ti, Zr, Hf, in *bcc* Mo, W, in *fcc* Rh, Ir, in *fcc* Pd, Pt, and in *fcc* Cu, Ag, Au; and nonmagnetic in *bcc* V, Nb, Ta, in *hcp* Tc, Re, and in *hcp* Ru, Os. Most probably the interaction of the Fe $3d$ electrons with the structure and symmetry dependent host d bands governs the intricate host dependence of moment formation on Fe in transition metal hosts via the shape of $N(E)$ in a rather general manner. Furthermore, this interpretation provides a physical basis for the lack of an observed correlation of Fe magnetism with the host lattice volume (compare Fig. 4).

5. Iron Impurities on Interstitial Sites in Metal Hosts

Experiments employing TDPAD (Metz *et al.* 1993; Kapoor *et al.* 1993) and its combination with in-beam Mössbauer spectroscopy (Sielemann 1993; Keck *et al.* 1993) show that implantation of Fe into hosts where it has a limited or vanishing solubility yields a considerable fraction (up to 90%) of interstitial-site

occupation. This confirms indications seen in earlier work, e.g. on Fe in Hg (Mishra *et al.* 1989). On the other hand, in alloying systems, only substitutional sites are observed by TDPAD for the implanted impurities. By comparison of the measured isomer shifts at the different implantation sites with calculated values (Frota-Pessôa *et al.* 1993; Terrazos and Frota-Pessôa 1997), a reliable site identification can be performed.

Recently, systematic TDPAD measurements on Fe (and Mo) implanted into a wide variety of nonalloying host metals (Andres 1996; Andres *et al.* 1998) have shown the occupation of interstitial sites to be a very general phenomenon and have revealed clearcut trends within different groups of host metals. In the d-band hosts, a strong correlation of the site occupation probability with host lattice volume is found, giving a straightforward linear dependence of the interstitial-site occupation fraction on host volume. This trend might be explained in terms of the rigidity of the respective host lattices (Frota-Pessôa 1997): the relatively hard d-band hosts, with their large bulk moduli, can be treated in terms of a simple hard-sphere model, where the volume mismatch between impurity and host lattice is decisive for the occupation of non-substitutional sites. In sp-metal hosts (except alkali metals), the interstitial fraction is often larger than the substitutional occupation. This has been found for Fe in e.g. Al, Sr, Yb, Ba and Pb (Andres 1996; Andres *et al.* 1998). In contrast to d-metal hosts, no simple dependence of site occupation on host volume is observed. The only prominent exception to these systematic trends occurs for $3d$ and $4d$ impurities in the extremely soft alkali-metal hosts, where—at least for temperatures above 50 K—apparently only substitutional sites can be observed (cf. the discussion in Section 2).

Aside from the interesting and potentially important question of site occupation, which is the subject of continuing experimental and theoretical investigations, the observation of interstitial impurities opens up a whole new field for magnetic studies. The interstitial sites, with their different symmetries and considerably reduced lattice volumes, should lead to quite different magnetic properties on the interstitial impurity ions from those of ions occupying substitutional sites in the same host. In contrast to the large number of studies of substitutional magnetic impurities, no reliable experimental evidence has been available for the existence of a local magnetic moment at an interstitial lattice site in a metallic host. Challenging motivations for studying magnetism and electronic structure at interstitial sites are provided by the expected drastic changes in basic parameters, e.g. in volume and electron density. Any attempt at such a study has to overcome the difficulties in the production of interstitial-site impurities; in addition one requires a method with high local sensitivity to the magnetic response of the interstitials produced. The production of interstitial atoms in metals can be carried out reasonably well for self-interstitials and for light impurities (muons, H, B, C, N and O) and much effort has been spent on investigating such systems, in particular with respect to site locations, formation energies, and diffusion processes. The $3d$ ions can also be produced as self-interstitials in metals, e.g. by electron beam irradiation. However, no macroscopic method seems to be available to disentangle the possible magnetic responses of the very few interstitials from those of the many substitutional magnetic $3d$ ions. Moreover, one might speculate that magnetic moment formation on interstitial sites seems

rather unlikely. Naively, one would expect much more broadened $3d$ band states and suppressed atomic spin correlations at interstitial lattice sites as compared to substitutional sites, because the considerably reduced interatomic distances should lead to a much stronger $3d$ shell hybridisation. However, it was found that such arguments should be regarded with caution. Below, we discuss as illustrative examples two groups of impurity systems with interstitial site occupation which have been investigated in recent years.
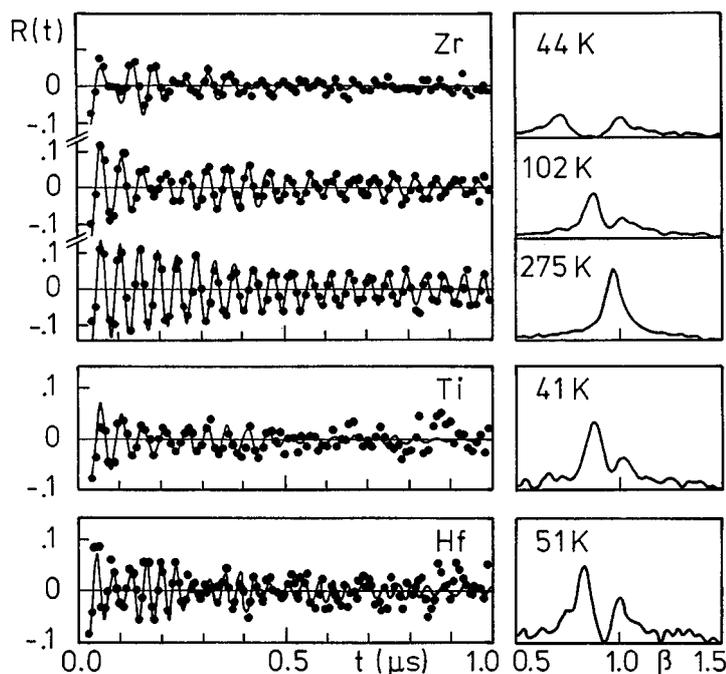
Fig. 6. Spin rotation patterns from ^{54}Fe implanted into the Group 4 hosts Zr, Ti and Hf. A 'beat' pattern is clearly seen in the time spectra, indicating the presence of two distinct Larmor frequencies and thus two different sites for the Fe impurities. Fourier transforms (right panel) confirm this conclusion and show one site (identified as the substitutional site in Zr) to be magnetic, and the other (interstitial) site to contain nonmagnetic Fe. [From Kapoor *et al.* (1993).]

The lack of magnetism on interstitial sites was in fact confirmed in hosts from the third and fourth columns of the Periodic Table (Metz *et al.* 1993; Kapoor *et al.* 1993). Results of TDPAD experiments on Fe implanted into Y, and Ti, Zr and Hf, show clearly two distinct sites, one exhibiting local magnetic moments and the other nonmagnetic (cf. Fig. 6). Comparison of the TDPAD results to in-beam Mössbauer effect data and to the theoretical predictions confirms the conclusion that the magnetic components correspond to Fe on substitutional sites, whereas the nonmagnetic components correspond to interstitial Fe sites in these hosts. Two theoretical methods were used to calculate properties of substitutional Fe impurity sites, and one of them was also applied to Fe ions on interstitial sites in Zr. The latter calculation 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 density approach (Frota-Pessôa 1992). The interstitial impurity was placed at the centre of an octahedral site in a cluster of 1200 atoms having the *hcp* structure. The six nearest neighbours were relaxed radially by 0·23 Å, in such a way as to distribute the overlap evenly among the close neighbours. The potentials at the impurity and the first three Zr neighbour shells (of six atoms each) were determined self-consistently. Interstitial Fe is predicted to be nonmagnetic and furthermore the isomer shift (IS) is calculated to be −0·59 mm/s. Both predictions are in excellent agreement with experiment. For Fe on the substitutional site, two independent calculations were performed using the RS–LMTO–ASA and the Kohn–Korringa–Rostoker (KKR) Green function methods.

The most important results of this work are (cf. Metz *et al*. 1993): (i) 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 interstitial diffusion. (ii) Substitutional Fe atoms in all three Group 4 hosts are found to be strongly magnetic with large local moments and, especially for Fe in Zr, low Kondo temperatures. (iii) Interstitial Fe atoms are observed to be nonmagnetic. (iv) *Ab initio* calculations have been successfully carried out for interstitial sites in a metal, using the RS-LMTO-ASA method. Calculations for the substitutional sites using this method and the well-established KKR Green function technique agree with each other and both show excellent agreement with the experimental results. More details of the calculations for interstitial sites are given by Frota-Pessôa *et al*. (1993).

More recently, TDPAD and IBMS experiments with Fe implanted into Yb (Kapoor *et al*. 1997) have been performed. Fe ions in this divalent host have shown—surprisingly—the formation of stable moments on both substitutional and interstitial sites; the results obtained from TDPAD measurements are summarised in Fig. 7. For substitutional Fe in Yb, the hyperfine field is positive, implying the presence of strong orbital magnetism, consistent with the behaviour of Fe in other *sp*-metal hosts. On the (probably octahedral) interstitial site, a weaker negative hyperfine field is observed. The occurence of magnetic moments on both lattice sites could be explained by LSDA calculations (see Fig. 8), which show that although the peaks in the local *d* band are in fact broader for Fe on interstitial sites, they are still sufficiently narrow to allow the formation of a stable local moment. The calculations were performed for different degrees of lattice relaxation around the interstitial Fe impurities, indicating convergence with the experimental parameters at values above about 12% relaxation as compared to the unrelaxed octahedral interstitial site. The value of 14% adopted by Kapoor *et al*. (1997) gives results consistent with the observed isomer shift of the interstitial Fe impurities and with a picture in which Fe on a (relaxed) octahedral interstitial site in Yb occupies a lattice volume close to that of Fe in Fe metal. On a substitutional site, the Fe volume is much larger, since Fe assumes a more localised, ionic $3d^6$ configuration.

Further studies of Fe and Mo impurities on interstitial sites in a variety of (mostly divalent) hosts (Andres 1996; Andres *et al*. 1998) have shown that interstitial magnetism is not uncommon, even for the $4d$-ion Mo. Interstitial site occupation and magnetic-moment formation on interstitial Fe impurities were

also observed for Fe in Gd and Tb hosts (Brewer *et al.* 1995); here, however, the comparison with theory showed that the interstitial site moments were induced by the ferromagnetic host lattices. An induced moment in the case of interstitial Fe in Yb (due e.g. to lattice pressure causing a valence transition to magnetic Yb^{3+} in the neighbourhood of the interstitial Fe impurities) could be ruled out by comparison with Sc impurities, which have an even larger volume than Fe but show no induced moment in the Yb host.
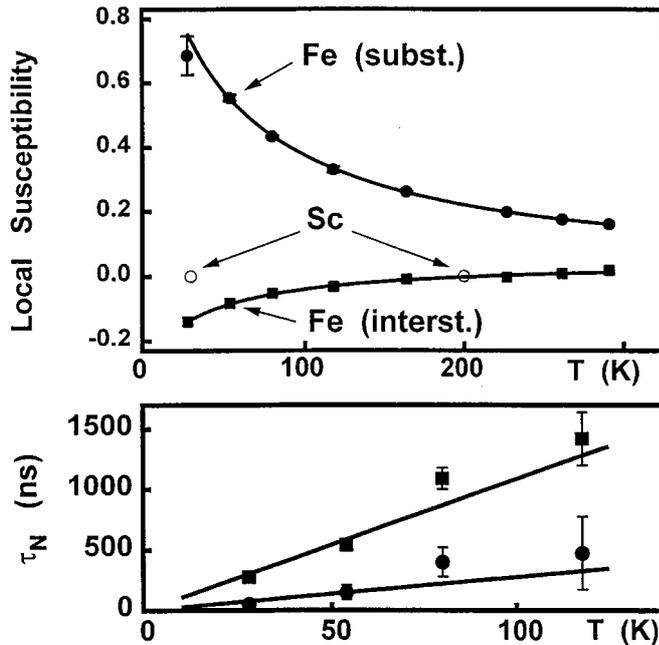
Fig. 7. Local susceptibility and damping times of Fe on substitutional (circles) and interstitial sites (squares) in Yb metal host as functions of temperature. The local susceptibilities of nonmagnetic Sc impurities are shown for comparison. Substitutional Fe has a Curie constant of $C = +54(4)$ K and a Kondo temperature T_K of 43(2) K, while interstitial Fe gives $C = -12 \cdot 3(1 \cdot 3)$ K and $T_K = 37(6)$ K. A Korringa law is obeyed by the damping times of Fe impurities on both sites. [From Kapoor *et al.* (1997).]

6. Summarising Remarks

In summary, we have emphasised that the TDPAD method applied to recoil-implanted ions following heavy-ion reactions and accompanied where appropriate by in-beam Mössbauer data is a powerful experimental tool for the study of the local electronic structure and magnetism of d- (and f-) impurity ions in a wide variety of host metals, including nonalloying systems. Combining these experimental results with calculations of the local density of states provided by modern LSDA theories allows considerable progress to be made in the understanding of basic trends in magnetic moment formation. We have described several areas where this combination has yielded interesting new results in the past few years: in Section 2, we discuss the discovery that Sc can form an ionic
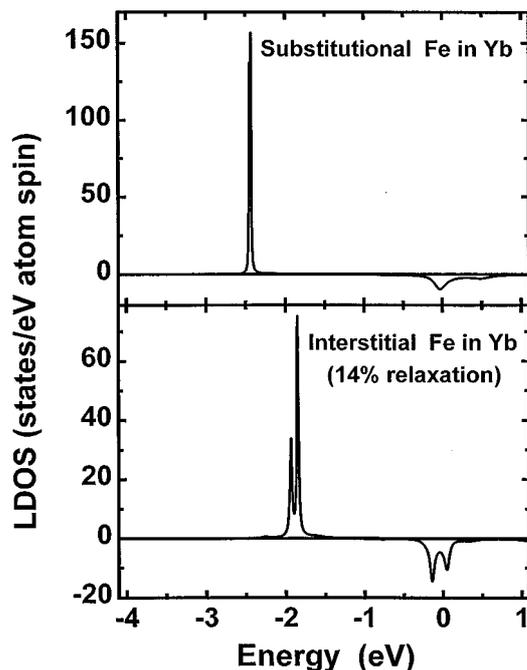
Fig. 8. Local density of states calculated by the RS-LMTO-ASA method for substitutional (above) and interstitial (below) Fe impurities in Yb. A relative lattice relaxation of 14% was taken into account in the interstitial-site calculation. In spite of some peak broadening for interstitial Fe, it clearly remains magnetic. [From Kapoor *et al.* (1997).]

$3d^1$ state in alkali-metal hosts and exhibits a Kondo effect similar to that seen in $4f^1$ systems, with a Kondo temperature related to the host lattice volume. These systems, while not completely described by current LSDA theories, provide a new test case for the development of theory. The Fe impurity (Section 3) exhibits similar behaviour, with a $3d^6$ ionic configuration in alkali hosts, but shows reduced magnetism in many other *sp*-metal hosts due to stronger overlap and hybridisation of its *d*-electrons with host band electrons; these effects can again be correlated to the host lattice volume. In *d*-band hosts (Section 4), on the other hand, Fe shows more complicated magnetic behaviour, and the completion of systematic studies of local moment formation on Fe impurities in the nonmagnetic *nd* hosts, combined with impurity and cluster calculations of its LDOS, have allowed for the first time a detailed understanding of the groupwise occurrence of local magnetism on Fe in these hosts to be gained. In nonalloying systems, a general tendency for the implanted ions to occupy interstitial sites has been observed (Section 5), with systematic regularities in the site occupation fraction as a function of host properties; these will be described in detail in a forthcoming paper. Such new interstitial systems provide another testing ground for theory, especially important now that theoretical methods are available to calculate the LDOS at an interstitial impurity in a metal host, including the effects of lattice relaxation around the impurity site. In all small-volume hosts

investigated thus far, interstitial Fe (and Mo) have been found to be nonmagnetic. In hosts with larger interstitial-site volumes, the new phenomenon of 'interstitial magnetism' has indeed been observed and is found to occur as predicted by theory.

This exciting field is the subject of ongoing experimental and theoretical studies, with emphasis on the understanding of magnetism at interstitial sites and of local environment effects in alloys and spin glasses, a topic which we could not take up in this brief review.

Acknowledgments

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