

First-Principles Calculations for Interstitial Fe Impurities in hcp Sc, Y, Ti, and Zr

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We have determined the electronic structure around interstitial Fe impurities in hcp Sc, Y, Ti, and Zr. The self-consistent calculations take lattice relaxation into account and were performed using the recently developed real space linear muffin-tin orbital scheme. This is the first time that such realistic calculations have been performed for isolated interstitial impurities in metals. In agreement with experiments, interstitial Fe was found to be nonmagnetic in these hosts; the calculated isomer shifts on both interstitial and substitutional Fe sites are also in excellent agreement with experiments.

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In recent years, due to advances in experimental techniques, there has been a renewed interest in the problem of impurities in metallic hosts. In particular, nonalloying systems can now be investigated, yielding information about moment formation and hyperfine fields at the impurity, as the host is varied throughout the periodic table [1]. The Fe impurity is especially suited for such studies, due to its interesting magnetic behavior and its flexibility when used as a probe. Several Fe impurity systems have been studied by combining time differential perturbed angular distribution (TDPAD) or in-beam Mössbauer spectroscopy (IBMS) methods with heavy ion recoil implantation of the impurity [1,2]. The results often show that the Fe impurity occupies more than one type of site, and the sites can have distinct magnetic and hyperfine properties. Theoretical results are important to understand these differences and identify the sites. Calculations for substitutional Fe in many hosts using different techniques are now available [3-5]; however, interstitial impurities break the structural symmetry of the Bravais lattice and often induce changes in the position of neighboring atoms. These features (due to practical problems or intrinsic limitations of the techniques) are difficult to incorporate in most of the existing methods and thus calculations for the interstitial sites could not be performed. The recently developed real space (RS) linear muffin-tin orbital atomic sphere approximation (LMTO-ASA) scheme [5,6] does not require any symmetry and can be used in the presence of lattice relaxation. Therefore it allows the study of both substitutional and interstitial impurities in metals.

Here we study the behavior of Fe in hcp Sc, Y, Ti, and Zr. These systems have been investigated recently using both TDPAD and IBMS, yielding interesting results. In all four hosts, two Fe sites with very different characteristics were observed [1,2,7]. The TDPAD experiments [1,7] indicate local moment formation at one of the Fe sites, while the other is found to be nonmagnetic. At one of the Fe sites the isomer shift is positive, but unusually large negative values are found at the other site [2,7]. Through theoretical calculations and empirical arguments, the magnetic site was associated with substitutional impurities, but several questions were left unanswered:

Why is the interstitial site nonmagnetic? Could this be due to a broadening of the peaks in the Fe local density of states due to larger overlap with neighbors? Is it reasonable to assume that the Fe impurities occupy an octahedral interstitial site in the hcp structure? Why are the values of the isomer shift so different at the two Fe sites? To address these questions in the present paper, we use the RS-LMTO-ASA scheme to determine, within the local spin density functional formalism, the electronic structure around Fe impurities in hcp Sc, Y, Ti, and Zr. The calculation is self-consistent and for the interstitial site, first-neighbor relaxation is included. This is, to our knowledge, the first time that such realistic calculations have been performed for isolated interstitial impurities in metals.

There are several ways of treating local perturbations within a first-principles approach [3,4,8]. One can use supercells in conjunction with standard reciprocal space methods, perform calculations for relatively small clusters, or use the Green's function (GF) approach within some well established formalism such as the Kohn-Korringa-Rostoker (KKR) or the LMTO. The Green's function describes correctly the embedding of the defect in the crystal and has been widely used to treat isolated impurities in metals. Substitutional impurities, which occupy a regular site of the Bravais lattice, are very well described within the Green's function formalism [3]. Interstitial sites in open structures such as the diamond structure of Si can also be treated, since the interstitial regions may be taken to be empty spheres when calculating the electronic structure of the host [9]. But metallic systems usually form closely packed structures and the inclusion of empty spheres tends to misrepresent the electronic structure of the host. The procedure may be used when no lattice relaxation is included, but even then only if the impurity atomic size is very small compared to that of the host [8]. In most cases, when interstitial impurities or self-interstitials in metals are considered, these conditions are far from satisfied and a more flexible approach is desirable. The RS-LMTO-ASA scheme is based on the well known LMTO-ASA formalism [10] and uses the recursion method [11]. The procedure is very similar to the usual reciprocal space LMTO-ASA formalism, but when

solving the eigenvalue problem to find the density of states, we substitute the k -space diagonalization by the real space recursion procedure. To avoid surface effects, large clusters of more than one thousand atoms are used. The RS-LMTO-ASA scheme has been tested with success in several metallic systems, and the results are in good agreement with those obtained using well established methods [5,6]. When applied to substitutional impurities in metals it yields results which agree well with those obtained with the KKR-GF formalism [5].

The RS-LMTO-ASA scheme is a linear method and makes use of the atomic sphere approximation, where the space is divided into Wigner-Seitz (WS) cells, which are then approximated by WS spheres of the same volume. To obtain the tight binding form of the Hamiltonian used in the real space formalism, the average WS sphere radius is used. In the case of interstitial impurities, the average WS radius in the impurity region is smaller than that of the rest of the system. Minor changes were made in the codes to describe correctly the basis functions for the LMTO-ASA most localized representation in this case [12]. In the present work, clusters of 1400 atoms, cut in order to keep the atoms of interest at a maximum distance from the surface, were used for both interstitial and substitutional impurities. For Sc, Zr, and Ti, a c/a ratio of 1.59 was used together with the experimental values for the lattice constant a . The c/a ratio is smaller in Y and the value 1.57 was taken. In all cases the impurity and its first shell of neighbors were treated self-consistently; the impurity and 12 neighbors (of two inequivalent types) in the substitutional case and the impurity and 6 neighbors (again of two types) in the interstitial case. The potential parameters of the remaining sites were fixed at bulk values. We have placed the interstitial site at the center of the octahedral void of the hcp structure. The Fe impurity is large and lattice relaxation must be included; here the first neighbors were relaxed radially by 10% of their distance to the impurity. The displacement is towards a neighboring void and not directly towards an occupied site. To work within the ASA, we have to define a WS sphere radius around all sites. These are well defined in the substitutional case, since the Fe occupies the site of a host atom, with the same WS sphere. In the interstitial case, the Fe impurity and its 6 neighbors occupy together 6 times the volume of a host WS sphere, but to make the choice unique we need an additional constraint. Here we chose the size of the WS radius to assure approximate charge neutrality at the interstitial Fe site [8]. Finally, in the present nonrelativistic calculations an exchange and correlation term of the form proposed by von Barth and Hedin was used [13].

Our calculations show that, in agreement with experimental evidence [1,2,7], the Fe impurity in Sc, Y, Ti, and Zr exhibits large local magnetic moments for substitutional sites and is nonmagnetic on interstitial sites. The substitutional sites will be discussed in detail in a future

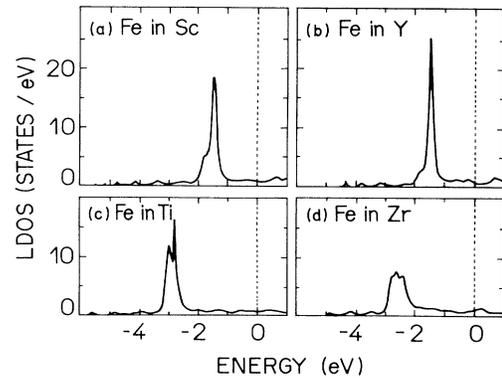


FIG. 1. Calculated LDOS at an interstitial Fe impurity in Sc, Y, Ti, and Zr hosts. Scale relative to the Fermi energy.

paper. Here we only mention that the “up” band in the local density of state (LDOS) of substitutional Fe in Sc and Y shows a very sharp peak at energies 2.5 eV below the Fermi level, while for Zr and Ti a much wider peak is observed at similar energies. In all cases, the “down” band has broad features around the Fermi level. Non-spin-polarized calculations in these systems yield high values of the LDOS at the Fermi level for the impurity site, and the Stoner criterion for magnetism is well satisfied.

In Fig. 1 we show the LDOS at the interstitial Fe site in Sc, Y, Ti, and Zr. In all cases the sharp peak which appears in the LDOS is part of a very broad d band which extends itself far above the Fermi level. It is clear that the naive picture, which attributes the lack of moment formation to the broadening of the peaks in the Fe LDOS as a result of compression, is incorrect. The peaks in the Fe LDOS at the interstitial sites are actually much sharper than those of the substitutional site in the corresponding non-spin-polarized calculation, but appear at energies further from the Fermi level. Therefore, the LDOS is very low near the Fermi level (see Fig. 1) and moment formation at the interstitial Fe site is not favored. In Table I, we show calculated values for the isomer shift at the Fe impurity nucleus in Sc, Y, Ti, and Zr for both substitutional and interstitial sites. Details of

TABLE I. Isomer shift in mm/s for substitutional and interstitial Fe impurities in Ti, Zr, Sc, and Y hosts.

	Substitutional		Interstitial	
	Theory	Expt.	Theory	Expt.
Ti	+0.03	+0.06 ^a	-0.75	-0.78 ^a
Zr	+0.16	+0.17 ^a	-0.58	-0.58 ^a
Sc	+0.18	+0.20 ^a	-0.49	-0.52 ^a
Y	+0.27	+0.29 ^b	-0.35	-0.48 ^b

^aFrom Ref. [2].

^bFrom Ref. [7].

the procedure used in the isomer shift calculations can be found elsewhere [14]. To convert the charge densities at the nucleus into isomer shift values, standard factors which vary between $-0.22a_0^3 \text{ mms}^{-1}$ and $-0.25a_0^3 \text{ mms}^{-1}$ are found in the literature [15]. In the present calculations following Akai *et al.*, a standard factor of $-0.24a_0^3 \text{ mms}^{-1}$, appropriate to nonrelativistic calculations, was used.

In Table I, the values of the isomer shift are arranged according to host size or WS radius. Taking Sc as reference, the WS radius is roughly 2% smaller in Zr, 10% smaller in Ti, and 10% larger in Y. Experimental IBMS values [2,7] for the isomer shift are also shown for comparison. The overall agreement is excellent and the trend is clear. As the Fe atom is compressed into smaller volumes, the isomer shift becomes more negative, indicating a larger electron density at the nucleus. Our results show that the core contribution to the isomer shift is roughly the same for interstitial and substitutional Fe sites in a given host. The large observed differences in isomer shift are mainly due to the contribution of valence ($4s$) electrons, which is positive for substitutional Fe sites and negative for interstitial Fe sites. The increase of the electron density at the nucleus can be associated with an increase of the value of the $4s$ radial part of the $4s$ orbital at the nucleus. This larger value at the nucleus, rather than an increase of the s occupation, is responsible for the negative sign and unusually large magnitude of the isomer shift at interstitial sites. We note that isomer shift values for the interstitial Fe site in Y show the largest discrepancy between calculated and experimental results. Since Y has the largest octahedral voids, we performed in this case calculations using a smaller first-neighbor relaxation, about 7% of the first neighbor distance. The variation in the isomer shift values was very small (around 0.03), indicating that the discrepancy in the Y host cannot be accounted for by lattice relaxation. Finally, we would like to use our results to comment on local moment formation in interstitial sites, where the impurity is much more compressed than in substitutional ones. It is clear from the figures that as the valence of the host decreases from 4 in Ti and Zr to 3 in Y and Sc, the peak in the Fe LDOS moves towards the Fermi level. The trend suggests that local magnetism at interstitial Fe sites is more likely to be found in hosts with two valence electrons than in those studied here; recent experimental evidence for a Yb host supports this hypothesis [16]. Motivated by the results, we performed non-spin-polarized calculations for an Fe impurity on an octahedral site in fcc Yb, with first-neighbor relaxation included. The LDOS at the Fe impurity shows a peak, but continuing the trend of Fig. 1, it is now only 0.4 eV below the Fermi level. Preliminary spin-polarized calculations for interstitial Fe in Yb indicate local moment formation at the Fe impurity. We note that, in contrast with the isomer shift at the non-magnetic sites, the value of the local moment is strongly

dependent on lattice relaxation. Finally, to complete our investigation, we should examine the behavior of the peak in the impurity LDOS as the number of valence electrons of the impurity is changed. Therefore, we have performed non-spin-polarized calculations for interstitial Cr and Ni impurities in the Sc host, including first-neighbor relaxation. From the results shown in Fig. 2, we see that the peak in the impurity LDOS moves towards the Fermi level as the valence of the $3d$ impurity is reduced, favoring the occurrence of local moments at the impurity site. Of course this is only true if the impurities occupy the same interstitial site: Being of similar size, Cr, Fe, and Ni probably all occupy the same position. But this might not be true when, for example, a self-interstitial in Sc is considered.

In summary, we have shown that the RS-LMTO-ASA scheme can be used to obtain the electronic structure around interstitial impurities in metals, in the presence of lattice relaxation. The present results should encourage the application of the RS-LMTO-ASA scheme to problems with similar characteristics, not easily solvable by other approaches. Our calculations for Fe impurities in Sc, Y, Ti, and Zr hosts show that, in agreement with experiment, substitutional sites exhibit local moments, while interstitial sites are nonmagnetic. We find that the LDOS at the interstitial Fe site shows a sharp peak below the Fermi level. The lack of moment formation at this site is due to the low values of the LDOS close to the Fermi level and not to broadening of the peaks in the LDOS of Fe as a result of compression. Our results show that the sharp peak in the LDOS of interstitial Fe moves towards the Fermi level as the number of valence electrons of the host decreases. The same behavior is observed when the number of valence electrons of the $3d$ interstitial impurity is decreased, for a given host. These trends suggest that local moment formation at Fe interstitial sites are more likely for hosts with two valence electrons than in the ones studied here. Results for interstitial Fe in Yb support this hypothesis and similar systems should be investigated. Our results also indicate that $3d$ impurities with lower valence than Fe could yield magnetic in-

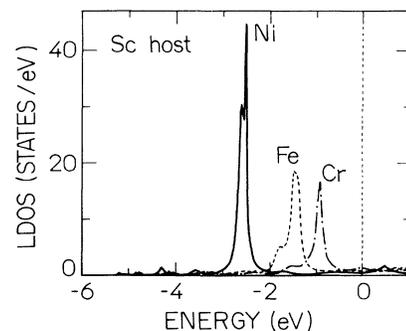


FIG. 2. Calculated LDOS at interstitial Ni, Fe, and Cr impurities in hcp Sc. Scale relative to the Fermi energy.

terstitials in Y or Sc, and should be investigated in this context. Finally, we have obtained the isomer shift at the Fe impurity in Sc, Y, Ti, and Zr hosts, and find agreement with experimental values for both sites.

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