

Magnetic behavior of interstitial Fe impurities in divalent Ca, Sr, and Yb hosts

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We have used a first-principles real-space approach to investigate the electronic structure and the magnetic behavior of interstitial Fe impurities in divalent Ca, Sr, and Yb hosts. The dependence of the local moment as a function of lattice relaxation around the impurity is obtained and contrasted with that of interstitial Fe in trivalent and tetravalent Zr, Y, Ti, and Sc hosts. The trends obtained for local moment formation at the impurity site are in agreement with experimental time-differential perturbed γ -ray angular distribution technique observations.

I. INTRODUCTION

The magnetic behavior of transition-metal impurities in metallic hosts is a classical problem and much has been learned about itinerant magnetism by investigating these systems. But in the past, due to limitations in experimental procedures and theoretical approaches, experiments have been restricted to thermally stable systems and interpretations were mostly based on simple phenomenological models. In the last decade, both experimental and theoretical tools for studying moment formation and other local properties around an impurity site in metallic hosts have considerably improved. Experimentally, many more systems can be investigated, partly due to the application of the time-differential perturbed γ -ray angular distribution technique¹ (TDPAD) and in-beam Mössbauer spectroscopy (IBMS),² which can be used to probe local properties of impurities implanted by recoiling into the host. Nonalloying systems are now accessible, yielding information about moment formation at the impurity site, as hosts are varied throughout the periodic table, even under these unusual extreme conditions. Theoretically, several *ab initio* approaches have been developed³⁻⁶ which can be used to investigate the electronic structure, magnetic behavior, and hyperfine interactions associated with impurities in metallic hosts. Recently, lattice relaxation of the host atoms around the impurity have been included in the calculations,⁷⁻⁹ interstitial impurities could be investigated,^{10,11} and orbital contributions to the hyperfine field at impurity sites have been evaluated.¹²

The Fe impurity in metallic hosts has attracted special attention due to its interesting magnetic properties and its flexibility when used as a probe.¹³ Several systems containing Fe impurities have been investigated by TDPAD and IBMS techniques and the results often show that the impurity occupies more than one type of lattice site, with distinct magnetic and hyperfine properties. Normally the sites have very different isomer shift values and can be clearly identified as Fe impurities occupying substitutional or interstitial positions in the host lattice.^{14,15}

Substitutional Fe impurities in metals have been studied using several different *ab initio* approaches and the agree-

ment between theory and experiment regarding moment formation at the impurity site is impressive. The mechanisms which govern moment formation in transition metal and simple metal hosts may differ considerably. In transition-metal hosts, moment formation at the impurity site is extremely sensitive to the lattice structure,^{6,16} while in simple metals where, at least to some degree, the valence electrons behave as an electron gas,¹⁷ the lattice structure seems to be less relevant. We note that the magnetic behavior of substitutional impurities is often harder to describe in simple metals than in transition-metal hosts. The agreement between theory and experiment is not as good and, even though progress has been made, a lot remains to be understood. In alkali metals and other hosts with very large volume per atom, the substitutional impurity seems to exhibit an ionic-like ground state for the d shell,¹⁸ with unquenched orbital moments. To describe the large positive hyperfine field values observed at substitutional Fe sites in these hosts, LS coupling has to be included in the calculations. Substitutional impurities in metals to the right of the periodic table (e.g., Al and Zn) can also be difficult to treat within *ab initio* local-spin-density-approximation (LSDA) approaches, due to the possibility of Kondo-like behavior.⁹ For substitutional Fe in Al, a borderline case with regard to the Stoner condition, moment formation is very sensitive to the distance between the impurity and its neighbors, and lattice relaxation of host atoms around the impurity should be included in the calculation.⁷⁻⁹

Interstitial impurities are even harder to describe using first-principles LSDA approaches, since realistic calculations require the inclusion of lattice relaxation around the impurity and break the structural order of the lattice. The lack of structural order makes the Green's-function-based Korringa-Kohn-Kostoker (KKR) and linear muffin-tin orbital (LMTO) procedures difficult to implement, while the extended nature of the defect renders the application of supercell approaches unrealistic. Some information about interstitial transition metal impurities in metallic hosts can be obtained using more flexible real-space approaches. The real-space muffin-tin orbital formalism, within the atomic-sphere approximation (RS-LMTO-ASA), has been used with success to understand

the magnetic and hyperfine behavior of $3d$ impurities in trivalent and tetravalent Y, Sc, Ti, and Zr hosts.^{10,15} Interstitial Fe impurities in these hosts were found to be nonmagnetic, in agreement with experiment, but the trends indicate that interstitial Fe in valence two hosts (Ca, Sr, Ba, and Yb) may develop a local moment.¹¹ Recent TDPAD experiments have observed interstitial magnetism at Fe sites in fcc Yb, a behavior which is compatible with results of RS-LMTO-ASA calculations for this system.¹⁴ The alkaline-earth metals represent a link between the alkaline metals where the jellium model seems to work reasonably well and the transition metals, and the magnetic behavior of substitutional Fe impurities in alkali-earth hosts has been investigated^{19,20} in this context. Interstitial sites require more flexible approaches, and no calculations for interstitial Fe impurities in alkaline-earth were reported.

Here, we use the RS-LMTO-ASA scheme^{5,21} to obtain the electronic structure and investigate the magnetic behavior of substitutional and interstitial Fe impurities in divalent fcc Ca, Sr, and Yb hosts. In the case of interstitial impurities we assume that the impurity occupies the octahedral site of the fcc structure and, to accommodate the Fe in the interstice, first-neighbor lattice relaxation around the impurity is included. Interstitial transition-metal impurities in Ca and Sr do exist and some, as in the case of interstitial Fe in divalent Yb,¹⁴ are probably magnetic. We hope that the present investigation will contribute to a better understanding of the mechanisms which lead to moment formation at interstitial impurity sites in metallic hosts.

The plan of the paper is as follows: in the next section, a brief account of the theory used in the calculations is given. A discussion of the Stoner criterion for magnetism as applied to impurities is also included. In Sec. III we show results for substitutional Fe impurities in divalent hosts and compare them with those in the literature. In Sec. IV we use non-spin-polarized calculations in conjunction with the Stoner criterion to discuss moment formation at interstitial impurity sites in metallic hosts. The magnetic behavior of interstitial transition metal impurities in divalent Yb, Ca, and Sr is considered in Sec. V. Finally, in Sec. VI we draw our main conclusions.

II. THE RS-LMTO-ASA SCHEME

In this section we give a brief outline of the RS-LMTO-ASA scheme used in our calculations. A detailed description of the method^{21,22} and its application to impurity systems^{5,23} can be found elsewhere. The RS-LMTO-ASA is a first-principles, self-consistent scheme which is based on the LMTO-ASA formalism^{24,25} and the recursion method.²⁶ It is a linear method, and the solutions are valid around a given energy E_ν , usually chosen to be the center of gravity of the occupied band. We work within the atomic-sphere approximation (ASA), where the Wigner-Seitz (WS) cell around each site is substituted by a WS sphere with the same volume. In the RS-LMTO-ASA scheme, the solutions of the Schrödinger-like equations within the WS spheres are obtained by the same procedures as those used in the usual k -space LMTO-ASA method and the approximations used to obtain the exchange and correlation terms are exactly the same.

In the RS-LMTO-ASA scheme we work in the orthogonal representation of the LMTO-ASA formalism,²⁵ for which the overlap is approximately given by the unit matrix, but express the Hamiltonian in terms of parameters of the tight-binding representation. In the first-order approximation, where only linear terms in $(E - E_\nu)$ are retained, we have a tight-binding Hamiltonian and the eigenvalue problem has the simple form^{5,21}

$$(H - E)u = 0, \quad (1a)$$

where

$$H = \bar{C} + \bar{\Delta}^{1/2} \bar{S} \bar{\Delta}^{1/2}. \quad (1b)$$

\bar{C} and $\bar{\Delta}$ are the potential parameters and \bar{S} is the structure constant in the tight-binding LMTO-ASA representation. \bar{S} is entirely determined by the lattice structure, i.e., by the position of the lattice sites. The potential parameters (\bar{C} and $\bar{\Delta}$) are related to the solutions of the Schrödinger-like equation inside the WS spheres around each site, and are determined self-consistently. To obtain the barred parameters of the tight-binding representation, the average value of the WS radius is used as a scale in the LMTO-ASA formalism. 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 introduced in the codes to correctly describe the LMTO-ASA parameters of the tight-binding representation in this case.

To obtain the local-density of states (LDOS), the occupations, and the charge transfers at each site, the Fermi level has to be determined. In crystalline systems the Fermi level is given at each iteration by filling the bands with the correct number of valence electrons. In the case of impurities and other local perturbations, the contribution of the disturbance to the electrostatic potential VES of the system goes to zero as we move away from the perturbed region. In this case, the Fermi level of the perturbed system is fixed by the Fermi level of the host, and the procedure has to be modified to take this into account. Therefore, when treating impurities, we first perform a RS-LMTO-ASA calculation for the host and obtain the Fermi level in the usual way, in the absence of perturbation. Then we set the Fermi level to this value and calculate self-consistently the occupation and other relevant quantities in the presence of the perturbation, in the region of interest. This region can include several shells of host atoms. It is clear that spin-polarized calculations should be used to investigate the magnetic behavior of metallic systems. But we argue that, since magnetism appears as consequence of an instability of the nonmagnetic state, to understand moment formation, non-spin-polarized calculations should be performed. Non-spin-polarized calculations in conjunction with the Stoner criterion for magnetism $N(E_F)I > 1$ will be used here to understand moment formation at impurity sites in metallic hosts. In the case of impurities, the Stoner condition can be applied locally,²⁷ using for $N(E_F)$ non-spin-polarized values of the LDOS at the impurity site and tabulated LDA Stoner parameters for transition metals for the constant I .²⁵ Experience shows that when the Stoner condition is satisfied locally, spin-polarized calculations lead to a local moment at the impurity, while nonmagnetic solutions are normally found when the condition is not obeyed. The criterion for

magnetism can be generalized^{25,27} by using the averaged values $\bar{N}(E_F)$ of LDOS over a small energy interval around E_F in the Stoner formula. As the energy interval tends to zero, the usual form of the Stoner criterion is retrieved. Sometimes, especially in the case of interstitial impurities, the generalized condition can be of use. We note that the simple Stoner condition does not give the values of the moments and may fail for borderline cases where $N(E_F)I$ is close to one: to obtain reliable values for the moments, spin-polarized calculations should be performed. But the simple Stoner condition gives a rather transparent picture of moment formation and will be used here, together with the first-principles results, to understand the magnetic behavior of interstitial impurities.

To obtain the electronic structure around impurities in divalent fcc Ca, Sr, and Yb hosts within the RS-LMTO-ASA formalism, large fcc clusters of ≈ 4000 atoms, with the experimental lattice parameter of the host, were used. We considered a basis set with nine orbitals per site, representing the valence s , p , and d electrons, and have used the Beer and Pettifor terminator,²⁸ with a cutoff parameter $LL=20$ in the recursion chain. We have worked within the LSDA, with the exchange and correlation potential of von Barth and Hedin.²⁹ We note that Yb is a divalent rare earth and $4f$ electrons must be considered in the calculations. Experimentally, Yb shows a fairly narrow $4f$ level approximately 2 eV below E_f which could, in principle, influence the Fe LDOS. But since $4f$ orbitals are very localized in space and the level is completely full we have, as was done previously, neglected hybridization and treated the $4f$ states of Yb as core levels in the calculations.

III. SUBSTITUTIONAL FE IN CA, SR, AND YB HOSTS

Here we will briefly present RS-LMTO-ASA results for substitutional Fe impurities in divalent Ca, Sr, and Yb. As we shall see, the moments at the impurity site are, in all cases, close to saturation. Under these conditions the presence of lattice relaxation around the impurity should not significantly change the magnetic behavior at the impurity site. Therefore, as done in previous calculations,^{14,19,20} lattice relaxation around the substitutional impurity site was not included. To investigate moment formation at the impurity site we have performed non-spin-polarized calculations for the substitutional Fe impurities in the three hosts. In all cases the LDOS at the Fermi level at the impurity site is very large and the Stoner criterion is easily fulfilled. This is to be expected in hosts with a large volume per atom and low valence, where the d levels of Fe show little hybridization with the host and are rather narrow. Since the d states at the Fe impurity are not totally occupied, non-spin-polarized calculations yield a sharp peak at the Fermi level, high values of $N(E_F)$ and a strong tendency towards magnetism. The spin-polarized results confirm this tendency and, in agreement with previous calculations,^{14,19,20} yield large values for the local moments. In Table I we show RS-LMTO-ASA values for the local moments at a substitutional Fe site in divalent Yb, Ca, and Sr hosts. Results of discrete variational method (DVM) (Ref. 19) and KKR Green's function (GF) (Ref. 20) calculations are also shown for comparison. In all cases, as expected for these hosts of large volume per atom and low

TABLE I. Local magnetic moments (in μ_B) for substitutional impurities in Yb, Ca, and Sr obtained using the RS-LMTO-ASA scheme. KKR-GF and DVM results from the literature are also shown for comparison.

Host	Yb	Ca	Sr
RS-LMTO-ASA	3.14	3.24	3.28
KKR-GF (Ref. 20)		3.28	3.33
DVM (Ref. 19)		2.93	3.01

valence, the moment at the substitutional Fe impurity is close to saturation.

IV. MOMENT FORMATION AT INTERSTITIAL IMPURITY SITES IN METALLIC HOSTS

We have used real-space non-spin-polarized calculations, in conjunction with the Stoner criterion, to investigate magnetic moment formation in interstitial transition-metal impurities in metallic hosts.^{10,11} As noted in Sec. II, spin-polarized calculations give information about the magnetic behavior of the system, while non-spin-polarized calculations should be used to understand moment formation (whether the system will exhibit magnetism or be nonmagnetic).

Some of our conclusions may be generally useful and will be reviewed here. In a naive picture one might expect the LDOS at interstitial sites to show broad peaks as result of compression. We found this to be incorrect.¹⁰ The peaks of the LDOS at interstitial Fe sites are often sharper than those of substitutional Fe in corresponding non-spin-polarized calculations. Interstitial Fe impurities in tetravalent Zr and Ti and trivalent Sc and Y hosts do not develop a moment because these sharp peaks appear far from the Fermi energy: as a consequence, $N(E_F)$ is small and the Stoner condition for magnetism is not satisfied. As the valence of the host is decreased, the peak in the LDOS gets closer to E_F , leading to higher values of $N(E_F)$. This behavior is clear from Fig. 1 where non-spin-polarized results for the LDOS of interstitial Fe impurities in tetravalent hcp Zr and trivalent hcp Y hosts¹⁰ are shown together with non-spin-polarized results for interstitial Fe in divalent fcc Sr. A similar behavior was

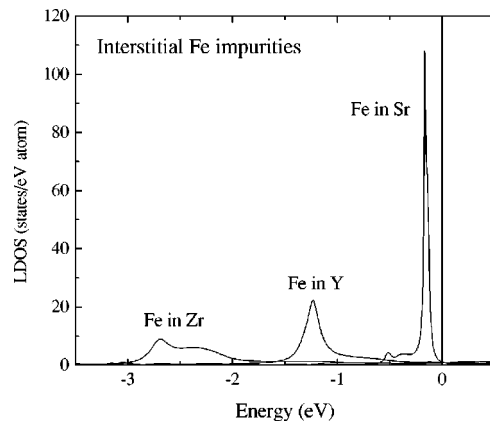


FIG. 1. Non-spin-polarized local density of states for interstitial Fe impurities in tetravalent Zr, trivalent Y, and divalent Sr. In all cases, a lattice relaxation of 10% of the first-neighbor distance to the impurity was assumed in the calculations.

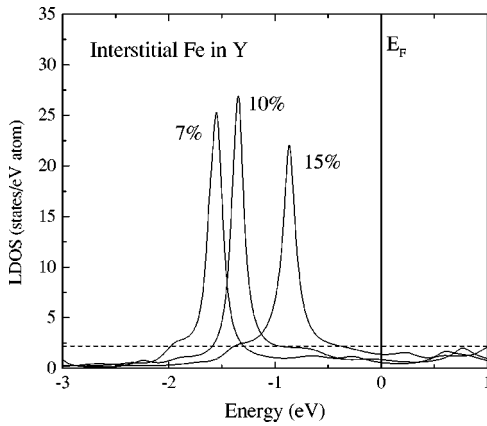


FIG. 2. Non-spin-polarized local density of states for interstitial Fe impurities in Y for three different values of the lattice relaxation (in units of % of first-neighbor distance to the impurity). The Stoner limit $N(E_F) = (I)^{-1}$ for Fe is also shown.

observed when non-spin-polarized results for Ti, Sc, Ca, and K hosts were calculated.¹¹ It is clear that for divalent hosts, where the peak in the LDOS appears close to E_F , the Stoner criterion (in its usual or generalized form) is often satisfied, and magnetic moments can be present.¹¹ A local moment associated with interstitial Fe impurities in Yb was in fact observed in TDPAD experiments.¹⁴ When other 3d impurities are considered, the peak moves towards E_F for elements to the left of Fe (e.g., Cr) and away from E_F for elements to the right of Fe. These trends, obtained from first-principles RS-LMTO-ASA calculations, can be qualitatively understood¹¹ using an extension of the Wolff model,³⁰ which was originally proposed to explain the behavior of substitutional impurities in transition metal hosts. According to the model, the peaks in the impurity LDOS are sharp resonances in a broad d band which extends far above the Fermi level. The position of the resonance will depend on the impurity potential and on the characteristics (valence) of the host. *It is the appearance of this resonant peak which is responsible for magnetic moment formation at d -series impurities on interstitial sites.* It is interesting to note that, in contrast with the more familiar case of virtual bound states, the resonant peak does not contain all of the d -electron states. The peaks of Fig. 1 exhibit this kind of resonant behavior. Even in the case of trivalent and tetravalent hosts, for which the resonant peak appears far below E_F , there are only about 6.8 d electrons at the Fe site, the other d states being located in the broad part of the d band which extends above E_F and are therefore unoccupied. This unusual behavior should be kept in mind when analyzing the LDOS at interstitial impurity sites.

Transition-metal impurities are usually too large to occupy interstices of the fcc or hcp structures of the hosts, and lattice relaxation around the impurity site will inevitably occur. We have investigated the dependence of the LDOS at the impurity site as a function of lattice relaxation and have verified that as relaxation increases, the resonant peak shifts towards the Fermi level. The shift is relatively small and does not affect the magnetic properties of interstitial Fe impurities in trivalent and tetravalent hosts; the interstitial Fe site remains nonmagnetic. This is illustrated in Fig. 2 where we show the position of the resonant peak in the LDOS at

the interstitial Fe impurity in Y, for three different values of first-neighbor relaxation, given in units of the unrelaxed distance to the impurity. The Stoner limit $N(E_F) = (I)^{-1}$, above which magnetism is favored, is also shown. It is clear from Fig. 2 that the effect of lattice relaxation is to move the resonant peak towards E_F . But for the Y host, even when large, unrealistic lattice relaxations of 15% are assumed, $N(E_F)$ remains below the Stoner limit and magnetic moment formation is not favored. In divalent hosts, in which the resonant peak in the LDOS of Fe appears very close to E_F (see Fig. 1), the situation is different and, as we shall see in the next section, lattice relaxation can drastically affect the magnetic properties of interstitial Fe in these hosts.

The position of the resonant peak as a function of the valence of the host, in conjunction with the Stoner criterion of magnetism, gives a clear picture of moment formation at interstitial Fe impurities in hosts to the left of the periodic table.¹¹ Interstitial Fe impurities are expected to be nonmagnetic in early transition metals such as Sc, Ti, V, etc., since the resonant peaks will be located far below E_F , leading to low values of $N(E_F)$. In the monovalent alkali hosts with low electron density such as K or Rb, the peak is pinned to E_F and the interstitial Fe site should exhibit a local moment. Divalent hosts are borderline cases regarding moment formation and the simple model given above suggests that lattice relaxation may play a crucial role.¹¹ In the next section we verify this point and present a careful analysis of the behavior of the local moment at interstitial Fe sites in divalent hosts, as a function of lattice relaxation.

The investigation of interstitial magnetism is a complex problem and presents difficulties which are hard to overcome. Due to the lack of periodicity and to the extended nature of the defect, the powerful k -space techniques cannot be applied and more flexible approaches must be used. The RS-LMTO-ASA is especially suited to deal with extended defects and other complex situations for which more traditional approaches may fail. But, in the case of interstitial impurities, one technical problem requires attention: when working within the ASA one must assign a WS radius to the impurity and, as we shall see, especially in the case of the divalent hosts considered here, the choice is not unique. We note that the size of an element in metals is not well defined, but it can have a physical meaning within a given model, and size-related concepts such as charge transfers and electronegativities are often cited in the literature. Therefore, before we proceed, we would like to explain our choice of WS radius and discuss some physical aspects associated with the simple models used here to define a reasonable range of values for the size of interstitial Fe impurities in divalent hosts.

When an impurity is placed in an interstitial position, some of the space previously occupied by host atoms will now be occupied by the impurity. For the divalent hosts considered here, the impurity is placed in octahedral interstitial sites of the fcc structure (center of the fcc cubic cell) and has six close nearest neighbors (at the faces). Here we assume that the impurity and its six neighbors share the space previously occupied by the neighbors alone, equal to six times the volume per atom in the host. But to make the choice of the impurity WS radius unique one needs an additional constraint. Two kinds of conditions are often used to define the WS radius in binary compounds: the space can be divided

TABLE II. In this table we give the values in atomic units of the WS radius for interstitial impurities in divalent hosts using both the charge neutrality condition (CT) and proportionality to size (PS). The average between these values (WSA) in the calculations for the interstitial Fe impurities and the host value (WSH), used in substitutional impurity calculations are also shown.

	Ti	Zr	Sc	Y	Yb	Ca	Sr
CN	2.53	2.59	2.66	2.75	2.90	2.95	3.15
PS	2.57	2.59	2.60	2.61	2.62	2.62	2.63
WSA	2.55	2.59	2.63	2.68	2.77	2.79	2.89
WSH	3.05	3.34	3.42	3.76	4.05	4.12	4.49

proportionally to the size of the elements (defined as the volume per atom which they occupy in the pure metals), or the WS radius can be defined in such a way as to assure approximate charge neutrality at all sites. In Table II we show the WS radius for interstitial Fe impurities in Zr, Ti, Y, and Sc hosts and in divalent Ca, Sr, and Yb using the two types of constraints: approximate charge neutrality at the impurity site (CN) and proportionality to size (PS). The WS radius of the host (WSH), related to the volume per atom of the host, is also shown. It can be seen from Table II that the two criteria give similar values of WS radius for Fe in transition metal hosts, but they differ considerably in the case of the softer divalent hosts. The WS defined by PS agree within 2% for all hosts, being slightly smaller than the WS of pure bcc Fe (2.662 a.u.), due to compression. But to get charge neutrality at the Fe site in divalent hosts, the WS radius at the Fe site has to be considerably larger than 2.662 a.u. Most transition metals encountered in nature respect the size of the atom as defined by the CN and PS criteria, which thus yield similar solutions for the radii of the WS spheres in intermetallic compounds. The same seems to be true, in a completely different context, for the trivalent and tetravalent hosts considered here, suggesting that the PS and CN criteria may give a consistent definition of size in transition-metal systems. A physical meaning may still be attributed to impurity size in divalent hosts, but it will probably depend on the model used. When size is defined by CN, the large WS radii of Fe in divalent hosts in Table II, which are considerably larger than that of Fe (2.662 a.u.), have an explanation: the Fe atom expands against these soft hosts which have rather low values of the bulk modulus. If the size of the Fe impurity is taken as approximately constant ($WS \approx 2.662$ a.u.), the results might indicate that the impurity is losing some of its $s-p$ electrons to the host and slowly acquiring a more ionic character. Here we use the PS and CN criteria to define a range of reasonable WS values for interstitial impurities. An average between the two values [(WSA) in Table II] was in fact used in the calculations. The magnetic behavior of interstitial impurities studied here is dominated by d states and is not sensitive to the choice of WS radius, rendering the above discussion unnecessary. But some properties, such as the isomer shift,³¹ have a stronger dependence on the choice of the WS radius used in the calculations, and more precise methods for determining the WS radius and evaluating the errors introduced by the ASA approximation would be useful.

TABLE III. Local magnetic moments (in μ_B) at an interstitial Fe site and induced moments at the neighboring host atom in Yb, Ca, and Sr divalent hosts for two different values of first-neighbor lattice relaxation. The radial displacement of the first-neighbor shell is also given, both in units of lattice constant $a(D)$ and in percentage of the distance to the impurity (%).

		M (μ_B)		Relaxation	
		Fe	First neighbor	%	D
Yb	LJ	0.73	-0.01	9.44	0.047
	LJ+20%	1.95	-0.02	11.30	0.056
Ca	LJ	1.29	-0.02	8.60	0.043
	LJ+20%	2.33	-0.03	10.40	0.052
Sr	LJ	2.43	-0.06	6.80	0.034
	LJ+20%	2.63	-0.04	8.20	0.041

V. RESULTS FOR INTERSTITIAL FE IMPURITIES IN FCC YB, CA, AND SR

Here we present our results for the electronic structure and magnetic properties of interstitial Fe impurities in divalent fcc Ca, Sr, and Yb hosts. The calculations were performed using large clusters of around 4000 atoms. In the calculations the interstitial site was placed at the center of the octahedral void of the fcc structure and lattice relaxation was included by displacing the six first neighbors to the impurity radially outwards, while leaving the position of all other sites unchanged.

We initially attempted to calculate values for the lattice relaxation using Lennard-Jones pair potentials obtained from the pure elements, where a linear and a constant term were added in order to make the potentials and the forces vanish after three lattice parameters.³² These short-range modified Lennard-Jones pair potentials had been used previously in studies of amorphous metals.^{21,32,33} To obtain values for the first-neighbor relaxations, we fixed the impurity and its second neighbors to their unrelaxed positions and allowed the six host atoms closest to the impurity to move radially under the forces generated by the pair potentials, until equilibrium was reached. Later, we realized that for the soft divalent hosts considered here, Lennard-Jones-like potentials probably underestimate the relaxation¹⁴ and decided that it would be useful to obtain results considering larger values for the relaxations. In Table III we show values of the local moment at the interstitial impurity site (in units of μ_B) for two different values of the lattice relaxation: the Lennard-Jones relaxation (LJ) and with a value approximately 20% larger (LJ+20%). It is clear that the local moment at the Fe sites is extremely sensitive to lattice relaxation and increases as the distance between the impurity and the first shell of neighbors increases. A similarly strong dependence of the local moment on first-neighbor relaxation around an impurity was found recently for substitutional Fe impurities in Al.⁷⁻⁹ In that case DVM, KKR, and RS-LMTO-ASA results show that the local moment at the substitutional Fe site in Al, which is quite large for the unrelaxed situation, diminishes and even vanishes when the distance between the impurity and its first shell of neighbors is reduced by relaxation towards the impurity. The results in Table III show that the local moment at the Fe site depends on the size of the host atom (see WSH in

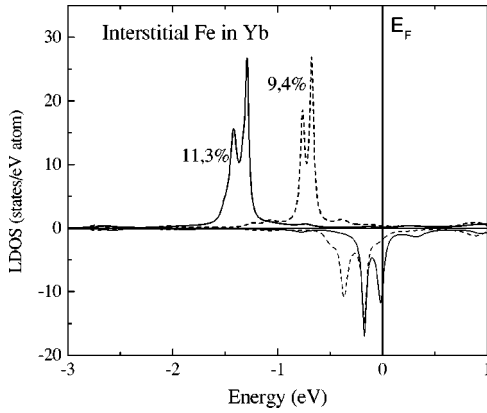


FIG. 3. Spin-polarized local density of states at the interstitial site for Fe in Yb, with the two values of relaxation shown in Table III.

Table II), defined as the volume per atom in that host. For these divalent hosts, the density of valence electrons decreases as the volume per atom increases, leading to a decrease of the hybridization between the impurity and the host and higher local moments. In Fig. 3 we show spin-polarized results for the LDOS of interstitial Fe in Yb for the two relaxation values of Table III. The energy range for the Fe states is very broad and we have restricted the plot to a smaller energy range which includes the resonant peaks. For the LJ relaxation the resonant peaks for both up and down states are located below E_F . This is in contrast to the behavior found for substitutional Fe impurities in these hosts, where the virtual bound state-like peak of the LDOS of Fe is always partially occupied and pinned to E_F . As we mentioned before, the resonant peaks in the LDOS of interstitial sites appear in a broad d band and may contain only a small number of states. If we integrate the LDOS for the LJ value of relaxation up to E_F we obtain around 3.7 d electrons with spin up and 3.2 with spin down. Since the resonant peak in the minority band contains a small number of electrons, it can appear below E_F for reasonable values of charge transfer around the Fe site. For the higher relaxation values (LJ +20%) the minority band moves up and contains empty states.

It is clear that the magnetic behavior of interstitial Fe

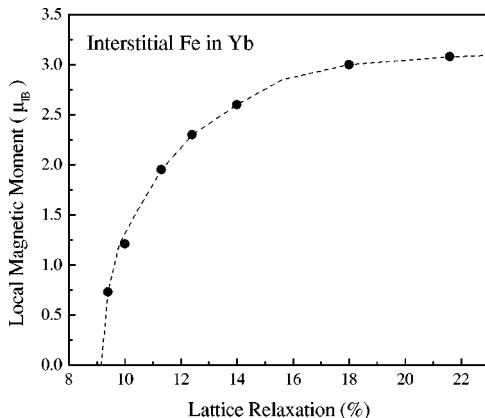


FIG. 4. Local magnetic moment (in μ_B) as a function of lattice relaxation (in percent of nearest-neighbor distance to the impurity) for interstitial Fe impurities in Yb.

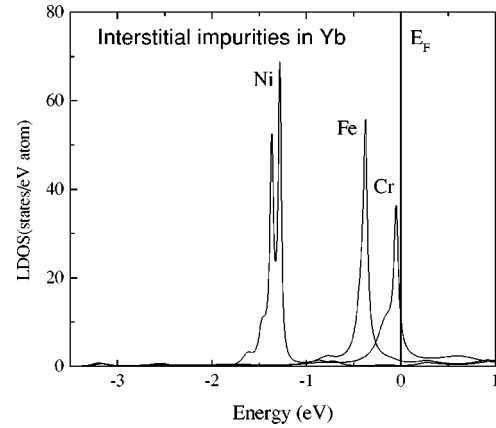


FIG. 5. Non-spin-polarized local density of states for interstitial Cr, Fe, and Ni impurities in Yb.

impurities in divalent hosts is extremely dependent on lattice relaxation. Since exact values for the lattice relaxation are difficult to obtain, to improve our understanding of interstitial impurities in divalent hosts, we investigated the magnetic behavior at the Fe site as a function of relaxation. Results for the local moment at interstitial Fe sites in Yb as a function of first-neighbor lattice relaxation are presented in Fig. 4. The dots are calculated points, while the dashed line is a guide through the points. For low values of relaxation, where the first-neighbor shell is displaced by less than 8% of the first-neighbor distance, the Fe impurity does not develop a moment. For larger relaxations a moment appears, increases rapidly and reaches its saturation value of slightly more than $3\mu_B$ characteristic of Fe. Similar behavior is observed for Fe in Ca and Sr, but due to the larger volume per atom in these hosts, the curve is shifted to lower values of the lattice relaxation: moments form and saturate at lower relaxation values, if units of % of the distance to the impurity are used. We do not have the precision to study extremely small values of the moment, but the shape of the curve points to a second-order transition to the nonmagnetic state, similar to that suggested for the case of substitutional Fe impurities in Al.⁸

Finally, we use the Stoner criterion in conjunction with non-spin-polarized calculations to investigate moment formation at the interstitial site for other transition-metal impurities in divalent hosts. As in the case of $3d$ impurities in Sc,¹⁰ for elements to the left of Fe the resonant peak moves towards the Fermi energy, while for those to the right of Fe it moves in the opposite direction. This behavior is illustrated in Fig. 5 where the position of the resonant peaks for interstitial Cr, Fe, and Ni impurities are shown. According to our calculations, for tabulated values of the Stoner I (Ref. 25) a moment will certainly develop at V and Cr sites, while interstitial Ni impurities in Yb will be nonmagnetic. Recently TDPAD experiments have shown that interstitial Mo impurities in Yb, Ca, and Sr can exhibit local moments.³⁴ This is compatible with the present calculations for interstitial Mo impurities which show that Mo in Sr develops a moment for LJ values of the relaxation, while the Mo impurity should be magnetic in all three hosts if the larger values LJ+20% are taken for the relaxation.

VI. CONCLUSIONS

We have used first-principles electronic structure calculations implemented in real space to study the magnetic behav-

ior of substitutional and interstitial Fe impurities in divalent Yb, Ca, and Sr hosts. Moment formation for other interstitial transition-metal impurities in the same hosts were also investigated. We argue that, since magnetism appears as the consequence of an instability of the *nonmagnetic* state, to investigate moment formation non-spin-polarized calculations should be performed. Here we used non-spin-polarized RS-LMTO-ASA results in conjunction with a local version of the Stoner criterion and tabulated LDA Stoner parameters to understand local moment formation at impurity sites in metallic hosts. Subsequently, spin-polarized calculations were applied to investigate the quantitative magnetic behavior of these systems.

For substitutional Fe impurities in Yb, Ca, and Sr the non-spin-polarized results show a narrow peak, with virtual-bound-state-like characteristics, around the Fermi energy. As expected, in all cases the peak is partially occupied, leading to high values of $N(E_F)$ and a strong tendency towards moment formation. In agreement with results obtained by other approaches,^{14,3,4} the spin-polarized RS-LMTO-ASA calculations indicate that substitutional Fe impurities in Yb, Ca and Sr should exhibit large local moments, close to the saturation value for Fe.

We also use non-spin-polarized calculations in conjunction with the Stoner criterion to understand moment formation at interstitial transition-metal impurities in Yb, Ca and Sr. Results for these impurities in Y, Sc, Zr and Ti obtained previously were also reviewed. In all cases the LDOS at the impurity site exhibits a sharp resonance as part of a broad d band, which extends far above the Fermi level. Contrary to the more familiar virtual-bound-state peak, the resonant peak does not necessarily contain all of the d states: some fraction of these states are located in the broad, extended portion of the d band. The non-spin-polarized results show that the position of the resonant peak relative to E_F , which depends on the type of impurity and the host valence, is essentially responsible for interstitial magnetism in the hosts to the left of the periodic table considered here. For interstitial Fe in trivalent and tetravalent hosts, the resonant peak appears far below the Fermi level. As a consequence, $N(E_F)$ is low and the impurity is nonmagnetic. For monovalent hosts such as K or

Rb the resonant peak is pinned to E_F and a moment should develop at the impurity site. For interstitial Fe in the divalent Yb, Ca, and Sr hosts investigated here, the resonant peak is very close to E_F and moment formation is extremely dependent on first-neighbor lattice relaxation around the impurity. This was confirmed by spin-polarized calculations which show that for interstitial Fe in Yb, the impurity is nonmagnetic for first-neighbor relaxations smaller than 8%, in units of % of the unrelaxed distance to the impurity, while at relaxations of 20% in the same units, the moment is close to saturation. Similar behavior was observed for interstitial Fe in Ca and Sr, but especially in the case of Sr, due to the larger volume per atom of the host, the moments form and saturate at lower relaxation values.

We have also investigated moment formation at other interstitial transition-metal impurity sites in divalent hosts. We find that $3d$ impurities to the left of Fe (such as Cr) should develop magnetism, while those to the right of Fe will probably be nonmagnetic (or develop moments at much higher values of lattice relaxation). In the case of Mo impurities, spin-polarized calculations were performed, motivated by TDPAD experiments.³⁴ We find that interstitial Mo impurities in Yb can develop a moment for first-neighbor relaxations of around 15% or more. Since Mo is a rather large impurity, we think that these relaxation values are realistic.

Finally, we should note that our findings regarding moment formation at interstitial impurity sites in metallic hosts are consistent with experimental results in these systems. TDPAD experiments find that interstitial Fe atoms in Y, Sc, Zr, and Ti are nonmagnetic,¹⁵ while magnetic behavior was observed for Fe and Mo interstitial impurities in divalent Yb, Ca, and Sr hosts.^{14,34}

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