

Understanding the isomer shift of Fe impurities in metallic hosts

L. A. Terrazos and S. Frota-Pessôa

Instituto de Física, Universidade de São Paulo, Caixa Postal 66318, 05315-970 São Paulo, SP, Brazil

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We have used first-principles linear muffin-tin orbital (LMTO) electronic structure calculations in the atomic sphere approximation (ASA), implemented directly in real space (RS) to investigate theoretically the behavior of the isomer shift of substitutional Fe impurities in metallic hosts. We find that the isomer shift in these systems is dominated by the $4s$ contribution at the Fe site. Since both the volume occupied by the impurity and the valence of the metallic host vary widely in the systems studied here, the influence of these factors on the isomer shift could be investigated. When RS-LMTO-ASA basis functions are used, a simple picture emerges, which allows us to understand the observed trends of the isomer shift in terms of two quantities: the number of $4s$ electrons at the impurity site and the probability of finding one of these electrons close to the nucleus. We find that probability follows a nearly universal curve as a function of the volume occupied by the impurity in the host, which leads to more negative isomer shift values as the Fe is compressed into smaller volumes. The number of $4s$ electrons at the Fe site depends both on the volume occupied by the impurity in the host and on the host valence. Our approach can partially deconvolute these dependences, calling attention to the interesting processes which regulate the isomer shift trends. [S0163-1829(97)01635-4]

I. INTRODUCTION

The isomer shift (IS) of Fe as measured by Mössbauer effect is a measure of the local charge density at the nuclear position and provides information about the local surroundings of the Fe probe. The volume occupied by the Fe atoms in the sample is one of the factors which can affect IS values. This has been known for a long time and is confirmed by the behavior of the IS of Fe in bcc Fe as a function of pressure.¹ Volume (or “size”) effects are especially important when one considers substitutional Fe impurities in metallic hosts, where due to the large variations of the host volume per site, the size of the substitutional Fe impurity can vary drastically from one host to another. An impressive amount of experimental data for the IS at the impurity site exists for these systems,^{2,3} but to deconvolute the effect of size from other effects, a theoretical model is needed. In the absence of more reliable approaches, empirical volume corrections⁴ are often used to compensate differences in size when investigating the influence of other quantities on the IS. Interesting trends emerge when the volume-corrected data are plotted against the valence of the host.³ But because the volume occupied by the substitutional impurity changes in a systematic way when the valence of the host is varied, “size effects” may still be present. The isomer shift of Fe depends on the electronic charge density at the nucleus (ECDN) and is strongly influenced by the behavior of valence electrons around the Fe probe. Therefore any reliable theoretical prediction of this quantity requires a precise description of the electronic structure around the impurity. Since impurities break the periodicity of the Bravais lattice, the usual k -space approaches cannot be applied and, although a few isolated calculations have been carried out, virtually no systematic theoretical study of the IS in the context of impurities in metallic hosts exists. One notable exception is the work of Akai *et al.*,⁵ which has contributed most of the present theoretical understanding of the problem. They used the Korringa-Kohn-Rostoker

Green’s function approach⁵ to study the electronic structure around impurities with atomic numbers between 1 and 56 in bcc Fe and calculate the IS of Fe atoms which are nearest neighbors to the impurity. The agreement between theory and experiment is impressive; the trends were well described and a general picture emerged. It was shown that the IS is directly proportional to changes in the $4s$ occupation of the Fe probe due to the presence of the impurity, and that the experimental trends could be explained in terms of this quantity. The contribution of core ($1s$, $2s$, and $3s$) states to the IS was found to be negligible and, contrary to the previously accepted view, influence of the $3d$ states of Fe is also of minor importance. Unfortunately, since the volume occupied by the Fe atom in this case does not vary with the inclusion of the impurity, the results of Akai *et al.* give no information about size effects.

In this paper we use the real-space (RS) linear muffin-tin orbital (LMTO) approach in the atomic sphere approximation (ASA) to study the IS of substitutional Fe impurities in metallic hosts, where volume effects play a major role. We use results of electronic structure calculations to deconvolute the various contributions to the IS and determine their relative importance. We also give a brief discussion of the basis functions used in the RS-LMTO-ASA scheme, since they will be used in our description of the IS. Finally, using the calculations as a guide, we develop a model which allows one to understand, in simple physical terms, the observed trends for the IS of Fe impurities in metallic hosts. The model shows the importance of volume effects to the IS of Fe and provides a simple way to estimate this quantity.

The paper is organized in the following way. In Sec. II we use the RS-LMTO-ASA scheme⁶ to obtain the IS of substitutional Fe impurities in metallic hosts. In Sec. III we discuss the RS-LMTO-ASA basis and introduce a simple physical model which allows us to describe the behavior of the IS. The model is used in Sec. IV to understand the observed IS trends. Finally in Sec. V we present our conclusions.

II. RS-LMTO-ASA RESULTS FOR THE ISOMER SHIFT OF Fe IN METALLIC HOSTS

Here we use the first-principles, self-consistent, density functional RS-LMTO-ASA scheme⁶ to obtain the electronic structure and the IS around substitutional Fe impurities in Al and in a large number of hosts of the $3d$ and $4d$ rows of the Periodic Table. A brief description of the method will be given here to state a few approximations and establish notation. A detailed description of the scheme and its application to impurities can be found elsewhere.⁶ The LMTO is a linear method⁷ and its solutions are valid around an energy E_ν , normally taken to be at the center of gravity of the occupied part of the band. We work within 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. In the RS-LMTO-ASA scheme⁶ a tight-binding Hamiltonian H , which allows interactions only between close neighbors, is used and the wave function Ψ_E can be expressed in terms of $\varphi_{l\nu}(r_R)$ and $\dot{\varphi}_{l\nu}(r_R)$, energy independent functions defined inside the WS sphere around site R . The eigenvalue problem has the simple form given below and can be solved in real space using the recursion method:⁸

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

$$\Psi_E = \sum_{RL} [\varphi_{l\nu}(r_R) + (E - E_\nu)\dot{\varphi}_{l\nu}(r_R)] Y_L(\hat{r}_R) u_{RL}(E).$$

Within the RS-LMTO-ASA scheme, the radial part $\varphi_l(E, r_R)$ of the basis function for each angular momentum l and each site R is expanded around the energy E_ν and higher order terms in the expansion are neglected. Actually $\varphi_{l\nu}(r_R)$ and $\dot{\varphi}_{l\nu}(r_R)$ are the solutions of a Schrödinger type equation with quantum numbers $L = (l, m)$, and its first energy derivative. The potential used to solve the equation is the self-consistent spherical potential inside the WS sphere around site R and the values are calculated at energy E_ν . These functions are defined to be zero outside their own WS sphere and this has some advantages. When the RS-LMTO-ASA scheme is applied to obtain the IS, one does not have to worry about contributions to the ECDN for the probe arising from tails of orbitals at neighboring sites, a major concern when the linear combination of atomic orbitals (LCAO) is used as the basis. In the real-space formalism used here, the valence contribution to the ECDN at the Fe probe is completely determined by the $4s$ electrons associated with the probe site.

The IS at the Fe site can be obtained in terms of the calculated electronic charge densities $\rho^{\text{imp}}(r)$ at the Fe impurity and $\rho^{\text{Fe}}(r)$ at the Fe site in bcc Fe (taken here as reference), both substituted at the nuclear region by taking $r=0$. In units of mm/s we have

$$\text{IS} = \alpha [\rho^{\text{imp}}(0) - \rho^{\text{Fe}}(0)]. \quad (2)$$

The constant $\alpha = -0.24$ is given in units of a_0^3 mm/s.⁵ We have used superscripts to indicate either the impurity or bcc Fe. This notation will be kept throughout the work. To calculate the IS we need the ECDN at the probe site, which can be obtained from electronic structure calculations. The electronic charge densities used here were obtained from RS-

LMTO-ASA calculations performed by us or from previous calculations by members of our group.⁹ In a few cases the IS results have already been published.¹⁰ To perform electronic structure calculations in real space with the RS-LMTO-ASA scheme, large clusters are normally used. The IS values shown here were obtained for clusters of 1600 atoms or more, cut in order to keep the impurity at a maximum distance from the surface. In all calculations, experimental values of the lattice constant were used. The calculations were performed within the local spin density functional approximation with an exchange and correlation term of the form proposed by von Barth and Hedin.¹¹ Valence s , p , and d electrons were considered in the basis, a total of nine orbitals per site. The eigenvalue problem of Eq. (1) was solved in real space using the recursion method.⁸ For all sites and orbitals considered here, a cutoff parameter $L_{\text{max}} = 20$ was taken in the recursion chain and the Beer and Pettifor terminator¹² was used. The impurity and first shell of neighbors were included self-consistently in the calculations, while the potential parameters at the other sites were kept at the bulk values of the host. In some cases a larger number of shells around the impurity were included self-consistently, but there were no significant changes in the IS of the Fe impurity. Finally we should note that, as is usually done in the literature, we have taken the WS radius around the substitutional Fe impurity to be the same as that of the host. This choice gives the minimum overlap between the WS spheres and has also some physical significance: if we neglect the structural relaxation of the neighbors, which is usually small,¹³ the volume available for the substitutional Fe impurity is determined by the volume of the missing host atom that it replaces. In this sense, the WS radius of the host gives a measure of the ‘‘size’’ of the Fe impurity in the given metal.

We have used results of the RS-LMTO-ASA electronic structure calculations for the impurity systems and for bcc Fe, to obtain the ECDN at the Fe site. These values were used in Eq. (2) to determine the IS of the substitutional Fe impurities in several metallic hosts. In Fig. 1 we show the calculated IS values (full squares), plotted as a function of the WS radius of the host, which has been used to characterize the ‘‘size’’ of the Fe impurity in the metal. We have divided the hosts into two classes according to their position in the Periodic Table; those to the left of Fe, such as Zr and Cr, are shown in Fig. 1(a), while those to the right of Fe, such as Cd and Al, are shown in Fig. 1(b). Experimental values^{2,3} (open circles) for the IS are also given for comparison. The agreement, excellent in the case of transition metal hosts, is less impressive when simple metals are considered. But, in all cases, the observed experimental trends are very well described by the calculations. We should note that spin-polarized calculations were used to obtain the IS values of Fig. 1 for systems in which the Fe impurity develops a local moment. Magnetism tends to make the IS results more negative, typically by a few hundredths of mm/sec. These changes are small in the scale of Fig. 1 and a similar overall agreement between theory and experiment would have been obtained if non-spin-polarized calculations had been used.

III. THE RS-LMTO-ASA BASIS AND A SIMPLE MODEL FOR THE ISOMER SHIFT

Having established that the experimental trends are well described by RS-LMTO-ASA calculations, we will proceed

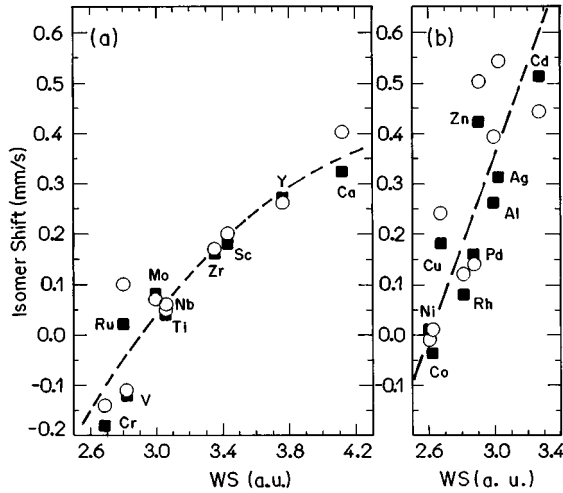


FIG. 1. Theoretical (full squares) and experimental (empty dots) values for the IS of Fe in metals as a function of the WS radius of the host. Hosts to the left (a) and right (b) of Fe in the Periodic Table are shown.

to use the theoretical results as a guide, and try to understand the behavior of the IS of Fe in metallic hosts. In this section, we explore the simplicity of the present real-space approach, in order to determine which are the quantities which influence most the IS behavior. By neglecting the unimportant contributions, we introduce a physical model which allows one to understand the behavior of the IS in terms of two simple quantities; the number of $4s$ electrons at the impurity site and the probability to find one of these electrons close to the Fe nucleus.

It is usual to decompose the IS into a core contribution from $1s$, $2s$, and $3s$ core electrons and a valence contribution associated with the $4s$ electrons at the impurity site. Akai *et al.* have shown that, for impurities in bcc Fe, the core contribution to the IS at an Fe first neighbor to the impurity is negligible.⁵ For the Fe impurities in metallic hosts studied here, core contributions are usually slightly negative and not negligible. But they show no systematic behavior and therefore do not influence the trends. When we plot the core contributions to the IS at the Fe site as a function of the WS radius of the host for all hosts considered here, the points scatter randomly around an average value of -0.08 mm/s, with a dispersion (given by the variance) of less than 0.05 mm/s. We note that the behavior of the IS shows very definite trends, which cannot be related to the random behavior of the core contributions. We also note that the variation of the IS values is one order of magnitude larger than the observed variations of the core contribution, rendering these contributions unimportant on the scale of Fig. 1. Here, to make the model more transparent, we will neglect these unimportant core contributions and concentrate on the dominant valence $4s$ contribution.

To evaluate the valence contribution to the IS we consider the wave function Ψ_E given in Eq. (2). As in the case of the electric field gradient¹⁴ (and for similar reasons), the influence of the linear term in $(E-E_\nu)$ to the IS is extremely small and can be neglected. The wave function Ψ_E can then be written as

$$\Psi_E = \sum_{RL} \varphi_{l\nu}(r_R) Y_L(\hat{r}_R) u_{RL}(E). \quad (3)$$

The above expression shows Ψ_E expanded in terms of an energy independent basis of s , p , and d orbitals ($l=0, 1, 2$), characterized by radial functions $\varphi_{l\nu}(r_R)$, at each site R . As in the case of the more familiar LCAO basis, the radial part depends on the quantum number l and the corresponding angular part given by the usual set of spherical harmonics Y_L , where $L=(l,m)$. The radial functions $\varphi_{l\nu}(r_R)$ are normalized solutions of the Schrödinger equation inside the WS sphere at site R , taken at energy E_ν and subjected to appropriate conditions at the sphere boundary. One could think of the elements of the simple RS-LMTO-ASA basis defined above as being a sophisticated version (since they are solutions of a self-consistent potential) of “renormalized atom” orbitals, in the same sense that atomic orbitals constitute the basis elements in the LCAO formalism. The main disadvantage of the renormalized atom orbitals when compared to the atomic orbitals is that they are obtained numerically and cannot in general be represented by a simple function. On the other hand, there are important advantages: the renormalized-atom-like orbitals constitute a rather good basis for metals, since inside their own sphere, they can be used to simulate reasonably well the charge density of metallic systems. The metal could then be seen as a collection of closely packed spheres. As a consequence, even the simple renormalized atom theory¹⁵ can give a reasonable qualitative description of the cohesive energy and bulk modulus of metals. Another advantage of our renormalized atom basis functions is that they are defined to be zero outside their own sphere (no tails), and are orthogonal to each other and to the core levels.

Finally we should stress that the quantities used to describe physical systems may be basis dependent and models which are introduced to guide our intuition, when investigating a given phenomena, are not unique. The description of the IS given in terms of the renormalized-atom-like RS-LMTO-ASA basis will differ from the more familiar description based on LCAO-like orbitals. The RS-LMTO-ASA basis can be in some cases simpler and more transparent, being especially well suited to the study of local properties. For example, in the LCAO description of the IS, orbitals located at neighboring sites contribute to the ECDN at the probe through their extended tails. The evaluation of this contribution adds to the complexity of the problem. In the present treatment, since the values of $\varphi_{s\nu}(r_R)$ are zero outside their own WS sphere, the neighboring sites give no direct contribution to the IS at the probe.

We proceed to use the renormalized-atom-like basis introduced above in order to obtain expressions for the ECDN and the IS. The valence contribution to the IS at the Fe impurity, $\rho_{4s}(0)$, is given by an integral up to the Fermi level of $|\Psi_E|^2$, taken at the position of the nucleus. With Ψ_E given by Eq. (3), the electronic charge density $\rho_{4s}(0)$ can be simply written in terms of the $4s$ occupation n_{4s} at the impurity site and the function $\varphi_{s\nu}(r)$ taken at the nuclear position $r=0$ as

$$\rho_{4s}(0) = (4\pi)^{-1} |\varphi_{s\nu}(0)|^2 n_{4s}. \quad (4)$$

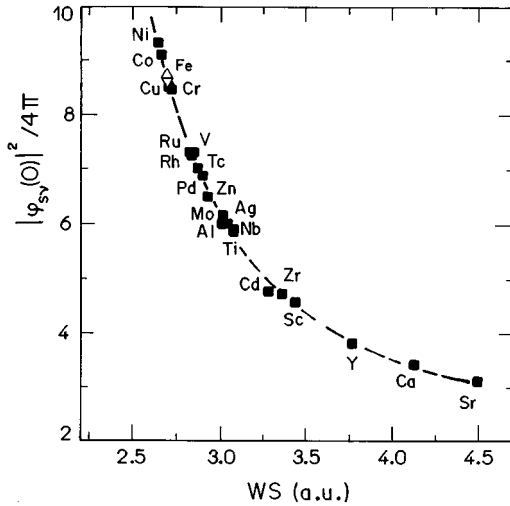


FIG. 2. Values of the probability $(4\pi)^{-1}|\varphi_{s\nu}(0)|^2$ of finding a $4s$ electron at the impurity nucleus as a function of the WS radius of the host. The empty triangles give values for the probability associated with the up and down $4s$ states of Fe in bcc Fe.

Here, n_{4s} is given as an integral, up to the Fermi level, of the local density of states associated with the $4s$ states at the probe, defined at site R by $|u_{RL}(E)|^2$ with quantum numbers $L=(0,0)$. The factor $(4\pi)^{-1}$ comes from the spherical harmonics Y_0 in Eq. (3). The expression for the $\rho_{4s}(0)$ has a simple physical interpretation, if we notice that the occupation n_{4s} gives the number of $4s$ electrons around the impurity, while $|\varphi_{s\nu}(0)|^2$ can be associated with the probability of finding one of these electrons at the Fe nucleus. [We note that the occupations n_p and n_d of p and d orbitals at the Fe site are significant, but the p and d electrons do not contribute to $\rho(0)$ because $\varphi_{l\nu}(0)=0$ for $l=1,2$ associated with these states.] When core contributions are neglected, the IS can be obtained from Eq. (2), by using the $4s$ contribution to the ECDN at the impurity site [$\rho_{4s}^{\text{imp}}(0)$] and at the Fe site in bcc Fe [$\rho_{4s}^{\text{Fe}}(0)$] given in Eq. (4), instead of the total ECDN. Therefore in the simple model introduced the IS will be given by

$$\text{IS} = \alpha(4\pi)^{-1} [|\varphi_{s\nu}^{\text{imp}}(0)|^2 n_{4s}^{\text{imp}} - |\varphi_{s\nu}^{\text{Fe}}(0)|^2 n_{4s}^{\text{Fe}}]. \quad (5)$$

The charge density $\rho_{4s}^{\text{Fe}}(0)$ is a constant and the IS value is determined by $\rho_{4s}^{\text{imp}}(0)$, being negative if the charge density at the Fe impurity nucleus is larger than that in bcc Fe and positive otherwise. In the next section we will use the simple model developed here to understand the observed experimental trends for the IS of substitutional Fe impurities in metals.

IV. APPLICATION OF THE MODEL TO STUDY ISOMER SHIFT TRENDS

According to our simple model, $\rho_{4s}^{\text{imp}}(0)$ and the observed trends of the IS of Fe impurities in metallic hosts can be understood in terms of the behavior of the $4s$ occupation n_{4s}^{imp} and the probability $(4\pi)^{-1}|\varphi_{s\nu}(0)|^2$ at the impurity site. In Fig. 2, we show calculated values of the probability $(4\pi)^{-1}|\varphi_{s\nu}(0)|^2$ as a function of impurity ‘‘size,’’ repre-

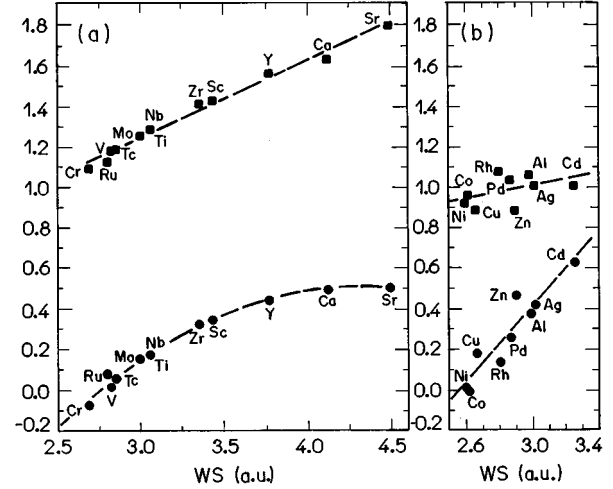


FIG. 3. Values of $n_{4s}^{\text{imp}}/n_{4s}^{\text{Fe}}$ (full squares) and of the IS (full dots) at the impurity site are shown as a function of the WS radius. Hosts to the left (a) and to the right (b) of Fe in the Periodic Table are considered.

sented here by the WS radius of the host. Since the orbital $\varphi_{s\nu}(0)$ is normalized to one within the WS sphere, we expect the value $\varphi_{s\nu}(0)$ to decrease as the volume of the WS sphere increases. But it is interesting that all the points fall on a universal curve, dictated by the behavior of $\varphi_{s\nu}(0)$ under ‘‘compression.’’ The curve is very steep for small values of the WS radius and becomes gradually flatter as the size of the impurity increases. The value of $\varphi_{s\nu}(0)$ does not seem to be sensitive to the conditions imposed at the sphere boundary when solving the Schrödinger-like equation around the Fe site. Even though the hosts have different valences and form different structures, the probability values of Fig. 2 seem to depend exclusively on the size of the impurity. For example, Mo and Al are totally distinct: one is a simple metal and the other a transition metal, they form different structures and are on opposite sides of the Periodic Table. But they have approximately the same volume per atom in their respective structures, and as a consequence the $4s$ electrons at the Fe impurity have a similar probability of being found close to the nucleus (see Fig. 2). Therefore we associate the influence of $|\varphi_{s\nu}(0)|^2$ over the IS with ‘‘size effects’’ and, in the simple model introduced here, changes in the IS due to differences in the volume available for the Fe impurity in the system will be described in terms of this quantity. In Fig. 3 we show values of n_{4s}^{imp} (which for convenience were divided by $n_{4s}^{\text{Fe}}=0.66$, the calculated $4s$ occupation of Fe in bcc Fe) and the calculated valence contribution to the IS shift [governed by the product of n_{4s}^{imp} and $(4\pi)^{-1}|\varphi_{s\nu}(0)|^2$] as a function of the WS radius of the host. The behavior is rather unexpected since the calculated values follow two different curves: one for hosts to the left of Fe [Fig. 3(a)] and one for those to the right of Fe [Fig. 3(b)] in the Periodic Table. Hosts to the left of Fe show a linear increase of n_{4s}^{imp} with the WS radius, while for hosts to the right the points are more dispersed and the curve is nearly flat. For similar values of the WS radius [and therefore similar values of $|\varphi_{s\nu}(0)|^2$], the $4s$ occupations for hosts to the left of Fe are systematically higher. As a consequence, if

similar values of the WS are considered, hosts to the left of Fe have higher ECDN and smaller values of the IS. This can be seen if we compare the IS values for hosts to the left [Fig. 3(a)] and to the right of Fe [Fig. 3(b)]. If we vary the impurity size, here represented by the WS radius of the host, the curves for hosts to the left and to the right of Fe have a similar behavior; in both cases the number of 4s electrons at the impurity site increases with size. But due to the shape of the universal curve of Fig. 2, the probability of finding one of these 4s electrons at the nucleus decreases with size. The decrease can be very drastic, if the steep part of the curve is considered. As a consequence, the ECDN decreases and the IS values generally increase as the WS radius of the host increases. We note that the IS values grow steeply for small values of the WS, but the curve gets flatter for large WS values, reflecting the behavior of the probability. A similar trend is seen in the IS behavior shown in Fig. 1.

Our results demonstrate that size effects can play a significant and often predominant role in determining the trends of the IS. The variation of the IS of Fe in bcc Fe with pressure constitutes an interesting example of how the importance of size effects can be estimated using the procedure introduced here. To obtain the variation of the IS of Fe in bcc Fe within our model we use the expression for the IS given in Eq. (5). The first term $\alpha(4\pi)^{-1}|\varphi_{s\nu}^{\text{imp}}(0)|^2 n_{4s}^{\text{imp}}$ will be associated with Fe in the compressed bcc lattice, while the second term refers to the uncompressed Fe (taken as reference) and is a constant. Under these assumptions the variation of the IS with the WS radius can be estimated from Eq. (5). It is clear that the derivative of the IS with respect to the WS radius has two terms; one fixes n_{4s}^{imp} at the equilibrium value and takes the derivative of the probability while the other fixes the probability (size) and takes the derivative of n_{4s}^{imp} . The first term is associated with size effects while the second gives the contribution due to changes of the 4s occupation under pressure. The variation of the probability with the WS radius (and the value of the probability itself) can be easily estimated from Fig. 2, but the 4s occupation and its variation with the WS radius depend on details of the band structure and are more difficult to obtain.¹⁶ For the 4s occupation of Fe we used our calculated value of 0.66, while for the variation of the 4s occupation of Fe in bcc Fe with the WS radius we used the tabulated value of Andersen *et al.*,¹⁷ $d(n_{4s})/d\ln(\text{WS})=0.253$. Since the variation of the probability with WS radius is negative (see Fig. 2), the two terms which determine the derivative of the IS with respect to the WS radius have opposite signs. We find that the derivative is dominated by size effects, which give a contribution almost nine times larger than the one due to the variations in n_{4s}^{imp} . Finally, we use the relation $3d(\text{IS})/d\ln(V)=d(\text{IS})/d\ln(\text{WS})$, valid for a system of atoms with the same WS radius, to estimate the variation of the IS of bcc Fe under pressure with volume. We find $d(\text{IS})/d\ln(V)=1.3$ mm/s, which agrees well with the experimental value of 1.34 mm/s given in the literature.¹

In the present paper we have studied Fe impurities in metallic hosts using the simple RS-LMTO-ASA model introduced here. The treatment in terms of the renormalized-atom-like basis originates on the real-space LMTO-ASA formalism and can be used to study other systems. So it is interesting to say a few words about the transferability of our

results. If the core contributions can be neglected, the IS can still be written in terms of the 4s occupation at the Fe probe and the probability of finding a 4s electron close to the nucleus. The 4s occupation is determined by the interaction of the probe with its surroundings and is clearly dependent on the system being considered. Electronic structure calculations for the specific system being studied must be performed to obtain information about this quantity. On the other hand, in our model, the probability is practically independent of the surroundings, and seems to be a (size dependent) property of the probe. We believe that the information about the probability is transferable and that the universal curve of Fig. 2 can be used to estimate the influence of size effects on the IS of Fe in other systems. It could, for example, be used to estimate the influence of size effects to the IS of Fe, and separate it from other effects, in binary systems, where the lattice parameter, and therefore the volume, can be changed by alloying. Finally it is interesting to notice that when a similar RS-LMTO-ASA model is used to study electric field gradients (EFG), the elements of the EFG tensor can be expressed in terms of two quantities:¹⁴ angular asymmetries which come from differences between the occupations of orbitals with different symmetries¹⁸ and radial integrals related to the behavior of the orbitals close to the probe nucleus. To determine the angular asymmetries a detailed electronic structure calculation for the system is required, but the radial integrals are transferable quantities associated with the probe.

It is useful to compare our results for the IS of Fe impurities in metallic hosts to those obtained by Akai *et al.*⁵ for the IS of an Fe atom close to an impurity in bcc Fe. In both cases the trends of the IS are dominated by the 4s valence contribution, but in the problem investigated by Akai *et al.* the IS behavior was dictated by the n_{4s} , while here both the occupation n_{4s} and the probability are important. In the problem studied by Akai *et al.* the volume occupied by the Fe probe was assumed not to vary when different impurities were introduced in its neighborhood in bcc Fe. We note that if the size of the Fe is kept constant, the probability (see Fig. 2) does not change and the IS is governed by the 4s occupation. This is consistent with the results obtained by Akai *et al.*⁵

It has often been suggested that electronegativity may play a role in the IS behavior.^{3,19} If it does, there must be a correlation between the total charge transfer (governed by electronegativity) and the 4s occupation. Since 4p and 3d orbitals are also available, it is not clear how much of the transferred charge will go into 4s states. Actually, in a rigid band type of picture one would expect most of the transferred charge to go into the 3d orbitals, since the density of states at the Fermi level in Fe is dominated by 3d states and not many 4s states are available. To investigate this point, we have calculated the total charge transfer, defined as the number of valence electrons in excess of eight (valence of Fe) at the impurity site. In Fig. 4(a) we show the total charge transfer at the impurity as a function of the WS radius of the host. As a general trend, the total charge transfer increases with the WS of the host. For similar WS radii, the values of charge transfer in hosts to the left of Fe are systematically higher than those in hosts to the right of Fe in the Periodic Table. This behavior is rather similar to that observed for

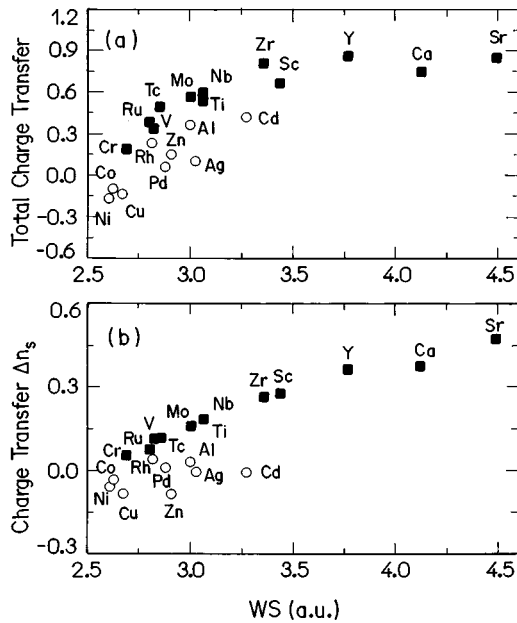


FIG. 4. The total charge transfer (a) and the charge transfer Δn_s (b) at the impurity site as a function of the WS radius of the host. Values for hosts to the left (full squares) and to the right (empty dots) of Fe in the Periodic Table are shown.

$n_{4s}^{\text{imp}}/n_{4s}^{\text{Fe}}$ in Fig. 3, which is associated with $4s$ states. We have also calculated the charge transfers associated with the $4s$, $4p$, and $3d$ orbitals at the impurity, given as the difference between their occupations and that of Fe in bcc Fe. The charge transfers Δn_s associated with the $4s$ states of the Fe impurity are shown in Fig. 4(b). They constitute a significant fraction of the total charge transfer and are of the same order as the charge transfers associated with $3d$ states. It can be seen from Fig. 4 that the total charge transfer correlates quite well with the charge transfer Δn_s . Such a correlation is not present when $3d$ charge transfers are considered. The above results suggest that the peculiar behavior of $n_{4s}^{\text{imp}}/n_{4s}^{\text{Fe}}$ in Fig. 3 can be related to the charge transferred between the impurity and the host and therefore to the concept of electronegativity.

V. CONCLUSIONS

We have calculated the IS of substitutional Fe impurities in Al and a large number of hosts of the $3d$ and $4d$ rows of the Periodic Table and shown that the theoretical results reproduce well the experimentally observed IS trends. Our results indicate that core contributions are small and that the behavior of the IS is dominated by the $4s$ valence electrons of the Fe. By neglecting the core and other unimportant contributions we introduce a simple model which retains the relevant information. In this model the IS is obtained using a set of renormalized-atom-like orbitals as basis functions. This description of the IS is conceptually different from the more familiar one, in which LCAO type orbitals are used as basis. The new formulation allows one to understand the IS behavior in terms of two quantities which have simple physical meaning: one is the number of $4s$ electrons at the probe site and the other the probability of finding one of these

electrons close to the nucleus. In the present model, size effects are associated with the probability of finding the $4s$ electrons close to the nucleus and can be simply described in terms of this quantity. We show that when the probability is plotted in terms of the impurity size, the points follow a universal curve, which can be used to estimate the influence of size effects on the IS of Fe, whenever changes in the volume occupied by the Fe probe are known.

When the $4s$ occupations n_{4s} are plotted as a function of the impurity size the behavior is rather unexpected. The calculated values follow two distinct curves; one for hosts to the right of Fe (with occupation values similar to Fe in bcc Fe) and one to the left of Fe in the Periodic Table, with larger values of occupation. In both cases there is an overall increase in occupation as the size of the WS increases, tending to make the IS more negative. This is compensated by the size effects which are often dominant and tend to make the values of IS at the Fe impurity more positive as the WS of the host increases. To study the origin of the peculiar behavior of the $4s$ occupation, we investigate the charge transfers at the Fe impurity site. We find that the $4s$ occupation correlates well with the total charge transfer into the site, confirming that electronegativity may be an important factor in understanding the IS of Fe impurities in metals.

Finally, as an example, we applied the new approach to study the behavior of the IS of bcc Fe under pressure. The model is used to obtain the variation of the IS with volume under pressure and separate contributions due to size effects from those that come from changes in the $4s$ occupation due to compression. We find that the two contributions have different signs and that the model gives results which are compatible with experiment. We show that size effects are dominant, being close to an order of magnitude larger than those associated with changes in the $4s$ occupation.

We note that the behavior of the $4s$ occupation is dictated by the interactions between the Fe probe and its surroundings. Since these are system dependent, the information obtained here is not transferable to other problems. But the probability, as defined in our model, is practically independent of the surroundings; it seems to be a (size dependent) characteristic of the Fe probe. Therefore the universal curve for the probability given here can be used to evaluate the influence of size effects on the IS in other systems. It can, for example, be used to estimate the importance of size effects to the IS of Fe in binary systems, where changes in the lattice constant can be introduced by alloying. So we hope that the simple procedure introduced here will be of help to experimentalists, who are interested in evaluating the influence of size effects on the IS shift of Fe in their samples.

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- ¹D. N. Pipkorn *et al.*, Phys. Rev. **135**, A1604 (1964).
- ²S. M. Quaim, Proc. Phys. Soc. London **90**, 1063 (1967).
- ³B. Keck, R. Sielemann, and Y. Yoshida, Phys. Rev. Lett. **71**, 4178 (1993); Hyperfine Interact. **80**, 1239 (1993), and references therein.
- ⁴R. Ingalls, Solid State Commun. **14**, 11 (1974); A. R. Miedema and F. vander Woude, Physica B & C **100B**, 145 (1980); I. Dezsi *et al.*, Phys. Rev. Lett. **62**, 1659 (1989).
- ⁵H. Akai *et al.*, Phys. Rev. Lett. **56**, 2407 (1986).
- ⁶S. Frota-Pessôa, Phys. Rev. B **46**, 14 570 (1992); P. R. Peduto *et al.*, *ibid.* **44**, 13 283 (1991).
- ⁷O. K. Andersen, Phys. Rev. B **12**, 3060 (1975); O. K. Andersen and O. Jepsen, Phys. Rev. Lett. **53**, 2571 (1984).
- ⁸R. Haydock, in *Solid State Physics: Advances in Research and Applications*, edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1980), Vol. 35.
- ⁹Some of the IS values at the substitutional Fe impurities were obtained from available RS-LMTO-ASA electronic structure calculations by P. G. Gonzales and H. M. Petrilli (in Cd and Zn), S. B. Legoas and S. Frota-Pessôa (in Tc and Ru), L. A. de Mello and S. Frota-Pessôa (in Ca and Sr), and A. B. Klautau and S. Frota-Pessôa (in Pd). See also Ref. 10.
- ¹⁰S. Frota-Pessôa *et al.*, Phys. Rev. Lett. **71**, 4206 (1993); H. M. Petrilli and S. Frota-Pessôa, Phys. Rev. B **48**, 7148 (1993).
- ¹¹V. von Barth and L. Hedin, J. Phys. C **5**, 1629 (1972).
- ¹²N. Beer and D. G. Pettifor, in *The Electronic Structure of Complex Systems*, edited by W. Temmermann and P. Phariseau (Plenum, New York, 1984).
- ¹³U. Scheuer and B. Lengeler, Phys. Rev. B **44**, 9883 (1991).
- ¹⁴H. M. Petrilli and S. Frota-Pessôa, J. Phys. Condens. Matter **5**, 8935 (1993); S. Ferreira and S. Frota-Pessôa, Phys. Rev. B **51**, 2045 (1995).
- ¹⁵C. D. Gelatt, H. Ehrenreich, and R. E. Watson, Phys. Rev. B **15**, 1613 (1977).
- ¹⁶This will always be the case, since the volume effects do not depend on details of the environment around the probe while the occupation n_{4s} as well as the variations in the $4s$ occupation are system dependent and must be calculated.
- ¹⁷O. K. Andersen *et al.*, in *Highlights of Condensed Matter Theory*, edited by F. Bassani, F. Fumi, and M. P. Tosi (North-Holland, Amsterdam, 1985).
- ¹⁸P. Blaha, K. Schwarz, and P. H. Dederichs, Phys. Rev. B **37**, 2792 (1988).
- ¹⁹R. E. Watson and L. H. Bennett, Phys. Rev. B **15**, 5136 (1977).