

Site preference energies for 3d impurities in ZrFe₂

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For calculating the preferred site of isolated impurities in complex intermetallic compounds, we suggest an alternative approach that assumes that the displaced atom lands on an existing vacancy, and compare total energies for different site configurations. To obtain the electronic structure and total energies in the presence of the impurities and vacancies, we use the linear muffin-tin method and perform self-consistent, first-principles calculations within the local spin density functional approximation, directly in real space. Here, as an example, we calculate the site preference and corresponding local moments for 3d impurities in the Laves phase compound ZrFe₂. Our results are compared to experiment.

The investigation of the magnetic and hyperfine properties of impurities and additions in metals has been an active field of research, and has helped to enhance our understanding of the physical phenomena involved. An intense experimental effort was backed by the development of powerful theoretical methods: The Korringa, Kohn, and Rostoker Green function,¹ (discrete variational method),² and RS-LMTO-ASA (real space–linear muffin-tin orbital–atomic-sphere approximation)³ in the case of impurities, and the first principles coherent potential approximation⁴ approaches for solid solutions and binary additions. But, due to the difficulties involved, in spite of the considerable amount of data obtained by several experimental techniques,^{5–7} very few first-principles theoretical investigations regarding the behavior of isolated impurities and ternary additions in binary metals with complex structures have been performed.

In this work, motivated by experiments,^{6,7} we use first-principles, self-consistent LMTO-ASA calculations implemented in real space to investigate the magnetic behavior of 3d impurities in ZrFe₂. It is clear that the magnetic behavior of the system depends on whether the impurity occupies a Zr or an Fe site in the ZrFe₂ Laves phase, and the calculation of site preference energies becomes important in this context.

Very few calculations of site preference for impurities and additions in complex metals exist and they are usually performed for finite concentrations using supercells. Recently, LMTO-ASA calculations on 16-atom supercells were performed to understand site preference energies in NiAl and FeAl B2 intermetallics.⁸ In the same paper, to investigate lattice relaxation around the impurities, full potential (FP) LMTO calculations in the same supercells were carried out. Previously, in their pioneering work, Khowash, Price, and Cooper had also used the FPLMTO and the LMTO-ASA approaches to evaluate site preference energies for Mn, Cr, and V impurities in γ -TiAl alloys.⁹ The differences between the site preference energies calculated by the two approaches were in all cases smaller than 4 mRy. This gives us an idea of the order of the accuracy of the ASA approximation, which should not be trusted beyond this limit. On the other hand, using the LMTO-ASA formalism, these authors have also calculated site preference energy for one Cr or V impurity in γ -TiAl alloys using supercells of 8 and 54 atoms. The difference in site preference energy when the size of the cell

is varied is four times larger than the errors introduced by the ASA approximation. It is clear from their analysis that the concentration (and even the distribution) of impurities affects considerably the site preference energy. Therefore, when investigating site preference energies for dilute impurities in complex hosts, the use of supercells should, if possible, be avoided.

First-principles calculations using supercells have been used with some success to obtain magnetic moments and other properties of isolated impurities in metals, but the electrostatic potentials and therefore total energies are usually badly described. The isolated impurity produces local disturbances and, at large distances, one has mainly the unperturbed host. Charge transfers are important only in the region close to the impurity, and the Fermi level of the system is defined by that of the host. In the case of the supercell the disturbances extend throughout the system and the resulting electrostatic potential is usually given by Ewald sums. Therefore it is not surprising that the errors introduced by the use of the ASA are smaller than those that come from interactions in the supercell or, when simulating an isolated impurity, by badly described electrostatic potentials.

To calculate site preferences, one should compare the energies required to add a substitutional atom at different lattice sites in the compound, while the number of atoms in the system is kept constant. The site preference energy is usually determined as the difference between the total energies of supercells with impurities on both sublattices, and of the bulk metals. Physically, this model implies that the atom displaced by the addition does not disappear from the system, but is returned to a state similar to that of the bulk metal. This assumption is not exact, but gives reference states that make the comparison between the energies for different site occupations possible; it has been used with success in first-principles calculations to evaluate site preference energies in γ -TiAl alloys⁹ as well as in NiAl and FeAl alloys.⁸

Here we report *ab initio* RS-LMTO-ASA calculations for the local moment and energy preference for site selection of isolated substitutional 3d impurities in the cubic Laves phase ZrFe₂. We also suggest an alternative approach to obtain site preference energies, which is particularly suitable for dilute impurities in complex intermetallic compounds. The Laves

phase structure has to accommodate atoms of different sizes (Zr is much larger than Fe) and bears no resemblance to the bcc (or hcp) structure of Fe (or Zr); thus the usual assumption that the displaced Fe (or Zr) atom would occupy sites with energies comparable to those for pure Fe (or Zr) does not seem appropriate. In the following, we suggest an alternative procedure to obtain site preference energies, which also conserves the number of atoms in the system, but seems, in the present case, more realistic.

It is known that in Laves phase compounds vacancies are usually present.¹⁰ Here we assume that the displaced Fe (or Zr) atom finds and occupies an existing Fe (or Zr) vacancy, keeping the number of atoms in the system constant. The physical situation is the following: initially one has the impurity and a system with vacancies. In the final situation we find the impurity at an Fe (or Zr) site and one fewer Fe (or Zr) vacancy in the system. Since the initial state is the same, to obtain the site preference one should compare the energies of the final states, which are essentially given by adding the impurity and subtracting a vacancy at the same site. If we define positive energies as giving preference to the Fe site, the expression for the site preference energy ΔE can be written as

$$\Delta E = [E_i(\text{Zr}) - E_v(\text{Zr})] - [E_i(\text{Fe}) - E_v(\text{Fe})]. \quad (1)$$

Here the subscript indicates an impurity or a vacancy at the site shown in parentheses. It is clear from Eq. (1) that, to calculate the site preference energy, four different situations must be considered, i.e., impurities and vacancies at both Zr and Fe sites.

To obtain the electronic structure, total energies, and local moments around impurities and vacancies in ZrFe_2 , the RS-LMTO-ASA method was used. The procedure is similar to the usual LMTO-ASA approach,¹¹ but uses the recursion method¹² to solve the eigenvalue problem directly in real space. To simulate the system we have used a large cluster of 4000 atoms for the Laves phase structure, with the experimentally observed lattice parameter. The size of the Wigner-Seitz (WS) spheres of Fe and Zr were determined in order to keep the sphere overlap at a minimum. The energy reduction associated with lattice relaxation around the sites is usually small.¹³ Therefore, to reduce the errors when comparing the total energies, the same unrelaxed configuration was used in calculations for vacancies and impurities. We note that the accuracy of the procedure can be further increased by going beyond the ASA and using the nonspherical charge distribution inside the spheres, when computing the energies as a last step after self-consistency. These corrections, which were not introduced in this first application of the method, are essential to avoid a systematic overestimation of vacancy formation energies.¹⁴ For site preference energies, the errors introduced by the ASA will be probably smaller, since the subtraction of Eq. (1) will lead to their partial cancellation.

The first step in the present calculations was to obtain the electronic structure of the unperturbed ZrFe_2 , since the defect will be embedded in this system. The calculation was performed using the RS-LMTO-ASA procedure for crystalline systems;^{15,16} our results are in very good agreement with those in the literature.¹⁷ The calculation for the unperturbed ZrFe_2 Laves phase determines the Fermi level of the system, which does not change when the defect is introduced. It also

defines the unperturbed potential parameters, charge transfers and electrostatic potentials to be used at sites far from the defect, which are not significantly affected by its presence. We note that the unperturbed electrostatic potentials $(V)_0$ at the Zr and Fe sites are obtained in terms of the unperturbed charge transfers $(\Delta Q)_0$ and include the Madelung potentials given by the usual three-dimensional Ewald sums. Here we use the subscript zero to indicate unperturbed quantities, to distinguish them from the charge transfers ΔQ and corresponding electrostatic potentials V in the presence of the defect. The differences between the perturbed and unperturbed quantities tend to zero far from the defect, and it is convenient to define local charge transfers $(\Delta Q)_{local}$ as

$$(\Delta Q)_{local} = \Delta Q - (\Delta Q)_0. \quad (2)$$

The charge transfer ΔQ at each site in the presence of the perturbation can be written as a sum of the unperturbed charge transfer plus a local charge transfer due to the presence of the impurity or vacancy. Since the electrostatic potential obeys the superposition principle, the potential V associated with the charge transfer ΔQ can also be written as a sum of the unperturbed potential $(V)_0$ plus a potential $(V)_{local}$ generated by the local charge transfers $(\Delta Q)_{local}$. We have

$$(V)_{local} = V - (V)_0. \quad (3)$$

To obtain the electronic structure in the presence of the local perturbation (impurity or vacancy), we fix the Fermi level to the given unperturbed value. The space then is divided into a region around the defect (where potential parameters are significantly affected by the perturbation) and the rest of the system in which this region is embedded. In the region around the defect the potential parameters, charge transfers, etc., at each site are calculated self-consistently, while for the remaining sites of the large 4000-atom cluster, the parameters are kept at their unperturbed values. Here we determine self-consistent parameters in a relatively large region containing 45 sites around the central impurity or vacancy in ZrFe_2 . It includes four shells of atoms in the case of a defect at the Zr site and five shells of atoms when a defect at the Fe site is considered. We have verified that the inclusion of one extra shell in the self-consistent procedure changes the site preference energies by less than 2 mRy. To perform the calculations we build the Hamiltonian taking initial guesses for the unknown potential parameters, and use the recursion method to obtain the local density of states (LDOS) at each site in the region close to defect. We integrate the LDOS up to the fixed Fermi level in order to find the charge transfer ΔQ at each site and, using the unperturbed values $(\Delta Q)_0$ in Eq. (2), we obtain the local charge transfer $(\Delta Q)_{local}$ and the corresponding electrostatic potential $(V)_{local}$. Finally, using Eq. (3) and the unperturbed electrostatic potential $(V)_0$, we obtain a new value for V at each site. New values of potential parameters are obtained in the usual way, by solving the Schrödinger equation inside the WS sphere around each inequivalent site. The new values of potential parameters, charge transfers, and electrostatic potentials in the region around the defect give a new Hamiltonian and the process is continued until self-consistency in the region around the impurity is achieved.

TABLE I. Site preference energies (in mRy) for 3d impurities in ZrFe_2 .

Impurity	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
Site	Zr	Zr	Zr		Fe	Fe	Fe	Fe	
ΔE	-233	-125	-46	2	6	41	60	56	4

It is clear from Eq. (1) that one can use any convenient system as reference to measure the energies. Here energies $E_i(\text{Zr})$, $E_v(\text{Zr})$, $E_i(\text{Fe})$, and $E_v(\text{Fe})$ are all defined with respect to the energy of the unperturbed ZrFe_2 system. In the LMTO-ASA formalism, the total energies are usually written as a sum of two contributions: (i) sum of kinetic, electrostatic, and exchange and correlation energies inside each WS sphere, and (ii) a term that depends on the charge transfer ΔQ and electrostatic potential V at each site. When the unperturbed ZrFe_2 Laves phase is used as reference, the total energy is given in terms of (i) differences between the energies associated with each WS sphere in the presence of the perturbation (impurity or vacancy) and the energies at the same spheres in the unperturbed system, and (ii) an electrostatic contribution that depends on the differences between charge transfers and corresponding electrostatic potentials at each WS sphere with and without the perturbation. Using Eqs. (2) and (3), these charges and corresponding potentials can be easily identified with the values of $(\Delta Q)_{local}$ and $(V)_{local}$ in each sphere. The differences (i) and (ii) are important at sites close to the defect, but tend to zero at sites that are well represented by bulk parameters. Therefore, in the present calculations, the information needed to obtain site preference energies is restricted to a region that includes only 45 sites around the defect.

In Table I we present results for the site preference ΔE of 3d impurities from Sc to Cu in ZrFe_2 . By definition, the impurity will prefer the Zr site if ΔE is negative and the Fe site if it is positive. According to the calculations, Sc, Ti, and V impurities prefer the Zr sites, while Fe, Co, and Ni prefer the Fe sites of the ZrFe_2 host. As noted before, our results are accurate within a few mRy; thus the sign of the energies of Cr, Cu, and even Mn cannot be completely trusted. The only reliable information we have is that the site preference (in whichever direction) for these impurities is weak. From Table I it is clear that the site preference energies ΔE do not vary monotonically as one considers impurities across the 3d series in the Periodic Table. They are initially negative, indicating preference for the Zr site, and rise steadily from Sc to Fe, changing sign and site preference around Cr and Mn. ΔE reaches a maximum for Co and decreases again for Ni and Cu, as the 3d shell is completed. The small value of site preference energy found for Cu is compatible with the results of nuclear magnetic resonance (NMR) experiments,⁷ which suggest that Cu atoms can be found in both sites in the ZrFe_2 host.

We have also calculated local moments for the 3d impurities in this Laves phase and we can use the values for Cr and Mn to try to establish the site preference of these impurities in ZrFe_2 . It is convenient to define the direction of the local moment at impurity as positive (or negative), if it aligns with (or against) the local moment of Fe sites in the host. We find that the magnetic moment at the Cr impurity depends

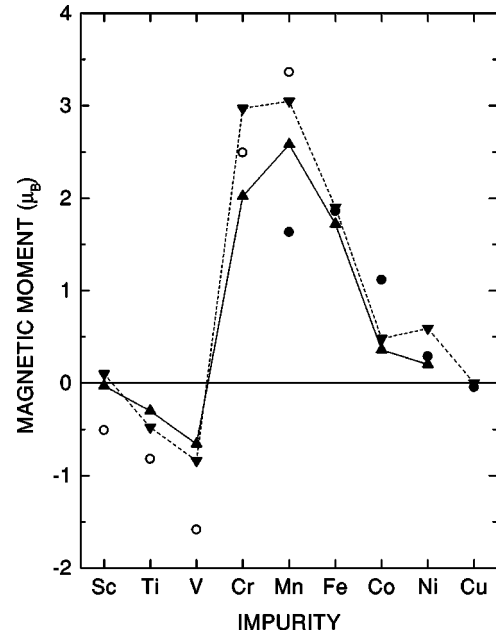


FIG. 1. Magnetic moments at 3d impurity sites in ZrFe_2 . Theoretical results are shown with open (filled) circles for impurity at Zr (Fe) site. Experimental values are shown with filled triangles: up (see Ref. 6) and down (see Ref. 7).

drastically on site preference: when placed at an Fe site, Cr develops a small negative moment of around $0.5\mu_B$, but when placed at the Zr site its moment is positive and large, with value around $2.5\mu_B$. The experimentally observed moment for Cr impurities are large and positive,^{6,7} indicating that the Cr impurity occupies the Zr site. For Mn, the local moments at both sites were found to be positive and compatible with experiment. Therefore, in contrast to Cr, no reliable assignment of site preference for Mn could be made. In Fig. 1 we plot the calculated moments of the 3d impurities at their preferred sites. In the case of Mn both sites were included. White (black) circles are used for impurities at Zr (Fe) sites. For comparison, local moments at the impurity sites inferred from the nuclear orientation⁶ (full line with triangles) and NMR (Ref. 7) (dashed line with triangles) experiments are also shown. There are certainly discrepancies between the calculated results and the values inferred from experiments, probably due to the theoretical simplifications and the difficulties in deconvoluting and analyzing the experimental data. But observed and calculated trends are the same and, considering the complexity of the problem, the overall agreement is quite good. The calculated moments are negative for Sc, Ti, and V, compared to the negative experimental moments that are smaller, but they follow the same trends. Both theory and experiment show a considerable positive moment for Cr and Mn, while for Co and Ni the local moment is also positive, but smaller in magnitude. In the case of Cu the calculated moment is close to zero (for both the Zr and Fe sites), in agreement with experiment.

In conclusion, we have presented an alternative first-principles approach to obtain site preference energies for impurities in binary metallic hosts with complex structures. The calculations are implemented in real space using the RS-LMTO-ASA method and, to compare total energies, we assume that the atom displaced by the impurity lands at an

existing vacancy. The present real space approach can also be applied to investigate other extended defects in complex metallic hosts.

The scheme has been applied to obtain site preference for $3d$ impurities in the Laves phase compound $ZrFe_2$. Local moments at the impurity site were also calculated and the results show tendencies that are in good agreement with those inferred from experiment. We conclude that Sc, Ti, V, and Cr impurities should occupy the Zr site of the Laves phase compound $ZrFe_2$, while Co and Ni prefer the Fe site. For Mn, impurities probably have a weak preference for the

Fe site, but a definite site assignment could not be made. We find that the energy difference ΔE associated with site preference does not vary monotonically for impurities along the $3d$ line of the Periodic Table. While Co and Ni clearly prefer the Fe site, the site preference of Cu is very weak. This is consistent with experimental evidence for Cu impurities in $ZrFe_2$, which suggest they can be found in both sites.⁷

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