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Theoretical studies of vacancies in Al and Cu

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We use the real-space linear-muffin-tin-orbital approach, within the atomic-sphere approximation to calculate the electronic structure around vacancies in Al and Cu and divacancies in Al. A defect consisting of a Cd-monovacancy pair in Al is also considered. The electric-field gradient at the nucleus and the asymmetry parameter η for sites in the near neighborhood of the vacancy in these various situations were also obtained. The calculated values are in good agreement with experiment when available. Our results confirm the failure of the point-charge model when applied to obtaining the electric-field gradient at the nucleus in metallic systems and show that the defect with quadrupole frequency $\omega_0 = 64$ Mrad/sec, created by low-temperature implantation of In in Al, can indeed be assigned to a Cd-monovacancy pair.

I. INTRODUCTION

Impurities, vacancies, and other lattice imperfections are often found in metals. These defects distort the local charge distribution, changing the electric and magnetic fields in their neighborhood. Hyperfine interactions are sensitive to these fields and can be used to characterize defects in solids. The electric-field gradient (EFG) due to imperfections in cubic lattices can be measured by several techniques and has often been used to trace vacancy migration, trapping, and clustering in fcc metals. A large number of experiments using perturbed angular correlation (PAC), perturbed angular distribution, and nuclear magnetic resonance (NMR) give detailed information about the EFG in the vicinity of vacancy-related defects.[1-7] But to associate the measured values with each of the possible defects is not an easy task and some theoretical support is usually needed. One interesting example is the case of a defect created by low-temperature implantation of In in Al. It is characterized in PAC experiments by a quadrupole frequency $\omega_0 = 64$ Mrad/sec, an asymmetry parameter $\eta = 0.41$, and a V_{zz} directed along the $\langle 110 \rangle$ direction of the fcc lattice. The In decays into Cd during the experiment and the measured EFG corresponds to that of a Cd probe. A study of the dilute alloy of Al containing In after quenching is compatible with the assignment of this defect to a Cd-monovacancy pair in Al.[2] But point-charge-model calculations for the EFG seem to exclude this possibility and other authors suggest that it represents a more complex structure, consisting of Cd and four vacancies.[3] Simple point-charge models and Steinheimer factors have been used often to obtain values for the EFG, but recent first-principles calculations for a series of hcp metals cast serious doubts on the validity of point-charge-model calculations when applied to metallic systems.[8] Therefore, to understand the behavior of the EFG around these vacancy-related defects, it is desirable to have reliable self-consistent electronic-structure calculations performed for these systems. The lack of periodicity due to the introduction of the defect prevents the direct application of the powerful k-space formalism and increases the complexity of the problem. But under some assumptions (different in each of the various existing methods) the electronic structure around localized defects can be obtained. Several approaches can be used to treat the defects within a first-principles self-consistent method.[9-12] One can use supercells in conjunction with reciprocal space methods, one can perform calculations in a small cluster of atoms, or one can use the Green's function (GF) formalism within some well-established method such as the Korringa-Kohn-Rostoker (KKR) or linear-muffin-tin-orbital (LMTO) methods, among others. The advantage of the GF approach as compared to the others is that the embedding of the defect is correctly described and it has been frequently applied to study impurities in metals. In recent years a first-principles, self-consistent, density-functional procedure,[13] implemented directly in real space (RS), has been shown to describe well the electronic structure around local perturbations in metallic systems.[14] It is based in the linear-muffin-tin-orbital formalism within the atomic-sphere approximation[15,16] (ASA) and makes use of the recursion method[17] to solve the eigenvalue problem in real space. The RS LMTO ASA scheme has been applied to study substitutional impurities in metals, yielding results for local magnetic moments, charge transfers, and hyperfine fields that are in excellent agreement with those obtained by KKR GF calculations.[14,18] We should note that the RS LMTO ASA scheme is very flexible, can be applied to study interstitial impurities, and is very useful in the presence of lattice relaxation.[19]

The first realistic calculation of the electronic structure around a monovacancy in Al was performed in a supercell of 26 Al atoms plus a vacancy, using the pseudopotential approach.[10] The electronic structure around an isolated vacancy was later obtained using the KKR GF formalism.[11] In this calculation, the potential of the vacancy was treated self-consistently and charge neutrality was imposed, but the potential of the Al sites was kept at bulk value. Due to the approximations involved, no results could be obtained for the EFG or the asymmetry parameter at the Al site close to the vacancy in these pa-

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pers.[10,11]

Here we are interested in the behavior of the EFG around vacancies in Al, for which a considerable amount of experimental data are available. There are few first-principles calculations of the EFG in nonperiodic systems and we did not find one for vacancy-related defects in Al. But a calculated value of V_{zz} for a Cu first neighbor to a monovacancy in Cu was recently cited in a KKR GF study of the EFG for Cu sites in the neighborhood of 3*d* and 4*sp* impurities in Cu.[12] The study is rather complete and several shells of Cu atoms around the vacancy were treated self-consistently. The work shows that, as in the case of hcp metals,[8] the lattice contributions to the EFG at the calculated sites are very small, typically less than 5% of the total value. This is true for most metallic systems. It is interesting to have reliable theoretical EFG values to compare with those obtained here using the RS LMTO ASA scheme. Therefore we have also calculated the electronic structure around a vacancy in Cu and evaluated the EFG at a Cu site in the neighborhood of the vacancy.

The paper is divided in the following way. In Sec. II we give a brief description of the RS LMTO ASA scheme, used in the electronic-structure calculations. We also describe the procedure used in the calculation of the EFG tensor and its components along the principal axis. In Sec. III we show results for vacancies and divacancies in Al and vacancies in Cu. In Sec. IV we discuss the case of the Cd-monovacancy pair in Al. Finally, in Sec. V we present conclusions.

II. THEORETICAL APPROACH

In the present work we use the RS LMTO ASA scheme to describe the electronic structure around the vacancies. It is based on the well-known LMTO ASA formalism[15,16] and makes use of the recursion method[17] to solve the eigenvalue problem directly in real space. A brief description of the RS LMTO ASA will be given here to state the approximations used and establish notation. A detailed description of the scheme[13] and its application to obtaining the electronic structure around defects[14,19] can be found elsewhere.

The LMTO is a linear method and its solutions are valid around a given energy E_v, normally taken at the center of gravity of the occupied part of the band. Here we use the ASA LMTO approach, where the space is divided into Wigner-Seitz (WS) cells, which are then approximated by WS spheres of the same volume. The LMTO ASA basis functions can be chosen in a variety of ways, to optimize the efficiency when solving a given problem. There are three very important representations:[16] the standard, the orthogonal, and the tight binding (TB) (or most localized). Up to the first order in $E-E_v$, the orthogonal and TB representations coincide and we can take advantage of both features. In the RS LMTO ASA scheme we use a first-order Hamiltonian, where terms of order of $(E-E_v)^2$ and higher are neglected. Within these approximations, we have a TB Hamiltonian and an orthogonal basis, yielding a simple eigenvalue problem, easily solvable in real space by the recursion method:

$$(H-E)u=0\ , \tag{1}$$

$$H=\bar{C}+\bar{\Delta}^{1/2}\bar{S}\bar{\Delta}^{1/2}\ . \tag{2}$$

To build the Hamiltonian we have to determine the TB structure constant $\bar{S}$ and obtain the TB potential parameters $\bar{C}$ and $\bar{\Delta}$. The structure constant $\bar{S}$ is calculated only once, since it depends on the position of the sites, which is not changed during the iterative process towards self-consistency. To obtain the potential parameters $\bar{C}$ and $\bar{\Delta}$ for a given site, one has to solve the Schrödinger equation for $E=E_v$ within the WS sphere around the site. All inequivalent sites (with different values of $\bar{C}$ and $\bar{\Delta}$) should be considered. Since the potential inside the WS spheres changes, the potential parameters $\bar{C}$ and $\bar{\Delta}$ should be recalculated at each iteration, until self-consistency is achieved. The main difference between the present real-space scheme and the usual LMTO ASA formalism regards the way by which the eigenvalue problem is solved for the given Hamiltonian. We note that the solution of the Schrödinger equation within each WS sphere is treated in exactly the same way in both the LMTO ASA formalism and the RS LMTO ASA scheme. Therefore the approximations used for the exchange and correlation terms when solving the Schrödinger equation inside the WS spheres are exactly the same in the two approaches. In the case of the vacancy, the Schrödinger equation is solved inside a WS sphere without a nuclear charge, usually called an empty sphere.

Normally, when calculating the electronic structure of a periodic system, the Fermi level is determined at each iteration, by filling the bands with the correct number of valence electrons. In the case of local perturbations, such as impurities or vacancies, the Fermi level is determined by that of the host and the procedure has to be modified. Here we first perform a RS LMTO ASA for the perfect system (no vacancies) to determine the Fermi level. Then we fix the Fermi level at this value and introduce the vacancy (empty sphere) or any other perturbation of interest. We calculate the occupation and other relevant quantities as the vacancy site up to the fixed Fermi level, keeping the potential parameters of the rest of the system at bulk value. The extra charge found at the site is placed in the first neighboring shell in order to preserve charge neutrality, when determining the electrostatic potential at the vacancy. The process is repeated until self-consistency is achieved. Then we include the first shell of atoms in the self-consistent calculation and proceed in a similar way, placing the extra charge on the second neighbor shell. When the potential of the vacancy of that of the first neighbors to the vacancy are determined self-consistently, we include the next shell. The process continues until the self-consistent value for the potential of the last shell included differs from that of the bulk by a negligible amount. In the case of a larger vacancy-probe defect, the process is analogous, but the concept of the first shell, second shell, etc. is redefined accordingly. A diagram showing in detail the steps required to obtain the self-consistent solution to the electronic structure around defects within the RS LMTO ASA scheme is available in the literature.[14]

We should now comment on how to determine the

EFG tensor and values for V_{zz} and η, once the converged results for the electronic structure are known. Again we refer to the literature for a detailed description of the theory used to obtain the EFG tensor.[20,21] Just a brief overview stressing the approximations used and some interesting consequences of the present treatment is given here. There are several contributions to the EFG at a given site. They are often divided according to the spatial distribution of the charges from which they originate. Here we designate by lattice contribution the part that originates from charges located outside the WS cell which encloses the given nucleus, and by electronic contribution the part that originates from charges inside this WS cell. It has been shown[8] that for metallic systems, the lattice contribution is small (less than 10% of the total) and we neglect it in the present calculations. We also do not consider the contribution coming from core electrons around the probe. These electrons have a nearly spherical charge density and give negligible contributions (of order of 1%) to the EFG. The relevant contribution to the EFG in metallic systems comes from the valence electrons around the nucleus. It accounts for 90% of the effect in most cases and is the term we calculate here.

The components V_{ij} of the EFG tensor can be obtained by taking the quantum-mechanical average of the corresponding classical operator for an electronic state of energy E and integrating over all occupied states up to the Fermi level (E_F). When this is done and small terms are neglected, we find that the components of the EFG tensor can be tabulated in terms of radial integrals I_{ll} and generalized occupations $n_{m,m'}$ given below. A table with expressions for all the V_{ij} in terms of these quantities can be found elsewhere:[20]

$$I_{ll}=\int_0^s \frac{|\varphi_{l(r)}|^2}{r} d^3r \ , \tag{3}$$

$$n_{m,m'}=\int^{E_F} u_m^*(E)\,u_{m'}(E)\,dE \ . \tag{4}$$

Here the radial functions $\varphi_l(r)$ are solutions of angular momentum l for the Schrödinger equation inside the WS sphere of radius s around the probe and the quantities u_m are the coefficients corresponding to the orbital with angular part designated by cubic harmonics ($m=x, y$, and z for p orbitals and $m=xy, xz, yz, x^2-y^2$, and $3z^2-r^2$ for d orbitals) in the wave-function expansion. We note that $|u_m|^2$ is the local density of states associated with the orbital m. Therefore the quantity $n_{m,m}$ ($m=m'$) is just the occupation of the orbital of symmetry m and the quantities $n_{m,m'}$ are called generalized occupations. If we look at the expressions for the EFG tensor in terms of these quantities we find that, within the RS LMTO ASA approach, the EFG, to a good approximation, can be decomposed into a product of two terms. One term is due to small differences between occupations $n_{m,m'}$ associated with orbitals of different symmetries. These differences can be positive or negative and are usually of the order of 0.01 electrons. Therefore, to obtain this term, very accurate electronic-structure calculations are required. The other term is given by the integrals I_{ll} and is always positive. Due to the r^{-1} dependence of the integrand, I_{ll} is governed by the behavior of the radial solution for p and d orbitals close to the nucleus. This quantity is not very sensitive to the environment in which the atom is placed and can be tabulated for a given element in a metallic environment (see Table I). The order of magnitude of the EFG and the relative importance of p and d contributions can often be predicted without elaborate calculations, since the radial integrals are known. But to obtain the sign and a precise evaluation of the EFG is rather difficult. They depend on very small differences in occupation numbers and large errors are to be expected.

The radial integrals and generalized occupations can be determined from the converged RS LMTO ASA for the electronic structure. The EFG tensor is then easily obtained using tabulated expressions for its components. The tensor is not diagonal in general, but is always traceless. Finally, we use the calculated EFG tensor to obtain values for V_{zz} and η, which can be directly compared to experiment. To obtain these values we diagonalize the EFG tensor and find principal axes. The largest component in magnitude of the diagonal EFG tensor is usually associated with V_{zz} and the smallest with V_{xx}. With this convention the asymmetry parameter η is defined as $(V_{xx}-V_{yy})/V_{zz}$. It is always positive and can vary between zero and one. The direction of V_{zz} (or any other component) is given by the direction of the corresponding principal axis.

III. RESULTS FOR VACANCIES IN Al AND Cu

Here we use the RS LMTO ASA scheme to obtain the electronic structure around a vacancy in Cu and Al and divacancies in Al. Both Cu and Al form in fcc structures and experimental lattice constants, corresponding to a WS sphere radius of 4.05 Å for Al and 3.61 Å for Cu, were used in the calculations. The calculations were performed using a large cluster of 1700 atoms, cut in order to keep the atoms of interest at a maximum distance from the surface. Valence s, p, and d electrons were considered in the calculation, in a total of nine orbitals per site. For all the sites and orbitals a cutoff parameter $L_{\max}=20$ was taken in the recursion chain[17] and a Beer and Pettifor terminator was used.[22] We work within the local-spin-density-functional approximation with an exchange and correlation term of the form proposed by von Barth and Hedin.[23] To test the accuracy of the real-space calculations for vacancies, we have performed calculations in a fictitious fcc lattice with four atoms (three Al atoms and one empty sphere) in the unit cell, using both the RS LMTO ASA scheme and the standard k-space LMTO ASA formalism. Calculations for bulk Cu and bulk Al were also performed using the two approaches. In all cases, within the limitations of the first-order Hamiltonian,[13] the agreement between the two calculations was excellent.

To obtain the electronic structure around a monovacancy in Cu and Al, the potentials at the vacancy and four shells of neighbors, in a total of 55 sites, were included self-consistently. For the remaining atoms of the cluster, the bulk potentials were used. Due to the symmetry of the problem, the local density of states (LDOS) and the potential parameters are the same for all atoms belonging to the same shell. Therefore these quantities could be obtained using five representative sites (the vacancy and one atom of each shell) in each iteration, simplifying considerably the calculation.

In Table I we show the charge transfer (number of electrons transferred relative to the neutral site) at the vacancy and at an atom in each of the four neighboring shells in Cu and Al. The number of atoms in each shell is also given. Qualitatively, the behavior of the charge distribution is the same for Cu and Al. There is a positive charge transfer of around 0.9 electrons at the vacancy site and a negative charge transfer of about -0.1 electrons at each of the first neighbors to the vacancy. Since there are 12 of these, there is an overscreening, which is compensated by a positive charge transfer in the subsequent layers. In both cases we observe a charge transfer for atoms in the third shell that is larger than that in the second shell. A similar behavior was observed in the case of $3d$ impurities in Cu.[14] There the impurity has a negative charge transfer (loses electrons to the host), which is overscreened by the positive charge transfers of the first Cu shell, resulting in predominantly negative charge transfers in the second and third shells. Both the KKR GF and RS LMTO ASA results for $3d$ impurities in Cu also show a larger charge transfer at the third shell as compared to that of the second shell of neighbors. It is interesting to compare our results, which include four shells around the vacancy, with KKR GF results[11] obtained for a vacancy in Al, within the single-site (SS) approximation. We note that in this approximation the vacancy is treated self-consistently, but the potential of the remaining atoms are kept at a bulk value. The SS calculations[11] were performed in two ways: in the usual way (without charge conservation) and using corrections to account for the charge neutrality of the system. The charge transfer obtained at the vacancy using charge neutrality corrections (0.81 electrons) agrees much better with our more exact value (see Table I) than the one obtained by the usual procedure (0.43 electrons). We note that the SS value obtained correcting for charge neutrality is roughly twice that obtained without these corrections. A similar situation is also observed for $3d$ impurities in Cu,[14] indicating that the simple inclusion of charge conservation, when calculating the Madelung term at the site considered, can greatly improve the results of SS calculations at no additional cost.

TABLE I. Charge transfer at each atom around vacancies in Cu and Al. Also given is the number of atoms in each shell.

	Al	Cu	Number of atoms
vacancy	0.919	0.927	1
first shell	-0.113	-0.108	12
second shell	0.014	0.008	6
third shell	0.017	0.010	24
fourth shell	0.000	0.000	12

We have used our results for the electronic structure around a monovacancy to obtain the EFG tensor at an Al (or a Cu) site, first neighbor to the vacancy. As we have mentioned, the dominant contribution for the EFG in metallic systems comes from the charge distribution of p and d valence electrons around the nucleus. Other contributions (lattice and core) are small and were neglected in the present calculations. The relative importance of p and d contributions is roughly determined by the relative values of the radial integrals I_{pp} and I_{dd}, discussed in Sec. II. In Table II we give the value of these integrals for Al, Cu, and Cd probes in a metallic environment. From these values we see that the d contribution to the EFG can probably be neglected in the case of Al, but not in the case of Cu (or of the Cd probe to be considered later). The radial integrals also indicate that the magnitude of the EFG should be larger in the case of Cu than in the case of Al.

In Table III we show the components of the diagonal EFG tensor for sites close to a vacancy in Cu and Al. The direction of the principal axis associated with each of the components is also indicated. The measurements give the largest component (in magnitude) of the diagonal EFG tensor, usually designated by V_{zz} and the asymmetry parameter η. The asymmetry parameter is defined as the difference between the smallest components, divided by V_{zz}. In Table IV we show the calculated values of V_{zz} and η for first neighbors of a monovacancy in both Cu and Al. The direction of V_{zz} relative to the fcc lattice is given in parentheses in each case. As expected from the values of the radial integrals (see Table II), the value of V_{zz} is larger for Cu than for Al. In the case of Al the largest component of the tensor (see Table III) is clearly associated with the (1,1,0) direction and is directed along the line connecting the Al site to the vacancy. The calculated values for V_{zz} and η given in Table IV are in very good agreement with the values $V_{zz}=4.0\times10^{20}$ V/m^2 and $\eta=0.65$ obtained by NMR experiments.[6] In the case of Cu one of the components of the EFG tensor is very small, while the other two have nearly the same magnitude (η close to one). In the situation, within our precision, the magnitude of V_{zz} is well defined, but we have two possibilities for the sign. Therefore two numbers (with the corresponding directions) are quoted for Cu in Table IV. The numbers compare well in magnitude with the value of 11.3 obtained by KKR GF calculations[12] and the experimental value[7] of 13.5, given in the same units. The theoretical result is positive, but no value of η is given. The sign of V_{zz} has not been measured. We proceed to study divacancies in Al.

To obtain the electronic structure around divacancies

TABLE II. Radial integrals I_{pp} and I_{dd} used in the EFG calculations in units of 10^{-30} m^{-3} atoms in each shell.

	Al	Cu	Cd
I_{pp}	15.1	49.5	80.7
I_{dd}	0.66	53.3	69.9

TABLE III. The three components of the diagonal EFG tensor at the site (0.5, 0.5, 0.0), close to a vacancy in Cu and Al. The components are given in units of 10^{20} V/m^2 and the directions of the principal axis relative to the fcc lattice are also shown.

	EFG	p	d	Total	Direction
Al	V_1	-0.68	-0.08	-0.77	$\langle -1,1,0\rangle$
	V_2	-2.73	-0.09	-2.82	$\langle 0,0,1\rangle$
	V_3	3.42	0.17	3.57	$\langle 1,1,0\rangle$
Cu	V_1	0.10	-0.05	0.05	$\langle 0,0,1\rangle$
	V_2	18.52	-4.67	13.85	$\langle 1,1,0\rangle$
	V_3	-18.62	4.72	-13.90	$\langle 1,-1,0\rangle$

in Al we have used the same 1700 atoms cluster with the vacancy at the origin and added a second vacancy at a neighboring site (0.5, 0.5, 0.0) of the fcc lattice. Here we use reduced coordinates to indicate atomic positions. One can easily obtain the real coordinates by multiplying the numbers by the lattice parameter of Al. Again, the RS LMTO ASA scheme was used to obtain the electronic structure around the divacancy. The potential was calculated self-consistently at the vacancies and up to the third shell of neighbors around each vacancy for a total of 60 sites. The potential at the remaining sites was kept at bulk value. As before, we have used symmetry to simplify the numerical effort. For example, the first shell, which includes all the first neighbors to both vacancies, has a total of 18 atoms. But only four atoms are inequivalent with respect to the LDOS and the potential parameters and have to be considered to calculate these quantities. In Table V we show the position of these representative atoms (Al1, Al2, Al3, and Al4) and the number of atoms of each type present in the first shell. We obtain a charge transfer of 0.82 electrons to each of the vacancies, slightly smaller than the one obtained for monovacancies. The Al1 site, which is a first neighbor to both vacancies, shows a charge transfer of -0.23 electrons, while the remaining first-neighbor sites (Al2, Al3, and Al4) show transfers of around -0.1 electrons. In Table V we calculated values of V_{zz} and η for all representative Al sites in the first shell around the divacancy. We see that the largest value of V_{zz} correspond to Al1, a first neighbor to both vacancies, and is directed towards the center of the line connecting the two vacancies. The fourth site (Al4) is collinear with the vacancies and has a negative value of V_{zz}, directed along the z axis in the fcc structure. In all cases, due to the relative magnitude of the radial integrals of Al (see Table II) the p contribution to the EFG tensor is dominant.

TABLE IV. Calculated values of V_{zz} and η for a first neighbor of the monovacancy in both Cu and Al. The direction of the EFG relative to the fcc lattice is also given. V_{22} is given in units of 10^{20} V/m^2.

Al	$+3.6$ (110)	0.57
Cu	$+13.9$ (110)	~ 1
	-13.9 (1-10)	

TABLE V. Values of V_{zz} and η for atoms in the first shell around a divacancy in Al. V_{zz} is given in units of 10^{20} V/m^2.

	V_{zz}	η	Position	Number of atoms
Al1	7.1	0.29	0.0, 0.5, 0.5	4
Al2	4.4	0.36	0.5, -0.5,0.0	4
Al3	-3.6	0.43	-0.5,0.0, -0.5	8
Al4	-2.7	0.54	-0.5, -0.5,0.0	2

IV. RESULTS FOR A Cd PROBE IN Al

Most of the information for defects in Al has been obtained by PAC using a Cd probe[1–4] (an In atom is introduced, but it decays to Cd for the measurement of the EFG). Several values of the EFG can be observed experimentally in the presence of a Cd probe and the assignment of the measured values to each type of defect is not easily done. It is clear that reliable theoretical calculations for the EFG can contribute to the identification of the defect in this case.

Here we use the RS LMTO ASA to obtain the EFG at the Cd site of a monovacancy-Cd pair in Al. We use a 1700 atoms cluster, similar to the one used to study divacancies in Al, but replacing the vacancies at position (0.0, 0.0, 0.0) by a Cd atom. The problem is more complicated, since we lose the reflection symmetry around the plane perpendicular to the line connecting the two vacancies. In this case, two shells around the monovacancy-Cd pair are made self-consistent. This region contains all the first and second neighbors of both the vacancy and the Cd probe, for a total of 28 atoms. The potential of the remaining sites are kept at bulk value. Due to the lower symmetry of the defect, the first shell has seven inequivalent atoms instead of the four inequivalent sites observed in the case of the divacancy. The atom equally distant from the Cd and the vacancy still has the equivalence four of site Al1 of Table V. But each of the others (Al2, Al3, and Al4) are subdivided into two inequivalent sites, one closer to the Cd probe and the other closer to the vacancy. For the same reasons we have four inequivalent sites (instead of two) in the second-neighbor shell. Therefore, with the Cd and the vacancy, we include a total of 13 inequivalent potentials in the self-consistent process. We calculate the electronic structure around the defect using the same cutoff parameter and the same terminator as in the previous calculations. We find a charge transfer (number of electrons transferred relative to the neutral site) of 0.922 at the vacancy, very similar to the ones obtained for monovacancies in Al and Cu. The charge transfer at the Cd atom is -0.19 and all the other first neighbors of the vacancy, including the common neighbor with the Cd, have a charge transfer around -0.1. The charge transfer at the other atoms in the first shell, first neighbors of the Cd probe, is 10 times smaller. In the second shell, the charge transfer of the two atoms closer to the vacancy probe is positive, around 0.03, while the charge transfer for those closer to the Cd is again much smaller. We conclude that the behavior of the charge transfer in the presence of the Cd probe is very similar to that of the monovacancy, with a negative charge transfer in the first-neighbor shell of the vacancy and a smaller positive charge transfer in the second.

The components of the diagonal EFG tensor for the Cd probe and corresponding directions of the principal axis relative to the fcc lattice are shown in Table VI. We have used the conventional notation to assign the largest component in magnitude to V_{zz} and the smallest to V_{xx}. As in the case of the EFG for an Al first neighbor to a monovacancy, V_{zz} is directed along the line which connects the vacancy to the probe. But due to the higher values of the radial integrals of Table I, the value of V_{zz} in Cd is about six times larger than the one found for Al.

As we have mentioned before, there has been some interesting discussion in the literature regarding the identification of defects created by low-temperature implantation of In (decaying into Cd) in Al. Two signals are clearly observed in perturbed angular correlation experiments. Defect 1 has a quadrupole frequency $\omega_0=64$ Mrad/sec, asymmetry parameter $\eta=0.41$, and V_{zz} along the $\langle 110 \rangle$ direction, while defect 2 has a larger quadrupole frequency $\omega_0=123$ Mrad/sec $\eta=0$, and V_{zz} along the $\langle 111 \rangle$ direction.[1-4] It is generally agreed that defect 2 is due to a divacancy-Cd probe association and we did not attempt to calculate the EFG associated with this defect. But there is some controversy regarding the identification of defect 1. The simplest choice for a defect that appears when low-temperature implantation is used is the monovacancy-probe pair. But point-charge model calculations predict a value of η close to zero for this type of defect. Therefore, in a general study of several fcc metals,[1] the monovacancy-probe pair has been associated with a class A defect, oriented along the $\langle 110 \rangle$ direction, having $\eta=0$. Class A defects were encountered in several fcc metals, but a defect with these characteristics is missing in Al. The point-charge model would be compatible with larger values of η if relaxation of the probe towards the vacancy is allowed. But the value of V_{zz} predicted by the model is already three times larger than that associated with defect 1 and its values increases further with relaxation.[1] Based on these considerations defect 1 was assigned to a more complex structure, consisting of Cd and four vacancies. On the other hand, a PAC study of the formation of defect 1 and defect 2 after quenching[2] has indicated that defect 1 consists of fewer vacancies than defect 2. Since it is agreed that defect 2 has two vacancies, this experiment would be consistent with the assignment of defect 1 to the monovacancy-Cd pair in Al. Linear augmented plane-wave calculations for several hcp metals,[8] which agree rather well with experiment, make it clear that the point-charge model often fails to give the correct magnitude and sign for the EFG in these simple systems. Due to its simplicity, the point-charge model is still used, but it is agreed that it frequently fails when applied to metals and more reliable calculations are needed. Here we use our RS LMTO ASA results for the Cd-monovacancy pair to help to understand the structure of defect 1.

TABLE VI. The three components of the diagonal EFG tensor for the Cd probe in a Cd-monovacancy pair in Al. The components are given in units of 10^{20} V/m^2 and the directions of the principal axis are shown.

	EFG	p	d	Total	Direction
Cd	V_{xx}	-7.8	3.1	4.7	$\langle 1,-1,0 \rangle$
	V_{yy}	-16.3	0.9	-15.4	$\langle 0,0,1 \rangle$
	V_{zz}	24.1	-4.0	20.1	$\langle 1,1,0 \rangle$

TABLE VII. Experimental and calculated values of V_{zz} (units of 10^{20} V/m^2) and η for the Cd probe in a Cd-monovacancy pair in Al.

	RS LMTO ASA	Expt.	Point charge
V_{zz}	$+20.1$	34.2	-112
η	0.54	0.41	0.0

In Table VII we show the RS LMTO ASA calculated values of V_{zz} and η for a Cd probe in a Cd-monovacancy pair, together with experimental values obtained for the same quantities.[1-4] Results inferred from point-charge model calculations[1] are also shown for comparison. Contrary to the point-charge model, our results associate a high value of η to the Cd-monovacancy pair. We can see that the point-charge value for V_{zz} is much larger than both the calculated RS LMTO ASA and experimental values. Also its sign is negative, while the present work predicts a positive sign for V_{zz}. A similar situation is observed for the V_{zz} at an Al probe close to a vacancy in Al. We find (see Table IV) $V_{zz}=3.6\times10^{20}$ V/m^2, while the point-charge calculations yields -12.8 in the same units.[1] This is to be compared with an experimental value of 4.0×10^{20} V/m^2 obtained in the NMR experiment,[6] where the sign was not determined. We note that exact values for the EFG are difficult to obtain since it depends on very small differences (of the order of one hundredth of an electron) between occupations of orbitals of different symmetries. Within the expected errors, the agreement between the calculated RS LMTO ASA values of Table VII and experiment is quite good. Our calculations clearly indicate that defect 1 can indeed be assigned to a Cd-monovacancy pair.

V. CONCLUSION

We have performed first-principles self-consistent calculations to obtain the electronic structure around monovacancies in Cu and Al and divacancies in Al. The case of a monovacancy-Cd probe defect in Al was also considered. In all cases we observed a large transfer of electrons (0.8–0.9) into the vacant site. For monovacancies in Cu and Al, there is an overscreening of this charge by the first shell of atoms (which loses electrons), compensated by a gain of electrons by the second and third shells. The behavior around the vacancy is qualitatively the same for the divacancy and the monovacancy-Cd defect in Al.

The electronic-structure results were used to obtain the EFG tensor and values of V_{zz} and η for atoms close to the vacant sites. For a monovacancy in Cu, our absolute value of V_{zz} at the Cu site is in excellent agreement with experiment and previous KKR GF calculations. Since we find η close to one, the sign of V_{zz} could not be determined.

We also calculate the EFG tensor for atoms close to vacancies in Al. We find $V_{zz}=3.6\times10^{20}$ V/m^2 and $\eta=0.57$ at an Al atom close to a monovacancy and $V_{zz}=20.1\times10^{20}$ V/m^2 with $\eta=0.54$ if a Cd probe is used. These values are to be compared with experimental values of $V_{zz}=4.0\times10^{20}$ V/m^2 with $\eta=0.65$ for the Al atom and $V_{zz}=34.2\times10^{20}$ V/m^2 with $\eta=0.41$ for the Cd probe. Considering the subtlety of the effect, which depends on small differences between large numbers, the agreement is rather good. Our calculated results for the Cd probe allow us to identify the defect with quadrupole frequency $\omega_0=64$ Mrad/sec, which appears on low-temperature implantation of In (decaying into Cd) in Al, as a monovacancy-Cd pair.

Finally, the present calculations confirm that the point-charge model fails when applied to metallic systems and can be misleading when used to identify defects. Here, not only were the sign and the magnitude of V_{zz} badly described, but we have also shown that the point-charge model can lead to incorrect values of the asymmetry parameter η.

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