# Self-consistent molecular-cluster calculations of the electric field gradient of 5 sp impurities ( $_{47}Ag - _{54}Xe$ ) in cadmium

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The electric field gradients (EFG's) of 5sp impurities ( $_{47}Ag - _{54}Xe$ ) are calculated within the selfconsistent local-density molecular-cluster approach using 27 atoms. The experimentally observed oscillation of the EFG, from  $_{47}Ag$  to  $_{54}Xe$ , originates from the conduction-electron contribution. The 5p impurity electrons hybridize with the conduction band into bonding and antibonding states, the  $p_x, p_y$  bonding states having the lowest energy. A successive population of these states, with increasing impurity charge, explains the change in sign that occurs close to  $_{51}Sb$ .

# I. INTRODUCTION

The theoretical understanding of the origin of electric field gradients (EFG's) in metals has been a subject of great interest in the past decade. A significant increase in the amount of experimental data, in particular sign determinations, has occurred and various theoretical approaches have been employed to explain observed trends. Excellent reviews of both the experimental and theoretical aspects have been given by Kaufmann and Vianden.<sup>1,2</sup>

Very often estimates and calculations of the EFG's at a nucleus are based on the parametrization into one part,  $q_{ext}$ , originating from sources external to the electron shell and another part,  $q_{el}$ , from the valence electrons or unfilled atomic orbitals local to the nucleus:

$$q = (1 - \gamma_{\infty})q_{\text{ext}} + (1 - R)q_{\text{el}} .$$
 (1)

The polarization of the charge distribution in the core is accounted for by the Sternheimer antishielding factors  $\gamma_{\infty}$ and R. The first term in Eq. (1) is often calculated by a lattice summation and the importance of including the screening from conduction electrons, instead of just summing over bare ionic charges, has been demonstrated by Nishiyama and Riegel<sup>3</sup> and Butz.<sup>4</sup> Relying on the socalled "universal correlation," discovered by Raghavan et al.,<sup>5</sup> the second term is then estimated to be three times the first term but of opposite sign. In recent years, with an increasing amount of available experimental data, this proportionality is questioned in many systems.<sup>2</sup> The reason for this may be found in the second term of Eq. (1), which requires evaluation of electronic wave functions. For the pure metals, the electronic states are best determined by a band-structure approach, but despite the large number of such calculations presented in the past decades, only a few of them deduce the EFG's in noncubic metals.<sup>1</sup> The works by Das and co-workers<sup>6,7</sup> show, however, that the EFG's from the electronic states in the conduction band and close to the Fermi level are important as well as a properly calculated antishielding factor, accounting for the overlap of the conduction band with the core.

Most of the measured electric field gradients are for impurities in noncubic metals. The broken periodicity of the lattice in these systems almost prevents the use of bandcalculation methods, requiring very large unit cells to exclude impurity-impurity interactions. Another approach, however, that has proven to be a useful tool for impurity systems is the molecular-cluster method, where selfconsistent solutions are found for the electronic wave functions in a cluster of a limited number of atoms.

This paper presents self-consistent molecular-cluster calculations of the EFG's at 5sp impurities ( $_{47}Ag_{-54}Xe$ ) in hexagonal cadmium metal. The EFG's for these impurities show a sign-reversal around Sb,<sup>8</sup> hence not proportional to any antishielding factor. The method, which is described in Sec. II, treats all the electrons and does not require the use of antishielding factors. Section III discusses the results for a pure Cd cluster and in Sec. IV the calculated values along the impurity series is presented. A short summary and final comments are given in Sec. V.

#### **II. THEORETICAL MODEL**

### A. Computational procedure

The theoretical basis for the electronic structure calculations used here is the self-consistent one-electron localdensity formalism in the Hartree-Fock-Slater model.<sup>9-11</sup> The essential point of this theory is the replacement of the nonlocal Hartree-Fock exchange operator by a potential depending only on the local electron density.

In a nonrelativistic approach the one-electron Hamiltonian for the molecule can be written (in Hartree atomic units) as

$$H = -\frac{\nabla^2}{2} + V_C + V_{\rm xc} , \qquad (2)$$

where the first two terms are the kinetic energy and Coulomb potential.

The Hedin-Lundqvist potential<sup>12</sup> was adopted for the exchange-correlation potential

$$V_{\rm xc}(\mathbf{r}) = (3\rho/\pi)^{1/3} - 0.0225 \ln[1 + 21(4\pi\rho/3)^{1/3}], \qquad (3)$$

where  $\rho$  is the electron density at a point **r**.

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As in the usual linear-combination-of-atomic-

orbital-molecular-orbital (LCAO-MO) method, the molecular-orbital eigenfunctions are expanded in terms of symmetry orbitals:

$$\Psi_i(\mathbf{r}) = \sum_i \chi_j(\mathbf{r}) C_{ji} .$$
<sup>(4)</sup>

The symmetry orbitals  $\chi_j(\mathbf{r})$  are chosen here as linear combinations of atomic orbitals located on the different atoms in the molecule corresponding to the cluster point-group symmetry, i.e.,

$$\chi_j(\mathbf{r}) = \sum_{\nu,m} W_{\nu m}^{jl} U_{nl}(\mathbf{r}_{\nu}) Y_{lm}(\hat{\mathbf{r}}_{\nu}) , \qquad (5)$$

where  $U_{nl}(r_v)$  is the atomic radial wave function centered on the vth nucleus, with principal quantum number n and orbital number l.  $U_{nl}$  is obtained numerically by solving a self-consistent free atom or ion problem, and  $Y_{lm}$  is a spherical harmonic function with magnetic quantum number m.  $W_{vm}^{jl}$  are symmetrization coefficients which can be obtained by group-theoretical projection operators.

The expansion coefficients [variational coefficient  $C_{ji}$  in Eq. (4)] are obtained using standard procedures by solving the matrix secular equation

$$(H - \varepsilon S)C = 0, \qquad (6)$$

where  $\epsilon$  is the eigenvalue matrix.

The Hamiltonian matrix H and the symmetry orbital overlap matrix S are obtained in the discrete variational method (DVM) as a weighted sum over a set of sample points. The sample points set used in our study includes not only a pseudorandom Diophantine points set,<sup>13,14</sup> but also a regular spherical-volume mesh. The Diophantine distribution is mapped onto an infinite domain representing the region exterior to atomic spheres of some arbitrary radius, using a Fermi distribution.<sup>14</sup> In order to get good wave-function accuracy in core regions near the nucleus, we use an optimized Gaussian surface mesh in conjunction with a radial Simpson's rule scheme in spheres around the nuclei.

The Fermi energy and occupation numbers  $f_i(\epsilon)$  for each molecular orbital (MO) in Eq. (4) are obtained by using Fermi-Dirac statistics on these MO eigenstates. The cluster charge density was then constructed by summing over all MO's:

$$\rho_{\text{cluster}}(\mathbf{r}) = \sum_{i=1}^{N} f_i |\Psi_i(\mathbf{r})|^2 .$$
(7)

In order to calculate the potential by one-dimensional integrations, this charge density was cast in a multicenteroverlapping multipolar form:<sup>15</sup>

$$\rho_{\text{model}}(\mathbf{r}) = \sum_{n,j,l,m} d_{jlm}(n) \rho_j(r_n) Y_{lm}(\hat{\mathbf{r}}_n) , \qquad (8)$$

where  $\mathbf{r}_n = \mathbf{r} - \mathbf{R}_n$ ,  $\mathbf{R}_n$  are atomic sites, and (j, l, m) denotes multipoles centered on various nuclear sites.

The coefficients  $\{d_{jlm}\}\$  were determined by leastsquares fitting to the eigenvector density of Eq. (7). The radial density basis set of  $\{\rho_j\}\$  was constructed from spherical atomic densities calculated from the wavefunction variational basis, and from several radial functions for each  $l \leq 2$  in the fully symmetric representation



FIG. 1. Upper half of the 27-atom cluster, used in the calculations. The threefold rotation axis (z axis) of the  $D_{3h}$  pointgroup symmetry is equivalent to the c axis of the hcp structure. The open symbol shows the center atom where the EFG was calculated. The plane with this atom is the horizontal mirror plane.

of the molecular point group.

In the self-consistent multipolar (SCM) procedure the potential calculated from this representation of the cluster density is used to determine new wave functions and hence a new cluster density, until self-consistency is obtained.

#### **B.** Variational basis

The impurity atom was placed in the center of a 27atom cluster (Fig. 1), with the symmetry point group  $D_{3h}$ . All the electrons were treated for the center atom while the core 1s-4d were frozen for the other atoms. Since the local-density eigenfunctions are orthogonal to each other, the nonlocal pseudopotential of the frozen core can be fully accounted for by orthogonalizing the valence wave functions of one atom to the core functions of all the other atoms—a procedure followed here.

A double basis composed of neutral and ionized atoms was used for the center atom and its 12 nearest neighbors. This kind of basis is known to have enough variational freedom to reproduce all major rearrangements in the valence electron density.<sup>15</sup> With the pure 27-atom Cd cluster, an extra 4s, 4p basis was also added in order to investigate the influence on the core EFG contribution. A single basis from neutral Cd atoms was used for the outer 14 atoms of the cluster.

#### C. Cluster embedding

In the case where one is trying to represent a solid by a finite cluster of atoms, it is necessary to consider the embedding problem. For treating some properties of metals which may depend more or less sensitively on the band structure, it is desirable to broaden the discrete energy levels of the isolated cluster into bands. This can be accomplished by empirical level-smearing schemes, or by modifying the cluster boundary conditions. The asymptotic form of the wave function can be controlled by mixing in a selected continuum state into the cluster wave functions



FIG. 2. Valence energy levels for the 27-atom Cd cluster and the corresponding density of states (DOS) obtained with the empirical smearing parameter  $\beta = 100$  and 50, respectively. With  $\beta = 100$  some structure is still present in the DOS, while  $\beta = 50$  gives a smooth parabola-shaped DOS representative for a free-electron-like metal.

and solving an inhomogeneous Schrödinger equation.<sup>16</sup> The net result is an energy-dependent broadening of cluster levels and a smooth spectral representation of properties like the charge density. Such a scheme is necessary for systems with bands of different widths like the d and sp bands in the 3d metals.<sup>16-18</sup> However, for the more or less free-electron-like sp bands in cadmium metal, the empirical level smearing was adopted in this work. Each discrete energy level was broadened by

$$L_i(E) = (\beta/4) \cosh^{-2}[\beta(E - \varepsilon_i)/2] . \tag{9}$$

The density of states (DOS) obtained for the 27-atom Cd cluster in this way is shown in Fig. 2 for two different values of the empirical parameter  $\beta$ . The actual population for each single-particle state is obtained by integrating up to the Fermi energy  $\epsilon_F$ 

$$f_i = \int_{-\infty}^{\epsilon_F} L_i(E) dE \tag{10}$$

or by the well-known Fermi distribution function

$$f_i = \{1 + \exp[\beta(\epsilon_i - \varepsilon_F)]\}^{-1}.$$
(11)

The choice of smearing function was arbitrary. Fine details in the DOS are not significant since it is only the integral value of each line (10) that is controlled selfconsistently through Eq. (7). Results using both  $\beta = 100$ and  $\beta = 50$  will be given.

#### D. Electric field gradient

In a hexagonal structure an axially symmetric field gradient is present and given (in a.u.) by

$$q = -\int \rho(\mathbf{r}) (3\cos^2\theta - 1)r^{-3} d\mathbf{r} + q_{\text{nucleus}}$$
(12)

or with Eqs. (7) and (4),

$$q = -\sum_{n} f_{n} \sum_{i,j} \left\langle \chi_{i}(\mathbf{r}) \, | \, (3\cos^{2}\theta - 1)/r^{3} \, | \, \chi_{j}(\mathbf{r}) \right\rangle \\ \times C_{in} C_{jn} + q_{\text{nucleus}} .$$
(13)

TABLE I. Free neutral atomic  $\langle 5p | r^{-3} | 5p \rangle$  integrals (in a.u.) obtained with the Hedin-Lundqvist exchange-correlation potential.

Atom	Configuration	$\langle 5p   r^{-3}   5p \rangle$	
47Ag	$5s^{1}p^{0}$	2.46	
48Cd	$5s^2p^0$	3.66	
49In	$5s^{2}p^{1}$	5.77	
50Sn	$5s^2p^2$	8.22	
51Sb	$5s^{2}p^{3}$	10.91	
5. 57Te	$5s^{2}p^{4}$	13.83	
51 51	$5s^2p^5$	16.99	
54Xe	$5s^2p^6$	20.39	

Here r refers to the site of the probe nucleus, i.e., the center of the cluster. All terms in the sum belonging to this atom and its neutral basis set, including the core orbitals (see Sec. III B), were treated separately by using the integrals  $\langle u_{nl} | r^{-3} | u_{n'l'} \rangle$  obtained from the atomic basis calculation. The other terms were integrated numerically on the same point mesh as used for the integration of the Hamiltonian. Since core electrons are included self-consistently in the molecular-orbital calculation, the Sternheimer core antishielding factors are not needed. The overall numerical accuracy is estimated to be better than  $0.1 \times 10^{17}$  V/cm<sup>2</sup> within the model and basis functions used. (The conversion factor between atomic and SI units is  $9.72 \times 10^{17}$  V/cm<sup>2</sup> a.u.)

The atomic  $\langle u_{nl} | r^{-3} | u_{n'l'} \rangle$  integral depends on the exchange-correlation potential used. The  $\langle 5p | r^{-3} | 5p \rangle$  integrals obtained with the Hedin-Lundqvist potential are given in Table I. Considerably higher values may be calculated with the Slater exchange<sup>9</sup>  $V_{xc} = 1.5(3\rho/\pi)^{1/3}$  but the total EFG for the cluster was less sensitive. Relativistic effects are not included. They are estimated from relativistic atomic calculations<sup>19</sup> to increase the obtained magnitudes by about 15%.

#### III. RESULTS FOR Cd

The calculated EFG's, obtained with a Cd atom also at the center of the cluster in Fig. 1, are summarized in Table II for two different values of the broadening parameter  $\beta$ . The EFG's from unscreened 2 + ions is slightly less than  $-0.1 \times 10^{17}$  V/cm<sup>2</sup>. Using  $\gamma_{\infty} = -29.27$  for a Cd<sup>2+</sup> ion,<sup>20</sup> one obtains a core EFG of  $-3.1 \times 10^{17}$ V/cm<sup>2</sup>. Since the valence charges of the nearest-neighbor atoms overlap with the center atom and are not complete-

TABLE II. Calculated EFG's in units of  $10^{17}$  V/cm<sup>2</sup> for different broadening parameter  $\beta$ .

β	Core 1s-4d	Valence 5 sp	Total (including $q_{nucl}$ )	Experimental value (Ref. 21)
100	-1.5	+ 4.9	+ 3.3	+ 6.28
50	-1.5	+ 5.8	+ 4.3	1 0.20

ly external, another antishielding factor other than  $\gamma_{\infty}$  might be more appropriate to use. This problem is avoided in the current study where all the core electrons are treated self-consistently. Instead one must worry about the variational freedom of the core basis, in particular, the 4p basis which is responsible for more than 90% of the antishielding of the ion.<sup>20</sup> Extra 4s and 4p basis generated from the Cd<sup>7+</sup>( $4s^2p^6d^5$ ) ion indeed increases the magnitude of the core contribution from -1.5 to  $-1.9 \times 10^{17}$  V/cm<sup>2</sup>. This correction is, however, small compared to the total EFG and will be neglected hereafter.

As is evident from Table II the total EFG is dominated by the valence part. The contributions,  $\delta q(E)$ , from states at different energies (spectral distribution) are shown in Fig. 4. At the low-energy part of the band the EFG is positive, corresponding to a predominant  $p_x, p_y$  character of those states. This positive EFG is then partly reduced by states with  $p_z$  characters lying close to the Fermi energy. The actual population of those states determines critically the calculated value of the EFG, which explains the different results for the two  $\beta$  values used. Mixing in continuum states in the cluster wave functions (see Sec. II C) could not improve the calculated EFG. A more-detailed knowledge of the Fermi surface and its electron states than can be obtained by the present method and cluster size is needed in order to obtain better agreement with experiments. However, for systematic comparisons with, e.g., different impurity atoms, this accuracy is enough as will be obvious in Sec. IV.

An inspection of one of the eigenvectors at the Fermi level, showed that about 70% of the EFG came from 5p-5p integrals, while about 17% was due to 5p-4p integrals. Freezing all the core electrons, up to 4d, changed the eigenvalues by less than a few meV. Hence the coreelectron admixture in the final molecular valence wave functions is mainly due to the overlap matrix elements and the core orthogonalization. This "core-electron contribution" is comparable to what is obtained with the local Sternheimer factor R = -0.2,<sup>1</sup> but the origin is rather nonlocal. In the variational basis the 5p and 4p wave functions are already orthogonal within one atom and it is the overlap with neighboring atoms that mixes in with the core contribution into the valence wave functions.

Different cluster sizes and geometries were also investigated. The point ion EFG obtained for the cluster in Fig. 1 is about 15% less than that of an infinite lattice. Removing the two atoms at the c axis leads to a 40% too large value but the valence part of the EFG does not follow this increase in magnitude. These two atoms are crucial for the correct bonding and antibonding or hybridization of the  $p_z$  orbitals of the center atom. Reducing the distance of those two atoms pushes up and depopulates the  $p_z$ -like orbital at the Fermi energy, increasing the total EFG. If the atoms are removed the orbital is lowered in energy, hence reducing the EFG or even changing the sign. Decreasing all the z-coordinates of the atoms to values corresponding to the ideal  $c/a = \sqrt{8/3}$  of the hcp lattice, reduces the total EFG as expected. The obtained value,  $-0.9 \times 10^{17}$  V/cm<sup>2</sup>, may indicate the systematic error in the EFG due to the finite cluster size, if the true value is assumed to be zero for ideal c/a.

# IV. RESULTS FOR Ag-Xe IN CADMIUM

The EFG for different substitutional 5sp-impurity atoms in the Cd cluster are compared with experimental data<sup>21</sup> in Fig. 3. The change in sign by increasing the impurity charge is well reproduced. The spectral distributions  $\delta q(E) = dq/dE$  are shown in Fig. 4, left-hand side of diagram. The bottom of the band is predominantly of  $p_x, p_y$  character and contributes positively. Then a  $p_z$  region with a negative contribution appears. This can be understood in terms of bonding and antibonding states of the p orbitals of the center atom with the rest of the cluster electrons, i.e., they hybridize with the conduction band of the host. In Cd metal, where  $c/a > \sqrt{8/3}$ , the bonding and antibonding of the degenerate  $p_x, p_y$  states are stronger than for the  $p_z$  states. This is schematically illustrated in Fig. 5. For Ag and Cd, where the p orbitals are not bound in the free atom, the bottom of the conduction band gets a small  $p_x, p_y$  character due to the hybridization. In Fig. 4 (left-hand side)  $\delta q$  is positive below the Fermi energy  $E_F$ . With increasing impurity charge, and hence deeper impurity potential, the orbitals illustrated in Fig. 5 are successively populated. A negative  $\delta q$  is shifted down through  $E_F$  in Fig. 4. After Sb, with its almost spherical half-filled p shell and small EFG, the first antibonding states, which are of  $p_z$  type, become populated and the EFG's change sign. This is also observed in the right-hand side of Fig. 4 which shows the energy dependence of the valence EFG  $q(E) = \int_{-\infty}^{E} \delta q(E) dE$ . The total valence EFG is given by the value at  $E_F, q(E_F)$ . A similar interpretation has previously been given by Haas and co-workers.<sup>8</sup> They adopted a tight-binding model with different widths of the  $p_x$ ,  $p_y$ , and  $p_z$  bands.

Despite the change in sign of the EFG, the core contribution is negative for all the different impurities. The EFG from charges external to the center atom is also neg-



FIG. 3. Calculated and experimental EFG's for 5sp-impurity atoms in cadmium metal. The solid curve shows results obtained with  $\beta = 50$  and the dashed curve for  $\beta = 100$ . The solid circles show experimental data (Ref. 21). The Sb-EFG sign is not known and the *I* value is very uncertain.



FIG. 4. Left diagram: The spectral distribution of the EFG,  $\delta q(E) = dq/dE$ , for different atoms in Cd. Right diagram: The valence part of the EFG as a function of energy,  $q(E) = \int^{E} \delta(E) dE$ . The total valence contribution is given by the value at the Fermi energy. All scales are proportional to  $\langle 5p | 1/r^3 | 5p \rangle$  for the respective impurity atom,  $\beta = 50$ .

ative and in Fig. 6 this EFG and its antishielding<sup>20</sup> of the core [Eq. (1)] is compared to the calculated core contribution. For Ag the 4*d* levels lie on the bottom of the conduction 5sp band and for Cd just below, making the separation into core EFG and valence EFG more ambiguous than for the other atoms.

As already mentioned in Sec. III, the contribution to the EFG from states at the Fermi level is important and a detailed knowledge of the Fermi surface and its electron states is necessary in order to obtain better agreement with



FIG. 5. Schematic illustration showing the splitting of the valence *p*-orbitals into bonding and antibonding states due to the hybridization with neighboring atomic orbitals. In a prolate structure  $(c/a > \sqrt{8/3})$  the  $p_{xy}$  orbitals are more split than the  $p_z$  orbitals. In a tight-binding model (Ref. 8), more appropriate for a solid, this implies a broader  $p_{xy}$  band than the  $p_z$  band (solid curve).



FIG. 6. Solid curve: The core EFG contribution (from levels below 4d) for different 5sp atoms. Dashed curve: EFG from charges external to the center atom and its antishielding of the core electrons [Eq. (1)].

experimental values. Some of the deviations may, however, also be ascribed to uncertain quadrupole moments of the nuclear levels. Values for, e.g., <sup>119</sup>Sn, range from -0.06 b (Ref. 22) to -0.11 b (Ref. 23). The values quoted in Ref. 21 were used for the experimental points in Fig. 3.

Another important factor is the lattice relaxation due to the impurity atoms. From the valence charge-density maps in Fig. 7, it is clear that some relaxation of the



FIG. 7. Valence charge-density maps in a ca plane of the hcp structure. Contour intervals are 0.002 a.u., linearly.

neighboring atoms is to be expected. The equilibrium distances can in principle be calculated from the total energies of different cluster geometries, but this was beyond the scope of the present work. Interatomic distances representative for the pure Cd metal were used. Hence, the systematic trend in the EFG for the different impurities, reproduced by the calculations, is due to the hybridization of the impurity electrons with the host conduction band, and not because of different impurity-host distances.

# V. SUMMARY

The EFG of 5sp impurities in Cd metal was found to depend strongly on the valence band and in particular on details of the Fermi level. Although a finite molecularcluster model cannot calculate the Fermi surface and accurate electronic states there, the systematic trend and sign reversal were well reproduced. The merit in the molecular-cluster model lies, instead, in the more simple interpretation of the results in terms of orbitals associated with certain atoms. It was found that the systematic trend originated from a bonding and antibonding hybridization of the *p* electrons of the impurity atom with the

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host conduction band. The impurity-host system here gives us a unique possibility to study this. In principle the same trend with sign reversal should be seen in the pure metals going from Ag to Xe, but the structure and c/a also change when  $p_x, p_y$ , and  $p_z$  bonding and antibonding states successively become populated.

The hyperfine field of impurity atoms in ferromagnetic metals follow a similar oscillating dependence on the impurity charge. In, e.g., Fe, Co, and Ni, the Ag-hyperfine field is negative while the I field is positive and the sign reversal occurs close to Sn.<sup>24</sup> This systematic behavior is also explained by successive population of impurity associated electron states close to the Fermi level.<sup>18</sup> Care must therefore be taken when hyperfine data of impurities are used to extract information about host properties. "Unexpected" temperature dependence, etc., may appear if the hyperfine parameter critically depends on a narrow impurity level at the Fermi energy.

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