

## Point-ion versus density functional calculations of electric field gradients in ordered GaInP 2

Su-Huai Wei and Alex Zunger

Citation: *The Journal of Chemical Physics* **107**, 1931 (1997); doi: 10.1063/1.474544

View online: <http://dx.doi.org/10.1063/1.474544>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/107/6?ver=pdfcov>

Published by the [AIP Publishing](#)

---

### Articles you may be interested in

[Calculation of electric-field gradients based on higher-order generalized Douglas–Kroll transformations](#)  
*J. Chem. Phys.* **122**, 204107 (2005); 10.1063/1.1904589

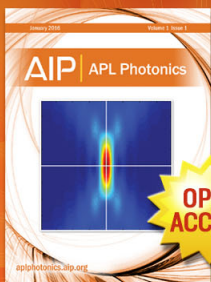
[The quadrupole moment of the  \$3/2 +\$  nuclear ground state of Au 197 from electric field gradient relativistic coupled cluster and density-functional theory of small molecules and the solid state](#)  
*J. Chem. Phys.* **122**, 124317 (2005); 10.1063/1.1869975

[Comparison of ab initio and density functional calculations of electric field gradients: The 57 Fe nuclear quadrupole moment from Mössbauer data](#)  
*J. Chem. Phys.* **115**, 5913 (2001); 10.1063/1.1398095

[Density functional calculations of nuclear quadrupole coupling constants in the zero-order regular approximation for relativistic effects](#)  
*J. Chem. Phys.* **112**, 8279 (2000); 10.1063/1.481433

[The accuracy of current density functionals for the calculation of electric field gradients: A comparison with ab initio methods for HCl and CuCl](#)  
*J. Chem. Phys.* **111**, 3357 (1999); 10.1063/1.479620

---



Launching in 2016!

The future of applied photonics research is here

OPEN  
ACCESS

**AIP** | APL  
Photonics

# Point-ion versus density functional calculations of electric field gradients in ordered GaInP<sub>2</sub>

Su-Huai Wei and Alex Zunger

National Renewable Energy Laboratory, Golden, Colorado 80401

(Received 29 January 1997; accepted 1 May 1997)

We investigate whether the electric field gradient (EFG) at an atomic site in the unit cell of a periodic solid can be modeled via the electrostatic field gradient set up by atomic *point charges* outside that site. To test this approach we contrast the EFG predicted by such point-ion models for long-range ordered GaInP<sub>2</sub> alloys with the results obtained from self-consistent all-electron calculations in the local density approximation (LDA). We first tested our LDA approach for ZnAl<sub>2</sub>O<sub>4</sub>, for which experimental data exist, finding the quadrupole coupling constant  $Q_{cc}({}^{27}\text{Al})=3.94$  MHz, compared with the measured value of  $|Q|=3.68$  MHz. Applying next the LDA approach to perfectly ordered GaInP<sub>2</sub> (for which experimental data do not exist), we find the LDA quadrupole coupling constant  $Q_{cc}=-4.83, -2.84,$  and  $13.08$  MHz for <sup>69</sup>Ga, <sup>71</sup>Ga, and <sup>115</sup>In, respectively. We further find that more than 95% of these EFGs originate from the anisotropic electron charge distribution *within* a small sphere of radius  $\sim 0.2$  Å about the respective atomic site. Hence, the point-ion model significantly underestimates the magnitude of the EFG (and in some cases also gives an incorrect sign). The point-ion model also fails in reproducing the relative trends in the EFG as the crystal structure changes. We conclude that the point-ion model is not a viable alternative to calculate EFG in periodic covalent solids. © 1997 American Institute of Physics. [S0021-9606(97)50930-5]

## I. INTRODUCTION

Substitutional solid solutions  $A_{1-x}B_xC$  of fourfold coordinated covalent semiconductors  $AC$  and  $BC$  (e.g., GaAs, GaP, InP, etc.) are rarely random.<sup>1</sup> The two leading forms of deviation from random are ‘‘short-range order’’ (where the number of local  $A-A$ ,  $B-B$ , and  $A-B$  pairs is different from what random statistics would grant) and ‘‘long-range order’’ (where  $A$  and  $B$  order crystallographically). Spontaneous, CuPt-like long-range ordering of III-V semiconductor alloys<sup>1</sup> (e.g.,  $\text{Ga}_{1-x}\text{In}_x\text{P}$ ,  $\text{Al}_{1-x}\text{In}_x\text{As}$ ), has been widely observed in vapor phase growth. This ordered phase consists of alternate cation monolayer planes  $A_{x+\eta/2}B_{1-x-\eta/2}$  and  $A_{x-\eta/2}B_{1-x+\eta/2}$  stacked along the  $[111]$  direction, where  $0 \leq \eta \leq 1$  is the long-range order parameter.<sup>2</sup> Perfect ordering ( $\eta=1$ ) corresponds to successive planes of pure  $A$  followed by pure  $B$ , etc.

The interest in atomic-scale deviations from randomness stems from the profound effects they have on optical properties<sup>3</sup> (including level splittings, level shifts, new allowed transitions, and new light polarization rules), and from the implication of such nonrandom distribution on alloy thermodynamics.<sup>4</sup> These deviations from randomness can be observed directly through diffraction<sup>5</sup> and scattering<sup>6</sup> techniques, or indirectly via their optical fingerprints.<sup>3</sup> Another approach, suggested recently,<sup>7</sup> is to measure the quadrupole interactions between the nuclei and the local electric field gradient (EFG) using nuclear magnetic resonance (NMR), which is sensitive to the local symmetry about a nucleus. Mao *et al.*<sup>7</sup> deduced the degree  $\eta$  of long-range order in  $\text{Ga}_{0.52}\text{In}_{0.48}\text{P}$  from the measured EFG through a point-ion model. Here we utilize self-consistent local density electronic structure theory to compute the EFG directly from the

variational potential. We show that more than 95% of the Ga, In, or P EFG originates from the anisotropic electron charge distribution *within* a small sphere of radius  $\sim 0.2$  Å about the atomic site. Hence, the point-ion model, which considers charge only on lattice sites, significantly underestimates the magnitude (and in some cases also gives an incorrect sign) of the EFG. The point-ion model is further found to fail in reproducing the relative trends in the EFG as the crystal structure changes.

## II. METHOD OF CALCULATION AND TESTS

We use the local density functional formalism<sup>8</sup> to calculate the self-consistent crystalline charge density  $\rho(\mathbf{r})$  and Coulomb potential  $V_C(\mathbf{r})$ , which is needed to obtain the EFG. Using the local density functional approximation,<sup>9</sup> we first solve the self-consistent single particle equation

$$[K_{\text{op}} + V_C(\rho) + V_{\text{xc}}(\rho)]\psi_i = \epsilon_i\psi_i, \quad (1)$$

where  $K_{\text{op}}$  is the kinetic energy operator,  $V_C(\rho)$  is the Coulomb potential, and  $V_{\text{xc}}(\rho)$  is the electronic exchange-correlation potential. The electron charge density is obtained by

$$\rho_e(\mathbf{r}) = \sum_i |\psi_i(\mathbf{r})|^2, \quad (2)$$

where the summation runs over all the occupied states. We solve Eq. (1) using the all-electron full-potential linearized augmented plan wave (LAPW) method,<sup>10,11</sup> which is highly precise and a generally applicable technique for studying ground state properties in periodic solids.<sup>10-15</sup> In this approach, space is divided into two regions: the (nonoverlapping) muffin-tin (MT) spheres (with radii  $R_{\text{MT}}$ ) centered

TABLE I. Cartesian coordinates ( $x, y, z$ ) $a$  of atoms in the relaxed GaInP<sub>2</sub> crystal having the CuPt structure. Here,  $a=5.671$  Å is the calculated equilibrium lattice constant. The two types of P atoms are denoted P(Ga<sub>3</sub>In) and P(GaIn<sub>3</sub>), respectively.

	$x$	$y$	$z$
Ga	0.000 00	0.000 00	0.000 00
In	1.003 25	1.003 25	1.003 25
P(Ga <sub>3</sub> In)	1.262 31	1.262 31	1.262 31
P(GaIn <sub>3</sub> )	0.239 93	0.239 93	0.239 93

about each atom, and the interstitial region between the atoms. The total (electrons and nuclei) charge density  $\rho(\mathbf{r})$  in the solid is expanded as

$$\rho(\mathbf{r}) = \begin{cases} \sum_{l,m} \rho_{lm}(r) Y_{lm}(\hat{r}) & \text{inside the MT spheres,} \\ \sum_{\mathbf{G}} \rho_{\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{r}} & \text{in the interstitial region} \end{cases} \quad (3)$$

For a given total charge density  $\rho(\mathbf{r})$ , the Coulomb potential of the crystal is obtained by solving the Poisson's equation using a method proposed by Weinert.<sup>16</sup> The resulting Coulomb potential  $V_C = V(\mathbf{r})$  is expanded in analogy with Eq. (3) as

$$V(\mathbf{r}) = \begin{cases} \sum_{l,m} V_{lm}(r) Y_{lm}(\hat{r}) & \text{inside the MT spheres,} \\ \sum_{\mathbf{G}} V_{\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{r}} & \text{in the interstitial region} \end{cases} \quad (4)$$

Given the Coulomb potential  $V(\mathbf{r})$ , the electric field gradient (EFG) tensor  $V_{ij}^\alpha$  at the  $\alpha$ th nuclear site can be defined as

$$V_{ij}^\alpha = \left. \frac{\partial^2 V^\alpha}{\partial x_i \partial x_j} \right|_{r_\alpha=0}, \quad (5)$$

where  $i$  and  $j$  are Cartesian coordinates. (For simplicity, we will ignore the index  $\alpha$  below.) Since the potential of Eq. (4) near the nucleus at  $r=0$  has the asymptotic form<sup>17</sup>

$$V(r \rightarrow 0) = \sum_{l,m} r^l \Phi_{lm} \left[ \frac{4\pi}{2l+1} \right]^{1/2} Y_{lm}(\hat{r}), \quad (6)$$

only the  $l=2$  ( $m=-2$  to  $2$ ) terms give nonzero EFG. Specifically, the EFGs at a nuclear site are

TABLE II. Calculated principle components of the electric field gradient  $V_{z'z'}$  (in Ry/bohr<sup>2</sup>) of CuPt ordered GaInP<sub>2</sub>. Here,  $z'$  is along the [111] direction.  $\text{EFG}_{\text{NN}}^{\text{ion}}$  are obtained from Eq. (13) by summing over only nearest neighbor ions,  $\text{EFG}_{\text{total}}^{\text{ion}}$  are obtained from the full sum of Eq. (13), while  $\text{EFG}^{\text{LDA}}$  are obtained from first-principles all-electron LDA calculations.

Sites	$\text{EFG}_{\text{NN}}^{\text{ion}}$	$\text{EFG}_{\text{total}}^{\text{ion}}$	$\text{EFG}^{\text{LDA}}$
Ga	-0.003 27	0.003 86	-0.241 62
In	-0.000 38	-0.007 39	0.137 46
P(Ga <sub>3</sub> In)	-0.003 47	-0.003 88	-0.249 58
P(GaIn <sub>3</sub> )	0.006 34	0.007 74	0.273 66

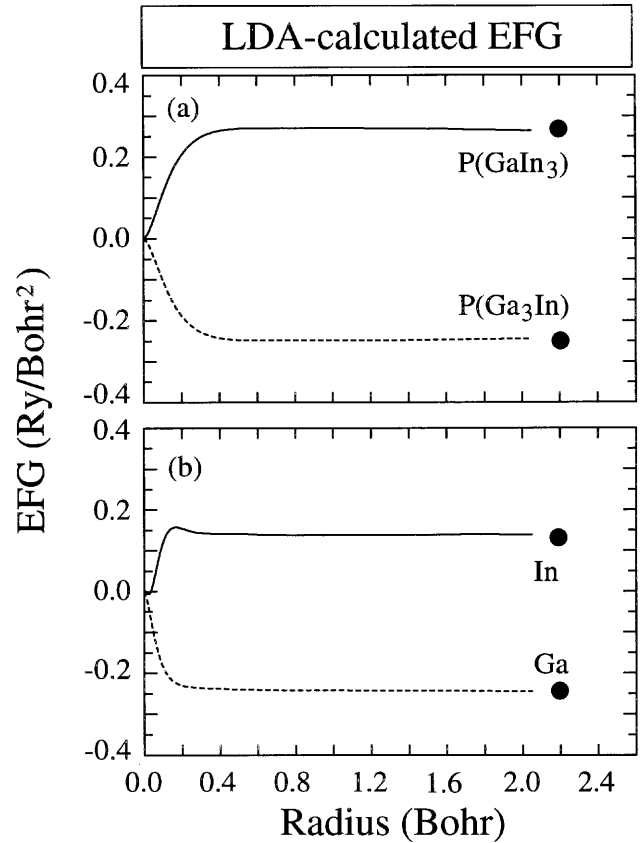


FIG. 1. Calculated EFG of CuPt ordered GaInP<sub>2</sub>. The lines show the contributions to EFG from charges inside a sphere as a function of the sphere's radius  $R$  [Eq. (11)]. The solid dots on the right hand side of the figures give the total EFG; (a) for the two types of P atoms and (b) for Ga and In.

$$\begin{aligned} V_{xx} &= \left(\frac{3}{2}\right)^{1/2} (\Phi_{2,-2} + \Phi_{2,2}) - \Phi_{2,0}, \\ V_{yy} &= -\left(\frac{3}{2}\right)^{1/2} (\Phi_{2,-2} + \Phi_{2,2}) - \Phi_{2,0}, \\ V_{xy} &= -i \left(\frac{3}{2}\right)^{1/2} (\Phi_{2,-2} - \Phi_{2,2}), \\ V_{yz} &= -i \left(\frac{3}{2}\right)^{1/2} (\Phi_{2,-1} + \Phi_{2,1}), \\ V_{zx} &= \left(\frac{3}{2}\right)^{1/2} (\Phi_{2,-1} - \Phi_{2,1}). \end{aligned} \quad (7)$$

Here,

$$\Phi_{2m} = \Phi_{2,-m}^* = \lim_{r \rightarrow 0} \left[ \frac{5}{4\pi} \right]^{1/2} \frac{V_{2m}(r)}{r^2}, \quad (8)$$

and the traceless condition of the EFG requires

$$V_{zz} = -(V_{xx} + V_{yy}) = 2\Phi_{2,0}. \quad (9)$$

As we can see from Eqs. (3)–(8), the EFG can be easily obtained once the self-consistent charge density of Eq. (3) is known. Further, one can always find principal axes ( $x', y', z'$ ) of the potential  $V$  such that  $V_{ij} = 0$  if  $i \neq j$ . Con-

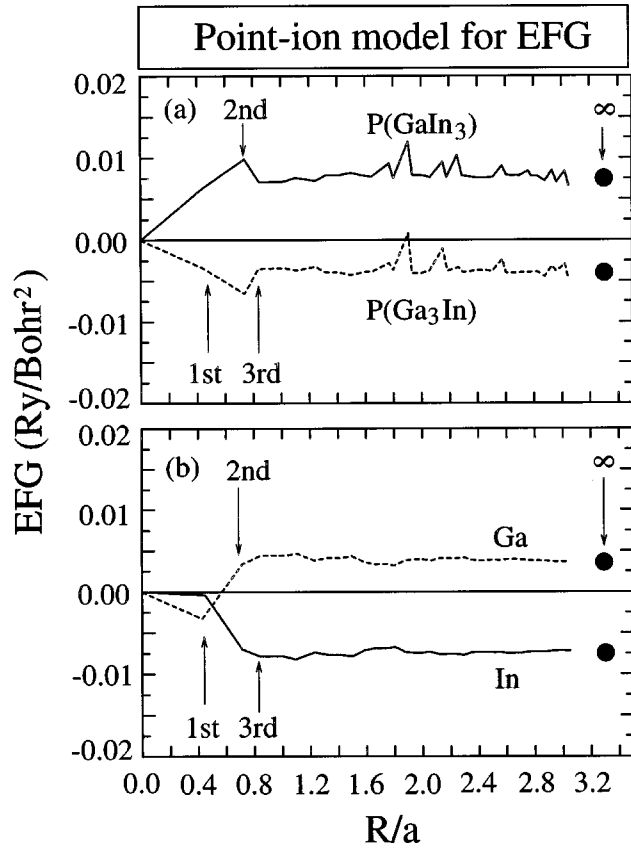


FIG. 2. Calculated point-ion  $EFG^{\text{ion}}$  of CuPt ordered GaInP<sub>2</sub>. The lines show the  $EFG^{\text{ion}}$  as a function of the ratio between the coordination shell radius  $R$  and the lattice constant  $a$ , where only ions inside the sphere are included in the summation of Eq. (13). The solid dots on the right hand side of the figures are the total ionic EFG: (a) for the two types of P atoms and (b) for Ga and In.

ventionally, one orders the Cartesian components according to their magnitude so that  $|V_{z'z'}| > |V_{y'y'}| > |V_{x'x'}|$ . Thus, the EFGs are usually specified by just two parameters: the principal component  $V_{z'z'}$  and the anisotropy parameter

$$\lambda = (V_{x'x'} - V_{y'y'}) / V_{z'z'}, \quad (10)$$

where  $0 < \lambda < 1$ .

Before performing the EFG calculations for the CuPt ordered structure of GaInP<sub>2</sub>, we tested our procedure by calculating the Al EFG in ZnAl<sub>2</sub>O<sub>4</sub>. We chose this system because accurate experimental data<sup>18–20</sup> are available for comparison.

ZnAl<sub>2</sub>O<sub>4</sub> has the normal spinel structure. The Al atoms are located at the octahedral sites with a local trigonal ( $D_{3d}$ ) symmetry. Hence, the EFG at the Al site is axially symmetric ( $\lambda = 0$ ) with the principal component  $V_{z'z'}$  oriented along the [111] direction. We calculated the EFG of Al in ZnAl<sub>2</sub>O<sub>4</sub> at the measured structural parameters  $a = 8.0813 \text{ \AA}$  and  $u = 0.3887$ . The calculated  $V_{z'z'} = -0.2390 \text{ Ry/bohr}^2$  is in good agreement with the experimentally measured value<sup>19,20</sup> of  $|V_{z'z'}^{\text{exp}}| = 0.2233 \text{ Ry/bohr}^2$ , and is also in good agreement with the recent first-principles all-electrons Hartree–Fock cluster calculations of Mitchell

TABLE III. Cartesian coordinates  $(x, y, z)a$  of atoms in the relaxed GaInP<sub>2</sub> crystal having the Z2 structure. Here,  $a = 5.671 \text{ \AA}$  is our calculated equilibrium lattice constant. Only symmetry nonequivalent atomic positions are given. The three types of P atoms are denoted P(Ga<sub>4</sub>), P(Ga<sub>2</sub>In<sub>2</sub>), and P(In<sub>4</sub>), respectively.

	$x$	$y$	$z$
Ga	0.000 00	0.000 00	0.000 00
In	0.000 00	0.000 00	0.960 76
P(Ga <sub>4</sub> )	0.250 00	0.250 00	0.230 46
P(Ga <sub>2</sub> In <sub>2</sub> )	0.250 00	0.750 00	0.689 68
P(In <sub>4</sub> )	0.250 00	0.250 00	1.230 46

*et al.*,<sup>18</sup> who find  $V_{z'z'} = -0.2102 \text{ Ry/bohr}^2$ . This test demonstrated that it is possible to obtain reliable EFG from first-principles LDA band structure calculations.

In the study of GaInP<sub>2</sub>, a local orbital extension<sup>12</sup> is applied to the full-potential LAPW method. Local orbitals are used to treat accurately the extended Ga 3*d* and In 4*d* semicore states. We use the Ceperley–Alder exchange correlation potential<sup>21</sup> as parameterized by Perdew and Zunger.<sup>22</sup> Core states are treated relativistically using a spherical approximation (so they do not contribute in this approximation directly to the EFG), while the valence states are treated semirelativistically with the full potential. Highly converged basis sets with a cutoff energy of 19.3 Ry is used (corresponding to  $\sim 230$  LAPW basis functions per atom). The Brillouin-zone integration is performed using special  $k$ -points corresponding to the ten special  $k$ -points in the zinc-blend structure.<sup>23</sup>

### III. RESULTS AND ANALYSIS

#### A. First-principles LDA calculations

The equilibrium lattice parameters and cell-internal crystallographic parameters of the ordered GaInP<sub>2</sub> were determined by minimization of the total energies. The calculated structural parameters of CuPt ordered GaInP<sub>2</sub> are given in Table I. In this ordered structure there are two chemical types of cations (Ga and In) and two crystallographic types of anions inside the trigonal primitive unit cell. Each cation is surrounded by four nearest neighbor (NN) P atoms. One anion P is surrounded by three Ga and one In atoms [denoted as P(Ga<sub>3</sub>In)], while the second P is surrounded by one Ga and three In atoms [denoted as P(GaIn<sub>3</sub>)]. All atoms have locally a trigonal ( $C_{3v}$ ) symmetry, thus the EFGs at all sites are axially symmetric ( $\lambda = 0$ ) with the principal component  $V_{z'z'}$  oriented along the ordering [111] direction. The last column of Table II shows our calculated  $V_{z'z'}$  (denoted as  $EFG^{\text{LDA}}$ ) for the four atoms in perfectly ordered ( $\eta = 1$ ) GaInP<sub>2</sub>.

To understand the different contributions to the EFG of GaInP<sub>2</sub>, we have decomposed the  $V_{z'z'}$  into two parts: (i)  $V_{z'z'}^{\text{sphere}}(R)$  from the anisotropic charge distribution *inside* a sphere of radius  $R$  centered at the nuclear site and (ii)  $V_{z'z'}^{\text{latt}}(R)$  from charges *elsewhere in the lattice*. Clearly, by definition  $V_{z'z'} = V_{z'z'}^{\text{sphere}}(R) + V_{z'z'}^{\text{latt}}(R)$ . The sphere's contribution  $V_{z'z'}^{\text{sphere}}(R)$  is given by

TABLE IV. Calculated principal component  $V_{z'z'}$  (in Ry/bohr<sup>2</sup>), the principal axis  $z'$ , and the anisotropy parameter  $\lambda$  [Eq. (10)] of relaxed GaInP<sub>2</sub> in the Z2 structure. The definition of different approaches can be found in the caption of Table II.

Sites	EFG <sub>NN</sub> <sup>ion</sup>			EFG <sub>total</sub> <sup>ion</sup>			EFG <sup>LDA</sup>		
	$V_{z'z'}$	$z'$	$\lambda$	$V_{z'z'}$	$z'$	$\lambda$	$V_{z'z'}$	$z'$	$\lambda$
Ga	-0.011 52	[1 $\bar{1}$ 0]	0.89	0.012 35	[001]	0.93	0.327 92	[001]	0.34
In	-0.009 94	[001]	0.93	-0.011 75	[001]	0.70	-0.553 32	[001]	0.37
P(Ga <sub>4</sub> )	-0.009 85	[001]	0.00	-0.004 50	[001]	0.00	-0.180 07	[001]	0.00
P(Ga <sub>2</sub> In <sub>2</sub> )	0.003 88	[110]	0.99	-0.004 32	[1 $\bar{1}$ 0]	0.84	-0.254 78	[1 $\bar{1}$ 0]	0.83
P(In <sub>4</sub> )	0.010 11	[001]	0.00	0.006 70	[001]	0.00	0.247 14	[001]	0.00

$$V_{z'z'}^{\text{sphere}}(R) = \left[ \frac{4\pi}{5} \right]^{1/2} \int_0^R \frac{\rho_{z'z'}}{r^3} r^2 dr. \quad (11)$$

Here the relation between  $\rho_{ij}$  and  $\rho_{2,m}$  is the same as that between  $V_{ij}$  and  $V_{2,m}$  given in Eq. (7). Figure 1 shows  $V_{z'z'}^{\text{sphere}}(R)$  as a function of the sphere radius  $R$  for the four atom types in the GaInP<sub>2</sub> unit cell. The values of the total  $V_{z'z'}$  are shown on the right hand side of Fig. 1 as solid dots. The difference between the total  $V_{z'z'}$  and  $V_{z'z'}^{\text{sphere}}(R)$  is  $V_{z'z'}^{\text{latt}}(R)$ . We see that *most of the EFG comes from the anisotropic charge distribution of the electron inside a sphere radius  $R_0$  of about 0.4 bohr*. Since the core orbitals are assumed in our calculation to be spherically symmetric, the entire EFG results from the valence orbitals.<sup>24</sup> The contribution to the EFG of charges *outside*  $R_0$  is very small (Fig. 1) because of the  $1/r^3$  dependence of the EFG to a point charge [Eq. (11)]. We find that  $V_{z'z'}^{\text{latt}}(R_0)/V_{z'z'} < 4\%$ .

Our calculated  $V_{z'z'}$  can be used to compute the nuclear quadrupole coupling constant<sup>25</sup>  $Q_{cc} = e^2 q Q$ , where  $eq = V_{z'z'}$ , and  $Q$  is the quadrupole moment of the nucleus. Using the values<sup>26</sup> of  $Q = 0.17, 0.10,$  and  $0.81$  barn for <sup>69</sup>Ga, <sup>71</sup>Ga, and <sup>115</sup>In, respectively, we find the LDA values of the quadrupole coupling constants

$$\begin{aligned} Q_{cc}(\text{}^{69}\text{Ga}) &= -4.83 \text{ MHz}, \\ Q_{cc}(\text{}^{71}\text{Ga}) &= -2.84 \text{ MHz}, \\ Q_{cc}(\text{}^{115}\text{In}) &= 13.08 \text{ MHz} \end{aligned} \quad (12)$$

for perfect ordered GaInP<sub>2</sub>. <sup>31</sup>P has no quadrupole moment, so  $Q_{cc}(\text{}^{31}\text{P})$  is zero.

## B. Simple point-ion models

Our first-principles calculated EFG results can be compared with those obtained from simple model calculations. In particular, we will study the ionic model of Mao *et al.*<sup>7</sup> In this model, the EFG on a nuclear site is calculated from point-ion electrostatic potentials of surrounding atoms. Following Mao *et al.*, we use the Harrison's bond-polarity model<sup>7,27</sup> to assign point charges on each atomic site. This gives  $Q_{\text{ion}}(\text{Ga}) = 1.08 e$  and  $Q_{\text{ion}}(\text{In}) = 1.32 e$ . Since there are five types of P atoms in the Ga<sub>1-x</sub>In<sub>x</sub>P alloy (depending on the P nearest neighbor coordination shell Ga<sub>4-n</sub>In<sub>n</sub>, where  $n = 0, 1, 2, 3,$  and  $4$ ), we have five  $Q_{\text{ion}}(\text{P}_n)$  values. In Harrison's model they are  $-1.08, -1.14, -1.20, -1.26,$

and  $-1.32 e$  for  $n = 0, 1, 2, 3,$  and  $4$ , respectively. The point-ion EFG at an atomic position  $\mathbf{r} = \mathbf{0}$  due to all ions outside the origin can be obtained as

$$\begin{aligned} V_{ij}^{\text{ion}} &= \sum_{\alpha} Q_{\text{ion}}^{\alpha} (3x_{\alpha,i}^2 - r_{\alpha}^2) / r_{\alpha}^5 \quad \text{for } i=j, \\ V_{ij}^{\text{ion}} &= \sum_{\alpha} Q_{\text{ion}}^{\alpha} 3x_{\alpha,i}x_{\alpha,j} / r_{\alpha}^5 \quad \text{for } i \neq j. \end{aligned} \quad (13)$$

Table II shows our calculated point-ion model EFG for CuPt ordered GaInP<sub>2</sub> using Eq. (13). Two results are shown in Table II: First, when the summation over  $\alpha$  in Eq. (13) is limited to first nearest neighbor shell (denoted as EFG<sub>NN</sub><sup>ion</sup>) as done by Mao *et al.* Second, the summation is carried over all the atoms in the crystal (denoted as EFG<sub>total</sub><sup>ion</sup>). Figure 2 shows how fast the point-ion EFGs converge as a function of the number of shells included in the sum of Eq. (13).

We see from Table II and Fig. 2 that:

- (i) The point-ion EFG<sup>ion</sup> is much smaller than the EFG calculated using the full, continuous charge distribution. For the cations, the signs of the point-ion EFG are reversed. The underestimation of the magnitude of the EFG by the point-ion model is consistent with the results we plotted in Fig. 1, which show that the EFG originates mostly from the valence charge distribution *within* a sphere of radius  $R_0 < 0.4$  bohr about the nuclei. Thus, it appears that the point-ion model is not capable of reproducing the EFG in such covalent alloy systems.
- (ii) We see that EFG<sub>NN</sub><sup>ion</sup> and EFG<sub>total</sub><sup>ion</sup> are quite different. In fact, Fig. 2 shows that EFG<sup>ion</sup> at the Ga and In sites are relatively converged only after the sum of Eq. (13) extends at least up to the third neighbor shells. This can be understood by noticing that despite the  $1/r^3$  dependence of the point-ion EFG [Eq. (13)], in the zinc-blende structure the ratio  $R(2\text{nd})/R(1\text{st}) = 1.633$  of the second to the first neighbor distance and  $R(3\text{rd})/R(1\text{st}) = 1.915$  between the third and first neighbor distance are not very large. Furthermore, there are 12 atoms in both second and third coordination shells, but only 4 atoms in the first shell. Thus, the contributions to EFG<sup>ion</sup> of Eq. (13) from second and third neighbor shells are not negligible.

### C. Relative EFG of two structures

While the previous section showed that the point-ion model captures only a small piece of the total EFG of a given crystal structure, one might wonder if it correctly predicts the *trend* in EFG between different structures. If it does, it could still be used to compare, e.g., ordered versus disordered alloys using the Sternheimer factor.<sup>25</sup> To test this we have compared the calculated point-ion EFG of two structures to the values obtained by the LDA calculation. We selected the Z2 structure, which is a (2,2) superlattice along the [001] direction. There are three types of P atoms in the Z2 structure: P(Ga<sub>4</sub>), P(In<sub>4</sub>), and P(Ga<sub>2</sub>In<sub>2</sub>). The first two types of P atoms have local  $D_{2d}$  symmetry, so the principal axis is along the [001] direction and  $\lambda=0$ . On the other hand, P(Ga<sub>2</sub>In<sub>2</sub>) and the cations (Ga and In) have local  $C_{2v}$  symmetry, so the principal axis can be [001], [110], or [110] and  $\lambda \neq 0$ . Table III gives the calculated equilibrium atomic positions in the Z2 structure and Table IV gives our calculated principal component of the EFG, the principal axis, and the anisotropy parameter  $\lambda$  using the three different approaches. We see again from Table IV that the calculated EFG from point-ion approaches (including either the NN point-ion model or the model that includes all ions) are much too small compared with the first-principles LDA results. The trend in EFG with changing chemical environment is also not described well by the point-ion model: Using the first-principles LDA results the ratios  $EFG_{\alpha}^{CP}/EFG_{\alpha}^{Z2}$  are  $-0.74$  and  $0.248$ , respectively, for  $\alpha$ =Ga and In, while in the point-ion model the ratios are  $0.31$  and  $0.63$ , respectively.

### IV. SUMMARY

Using the first-principles LAPW method and the local density functional approximation we have calculated the electric field gradient of long-range ordered GaInP<sub>2</sub> alloys. We find the quadrupole coupling constant  $Q_{cc} = -4.83$ ,  $-2.84$ , and  $13.08$  MHz for <sup>69</sup>Ga, <sup>71</sup>Ga, and <sup>115</sup>In, respectively. We find that more than 95% of the Ga, In, or P EFG originates from the anisotropic electron charge distribution *within* a small sphere of radius  $\sim 0.2$  Å about the atomic site. The calculated results are compared with a simple point-ion model. We find that the point-ion model significantly underestimates the magnitude (in some cases also gives the incorrect sign) of the EFG. The point-ion model also fails to reproduce the relative trends in the EFG as the crystal structure changes.

### ACKNOWLEDGMENTS

This work was supported in part by the U.S. Department of Energy, Grant No. DE-AC36-83-CH10093. We thank P. C. Taylor, Sarah R. Kurtz, W. A. Harrison, and S. Froyen for useful discussions.

- <sup>1</sup>A. Zunger and S. Mahajan, in *Handbook of Semiconductors*, 2nd ed. (Elsevier, Amsterdam, 1994), Vol. 3, p. 1339, and references therein.
- <sup>2</sup>S.-H. Wei, D. B. Laks, and A. Zunger, *Appl. Phys. Lett.* **62**, 1937 (1993).
- <sup>3</sup>S.-H. Wei, A. Franceschetti, and A. Zunger, in *Optoelectronic Materials—Ordering, Composition Modulation, and Self-Assembled Structures*, edited by E. D. Jones, A. Mascarenhas, and P. Petroff (MRS, Pittsburgh, 1996), p. 3, and references therein.
- <sup>4</sup>R. Osorio, J. E. Bernard, S. Froyen, and A. Zunger, *Phys. Rev. B* **45**, 11,173 (1992).
- <sup>5</sup>C. S. Baxter, R. F. Broom, and W. M. Stobbs, *Surf. Sci.* **228**, 102 (1990).
- <sup>6</sup>S. Yasuami, K. Koga, K. Ohshima, S. Sasaki, and M. Ando, *J. Appl. Crystallogr.* **25**, 514 (1992).
- <sup>7</sup>D. Mao, P. C. Taylor, S. R. Kurtz, M. C. Wu, and W. A. Harrison, *Phys. Rev. Lett.* **76**, 4769 (1996).
- <sup>8</sup>P. Hohenberg and W. Kohn, *Phys. Rev.* **136**, B864 (1964).
- <sup>9</sup>W. Kohn and L. J. Sham, *Phys. Rev.* **140**, A1133 (1965).
- <sup>10</sup>O. K. Andersen, *Phys. Rev. B* **12**, 3060 (1975); D. D. Koelling and G. O. Arbman, *J. Phys. F* **5**, 2041 (1975); E. Wimmer, H. Krakauer, M. Weinert, and A. J. Freeman, *Phys. Rev. B* **24**, 864 (1981); S.-H. Wei and H. Krakauer, *Phys. Rev. Lett.* **55**, 1200 (1985).
- <sup>11</sup>D. J. Singh, *Planewaves, Pseudopotentials and the LAPW Method* (Kluwer, Boston, 1994), and references therein.
- <sup>12</sup>D. J. Singh, *Phys. Rev. B* **43**, 6388 (1991).
- <sup>13</sup>K. Schwarz, C. Ambrosch-Draxl, and P. Blaha, *Phys. Rev. B* **42**, 2051 (1990).
- <sup>14</sup>J. Yu, A. J. Freeman, R. Podloucky, P. Herzig, and P. Weinberger, *Phys. Rev. B* **43**, 532 (1991).
- <sup>15</sup>D. Singh, K. Schwarz, and P. Blaha, *Phys. Rev. B* **46**, 5849 (1992).
- <sup>16</sup>M. Weinert, *J. Math. Phys.* **22**, 2433 (1981).
- <sup>17</sup>P. Blaha, K. Schwarz, and P. Herzig, *Phys. Rev. Lett.* **54**, 1192 (1985).
- <sup>18</sup>D. W. Mitchell, T. P. Das, W. Potzel, W. Schiessl, H. Karzel, M. Steiner, M. Köfferlein, U. Hiller, G. M. Kalvins, A. Martin, W. Schäfer, G. Will, I. Halevy, and J. Gal, *Phys. Rev. B* **53**, 7684 (1996).
- <sup>19</sup>P. Ruggsegger, F. Waldner, and E. Burn, *Helv. Phys. Acta* **43**, 799 (1970).
- <sup>20</sup>D. Sundholm and J. Olsen, *Phys. Rev. Lett.* **68**, 927 (1992).
- <sup>21</sup>D. M. Ceperly and B. J. Alder, *Phys. Rev. Lett.* **45**, 566 (1980).
- <sup>22</sup>J. P. Perdew and A. Zunger, *Phys. Rev. B* **23**, 5048 (1981).
- <sup>23</sup>S. Froyen, *Phys. Rev. B* **39**, 3168 (1989).
- <sup>24</sup>Treating the “outer core” states (Ga 3s, 3p and In 4s, 4p) as valence bands does not change our calculated results.
- <sup>25</sup>C. P. Slichter, *Principles of Magnetic Resonance* (Springer-Verlag, New York, 1978).
- <sup>26</sup>*CRC Handbook of Chemistry and Physics*, 76th ed., edited by A. R. Lide and H. P. R. Frederikse (CRC, New York, 1996).
- <sup>27</sup>W. A. Harrison, *Electronic Structure and the Properties of Solids* (W. H. Freeman, Oxford, 1979).