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Point-ion versus density functional calculations of electric field gradients in ordered GaInP₂

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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 GaInP₂ alloys with the results obtained from self-consistent all-electron calculations in the local density approximation (LDA). We first tested our LDA approach for ZnAl₂O₄, for which experimental data exist, finding the quadrupole coupling constant $Q_{cc}^{27}\text{Al} = 53.94$ MHz, compared with the measured value of $Q_{cc} = 53.68$ MHz. Applying next the LDA approach to perfectly ordered GaInP₂ -for which experimental data do not exist!, we find the LDA quadrupole coupling constant $Q_{cc} = 24.83, 22.84,$ and 13.08 MHz for ⁶⁹Ga, ⁷¹Ga, and ¹¹⁵In, respectively. We further find that more than 95% of these EFGs originate from the anisotropic electron charge distribution *within* a small sphere of radius ≈ 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 $A_{1-2x}B_xC$ of fourfold coordinated covalent semiconductors AC and BC -e.g., GaAs, GaP, InP, etc.! are rarely random.¹ 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 alloys¹ -e.g., $\text{Ga}_{1-2x}\text{In}_x\text{P}$, $\text{Al}_{1-2x}\text{In}_x\text{As}$!, has been widely observed in vapor phase growth. This ordered phase consists of alternate cation monolayer planes $A_{x+1/2}B_{1-2x+1/2}$ and $A_{x+1/2}B_{1-2x+1/2}$ stacked along the $[111]$ direction, where $0 < h < 1$ is the long-range order parameter.² Perfect ordering ($h=1$) corresponds to successive planes of pure A followed by pure B , etc.

The interest in atomic-scale deviations from randomness

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

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

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.¹⁶ The resulting Coulomb potential $V_C(\mathbf{r})$ is expanded in analogy with Eq. (3) as

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

Given the Coulomb potential $V(\mathbf{r})$, the electric field gradient -EFG! tensor V_{ij}^a at the

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

$$I = \frac{3}{2} \frac{V_{x\bar{x}} - V_{y\bar{y}}}{V_{z\bar{z}}}, \quad (10)$$

where $0 \leq I \leq 1$.

Before performing the EFG calculations for the CuPt ordered structure of GaInP₂, we tested our procedure by calculating the Al EFG in ZnAl₂O₄. We chose this system because accurate experimental data^{18–20} are available for comparison.

ZnAl₂O₄ 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 ($I = 0$) with the principal component $V_{z\bar{z}}$ oriented along the $[111]$ direction. We calculated the EFG of Al in ZnAl₂O₄ at the measured structural parameters $a = 8.0813 \text{ \AA}$ and $u = 0.3887$. The calculated $V_{z\bar{z}} = 2.02390 \text{ Ry/bohr}^2$ is in good agreement with the experimentally measured value^{19,20} of $|V_{z\bar{z}}^{\text{exp}}| = 0.2233 \text{ Ry/bohr}^2$, and is also in good agreement with the recent first-principles all-electrons Hartree–Fock cluster calculations of Mitchell

et al.,¹⁸ who find $V_{z\bar{z}} = 2.02102 \text{ Ry/bohr}^2$. This test demonstrated that it is possible to obtain reliable EFG from first-principles LDA band structure calculations.

In the study of GaInP₂, a local orbital extension¹² is applied to the full-potential LAPW method. Local orbitals are used to treat accurately the extended Ga $3d$ and In $4d$ semicore states. We use the Ceperley–Alder exchange correlation potential²¹ as parameterized by Perdew and Zunger.²² 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 ; 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.²³

III. RESULTS AND ANALYSIS

A. First-principles LDA calculations

The equilibrium lattice parameters and cell-internal crystallographic parameters of the ordered GaInP₂ were determined by minimization of the total energies. The calculated structural parameters of CuPt ordered GaInP₂ 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-Ga₃In!#, while the second P is surrounded by one Ga and three In atoms @denoted as P-GaIn₃!#. All atoms have locally a trigonal (C_{3v}

$$V_{z\bar{z}\bar{z}}^{\text{sphere}} \sim R! \int_0^R \frac{4\rho}{5} \left[\frac{r_{z\bar{z}\bar{z}}}{r^3} \right]^{1/2} r^2 dr. \quad -11!$$

Here the relation between r_{ij} and $r_{2,m}$ is the same as that between V_{ij} and $V_{2,m}$ given in Eq. -7!. Figure 1 shows $V_{z\bar{z}\bar{z}}^{\text{sphere}}(R)$ as a function of the sphere radius R for the four atom types in the GaInP₂ unit cell. The values of the *total* $V_{z\bar{z}\bar{z}}$ are shown on the right hand side of Fig. 1 as solid dots. The difference between the total $V_{z\bar{z}\bar{z}}$ and $V_{z\bar{z}\bar{z}}^{\text{sphere}}(R)$ is $V_{z\bar{z}\bar{z}}^{\text{latt}}(R)$. 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.²⁴ 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 $V_{z\bar{z}\bar{z}}^{\text{latt}}(R_0)/V_{z\bar{z}\bar{z}}$, 4%.

Our calculated $V_{z\bar{z}\bar{z}}$ can be used to compute the nuclear quadrupole coupling constant²⁵ $Q_{cc} \sim e^2 q Q$, where $eq \sim V_{z\bar{z}\bar{z}}$, and Q is the quadrupole moment of the nucleus. Using the values²⁶ of $Q \sim 0.17, 0.10,$ and 0.81 barn for ⁶⁹Ga, ⁷¹Ga, and ¹¹⁵In, respectively, we find the LDA values of the quadrupole coupling constants

$$\begin{aligned} Q_{cc} \text{ } ^{69}\text{Ga} &\sim 24.83 \text{ MHz}, \\ Q_{cc} \text{ } ^{71}\text{Ga} &\sim 22.84 \text{ MHz}, \\ Q_{cc} \text{ } ^{115}\text{In} &\sim 13.08 \text{ MHz} \end{aligned} \quad -12!$$

for perfect ordered GaInP₂. ³¹P 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.*⁷ 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^{7,27} to assign point charges on each atomic site. This gives $Q_{\text{ion}}\text{-Ga} \sim 1.08 e$ and $Q_{\text{ion}}\text{-In} \sim 1.32 e$. Since there are five types of P atoms in the Ga_{1-2x}In_xP alloy -depending on the P nearest neighbor coordination shell Ga_{4-2n}In_n, where $n \sim 0, 1, 2, 3,$ and $4!$, we have five $Q_{\text{ion}}(\text{P}_n)$ values. In Harrison's model they are $\geq 1.08, \geq 1.14, \geq 1.20, \geq 1.26,$

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

$$\begin{aligned} V_{ij}^{\text{ion}} &\sim \sum_a Q_{\text{ion}}^a \frac{3x_{a,i}^2 - 2r_{a,i}^2/r_a^5}{r_a^5} \quad \text{for } i \sim j, \\ V_{ij}^{\text{ion}} &\sim \sum_a Q_{\text{ion}}^a \frac{3x_{a,i}x_{a,j}}{r_a^5} \quad \text{for } i \neq j. \end{aligned} \quad -13!$$

Table II shows our calculated point-ion model EFG for CuPt ordered GaInP₂ using Eq. -13!. Two results are shown in Table II: First, when the summation over a in Eq. -13! is

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.²⁵ 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 $\sqrt{2} \times \sqrt{2}$ superlattice along the $[001]$ direction. There are three types of P atoms in the Z2 structure: P-Ga₄, P-In₄, and P-Ga₂In₂. The first two types of P atoms have local D_{2d} symmetry, so the principal axis is along the $[001]$ direction and $\parallel \mathbf{z}$. On the other hand, P-