

VIRTUAL LATTICE TECHNIQUE AND THE INTERATOMIC POTENTIALS OF ZINC-BLEND-TYPE BINARY COMPOUNDS

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Chen's lattice inversion method is expanded to calculate the interatomic potentials of zinc-blend-type binary compounds with the virtual lattice technique, which proposes a scheme to obtain the non-empirical interatomic potentials based on the first principle calculation.

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The interatomic potentials are widely used in the simulation of the structures, defects, dynamical properties, etc. for various materials. A number of empirical interatomic pair-potential forms have been developed such as the rigid-sphere model, the Buckingham potential, the Lennard–Jones potential, the Morse potential and the Born–Mayer potential [1], which are widely used in many simulations. In the early 1980s, Carlsson *et al.* developed a non-empirical pair potential with an iterative form²:

$$E(r) = \sum_{p=1}^{\infty} n_p \varphi(d_p r), \quad (1)$$

$$\begin{aligned} \varphi(r) = & \frac{1}{n_1} E(r) - \sum_{s=2}^{\infty} \frac{n_s}{n_1^2} E(d_s r) + \sum_{p,q=2}^{\infty} \frac{n_p n_q}{n_1^3} E(d_p d_q r) \\ & - \sum_{p,q,l=2}^{\infty} \frac{n_p n_q n_l}{n_1^4} E(d_p d_q d_l r) + \dots, \quad (2) \end{aligned}$$

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where r is the lattice constant, $E(r)$ is the cohesive energy, n_p and $d_p r$ are the number and the distance of the n th set of lattice points, respectively, and $\varphi(r)$ is the pair potential function. This is an initial investigation to obtain exactly the interatomic potentials from the cohesive energy curves. In 1990, a number-theoretic Möbius inversion method^{3,4} was applied creatively to a few physical inversion problems, which resulted in the solution of a series of problems such as the capacity inverse problem,⁵ the lattice inverse problem⁶ and the inverse problems in astrophysics,⁷ etc. Particularly, in the application for lattice inverse,⁶ the modified Möbius inverse formula was obtained:

$$U(x) = \frac{1}{2} \sum_{n=1}^{\infty} r_0(n) \Phi(b_0(n)x), \quad (3)$$

$$\Phi(x) = 2 \sum_{n=1}^{\infty} I(n) U(b(n)x), \quad (4)$$

where x is the nearest-neighbor distance, $I(n)$ is determined by

$$\sum_{b(d)|b(n)} I(d)r \left(b^{-1} \left[\frac{b(n)}{b(d)} \right] \right) = \delta_{n1}. \quad (5)$$

The series $\{b(n)\}$ is a multiplicatively closed semi-group extended from $\{b_0(n)\}$, and

$$r(n) = \begin{cases} r_0(b_0^{-1}[b(n)]), & b(n) \in \{b_0(n)\}, \\ 0, & b(n) \notin \{b_0(n)\}. \end{cases} \quad (6)$$

This is a concisely analytic method to obtain the interatomic potentials from the *ab initio* cohesive energy curves, and has been applied to the solutions of some physical problems.⁷⁻⁹

Obtaining the interatomic potentials of the binary alloys and compounds has been an intractable problem. Generally, the interatomic potentials of the element crystal are directly transferred to the alloys, which are verified in a feasible, approximate way by calculations.^{8,9} However, for the covalent and ionic crystals, the same transfer is not appropriate due to the large difference between the bond-types. The investigation of interatomic potentials for ionic crystals is limited in the empirical scheme. For example, a common model is the Buckingham potential or Lennard-Jones potential attached Coulomb potential.^{10,11}

In the present work, Chen's lattice inversion method is extended to calculate the interatomic potentials of the AB zinc-blend-type binary compounds with virtual lattice technique based on *ab initio* calculation. We suppose the potentials are transferable in the crystals with space groups $F\bar{4}3m$ and $P42/mmc$ (see Fig. 1) according to the similarity of the relative positions of the atoms in these two structures. Then, the cohesive energy difference at the same lattice constant between model 1 and model 2 depends only on the interatomic interaction Φ_{A-A} . According to the cohesive energy differences at different lattice constants, the interatomic

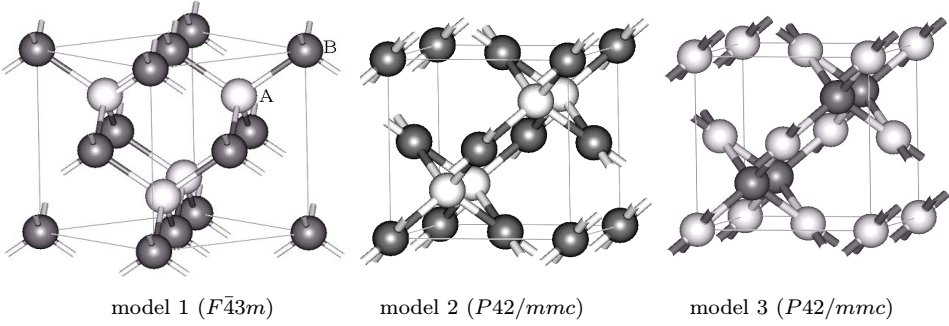


Fig. 1. The zinc-blend-type crystal cell (model 1 with space group $F\bar{4}3m$) and the virtual crystal cell (model 2 and model 3 with space groups $P42/mmc$) used in the calculations.

potential Φ_{A-A} is obtained using Chen's lattice inversion method. Similarly Φ_{B-B} can be obtained from the cohesive energy difference between model 1 and model 3. The potential Φ_{A-B} can be directly calculated based on the dependence of cohesive energy of model 1 on the lattice constants.

Following the above procedure, we calculate the interatomic pair-potentials of GaSb and GaAs based on *ab initio* cohesive energy curves. In the calculations the first principle norm-conserving pseudopotential in the LDA is used. The crystal wave-function is expanded by the plane-wave basis set, the cut-off energy for the plane-wave is 890 eV GaAs. The electronic minimization scheme is the density mixing with the conjugate gradient (CG) method for eigenvalues minimization. The calculations of the total energy and charge density are based on the density functional theory, a uniform mesh of k points in the irreducible Brillouin zone is produced by the Monkhorst–Pack scheme.¹² The quality of this representation can be verified by increasing the density of k points in the mesh. The self-consistent iteration of the total energy is converged to 2×10^{-6} eV/atom in our calculations. The total energy at the infinite lattice constant, i.e. the extrapolated value by fitting the curve of the calculated total energy with lattice constants, is set as zero of the cohesive energy. Given that an accurate calculation method is still in expectation and the experimental cohesive energy data for III–V compounds are so scarce up to now,¹³ the cohesive energy based on the LDA is rationally adopted in our calculations. The graphs of interatomic pair-potentials are shown in Fig. 2.

In our calculations, the Born stable conditions of the cubic crystal — i.e. the values of the nonzero elastic constants being positive and $c_{11} - c_{12} > 0$ — are not satisfied for the zinc-blend-type crystal only under the pair potential interaction, which results in structural unsteadiness with the small vibration of the atoms. So, the three-body term, a supplement to the isotropic two-body potentials, is necessary for describing accurately the interatomic interactions in the zinc-blend structure. In the present work, the Modified Stillinger–Weber (MSW)¹⁴ three-body potential is applied to modify the pair potentials:

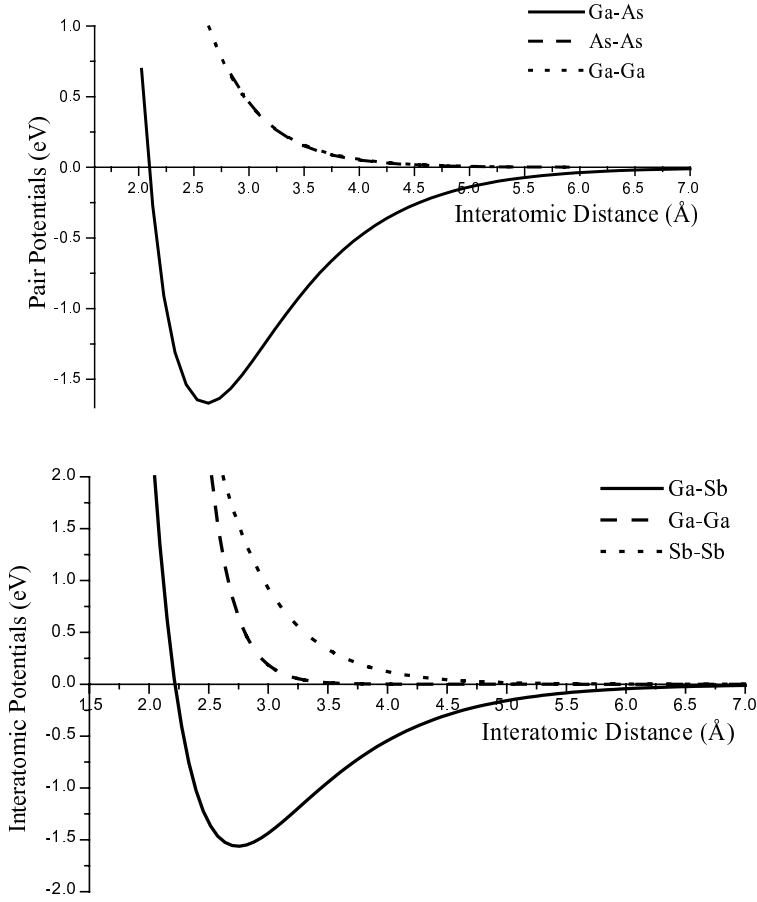


Fig. 2. The calculated interatomic pair potentials for GaAs and GaSb.

$$\Phi_3(r_{ij}, r_{ik}, \theta_{jik}) = \begin{cases} \lambda_i \exp \left[\frac{\gamma_i}{(r_{ij} - r_i^c)} + \frac{\gamma_i}{(r_{ik} - r_i^c)} \right] (\cos \theta_{jik} - \cos \theta_{jik}^c)^2, & r_{ij} < r_i^c \text{ and } r_{ik} < r_i^c, \\ 0, & \text{otherwise,} \end{cases} \quad (7)$$

where λ_i , r_i^c and θ_{jik}^c are constants and θ_{jik}^c is the angle subtended by r_{ij} and r_{ik} with the vertex at i . The function $\Phi_3(r_{ij}, r_{ik}, \theta_{jik})$ determines the three-body contribution to atom i that comes from the three atoms i , j and k , with i as the central atom and j and k as two of its covalently bonded neighbors, the value of r_i^c being within the nearest and next-nearest distance. The MSW three-body potential is applied widely to the surface, interface, defect, mechanical property and melting, etc.^{14,15} Define $\theta_{jik}^c = \arccos(-1/3)$. Obviously, the MSW three-body potential has no contribution to the cohesive energy either for model 1, model 2 or model 3. It operates only when the atom deviates from the lattice points or has the

Table 1. The MSW parameters for GaAs and GaSb.

	As–Ga–As	Ga–As–Ga	Sb–Ga–Sb	Sb–Ga–Sb
D_1 (eV)	1290.05	1276.19	1249.713	1247.103
γ_1 (Å)	2.728	2.728	3.0013	3.0013
R_{C1} (Å)	3.299	3.299	3.5254	3.5254

Table 2. The structure and mechanical properties of GaAs and GaSb.

	Experimental data ¹⁶		by <i>ab initio</i>		by potentials		
	GaAs	GaSb	GaAs	GaSb	GaAs	GaSb	
Lattice constant (Å)	5.653	6.096	5.646	5.983	5.646	5.982	
Cohesive energy (eV/atom)	—	—	4.290	3.906	4.309	3.905	
Bulk modulus (10^{11} N/m ²)	0.754	—	0.747	0.620	0.747	0.618	
Elastic constants (10^{11} N/m ²)	C_{11}	1.181	0.884	1.060	1.052	1.060	0.884
	C_{12}	0.532	0.403	0.501	—	0.590	0.486
	C_{44}	0.594	0.432	0.687	0.734	0.431	0.352

trend to deviate. So, the adoption of the MSW three-body potential can logically be self-consistent with previous pair potential calculation methods.

Based on the pair potential parameters, the contribution of the pair-potentials to the elastic constants is calculated. Furthermore, the component of the elastic constants contributed by three-body potentials $c_{ij,\text{three-body}} = c_{ij} - c_{ij,\text{pair}}$ is evaluated, in which c_{ij} is obtained from *ab initio* calculations except for c_{12} of GaSb. The latter is an experimental value because its *ab initio* calculation is not a suitable result. Then, the MSW three-body potential parameters are determined by fitting the $c_{ij,\text{three-body}}$. The results are listed in Table 1. The lattice constants, bulk modulus and the elastic constants of GaAs and GaSb are evaluated according to the calculated interatomic potentials. The results are listed in Table 2.

In the present work, based on the interatomic potentials without disposable parameters, the phonon dispersion curves of GaAs and GaSb are calculated using the Born–von Karman model (see Fig. 3). It is in good agreement with the neutron scattering experimental results.¹⁶ In our calculation, the absence of the Coulomb potential results in degeneration of phonon LO and TO at $q = 0$, while the experimental results show that the LO and TO have a little split. The deviation of the calculations from experiment will be eliminated when the effective charges are increased and the electrostatic interaction is summed with the Ewald method.¹⁷ However, the use of the adjustable effective charge will not preserve the characteristics of the interatomic potentials obtained from *ab initio* calculations without any disposable parameters in this work.

The interatomic potentials are a powerful tool to investigate the structure and the mechanical properties. Figure 4 is one of the applications of these interatomic potentials. It represents the atom arrangement when there exists a Ga vacancy

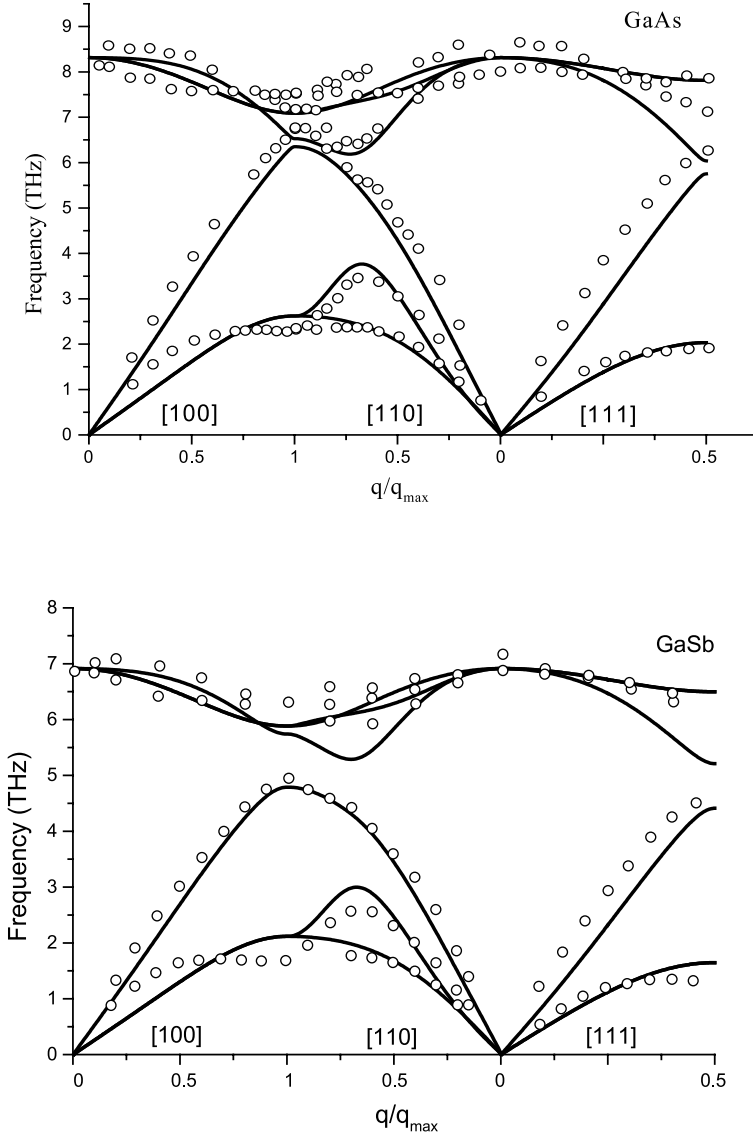


Fig. 3. The calculated phonon dispersion curves of GaAs and GaSb (circles represent the experimental data in Ref. 16).

in a $4 \times 4 \times 4$ GaSb supercell. The structure and elastic parameters change to $a_0 = 23.89464 \text{ \AA}$, $c_{11} = 0.872 \times 10^{11} \text{ N/m}^2$, $c_{12} = 0.492 \times 10^{11} \text{ N/m}^2$ and $c_{44} = 0.348 \times 10^{11} \text{ N/m}^2$, respectively.

We do not intend to provide detailed analyses of the structure, the mechanical properties or lattice dynamics for GaAs and GaSb, but test the potentials obtained with the method in this paper. This proposes an approach to evaluate more accu-

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