

Ionicity and the Structural Stability of Solids

James R. Chelikowsky

Corporate Research Science Laboratories, Exxon Research and Engineering Company, Annandale, New Jersey 08801

and

Jeremy K. Burdett

Department of Chemistry, University of Chicago, Chicago, Illinois 60637

(Received 5 December 1985)

The dielectric theory of Phillips and Van Vechten defines crystalline ionicity in terms of optical properties and predicts first-order structural phase transitions. Their approach, while very successful, is, nonetheless, empirical and has yet to be justified via an *ab initio* quantum mechanical approach. We present such an approach for examining the relationship between spectroscopic crystal ionicity and spatial structure. We demonstrate that the structural predictions based on ionicity scales derived from the dielectric theory are consistent with a microscopic point of view.

PACS numbers: 71.45.Nt, 61.50.Lt

The microscopic dielectric theory of Phillips and Van Vechten¹ provides a basis for understanding the structural trends, elastic properties, energy bands, optical properties, and thermochemistry of semiconductors. Perhaps the greatest success of their theory is in its application to the classification of crystal structure. For example, if one considers the octet *AB* crystal family, where *A* and *B* are simple metals or metalloids and the bonds are fully saturated, two main types of structures exist: fourfold coordinated and sixfold coordinated. The bonding forces which dictate which structure is more stable for a given chemical composition involve very fine energy distinctions, often less than kT and certainly beyond the accuracy of traditional computational tools. For these latter reasons, it was presumed for many years to be impossible for any theory to predict the relationship between the nature of the chemical bond and crystal structure stability. However, with the dielectric theory it became possible to establish a criterion based on an ionicity scale which divided the fourfold and sixfold structures.

While the prediction of a critical ionicity is well established from an empirical point of view, the realization of an *ab initio* quantum mechanical justification has yet to be achieved. Several microscopic calculations have attempted to describe the structural transition of fourfold to sixfold structures with increasing ionicity, but these calculations have been limited in scope and have concerned themselves with a particular material, or with a microscopic index not directly related to ionicity or total crystalline energies.² The difficulty involved with such calculations resides with the lack of a theoretical framework which can describe the structural properties of crystals as a function of such parameters as charge transfer, atomic size, and nonlocality of the crystalline potential. For example, consider a simple question such as what will be the influence

of a weakening of the cation potential and a strengthening of the anion potential. To obtain accurate trends, a series of calculations would have to be performed which involve a self-consistent calculation for each structure, as a function of both volume and proposed crystalline potential. Until recently such calculations were beyond the scope of state-of-the-art *ab initio* methods. In this paper we indicate a method which will allow us to alter in a systematic fashion the total crystalline potential and examine the factors involved in determining structural stability without invoking empirical, or parametrized, solution techniques for the single-particle Schrödinger equation.

Our study starts with a prototypical zinc-blende structure and determines the effects of an altering of the strength of the anion and cation potentials. As a first test of the dielectric theory we propose to model the effect of "charge transfer" and determine whether our microscopic calculations are consistent with the Phillips-Van Vechten predictions. Our study incorporates recent total-energy methods³ and examines several crystal-structure types to determine the relative structural properties of each. For our reference crystal we chose GaAs as previous structural work has been done on this species. The structures that we will examine include the zinc-blende, β -Sn, and rocksalt structures. These three types of structures encompass essentially all the experimentally accessible types for the *AB* crystal family; qualitatively they are thought to represent covalent, metallic, and ionic bonding configurations, respectively. The details of our total-energy method have been published elsewhere.³ The essential ingredients of this method include *ab initio* pseudopotentials⁴ and a Gaussian basis. The basis here was taken to be structurally independent and consisted of thirty Gaussian orbitals per atom. The starting potential was constructed from a superposition of atomic

charge densities. Self-consistency was incorporated by inclusion of on-site corrections.⁵

Once we have arrived at a self-consistent solution for a given structure, we alter the volume and repeat the process. We then fit several energy-versus-volume points with an equation of state of the form⁶

$$E(V) = B_0 V \frac{B'_0 (1 - V_0/V) + (V_0/V)^{B'_0} - 1}{B'_0 (B'_0 - 1)} + E_0, \quad (1)$$

where B_0 is the equilibrium bulk modulus, V_0 is the equilibrium volume, V is the volume, E_0 is the equilibrium total energy, and B'_0 is the derivative of the bulk modulus with pressure at equilibrium. We do this for each structural type. The results are shown in Fig. 1 for GaAs in the three structures of interest and are in good agreement with the work of Froyen and Cohen.⁷

Given an accurate reference system, we are in a position to alter the ionic potentials of the cation and anion, and examine the detailed effect of charge transfer. To modify the potentials, we added a simple Gaussian correction: a repulsive one on the cation and an attractive one on the anion. The well depths of the Gaussians were chosen to be equal but opposite in sign and the well sizes were constrained to be roughly the size of ion cores. This selection alters the ionic components such that the average core potential remains unchanged. Moreover, we now have only one parameter to vary and determine its role on the structural properties of AB crystals. We proceeded by altering the ionic potential and then determining the equation of state for each structure. The computational component of this study requires approximately eighty independent total-energy calculations; i.e., we have three structures, we examined six different ionic-potential configurations, and ran four or more volume points for each potential and structure.

To organize our data base, we categorized our results by examining the charge configuration for a reference structure. We chose the zinc-blende structure and did a population analysis⁵ to determine what type of material our ionic potentials represented. For example, if the altered potential resulted in a population analysis with two electrons around the cation and six around the anion, we labeled this potential as replicating a II-VI material. The choice of this categorization scheme in principle is not unique as the charge assignments are not unique. For example, if we were to change the basis, we would alter the assignments. To obtain physically meaningful results, we have used a chemically realistic basis which reproduces the known band structures of these crystals and we have not altered this basis from one crystal structure to another. Thus, we expect the *relative* charge assignments to be

correct. To test this assumption, we have used a very restricted basis of only eight s and p orbitals per atom and reproduced the results of our extended basis of thirty orbitals per atom. We note that a similar treatment based on a Mulliken population analysis has been used with good success for surface studies.⁵ In addition, we have examined the dependency of our

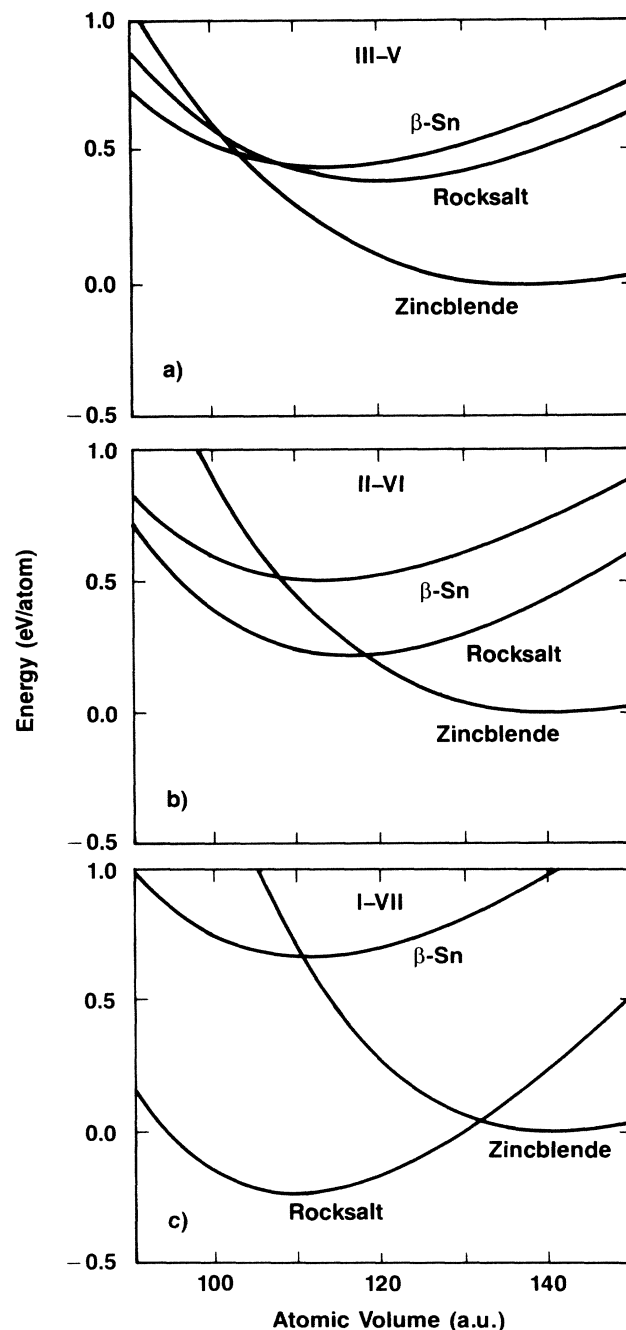


FIG. 1. (a) Equation of state for GaAs in the β -Sn, rock-salt, and zinc-blende structures. (b) Equation-of-state curves for a prototypical II-VI compound. (c) Equation-of-state curves for a prototypical I-VII compound.

charge-density analysis on which structure we used as a reference. For example, if we consider the charge population for the rocksalt structure as a reference instead of the zinc-blende structure, the results are not significantly altered. We find as we change the potential that the charge densities scale in similar fashion independent of structure. If the charge assignments yield a specific charge transfer relative to the zinc-blende structure, the rocksalt-referenced charge transfer would be the same to within 0.1 electron. This accuracy in terms of an ionicity scale would be on the order of an error of 5%, at worst, as discussed below.

Using the above definition for characterizing our potential modifications, we can determine the equation of state for representative II-VI and I-VII materials. In Fig. 1, we illustrate the equation of state for each configuration. The chief qualitative result is that with increasingly ionic materials, i.e., from III-V to I-VII, the β -Sn structure moves up in energy and the rocksalt structure moves down in energy relative to the zinc-blende structure. Another distinctive feature is that the lattice constant of the zinc-blende structure hardly changes from the III-V to the I-VII configuration, in good agreement with the lattice constants in the horizontal sequence Ge-GaAs-ZnSe-CuBr.

Given that we can determine accurate ground-state properties, we can derive a global picture of crystal stability as a function of a particular attribute of the crystalline potential. For example, here we examine the modification of the structural energies by varying the relative cation to anion potential strengths. We could have chosen another attribute such as size or nonlocality, i.e., we could have made an individual l component of the potential weaker or stronger and followed the effect of this modification on structural stability. However, within the Phillips-Van Vechten work, the strongest parameter is that of "charge

transfer." To determine the phase stability of a given structure, we consider the free energy:

$$G(p) = B_0 V_0 [(1 + pB'_0/B_0)^\gamma + 1] + E_0, \quad (2)$$

where $\gamma = (B'_0 - 1)/B'_0$ and p is pressure. By considering a sequence of different ionic potentials, we can determine $G(p)$ for prototypical III-V, II-VI, and I-VII materials, and Fig. 2 is the result of such a calculation. Previous structural characterizations⁸ have concentrated on empirical indices; however, this overview in Fig. 2 is based on indices which have a direct microscopic interpretation.

The fields in Fig. 2 are compatible with the known structural behavior of the AB compounds.^{1,9} For example, the more covalent species are predicted to transform to β -Sn under pressure and the more ionic II-VI species transform to rocksalt. Moreover, we are able to predict generic trends in that our diagram predicts that a zinc-blende to β -Sn to rocksalt transformation cannot occur. We do predict that a zinc-blende to rocksalt to β -Sn transition can occur. We note that the possibility of other structures intervening is a real one and we present only the result for these archetypal structures.

Finally, we note that it is possible to construct an ionicity scale by employing our calculated population analyses. In analogy to the work of Coulson, Redei, and Stocker,¹⁰ we can write the ionicity of a crystal as

$$f_i(\delta Q) = (4 - N_c)/4 + \alpha \delta Q, \quad (3)$$

where N_c is the number of valence electrons on the cation, δQ is the charge transfer relative to neutral atoms accompanying the formation of the solid state, and α is a parameter. Our purpose in writing this ionicity definition is twofold. First, we can establish a mapping from the Phillips scale to our definition in (3). This will allow us to place real materials on our phase diagram. Second, we can estimate for our calculated ionicity the critical value which separates the fourfold and sixfold structures.

With respect to the first point, we fix α so that Phillips's f_i for GaAs and our value for GaAs are identical.¹¹ With this prescription and our calculated values of δQ we can determine a correspondence between the Phillips scale and our ionicity definition. We have indicated in Fig. 3 some II-VI materials and the pressure of transition from the zinc-blende (or wurtzite) structure to the rocksalt structure as a function of our ionicity. We do not expect detailed agreement with the observed transition as our potentials do not include the effects of orbital sizes, or changes in the "covalent" bonding components. Nonetheless, we obtain semiquantitative agreement with experiment. Specifically, we find MgS and MgSe to fall on the transition boundary of zinc blende and rocksalt and we are able to predict the differences between the Zn

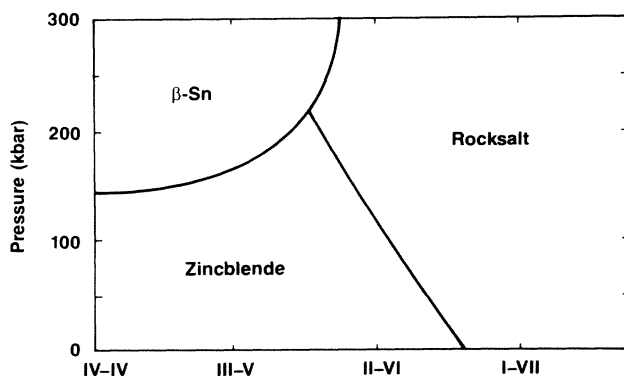


FIG. 2. Phase diagram for prototypical crystal-structure types. The diagram is categorized by material and by pressure. Orbital or size effects are not included. The reference structure is GaAs.

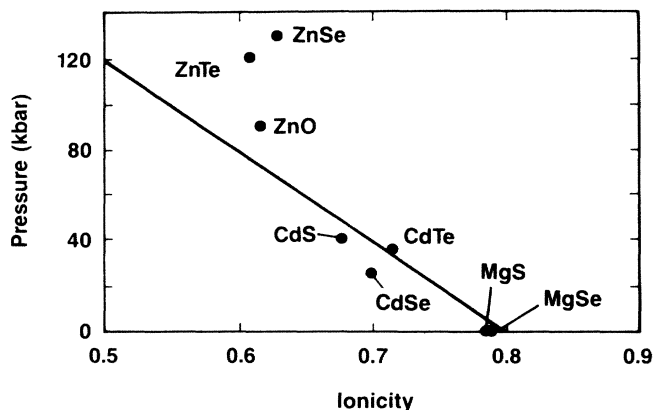


FIG. 3. Transition pressure for transformations from fourfold-coordinated structures to sixfold-coordinated structures. The ionicity scale is defined by Eq. (3). The experimental data are from Ref. 9.

and Cd salts. This somewhat surprising accuracy is consistent with the ideas that one can characterize trends of these materials with the "charge transfer" parameter as in the Phillips-Van Vechten theory.

With respect to our second point, we find that our predicted critical ionicity is consistent with the Phillips value. We find from our discussion above that $f_i^c = 0.80$ whereas the Phillips value is $f_i^c = 0.795$. Although we have not attempted to define the value for a wide range of starting lattices and potentials, we have considered a variety of potentials and varied the size of the cation and anion wells. We find our critical value to be fairly insensitive to the details of these variations, or to variations in the basis. Moreover, the fact that we find the crossover near the more ionic II-VI's puts our results in agreement with experiment and is independent of the details of a particular scale.

In summary, we note that our general approach will allow us to examine global trends in a wide variety of crystal structures. We may systematically alter a number of pertinent attributes in the crystalline poten-

tial such as depth, size, and angular dependence and investigate the effect of such alterations on the crystalline stability in a microscopic fashion.

¹J. C. Phillips, *Bonds and Bands in Semiconductors* (Academic, New York, 1973).

²See, for example, *Structure and Bonding in Complex Crystals*, edited by M. O'Keeffe and A. Navrotsky (Academic, New York, 1981); J. P. Walter and M. L. Cohen, Phys. Rev. Lett. **26**, 17 (1971); W. D. Grobman, D. E. Eastman, and M. L. Cohen, Phys. Lett. **43A**, 49 (1973); C. Varea de Alvarez and M. L. Cohen, Phys. Rev. B **8**, 1603 (1973).

³J. R. Chelikowsky and S. G. Louie, Phys. Rev. B **29**, 3470 (1984); J. R. Chelikowsky, S. G. Louie, D. Vanderbilt, and C. T. Chan, Int. J. Quantum Chem. **18**, 105 (1984).

⁴D. R. Hamann, M. Schluter, and C. Chiang, Phys. Rev. Lett. **43**, 1494 (1979).

⁵D. Vanderbilt and S. G. Louie, Phys. Rev. B **30**, 6118 (1984). The population analysis in this paper is based on the work of R. S. Mulliken, J. Chem. Phys. **23**, 1833 (1955).

⁶F. D. Murnaghan, Proc. Natl. Acad. Sci. U.S.A. **3**, 244 (1944).

⁷S. Froyen and M. L. Cohen, Solid State Commun. **43**, 447 (1982).

⁸See, Ref. 2 and J. R. Chelikowsky and J. C. Phillips, Phys. Rev. B **17**, 2453 (1978), and references therein.

⁹C. W. F. T. Pistorius, Prog. Solid State Chem. **11**, 1 (1976); A. L. Ruoff and M. A. Baublitz, Jr., in *Physics of Solids under High Pressure*, edited by J. S. Schilling and R. N. Shelton (North-Holland, New York, 1981), p. 81; C. J. M. Rooymans, Phys. Lett. **4**, 186 (1963); A. N. Mariano and E. P. Warekoi, Science **142**, 672 (1963); N. B. Owen, P. L. Smith, J. E. Martin, and A. J. Wright, J. Phys. Chem. Solids **24**, 1519 (1963).

¹⁰C. A. Coulson, L. B. Redei, and D. Stocker, Proc. Roy. Soc. London **270**, 352 (1962); J. C. Phillips, Rev. Mod. Phys. **42**, 317 (1970).

¹¹We find $\delta Q = 0.12$ for GaAs relative to the neutral atoms. With Phillips's value of $f_i(\text{GaAs}) = 0.31$, we find that $\alpha = 0.5$.