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Crystal Stability and Structural Transition Pressures of *sp*-Bonded Solids

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It is shown that the structural phase transformations and relative stabilities among cubic phases of *sp*-bonded nonmetals can be successfully predicted within a simple, universal tight-binding model by a total-energy–minimization procedure. The model elucidates the physical mechanisms determining the chemical trends and predicts semiquantitatively the stable crystal structures, bond lengths, bulk moduli, and transition pressures of structural phase transformations. The theory explains the puzzling strong cation and weak anion dependence of the observed structural transition pressures.

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It is widely believed that a prediction of the relative stability of two crystal structures, which usually differ by an energy of the order of 0.1 eV, requires an extremely accurate theory, such as the state-of-the-art density-functional calculations.[1] On the other hand, several empirical models have uncovered clear chemical trends in the structural stabilities of solids and suggest that the key for predicting relative structural energies of nonmetals is not absolute accuracy but a theory which carefully incorporates the chemical trends in the atomic characteristics.[2,3]

First-principles calculations have reached a stage where they permit the calculation of the cohesive properties of a variety of solids with often a high degree of accuracy.[1] However, these techniques do not easily provide insight into the dominant physical mechanisms and do not provide a conceptual framework for the understanding of chemical trends in the structural properties of crystals. Conversely, the phenomenological models[3-5] are often applicable only to a restricted class of materials and are interpretative rather than predictive.[6] In view of this situation, there is currently much interest in providing a link between accurate *ab initio* calculations and a physical understanding of the stability of phases.[7]

In this Letter we present a simple yet realistic and universal semiempirical tight-binding model which predicts the chemical trends in the static and dynamic structural properties of a wide range of nonmetals. We present results for *sp*-bonded *AB* compounds in the cesium-chloride, rocksalt, and zinc-blende phases. The model is based on a microscopic total-energy–minimization procedure and requires only properties of the isolated atoms as empirical input. The method does not discriminate between "ionic" or "covalent" solids but treats both on an equal footing. Formally, this approach follows closely the *ab initio* methods by expressing the total energy in terms of electronic Hamiltonian matrix elements. The crucial simplification is that these solid-state matrix elements are determined approximately by scaling arguments and by incorporation of the chemical trends in the atomic energies rather than explicit calculation of these matrix elements.[8]

We write the total energy as a sum of occupied band energies, minus the (doubly counted) electron-electron interaction and plus the core-core interaction. The electronic band energies are calculated in a minimal tight-binding basis. The off-diagonal elements $t_{ll'm}$ are taken to be nonzero only for nearest and second-nearest neighbors and are assumed to follow Harrison's[8] universal d^{-2} scaling, $t_{ll'm}=\eta_{ll'm}\hbar^2/md^2$, where d denotes the distance between two atoms in the crystal and l,l' and m denote the appropriate angular-momentum quantum numbers. The five universal constants $\eta_{ss\sigma}, \eta_{pp\sigma}, \eta_{pp\pi}, \eta_{sapc\sigma}, \eta_{scpa\sigma}$, which couple the neighboring s and p anion (a) and cation (c) states are from the work of Vogl, Hjalmarson, and Dow.[9] In addition, two nonzero constants of type $\eta_{ss\sigma}, \eta_{pp\sigma}$ for next-nearest neighbors have been fitted to obtain adequate overall band structures for binary semiconductors and insulators. The details will be given in a forthcoming publication.[10]

The on-site Hamiltonian elements $\epsilon_{\lambda,i}$ differ from free atomic orbital energies by charge-transfer effects and nonorthogonality corrections,[11,12] which we take into account as follows:

$$\epsilon_{\lambda,i}=w_{\lambda,i}-(U_i-U_M)(Z_i-Q_i)$$
$$-\tfrac{1}{2}(SH_{\rm el}+SH_{\rm el})_{\lambda,i;\lambda,i}. \qquad (1)$$

Here, $w_{\lambda,i}$ are the λ-symmetric orbital energies of the free, neutral atoms of type i, and U_i is an average intra-atomic Coulomb repulsion matrix element. These atomic quantities have been tabulated in Ref. 11. U_M is the electrostatic energy of an electron in orbital λ,i due to the cores of charge Z_j and the valence electrons in the crystal at all sites j different from i. This energy can be approximated by the Madelung energy.[11,13] The electron occupancies Q_i are calculated self-consistently with the Bloch eigenstates of the one-electron Hamiltonian. The overlap matrix ele-

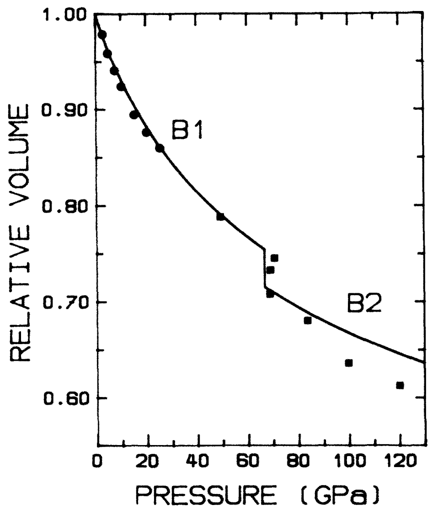

FIG. 1. Calculated equation of state for CaO. Experimental data are from Ref. 16 (dots) and from Ref. 17 (squares).

ments S_{AB} between atoms A and B are assumed to have a d^{-3} dependence and to be proportional to the electron-transfer matrix elements η_{AB} and inversely proportional to the average atomic orbital energies $(w_A+w_B)/2$, with a universal numerical constant K depending only on the row of the elements A and B in the periodic table.[14] These five universal constants K were fitted to obtain overall agreement between the experimental and theoretical bulk moduli of semiconductors and insulators.[10] The electron-electron interaction in the total energy is split into an intra-atomic and interatomic term and is calculated consistently with Eq. (1) in the Hartree approximation. It contains a term proportional to U_l and another term proportional to U_M, which incorporates the core-core interaction.

The cohesive energy is given by the difference between the energy of the neutral atoms and the total crystal energy per unit cell. By minimizing the total crystal energy E_{tot} as a function of volume, we can calculate the equations of state and—by equating the zero-temperature Gibbs energies of two phases—the relative stability of phases and phase transition pressures.[15] Once the universal constants η and K have been determined, the only empirical inputs required for any given solid are the tabulated[11] atomic orbital energies w_s, w_p, and the intra-atomic Coulomb repulsion U. We would like to emphasize that these three atomic energies per constituent atom completely characterize a compound in the present approach. This is in accord with and elucidates the success of the empirical concepts of electronegativity and atomic size.[2-5]

The model's ability to predict realistic cohesive properties such as the equilibrium volume, the bulk modulus, its derivative with pressure, the relative stability of crystal structures, and transition pressures and volumes is exemplified in Fig. 1. The predicted relative stability of the cubic phases of CaO is shown in Fig. 2. In Fig. 3 we show the predicted and the experimental transition pressures for several II-VI compounds. These compounds lie on the borderline between "covalent" and "ionic" solids and are thus

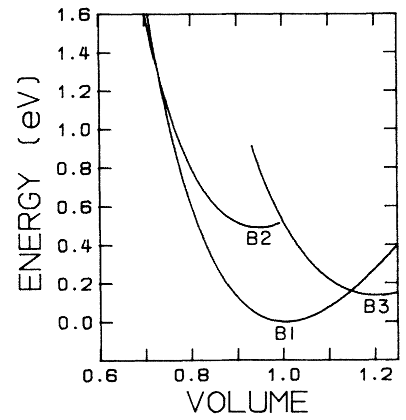

FIG. 2. Calculated total energy per unit cell as a function of volume for the rocksalt ($B1$), the cesium-chloride ($B2$), and the zinc-blende ($B3$) phases of CaO.

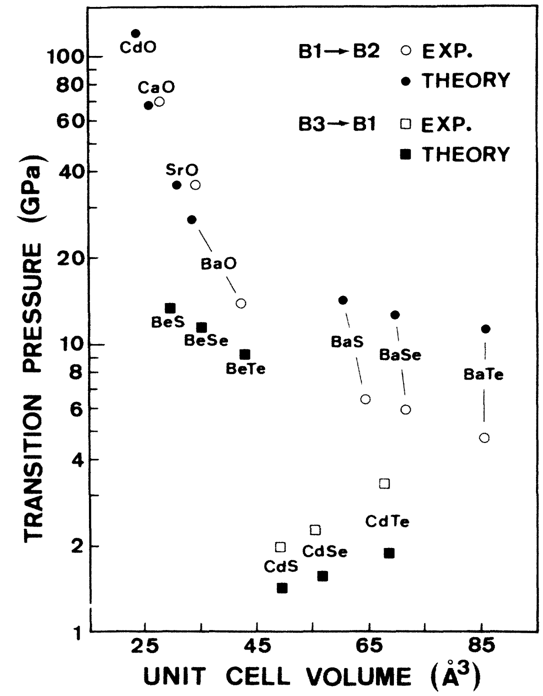

FIG. 3. Predicted transition pressures for the indicated structural phase transitions vs the calculated equilibrium volume at zero pressure. The experimental data for volumes are from Ref. 18; the experimental data for the transition pressure from the rocksalt ($B1$) to the cesium-chloride ($B2$) phase are given in Ref. 19; the data for the zinc-blende ($B3$) to rocksalt ($B1$) transitions are from Ref. 20.

often described from diametrically opposed perspectives by phenomenological models. Our model is also able to reproduce the major chemical trends in the cohesive energies, although absolute energies are less accurately predicted than relative structural energies. A few examples, in electronvolts, of theoretical cohesive energies are (experimental results[21] given in parenthesis) CaO 20.7 (11.6), SrO 18.8 (10.4), CaS 11.1 (9.7), SrS 10.4 (9.3), CaSe 9.3 (7.8); NaCl 9.54 (6.8), NaBr 8.14 (6.1), NaI 6.70 (5.2). We have applied the present model to the static and dynamic cohesive and structural properties of more than 60 binary compounds and find generally good agreement between theory and experiment, as will be shown in a forthcoming paper.[10] Particularly, we find the chemical trends in our results to be insensitive to the parameters in the electron Hamiltonian, as long as they are chosen consistently and in accord with the trends in the atomic data.

In order to obtain a physically transparent interpretation of the results it is useful to split the cohesive energy $E_{\rm coh}$ into three individual terms which have trends following one's intuition (even though such a breakup is not unique, of course).

(i) The covalent energy is the sum over the occupied band energies, with the on-site contribution subtracted. It vanishes if all electron-transfer matrix elements $t_{ll',m}$ are zero. It is therefore a measure for the tendency of the ions in the crystal to form bonds. It represents an effectively attractive energy contribution to $E_{\rm tot}$ and becomes increasingly attractive with decreasing difference in the atomic orbital energies of anion and cation. The covalent energy scales approximately as d^{-2}.

(ii) The overlap energy contains the terms in $E_{\rm coh}$ proportional to the orthogonalization correction in Eq. (1) and can be predominantly ascribed to the increase of the kinetic energy of the electrons upon compression of the solid. It is a strongly repulsive contribution to $E_{\rm tot}$ and the calculations show that it scales approximately as d^{-5}.

(iii) The remaining terms in $E_{\rm coh}$ depend weakly on d and represent the charge-transfer energy which is proportional to the Madelung energy and a second term which takes into account the different populations of the orbitals in the solid compared to neutral atoms.

In contrast to the classical point-charge type models, we find the chemical trends in the structural properties of *all* II-VI compounds to be governed by a competition between the short-range covalent and the overlap interaction because these terms depend most strongly on the interatomic distance d. The long-range electrostatic interaction, on the other hand, depends only weakly on d, and therefore plays only a minor role. This implies that any trends in a given compound as a function of the crystal structure will be governed by the space filling ratio $r = d/\Omega^{1/3}$, where d is the nearest-neighbor distance and Ω the unit-cell volume. This ratio is given by 0.86, 0.79, 0.68 for the cesium-chloride, the rocksalt, and the zinc-blende structures, respectively. Any trends in a series of different compounds in the same structure, on the other hand, depend decisively on the difference in the atomic orbital energies of the constituent atoms. (One may use the difference $w_{s,\rm cation} - w_{p,\rm anion}$ for heteropolar compounds, for example.)

The equilibrium volume V_0 is mainly determined by that term in the total energy which depends most strongly on volume, and this is the overlap energy. For given unit-cell volume, this energy is proportional to r^{-5} and therefore becomes more repulsive in the order cesium-chloride $(B2) \rightarrow$ rocksalt $(B1) \rightarrow$ zinc-blende $(B3)$. Correspondingly, it shifts the equilibrium volumes to larger values in this order, i.e., $V_0^{B2} < V_0^{B1} < V_0^{B3}$. This theory therefore predicts a *universal* sequence of structural phase transitions among the cubic phases of a given compound. As a function of pressure, structural phase transformations can occur only in the sequence zinc-blende → rocksalt → cesium-chloride but not in the reverse order. We note that this result is independent of the relative energies of these phases at their equilibrium volumes. If, for example, the rocksalt phase has the lowest equilibrium energy, such a crystal can only transform to the cesium-chloride but not to the zinc-blende phase as a function of pressure. To our knowledge, no exception to this finding is known experimentally. We find the overlap energy to increase with atomic number in any series of compounds where one type of atom is fixed and the other species varies within a given column of the periodic table (e.g., CaO, SrO, BaO). Therefore, the equilibrium volumes are predicted to increase in any such series of compounds, irrespective of the crystal structure. This is also in agreement with the experimental data.

Importantly, the present model is able to explain the puzzling strong cation and weak anion dependence of the observed structural transition pressures in II-VI and I-VII compounds.[22] We shall specifically consider the transition from the $B1$ to the $B2$ phase. For a qualitative discussion, we can approximate the transition pressure by

$$P_t = [E_{\rm tot}^{B2}(V_0^{B2}) - E_{\rm tot}^{B1}(V_0^{B1})]/(V_0^{B1} - V_0^{B2}), \qquad (2)$$

where the transition volumes have been replaced by the corresponding equilibrium volumes.[5] The trends in P_t therefore arise from two factors: (i) the equilibrium unit-cell volumes in the denominator of Eq. (2), and (ii) the difference in total energies of the $B1$ and $B2$ phases in the numerator of Eq. (2). Since V_0 is controlled by the overlap energy, one has

$V_0^{B1} \propto V_0^{B2}$. Therefore, the denominator in Eq. (2) causes P_t to decrease with increasing equilibrium volume and, subsequently, with increasing atomic number.

In order to understand the chemical trends in the numerator of Eq. (2) we consider a crystal with a given unit-cell volume in the $B1$ and $B2$ phases. Since the overlap energy is repulsive and proportional to r^{-5} it always favors energetically the cesium-chloride phase. (It therefore dominates the total energy at small volumes; see Fig. 2.) Since the covalent energy, on the other hand, is attractive and proportional to $-r^{-2}$, it is more attractive in the rocksalt phase than in the cesium-chloride phase. Let us now consider a series of compounds with increasing equilibrium volume. If $w_{s,\mathrm{cation}} - w_{p,\mathrm{anion}}$ decreases in this series, the covalent energy becomes relatively more attractive in the rocksalt phase than in the cesium-chloride phase. As a consequence, the numerator in Eq. (2) increases in this series.

Consider now oxides in the series of increasing atomic number, e.g., CaO, SrO, BaO. The difference in cation-*s* and oxygen-*p* orbital energy increases in this series.[8] Therefore, both the denominator and the numerator in Eq. (2) cooperate and give a strong reduction in P_t in this series of compounds. On the other hand, in any series of chalcogenides, e.g., BaO, BaS, BaSe, BaTe, the Ba-*s* and anion-*p* energy difference decreases and the numerator and denominator in Eq. (2) counteract. This explains the empirically observed weak anion-related dependence in P_t.

In summary, we have developed a realistic tight-binding model which provides a semiquantitative *and* conceptual framework for an understanding of the chemical trends in the structural properties of a wide range of solids. The model predicts a universal sequence of the three cubic phases for nonmetallic binary compounds as a function of pressure. It also explains the strong cation and weak anion dependence of phase transition pressures. We have shown that the trends in all major structural properties of semiconductors as well as ionic solids result from a competition between short-range bonding and overlap interactions, whereas long-range electrostatic forces play only a perturbative role.

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