

Covalent-Ionic and Covalent-Metallic Transitions of Tetrahedrally Coordinated $A^N B^{8-N}$ Crystals Under Pressure

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A microscopic analysis of the differences in Gibbs free energy between covalent, ionic, and metallic forms of $A^N B^{8-N}$ compounds is described. The analysis explains the success of the spectroscopic theory of chemical bonds in predicting the covalent-ionic transition at zero pressure as a function of A and B . It also suggests that bond charge may play the role of a microscopic order parameter which determines the magnitude of the differences in energy between ionic and covalent structures at zero pressure and temperature.

Quantitative theories of phase transitions in dense systems have been developed chiefly for second-order transitions where an order parameter can be defined.¹ The microscopic problem of first-order transitions away from the critical point has generally been regarded as an insoluble one because of the discontinuous change in interaction energies which accompanies a large volume change ΔV . However, in the homologous family of $A^N B^{8-N}$ crystals the first-order phase transition at zero pressure obtained by varying A and B chemically can be explained quantitatively in terms of variations in spectroscopic ionicity.² The spectroscopic chemical theory is an approximate one because it neglects most of the interaction energies associated with the atomic cores, but it still appears to be accurate to about 1%. Under pressure, on the other hand, core interaction energies are expected to increase in importance with decreasing atomic volume. In this Letter it is shown that although this is indeed the case, the spectroscopic model can still be used to identify the valence forces which play a critical role in pressure-induced covalent-ionic transitions. My description includes a generic phase diagram which indicates the relations between covalent, ionic, and metallic forms of these compounds.

The experimental data upon which the analysis is based are summarized in Table I. In some cases the crystal structure of the high-pressure phase or phases has been determined by x-ray diffraction *in situ* but for many cases (especially at pressures above 50 kbar) the structure must be inferred. Broadly speaking, three situations arise, depending on the ionicity f_i of the A - B bond (see Fig. 1): (a) For $0 \leq f_i \leq 0.3$, the low-pressure phase is usually tetrahedral, and the crystal transforms to a white Sn or orthorhombic structure under pressure. For $f_i = 0$ (diamond-type elemental crystals) the pressure and Gibbs

free-energy difference of the covalent-metallic transition decrease with increasing atomic number, so that at STP Sn can be found in either form, while Pb is metallic at STP. This trend is called metallization, and it has already been analyzed quantitatively in connection with our theory of heats of formation.³ (b) For $0.3 \lesssim f_i \leq 0.785$, the low-pressure phase is still tetrahedrally coordinated, but under pressure the crystal first transforms to the NaCl structure at a relatively low pressure and then at a higher pressure transforms to a metallic structure (probably orthorhombic). At least for the $N=1$ and $N=2$ compounds I believe that the intermediate NaCl phase is intrinsically an insulating one; i.e., there is a minimum energy gap ΔE_{cv} between the conduction and valence bands which is greater than zero. This is definitely known to be the case only for CdS,^{4,5} but the apparently semimetallic character⁵ of the remaining compounds in the NaCl form may be associated with a high density of native defects. (All the $N=2$ compounds, with the exception of CdTe, are known to be self-compensating.⁹) It would be interesting to examine this question with pseudopotential band calculations, especially in the light of the discussion of core effects given below. (c) For $f_i > 0.785$, the low-pressure phase usually has the NaCl structure, and it presumably transforms to a metallic structure at high pressure. This transition has been studied less extensively and it will not be discussed here.

The differences ΔG in Gibbs free energy at STP between the various structures can be estimated quite accurately if the volume discontinuity ΔV_t and the transition pressure P_t are known. (The differences in compressibility between structures contribute less than 10% of ΔG , and neither ΔV_t nor P_t are known to better than this accuracy in most cases.) In cases where ΔV_t has been measured, the ratio $\Delta V_t/V_t$, where V_t

TABLE I. Thermodynamic parameters for covalent-metallic and covalent-ionic transitions. In cases where $\Delta V_t/V_t$ is not known experimentally, the average values quoted in the text have been used, and V_t has been computed from second- and third-order elastic constants.

Substance	New Phase	P_t (kbar)	ΔV_t (cm ³ /mole)	$P_t \Delta V_t$ (eV/atom pair)	$\frac{\Delta V_t}{V_t}$	$\frac{\Delta H_a}{\text{atom pair}}$ (eV/atom pair)	$\frac{\Delta G_t}{\Delta H_a}$	f_1
Sn	Met	0	2.15 ^a	0.006	0.21 ^a	6.30	0.001	0.00
Ge	Met	105 ^b	2.85 ^a	0.56	0.21 ^a	7.82	0.072	0.00
Si	Met	150 ^b	2.73 ^a	0.84	0.23 ^a	9.13	0.092	0.00
InSb	Met	22 ^b	7.6 ^a	0.18	0.19 ^a	5.56	0.032	0.32
GaAs	---	180 ^b	5.5 ^a	1.0	----	6.73	0.149	0.31
GaSb	Met	70 ^b	5.2 ^a	0.38	0.17 ^a	6.04	0.063	0.26
AlSb	Met	110 ^b	5.0 ^a	0.52	0.16 ^a	6.95	0.075	0.25
InAs	Met	85 ^b	5.8 ^a	0.47	0.19 ^a	6.26	0.075	0.36
InP	NaCl	110 ^b	5.5 ^a	0.58	0.20 ^a	6.73	0.086	0.42
CdTe	NaCl	28 ^b	6.3 ^g	0.17	0.17 ^g	4.18	0.041	0.72
CdSe	NaCl	32 ^b	5.6 ^h	0.18	0.18 ^h	4.82	0.037	0.70
CdS	NaCl	25 ^b	5.9 ^h	0.14	0.21 ^h	5.78	0.024	0.69
ZnTe	NaCl	110 ^b	---	0.55	----	4.61	0.120	0.61
ZnS	NaCl	180 ^b	---	0.57	----	6.50	0.105	0.62
ZnSe	NaCl	125 ^b	4.7 ^d	0.56	0.17 ^d	5.18	0.108	0.63
MgS	NaCl	0	4.6 ^f	0.00	0.18 ^f	8.08	0.000	0.78
MgSe	NaCl	0	5.7 ^f	0.00	0.19 ^f	7.08	0.000	0.79
AgI	NaCl	3.5 ^c	7.3 ^c	0.02	0.18 ^c	4.68	0.004	0.77
CuBr	NaCl	43 ^d	---	0.19	----	5.78	0.033	0.73
ZnO	NaCl	95 ^e	6.0 ^e	0.54	0.18 ^e	6.70	0.081	0.65

^aRef. 3.

^bRefs. 4-7.

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is the volume of the low-pressure phase at the transition pressure, has been found to be (20 ± 3)% for the covalent-metallic transition, (19 ± 2)% for the covalent-ionic one, and <3% for the ionic-metallic one. The constancy of these values is noteworthy, and in itself it provides justification for constructing a microscopic model of the type described here. Values of $\Delta V_t/V_t$ are also listed in Table I where available.

There is also uncertainty in the choice of the values of P_t . For the covalent-metallic transition, which might proceed by means of a macroscopic shear, Jamieson has argued³ that the measured values of P_t may *underestimate* the thermodynamic values because of experimental deviations from purely hydrostatic pressure. Drickamer, on the other hand, has compared⁶ powder values of P_t with single-crystal values, and has concluded that metastability may lead to experi-

mental *overestimates* of P_t for covalent-ionic transitions. The values of P_t quoted in Table I

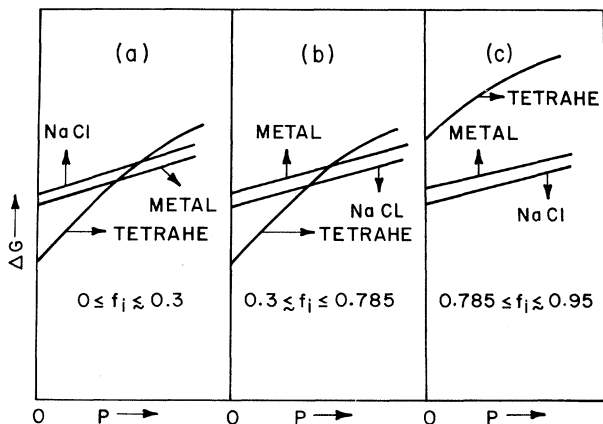


FIG. 1. A sketch of the Gibbs free energies of $A^N B^{8-N}$ compounds as a function of pressure, in three domains of ionicity $f_i(AB)$.

reflect these two comments, as well as the recent recalibration⁷ of P_i .

When the crystal structures of the $A^N B^{8-N}$ compounds are plotted in the (E_h, C) plane, it is found² that they separate exactly into two domains, separated by the line $f_i = 0.785$. Here E_h and C are the spectroscopically defined covalent and ionic contributions to the average energy gap $E_g^2 = E_h^2 + C^2$ and $f_i = C^2/E_g^2$. No gap is found between the two domains, so that this thermodynamically first-order phase transition appears to be microscopically continuous. Therefore, we seek a dimensionless reduction of $\Delta G_i = P_i \Delta V_i$ which will facilitate comparison of different compounds with f_i below but near 0.785. The most natural approach is to normalize relative to ΔG_a , the Gibbs free energy of sublimation (atomization) of these compounds at STP. In some cases ΔH_a (the enthalpy of sublimation at STP) is quoted in the thermodynamic tables⁸ but not ΔG_a . The two quantities are nearly the same in most cases, and to avoid introducing unnecessary ambiguities, I have normalized ΔG_i by ΔH_a in Table I and plotted these reduced values for f_i near 0.785 in Fig. 2.

In Fig. 2 the values of $\Delta G_i/\Delta H_a$ are fitted by linear and parabolic functions proportional to x and to x^2 , respectively, where $x = 0.785 - f_i$. The linear fit appears to be slightly superior to the quadratic one, except for the case of CdS. (Samples of the latter have been found to exhibit different phase diagrams depending on the origin of the sample. See references of Table I.)

It is interesting to compare these results with those based on the ratio ρ_A/ρ_B , where ρ_A and ρ_B are the "atomic radii" of the cation A and the anion B in the $A^N B^{8-N}$ compound. In the rigid-ion model the phase change from sixfold to fourfold coordination is explained as arising from the disparity of ρ_A and ρ_B . Small values of ρ_A/ρ_B lead to anion-anion contact in the NaCl structure, which is supposed to cause a phase change to a tetrahedral structure, the critical value being $\rho_A/\rho_B = 0.33$. Calculations based on the Born-Mayer model of ionic crystals have shown that "the predictions of the rigid-ion model, however, have little quantitative value."¹⁰ These calculations approach the first-order phase transition by extrapolation from the ionic side ($f_i \sim 0.9$, as in the alkali halides). When the same phase transition is approached from the covalent side the failure of the radius ratio rule becomes even more dramatic because Pauling's *covalent* radii make $\rho_A/\rho_B > 0.6$ in all cases. According to the radius ratio rule, this would make all covalent

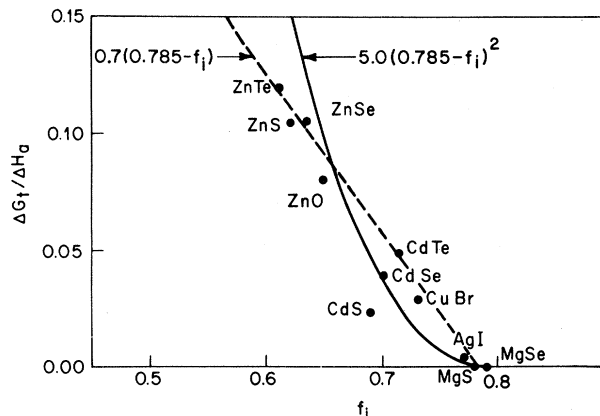


FIG. 2. The reduced free-energy difference $\Delta G_i/\Delta H_a$ as a function of $f_i(AB)$ for f_i near but below the critical value 0.785.

crystals have the rocksalt structure, which is absurd. Equally absurd results are obtained when ionic radii are used, as then the diamond structure can only be explained by assuming that the C atoms on one sublattice are in 4^+ states, while those on the other sublattice are in 4^- states.

By contrast to these results, the analysis given in Fig. 2 shows that $\Delta G_i/\Delta H_a$ goes to zero smoothly as a function of x , a quantity which depends primarily on $y = Z_A/r_A - Z_B/r_B$. The only part of the story that is missing is the value of $\Delta G_i/\Delta H_a$ for $f_i > 0.785$. This is not measurable by pressure experiments because we cannot apply a negative pressure to cause a transition from the more dense NaCl structure to the less dense tetrahedral structure. However, the energy difference ΔG_i can also be measured directly by extrapolating activity-composition data in alloy systems. This has been done¹¹ for ZnO in the rocksalt hosts CoO and NiO, and the results for ΔG_i obtained agree with those quoted in Table I to within 10%, after allowance for recalibration⁹ of P_i . Activity-composition measurements of MgO in ZnO, and AgBr and AgI in CuBr and CuI, respectively, should yield ΔG for $f_i > 0.785$, thus completing the description of the phase transition shown in Fig. 2.

We have seen that the natural parameter which governs the covalent-ionic transition is $x = 0.785 - f_i$. Walter and Cohen¹² have recently identified the valence bond charge Z_b , whose structural importance had previously been emphasized.¹³ They have found that $Z_b \propto x$, which suggests that the microscopic force which drives the transition is electrostatic. Because of the limitations inherent in any quantum-mechanical study, their plot

of Z_b against f_i does not establish conclusively that $Z_b=0$ for (metastable) tetrahedrally coordinated compounds with $f_i > 0.785$. The activity-composition measurements suggested here may provide further information on this basic question.

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Strain Fields and the Apparent Size of Donor Ions in GaP

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We report the first experimental determination of the microscopic strain fields surrounding substitutional impurities in a crystal. We have used pair spectra in GaP to reveal the splitting of Zn or C acceptor levels in the strain fields generated by O, S, Se, or Te donor ions. The anisotropic splitting, which agrees with a simple effective-mass theory, is the same for all four donors. We conclude that effects associated with the size of these impurities are distributed over a volume of the crystal extending more than 20 Å from the impurity.

Point imperfections in crystals generate local strain fields which can modify the properties of degenerate electronic states bound to them.¹ The experiment described in this Letter enables us not only to determine the magnitudes of the fields but also to measure their dependence on distance and direction from their sources. The method, which uses a careful analysis of the donor-acceptor pair lines from GaP which are split by these internal fields, generates a map of the strain field surrounding a donor through its effect on the energy levels of the nearby acceptors.

Sharp-line donor-acceptor pair spectra² provide a convenient indicator of interactions between donor and acceptor impurities at varying separations R . The major interaction term, the Coulomb energy of the bare ions, $e^2/\epsilon_0 R$, disperses the spectrum so that lines corresponding to different separations are resolved and can be identified and classified according to the interion separation vector \vec{R} . Once the pair lines have been classified by this gross structure, their properties can be correlated with the now known values of \vec{R} .³

We consider a donor ion which, because of its

intrinsic "size" relative to the atom it replaces or because of its (Coulomb) interaction with its neighbors, displaces its nearest neighbors from their normal radius R_0 by δR .⁴ This generates a strain field approximately equal to that produced in a homogeneous solid by a displacement (by δR) of a spherical shell of initial radius R_0 . It may be described by the displacement vector $\vec{u}(\vec{r})$ at a point \vec{r} measured from the donor site,⁵

$$\vec{u}(\vec{r}) = (A/r^3)\vec{r}, \quad (1)$$

where $A = R_0^2 \delta R$. In a cubic crystal the strain field may be anisotropic⁶—a complication which we discuss below. We seek the interaction of such a field with a hole bound to a nearby acceptor. In a cubic crystal this interaction depends upon two deformation-potential constants D_u and D_u' as expressed in the Kleiner and Roth Hamiltonian.⁷ The constants are those appropriate for the acceptor state and are in general different from those of the band edge.^{1,8} For holes in the strain field of Eq. (1) this Hamiltonian may be written [see Eqs. (2)–(4) of Ref. 1]

$$H_s(\vec{r}) = (2A/r^3)[D_u q(\vec{r}) + D_u' Q(\vec{r})], \quad (2)$$

where the operators $q(\vec{r})$ and $Q(\vec{r})$ reflect the