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Ionicity and phase transitions at negative pressures

A. Navrotsky*
Department of Chemistry, Arizona State University, Tempe, Arizona 85281

J. C. Phillips
Bell Laboratories, Murray Hill, New Jersey 07974

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The Gibbs-free-energy difference ΔG_t which determines the phase transition from fourfold to sixfold coordination in A^NB^{8-N} compounds is presented for three compounds (CdO, MgO, and AgBr) which are stable at STP in the more-dense (NaCl) structure. The additional data follow a linear trend in spectroscopic ionicity predicted previously from high-pressure data on compounds stable in fourfold coordinated structures. These data resolve ambiguities concerning the proper definition of ionic character in partially covalent compounds with the NaCl structure.

A chemical description of the first-order transition from tetrahedral to octahedral coordination of A^NB^{8-N} compounds under pressure has been given[1] based on the spectroscopic theory of ionicity.[2] Because of the presence of the term $P_t\Delta V_t$ in the Gibbs free energy the transitions associated with $P_t > 0$ go from the less dense tetrahedral phases to the more dense octahedral (NaCl) phase. Thus the chemical trends in measured transition pressures P_t and transition changes in volume ΔV_t test the spectroscopic definition of ionicity for compounds which are tetrahedrally coordinated in the ground state. In this paper measurements of activity-composition data in the alloy systems (Mg, Zn)O and (Cd, Zn)O are reported from which the free-energy difference $\Delta G_t = G_t^{(\text{octa})} - G_t^{(\text{tetra})}$ can be estimated when $\Delta G_t < 0$; thus the data correspond to measurements of the phase transition for $P_t < 0$. Previously published data for Ag(Br, I) are also analyzed to yield values of $\Delta G_t < 0$ for AgBr in addition to MgO and CdO.

Although the $N = 2$ compounds MgO and CdO and the $N = 1$ compound AgBr have the NaCl structure, their physical properties are quite different from those of alkali halides. The pressure derivative of the electronic dielectric constant, $d\epsilon_0/dP$, is negative for MgO and for all the tetrahedrally coordinated A^NB^{8-N} compounds, whereas it is positive for all the alkali halides, as predicted by the Clausius-Mossotti model.[3] Crystals of CdO generally contain ~ 10^{18} cm^{-3} interstitial Cd.[4] A variety of chemical trends in physical properties suggest[3] that, in addition to the crystallographic covalent-ionic transition at ionicity $f_i = F_i = 0.78-0.79$, an electronic "open-shell"–"closed-shell" transition takes place near $f_i = 0.85$. Thus octahedral CdO, MgO, and AgBr, which lie in the interval $0.78 < f_i < 0.85$, are still partially covalent open-shell compounds and should be describable in terms of the spectroscopic ionicity f_i, which is successful for the tetrahedrally coordinated compounds.

Navrotsky and Kenny[5] determined activity-composition relations at 1205 °C in the system ZnO-MgO. The experiments involved determining subsolidus phase relations in the system ZnO-MgO-Al_2O_3. In this system the (Zn, Mg)O terminal solid solutions of wurtzite and rocksalt structure coexist with a continuous $(Zn_xMg_{1-x})Al_2O_4$ spinel phase which was known to be very nearly an ideal solution.[5] Thus, from the positions of tie lines (compositions of coexisting spinel and rocksalt or coexisting spinel and wurtzite phases), the activity-composition relations along the ZnO-MgO join could be calculated.[5] The free energy of the transformation of MgO to the ZnO structure can be estimated from the limiting activity coefficient of MgO in the wurtzite phase as its mole fraction approaches zero; $\Delta G_t = RT\ln\gamma^0 = 9.6 \pm 1.0$ kcal/mol.[5]

Preliminary experiments on ZnO-CdO solid solutions[6] suggest a free-energy change of 2 ± 0.5 kcal/mol for the transformation CdO (rocksalt) → CdO (wurtzite).

Phase relations in the system AgBr-AgI were reported by Stasiv and Teltow.[7] Below 146 °C, AgI has the zinc-blende structure. At 100 °C the solubility of AgBr in AgI is ~ 9 mol% and that of AgI in AgBr is ~ 55 mol%. Assuming that Henry's law holds over the entire composition range of each solid solution [that is, γ_{AgI} (in AgBr) and γ_{AgBr} (in AgI) are constant] we estimate that for AgBr (rocksalt → zinc blende) $\Delta G^0 = RT\ln(0.45/0.09) = 1.2$ kcal/mol, while for AgI (zinc blende → rocksalt), $\Delta G^0 = RT\ln(0.91/0.55) = 0.37$ kcal/mol. The latter value is in good agreement with that calculated from the high-pressure transition in AgI ($\Delta G_t = 0.46$ kcal/mol).

Values of $\Delta G_t/\Delta H_a$ for MgO, CdO, and AgBr were calculated using vaporization data[8] and these transition energies, normalized by the heat of vaporization ΔH_a, are shown in Fig. 1.

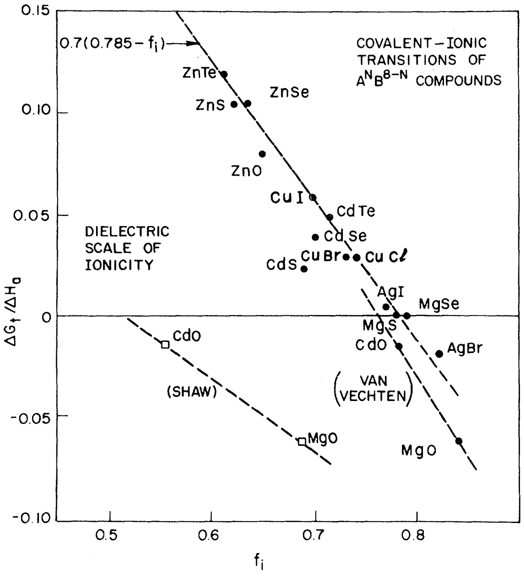

FIG. 1. Transition energies ΔG_t, normalized by the heats of vaporization, from covalent fourfold coordinated structures to ionic sixfold coordinated structures for $A^N B^{8-N}$ compounds. Data for $\Delta G_t > 0$ are summarized in Ref. 1, whereas data for $\Delta G_t < 0$ are presented in the text. The partial ionic character f_i for fourfold coordinated structures is defined spectroscopically (Ref. 2). for sixfold coordinated structures two definitions have been proposed, by Van Vechten (Ref. 3) and Shaw (Ref. 9). For the oxides Van Vechten's definition gives rise to a small and not unexpected discontinuity ($\Delta f_i \approx 0.02$) at $\Delta G_t = 0$, but the AgBr data fall on the extrapolation of the line for $\Delta G_t > 0$ to $\Delta G_t < 0$. Shaw's definition yields a large discontinuity, as indicated in the figure for the oxides only.

Van Vechten has defined[3] $f_i^{(\text{octa})}$ by assuming that the covalent contribution E_h to the average energy gap E_g scales with bond length in the same way in both tetrahedral and octahedral structures. With this definition the tetrahedrally and octahedrally coordinated phases are separated on the ionicity scale, those with $f_i < F_i$ being tetrahedral and those with $f_i > F_i$ octahedral. From Fig. 1 we see that this separation is a quantitative one with nearly the same value for $d(\Delta G_t/\Delta H_a)/df_i$ in both phases and a (possible) discontinuity $\Delta f_i = 0.02$ at the phase transition for oxides. This discontinuity is very small compared to the volume discontinuity $\Delta V_t/V_t \approx 0.2$ of the transition.[1]

A different scaling procedure, based on atomic volume rather than bond length, was proposed by Shaw.[9] With Shaw's choice the (nonobservable) and much more widely scattered dispersive energies proposed by Wemple and DiDomenico[10] become approximately continuous through the phase transition, but, as Shaw notes, there is "a small range of ionicity overlap between covalent and ionic structures, a situation which in many ways has stronger physical appeal than the sharp separation obtained with Van Vechten's definition." Actually, the "small range" corresponds to $\Delta f_i = 0.2$; i.e., it is approximately the same as the volume discontinuity. Near the transition Shaw, in effect, replaces Van Vechten's $f_i^{(\text{octa})}$ by $f_i'^{(\text{octa})}$, where

$$f_i'^{(\text{octa}, S)} = 2 f_i^{(\text{octa}, V)} - 1 . \qquad (1)$$

When the CdO and MgO data points are added to Fig. 1 using Shaw's f_i' from Eq. (1), the discontinuity in the basic observable ΔG_t becomes physically unappealing. In metals many phase transitions preserve atomic volume, but from this discussion it appears that in partially covalent semiconductors and insulators bond lengths are a better scaling parameter. We also see that the particular moments of the optical spectrum used by Phillips and Van Vechten (PVV) to construct E_h and E_g are more satisfactory from a *thermodynamic* viewpoint than the moments used[10] to define dispersion energies. Indeed, the results shown in Fig. 1 provide strong evidence for preferring the moments used by PVV to others, so that the theory is far less arbitrary than has sometimes been supposed.[9]

The new data reported here confirm the linearity of $\Delta G_t/\Delta H_a$ as a function of f_i for $0.60 \leq f_i \leq 0.85$, which was suggested by the previous data.[1] A microscopic explanation for the previous trend has been offered by Walter and Cohen (WC)[11] in terms of the linear dependence of the bond charge Z_b on $F_i - f_i$. With WC's definition $Z_b \to 0$ as $f_i \to F_i$ from below, which does not explain the continuation of the linear trend for $f_i > F_i$. However, WC have suggested[12] that as an alternate interpretation of their calculated charge densities one may assume that the magnitude of Z_b stays nearly constant, while the center of gravity of the bond charge moves toward the anion, becoming coincident with the anion for $f_i = F_i$. To test this interpretation, pseudopotential calculations were performed for NaCl in a hypothetical sphalerite structure, with the interesting result that the bond charges were found to be centered on the antibonding (or back) sides of the O anions.[12] Thus this interpretation properly anticipated the experimental results reported here.

Crystal chemical theories of phase transitions of ionic crystals have traditionally emphasized the importance of bond lengths through a steric factor, namely, anion-anion contact, in giving rise to changes of coordination configuration in complex ionic crystals. Attempts to apply steric arguments to covalent-ionic transitions in simple $A^N B^{8-N}$ compounds produce absurd results.[1] However, the success of bond-length scaling argu-

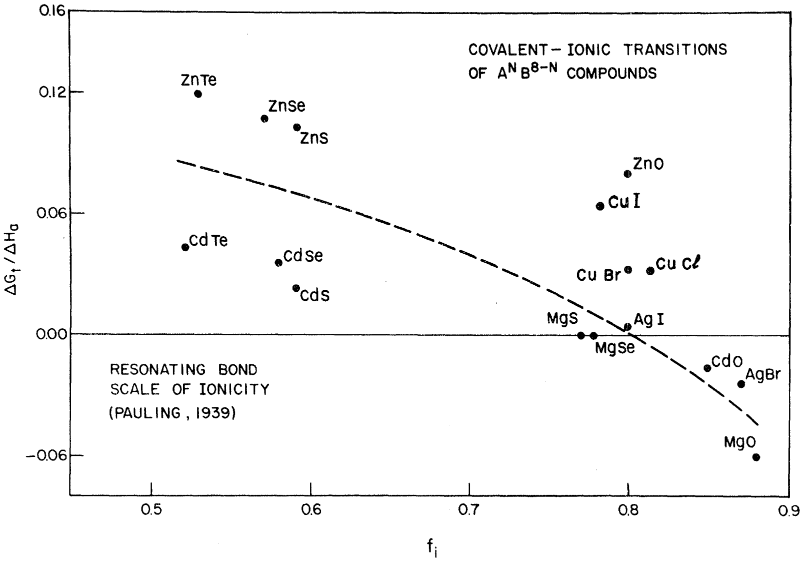

FIG. 2. Similar to Fig. 1, the normalized transition energies are plotted as a function of Pauling's resonating bond ionicity. The scatter is much larger, but the general trend is apparently similar to that shown in Fig. 1.

ments combined with the spectroscopic scale of ionicity f_i in describing ΔG_t makes it worthwhile to plot ΔG_t against Pauling's closely related[2] resonating bond scale f_i'. This is shown in Fig. 2. The same general trends are evident, but the scatter is much greater, which emphasizes the difference between the two ionicity scales. There are a number of differences between the definitions of f_i and f_i', but one of the most interesting ones is that the dielectric electronegativity difference used in calculating f_i specifically includes only s-p contributions, whereas Pauling's electronegativity includes valence d as well as s and p contributions. St. John and Bloch have shown[13] that the orbital dependence of the two electronegativity scales can be understood from free-ion-term values. One can conclude that the tetrahedral-octahedral transformation in $A^N B^{8-N}$ compounds primarily involves changes in s-p hybridization (from sp^3 to p^3) and that d orbital admixture effects are small. Conversely, the success of the Mooser-Pearson plots in describing phase transitions in intermetallic compounds[14] using Pauling's electronegativity shows that d-electron effects are necessary in structures where coordination numbers are large and metallic binding predominates.

Note added in proof. The high-pressure phases of the cuprous halides have been discussed recently by V. Meisalo and M. Kalliomäki, High Temp.-High Press. 5, 663 (1973). Many transitions are observed, especially for CuI. However, the transition pressures at room temperature for the transitions with large volume discontinuities are about 50 kbar for CuCl and CuBr, and about 90 kbar for CuI. The respective values for f_i are 0.74, 0.74, and 0.69, so that when CuCl and CuI are added to Fig. 1, along with CuBr they fall very close to the over-all straight line. On Pauling's scale the respective values are $f_i' = 0.82$, 0.80, and 0.78, which again provides much less satisfactory agreement (Fig. 2); it predicts equal differences between CuCl, CuBr, and CuI, whereas the former two are very similar while ΔG_t (CuI) $\approx 2\,\Delta G_t$ (CuCl or CuBr).

The Mn chalcogenides form in the zinc-blende structure. From the data on solid solutions of MnSe and CdSe (A. G. Sigai and H. Wiedemeier, J. Chem. Therm. 983 (1974)) by using activity-composition relations[5] one can obtain ΔG_t (MnSe) ≈ -1 kcal/mole and ΔG_t (CdSe) ≈ 4 kcal/mole, in good agreement with high-pressure data for CdSe.[1] Thus MnSe (and probably MnS) lie between MgS and MgSe, and CdO (see Fig. 1).

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*Alfred P. Sloan Fellow.

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