PHYSICAL REVIEW B VOLUME 24, NUMBER 6 15 SEPTEMBER 1981

Effect of Frenkel defects on the high-pressure phase transitions in PbF_2 and $SrCl_2$

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(Received 9 September 1980; revised manuscript received 23 February 1981)

Significant curvature has been observed in a plot of transition temperature against transition pressure for the high-pressure cubic-orthorhombic phase transition in both PbF_2 and $SrCl_2$ at high temperatures. In the present paper it is shown that the presence of a high equilibrium concentration of Frenkel defects in one phase but not the other phase involved in the transition can provide an explanation for this curvature. A comment is also made on the applicability of the work to AgI and $RbAg_4I_5$.

I. INTRODUCTION

In recent years the behavior of the cubic ($C1$)-orthorhombic ($C23$) transition temperature as a function of pressure has been elucidated in PbF_2,[1-3] and more recently[2,4] in $SrCl_2$. The recent high-temperature results for these materials[2-4] exhibit significant curvature in a plot of transition temperature against transition pressure. Klement and Cohen[4] suggest that this curvature is due to the presence of an additional transition in the cubic phases of these materials and we will see that this is basically correct, though a thermodynamic phase transition is not required. The observed change in dT_c/dP_c can be explained by the presence of a high concentration of Frenkel defects in one of the two phases involved in the first-order transition.

If we follow through the derivation of the Clausius-Clapeyron equation, we find

$$\frac{dT_c}{dP_c}=\frac{\left[\dfrac{\partial G_d}{\partial P}\right]_T-\left[\dfrac{\partial G_o}{\partial P}\right]_T}{\left[\dfrac{\partial G_o}{\partial T}\right]_P-\left[\dfrac{\partial G_d}{\partial T}\right]_P}\ , \tag{1}$$

where G_d and G_o are the Gibbs free energies of the disordered and relatively ordered phases involved in the transition. Normally, the Gibbs energy is just written as $E+PV-TS$ and the right-hand side of Eq. (1) becomes $(V_d-V_o)/(S_d-S_o)$. Alternatively, we can use the form of the Gibbs free energy that is normally used to describe defects in solids

$$G_d=G_d^p+x_d\Delta G_d^f-kT\ln W\ . \tag{2}$$

The term $k\ln W_d$ is the configurational entropy due to the presence of Frenkel defects and is given by[5,6,7]

$$\ln W=-(1-x_d)\ln(1-x_d)-2x_d\ln x_d -(m-x_d)\ln(m-x_d)+m\ln m\ , \tag{3}$$

with x_d the concentration of defects in the disordered phase and m the number of interstitial sites per anion, which is normally taken to be $\frac{1}{2}$, although some data indicate[8,9] it may be 1 or $\frac{3}{2}$. With this form for the free energy we can explicitly display the effects of Frenkel defects on the phase-transition trajectory

$$\frac{dT_c}{dP_c}=\frac{V_d^p-V_o^p+x_d\Delta V_d^f-x_o\Delta V_o^f}{S_d^p-S_o^p+x_d\Delta S_d^f-x_o\Delta S_o^f+k\ln W_d-k\ln W_o}\ . \tag{4}$$

The Frenkel-defect-formation volumes and entropies are represented by the ΔV^f's and ΔS^f's, $\ln W$ is given by Eq. (3), and the V^p's and S^p's represent the inherent volumes and entropies of the two phases excluding contributions due to the defects. It is easy to see that Eq. (4) reduces to the conventional form of the Clausius-Clapeyron equation as x_d and x_o approach zero (low temperature). In going from Eq. (1) to Eq. (4) we have made the assumption that the various entropies and volumes do not change with temperature and pressure. It is possible to simplify Eq. (4) by dropping all terms linear in x_o. Experimental results indicate that this quantity is two to three orders of magnitude smaller than x_d (Ref. 2).

Some years ago it became evident that Eq. (2) was not adequate for handling high concentrations of defects,[7,10,11] so a term in x_d^2 was included to display the effects of defect interaction. More recently, it was noted that this may not be the correct dependence on x_d either,[12] and the actual form would be more like $x_d^{3/2}$. We will do the calculations with each of these forms for the free energy. It is easy to show that inclusion of these terms in Eq. (2) results in volume and entropy terms in Eq. (4) with similar dependences on x_d.

II. APPLICATION TO PbF_2 AND $SrCl_2$

In order to apply Eq. (4), or its modified forms, experimental values are needed for the various volumes and entropies. For the volume changes across the transition we use the values 2.9 (Ref. 13) and 6.1 cm^3/mole (Ref. 14) for PbF_2 and $SrCl_2$, respectively. These values represent the volume change at low temperature, i.e., excluding contributions from the Frenkel defects. The corresponding entropy changes are calculated from the experimental data[2–4] using the conventional version of the Clausius-Clapeyron equation. The average values of dT/dP from the data of Refs. 2–4 are 466 and 1790 K/GPa for PbF_2 and $SrCl_2$ at low temperatures. These values result in entropy differences between the phases of $0.75k$ and $0.41k$ for PbF_2 and $SrCl_2$. (The data of Klement and Cohen were given a bit more weight in determining the average dT/dP, because the experimental technique they used is normally more accurate.) The high-temperature values for dT/dP were taken to be 267 and 424 K/GPa for PbF_2 (Refs. 2 and 3) and $SrCl_2$.[4]

The Frenkel-defect-formation volumes determined from the conventional free energy are 5.5 and 6.0 cm^3/mole (Ref. 2) for PbF_2 and $SrCl_2$, respectively. The reported values for the formation entropy of Frenkel defects in fluorite-structured crystals vary widely,[15–19] so we will use several values.

The results of one calculation are shown in Fig. 1, where we have plotted dT/dP vs x for several values of the Frenkel-formation entropy for PbF_2. It was found that the form of the free energy was not terribly important as long as the same configurational entropy was used in each case. The curves in Fig. 1 were calculated using a term $-x_d^2\Delta G_d^i$ in Eq. (2), where $\Delta G_d^i = \Delta G_d^f/3$ represents the interaction free energy. The fact that the general shape of the curves in Fig. 1 does not depend strongly on the form chosen for the interaction term (i.e., $0, x^{3/2}, x^2$) means that this choice of magnitude for ΔG_d^i is unimportant for the present calculation. It is included because it is more nearly correct to do so. In Fig. 1 it is clear that the low-temperature dT/dP is correctly reproduced and the high-temperature value of 267 K/GPa for PbF_2 occurs at a defect concentration around 0.06—depending on the parameters and form of the free energy used. This is a very high defect concentration, but it is in reasonable agreement with values that can be inferred from other work.[8,9,12] Similar results were obtained for $SrCl_2$.

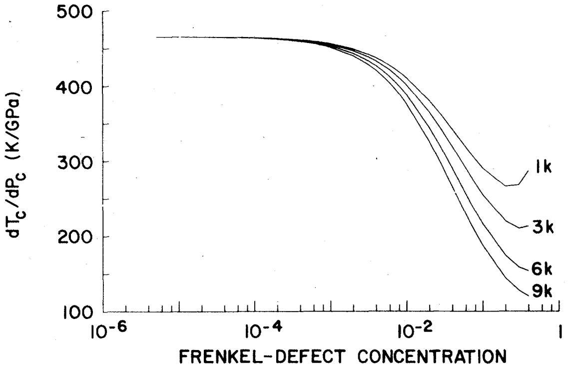

FIG. 1. Slope dT/dP calculated for the free energy similar to that used in Refs. 7, 10, and 11 as a function of x_d, the Frenkel-defect concentration for PbF_2. The curves are for the several values of the Frenkel-defect-formation entropy shown and $m = 1/2$.

The main conclusions are that the results do not depend strongly on the values of the formation entropy or on the form of the free-energy function (as long as the same configurational entropy and reasonable parameters are used). The results also did not strongly depend on m (the number of interstitial sites per anion) until $x_d \sim m$—as one might have expected. Stated another way, it appears that it is the configurational entropy which dominates the behavior of Eq. (4) at high equilibrium defect concentrations. This suggests that any modification of the form of Eq. (2) to more correctly describe high defect concentrations must include a modification of the configurational entropy. The simplest modification is to allow m to vary with defect concentration. One can imagine that repulsions by nearby interstitials would make some interstitial sites less likely to be occupied, thus one would expect that m will decrease as x increases. A simple thermodynamic model for a number of properties of crystals with the fluorite structure was recently published using this idea.[20]

It is evident that the presence of a high defect concentration can explain the observed behavior of the cubic-orthorhombic phase-transition trajectory in PbF_2 and $SrCl_2$. The concentration of defects required to produce the observed effects is quit high, but consistent with values reported elsewhere. It is also quite evident by examining Fig. 1 that such effects are quite unobservable unless the defect concentration is greater than 10^{-3}, i.e., a highly defective solid. Such a phenomenon can only occur when the transition is between a disordered phase and a relatively ordered phase, such as in a superionic material.

It is interesting to consider the behavior of first-order transitions in other superionic materials, such as AgI or $RbAg_4I_5$ (cf. Ref. 21 and references therein) in terms of the present discussion. As an example, one can imagine a material with a negative Frenkel formation volume large enough to dominate the numerator in Eq. (4); one can then expect that dT/dP will be negative. Other possibilities are also imaginable for various values of the parameters in one of the more complex forms for the free energy. In AgI the activation volume at temperatures just below the 420-K first-order transition is approximately -10 cm^3/mole and the activation volume at about 435 K is around 0.6 cm^3/mole. If we presume that the high-temperature phase is the disordered phase (relative to the low-temperature phase), then these values allow us to predict that the transition temperature increases as the pressure increases. However, in AgI the transition temperature decreases with increasing pressure. If we presume that the low-temperature phase is actually significantly more disordered than the high-temperature phase near the transition, then we have $\Delta V_d^f \sim -10$ cm^3/mole and $\Delta V_o^f \sim 0.6$ cm^3/mole. When these values are used, for example, in Eq. (4), then we could obtain the observed behavior of dT/dP. This would, of course, depend on the magnitudes of the inherent volume difference between the two phases and the relative values of x_d and x_o. In $RbAg_4I_5$ we have a rather different situation. The low-temperature activation volume (near the transition) is found to be around $+9$ cm^3/mole (Ref. 21), and the value found at temperatures just above the first-order transition is around -0.2 cm^3/mole. If, once again, we presume that the higher temperature phase is more disordered, then we could again obtain that the transition temperature decreases with pressure (depending on values of other parameters). The transition temperature is observed to increase with pressure, so either the inherent volume difference between the two phases dominates the contribution from the formation volumes, or the low-temperature phase is more disordered near the transition than the high-temperature phase. Both of these possibilities could be true at the same time as well. There is some evidence that the low-temperature phase in $RbAg_4I_5$ is disordered (cf. Ref. 21 and references therein). It is also possible that the approach taken in the present work is not applicable to either AgI or $RbAg_4I_5$, because the free-energy functions that have been used are not adequate to describe these materials.

ACKNOWLEDGMENT

I wish to thank W. Klement for some helpful discussions and for allowing me to see his results prior to publication.

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[1] G. A. Samara, J. Phys. Chem. Solids 40, 509 (1979).

[2] J. Oberschmidt and D. Lazarus, Phys. Rev. B 21, 2952 (1980).

[3] W. Klement and L. Cohen, J. Electrochem. Soc. 126, 1403 (1979).

[4] W. Klement and L. Cohen, Mater. Res. Bull. 15, 1079 (1980).

[5] N. N. Greenwood, *Ionic Crystals, Lattice Defects and Non-stoichiometry* (Chemical, New York, 1970).

[6] R. Fuller, *Point Defects in Solids,* edited by J. H. Crawford and L. Slifkin (Plenum, New York, 1972), Vol. I.

[7] B. A. Huberman, Phys. Rev. Lett. 32, 1000 (1974).

[8] S. M. Shapiro and F. Reidinger, in *Physics of Superionic Conductors; Topics in Current Physics,* edited by M. B. Salamon (Springer, Berlin, 1979).

[9] M. H. Dickens, W. Hayes, C. Smith, and M. T. Hutchings, in *Fast Ion Transport in Solids,* edited by P. Vashista, J. N. Mundy, and G. K. Shenoy (North-

Holland, New York, 1979).

[10] M. J. Rice, S. Strässler, and G. A. Toombs, Phys. Rev. Lett. 32, 596 (1974).

[11] D. O. Welch and G. J. Dienes, J. Phys. Chem. Solids 38, 311 (1977).

[12] C. R. A. Catlow, J. D. Comins, F. A. Germano, R. T. Harley, and W. Hayes, J. Phys. C 11, 3197 (1978).

[13] E.D.D. Schmidt and K. Vedam, J. Phys. Chem. Solids 27, 1563 (1966).

[14] L. H. Brixner, Mater. Res. Bull. 11, 1453 (1976).

[15] R. W. Bonne and J. Schoonman, J. Electrochem. Soc. 124, 28 (1977).

[16] A. B. Lidiard, AERE Harwell report T. P. 841 (unpublished) and references therein.

[17] M. Beniere, M. Chemla, and F. Beniere, J. Phys. Chem. Solids 40, 729 (1979).

[18] P. W. M. Jacobs and S. H. Ong, Cryst. Lattice Defects 80, 177 (1980).

[19] P. W. M. Jacobs and S. H. Ong, J. Phys. (Paris) 37, C7-331 (1978).

[20] J. Oberschmidt, Phys. Rev. B 23, 5038 (1981).

[21] P. C. Allan and D. Lazarus, Phys. Rev. B 17, 1913 (1978).