PHYSICAL REVIEW B VOLUME 45, NUMBER 15 15 APRIL 1992-I

Simple thermodynamic model for the specific heat of the fluorite crystals PbF_2, CaF_2, and $SrCl_2$

Yves Bouteiller
Laboratoire de Dynamique des Interactions Moléculaires, Université Pierre et Marie Curie, 4 place Jussieu,
75252 Paris CEDEX 05, France

(Received 22 January 1991; revised manuscript received 26 September 1991)

The excess specific heat for $SrCl_2$, PbF_2, and CaF_2 fluorite crystals has been computed by means of statistical mechanics using a model derived from the Welch and Dienes phenomenological model for phase transitions. The enthalpy is written in a form that partly takes the long-range interactions into consideration. It is shown that the transition temperature is always attained for low defect concentrations, as experimentally found by Schröter and Nöltig. The calculations are in quantitative agreement with available experimental data.

THEORETICAL MODEL

We are interested here in the excess specific heat which presents a diffuse transition for CaF_2, PbF_2, and $SrCl_2$ crystals. Experimental data are now available to specify these excess properties.[1–11] Theoretical calculations concern characteristic thermodynamic parameters.[12–19] The Oberschmidt[18] work is derived from the phenomenological Hubermann[20] or Welch and Dienes[21] model. In the work of Oberschmidt,[18] as well as in that of Makur and Ghosh,[19] there is a qualitative but no quantitative agreement between calculated and experimental data for excess specific heat C_p.

The purpose of the present work is to obtain a quantitative agreement between the calculation and available experimental data. In the phenomenological model of Welch and Dienes which is used, the excess enthalpy has been represented with an exponential dependence on the defect concentration. Preliminary results have been published[22] on specific heat for the $SrCl_2$ crystal. The variation of the excess Gibbs energy may be written $\Delta G=\Delta H-kT\ln W-T\Delta S$. The ΔH variation is assumed to be of the form

$$\Delta H=E_1 n_i e^{-\alpha n_i}\ , \tag{1}$$

where α is a parameter and n_i the defect concentration. By writing ΔH in the form (1) the exponential dependence with the defect concentration means that long-range interactions are roughly taken into consideration. The successive coefficients of the exponential expansion represent successive long-range interactions with three, four, and so on defects in interaction. The ΔS variation is written following Oberschmidt as

$$\Delta S=\Delta S_1 n_i-\Delta S_2 n_i^2\ , \tag{2}$$

where ΔS_1 and ΔS_2 are later written as $\Delta S_1/k=A$ and $\Delta S_2/k=B$. This form of ΔS has been chosen because it allows an easy self-consistent way of calculating ΔC_p. ΔS representing only a part of the total entropy, it is assumed that writing ΔS following (2) rather than with an exponential dependence will not give drastically different results. The $\ln W$ part of the configurational entropy is written[18]

$$\ln W=-2n_i\ln(n_i)-(m-n_i)\ln(m-n_i)-(\gamma-n_i)\ln(\gamma-n_i)+\gamma\ln(\gamma)+m\ln(m)\ .$$

In Ref. 18, m and γ are assumed to vary with the defect concentration. In the present work, m and γ are taken fixed at $m=1$ and $\gamma=0.5$.

At the thermodynamic equilibrium, the temperature is defined as

$$kT=E_1 e^{-\alpha n_i}(1-\alpha n_i)\times\{A-2Bn_i-\ln[(n_i^2)(m-n_i)^{-1}(\gamma-n_i)^{-1}]\}^{-1} \tag{3}$$

and ΔC_p is finally written as

$$kT^2\Delta C_p=C/D \tag{4}$$

with

$$C=E_1^2 e^{-2\alpha n_i}(1-\alpha n_i)^2\ ,$$

$$D=\alpha E_1(\alpha n_i-2)(kT)^{-1}e^{-\alpha n_i}+[2m\gamma-n_i(m+\gamma)][n_i(m-n_i)(\gamma-n_i)]^{-1}+2B\ .$$

This is the first model to carry out the specific heat, referred to as model I. If Eq. (1) is expanded in a Taylor series up to first order, at the thermodynamic equilibrium, the temperature is defined by

$$kT=(E_1-2n_iE_2)[\ln(1-n_i)(\alpha-n_i)n_i^{-2}+A-2n_iB] \tag{5}$$

and the ΔC_p expression stands as

$$kT^2\Delta C_p=C/D \tag{6}$$

with

TABLE I. Parameter values for models I and II.

	Model I					Model II				
	E_1	α	A	B	$n_i(T_c)$	E_1	α	A	B	$n_i(T_c)$
$SrCl_2$	1.9	1.67	17.2	32.37	7.8%					
	2.67	5.5	22.4	116.95	2.2%	2.67	5.5	23.98	154.33	3.6%
PbF_2	1.44	3.6	14.0	56.18	3.4%					
CaF_2	3.0	10.4	14.3	143.7	1.6%					

$$C=(E_1-2n_iE_2)^2 ,$$

$$D=\{[2\alpha-n_i(1+\alpha)]n_i^{-1}(1-n_i)^{-1}(\alpha-n_i)^{-1}+2B-2(kT)^{-1}E_2\} .$$

This second model to calculate the specific heat is referred to as model II. The following method has been used to calculate ΔC_p. E_1 is fixed while the parameters α, A, and B have to be determined. A trial value is chosen for α. In Eq. (4) [or (6)], B is a function of ΔC_p, T, and n_i. The B value is carried out for the $T=T_c$ value. For this T_c value, the corresponding ΔC_p value is fixed by the experimental data. In Eq. (3) [or (5)] A is a function of B which has been previously calculated, and of E_1, T_c, and n_i. The parameters A and B are calculated by varying n_i stepwise for a couple of α and E_1 values. Thus the A and B values are replaced in Eq. (3) [or (5)] which gives the T value and in Eq. (4) [or (6)] which provides the ΔC_p value. The n_i value gives again the maximum ΔC_p value for $T=T_c$. If this n_i value does not correctly reproduce the half-height width, the α value is changed and the calculation is repeated as far as the coincidence between experimental and calculated values is attained. The comparison with the experimental results is further made by deducing from the experimental ΔC_p value the part which is linear with the temperature.

APPLICATION TO $SrCl_2$, PbF_2, AND CaF_2 CRYSTALS

For all calculations, the n_i, A, and B values which have been determined using either model I or model II are reported in Table I.

The experimental data show for the $SrCl_2$ crystal[9] a peak for the specific heat located close to 1000 K, the half-height width being 65 K. In previously reported work,[18,19] the calculated corresponding value is 200 and 100 K, respectively. A first calculation is carried out with model I, using the Oberschmidt values, $E_1=1.9$ eV and $\alpha=1.67$. By looking at Table I, it is seen that n_i, A, and B values have closely related values with the corresponding Oberschmidt parameters.[18] All calculated and experimental ΔC_p values are reported in Fig. 1. The calculated half-height width is close to 200 K in agreement with the previously reported result[18] but far enough from the experimental data. The results prove that the variation of m and γ with the defect concentration is not a fundamental assumption for the $SrCl_2$ crystal. It will likely be the same for PbF_2 and CaF_2 crystals.

The formation enthalpy of defects in $SrCl_2$ is reported to be in the range 1.6–3.0 eV.[1,3,7,9,17] The higher values stand for diffusion and specific heat while values coming from conductivity are spread throughout this range. As the purpose of the present work is to represent the specific heat, the E_1 value has been fixed at the value of Schröter and Nöltig, i.e., $E_1=2.67$ eV. Using model I in a second calculation, the better agreement with the experimental data occurs for $\alpha=5.5$. The meaning of this large value for α is that long-range interactions make a large contribution to specific-heat data and that the main factor governing the half-height width is the parameter α. It is seen from Table I that n_i and A values are close to the values of Schröter and Nöltig. By looking at Fig. 1, it is seen that there is a quantitative agreement between the experimental data and the present calculation.

A third calculation of ΔC_p is made with model II using the values of E_1 and α determined above. It is shown in Table I that for the n_i value the better agreement stands for $n_i=3.6\%$, a higher value than in model I. By comparing the results of models I and II shown in Fig. 1, it is seen that without the long-range effects the curve is displaced on the left for all temperatures and that there is no quantitative agreement with experimental data.

The enthalpy variation has been calculated with model I using the parameters deduced from the first ΔC_p calculation. The experimental and calculated data[9] of enthalpy variation are reported in Fig. 2. It is seen that there is a close enough agreement with the experimental data. As

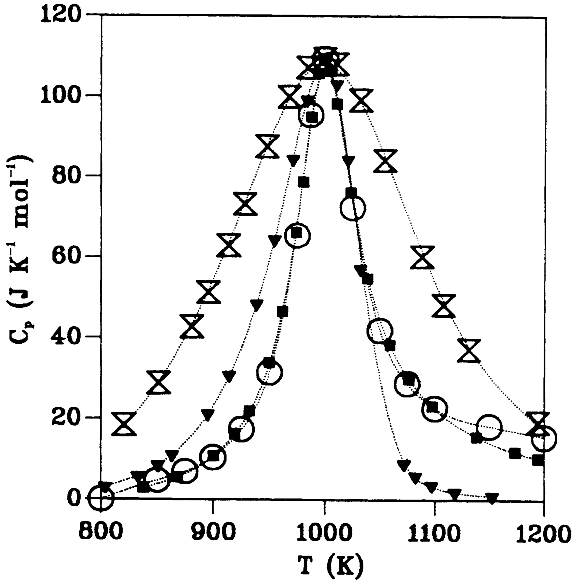

FIG. 1. $SrCl_2$ crystal: ○, experimental data; ◇, first calculation model I; ▼, second calculation model I; ■, third calculation model II.

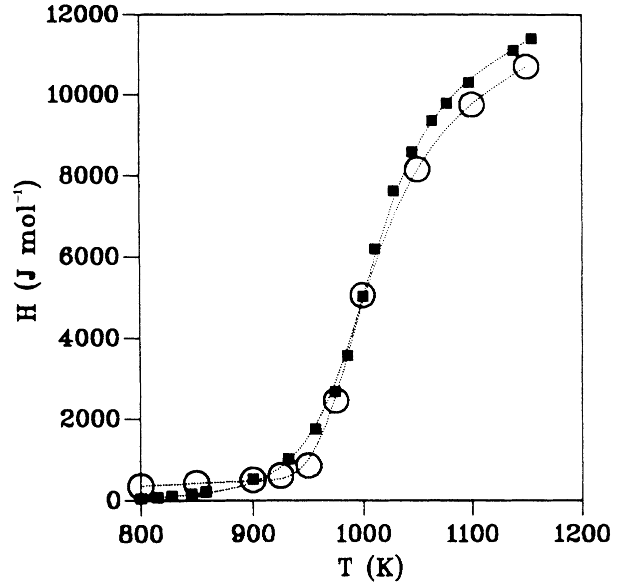

FIG. 2. $SrCl_2$ crystal: ○, experimental data; ■, calculation.

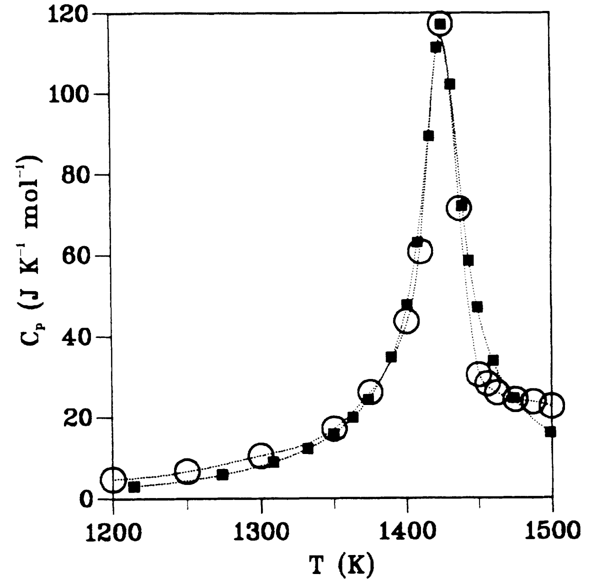

FIG. 4. CaF_2 crystal: ○, experimental data; ■, calculation.

the specific heat and enthalpy variation are in quantitative agreement with experimental results, it will be the same for the entropy variation which is not reported here.

For the PbF_2 compound the experimental data[10] exhibit a Schottky anomaly for the specific heat located at 714 K. The experimental half-height width is 100 K. For PbF_2, the E_1 formation enthalpy of Frenkel defects is reported to be in the range 0.95–1.45 eV.[2,4–7,9,12,18] In the present work, the E_1 value has been chosen $E_1=1.44$ eV, corresponding to specific-heat data.[18] The formation entropy for Frenkel defects has been reported to be in the range $(3.5\text{–}15)k$.[2,5,9,12,18] As seen from Table I, the A value is very close to the upper end of the above-defined range. The n_i value is close to the value of Schröter and Nöltig. The results of calculated specific-heat and experimental data are reported in Fig. 3 where it is seen that there is a quantitative agreement.

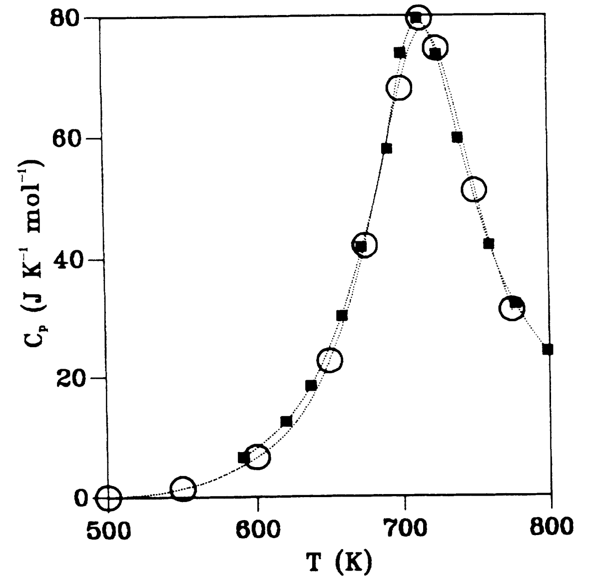

FIG. 3. PbF_2 crystal: ○, experimental data; ■, calculation.

For the CaF_2 crystal the experimental data[11] exhibit a Schottky anomaly for the specific heat located at 1425 K with a half-height width of 30 K. The E_1 formation enthalpy of Frenkel defects is reported to be in the range 2.71–3.17 eV.[8,13–16] As there is no defect formation energy coming from specific-heat measurements, a trial E_1 value, $E_1=3.0$ eV, has been assumed, close to ionic conductivity data.[8] The formation entropy for Frenkel defects has been reported to be in the range $(5.5\text{–}13.5)k$.[8,13–16] As seen from Table I, the A value is very close to the upper end of the above-defined range. The results of calculated specific heat are reported in Fig. 4, together with experimental data. It may be seen from this figure that there is still a quantitative agreement between experiment and calculation, but it is not as good as in the case of $SrCl_2$ and PbF_2 crystals.

CONCLUSION

It is possible to have a quantitative representation of the specific heat for three fluorites, even presenting a sharp Shottky anomaly as in the case of the CaF_2 compound. ΔH is fitted as well when experimental data are available. The half-height width is closely related to the strength of collective long-range interactions. The crudest approximation of the long-range interaction, depicted by pair defect interaction, is unable to fit the experimental data. In all cases, the fit to the experimental data occurs with very low defect concentration. The values determined in the present work for PbF_2, CaF_2, and $SrCl_2$ crystals cannot be considered as definitive. Our aim, nevertheless, is that further calculations on these crystals will not drastically change the present evaluation.

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

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

[3] A. V. Chadwick, F. G. Kirkwood, and R. Saghafian, J. Phys. (Paris) Colloq. **41**, C6-216 (1980).

[4] T. Y. Hwang, M. Engelsberg, and I. J. Lowe, Chem. Phys. Lett. **30**, 303 (1975).

[5] A. Azimi, V. M. Carr, A. V. Chadwick, F. G. Kirkwood, and R. Saghafian, J. Phys. Chem. Solids **45**, 23 (1984).

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

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

[8] J. Oberschmidt and D. Lazarus, Phys. Rev. B **21**, 5823 (1980).

[9] W. Schröter and J. Nöltig, J. Phys. (Paris) Colloq. **41**, C6-20 (1980); W. Schröter, Ph.D. thesis, University of Göttingen, 1979 (unpublished).

[10] A. S. Dworkin and M. A. Bredig, J. Phys. Chem. **72**, 1277 (1968).

[11] J. Nöltig (unpublished) [cited by C.R.A. Catlow, Comments Solid State Phys. **9**, 157 (1980)].

[12] P. Sekar and T. M. Haridasan, Philos. Mag. B **58**, 339 (1988).

[13] J. H. Harding, Phys. Rev. B **32**, 6861 (1985).

[14] P. W. M. Jacobs and S. H. Ong, J. Phys. (Paris) Colloq. **37**, C7-331 (1976).

[15] W. Bollman and H. Henniger, Phys. Status Solidi A **11**, 367 (1972).

[16] R. W. Ure, J. Chem. Phys. **26**, 1363 (1957).

[17] M. Dixon and M. J. Gillan, J. Phys. C **13**, 1901 (1980); **13**, 1919 (1980).

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

[19] M. Makur and S. Ghosh, J. Phys. (Paris) **50**, 431 (1989).

[20] B. A. Hubermann, Phys. Rev. Lett. **32**, 1000 (1974).

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

[22] Y. Bouteiller, J. Chim. Phys. (Paris) **87**, 1701 (1990).