

## Equation of state and temperature variation of the bulk modulus of the alkaline earth fluorides

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MS received 25 September 1975; in revised form 20 November 1975

**Abstract.** The isotherms for the alkaline earth fluorides ( $\text{CaF}_2$ ,  $\text{SrF}_2$  and  $\text{BaF}_2$ ) have been computed using the expression for the total free energy of a crystal in the quasi-harmonic approximation. The theoretical points for  $\text{SrF}_2$  and  $\text{BaF}_2$  have been compared with the points derived from Bridgman's experimental relation.

The temperature variation of the isothermal bulk modulus of the alkaline earth fluorides has been worked out on the basis of Axe's shell model. The theoretical points are compared with the points obtained from the temperature variation of the elastic constants data. It is found that the vibrational contribution to the temperature variation of the elastic constants in these crystals is significant.

**Keywords.** Equation of state; temperature variation of bulk modulus; alkaline earth fluorides; mechanical pressure; vibrational pressure; compression ratio.

### 1. Introduction

The total free energy of a crystal in the quasi-harmonic approximation consists of two parts

$$F = F^{\text{Mech}} + F^{\text{Vib}}. \quad (1.1)$$

The mechanical free energy  $F^{\text{Mech}}$  is the potential energy of interaction between the ions and the vibrational free energy  $F^{\text{Vib}}$  arises from the lattice vibrations. The two contributions for the fluorite structure on Axe's shell model are:

$$F^{\text{Mech}} = -\frac{\alpha_M e^2}{a} + 8\Phi_1(r) + 6\Phi_2(R)$$

$$F^{\text{Vib}} = \frac{k_B T}{N} \sum_{q=1}^N \sum_{s=1}^9 \ln [2 \sinh X_{q,s}] \quad (1.2)$$

Here  $\alpha_M$  is the Madulung constant referred to half the lattice constant,  $\Phi_1(r)$  is the potential energy of interaction between nearest neighbour cation-anion and  $\Phi_2(R)$  is the potential energy of interaction between nearest neighbour anion-anion. The unit cell volume  $v$ , the distances  $r$  and  $R$  are related to  $a$  as

$$v = 2a^3, \quad r = \frac{\sqrt{3}}{2} a, \quad R = a \quad (1.3)$$

The potential energies  $\Phi_1$  and  $\Phi_2$  are taken to vary as the inverse powers of the distances  $r$  and  $R$  with indices  $n_1$  and  $n_2$  respectively. The values of  $v$ ,  $r$ ,  $R$  and  $a$  pertaining to the minimum of the mechanical free energy will carry a subscript 0.  $N$  is the total number of wave-vectors  $q$  in the Brillouin zone.

$$X_{\mathbf{q},s} = \frac{\hbar\omega_{\mathbf{q},s}}{k_B T} \quad (1.4)$$

where  $\omega_{\mathbf{q},s}$  is the frequency of the normal mode belonging to branch  $s$  for wave vector  $\mathbf{q}$ , and  $k_B$  is the Boltzmann constant. The pressure  $P$  on the crystal is given by

$$P = -\left. \frac{\partial F}{\partial v} \right|_T = P^{\text{Mech}} + P^{\text{Vib}} \quad (1.5)$$

where

$$P^{\text{Mech}} = -\left. \frac{\partial F^{\text{Mech}}}{\partial v} \right|_T \quad \text{and} \quad P^{\text{Vib}} = -\left. \frac{\partial F^{\text{Vib}}}{\partial v} \right|_T.$$

Expressing  $\Phi_1(r)$  and  $\Phi_2(R)$  in terms of the parameters  $B_1$  and  $B_2$  defined by

$$\frac{e^2}{2v_0} B_1 = \frac{1}{r_0} \left( \frac{d\Phi_1}{dr} \right)_{r=r_0}; \quad \frac{e^2}{2v_0} B_2 = \frac{1}{R_0} \left( \frac{d\Phi_2}{dR} \right)_{R=R_0}. \quad (1.6)$$

We get

$$P^{\text{Mech}} = -\frac{e^2}{6a_0^4} \left[ \alpha_M \left( \frac{v_0}{v} \right)^{4/3} + \frac{B_1}{2} \left( \frac{v_0}{v} \right)^{(n_1+3)/3} + \frac{B_2}{2} \left( \frac{v_0}{v} \right)^{(n_2+3)/3} \right] \quad (1.7)$$

$$P^{\text{Vib}} = \frac{k_B T}{Nv} \sum_{\mathbf{q}=1}^N \sum_{s=1}^g \gamma_{\mathbf{q},s} X_{\mathbf{q},s} \coth X_{\mathbf{q},s} \quad (1.8)$$

$$\gamma_{\mathbf{q},s} = -\frac{\partial \ln \omega_{\mathbf{q},s}}{\partial \ln v},$$

is the Gruneisen parameter of mode  $(\mathbf{q},s)$  at the volume  $v$ . The equilibrium volume  $v_e(T)$  of a crystal at a temperature  $T$  is obtained by putting  $P = 0$ . The values of  $v$ ,  $r$ ,  $R$  and  $a$  pertaining to the equilibrium situation will carry a subscript  $e$ . From 1.5 we obtain  $P$  as a function of  $v$  at a temperature  $T$ . The experimental isotherms are normally plots of  $P$  versus the compression ratio  $(v - v_e)/v_e$ . Such a plot represents the equation of state of the crystal at temperature  $T$ .

The isothermal bulk modulus  $B_T$  of the solid is given by

$$B_T = -v_e \left. \frac{\partial P}{\partial v} \right|_{v=v_e(T)} = B^{\text{Mech}} + B^{\text{Vib}} \quad (1.9)$$

Here

$$\begin{aligned} B^{\text{Mech}} &= \frac{1}{3v_e} \left[ -\frac{4}{3} \frac{\alpha_M e^2}{a_e} + 8(n_1 + 3) n_1 \Phi_1(r_e) + 6(n_2 + 3) n_2 \Phi_2(R_e) \right] \\ &= -\frac{e^2}{6a_0^4} \left[ \frac{4}{3} \alpha_M \left( \frac{v_e}{v_0} \right)^{4/3} + \frac{B_1}{2} (n_1 + 3) \left( \frac{v_e}{v_0} \right)^{(n_1+3)/3} \right. \\ &\quad \left. + \frac{B_2}{2} (n_2 + 3) \left( \frac{v_e}{v_0} \right)^{(n_2+3)/3} \right] \end{aligned} \quad (1.10)$$

The vibrational bulk modulus  $B^{\text{Vib}}$  can be most conveniently obtained by finding the slope of the plot of  $P^{\text{Vib}}$  against  $v$  at  $v_e(T)$ . Thus the temperature variation of the isothermal bulk modulus can be found.

## 2. Results and Discussion

A program was written for the IBM 370 computer to compute  $P^{\text{Mech}}$ ,  $P^{\text{Vib}}$  and  $B^{\text{Mech}}$  for a set of equally spaced volumes around  $v_0$  for temperatures  $T = 5, 50, 100, 200$  and  $300^\circ \text{K}$ . In computing  $P^{\text{Vib}}$  the summation was performed over 151 wave vectors in the irreducible volume of the Brillouin zone giving the proper statistical weight for each wave vector. Tables 1, 2 and 3 give the values of  $P^{\text{Mech}}$ ,  $P^{\text{Vib}}$  and total pressure  $P$  as a function of volume  $v$  of the unit cell for  $\text{CaF}_2$ ,  $\text{SrF}_2$  and  $\text{BaF}_2$  respectively for a temperature of  $300^\circ \text{K}$ . Figures 1, 2 and 3 show a plot of pressure  $P$  versus compression ratio  $(v - v_0)/v_0$  for the three crystals. There are no experimental measurements of the equation of state of  $\text{CaF}_2$ . For  $\text{BaF}_2$  and  $\text{SrF}_2$  the only data available are from the early work of Bridgman (1958) up to a pressure of 12 kbars. From his experimental data Bridgman (1958) gave the following formula for the compression ratio  $\xi = (v - v_0)/v_0$  as a function of pressure  $P$  in  $\text{kgm/cm}^2$ .

**Table 1.** Equation of state of  $\text{CaF}_2$

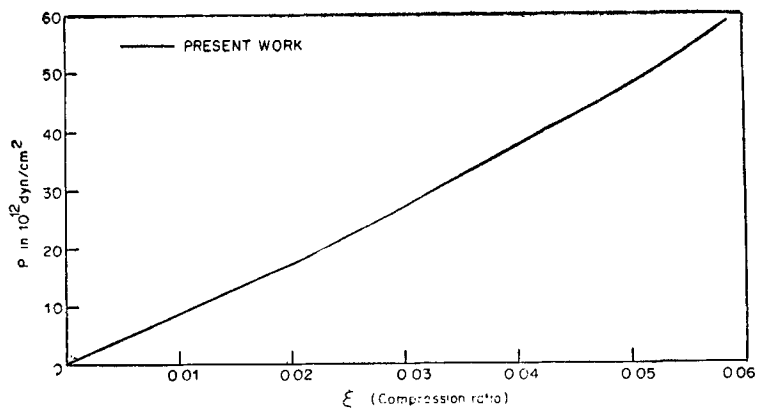
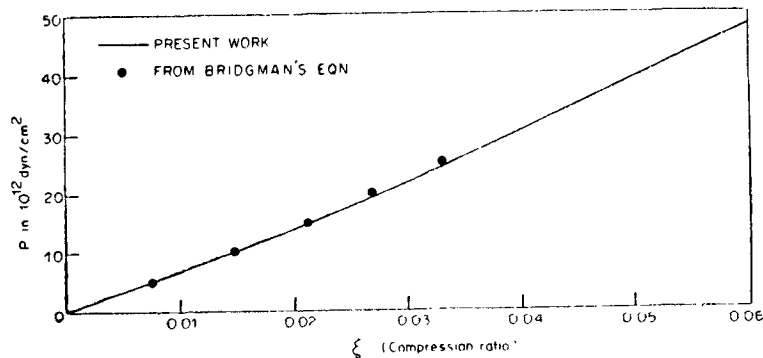
$v_0 = 41.2422 \text{ \AA}^3$		$T = 300^\circ \text{K}$		
$v$ in $\text{\AA}^3$	$\xi$	$P^{\text{Mech}}$	$P^{\text{Vib}}$	$P$ in $10^9$ dynes/cm $^2$
38.8361	-0.0583	39.82	18.59	58.41
39.3361	-0.0462	25.24	18.79	44.03
39.8361	-0.0341	12.68	18.97	31.65
40.3361	-0.0220	0.12	19.15	19.27
40.8361	-0.0098	-10.65	19.32	8.62
41.3361	0.0023	-21.55	19.50	-2.05
41.8361	0.0144	-30.90	19.65	-11.25

**Table 2.** Equation of state of  $\text{SrF}_2$

$v_0 = 49.2370 \text{ \AA}^3$		$T = 300^\circ \text{K}$		
$v$ in $\text{\AA}^3$	$\xi$	$P^{\text{Mech}}$	$P^{\text{Vib}}$	$P$ in $10^9$ dynes/cm $^2$
46.2752	-0.0602	34.31	14.05	48.36
46.7752	-0.0500	24.71	14.17	38.88
47.2752	-0.0398	15.69	14.28	29.97
47.7752	-0.0297	7.22	14.38	21.60
48.2752	-0.0195	-0.74	14.49	13.75
48.7752	-0.0094	-8.21	14.60	6.39
49.2752	0.0008	-15.24	14.70	-0.54
49.7752	0.0109	-21.85	14.80	-7.05

Table 3. Equation of state of BaF<sub>2</sub>

$v_0 = 59.9821 \text{ \AA}^3$ $v \text{ in } \text{ \AA}^3$	$\xi$	$P^{\text{Mech}}$	$P^{\text{Vib}}$	$T = 300^\circ \text{ K}$ $P \text{ in } 10^9 \text{ dynes/cm}^2$
55.3974	-0.0765	44.18	10.74	54.92
55.8974	-0.0682	36.72	10.82	47.54
56.3974	-0.0598	29.66	10.90	40.56
56.8974	-0.0515	22.96	10.97	33.93
57.3974	-0.0432	16.60	11.05	27.65
57.8974	-0.0348	10.58	11.12	21.70
58.3974	-0.0265	4.86	11.20	16.06
58.8974	-0.0181	-0.56	11.27	10.71
59.3974	-0.0098	-5.71	11.34	5.63
59.8974	-0.0015	-10.59	11.41	0.82
60.3974	0.0069	-15.22	11.48	-3.74
60.8974	0.0152	-19.62	11.54	-8.08

Figure 1. Equation of state of CaF<sub>2</sub>.Figure 2. Equation of state of SrF<sub>2</sub>.

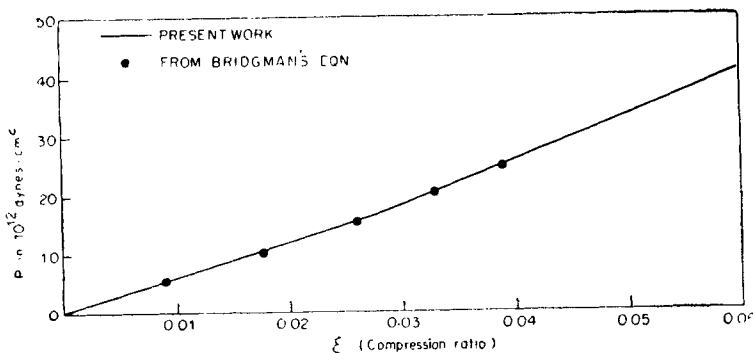


Figure 3. Equation of state of  $\text{BaF}_2$ .

$$-\xi = (a \times 10^{-7} P) - b \times 10^{-12} P^2$$

where

for  $\text{BaF}_2$  at  $300^\circ \text{K}$   $a = 19.33$  and  $b = 14.8$

and

for  $\text{SrF}_2$  at  $300^\circ \text{K}$   $a = 15.78$  and  $b = 10.3$ .

The points shown in figures 2 and 3 are derived from the above equations.

Tables 4, 5 and 6 give the values of the bulk moduli  $B_T$  at different temperatures. It should be remembered that in obtaining the parameters of the Axe's shell model, we have taken the equilibrium separation  $a_0$  corresponding to the minimum of  $F^{\text{Mech}}$  as the observed lattice constant at  $0^\circ \text{K}$ , which is only an approximation. Now  $a_s$  is derived by minimising the total free energy and so  $a_s$  will be different from the actual lattice constant at  $0^\circ \text{K}$ . Hence the bulk modulus calculated at absolute zero including the vibrational free energy will be different from the measured value. Therefore in comparing with experiment it is more meaningful to plot

$$\frac{B(T) - B(300)}{B(300)} \times 100 \text{ versus } T,$$

where  $B(T)$  is the isothermal bulk modulus at temperature  $T$ . Figure 4 shows such theoretical plots for  $\text{BaF}_2$ ,  $\text{SrF}_2$  and  $\text{CaF}_2$ . The bulk moduli at different temperatures obtained from the temperature variation of the second order elastic constants would obviously be the adiabatic bulk moduli, since the elastic constants measured experimentally by ultrasonic techniques are the adiabatic moduli. The relation

$$B_T = B_s (1 - \gamma \beta T) \quad (2.1)$$

helps one in converting  $B_s$  to  $B_T$  where  $\gamma$  is the bulk Gruneisen parameter, and  $\beta$  the volume expansion coefficient. For  $\text{CaF}_2$  experimental data on the temperature variation of the adiabatic elastic constants have been taken from Huffmann and Norwood (1960) and Ho and Ruoff (1967). For  $\text{SrF}_2$  the data are those of Gerlich (1964 *a*) and for  $\text{BaF}_2$  again from Gerlich (1964 *b*). To convert the adiabatic to the isothermal moduli the values of  $\gamma$  and  $\beta$  are taken from Bailey and Yates (1967). From a study of figure 4, it is obvious that there is good agreement between theory and experiment in  $\text{CaF}_2$  and  $\text{SrF}_2$ . In  $\text{BaF}_2$  on the other

**Table 4.** Temperature variation of the isothermal bulk modulus in  $\text{CaF}_2$ 

$T^\circ \text{K}$	Eq. volume $v_e$ in $\text{\AA}^3$	$B^{\text{mech}}$	$B^{\text{vib}}$	$B$ in $10^{10}$ dynes/cm <sup>2</sup>
5	40.8031	8.8821	0.0571	8.9392
50	40.8061	8.8789	0.0539	8.9328
100	40.8405	8.8377	0.0221	8.8598
200	41.0105	8.6556	-0.0656	8.5900
300	41.2398	8.4161	-0.1443	8.2718

**Table 5.** Temperature variation of the isothermal bulk modulus of  $\text{SrF}_2$ 

$T^\circ \text{K}$	Eq. volume $v_e$ in $\text{\AA}^3$	$B^{\text{mech}}$	$B^{\text{vib}}$	$B$ in $10^{11}$ dynes/cm <sup>2</sup>
5	48.6871	7.1367	0.0487	7.1854
50	48.6924	7.1327	0.0419	7.1746
100	48.7432	7.0941	0.0029	7.0970
200	48.9608	6.9382	-0.0480	6.8902
300	49.2370	6.7403	-0.1083	6.6320

**Table 6.** Temperature variation of the isothermal bulk modulus of  $\text{BaF}_2$ 

$T^\circ \text{K}$	Eq. volume $v_e$ in $\text{\AA}^3$	$B^{\text{mech}}$	$B^{\text{vib}}$	$B$ in $10^{11}$ dynes/cm <sup>2</sup>
5	59.3010	6.0015	0.0366	6.0381
50	59.3326	5.9845	0.0319	6.0164
100	59.3924	5.9519	0.0065	5.9584
200	59.6522	5.8189	0.0439	5.7750
300	59.9821	5.6909	-0.0847	5.5662

hand the observed total temperature variation between 0 and 300° K is roughly twice the calculated value. No reason is apparent for this discrepancy. Our theoretical studies predict a total variation of 8% in the bulk moduli of all the three crystals from 0–300° K. While experimental results on  $\text{CaF}_2$  and  $\text{SrF}_2$  also indicate about the same total variation for these two crystals, the total variation in  $\text{BaF}_2$  observed experimentally appears to be out of line with what has been observed in the other two crystals. It will perhaps be worthwhile to repeat the experimental measurements on the temperature variation of the elastic constants of  $\text{BaF}_2$ .

There is one striking feature from the results in the tables 4, 5 and 6. The vibrational contribution of the bulk modulus changes sign from positive to negative as

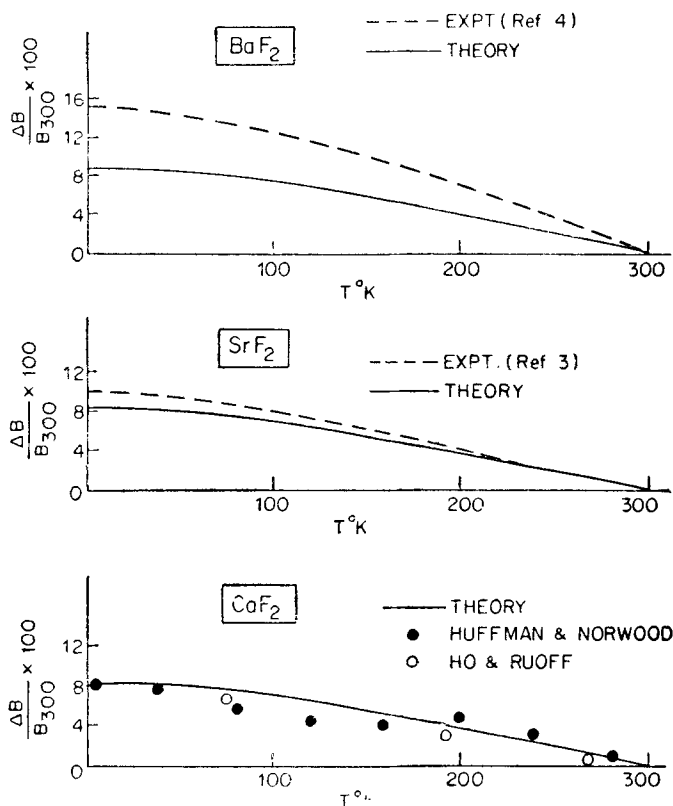


Figure 4. Temperature variation of the bulk modulus of the alkaline earth fluorides.

the temperature is increased.  $B^{\text{Vib}}$  depends upon the slope of the P-V-T graph, which is an involved function of the Gruneisen parameters and the frequencies.

In fact the vibrational contribution accounts for about one-third the total change in the isothermal bulk modulus of all the three fluorides from 0° K to 300° K. Hence, for the temperature variation of the elastic constants the vibrational contribution plays an important role.

### Acknowledgement

We thank K S Girirajan for help in computations.

### References

- Bailey A C and Yates B 1967 *Proc. Phys. Soc.* **91** 390
- Bridgman P W 1958 *Physics of High Pressure*, p. 163 (G Bell and Sons Ltd., London)
- Gerlich D 1964 *a Phys. Rev.*, **136 A** 1366
- Gerlich D 1964 *b Phys. Rev.* **135 A** 1331
- Ho P S and Ruoff A L 1967 *Phys. Rev.* **161** 864
- Huffman D R and Norwood M H 1960 *Phys. Rev.* **117** 709