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

R SRINIVASAN and V RAMACHANDRAN

Department of Physics, Indian Institute of Technology, Madras 600036

Abstract. The isotherms for the alkaline earth fluorides (CaF_2, SrF_2 and 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 SrF_2 and 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 theoretica 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

$$F = F^{\text{Mech}} + F^{\text{Vib}}. \tag{1.1}$$

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

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

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

Here a_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

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

The potential energies Φ_1 and Φ_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

N is the total number of wave-vectors q in the Brillouin zone.

$$X_{q,s} = \frac{\hbar \omega_{q,s}}{k_B T} \tag{1.4}$$

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

$$P = -\frac{\partial F}{\partial v}\bigg|_T = P^{\text{Mech}} + P^{\text{Vib}} \tag{1.5}$$

where

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

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

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

We get

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

$$P^{\text{Vib}} = \frac{k_B T}{Nv}\sum_{q=1}^{N}\sum_{s=1}^{9}\gamma_{q,s}X_{q,s}\coth X_{q,s} \tag{1.8}$$

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

is the Gruneisen parameter of mode (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

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

Here

$$B^{\text{Mech}} = \frac{1}{3v_e}\left[-\frac{4}{3}\frac{a_M e^2}{a_e} + 8(n_1 + 3)n_1\Phi_1(r_e) + 6(n_2 + 3)n_2\Phi_2(R_e)\right]$$

$$= -\frac{e^2}{6a_0^4}\left[\frac{4}{3}a_M\left(\frac{v_e}{v_0}\right)^{4/3} + \frac{B_1}{2}(n_1 + 3)\left(\frac{v_e}{v_0}\right)^{(n_1+3)/3}\right.$$

$$\left. + \frac{B_2}{2}(n_2 + 3)\left(\frac{v_e}{v_0}\right)^{(n_2+3)/3}\right] \tag{1.10}$$

The vibrational bulk modulus B^{Vib} can be most conveniently obtained by finding the slope of the plot of P^{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^{Mech}, P^{Vib} and B^{Mech} for a set of equally spaced volumes around v_0 for temperatures $T = 5$, 50 100, 200 and 300° K. In computing P^{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^{Mech}, P^{Vib} and total pressure P as a function of volume v of the unit cell for CaF_2, SrF_2 and BaF_2 respectively for a temperature of 300° K. Figures 1, 2 and 3 show a plot of pressure P versus compression ratio $(v - v_e)/v_e$ for the three crystals. There are no experimental measurements of the equation of state of CaF_2. For BaF_2 and 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 $\xi = (v - v_e)/v_e$ as a function of pressure P in kgm/cm^2.
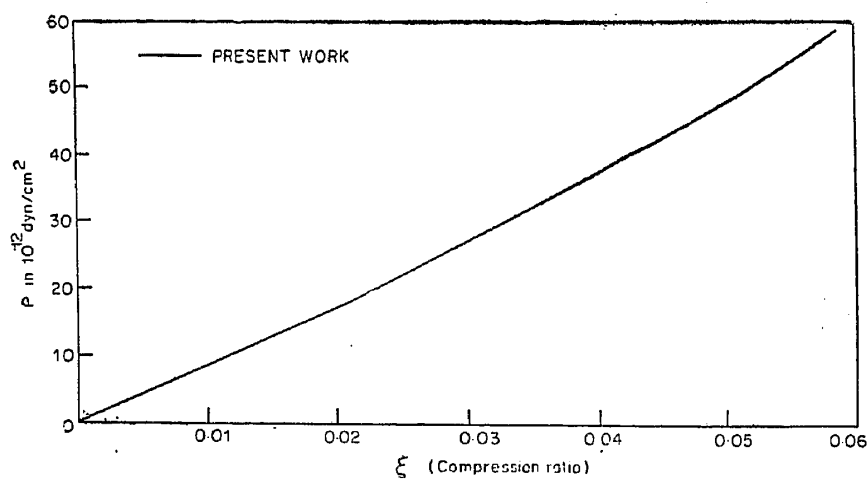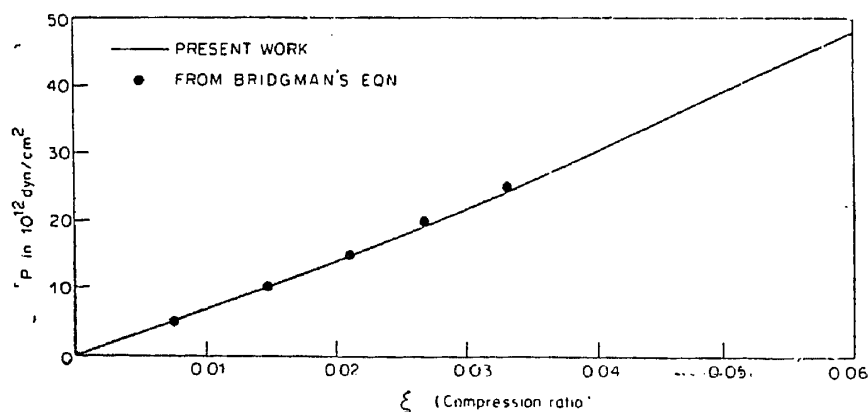
Table 1. Equation of state of CaF_2

$v_e = 41 \cdot 2422 \text{ Å}^3$				$T = 300° \text{ K}$
v in Å^3	ξ	P^{Mech}	P^{Vib}	P in 10^9 dynes/cm²
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 SrF_2

$v_e = 49 \cdot 2370 \text{ Å}^3$				$T = 300° \text{ K}$
v in Å^3	ξ	P^{Mech}	P^{Vib}	P in 10^9 dynes/cm²
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

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Table 3. Equation of state of BaF_2

| $v_e = 59 \cdot 9821$ Å^3 | | | | $T = 300°$ K |
v in Å^3	ξ	P^{Mech}	P^{Vib}	P in 10^9 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_2.

Figure 2. Equation of state of SrF_2.
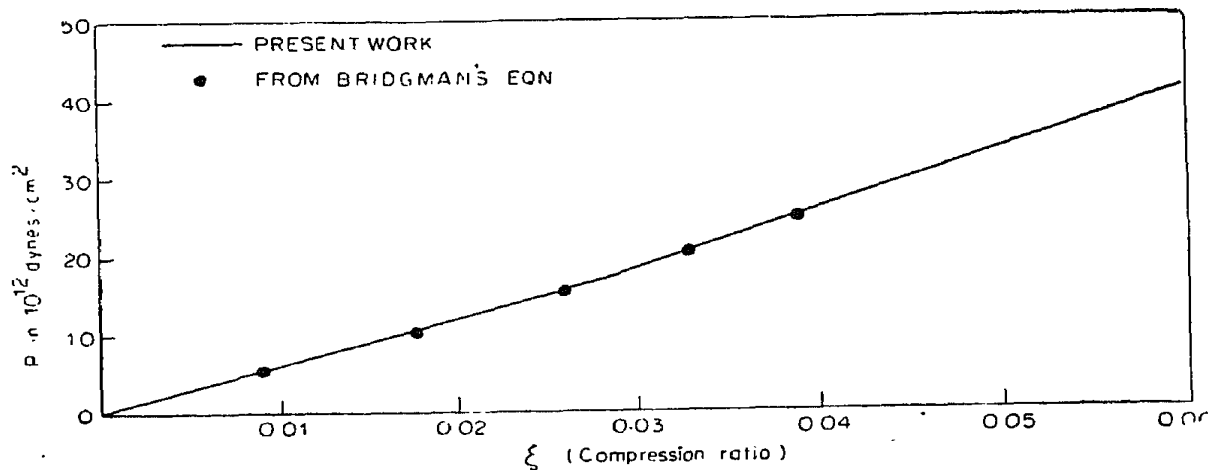
Figure 3. Equation of state of BaF_2.

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

where

for BaF_2 at $300°\,K$ $a = 19 \cdot 33$ and $b = 14 \cdot 8$

and

for SrF_2 at $300°\,K$ $a = 15 \cdot 78$ and $b = 10 \cdot 3$.

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 modulii 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^{Mech} as the observed latice constant at $0°\,K$, which is only an approximation. Now a_e is derived by minimising the total free energy and so a_e will be different from the actual lattice constant at $0°\,K$. 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

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

where $B(T)$ is the isothermal bulk modulus at temperature T. Figure 4 shows such theoretical plots for BaF_2, SrF_2 and CaF_2. The bulk modulii at different temperatures obtained from the temperature variation of the second order elastic constants would obviously be the adiabatic bulk modulii, since the elastic constants measured experimentally by ultrasonic techniques are the adiabatic modulii. The relation

$$B_T = B_s (1 - \gamma \beta T) \tag{2.1}$$

helps one in converting B_s to B_T where γ is the bulk Gruneisen parameter, and β the volume expansion coefficient. For 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 SrF_2 the data are those of Gerlich (1964 a) and for BaF_2 again from Gerlich (1964 b). To convert the adiabatic to the isothermal modulii the values of γ and β 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 CaF_2 and SrF_2. In BaF_2 on the other

Table 4. Temperature variation of the isothermal bulk modulus in CaF_2

$T°K$	Eq. volume v_e in $Å^3$	B^{Mech}	B^{vib}	B in 10^{10} dynes/cm^2
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 SrF_2

$T°K$	Eq. volume v_e in $Å^3$	B^{Mech}	B^{vib}	B in 10^{11} dynes/cm^2
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 BaF_2

$T°K$	Eq. volume v_e in $Å^3$	B^{Mech}	B^{vib}	B in 10^{11} dynes/cm^2
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 modulii of all the three crystals from 0–300° K. While experimental results on CaF_2 and SrF_2 also indicate about the same total variation for these two crystals, the total variation in 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 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
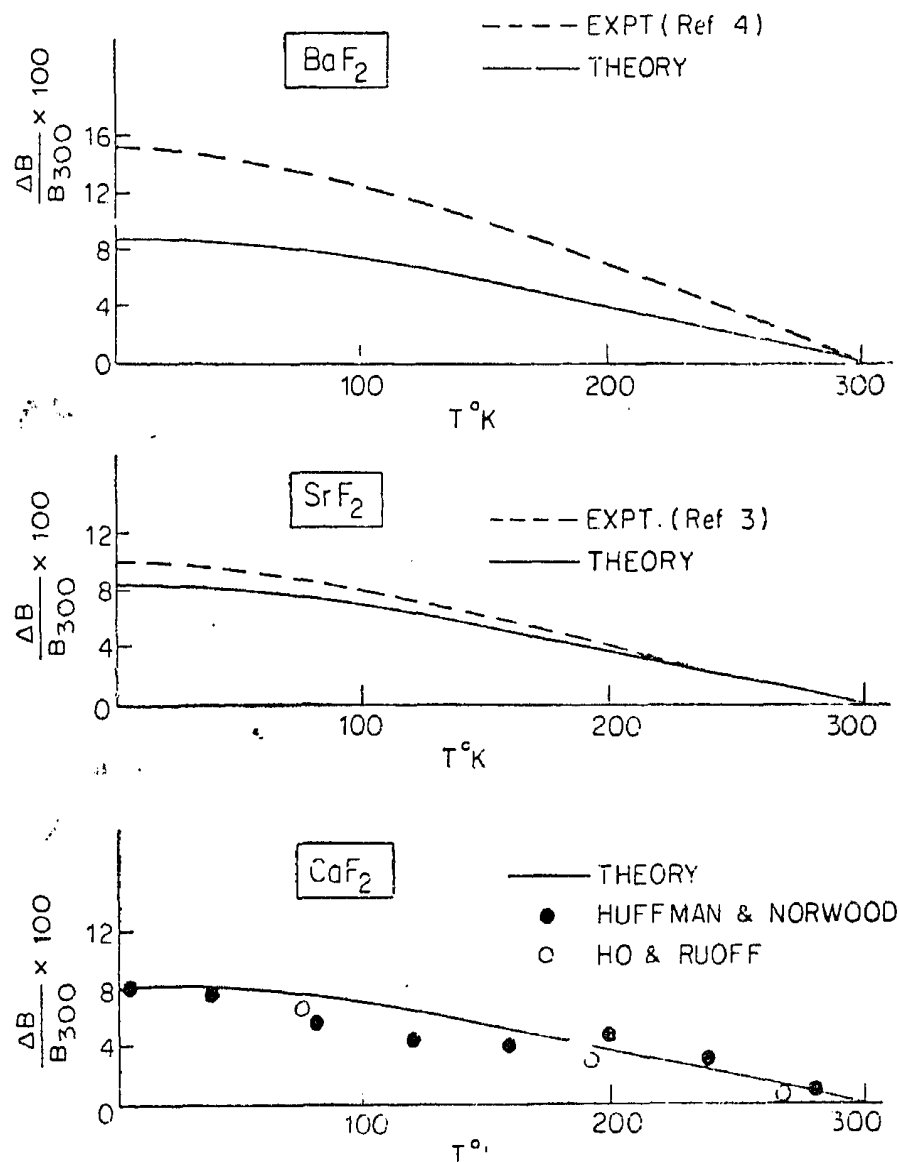
Figure 4. Temperature variation of the bulk modulus of the alkaline earth fluorides.

the temperature is increased. B^{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.

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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