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ON THE TEMPERATURE AND PRESSURE DEPENDENCE OF THE DEFECT FORMATION VOLUME IN IONIC CRYSTALS (*)

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Résumé. — Le volume de formation d'un défaut de Schottky dans les halogénures alcalins est supérieur au volume moléculaire, mais dépend aussi de la température et de la pression. Le coefficient β_v d'expansion thermique du volume du défaut est exprimé à l'aide du coefficient d'expansion β du matériau massif et de la dépendance en température des dérivées, par rapport à la pression, de ses constantes élastiques. Le coefficient β_v est beaucoup plus grand que β , et il croît légèrement avec la température. Le module isotherme du défaut B_v est aussi exprimé à l'aide du module macroscopique du matériau massif B et de ses dérivées premières et secondes par rapport à la pression. La valeur de B_v est beaucoup plus petite que celle de B et décroît avec la température. En outre, B_v décroît fortement avec la pression, 40 % pour 10 kbar. Les dépendances en température et en pression de B_v et β_v ont les comportements requis pour expliquer les mesures de diffusion et de conductivité sous pression hydrostatique.

Abstract. — The Schottky formation volume in alkali halides not only exceeds the molecular volume but also depends on temperature and pressure. The coefficient β_v for the thermal expansion of the defect-volume has been found in terms of the bulk expansivity β and the temperature dependence of the pressure derivative of the bulk elastic constants. The coefficient β_v is much greater than β and increases slightly with temperature.

The defect isothermal bulk modulus B_v has also been expressed in terms of the macroscopic bulk modulus B and its first and second pressure derivatives. The value of B_v is much smaller than that of B and decreases with temperature. Furthermore B_v decreases strongly with pressure, about 40 % up to 10 kbar.

The temperature and the pressure dependences of B_v and β_v have the same trend as required to explain the experimental diffusion and conductivity plots under hydrostatic pressure.

In recent publications [1-4] we have proposed that the anharmonicity of the solid plays a very important role in the determination of the formation parameters of a Schottky defect in alkali halides. On this basis, we hope that we have eliminated the old discrepancy, regarding the values of the formation entropy. We found that $s \approx 10$ k, in close agreement with the most recent experimental results [5]. Furthermore, we have shown [2, 3] that the coexistence of the strong decrease of the elastic constants with temperature T and the thermal expansion of the solid leads to a temperature dependence of h and s , where h denotes

the formation enthalpy per Schottky defect. We now turn our attention to another vexing question, i.e., to the calculation of the formation volume, v_f , per Schottky defect.

We note that all the calculations [6, 7, 8], up to now, have predicted a large contraction of the lattice around the defect, whereas all the available experimental techniques [9, 10, 11] showed a strong expansion. A more complete study of the v_f problem will be published elsewhere [4]. In the present treatment we restrict ourselves to the determination of the thermal-expansion coefficient β_v of the volume v_f and the isothermal defect-bulk modulus B_v . We note that no study of this problem has been published, due to the fact that in ionic crystals both β_v and B_v were

(*) To the memory of Antonios Varotsos.

arbitrarily assumed equal to zero [12]. We shall follow exactly the same procedure as before [1-4], keeping in mind the assumption that the value of C in the expression :

$$g = CB\Omega \quad (1)$$

does not depend on T and P , where P denotes the pressure, g the Gibbs formation energy and Ω the mean volume per atom. (B is the usual macroscopic bulk modulus.)

1. **Calculation of β_v and B_v .** — The value of C in eq. (1) can be determined [1-4] as follows : at $T = 0$ the energy g becomes equal to the formation enthalpy h_0 (hereafter the subscript 0 denotes the corresponding values at absolute zero). Thus eq. (1) gives :

$$C = \frac{h_0}{B_0 \Omega_0}. \quad (2)$$

A combination of eqs (1) and (2) shows :

$$g = \frac{h_0}{B_0 \Omega_0} B\Omega. \quad (3)$$

The quantities β_v and B_v are defined [13] as follows :

$$\beta_v = \frac{1}{v_f} \cdot \frac{dv_f}{dT}, \quad P = \text{const.} \quad (4)$$

and

$$B_v = -v_f \frac{dP}{dv_f}, \quad T = \text{const.} \quad (5)$$

Recalling that : $B = -\Omega \frac{dP}{d\Omega}$, $T = \text{const.}$, v_f can be found as follows :

$$v_f = \frac{dg}{dP} = \frac{h_0}{B_0 \Omega_0} \left(\frac{dB}{dP} - 1 \right) \Omega. \quad (6)$$

By inserting the value of v_f into eqs (4), (5) we finally get :

$$\beta_v = \beta + \frac{d}{dT} \ln \left(\frac{dB}{dP} - 1 \right)_P \quad (7)$$

and

$$\frac{1}{B_v} = \frac{1}{B} - \frac{d}{dP} \ln \left(\frac{dB}{dP} - 1 \right)_T. \quad (8)$$

2. **Remarks on eqs (7) and (8).** — (i) In a harmonic solid the elastic constants do not depend on temperature and pressure. Then eqs (7) and (8) give :

$$\text{harmonic solid : } \beta_v = \beta = 0 \quad \text{and} \quad B_v = B = B_0.$$

(ii) In the lowest order of anharmonicity [14, 15] the pressure derivative of dB/dP (and its temperature variation as well) is zero. Therefore we get : lowest order of anharmonicity : $\beta_v = \beta$ and $B_v = B$.

(iii) In a real solid (i.e. anharmonic) experiments [16, 17] showed that dB/dP depends on P and T . Especially in alkali halides, dB/dP decreases with pressure (for $T = \text{const.}$) and increases linearly with temperature (for each P). Thus eqs (7), (8) reveal : real solid : $\beta_v \neq \beta$ and $B_v \neq B$.

Important remark. — This last conclusion is *not inconsistent* with eq. (1). This equation is based on clear thermodynamic considerations : i.e. according to Zener [18] the creation of a vacancy is the *isothermal, isobaric* variation of the solid and hence the corresponding variation of the Gibbs energy of the solid must be proportional [19] to the bulk modulus and to the macroscopic change of the crystal-volume (which has a certain relation to the Ω).

3. **Application of equation (7).** — The first and the second pressure derivatives of B , in NaCl, have been measured by Spetzler *et al.* [16] up to 10 kbar. They have confirmed that dB/dP increases linearly with T (for each pressure) and we predicted its values, at higher and lower temperatures, by linear extrapolation. As for the volume expansivity, in NaCl, we have used the values reported by Srivastava and Merchant [20]. The β_v -values, obtained from eq. (7), have been inserted in column 5 of table I. In column 4 we give the values of β , for the sake of comparison, whereas in column 6 the ratio β_v/β is given.

TABLE I

Thermal expansion of a Schottky defect in NaCl

1	2	3	4	5	6
T K	$\frac{dB}{dP}$ $P = 0$ kbar	$\beta_v - \beta$ 10^{-4} grad $^{-1}$	β 10^{-4} grad $^{-1}$	β_v 10^{-4} grad $^{-1}$	$\frac{\beta_v}{\beta}$
300	5.352	3.61	1.17	4.78	4.08
550	5.745	3.31	1.55	4.86	3.14
800	6.138	3.06	1.91	4.97	2.60
900	6.295	2.97	2.05	5.02	2.45
1 000	6.452	2.88	2.19	5.07	2.32

We see that the *excess* expansivity $\beta_v - \beta$ (column 3) decreases with the temperature, but it consistently exceeds the bulk expansivity. The ratio β_v/β always exceeds unity and decreases from the value 4.1 (at R.T.) to 2.3 (at $T = 1\ 000$ K). The *surprising* result that $\beta_v > \beta$ has been also observed in metals and it has been used by Gilder and Lazarus [13] to explain the curvature in the diffusion plots. We note that in some metals β_v is proportional to $1/T$, whereas in our case β_v increases slightly with T .

For the confirmation of our results we recall two recent experimental results [10, 11] : (i) Yoon and Lazarus [10] remarked that the average slopes of $\ln \sigma$ -vs-pressure ($\sigma =$ conductivity) plots *decrease significantly with decreasing temperature*. These slopes correspond to the activation volume $v = \frac{v_f}{2} + v_m$,

where v_m is the migration volume. In other words, Yoon and Lazarus observed that v , and hence v_f , increases significantly with temperature. Therefore, experiment shows that $\beta_v > 0$, as our results predict. Unfortunately, in the case of NaCl, they give the $\ln \sigma$ -vs-pressure plot only at $T = 993.5$ K, and thus a direct check of our β_v -values is not possible. However, from the temperature dependence of their plots, in the other materials, we obtain $\beta_v > 0$. In the light of the present discussion, it should be interesting to reanalyse their results, in order to obtain the β_v -value, for each material.

(ii) Martin, Lazarus and Mitchell [11] studied cation diffusion in NaCl (with the tracer technique), under pressure, and they found that v increases with T (although this variation lies within the experimental error). By using their v -values, and assuming that v_m varies like v_f , we obtain that $\beta_v/\beta \approx 5$. Keeping in mind the large experimental error, we can say that our prediction, that $\beta_v > \beta$, is the right direction.

4. Application of equation (8). — Applying eq. (8), for $T = 936$ K and $T = 993.5$ K, for various pressures, we find B_v and the resulting values are given in tables II and III. In the last column of table III we

TABLE II

Defect-bulk modulus vs pressure in NaCl at $T = 936$ K

P kbar	1 $\frac{dB}{dP}$	2 B kbar	3 $\frac{d}{dP} \left(\frac{dB}{dP} \right)$ kbar ⁻¹	4 B_v kbar
0	6.351 8	135.37	- 0.095 5	39.63
2	6.154 6	147.90	- 0.101 7	37.75
4	5.945 0	160.00	- 0.107 8	35.66
6	5.723 5	171.68	- 0.115 03	33.14
8	5.484 9	182.90	- 0.123 0	30.41
10	5.231 7	225.05	- 0.130 3	28.39

TABLE III

Defect-bulk modulus vs pressure in NaCl at $T = 993.5$ K

P kbar	1 $\frac{dB}{dP}$	2 B kbar	3 $\frac{d}{dP} \left(\frac{dB}{dP} \right)$ kbar ⁻¹	4 B_v kbar	5 v_f Å ³
0	6.442	126.07	- 0.971 5	38.783	95.44
2	6.241 6	138.77	- 0.103 3	37.17	90.41
4	6.029	151.04	- 0.109 3	35.27	85.42
6	5.804 5	162.89	- 0.116 5	32.91	80.41
8	5.563	174.27	- 0.124 6	30.257	75.32
10	5.306 0	167.40	- 0.132 4	27.24	70.00

give the v_f -values, obtained from eq. (6), in order to show that it really gives correct results. We see that our value $v_f = 95.44$ Å³ $\approx 4 \Omega$ is in good agreement with the experimental value [11] : $v_f \approx 4.4 \Omega$ (we used the approximation $h_0 \approx h = 2.44$ eV [5]).

A comparison of the fourth columns of the tables II, III shows that B_v *decreases with temperature* (for $P = \text{const.}$), like B . However we must notice that the rate of the temperature decrease of B_v is much smaller than that of B . Furthermore, B_v *decreases strongly with pressure*, while for B the opposite holds. B_v is smaller than B by a factor $3 \sim 9$. This factor increases with pressure (for $T = \text{const.}$). We emphasize, again, that this last conclusion cannot lead to any confusion concerning the validity of eq. (1), for the same reasons discussed above. B_v is simply a measure of the v_f -variation with pressure, and thus it could be negative. In any case, B_v does not correspond only to the local reduction of the force constants, due to the fact that v_f is not only related to the relaxation of the nn atoms around the vacancies. If it were so, we would be very happy, because by applying the simple Einstein-model we would find :

$$s = 12 k \ln \sqrt{\frac{B}{B_v}} \approx 8 k ,$$

which is near the experimental value (!).

We try now to answer the following question : do our *strange* B_v -values correspond to the real situation ?

Both the above experimental techniques, i.e. conductivity and diffusion under hydrostatic pressure, have confirmed that the plots $\ln D$ vs P or $\ln \sigma$ vs P show a strong curvature (we may draw a continuous curve through the experimental points of ref. [11], instead of two distinct linear parts). According to Yoon and Lazarus *the curvature in such plots must represent real effects*. In other words, the experiments show that the slopes of these curves vary with the pressure, which means that v (and hence v_f) depends on P . As the curvature is always upwards, we can say that all the above experiments indicate that v_f decreases with

pressure, i.e. the B_v -value is positive, in accordance to our results. A very rough estimation, from the plot of Yoon and Lazarus (in NaCl, at $T = 993.5$ K), leads to the conclusion that, in the region (0... 6) kbar, v (and approx. v_f) decreases by $\sim 30\%$. By turning now to table III we see that, actually, at $P = 6$ kbar, our v_f -value is about 20% smaller than that corresponding to $P = 0$. Therefore, we conclude that the trend of our v_f -values to decrease strongly with P explains (partially) the curvature observed in the above mentioned plots.

Furthermore, our prediction that B_v is much smaller than B is not inconsistent with the experimental results. By using the initial and the final slopes of the plots, given in refs. [10] and [11], we easily find that they reveal : $B_v < B$, in accordance to our prediction.

5. Conclusions. — 1. The formation volume v_f , per Schottky defect, is not only greater than the

molecular volume but it depends also on temperature and pressure. Therefore $\beta_v \neq 0$ and $B_v \neq 0$, which is in contradiction with previous assumptions.

2. The defect-expansivity not only increases with T , but it even exceeds the bulk value.

3. The defect-bulk modulus B_v is much smaller than B , by a factor of $3 \sim 9$; B_v decreases strongly with pressure and slightly with temperature.

4. The conductivity and the diffusion plots vs pressure have continuously varying slopes, due to the fact that v_f depends strongly on pressure. Although all the above conclusions are in contradiction with current theoretical models, they are however strengthened by all the available experimental results.

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