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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	$\frac{dB}{dP}$ $P = 0 \text{ kbar}$	$\beta_v - \beta$ $10^{-4} \text{ grad}^{-1}$	β $10^{-4} \text{ grad}^{-1}$	β_v $10^{-4} \text{ grad}^{-1}$	$\frac{\beta_v}{\beta}$
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 $T = 1\,000\text{ K}$). 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 (σ = 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 $T = 993.5\text{ K}$, 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 $T = 936\text{ K}$ and $T = 993.5\text{ K}$, 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 $T = 936\text{ K}$

	1	2	3	4
P kbar	$\frac{dB}{dP}$	B kbar	$\frac{d}{dP} \left(\frac{dB}{dP} \right)$ kbar ⁻¹	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 $T = 993.5\text{ K}$

	1	2	3	4	5
P	$\frac{dB}{dP}$	B	$\frac{d}{dP} \left(\frac{dB}{dP} \right)$	B_v	v_f
kbar		kbar	kbar ⁻¹	kbar	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 $v_f = 95.44\text{ Å}^3 \approx 4\Omega$ is in good agreement with the experimental value [11] : $v_f \approx 4.4\Omega$ (we used the approximation $h_0 \approx h = 2.44\text{ eV}$ [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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