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Correlation of the individual vacancy-formation parameters in NaCl

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By using the thermodynamic defect parameters (i.e., the entropies s^i and the enthalpies h^i) just determined for NaCl we show that the quantity s^i/h^i is practically the same for the following three defect formation processes: cation vacancy, anion vacancy, and Schottky defect formation. The value of the quantity s^i/h^i is comparable to the value predicted by a model presented earlier by Varotsos and Alexopoulos.

Harris and Fiasson[1] have shown that experimental values of the surface potential measured on freshly cleaved surfaces of NaCl single crystals varied with temperature in a manner predicted by defect theory, the main difference being the presence of an additional charge on surface irregularities. They also presented equations for the surface potential derived from defect theory and indicated that measurements of isoelectric temperatures (i.e., temperatures at which the surface potential becomes zero) on crystal surfaces can provide an independent determination of the individual Gibbs energies g^f_- and g^f_+ for the formation of an anion vacancy and a cation vacancy, respectively. Harris[2] has just published such a determination for the case of NaCl and reported the following values:

$$h^f_+ = 1.15 \text{ eV}, \quad s^f_+ = 4.1k \ ,$$

$$h^f_- = 1.29 \text{ eV}, \quad s^f_- = 5.7k \ .$$

The symbols h^f_+ and h^f_- stand for the formation enthalpies of a cation vacancy and anion vacancy, respectively, whereas s^f_+ and s^f_- denote the corresponding formation entropies; the symbol k stands for the Boltzmann constant.

In a recent review, Varotsos and Alexopoulos[3] have suggested that the entropy s^i and the enthalpy h^i for a defect (formation *or* migration) process are *not* independent but obey the following rule: the quantity s^i/h^i depends only on bulk quantities and hence should be the same for various defect processes. More precisely they suggested the relation[3]

$$\frac{s^i}{h^i} = -\frac{\beta B + (dB/dT)\,|_P}{B - T\beta B - T(dB/dT)\,|_P} \ , \tag{1}$$

where β denotes the thermal volume expansion coefficient and B denotes the isothermal bulk modulus.

It is the scope of the present paper to check whether this suggestion of Varotsos and Alexopoulos holds also for the individual anion and cation vacancy-formation parameters just determined for NaCl. It is also worthwhile to carry out this check in view of the fact that Yamamoto, Ohno, and Anderson[4] have just published elasticity data for NaCl.

In view of the fact that $T\beta \ll 1$, Eq. (1) simplifies to

$$\frac{s^i}{h^i} = -\frac{\beta B + (dB/dT)\,|_P}{B - T(dB/dT)\,|_P} \ . \tag{2}$$

The two highest temperatures of the elastic data of Yamamoto *et al.* are $T = 745$ and 766 K. For these temperatures they reported the values $B = 165.6$ and 162.3 kbar, respectively, and hence $(dB/dT)\,|_P \simeq -0.152$ kbar/K. Furthermore, the data for Enck and Dommel[5] give, for $T = 766$ K, the value $\beta = 1.676 \times 10^{-4}$ K^{-1}. By inserting these data into the right-hand side of Eq. (2) we find, for $T = 766$ K, the value

TABLE I. Various defect-formation processes in NaCl.

	h^f eV	s^f k units	s^f/h^f 10^{-4} K^{-1}
Cation vacancy	1.15[a]	4.1[a]	3.1
Anion vacancy	1.29[a]	5.7[a]	3.8
Schottky (i.e., anion plus cation vacancy) process	2.44[b]	9.8[b]	3.5

[a] Reference 2.
[b] Reference 8.

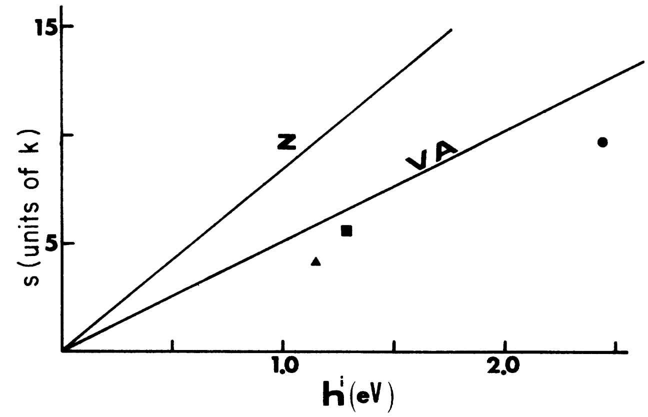

FIG. 1. Defect-formation enthalpies and entropies in NaCl: ●, Schottky formation; ■, anion vacancy formation; ▲, cation vacancy formation. The line labeled VA corresponds to the model of Varotsos and Alexopoulos [see Eq. (2)], whereas the line Z corresponds to the Zener's model [see Eq. (4)].

$$-\frac{\beta B+(dB/dT)|_P}{B-T(dB/dT)|_P}\simeq 4.5\times 10^{-4}\ \mathrm{K}^{-1}\ . \tag{3}$$

In Table I we have collected the values of the enthalpies and entropies that correspond to the following three formation processes of NaCl: cation vacancy, anion vacancy, and Schottky defect formation. We see that for these three processes the quantity s^i/h^i is practically the same if one also considers the experimental error. Furthermore, we note that the experimental value of the quantity s^i/h^i is only 15–30% lower than the aforementioned value predicted from the model of Varotsos and Alexopoulos (see also Fig. 1).

We proceed now to a comparison of the experimental data of Table I with the prediction of a model suggested long ago by Zener.[6,7] According to this model, the quantity s^i/h^i is given by

$$\frac{s^i}{h^i}=-\beta-\left.\frac{d\ln\mu}{dT}\right|_P , \tag{4}$$

where μ denotes the shear modulus. By using the two highest temperatures of the elasticity data of Yamamoto *et al.*, we find $(d\mu/dT)\simeq -9.5\times 10^{-2}$ kbar/K, whereas the μ value, for $T=766$ K, is 106.5 kbar. Therefore, the right-hand side of Eq. (4) is found to be

$$-\left\{\beta+\left.\frac{d\ln\mu}{dT}\right|_P\right\}\simeq 7.3\times 10^{-4} ,$$

which exceeds the experimental values of the quantity s^i/h^i (see Table I) by a factor of 2.

The recent experiment of Harris[2] indicates that the quantity s^i/h^i is practically the same for the three defect-formation processes in NaCl, i.e., anion vacancy, cation vacancy, and Schottky defect formation. The value of the quantity s/h^i agrees (within 15–30%) with the model of Varotsos and Alexopoulos. On the other hand, Zener's model deviates from the experimental values by a factor of around 2.

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