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THE TRUE AND THE EXPERIMENTAL ENTROPY VALUES OF VACANCIES

P. VAROTSOS and K. ALEXOPOULOS

Department of Physics, University of Athens, Solonos Str. 104, Athens 114, Greece

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Résumé. — L'enthalpie et l'entropie de formation d'un défaut de Schottky dépendent de la température à cause des effets anharmoniques. Pour cette raison les valeurs expérimentales des paramètres obtenus à haute température ne coïncident pas avec les valeurs réelles. Dans le cas de NaCl, la valeur expérimentale de l'enthalpie dépasse de 7% la valeur réelle au zéro absolu. En ce qui concerne l'entropie expérimentale elle n'est pas égale à la valeur réelle. La différence est due à un terme qui dépend de la dérivée par rapport à la température de l'enthalpie. Le calcul montre que la valeur expérimentale doit être 13 K en accord suffisant avec les valeurs publiées.

Abstract. — The formation enthalpy and entropy of a Schottky defect in alkali halides depend on temperature due to anharmonic effects. Thus the experimental values of these parameters obtained at high temperatures do not coincide with the true ones. In the case of NaCl the experimental value of the formation enthalpy exceeds by 7% the real formation enthalpy at absolute zero. The experimental value of the formation entropy is different from the true value. This is due to a term that depends on the temperature derivative of the formation enthalpy. The calculation shows that the experimental value should be 13 K in adequate agreement with the published values.

In a former paper [1] we indicated a method for calculating h/h_0 and s/s_0 from elastic constants of materials with bulk moduli B falling linearly with temperature. h and s are the enthalpy and the entropy for the formation of vacancies and the subscript zero indicates values at $T = 0$. The method disregarded the entropy s_{vib} due to the change of frequency of the vibrators surrounding the vacancy. The influence of expansivity was investigated separately [2]. Taking both effects into consideration one obtains

$$\begin{aligned} \frac{h}{h_0} &= \frac{b}{B_0} \left(B - T\beta B - T \frac{dB}{dT} \right); \\ \frac{s}{s_0} &= \frac{b}{B_0} \beta B + \frac{dB}{dT} + \frac{s_{\text{vib}}}{h_0} \end{aligned} \tag{1}$$

where β is the bulk thermal expansivity and

$$b = \exp \int_0^T \beta \, dT.$$

Although both parameters h and s change with temperature, in the analysis of conductivity or diffusion experiments they are assumed to be constants and are labelled as h_{exp} and s_{exp} . The present letter will compare

these parameters for NaCl with the values of h and s in the region where experiments are usually carried out.

Using published data for the bulk modulus [3] and expansivity [4] we have calculated and plotted in figure 1 h/h_0 and $(s - s_{\text{vib}})/h_0$ as a function of temperature. We have refrained from giving s/h_0 directly because s_{vib} can only be calculated in the approximation of an Einstein model [5]. We note that the bulk

FIG. 1. — Temperature dependence of formation parameters for NaCl.

modulus has only been measured up to 700 K. In this region it falls linearly with temperature ; we assume that it continues in the same way up to 1 073 K thus fulfilling the condition for the validity of eqs. (1).

The following simple numerical expressions fit these plots in the region 750 to 1 073 K

$$h/h_0 = AT + \Gamma \quad (2)$$

and

$$(s - s_{\text{vib}})/h_0 = E + \Delta/T \quad (3)$$

where

$$A = 8.33 \times 10^{-5} \text{ K}^{-1}, \quad \Gamma = 1.0047$$

$$\Delta = -704/11\,600 \quad \text{and} \quad E = 4.94/11\,600 \text{ K}^{-1}.$$

These forms of the equations are thermodynamically incompatible but they fit the plots with an accuracy of 1% for h/h_0 and 2.5% for $(s - s_{\text{vib}})/h_0$. From eqs. (2) and (3) we get for the Gibbs free energy

$$g = h_0(\Gamma - \Delta) - T(h_0 E - h_0 A + s_{\text{vib}}).$$

As the experimental results for intrinsic effects are obtained from the temperature region under consideration, one obtains :

$$h_{\text{exp}} = h_0(\Gamma - \Delta) \quad (4)$$

and

$$s_{\text{exp}} = h_0(E - A) + s_{\text{vib}}. \quad (5)$$

Inserting into eq. (4) the value [6] $h_{\text{exp}} = 2.44 \text{ eV}$ one gets $h_0 = 2.29 \text{ eV}$. We see that the experimental value from high temperature experiments is larger than h_0 by 6.5%. This difference has been noticed when h_0 is calculated from first principles [7].

Accepting the value of h_0 as determined above, and the approximation [5] $s_{\text{vib}} = 4.16 \text{ K}$ one can proceed to the application of eq. (5). The calculation gives $s_{\text{exp}} = 13.2 \text{ K}$ which agrees adequately with the published values [6, 8, 9] between 9 K and 13 K. By comparing eqs. (3) and (5) one sees that at high temperatures the difference $s - s_{\text{exp}}$ is essentially equal to $h_0 A$ where A is the temperature derivative of h .

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