# Comments on the formation entropy of a Frenkel defect in $BaF_2$ and $CaF_2$

P. Varotsos

*Department of Physics, University of Athens, Solonos Street, 104, Athens 144, Greece*

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The entropy for the formation of a Frenkel defect in alkaline-earth halides has been estimated using the defect's formation enthalpy and the temperature variation of the crystal's bulk modulus. The values obtained for $BaF_2$ and $CaF_2$ are in good agreement with the experimental results.

Several of the alkaline-earth halides such as $CaF_2$, $SrF_2$, $BaF_2$, and $SrCl_2$ have been studied fairly extensively. It has become customary to interpret their point-defect-controlled behavior of anion Frenkel defects as the overwhelmingly[1] predominant defects. In this paper we attempt an estimation of the formation entropy $S_F^F$ of a Frenkel defect using the formation enthalpy $h_F^F$ and the temperature variation of the bulk modulus $B$.

We assume that the formation of a Frenkel defect causes a uniform dilatation of the crystal. Thus, the corresponding free energy $g_F^F$ must be proportional to the bulk modulus[2]

$$g_F^F = aB, \qquad (1)$$

where the coefficient $a$ depends[2] on (i) the dilatation value and (ii) the "formation volume"[3,4] of the Frenkel defect.

At absolute zero, Eq. (1) gives

$$h_F^F = a_0 B_0, \qquad (2)$$

where $a_0$ and $B_0$ are the corresponding values at $T = 0$.

By differentiating Eq. (1) we have

$$-S_F^F = \frac{\partial g_F^F}{\partial T} = a\frac{\partial B}{\partial T} + \frac{\partial a}{\partial T}B. \qquad (3)$$

By ignoring[5] the temperature variation of the lattice parameter, i.e., $a\,\partial B/\partial T \gg (\partial a/\partial T)B$ and $a \simeq a_0$, Eq. (3) gives

$$S_F^F = -a_0\frac{\partial B}{\partial T}. \qquad (4)$$

A combination of Eqs. (2) and (4) gives

$$S_F^F = -\frac{h_F^F}{B_0}\frac{\partial B}{\partial T}. \qquad (5)$$

Experiments show that at low temperatures the slope $\partial B/\partial T$ is not constant, i.e., as it was expected $\partial B/\partial T \to 0$ when $T \to 0$. At higher temperatures Gerlich's measurements[6] show that the elastic constants $C_{11}$ and $C_{12}$ are decreasing linearly as the temperature is increasing and thus $\partial B/\partial T$ may be assumed as constant.

In the case of $BaF_2$ we have $h_F^F = 1.9$ eV,[7] $B_0 = 0.626$ erg/cm$^3$,[6,8] $\partial B/\partial T = 9.125\times10^{-4}$ erg cm$^{-3}$ K$^{-1}$.[6] Inserting the above values in Eq. (5) we find $S_F^F = 10.7k$. Also applying Eq. (5) in $CaF_2$ we find $S_F^F = 12k$. The above values obtained in both cases $BaF_2$ and $CaF_2$ are in good agreement with the experimental results.[7,9]

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