On the formation energy of Schottky defects in MgO

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Abstract- The formation entropy for Schotkky vacancies in magnesium oxide has been estimated for low and high temperatures, by using a recent value of the formation enthalpy and with the aid of a thermodynamic model which interrelates point defect parameters with bulk properties. Our calculated values obtained from macroscopic data, are comparable with recent theoretical results derived from detailed, microscopic calculations.

Index Terms- Schottky formation entropy, formation enthalpy, MgO , bulk modulus, thermal expansion coefficient, defect, thermodynamic model.

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1 INTRODUCTION

STUDIES on mass transport mechanisms in magnesium oxide have been extensively deployed and a sizeable portion of literature on experimental and theoretical results of diffusion processes and defect parameters is available [1], [2], [3], [4]. Among various theoretical approaches, studies of absolute diffusion rates showed in many cases a good agreement with experiments [5] although a scatter of orders of magnitude in between different experimental results has been observed [3], [6]. Recently, formation energies and entropies of Schottky defects in MgO by means of total energy and phonon calculations in supercell configurations have been estimated by Runevall and Sandberg [7].

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Here we propose an alternative theormodynamic model for the calculation of formation entropy of Schottky defects in MgO which interrelates bulk properties with defect parameters and we compare our findings to recent theoretical results.

2 THE THERMODYNAMIC MODEL

Defect parameters can be directly estimated by means of a thermodynamic model, termed as cBΩ model, which interrelates the Gibbs energy g^i with the isothermal bulk modulus B according to the formula [8], [9], [10], [11]

$$g^i = c^i \, B\Omega \qquad (1)$$

where the superscript 'i' refers to the different process mechanism, (formation, migration and activation), Ω is the mean atomic volume per atom and c^i is a dimensionless constant which can be considered as independent of temperature and pressure. This model has many successful applications such as in alkali and silver halides [12], in diamond [13], in fluorine superionic semiconductors [14], as well as in the case of seismic electric signals (SES) detected prior to large earthquakes [15], [16], [17], [18], [19], [20], [21].

The formation entropy s^f is obtained by inserting (1) into the relation $s^f = - (dg^f/dT)_P$ which leads to :

$$s^f = -c^f \Omega \left[\beta B + \frac{\partial B}{\partial T} \Big|_P \right] \qquad (2)$$

where β stands for the volume thermal expansion coefficient and T for the temperature. From the thermodynamic formula $h^f = g^f - T \, (dg^f/dT)_P$ and (1) the formation enthalpy h^f is given as:

$$h^{\mathrm{f}} = c^{\mathrm{f}} \Omega \left[B - T\beta B - T \frac{\partial B}{\partial T} \Big|_{P} \right] \tag{3}$$

Combining now (2) and (3) the formation entropy can be calculated through the formula:

$$s^{\mathrm{f}} = - \frac{\beta B + \dfrac{\partial B}{\partial T} \Big|_{P}}{B - T\beta B - T \dfrac{\partial B}{\partial T} \Big|_{P}} h^{\mathrm{f}} \tag{4}$$

3 DATA AND DISCUSSION

Here, we test the validity of the above thermodynamic model in the case of MgO by means of recent thermodynamic data derived from another theoretical model.

We estimate the formation entropy for Schottky vacancies first, at ambient conditions and then at temperature T =2000K and pressure P=0 GPa. We consider for the formation enthalpy h^{f} the value 5.79 eV found by Runevall and Sandberg [7] for Schottky defects by means of total energy and phonon calculations in supercell configurations. The isothermal bulk modulus and its temperature derivative dB/dT at ambient conditions are taken as B_{300}=162 GPa and (dB/dT)$_{300}$= -0.03 GPa/K while at T=2000K and P=0 GPa as B_{2000}=111 GPa and (dB/dT)$_{2000}$= -0.304 GPa/K respectively, (Table 6 of Sushil [22]). As far for the volume thermal expansion coefficient at T=300K and T=2000K we consider the values β_{300}=3.17x10^{-5} K^{-1} and β_{2000}=5.48x10^{-5} K^{-1} (Table 5 of of Sushil [22]). Inserting all the appropriate values in (4) we find for the formation entropy for Schottky defects, at room conditions, s^{f}_{300} =

(9.85 ± 0.05)k, which is more or less comparable with the calculated one 7.29k by Runevall and Sandberg [7]. Both these calculated values of the formation entropy are high compared to that in non ionic materials, as expected [11].

Next, we proceed to the estimation of the formation entropy s^{f}_{2000} at T=2000K. Applying (2) for T =300K and 2000K respectively, we get the ratio R as:

$$R = \frac{s^{\mathrm{f}}_{2000}}{s^{\mathrm{f}}_{300}} = \frac{\Omega_{2000}(\beta_{2000} B_{2000} + \frac{\mathrm{d}B}{\mathrm{d}T} 2000|_{P})}{\Omega_{300}(\beta_{300} B_{300} + \frac{\mathrm{d}B}{\mathrm{d}T} 300|_{P})} \tag{5}$$

where the value $\Omega_{2000}/\Omega_{300}$= V_{2000}/V_{300}=1.0801 at P=0 GPa is taken from Table 2 of Sushil [22]. The derived formation entropy has a somewhat of higher value, i.e., s^{f}_{2000} =(10.41 ± 0.05)k. Such a value is not unreasonable if we consider that in typical ionic crystals like NaCl, KCl, the s^{f} values for a Schottky defect is close to 10k (see [11], pp 288).

4 CONCLUSION

The formation entropy for Schottky defects in MgO has been estimated, for low and high temperature, by using a recent value of the formation enthalpy and with the aid of a thermodynamic model which interrelates bulk properties with defect parameters. Although our results are derived following a simple macroscopic model, they are comparable with recent theoretical values obtained through more sophisticated microscopic calculations.

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