



Applying the $cB\Omega$ thermodynamical model to LiF using its equation of state obtained from high pressure diamond anvil cell measurements

Efthimios S. Skordas*, Nicholas V. Sarlis, Panayiotis A. Varotsos

Section of Condensed Matter Physics, Department of Physics, National and Kapodistrian University of Athens, Panepistimiopolis, Zografos 157 84, Athens, Greece
Solid Earth Physics Institute, Department of Physics, National and Kapodistrian University of Athens, Panepistimiopolis, Zografos 157 84, Athens, Greece

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ABSTRACT

High pressure experiments using diamond anvil cells with a quasi-hydrostatic pressure transmitting medium (helium or neon) and coupled with X-ray diffraction have very recently been reviewed and provided equations of state parameters with a unified pressure metrology for all data. Focusing on such an equation of state for LiF, which is a unique crystal possessing the largest reported band gap of any material, here we show that a thermodynamical model, termed $cB\Omega$ model, satisfactorily describes the way that the point defect parameters, for various defect processes, are interrelated with bulk properties of the matrix material.

1. Introduction

Lithium fluoride (LiF) is a unique crystal exhibiting the largest reported band gap of any material. It is believed that remains transparent to visible light under stresses in excess of 1000 GPa [1]. Dynamic compression experiments have utilized LiF as an optical window to maintain high stress on a material boundary [2,3] since nearly 50 years. Despite its importance, the high-pressure static compression behavior of LiF has been determined before 2014 only up to 9 GPa under hydrostatic conditions [4] and approximately 30 GPa under non-hydrostatic compression [5]. Several measurements reported the zero-pressure bulk modulus of LiF using ultrasonic methods and Brillouin spectroscopy [6,7]. An average of 10 independent elasticity measurements after 1960 yielded $B = 66.2 \pm 1.5$ GPa (cf. the measured adiabatic bulk moduli have been corrected to give an average isothermal value), but the reported values of the pressure derivative of the bulk modulus spanned a wide range from 3.6 to 5.4 [4,5,8–15].

In 2014, the equation of state and compression behavior of LiF have been determined to 92 GPa by X-ray diffraction in a diamond anvil cell [16], which has become the primary tool for high-pressure research in the areas of physics, earth and planetary sciences, chemistry, and materials sciences (e.g., [17]). A neon pressure-transmitting medium was used to minimize the effect of differential stress on the sample and consistent results using multiple pressure standards were obtained. In addition, an independent very recent study [18] reported the equation of state of simple solids (including LiF, NaCl and Pb) measured under

ambient temperature in Mbar range focusing on experiments using diamond anvils cells with a quasi-hydrostatic pressure transmitting medium (helium or neon) and coupled with X-ray diffraction. Equation of state parameters has been listed with a unified pressure metrology for all data and the experimental methods were similar for all measurements.

It is the scope of this paper to study the applicability of the thermodynamical model termed $cB\Omega$ model (explained in the next section) by using the equation of state of LiF that has very recently been obtained by the aforementioned high-pressure diamond anvil cell measurements. The model under discussion has the following privilege: The thermodynamic parameters of point defects can be explicitly expressed through the bulk properties of the solid.

2. The thermodynamical model, termed $cB\Omega$ model. Background

The dielectric constant [19] as well as the formation Gibbs energy, g^f , and the migration Gibbs energy, g^m , vary upon changing the pressure (P). The entropy for the defect formation process (s^f) and the defect migration process (s^m), as well as the volumes for the defect formation process (v^f) and the defect migration process (v^m) are given by [20]:

$$\begin{aligned} s^f &= - \left. \frac{dg^f}{dT} \right|_P \quad \text{and} \quad s^m = - \left. \frac{dg^m}{dT} \right|_P \\ v^f &= \left. \frac{dg^f}{dP} \right|_T \quad \text{and} \quad v^m = \left. \frac{dg^m}{dP} \right|_T \end{aligned} \quad (1)$$

* Corresponding author at: Section of Condensed Matter Physics, Department of Physics, National and Kapodistrian University of Athens, Panepistimiopolis, Zografos 157 84, Athens, Greece.

E-mail addresses: eskordas@phys.uoa.gr (E.S. Skordas), nsarlis@phys.uoa.gr (N.V. Sarlis), pvaro@otenet.gr (P.A. Varotsos).

When both, i.e., the defect formation (f) and the defect migration (m) processes, are operating, an activation Gibbs energy g^{act} is employed, the temperature and the pressure derivative of which lead to the introduction of an activation entropy s^{act} and an activation volume v^{act} , respectively, as follows:

$$s^{act} = - \left. \frac{dg^{act}}{dT} \right|_P \quad \text{and} \quad v^{act} = \left. \frac{dg^{act}}{dP} \right|_T \quad (2)$$

When an aliovalent impurity attracts an adjacent bound (b) vacancy (v) or interstitial, the (re)orientation of the resulting electric dipoles is described with an activation energy g_b^{act} , associated with an activation volume $v_b^m \equiv (dg_b^m/dP)_T$. The relevant entropy and enthalpy for the bound vacancy motion are then designated by s_{bv}^m and h_{bv}^m , respectively. This mechanism explains [21,22] the generation of electric signals precursory of earthquakes [23–25], which appear when the stress before an earthquake attains a critical value [26–28].

The $cB\Omega$ model suggests the following: The defect Gibbs energy g^i , where i refers to the operating process, i.e., $i = f, m$ or act for the defect formation, migration and activation, respectively, can be expressed as: [20,29].

$$g^i = c^i B \Omega \quad (3)$$

where B is the isothermal bulk modulus of the matrix material, Ω stands for the mean volume per atom and c^i is approximately independent of temperature and pressure. The volume $v^i \equiv (dg^i/dP)_T$ resulting from Eq. (3) is found to be:

$$v^i = c^i \Omega \left(\left. \frac{dB}{dP} \right|_T - 1 \right) \quad (4)$$

which can be rewritten as:

$$v^i = \frac{g^i}{B} \left(\left. \frac{dB}{dP} \right|_T - 1 \right) \quad (5)$$

or

$$\frac{v^i}{g^i} = \frac{1}{B} \left(\left. \frac{dB}{dP} \right|_T - 1 \right) \quad (6)$$

The entropy $s^i = - (dg^i/dT)_T$ is found by differentiating Eq. (3) in respect to temperature and inserting it into the relation $h^i = g^i + Ts^i$ we finally get the enthalpy h^i [20].

Eq. (6) suggests that the ratio v^i/g^i is the same for various defect processes in the same matrix material [20,30].

This conclusion also holds for the ratio s^i/h^i [31] (the entropy, s^i , here differs from the dynamic entropy S defined in natural time [32]).

Beyond the recent applications to the case of silicon [33] and $\text{Si}_{1-x}\text{Ge}_x$ alloys [34–36], the $cB\Omega$ model has been earlier successfully applied to the study of various defect processes in a multitude of solids including metals [37,38] alkali halides [39,40], alkaline earth fluorides [41,42], silver halides (e.g., see Ref. [43]), fluoride superionic conductors, e.g., $\beta - \text{PbF}_2$ [30], in a variety of oxides, for example, in UO_2 and ThO_2 which are useful for nuclear fuel applications [44,45], in anatase TiO_2 [46], in Li_5FeO_4 [47] and Li_2CuO_2 [48] that are candidate materials as cathode in lithium ion batteries and in $\text{Na}_2\text{MnSiO}_4$ which is a promising positive electrode material in rechargeable sodium ion batteries [49] as well as for Si diffusing in silicates [50] and aluminum in MgO [51], oxygen self-diffusion in minerals [52,53] etc.

Remarkably, very recently [54] the $cB\Omega$ model inspired the explanation of the interconnection of the water solubility with ion diffusivity in the mantle silicates.

3. Data analysis and results

The Rydberg-Vinet equation of state of LiF in the Mbar range obtained recently by Dewaele [18] (see the third column of his Table 1) gives at $T = 300$ K: $B = 62.3$ GPa and $\left. \frac{dB}{dP} \right|_T = 5.01$ ($\Omega = 16.391 \text{ \AA}^3$).

Table 1
Defect parameters in LiF.

Process	h^i (eV)	s^i (k units)	v^i (cm^3/mol)	g^i (eV)
Free cation vacancy motions	0.75 ^a	2.3 ^a	3.2–4.0 ^a	0.69 ^c
Bound cation vacancy motions	0.66 ^b	2.3 ^c	3.2–4.0 ^c	0.62 ^c
Schottky defect formation	2.375 ^a	8.9 ^a	12.6–13.2 ^a	2.14 ^c

^a From Ref. [58].

^b From Ref. [55].

^c See the text.

Earlier, Dong et al. [16], after compression of LiF to 92 GPa, found $B = 66.2$ GPa and $\left. \frac{dB}{dP} \right|_T = 4.6 \pm 0.1$ by considering the 3rd-order Birch-Murnaghan equation of state.

McKeever and Lilley [55] have measured the thermally stimulated depolarisation currents (TSDC) and the thermally stimulated polarisation currents (TSPC) of LiF doped with Mg^{2+} . Their TSDC and TSPC curves showed a maximum (approximately around at $T_{max} = 211 \pm 3$ K) corresponding to a single relaxation process. An analysis of these results resulted in the following values [55]: $h_{bv}^m = 0.66$ eV and $\tau_0^{-1} = 1.9 \times 10^{14} \text{ s}^{-1}$ of the parameters τ_0 , h_{bv}^m in the Arrhenius relation:

$$\tau = \tau_0 \exp(h_{bv}^m/kT) \quad (7)$$

where h_{bv}^m is the enthalpy for the bound cation vacancy motion and τ_0 is the usual pre-exponential factor.

Following Ref. [41], the quantity s_{bv}^m for the bound vacancy motion in the (re)orientation process of the dipole ‘ Mg^{2+} -cation vacancy’ is estimated from

$$s_{bv}^m = k \ln(\tau_0^{-1}/2\nu) \quad (8)$$

where k is Boltzmann's constant, ν is the frequency of the (moving) ion vibrating in the direction of the potential barrier. Assuming to a first approximation [56] that $\nu = \nu_{TO}(k \rightarrow 0)$ where ν_{TO} is the frequency at very long wavelengths of the transverse optical mode, and inserting into Eq. (8) the values $\nu_{TO} = 0.92 \times 10^{13} \text{ s}^{-1}$ [57] and $\tau_0^{-1} = 1.9 \times 10^{14} \text{ s}^{-1}$, we find $s_{bv}^m = 2.3k$.

Since both parameters $h_{bv}^m = 0.66 \text{ eV}$ and $s_{bv}^m = 2.3k$ are now known, the g_{bv}^m value can be obtained by means of $g_{bv}^m = h_{bv}^m - Ts_{bv}^m$ at any temperature. Hence, at $T = T_{max} = 211$ K we find $g_{bv}^m = 0.62$ eV. The aforementioned value $s_{bv}^m = 2.3k$ is comparable to the value $s^m = 2.3k$ for the free cation vacancy motion obtained from the measurements in Ref. [58], which also resulted in $h^m = 0.75$ eV leading to $g^m = 0.69$ eV at $T = 300$ K for the cation vacancy motion.

Concerning the Schottky defect formation process, Lallemand [58] found the following values: $h^f = 2.37$ eV and $s^f = 8.9k$ which lead to $g^f = 2.14$ eV at $T = 300$ K. The experimental values for the defect volumes determined also in Ref. [58] are $v^f = (12.6\text{--}13.2) \text{ cm}^3/\text{mole}$ and $v^m = (3.2\text{--}4.0) \text{ cm}^3/\text{mole}$ for the cation vacancy migration process, thus the corresponding $\frac{v^i}{g^i}$ values are

$$\frac{v^f}{g^f} = (5.9 - 6.2) \times 10^{-2} \text{ GPa}^{-1} \quad (9)$$

and

$$\frac{v^m}{g^m} = (4.6 - 5.8) \times 10^{-2} \text{ GPa}^{-1} \quad (10)$$

for these two defect processes, respectively.

Furthermore, if we assume that the defect migration volume v_{bv}^m for the bound cation vacancy motion is approximately equal [20] to that of the free cation vacancy motion we find

$$\frac{v_{bv}^m}{g_{bv}^m} = (5.2 - 6.5) \times 10^{-2} \text{ GPa}^{-1} \quad (11)$$

According to the $cB\Omega$ model, see Eq. (6), the ratio $\frac{v^i}{g^i}$ should be equal

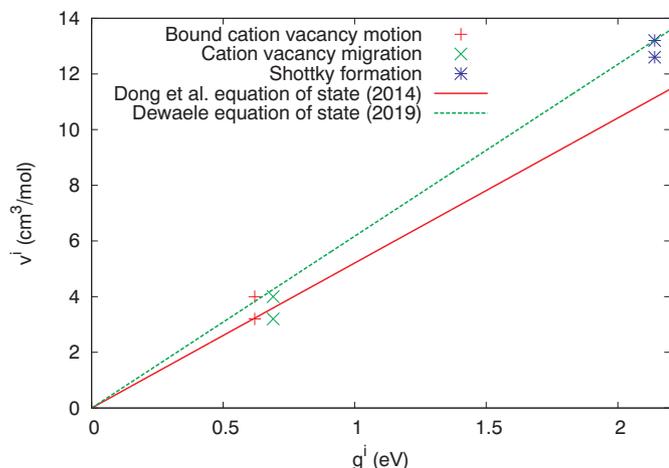


Fig. 1. The experimental values of the defect volumes v^j in LiF versus the defect Gibbs energy g^j for the following processes: Schottky defect formation (blue asterisks), free cation vacancy migration (green crosses), and bound cation vacancy motion (red pluses). The green broken straight line corresponds to the theoretical prediction for the $\frac{v^j}{g^j}$ of the $cB\Omega$ model (see Eq. (6)) using the equation of state deduced from the measurements reported in Ref. [18] while the red solid line from the measurements in Ref. [16]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

to $\frac{1}{B} \left(\frac{dB}{dP} \Big|_T - 1 \right)$ irrespective of the defect processes. By considering the values $B = 62.3$ GPa and $\frac{dB}{dP} \Big|_T = 5.01$ reported in the third column of Table 1 of Dewaele [18], as mentioned, we find

$$\frac{1}{B} \left(\frac{dB}{dP} \Big|_T - 1 \right) = 6.4 \times 10^{-2} \text{GPa}^{-1} \quad (12)$$

By the same token, the values $B = 66.2$ GPa and $\frac{dB}{dP} \Big|_T = 4.6$ obtained by Dong et al. [16] lead to

$$\frac{1}{B} \left(\frac{dB}{dP} \Big|_T - 1 \right) = 5.4 \times 10^{-2} \text{GPa}^{-1} \quad (13)$$

To visualize the extent of the agreement between the experimental $\frac{v^j}{g^j}$ values and the bulk quantity $\frac{1}{B} \left(\frac{dB}{dP} \Big|_T - 1 \right)$ predicted by the $cB\Omega$ model, we plot in Fig. 1 the v^j values versus the g^j values. In the same figure we also plot the straight lines corresponding to the predicted values $\frac{1}{B} \left(\frac{dB}{dP} \Big|_T - 1 \right)$ of the ratio $\frac{v^j}{g^j}$ from Eq. (6) deduced either from the above mentioned measurements by Dewaele [18] (broken green straight line) or by Dong et al. [16] (red straight line). An inspection of Fig. 1 reveals that for all three defect processes, the experimental results of $\frac{v^j}{g^j}$ agree with those deduced from the $cB\Omega$ model. Specifically, a more detailed inspection of Fig. 1 reveals that these experimental results of $\frac{v^j}{g^j}$ lie closer to the broken green straight line which interestingly corresponds to the latest equation of state obtained in the Mbar range that just appeared in the literature in Ref. [18]. Furthermore, we note that the positive $\frac{v^j}{g^j}$ value deduced from the $cB\Omega$ model also reveals [20] that the self-diffusion coefficients in LiF decrease upon increasing the hydrostatic pressure.

4. Conclusion

Here, we considered the most recent equation of state of LiF deduced from the very recent measurements by Dewaele [18] in the Mbar range at ambient temperature using diamond anvil cell with a quasi-hydrostatic pressure transmitting medium (helium) and coupled with X-

ray diffraction. In the light of this equation of state, we showed that the thermodynamic parameters obtained for three different defect processes in LiF (which is a unique crystal possessing the largest reported band gap of any material) satisfactorily obey the behavior predicted by the thermodynamical $cB\Omega$ model.

In other words, here we found that the thermodynamical $cB\Omega$ model conforms to the experimental results of various defect processes operating in a unique crystal, i.e., LiF, by using the most recent equation of state parameters [18] deduced from the highest pressure measurements available to date.

Author statement

Conceptualization, E.S.S., and P.A.V.; methodology, E.S.S., N.V.S., and P.A.V.; software, E.S.S.; validation, N.V.S., and P.A.V.; formal analysis, E.S.S., N.V.S., and P.A.V.; investigation, E.S.S., N.V.S., and P.A.V.; resources, E.S.S., N.V.S., and P.A.V.; data curation, E.S.S. and N.V.S.; writing-original draft preparation, E.S.S. and P.A.V.; writing-review and editing, E.S.S., N.V.S., and P.A.V.; supervision, P.A.V.

Declaration of competing interest

All authors declare no conflict of interest.

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