MIGRATION ENTHALPY OF THE CATION VACANCIES IN LiF:Be^{2+}

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Abstract—The energy parameters (h_m, τ_0) of the cation vacancies in the LiF:Be^{2+} system were measured using three experimental techniques involving measurements of (a) depolarization currents (DC); (b) dielectric loss (DL); and (c) ionic conductivity (IC). All the methods gave consistent results. Values of h_m in the range 0.60–0.68 eV were determined in agreement with recently reported TSDC (thermally stimulated depolarization currents) measurements. Our results might not be considered in accordance with a previous suggestion based on experimental findings that h_m increases as the ionic radius of the divalent impurity decreases.

1. INTRODUCTION

LiF, a material of considerable technological importance [1] has been the subject of many recent investigations mainly because of its high ionic conductivity (σ) at temperatures close to the melting point [2, 3]. At low temperatures ("extrinsic" region) σ depends on the kinds of added impurities and their concentration [4–6]. When positively charged divalent impurities are introduced in LiF they substitute for Li$^+$ ions leading to the formation of cation vacancies. The latter, due to their effective negative charge are attracted by the divalent impurities and form "complex dipoles". At every temperature T the number of the vacancies that remain "free" (the term "free" is used in contrast to the term "bound" used for the vacancies that participate in the dipoles) increases with T. The two kinds of vacancies have different migration enthalpies h_m. Moreover, it has been found that h_m of the "bound" vacancies decreases in LiF as the ionic radius of the divalent impurities increases [5, 6]. We should notice, however, that values of h_m found in the literature exhibit large diversities depending on the experimental technique employed. (A compelling case in point is LiF:Mg^{2+} where values of h_m ranging from 0.60 to 0.81 eV have been reported.) On the other hand, migration enthalpies of impurities with large ionic radius (for example Pb^{2+} ($R = 1.20$ Å) and Ba^{2+} ($R = 1.34$ Å) have not yet been reported.

In the present work we have made studies of the migration enthalpy h_m and the prefactor of the relaxation time τ_0 for the cation vacancies in Be^{2+}-doped LiF. To the best of our knowledge, studies of the parameters h_m and τ_0 in LiF:Be^{2+} have only once been reported so far using the TSDC method [7]. Three experimental techniques were employed here: (a) depolarization currents; (b) dielectric loss; and (c) ionic conductivity.

2. EXPERIMENTAL DETAILS

Two experimental set-ups were used to carry out the measurements. One for the depolarization currents experiment and the other for the dielectric loss and ionic conductivity experiments.

In the first case a vibrating reed electrometer (Cary 401) was used. The samples were placed between platinum electrodes in a vacuum of 10^{-3} torr. The crystals were annealed at ~ 900 K for 30 min and then quenched to room temperature. A polarization field, $E_p = 23$ kV m^{-1} was applied for 20 min at a constant temperature T between 232 and 240 K. After that the electrodes were shorted and the depolarization current as a function of time recorded.

In the second case a Boonton-Electronics Bridge (model 75c) was used operating between 5 and 500 kHz. The samples were also placed between platinum electrodes. The system was put inside a quartz tube which in turn was placed in an oven connected to a temperature controller. Measurements were taken in the range of 240–700°C.

The samples were LiF monocrystals with Be^{2+} (~ 50 ppm) as an added impurity. (They were purchased from the Crystal Growth Laboratory, University of Utah.) They were cut and prepared with typical dimensions: area $S \simeq 70$ mm^2, thickness $d = 1$–2 mm. In order to achieve good contacts between the electrodes and the samples the parallel surfaces of the latter were covered with a layer of graphite [8] painted on them. The measurements were repeated many times on every sample and were quite reproducible.

3. EXPERIMENTAL METHODS AND RESULTS

3.1. *The depolarization currents method*

According to this technique the crystal is polarized at a constant temperature T with the application of

an electric field for a time $t \gg \tau(T)$ where $\tau(T)$ is the dipoles' relaxation time at the above temperature. Then the crystal is shorted at this temperature.

The measured depolarization current obeys the relation

$$i = i_0 \exp(-t/\tau) \qquad (1)$$

from which we have

$$\ln i = \ln i_0 - \frac{t}{\tau}. \qquad (2)$$

In the graphical representation of eqn (2) we can distinguish three different parts [9]. The value of τ at a given T was extracted from the middle part of the curve ("fast depolarization") because the corresponding analysis gives values for the migration enthalpy h_m which are consistent with the results of other experimental methods for I–V dipoles. The first part of the curve ("very fast depolarization") is not observed at all the temperatures. This part is due to other types of dipoles which are not our concern in the present work. The last part of the curve ("slow depolarization") is due to the discharge of the system. The experiment is repeated at various temperatures. According to the Arrhenius relation

$$\tau = \tau_0 \exp(h_m/kT).$$

Using it in the form

$$\ln \tau = \ln \tau_0 + \frac{h_m}{k} \frac{1}{T} \qquad (3)$$

it is obvious that h_m, τ_0 could be determined from the plot of $\ln \tau$ against $1/T$.

Figure 1 corresponds to the relation (2) for the LiF:Be^{2+} system at $T = 240$ K. Figure 2 is the graphical representation of eqn (3). The determined values are:

$$h_m = (0.60 + 0.05)\,\text{eV}$$

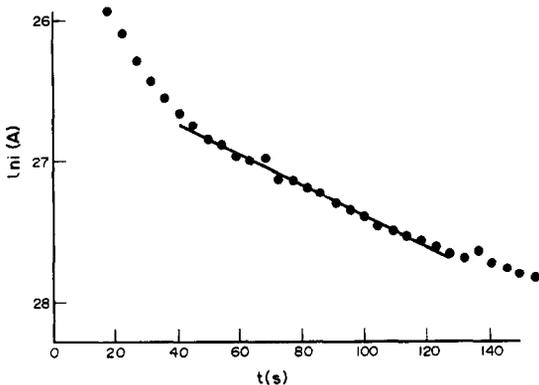$$\tau_0 = 2.05 \times 10^{-11}\,\text{s}.$$

Fig. 1. The logarithmic variation of the depolarization current as a function of time for the LiF:Be^{2+} system ($T = 240$ K).
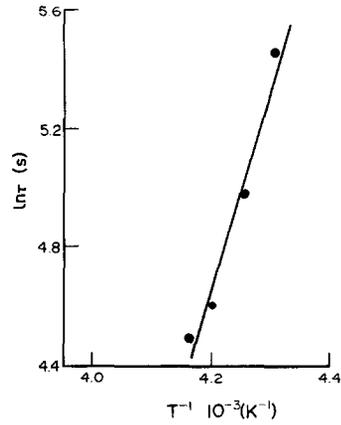

Fig. 2. Arrhenius plot for the DC technique.

The temperature range in which our results were obtained has been chosen such that the depolarization time is measurable. This range is known from previously reported ITC measurements [7].

3.2. The dielectric loss method

The dielectric constant of a crystal is in general a complex number ($\epsilon = \epsilon_1 + j\epsilon_2$). ϵ_2, the imaginary part of ϵ, is determined by the dielectric losses of the crystal. It is normally written as $\epsilon_2 = \epsilon_2' + \epsilon_2''$ to express its origin in the contribution of the "free" vacancies (ϵ_2') on the one hand and the "bound" vacancies (ϵ'') of the complex dipoles on the other. The variation of ϵ_2'' as a function of the circular frequency ω at a certain T has a maximum at ω_m which is equal to the inverse of the relaxation time of the dipoles at this temperature ($\omega_m = 1/\tau$). From the Debye equations we find

$$\epsilon_2 = \frac{\sigma_{dc}}{\epsilon_0 \omega}, \qquad (4)$$

where σ_{dc} is the d.c. conductivity and ϵ_0 the permittivity of free space. For frequencies low enough relative to ω_m the contribution of the dipoles to the dielectric constant is negligible (i.e. $e_2'' \rightarrow 0$ or $\epsilon_2 = \epsilon_2'$). Therefore, from eqn (4) we obtain

$$\epsilon_2' = \frac{\sigma_{dc}}{\epsilon_0 \omega}$$

from which

$$\log \epsilon_2' + \log \omega = \log\left(\frac{\sigma_{dc}}{\epsilon_0}\right). \qquad (5)$$

For low frequencies $\sigma_{ac} = \sigma_{dc}$ since only the free vacancies contribute to the conductivity. More specifically, σ_{dc} is constant. From eqn (5) it is clear that the plot of $\log \epsilon_2$ as a function of $\log \omega$ is linear with a slope equal to -1. For higher frequencies the above curve begins to deviate from the straight line because of the onset of the dipole contribution to the
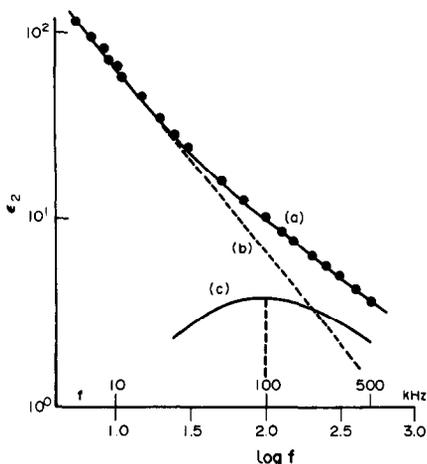
Fig. 3. Curve (a) is the plot of the imaginary part ϵ_2 of the dielectric constant against $\log f$ $(T = 720\text{ K})$. Curve (b) represents the contribution of free vacancies to ϵ_2. The net contribution of the dipoles (c) is found by the subtraction of curve (b) from (a).

Fig. 4. Arrhenius plot for the DL technique.

conductivity. At these frequencies the net contribution of the dipoles to the conductivity could be found by subtracting the straight line from the above curve. The resulting curve has a maximum at $\omega_m = 2\pi f_m$ which corresponds to the relaxation frequency of the dipoles. The experiment is repeated for various T and the corresponding f_m are determined. In this case the Arrhenius relation gives

$$\ln f_m = -\ln(2\pi\tau_0) - \frac{h_m}{k}\frac{1}{T}. \tag{6}$$

The plot of $\ln f_m$ vs $1/T$ is a straight line from which h_m and τ_0 are determined.

Figure 3 is the graphical representation of eqn (5) for LiF Be^{2+} at $T = 720$ K in the frequency range of 6–500 kHz. Figure 4 represents the plot of $\ln f_m$ against $1/T$ in the temperature range of 670–770 K. This range is specified by the frequency range of 5–500 kHz where our bridge is operated. The determined values are:

$$h_m = (0.60 \pm 0.050)\text{ eV}$$

$$\tau_0 = 1.04 \times 10^{-7}\text{ s}.$$

The width of the resulting peak [Curve (c), Fig. 3] is anomalously broad. This is presumably due to the contribution of other types of dipoles. Thus, the determined values of $\log f_m$, that is τ, contain large errors. Although this raises some doubt about the meaning of the extracted parameters, the good quantitative agreement between our values and those reported from other techniques strongly suggests that the prevailing dipoles are of the $I–V$ type.

The large error in τ leads to large scatter of the experimental points (Fig. 4). The two quantities h_m and τ_0 are not independent. We should stress at this
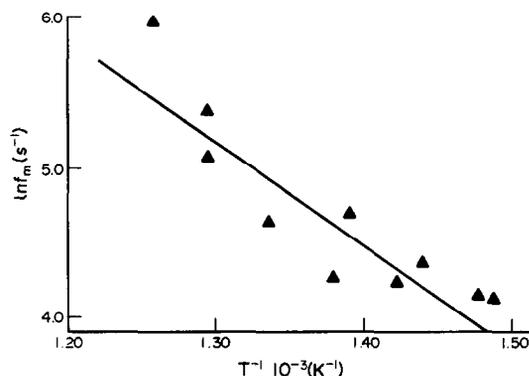
point that because of the exponential nature of relation (6) even a small error in the migration enthalpy h_m implies a much larger error in the pre-exponential factor τ_0.

3.3. The ionic conductivity method

The conductivity of ionic crystals is due to the motion of vacancies which exist for thermodynamic reasons and/or are created by added impurities in the crystal. The latter kind of vacancies prevail at low temperatures (extrinsic region). At high temperatures vacancies of the first kind dominate (intrinsic region). The ionic conductivity σ can be written [10, 11] as

$$\sigma = \frac{ne^2\alpha v l^2}{kT}\exp\left(-g_m/kT\right), \tag{7}$$

where n is the density of charge carriers, e is their charge α is a geometrical factor of order unity, v is the attempt frequency of the ion to hop over the Gibb's free-energy barrier g_m, l is the jump distance, k the Boltzmann's constant and T the absolute temperature. At low T, n is nearly constant and equal to the density of aliovalent impurities. Since $g_m = h_m - Ts_m$ eqn (7) gives

$$\ln \sigma T = \ln\left(\frac{ne^2\alpha v l^2}{k}\right) + \frac{s_m}{k} - \frac{h_m}{k}\frac{1}{T}. \tag{8}$$

The plot of $\ln \sigma T$ vs $1/T$ is linear and its slope yields h_m. It is worth noticing that when ionic conductivity measurements are taken it is necessary to work at low frequencies, in other words at a temperature range where only free cations contribute to the conductivity. At higher frequencies the measurements are affected by the contributions of the complex dipoles.

In Fig. 5, $\ln \sigma T$ vs $1/T$ is presented for LiF:Be^{2+}. Part I represents the "extrinsic" and part II the "intrinsic" region. The slope of part I gives

$$h_m = (0.68 \pm 0.03)\text{ eV}.$$

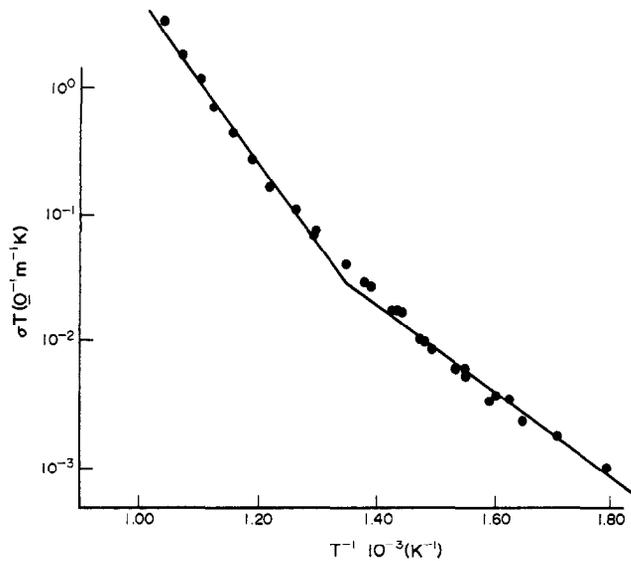The measurements were taken at the frequencies 8 and 12 kHz, which gave the same values for the conductivity.

Fig. 5. The temperature dependence of the conductivity of $LiF:Be^{2+}$.

Table 1. Migration enthalpies (h_m) of cation vacancies in $LiF:Be^{2+}$

τ_0 (s)	h_m (eV)	Experimental technique	Remarks	Ref.
1.82×10^{-12}	0.65 ± 0.04	TSDC	"Bound" vacancies	7
2.05×10^{-11}	0.60 ± 0.05	DC	"Bound" vacancies	Present work
1.04×10^{-7}	0.60 ± 0.05	DL	"Bound" vacancies	Present work
—	0.68 ± 0.03	IC	"Free" vacancies	Present work

4. DISCUSSION

Table 1 summarizes the results of our measurements and that of Ref. 7 for $LiF:Be^{2+}$. We note the consistency between the values of h_m found by the three methods TSDC, DC and DL. However, the value resulting from IC measurements is $\sim 10\%$ larger than the average value of the three other methods. This, in our opinion, is due to the fact that in the IC measurements only "free" vacancies contribute which have a different h_m from that of the bound vacancies.

In Table 2 the values of h_m for various impurities

Table 2. Migration enthalpies h_m, and prefactors τ_0 from several results and experimental methods reported in the literature

| Exp. method	Impurity	h_m (eV)	τ_0 (s)	Ref.
NMR	—	0.71	5.88×10^{-17}	12
IC	—	0.65	—	13
IC	Ti^{2+}	0.70	—	14
IC	Mg^{2+}	0.70	—	15
IC	Ca^{2+}	0.66	—	16
IC	—	0.68	—	17
IC	Be^{2+}	0.68 ± 0.03	—	Present work
DL	Mg^{2+}	0.75	3.12×10^{-15}	18
DL	Mg^{2+}	0.677	1.0×10^{-13}	19
DL	Be^{2+}	0.60 ± 0.05	1.04×10^{-7}	Present work
TSDC	Mg^{2+}	0.64	7.7×10^{-14}	5
TSDC	Ni^{2+}	0.62	9.1×10^{-14}	5
TSDC	Co^{2+}	0.61	2.8×10^{-13}	5
TSDC	Mn^{2+}	0.58	2.0×10^{-12}	5
TSDC	Cd^{2+}	0.54	1.0×10^{-11}	5
TSDC	Sr^{2+}	0.51	5.0×10^{-11}	5
TSDC	Mg^{2+}	0.86	1.0×10^{-19}	20
TCPC	Mg^{2+}	0.81	1.0×10^{-14}	21
TSDC	Mg^{2+}	0.66	1.0×10^{-14}	22
TSDC	Mg^{2+}	0.60	8.2×10^{-13}	6
TSDC	Ni^{2+}	0.60	1.3×10^{-12}	6
TSDC	Co^{2+}	0.59	1.3×10^{-12}	6
TSDC	Be^{2+}	0.65 ± 0.04	1.82×10^{-12}	7
DC	Be^{2+}	0.60 ± 0.05	2.05×10^{-11}	Present work
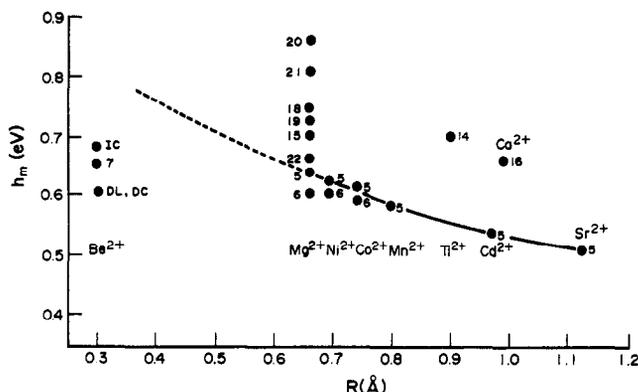
Fig. 6. The migration enthalpy h_m of the cation vacancies against the ionic radius of various divalent impurities in LiF. Numbers attached to the points indicate the corresponding references.

in LiF are cited. Data from the most significant works published to date have been collected. We remark that values of h_m attained from the IC method are independent of the kind of added impurity and are larger than those determined by the other methods. Our value of h_m determined with the IC method is in good agreement with the values reported by other authors with the same method. Figure 6 is the graphical representation of the results reported in Table 2. We observe that some impurities have been studied extensively (i.e. Mg^{2+}) while others are not reported at all in the literature (i.e. Pb^{2+}, Be^{2+}). Thus the law suggested by Laj and Bergé [5] claiming that h_m of the "bound" vacancies is decreased with the increase of the ionic radius of the added impurity may not yet be considered as well-established, even when values of h_m resulting from IC measurements are excluded. Our values of h_m from DL and DC studies seem to deviate from those predicted by the above law.

The values of τ_0 reported from these studies (see Table 1) show large divergences. This divergence can also be seen in the data reported by different authors using different experimental techniques (see Table 2).

It is worth noticing however, that our τ_0 value resulting from the DC method is within the range of most values in the literature. This cannot be claimed for the value of τ_0 from the DL method. We leave this point unanswered, although the scattering of the data of Fig. 4 for the DL method gives large errors for τ_0, which could at least partially account for the observed differences.

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