

Energy parameters of the migration of the bound cation vacancies in LiF:Ba²⁺

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LiF doped with 10⁻² mole fraction of Ba²⁺ impurity concentration was studied using two experimental techniques, namely thermally stimulated depolarization currents and depolarization currents at constant temperature. Both methods gave compatible results indicating the existence of three relaxation mechanisms. The activation enthalpies of reorientation, h_m , and the preexponential factors τ_0 were determined. The estimated parameters $h_m=0.24$ eV, and $\tau_0=6.59 \times 10^{-5}$ sec and $h_m=0.50$ eV and $\tau_0=1.78 \times 10^{-11}$ sec may be attributed, respectively, to reorientation of ion-vacancy dipoles by means of nearest-neighbor \rightarrow next-nearest-neighbor and nearest-neighbor \rightarrow nearest-neighbor jumps. A third mechanism with energy parameters $h_m=0.81$ eV and $\tau_0=4.93 \times 10^{-20}$ sec is attributed to a cluster.

I. INTRODUCTION

When a divalent impurity (M^{2+}) is introduced into an alkali halide lattice, a cation vacancy is formed (with negative electric charge), to preserve neutrality of the crystal. Because of their opposite effective charges, the divalent impurity and the cation vacancy are mutually attracted and form several kinds of dipoles, depending on their positions in the lattice. These dipoles are the nearest-neighbor (NN) type when the vacancy is the nearest neighbor to the divalent impurity and the next-nearest-neighbor and (NNN) type when the vacancy is the next nearest neighbor to the impurity.

LiF is a well-known and extensively studied material due to its technological importance.¹ A Ba²⁺-doped LiF crystal has not, to our knowledge, previously been studied. Since the Ba²⁺ ion has the largest ionic radius of all the divalent impurity metals, it is interesting to study the dependence of the migration enthalpy of the bound cation vacancies, h_m on the ionic radius.

In this paper we calculate the migration enthalpy h_m of the cation vacancies and the preexponential factor τ_0 of the Arrhenius plot of the relaxation time obtained from thermally stimulated depolarization currents (TSDC) data and depolarization current (DC) data at a constant temperature ($T = \text{const}$).

II. EXPERIMENTAL TECHNIQUES

The thermally stimulated depolarization currents method was proposed by Bucci and Fieschi^{2,3} and permits the study of dipoles which are created inside dielectrics. This method consists of applying an external electric field of intensity E_p to the crystal at a temperature T_p for a time t_p . When the crystal is cooled down to a temperature T_0 (usually the liquid-nitrogen temperature), at which the relaxation time $\tau(T_0)$ is practically infinite, the electric field is switched off and the crystal remains polarized. During a gradual increase of the temperature at a constant rate b , the relaxation time $\tau(T)$ of the dipoles decreases and the crystal is depolarized.

As the crystal is depolarized and connected to an electrometer, it gives rise to a current

$$i(T) = \frac{AP_0}{\tau_0} \exp\left[-\frac{h_m}{kT}\right] \times \exp\left[-\frac{1}{b\tau_0} \int_{T_0}^T \exp\left[-\frac{h_m}{kT'}\right] dT'\right], \quad (1)$$

where A is the end surface area of the sample, P_0 the initial polarization, h_m the migration enthalpy of the cation vacancy, k the Boltzmann constant, and τ_0 the preexponential factor of the Arrhenius relation

$$\tau = \tau_0 \exp(h_m/kT). \quad (2)$$

The curve that plots current versus temperature has a maximum at a temperature T_m , around which it appears nonsymmetrical. T_m is given by

$$T_m^2 = \frac{bh_m\tau(T_m)}{k}, \quad (3)$$

where $\tau(T_m)$ is the relaxation time at T_m . The relaxation parameters τ_0 and h_m are commonly determined by plotting $\ln i$ against T^{-1} for $T < T_m$, where $i(T) < 0.1i(T_m)$. (1) reduces to⁴

$$i(T) = \frac{AP_0}{\tau_0} \exp\left[-\frac{h_m}{kT}\right] \quad (4)$$

Another method⁴ for determining τ_0 and h_m is to use the relation

$$\tau(T) = \frac{1}{bi(T)} \int_T^{T_\infty} i(T') dT'. \quad (5)$$

By plotting $\ln \tau$ against T^{-1} we calculate τ_0 and h_m . If there are two straight lines in the plot, this indicates that we have two types of complexes or two relaxation mechanisms. In a TSDC spectrum, each relaxation process causes a current peak. Two overlapping peaks may be separated by the "peak-cleaning" technique³ and the individual mechanisms studied separately.

The depolarization current at a constant-temperature technique⁵ for determining the activation parameters of the cation vacancies is the measurement of the depolarization current after the application of an electric field. According to this technique the crystal is polarized at a constant temperature T by applying an external electric field for a time t which is much larger than $\tau(T)$, where $\tau(T)$ is the dipole relaxation time at the above temperature. Subsequently the crystal is shortcircuited at this temperature by a sensitive electrometer which measures the depolarization current. This current is given as

$$i = i_0 \exp(-t/\tau). \quad (6)$$

By varying the temperature T , the relaxation time $\tau(T)$ for different temperatures can be obtained and the values for τ_0 and h_m are then determined from Eq. (2).

III. EXPERIMENTAL DETAILS

In the experimental setup, 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 about 800 K for 45 min and then quenched to room temperature. In the TSDC method, a polarization field of $E_p = 15$ kV/cm was applied for $t_p = 5$ min at room temperature (T_p). The temperature of the sample was increased at a constant rate $b = 0.14$ K/sec. In the depolarization current at $T = \text{const}$ method the above-mentioned field strength was applied for $t_p = 20$ min at a constant temperature T_p in the range 200–230 K.

The samples were LiF single crystals having Ba^{2+} as an added impurity with a nominal concentration of 10^4 ppm. The samples were provided by the Crystal Growth Laboratory University of Utah. Typical dimensions of the samples were $1 \times 1 \times 0.2$ cm³.

IV. RESULTS

The TSDC spectrum for the $\text{LiF}:\text{Ba}^{2+}$ crystal consists of three overlapping peaks. This indicates that three activation mechanisms exist. In order to separate these peaks, we used the following peak-cleaning procedure. As the crystal is heated up at a constant rate b , starting from T_0 (the liquid-nitrogen temperature), it reaches 205 K, and at this point it is cooled down to T_0 . Therefore the a -type dipoles are already depolarized, the b -type dipoles are partly depolarized, while the c -type dipoles are not yet depolarized. Figure 1 shows the band A which, as our analysis indicates, consists of two overlapping peaks, which are due to two types of dipoles (a and b). By increasing the temperature again, at the constant rate b , the rest of the b -type and c -type dipoles are depolarized. Figure 2 shows the band B which also consists of two overlapping peaks that are due to b - and c -type dipoles. No signal was detected up to room temperature.

From relation (5) we calculate the relaxation time τ of the dipoles for several temperatures and, using the Arrhenius relation (2), we obtain the preexponential factor τ_0 and the activation enthalpies of reorientation, h_m , for each type of dipole.

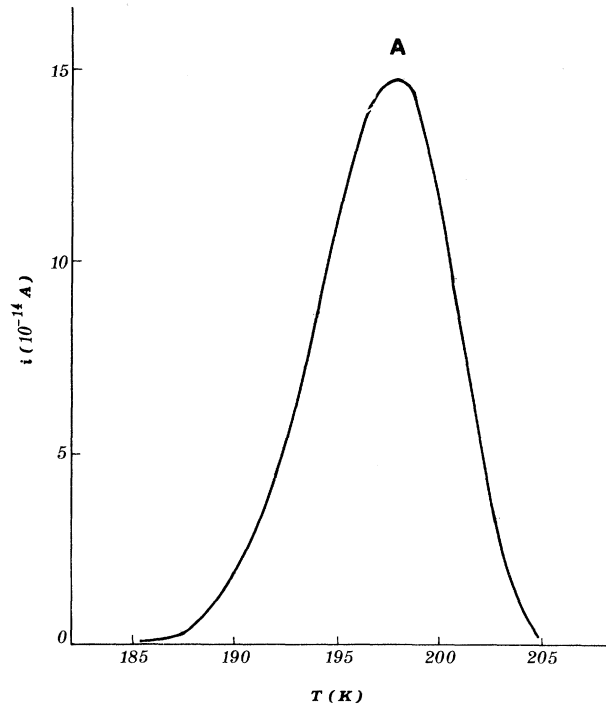


FIG. 1. The A band of the TSDC spectrum which is due to the depolarization of the a and b types of complexes.

Such a calculation for band A gives the plot $\ln \tau$ vs T^{-1} (Fig. 3). Because of the appearance of two straight lines, we conclude that we have two types of dipoles (a and b) or two relaxation mechanisms. From the first straight line [the high-temperature (HT) part] we obtain the energy parameters for the b type (Table I). The parameters of

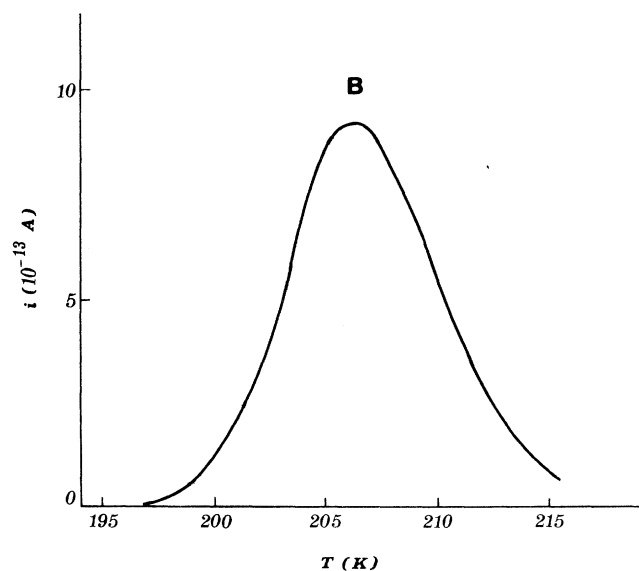


FIG. 2. The B band of the TSDC spectrum which is due to the b and c types of complexes.

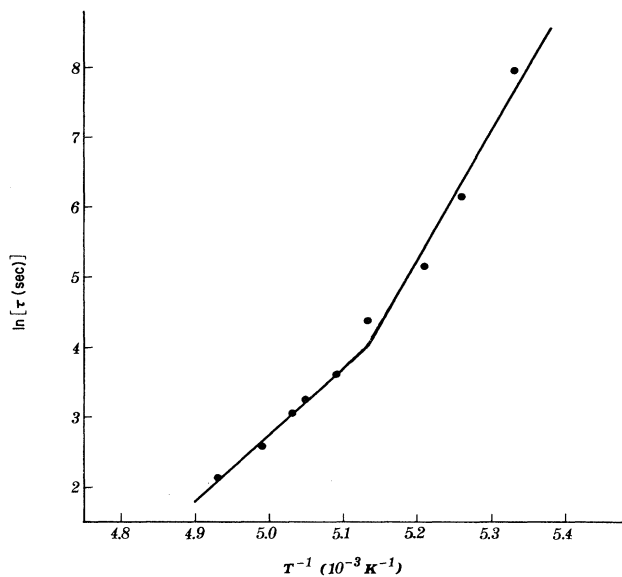


FIG. 3. The logarithm of the relaxation time τ (in sec) vs T^{-1} for the *A* band of the TSDC spectrum.

the *a*-type [second straight line in Fig. 3 or low-temperature (LT) part] are calculated using the plot $\ln i$ against T^{-1} [of relation (4)] and relation (3). The parameters of the *a* type cannot be calculated from the second straight line of Fig. 3, as long as both relaxation mechanisms are included in this part. These are calculated using the plot $\ln i$ vs T^{-1} of relation (4) (where no influence of the *b*-type mechanism exists) and relation (3) (Table I).

The same calculations for band *B* give the plot of Fig. 4. It appears that we have two types of dipoles (*b*, LT part and *c*, HT part) (Table I). The parameters for the *b* type were calculated twice and the values are in agreement.

According to the second technique we take a typical curve of depolarization current versus time shown in Fig. 5, where the solid points are experimental points whereas the solid line is the theoretical calculated depolarization current taking into account a sum of three exponential components. (A fit to a sum of two exponential components does not give satisfactory results.)

Results from depolarization measurements over the temperature range 200–230 K are shown in Fig. 6. In this figure we can see the Arrhenius plot for the three re-

TABLE I. Energy parameters for the three types of dipoles obtained from TSDC experiments.

| Complex | h_m (eV) | τ_0 (sec) | T_m (K) |
|----------|------------|------------------------|-----------|
| <i>a</i> | 0.24 | 6.59×10^{-5} | 194 |
| <i>b</i> | 0.81 | 4.93×10^{-20} | 198 |
| <i>b</i> | 0.80 | 1.28×10^{-19} | 198 |
| <i>c</i> | 0.50 | 1.78×10^{-11} | 206 |

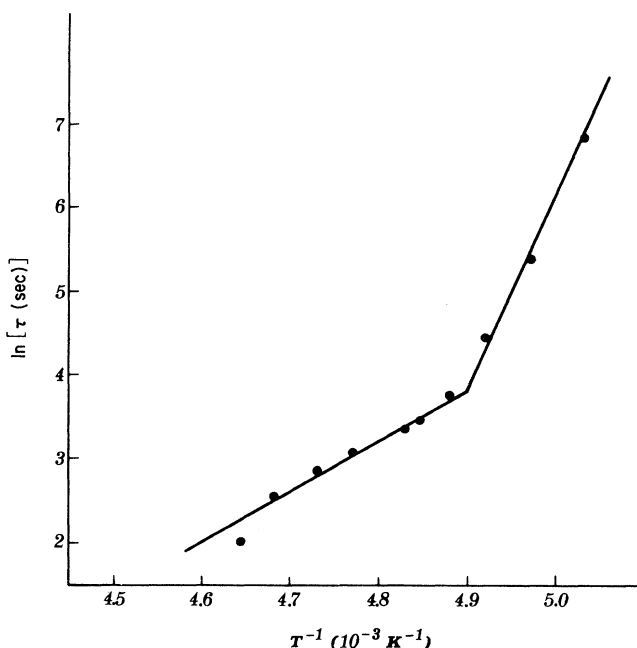


FIG. 4. The logarithm of the relaxation time τ (in sec) vs T^{-1} for the *B* band of the TSDC spectrum.

laxation times. From these plots we obtain values of the energy parameters h_m and τ_0 for the three types of dipoles (Table II).

V. CONCLUSION

Both experimental methods, TSDC and DC at $T = \text{const}$, suggest that three complexes are formed. The results of the second method (DC at $T = \text{const}$) are compatible with those obtained from the first method. The

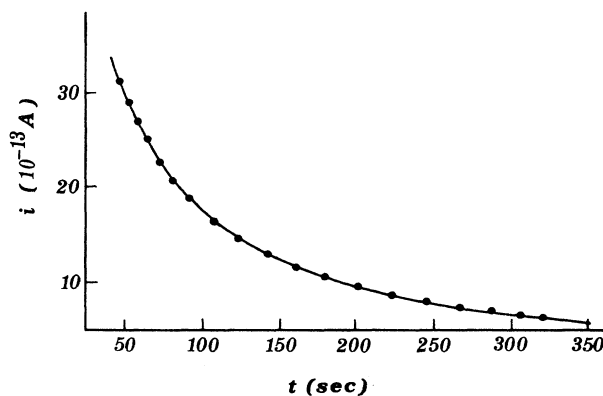


FIG. 5. The depolarization current vs time at $T = 215$ K. The solid line is the best fit to the experimental data (solid points) taking into account a sum of three exponential components.

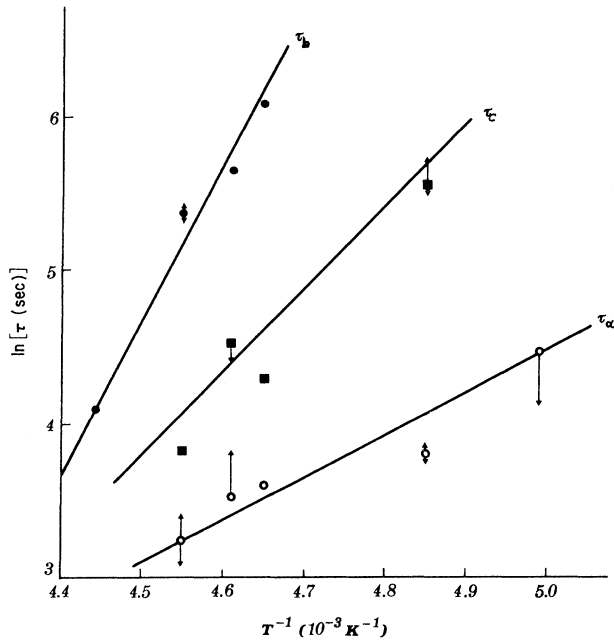


FIG. 6. The logarithm of the relaxation times τ (in sec) vs T^{-1} obtained from DC at $T = \text{const}$ measurements for the three types of dipoles.

derivation in the preexponential factor τ_0 for the b -type mechanism (appearing at a higher temperature in contrast to the TSDC method) can be attributed to the inability of this method to precisely evaluate relaxation times lower than 10^{-4} sec.⁵

TABLE II. Values of the energy parameters h_m and τ_0 for the three types of dipoles derived from DC at $T = \text{const}$ measurements.

| Complex | h_m (eV) | τ_0 (sec) |
|---------|------------|------------------------|
| a | 0.23 | 1.31×10^{-4} |
| b | 0.79 | 1.05×10^{-16} |
| c | 0.47 | 9.69×10^{-10} |

The c -type dipoles appear at the higher temperature, so one could attribute it to a cluster. The energy parameters are consistent with the values obtained for LiF doped with other divalent impurities. Additionally, they are in excellent agreement with the Cussó and Jaque model interconnecting the migration enthalpy with the ionic radius of the impurity for the reorientation of ion-vacancy dipoles via NN jumps (NN \rightarrow NN).⁶ Consequently, we attribute the c -type mechanism to a NN \rightarrow NN mechanism.

The energy parameters for a -type dipoles are in agreement with recently published papers⁷⁻⁹ suggesting that the bound cation vacancy may migrate by NN \rightarrow NNN jumps. The value of the activation enthalpy of reorientation of b -type centers, $h_m = 0.81$ eV, is quite high compared to the respective values for other impurities.⁶⁻⁹ We speculate that either annealing is unable to break up all the clusters or they are quickly reconstructed because of the high impurity density.¹⁰ Therefore, the b -type center might be a cluster. Our conclusions are supported by other measurements we have recently carried out on LiF doped with other impurities.

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