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Frequency-domain dielectric studies in LiF:Ca^{2+}

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Dielectric losses and conductivity studies in LiF:Ca^{2+} crystals were performed in the dissociation region in the frequency range from 5 to 500 kHz. Two dipolar contributions are revealed. The energy parameters of the high-frequency loss peak evidences the rotation of an impurity-cation vacancy dipole by NN→NN jumping of the bound-cation vacancy. This result is in agreement with previously reported ionic thermocurrent data of ours and directs us to the conclusion that the migration enthalpy of the bound cation vacancy decreases as a function of the ionic radius of the impurity.

I. INTRODUCTION

In alkali halide crystals, extrinsic point defects can be created by incorporating divalent cation dopants into the matrix by substituting host cations. In this case the excess positive electric charge of the crystal is compensated for the creation of a cation vacancy with negative effective electric charge. The Coulombic attraction of the impurity ion and cation vacancy leads to the formation of an impurity-vacancy (IV) dipole. The vacancy bound to the impurity is located at the nearest-neighbor (NN) or next-nearest-neighbor (NNN) lattice sites in relation to the lattice site occupied by the impurity. The orientation of an IV dipole corresponds to certain migration processes of the bound-cation vacancy around the impurity, which is assumed to occupy a fixed position, although, for dopants with small ionic radii, an interchange of the impurity with the bound-cation vacancy is also probable. Dielectric relaxation studies supply information about the dynamics of IV dipoles. Two parameters are evaluated from such experiments: the activation energy E, which is identical to the migration enthalpy h^m; and the preexponential factor τ_0 of the usual Arrhenius relation, that is directly correlated with the migration entropy of the jumping procedure.

In dilutely doped alkali halides the migration process of the bound vacancy is ruled by the host material structure and the impurity. By changing the dopant in a given matrix, one can probe the influence of the impurity to the migration of vacancies. Alkaline-earth divalent impurities (i.e., closed-shell ions) are the most likely ones for defect dipole relaxation studies, as they can be treated theoretically quite accurately. In alkali halides with alkaline-earth dopants, with the exception of lithium fluoride, it was observed that the migration enthalpy of the bound vacancy participating in NN defect dipoles is augmented as the size of the dopant increases. Theoretical work using Mott-Littleton techniques and employing appropriate potentials[1] showed that the jump of the bound-cation vacancy from one NN lattice site to another one needs more energy when the ionic radius of the dopant becomes larger, since the migrating vacancy travels closer to the dopant at the saddle point. The model was limited to certain systems, and could not explain the situation found experimentally for the case of LiF. Lithium fluoride exhibits a different behavior: The bound vacancy motion seems to be assisted the larger the impurity is. This aspect was based on a work by Laj and Bergé,[2] but a general picture was lacking since, in the latter work, from the alkaline-earth family, only Mg^{2+} and Sr^{2+} impurities were studied. Assuming a certain migration path and a lattice distortion around the dipole which depends upon the impurity size, Cussó and Jaque suggested that this situation can occur.[3] It was necessary to investigate the relaxation of LiF crystals doped with all the alkaline-earth ions (i) to ensure that indeed the activation energy decreases with the impurity size, and (ii) to understand the microscopic procedures going on through defect dipole relaxation, i.e., to judge whether the Cussó and Jaque proposal represents the reality or not. Notice that, to date, among the closed-shell alkaline-earth dopants larger than the substituted lithium (Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}), there are no dielectric relaxation data for Ca^{2+}. The present paper examines the contribution to the relaxation of LiF:Ca^{2+} resulting from the rotation of NN defect dipoles. Our data, combined with our recent thermocurrent results,[4] provide a complete view of the motion of the bound cation for impurities larger than lithium. Although ac measurements have lower resolution than ionic thermocurrent (ITC) experiments, they have the advantage that space-charge phenomena can be eliminated by avoiding very low frequencies and/or by setting a four-contact electrode system. Thus localized dipoles (i.e., complexes with nonzero dipolar moment) and delocalized dipoles developing on the interfaces separating two territories with different conductivities can be detected in the impendance spectra.

II. THEORY

The response of a dielectric to the application of an external ac electric field can be described by writing the dielectric constant of the crystal in a complex form:

$$\varepsilon=\varepsilon_1-i\varepsilon_2 \, , \tag{1}$$

where $i=\sqrt{-1}$. With the assumption that there is no interaction between the dipoles, the simple Debye theory gives the real and imaginary parts of the dielectric constant (i.e., ε_1 and ε_2, respectively):[5]

$$\varepsilon_1=\varepsilon_\infty+\frac{\varepsilon_s-\varepsilon_\infty}{1+\omega^2\tau^2}\ , \tag{2}$$

$$\varepsilon_2=\frac{\sigma_{\rm DC}}{\varepsilon_0\omega}+\frac{(\varepsilon_s-\varepsilon_\infty)\omega\tau}{1+\omega^2\tau^2}\ , \tag{3}$$

where ε_s and ε_∞ are the static and high-frequency dielectric constants, respectively. ω denotes the angular frequency ($\omega=2\pi f$) of the applied ac field, ε_0 the permittivity of free space, τ the relaxation time that governs the rotation of the dipoles and $\sigma_{\rm dc}$ is the dc conductivity. The imaginary part of the dielectric constant ε_2 is related according to Eq. (3) to the transport of free-cation vacancies expressed by the term $\sigma_{\rm dc}/\varepsilon_0\omega$, and to the relaxation of IV dipoles expressed by $[(\varepsilon_s-\varepsilon_\infty)\omega\tau]/(1+\omega^2\tau^2)$. By recalling that the relaxation time τ is provided by the usual Arrhenius formula

$$\tau(T)=\tau_0\exp(E/kT)\ , \tag{4}$$

where E and τ_0 are the activation energy and the preexponential factor describing the thermally activated rotation of the IV dipoles, it results that the term $[(\varepsilon_s-\varepsilon_\infty)\omega\tau]/(1+\omega^2\tau^2)$ is both temperature and frequency dependent. An isothermal logarithmic plot of ε_2 vs ω includes the contribution of free and bound vacancies. The subtraction of the free-carrier conductivity, dominating at low frequences, reveals a peak maximizing at a certain frequency

$$\omega_m=\frac{1}{\tau}=\frac{1}{\tau_0}\exp(-E/kT)\ . \tag{5}$$

A collection of (T,τ) pairs inserted into Eq. (4) permits the evaluation of E and τ_0.

In the dissociation region, the extrinsically created cation vacancies consist of the major defect population, and part of them is associated with the impurities while the remaining vacancies are free. In this case,[6] at low frequences, i.e., $\omega >> 1/\tau$, the ionic conductivity of the crystal originates from the free-cation vacancy migration:

$$\sigma=\frac{\sigma_0}{T}\exp\left[-\frac{g^m}{kT}\right]\ , \tag{6}$$

where σ_0 is a constant involving the geometrical features of the crystal structure and the vibrating frequency of the jumping species. Recalling that $g^m=h^m-Ts^m$, the last formula can be written so as to display two terms, one entropic and another enthalpic:

$$\sigma T=\sigma_0\exp\left[\frac{s^m}{k}\right]\exp\left[-\frac{h^m}{kT}\right]\ . \tag{7}$$

The last equation shows that the slope of ln σT versus $1/T$ leads directly to the evaluation of the migration enthalpy h^m of the free-cation vacancies, provided that the measurements are performed in the dissociation region.

III. EXPERIMENT

The lithium fluoride single crystals with a nominal 10^{-2} mole fraction of calcium as an added dopant in the melt were developed in Utah's Crystal Growth Laboratories. In lithium fluoride it is difficult to introduce large impurities. Thus we performed atomic absorbtion analyses that indicated the presence of less than 2000 ppm Ca^{2+}. In the present system the solubility limit is attained at a few tenths ppm,[7] therefore we may state that most of the impurities were in precipitated phases, an aspect that is certified from our ITC measurements.[4] Samples 1–1.5 mm thick were prepared, and care was taken to avoid contamination from the moisture.

The samples were placed between platinum electrodes in a specially designed holder introduced into an oven. Its temperature was continuously monitored by a temperature controller. Good contact with the electrodes was attained by painting the crystal surfaces with graphite.[6]

The conductivity of the sample was measured in the frequency range from 5 to 500 kHz with a Boonton Electronics 75c Bridge. The temperature region was selected so as to coincide with the dissociation region, as determined from previous measurements of ours.[8]

IV. RESULTS

In Fig. 1 the imaginary part of the dielectric constant ε_2 vs the ac field frequency f is depicted (curve a). At low frequencies, for reasons explained in Sec. II, the free charge transport component strongly dominates to the conductivity of the crystal. Hence Eq. (3) can be rewritten

$$\varepsilon_2=\frac{\sigma_{\rm DC}}{\varepsilon_0\omega}\ . \tag{8}$$

Then, logε_2 vs log$f$ should lie on a straight line with a slope equal to -1. In Fig. 1 the low-frequency points were fitted to a line with slope -1 (curve b). Its subtraction from curve a reveals the net dipolar contribution (curve c). Curve c exhibits two maxima that are closely

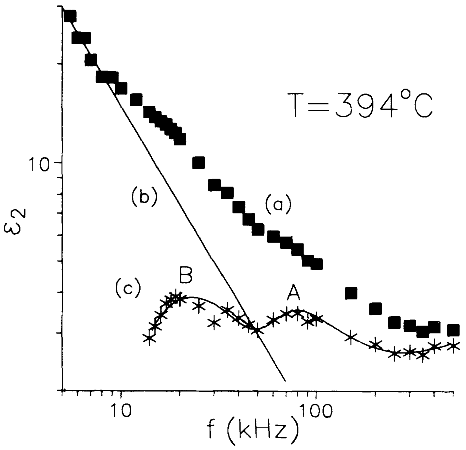

FIG. 1. Curve a: isothermal plot of the imaginary part of the dielectric constant ε_2 vs the frequency f of the applied field. Curve b: The dc conductivity straight line determined from the low-frequency part of our plot. Its slope is identical to -1. Curve c: The subtraction of Curve b from a reveals the dipolar contributions.

TABLE I. Relaxation mechanisms detected with the dielectric losses (DL) technique in the present work. Data from ionic thermocurrent (ITC) studies for thermally treated crystals are included.

Method Attribution	Dielectric losses (present work)	Ionic conductivity (present work)	ITC (Ref. 4)
NN→NN dipole relaxation	$E=0.58$ eV $\tau_0=7.49\times10^{-11}$ sec (A peak)		$E=0.59$ eV $\tau_0=1.66\times10^{-14}$ sec
Aggregate	$E=0.37$ eV $\tau_0=1.61\times10^{-8}$ sec (B peak)		
?			$E=0.98$ eV $\tau_0=1.39\times10^{-24}$ sec
?			$E=0.99$ eV $\tau_0=2.22\times10^{-23}$ sec
Free cation vacancies		$E=0.65$ eV	

separated, indicating that two loss peaks strongly overlap each other. Labeling the corresponding high- and low-frequency peaks participating to curve c A and B, the energy parameters E and τ_0 were evaluated (Table I) according to the Arrhenius plots shown in Fig. 2.

The interpretation of the loss spectra must be viewed critically. We present two qualitative comments that are striking.

(a) Peak A exceeds over the frequency range predicted by the Debye theory, while peak B is rather narrow.

(b) In Fig. 2 [$\ln\omega_m=f(T^{-1})$] the experimental points corresponding to peak B are dispersed, in contrast to these of peak A which lie quite well on a straight line.

The above aspects can be understood in terms of the standard analysis employed: The loss peaks are obtained by subtracting the dc conductivity contribution, which is determined from a very narrow frequency territory, as can be seen from Fig. 1. Subsequently the loss peaks located in the immediate neighborhood of the dc region are very sensitive to the selection of the dc straight line. On the other hand, small errors are introduced for the peaks far from the dc region. Therefore, the parameters evaluated for peak A are firmly established, while for peak B they are not highly accurate.

The same ac measurements can provide information about free-cation vacancy motion. The experiments were performed in the dissociation region, so the very low-frequency conductivity is due to the migration of free-cation vacancies. In Fig. 3, in a $\ln\sigma T=f(T^{-1})$ diagram, we have inserted the conductivity data for the 5.5-kHz ac frequency. According to Eq. (7) a linear fit yields the migration enthalpy h^m of the free-cation vacancies, which is found to be equal to 0.65±0.08 eV. Different low frequences (i.e., 6 and 6.5 kHz) give compatible results.

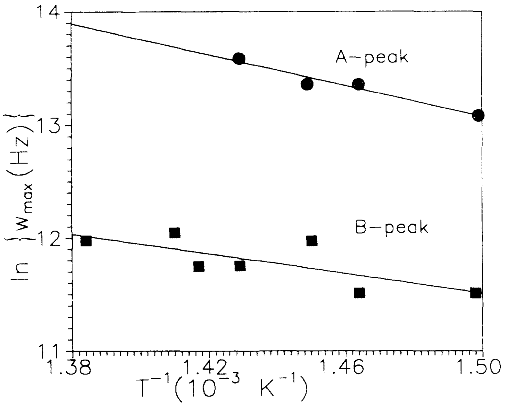

FIG. 2. The temperature dependence of the maxima of the loss peaks.

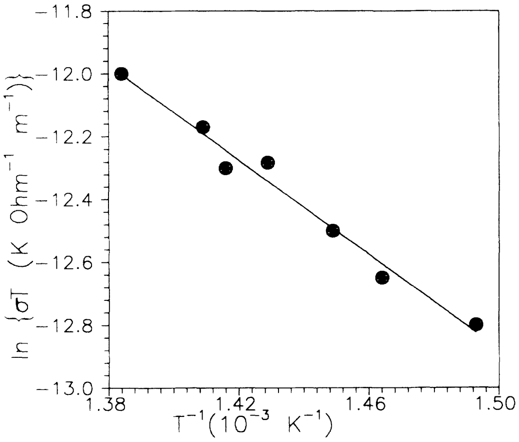

FIG. 3. Conductivity plot obtained from measurements recorded at 5.5 kHz.

V. DISCUSSION

Our dielectric loss measurements revealed two peaks which originate either from dipole rotation or from interfacial polarization.[4] The latter speculation must be rejected, since interfacial polarization contributions appear at very low frequences, i.e., far from the range our bridge operates. On the other hand, in the present system, the migrating species within highly conducting territories into the matrix are probably free-cation vacancies whose migration enthalpy is much different from the values reported in Table I.

The ac studies mutually complement the ITC technique. In the latter, the dipoles are aligned by the application of an external electric field, and the crystal is cooled down afterwards to the liquid-nitrogen temperature, where the relaxation time of the dipoles is practically infinite. Thus, by switching off the field, the sample remains polarized. By heating the sample, one detects a depolarization current peak at a certain temperature range, due to dipole reorientation. The analysis leads to parameters E and τ_0. The method is not destructive for the sample, is very sensitive and provides high resolution, but it suffers from space-charge contributions.

Our recent extensive ITC studies[4,9] revealed a peak that under certain physical arguments was firmly attributed to an IV dipole rotation occurring by NN→NN jumps of the bound-cation vacancy. The energy parameters found were $E=0.59$ eV and $\tau_0=1.66\times10^{-14}$ sec. These values, within experimental errors, are very close to those reported in Table I for peak A. Thus an attribution of peak A to the aforementioned dipole relaxation is justified.

In Fig. 4, we present the dependence of the activation energy E of defect dipole rotation in relation to the ionic radius R of the impurity, for alkaline-earth (i.e., closed shell) ions larger than the substituted cations. These data come from dielectric relaxation experiments, such as ITC, thermally stimulated polarization currents, and dielectric loss methods. It is obvious that the NN→NN migration of the bound-cation vacancy becomes energetically more favorable the larger the impurity is. A lattice distortion model proposed by Cussó and Jaque[3] seems to be justified from the experiments.

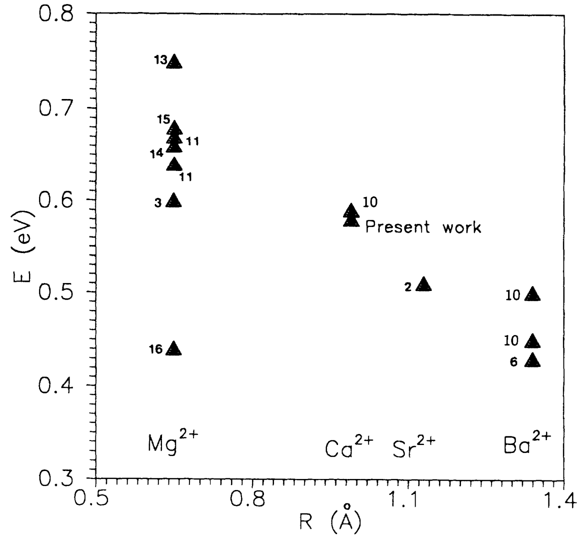

FIG. 4. The activation energy E of the IV dipole relaxation determined by different dielectric relaxation techniques vs the ionic radius R of the alkaline-earth ions introduced in LiF crystals. Each point is accompanied by a number indicating the reference.

Concerning peak B, one might relate it to the NN→NNN jumps of the bound-cation vacancy, as stated in some previous work by our group.[6,10,11] Having in mind that the ITC method is the most sensitive dielectric spectroscopy technique, one should look for the corresponding depolarization peak existing in the ITC spectrum. The temperature T_m, where the thermocurrent maximizes provided that the sample's temperature is raised at a constant rate b, is expressed by means of the formula[4]

$$T_m^2=\frac{bE}{k}\tau_0\exp(E/kT_m)\ . \tag{9}$$

For $b=0.1$ K/sec, and replacing E and τ_0 with the peak B values depicted in Table I, the solution of Eq. (9) is $T_m=191.7$ K. Our ITC thermograms[4] on as-received and thermally treated crystals proved that no depolarization due to the rotation of dipoles with peak B energy parameters appears (see Table I). We can therefore be directed to the speculation that the dipoles stimulating peak B might be some aggregates formed when the crystal remains at high temperature during the ac measurements.

Finally, the low-frequency conductivity plots provide the migration enthalpy value for the motion of free-cation vacancies which is in good agreement with previously published works.[12]

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