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Conductivity and dielectric constants of LiD

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The dielectric constant of LiD has been measured in the frequency region 5–500 kHz at different temperatures up to 340 °C. Compared to the results of other workers, the LiD conductivity curves are found to be displaced slightly to lower values than those of LiH. Furthermore, it is also proved that the high ac-conductivity values found by other workers at low temperature in the case of LiH correspond not to true conductivity but are caused by reorientation of complexes. Activation energies corresponding to the motion of a free cation vacancy or the reorientation of complexes have been determined.

INTRODUCTION

Properties of LiH, LiD, LiT, and their mixtures have been reported in a series of papers.[1-9] They bear out the predominantly ionic nature of crystalline LiH. However its optical properties differ from those expected by comparison with alkali halides or the other alkali hydrides. The latter difference is related to distortion and polarization effects on the hydride ion. In the lattice there is a tendency toward covalency which certainly contributes to the binding energy and this may also be responsible for its somewhat anomalous optical behavior.

The purpose of this paper is to study the ac conductivity and some dielectric properties of LiD. The ionic nature of the electrical conduction in LiH was first demonstrated by Moers[10] and Peters[11] and later by others.[4,12–14] It was realized that LiH conducts electricity by cation-vacancy migration, similar to the alkali halides.

We note that in LiH crystals there is a high vibrational frequency and high cation-vacancy mobility.[5]

THEORY

It is well known that the real part ϵ_1 and imaginary part ϵ_2 of the dielectric constant of an ionic crystal A^+B^- containing divalent impurities can be expressed according to simple Debye theory as follows:

$$\epsilon_1 = \epsilon_\infty + (\epsilon_s - \epsilon_\infty)/(1+\omega^2\tau^2) \tag{1}$$

and

$$\epsilon_2 = 4\pi\sigma_0/\omega + (\epsilon_s - \epsilon_\infty)\omega\tau/(1+\omega^2\tau^2)\,, \tag{2}$$

where σ_0 is the dc conductivity, τ is the relaxation time for the reorientation of complexes (dipoles consisting of a divalent ion and a bound vacancy), and ϵ_s and ϵ_∞ are the static and high-frequency dielectric constants, respectively. In Eq. (2) the first term $\epsilon_2' = 4\pi\sigma_0/\omega$ and the second term $\epsilon_2'' = (\epsilon_s - \epsilon_\infty)\omega\tau/(1+\omega^2\tau^2)$ determine, respectively, the contribution of free vacancies and complexes to the imaginary part of the dielectric constant.

When a crystal is under an ac field its total conductivity σ_{tot} can be expressed as follows:

$$\sigma_{tot} = \sigma_0 + \sigma_c = \sigma_0 + \frac{(\epsilon_s - \epsilon_\infty)\omega^2\tau}{4\pi(1+\omega^2\tau^2)} \tag{3}$$

where σ_c is the conductivity due to the reorientation of complexes. In a crystal containing a usual amount of divalent impurities, the number of free vacancies created because of thermodynamical reasons is much lower at low temperatures than the number of complexes. At these temperatures and at frequencies $\omega\tau \gg 1$, we have

$$\sigma_{tot} \simeq \sigma_c \simeq (\epsilon_s - \epsilon_\infty)/4\pi\tau \tag{4}$$

under the condition that all vacancies created due to the presence of divalent impurities are bound. If we assume that the Arrhenius expression $\tau = \tau_0 e^{(\phi/kT)}$ is valid, Eq. (4) gives

$$\sigma_{tot} \simeq \sigma_c \simeq \left(\frac{\epsilon_s - \epsilon_\infty}{4\pi\tau_0}\right) e^{(-\phi/kT)}\,, \tag{5}$$

where ϕ is the activation energy which is required for the reorientation of complexes. We wish to draw attention to the fact that ϕ corresponds to the orientation of complexes and that it is not the activation energy E for free vacancy migration.

The second term of Eq. (2) (ϵ_2'' of ϵ_2) has its maximum at a certain frequency

$$\omega_m = 1/\tau = (1/\tau_0)e^{-\phi/kT} \tag{6}$$

Plotting $\ln\omega_m = f(1/T)$ we find a straight line, and from its slope we calculate ϕ.

EXPERIMENTAL

The LiD polycrystalline material was grown by Pretzel. Samples with dimensions approximately 5×8×3 mm were measured with a Boonton 75*C* electronic direct capacitance bridge, with frequency range 5–500 kHz. They were held in a specially designed holder[15] and could be heated in an inert atmosphere of argon.

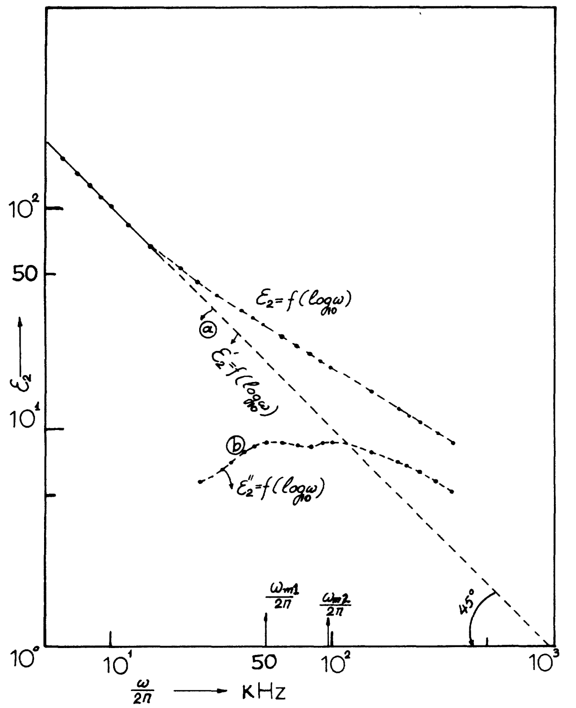

FIG. 1. Imaginary part ϵ_2 of the dielectric constant vs frequency, for a LiD crystal at 234 °C.

Figures 1 and 2 show, respectively, the results of measurements of ϵ_2 and ϵ_1 of LiD versus frequency at a constant temperature 234 °C.

Before measurement the crystals were heated up to about 350 °C for 2 h and rapidly quenched to the temperature of the measurement. We decided on this procedure because we observed that the experimental results then became reproducible. Maybe when the crystals are not quenched but only slowly cooled down most of the impurity ions form relatively larger clusters.

In Fig. 1 we observe that the curve of ϵ_2 vs $\omega/2\pi$ can be considered as the sum of the curves *a* and *b*.

Curve *a* is a straight line with unit slope and so represents [Eq. (2)] the dielectric loss ϵ_2' due to the drift of free vacancies. Using the form $\sigma_0 = \epsilon_2'\omega/4\pi$ we find $\sigma_0 = 5.52 \times 10^{-7}\ (\Omega\,\mathrm{m})^{-1}$ for the dc conductivity of LiD at 234 °C. Pretzel reported for LiH $\sigma_0 = 9 \times 10^{-7} (\Omega\,\mathrm{m})^{-1}$ at the same temperature.

Repeating the comparison for other temperatures, we find that the dc-conductivity curves of LiD are always displaced slightly to lower values than those of LiH. This slight reduction in conductivity for LiD is probably related to a similar reduction in the lattice parameter.[5]

Furthermore, by measurements of the dc conductivity at various temperatures, we obtain σ_0 vs T. From the slope of the curve $\ln\sigma_0 = f(1/T)$ we find that the activation energy for the migration of free cation vacancies is $E = 0.52$ eV, in agreement with the value of 0.53 eV which Pretzel[4] found for the LiH crystal.

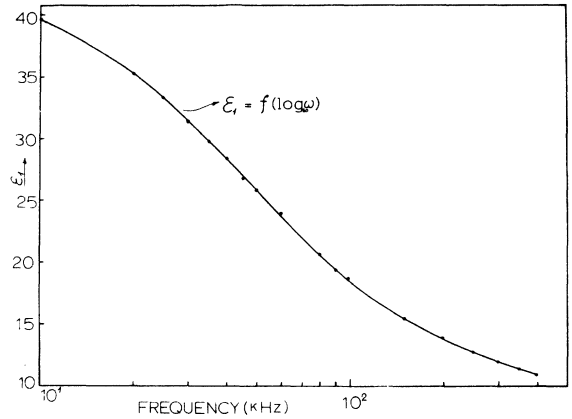

FIG. 2. Real part ϵ_1 of the dielectric constant vs frequency for a LiD crystal at 234 °C.

Curve *b* in Fig. 1 represents the losses ϵ_2'' due to the complexes. We observe that the curve $\epsilon_2'' = f(\log_{10}\omega)$ is wider than a Debye curve. Such

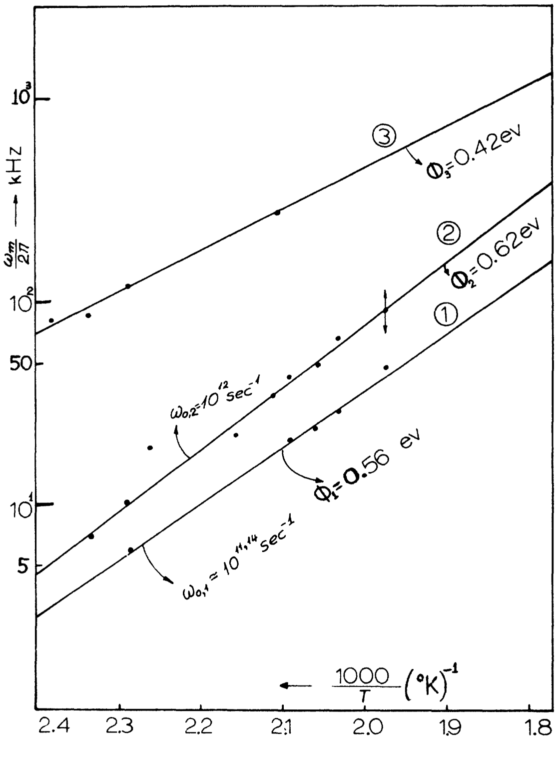

FIG. 3. Plot of ln $\omega_m/2\pi$ as a function of $1/T$ for (1)-, (2)-, and (3)-type peaks.

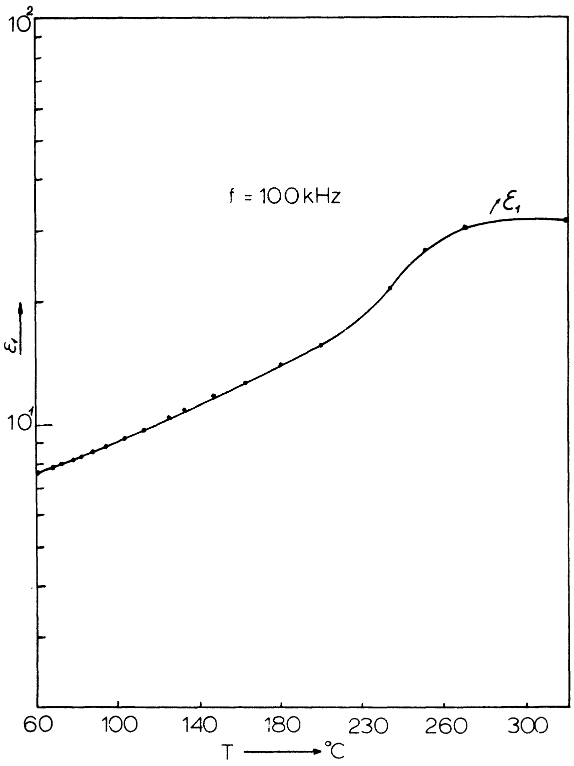

FIG. 4. Plot of $\log_{10} \epsilon_1$ as a function of T at a fixed frequency 100 kHz.

cases are usually described by a distribution of relaxation times (due to a coupling of the dipole moments to their surroundings[16]). As an alternative approach, we consider the experimental curve as a sum of two relaxation curves having their maxima at frequencies $\omega_{m1}/2\pi = 50$ kHz and $\omega_{m2}/2\pi = 95$ kHz, respectively.

Plotting the curves $\ln\omega_{m1} = f(1/T)$ and $\ln\omega_{m2} = f(1/T)$ (Fig. 3), we find from their slopes $\phi_1 = 0.62$ eV and $\phi_2 = 0.56$ eV.

In crystals which had not undergone the thermal treatment, a third relaxation mechanism appeared. Its activation energy is about $\phi_3 = 0.42$ eV (curve 3, Fig. 3).

Before attempting to explain the observed results the following points must be discussed.

(i) Space charge due to accumulation of electrons or other charge carriers at the electrodes or at internal subboundaries might produce relaxation losses similar to those due to dipole relaxation.

Studying the low-frequency (<1-kHz) capacitance at temperatures near 500 °C, we found no rapid increase of capacitance as the frequency is decreased. This proves that the above mechanism can not be a source of a dielectric-loss peak in our results.

Furthermore, as Kessler and Mariani[17] reported, the value of $\tan\delta = \epsilon_2/\epsilon_1$ in the case of the above mechanism depends on the thickness of the crystals. No such dependence was observed in our results.

(ii) Reorientation of aggregated complexes (clusters) might produce relaxation peaks.[18-20]

It is well known that upon heating, the clusters break up into simple complexes and their loss peak disappears. But in the present case, we observed that the heights of both peaks 1 and 2 increased on quenching the crystals from higher temperatures, thus indicating that they are not due to clusters.

Perhaps the third peak 3 is due to such a mechanism. For the interpretation of the experimental data of Figs. 1–3 it is sufficient to accept simple complexes that orient themselves under the application of an ac field. Such a complex probably consists of a divalent anion and a bound anion vacancy. The existence of such oxygen anions has been reported.[21]

It is necessary at this point to compare the present results with those reported by Bergstein *et al.*[21] on LiH at a frequency of 1 MHz. From their curve of conductivity versus temperature, we obtain at 234 °C a conductivity of 5×10^{-4} $(\Omega\,\mathrm{m})^{-1}$, i.e., much greater than the value $\sigma_0 = 5.52\times10^{-7}$ $(\Omega\,\mathrm{m})^{-1}$ that results from Fig. 1 or than that found by Pretzel.

Another fact is remarkable about the results of Bergstein *et al.* They found two knees in the conductivity curve, from which the high-temperature knee at 770 °K has been also reported by Pretzel and corresponds surely to the beginning of the intrinsic region of the ionic conductivity. The source of the low-temperature knee at 625 °K remained unexplained. A possible explanation of this knee is given below. At the frequency 1 MHz we obtain from Fig. 3 a maximum of ϵ_2'' at a temperature ~620 °K, which shows that at this temperature the contribution of complexes in the σ_{tot} has its maximum value. So the first knee in their conductivity curves[21] can be ascribed to the contribution of complexes to σ_{tot}.

Furthermore, the high-conductivity values reported by them do not contradict our much lower values, because they correspond to the σ_{tot} and not to the dc conductivity only. Also we note that the part of their conductivity curve towards lowest temperature gives an activation energy of 0.65 eV, which should be compared to the value $\phi_2 = 0.62$ eV found by us from the slope of $\ln\omega_m = f(1/T)$. The fit becomes still better if we replace 0.65 eV by 0.61 eV which is the value that they published for experiments under an inert atmosphere (Ar).

In Fig. 4, ϵ_1 is plotted at 100 kHz vs temperature. Although its form in general is similar to that given by the Debye model we notice a somewhat anomalous behavior.

ACKNOWLEDGMENT

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