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# Difference in conductivity between LiD and LiH crystals

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The LiD and LiH conductivities have been compared in the temperature range 300–900 °K. In both (LiD and LiH) the conductivity curve $\log_{10}(\sigma T) = f(1/T)$ shows three linear regions: (i) an intrinsic, (ii) a dissociation, and (iii) an association region. In all examined temperature ranges the conductivity values of LiD are smaller than those of LiH. The formation energy of Schottky defects is different in these two materials (2.40 and 2.33 eV, in LiD and LiH, respectively). Furthermore, the association energy of the $Mg^{+2}$–cation-vacancy complex is 0.76 eV in LiD and 0.84 eV in LiH; these values are unexpectedly much higher than those found in the alkali halides. Also large aggregation phenomena exist in crystals which have not undergone the usual thermal treatment.

## INTRODUCTION

There has been considerable interest in the theoretical and experimental analysis of LiH, LiD, LiT, and their mixtures. The physical properties of crystalline LiH, etc., especially their ionic conduction of electricity, give strong evidence for the basically ionic nature of these solids.[1–6] However, according to measurements of fundamental ultraviolet absorption, polarization properties, chemical stability, "Compton" profile, etc., the crystal displays some deviation from the properties of typical ionic crystals like the alkali halides. Many workers[7–14] in trying to explain these deviations have assumed that they depend on homopolar contributions (to binding energy in LiH or LiD crystals). Evidence for the partial covalent character (about 12.5%) of the bonds in crystalline LiH has been drawn[1] from (i) small differences in the electronegativities of the combining elements, (ii) the low "effective" charge, and (iii) the contraction of the lattice dimensions from the sum of the free-ion radii.[15] Using the lattice parameters[1] 4.084 ±0.001 Å for LiH and 4.060±0.001 Å for LiD and an ionic radius of 0.68 Å for $Li^+$,[16] we find that the "effective" $H^-$ and $D^-$ radii are $H^-$: 2.042 − 0.68 = 1.36 Å; $D^-$: 2.03 − 0.68 = 1.35 Å, instead of[1] 2.08 Å, which is the free-$H^-$-ion radius. (iv) Using the ionic model of Born and Mayer ($e^{-r/\rho}$), a high value for the repulsive parameter $\rho$ is found[17,18] in comparison with that found for the alkali halides.

Conductivity measurements have shown[1,19,20] that LiH and LiD conduct electricity by the cation-vacancy mechanism, as do the alkali halides, although for a period some authors supported just the opposite view.[21] Pretzel *et al.*,[1] reported that the LiH condictivity curve fits into the sequence of lithium halides by comparison with Haven's[22] results. The conductivity values of LiH in the intrinsic region were found[1] to be 1000 times greater than those of LiF (which has more nearly the same lattice parameter, 4.016 Å), being closer to the values obtained for LiCl. Bredig[19] remarked that the above is well understood as a result of the much higher polarizability of the (gaseous) ions $H^-$ (100 $\times 10^{-25}$), and $Cl^-$ ($36\times 10^{-25}$), compared with that of $F^-$ ($10\times 10^{-25}$), which leads to "a loosening up" of the crystal and endows a fraction of the lithium ions with much greater mobility.

It is extensively known that an ionic crystal containing small amounts of impurities has reproducible values of conductivity in its intrinsic region. However, comparing the conductivity curves of Pretzel *et al.*, Bredig,[19] and Bergstein,[23] we find a large discrepancy between them as to their slopes and shapes.

In a recent paper[24] we have reported that the LiD conductivity curves are found to be displaced slightly to lower values than those of LiH and that the cation-vacancy migration mechanism takes place with an activation energy of 0.52 eV. Also we have proved that the high ac conductivity values, found by other workers[23] at low temperature for LiH, are caused by reorientation of complexes, and so they do not correspond to an intrinsic property of the LiH material.

The purpose of this paper is to give some new information about the dc conductivity of LiD and its difference from that of LiH. Thus we give, for the first time, (i) the energy of formation of Schottky defects for LiD and its value compared with that of LiH and (ii) the association energy of the $Mg^{+2}$–cation-vacancy complex in LiD and its difference from that in LiH.

## II. dc CONDUCTIVITY. EXPERIMENTAL RESULTS AND DISCUSSION

The ionic conductivity of LiH and LiD crystals occurs almost entirely through the migration of cation vacancies, since the mobility of an anion vacancy is very much smaller than that of a cation vacancy. Such vacancies, as it is well known, may either of thermal origin (in the form of Schottky

pairs) or may be incorporated into the lattice together with divalent metallic impurities to maintain charge neutrality.[25] In a similar way, it is possible that anion vacancies are created owing to the presence of divalent anions, i.e., $O^{-2}$ in the LiD crystals, as has been reported in our previous paper.[24] But at high temperatures (intrinsic region), the number of thermally created Schottky defects is very large, so that the presence of a usual amount of divalent impurities does not appreciably change the vacancy density.

Figure 1 shows the conductivity curves of LiH and LiD crystals in the temperature region (300–900)°K obtained with a method described elsewhere.[24] (The absolute error of temperature was less than 1°K). The bridge relative error in the measurements of conductivity[25] was less than $2.5\times10^{-3}$. The curve can be separated into three linear regions: (a) intrinsic, (b) dissociation, and (c) association.

### A. "Intrinsic" region

In the intrinsic region (high temperature) we note that the LiD has *lower conductivity* but a *higher slope than* LiH.

The density of vacancies $n$ depends on $E_S$, the formation energy of Shottky defects and on $\Delta S_S$, the corresponding entropy of formation, according to the formula[26]

$$n = Ne^{(\Delta S_S/2k - E_S/2kT)}, \tag{1}$$

where $N$ is the concentration of $Li^+$ ion sites. The mobility of the free-cation vacancy is given by the formula

$$\mu = (4ea^2v_0/kT)e^{(-E_m/kT)}, \tag{2}$$

where $a$ is the nearest-neighbor distance and $E_m$ is

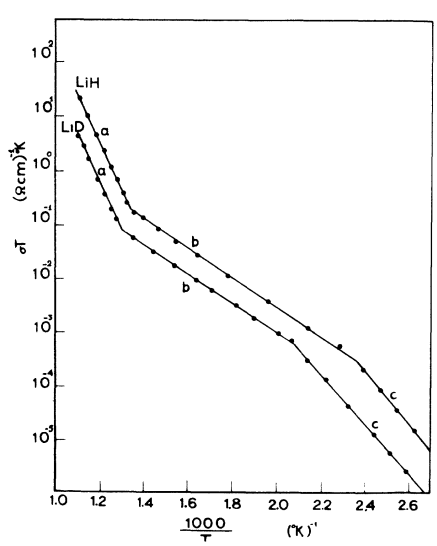


FIG. 1. Conductivity curves $\log_{10}\sigma T = f(1/T)$ for LiH (Ref. 1) and LiD. The lines $a$, $b$, and $c$ show the "intrinsic," "dissociation," and "association" regions, respectively.

the activation energy for the cation vacancy motion.

The "frequency factor" $v_0$ is given by the relation

$$v_0 = v_0^1 e^{\Delta S_m/k}, \tag{3}$$

where $\Delta S_m$ is the entropy of activation for migration of a cation vacancy and $v_0^1$ an effective lattice vibration frequency, usually taken as the Debye frequency. With the help of the equation

$$\sigma = ne\mu \tag{4}$$

we can obtain that the slope $\ln\sigma T$ vs $1/T$ is given by $E_m + \frac{1}{2}E_S$.

From the data of the intrinsic region, by using a least-squares fitting, we find for the slope $E_m + \frac{1}{2}E_S$ the values $1.720\pm0.005$ and $1.695\pm0.005$ eV for LiD and LiH, respectively. The errors of the above values were calculated from the least-square method, introducing also in the program the estimated errors of the temperature and conductivity.

Using for $E_m$ the values 0.53 (LiH) and 0.52 eV (LiD) obtained from the slope in the dissociation region (see below), we find for $E_S$ the values $2.33\pm0.01$ and $2.40\pm0.01$ eV for LiH and LiD, respectively.

We observe that the formation energy for a Schottky defect in LiD is greater than that in LiH. In the case of alkali and Lithium halides, Sastry and Mulimani[27] have found that a simple empirical relation exists between the Debye temperature $\Theta_D$ and the formation energy $E_S$ (which is analogous to that found by Mukherjee and March for metals). The relation which they proposed is

$$\Theta_D = 32.37(E_S/MV^{2/3})^{1/2}, \tag{5}$$

where $M$ and $V$ are respectively, the mass and the volume of a mole of the solid and $E_S$ is measured in cal/mole.

Applying Eq. (5) for LiH (unprimed) and LiD (primed quantities) we obtain

$$\Theta_D/\Theta_D' = 1.057\ (E_S/E_S')^{1/2}. \tag{6}$$

From x-ray[28] data $\Theta_D$ and $\Theta_D'$ are 851 and 638 °K for LiH and LiD, respectively. We therefore conclude that

$$E_S/E_S' = 1.6. \tag{7}$$

This result is in disagreement with our experimental results which give $E_S/E_S' = 0.97$. This difference is beyond the experimental error.

Thus we conclude the Sastry and Mulimani's relation is not valid in the case of LiH and LiD. The above result $E_S/E_S' = 0.97$ is consistent with the following consideration: In Fig. 2 we have plotted $E_S$ as a fit of the melting point $T_m$ for the lithium halides. A smooth curve drawn through the obtainable data shows that materials with higher $T_m$ have a high $E_S$. As LiD has a higher melting point[29] than LiH, $E_S/E_S'$ is smaller than 1. The value 0.97 given above cannot be checked, as the

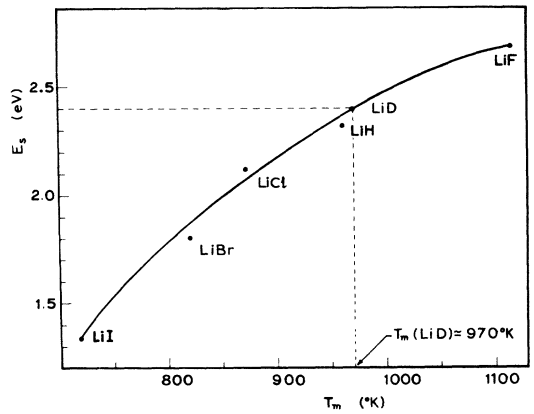


FIG. 2. Formation energy $E_S$ of a Schottky defect vs melting point $T_m$ for the lithium halides (Ref. 27) and LiH. The $E_S$ value of LiD corresponds to a melting point about 970 °K. The exact value of $T_m$ for LiD is not yet well known.

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### B. "Dissociation" region

Both the LiH and the LiD conductivity curves show a region which has been named in Fig. 1 the dissociation region. This is usually assumed[26] to represent the range in which the cation-vacancy concentration is nearly equal to the concentration of divalent cations contained in the crystal (in the present case $Mg^{+2}$, which was introduced during the growing of the crystal[1]). The slope of this linear part of the curve, obtained as described above, gives the activation energy $E_m$ required for a free cation-vacancy migration. Thus we find the values $0.520 \pm 0.002$ and $0.530 \pm 0.002$ eV for LiD and LiH, respectively.

We can therefore safely conclude that LiH and LiD display a dissociation region in a similar way to the alkali halides.

### C. "Association" region

The association region observed at lower temperature (Fig. 1) is probably due to the tendency of $Mg^{+2}$ impurities to associate with a cation vacancy to form a complex. The slope then gives an "effective" activation energy which must be equal to $E_m + \frac{1}{2}E_A$, where $E_A$ is the association energy of the complex. Since $E_m = 0.53$ and $0.52$ eV for LiH and LiD, respectively, we find, for LiH, $\frac{1}{2}E_A + E_m = 0.950 \pm 0.004$ eV $\Rightarrow E_A = 0.84 \pm 0.01$ eV, and for LiD, $\frac{1}{2}E_A + E_m = 0.900 \pm 0.004$ eV $\Rightarrow E_A = 0.76 \pm 0.01$ eV.

The above values are large compared to the simple-association values 0.3–0.4 eV which have been found in alkali halides doped with divalent cations.[30]

The association energy value of 0.76 eV does not reflect that of $O^{-2}$–anion-vacancy[24] complexes because the mobility of an anion vacancy is much smaller than that of a cation vacancy. So we must attribute this value to the association energy of the $Mg^{+2}$–cation-vacancy complex.

In comparing this value of 0.76 eV in LiD with that of 0.84 eV in LiH we conclude that the association-energy value in LiD is less than that in LiH.

The above result is not in accordance with the previous experimental results which show that in alkali-halide crystals with the same cation and the same divalent cation impurity, the association energy increases slightly as the mass of the anion is increasing, i.e.,[31]

$KCl + Pb^{+2}$, $E_A = 0.26$ eV,

$KBr + Pb^{+2}$, $E_A = 0.27$ eV,

$KI + Pb^{+2}$, $E_A = 0.28$ eV,

while in the case of cesium halides the opposite happens.[32] At this point we mention the fact that Dryden,[33] studying $LiF + Mg^{+2}$ at the same temperature region, found an activation energy of 0.92 eV from dc measurements and 0.65 eV from dielectric-loss measurements and was unable to explain that difference. That difference can be explained on the above context because activation energy from dc measurements represents $\frac{1}{2}E_A + E_m$, whereas dielectric-loss measurements give the activation energy required for the reorientation of the complex $Mg^{+2}$–cation-vacancy.

Bergstein's measurements under an ac field of 1 MHz showed that the LiH conductivity curve has three linear parts extending over the temperature intervals $T < 625$ °K $< T < 770$ °K, and $T > 770$ °K, with activation energies of 0.61, 1.1, and 1.7 eV,

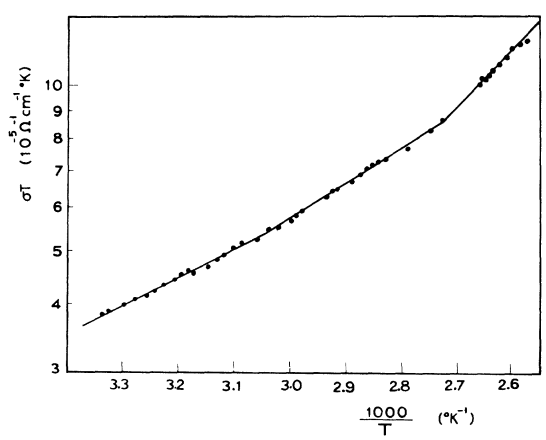


FIG. 3. Conductivity curve $\log_{10}\sigma T = f(1/T)$ under an ac field of 100 kHz of a sample which has not undergone the usual thermal treatment.

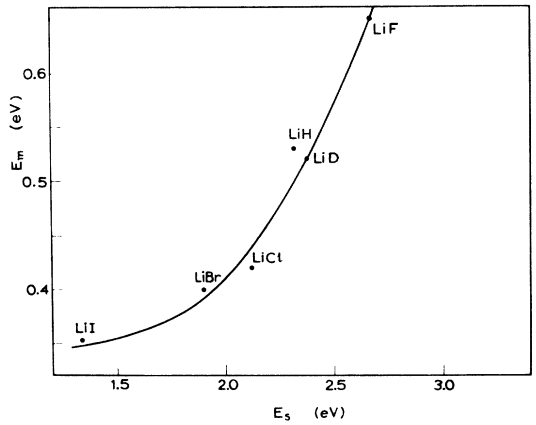


FIG. 4. Activation energy $E_m$ vs the formation energy $E_S$. The values, except those of LiH and LiD, are from Sastry and Mulimani's data (Ref. 27).

respectively. We have reported in a previous paper[24] that the activation energy 0.61 eV is that required for the reorientation of the complexes $O^{-2}$–anion-vacancy under the ac field and so there is not any comparison with our results at this temperature region. On the contrary, in the highest temperature region Bergstein's conductivity slope approximately coincides with ours because the number of thermally produced cation vacancies is much greater than that of complexes, and so the total ac conductivity is equal to that caused only by free cation-vacancy migration.

All the above measurements were made after the LiD crystals were heated for a long time (~2h) near the melting point. Measuring the conductivity of a crystal which has not been thermally treated before the measurement, we obtain the conductivity plot in Fig. 3 with an ac field of 100 kHz. In this figure we see that the "conductivity curve" shows three linear parts, which give the "effective" activation energies 0.1, 0.13, and 0.2 eV as we proceed from room temperature to higher temperatures. These linear parts can be attributed to aggregated impurity-vacancy dipoles; i.e., a certain number of impurity-vacancy pairs exist as larger aggregates which dissociate into simple pairs when the crystal is heated to higher temperature. But at present it is difficult for us to explain what the activation energies of 0.1, 0.13 and 0.2 eV really represent. However, it is extensively known that when the impurity forms aggregates, they may give rise to loss peaking (for this reason the conductivity measurements in Fig. 3 were made under an ac field).

## III. CONCLUSIONS

From the above experimental results and discussion it is evident that:

(i) In the intrinsic region the conductivity values of LiD are smaller than those of LiH, but the slope of the curve $\ln\sigma T$ vs $1/T$ in LiD is greater than that of LiH. The latter result leads to the conclusion that in LiD the value of $E_S$ is greater than that in LiH.

(ii) The formation energy of Schottky defects in LiD is greater than in LiH in accordance with the consideration that $E_S$ increases as $T_m$ is increasing.

(iii) Both LiD and LiH conductivity curves showed a dissociation region, as the alkali halides do. The slopes of these regions really give the activation energy for a free cation migration.

(iv) Previous experimental results show (Fig 4) that in lithium halides the energies $E_S$ and $E_m$ are decreasing as the mass of the anion is increasing. However, we found that the above rule is violated by LiH and LiD when compared with the lithium halides. Also $E_S$ for LiD is higher than in LiH in violation of the rule, but the opposite holds for $E_m$.

(v) The association energy of the $Mg^{+2}$–cation-vacancy complex in LiH is greater that that in LiD, while, as we have discussed above, the opposite is expected.

(vi) In spite of the fact that the samples which we have used contained a usual amount of impurities, large aggregation phenomena are observed when the crystals are not subjected to the usual thermal treatment.

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