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Electrical Conductivity in NH_4Cl and ND_4Cl Single Crystals

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Abstract – Electrical conductivity measurements are reported for normal and deuterated ammonium chloride single crystals in the temperature regions which characterize the pure and the impurity-dominated materials. We conclude from the data that conductivity in ammonium chloride is due to the formation of either cation or anion vacancies and a subsequent process controlled by a proton transfer. Our results are found to be consistent with a model proposed by Herrington and Staveley.

1. INTRODUCTION

It was noted, during studies on radiation-induced point defects in ammonium halide single crystals [1,2], that hydrogen migrates fairly rapidly through these crystals at room temperature. This effect may be seen directly in the electron paramagnetic resonance spectra of ND_3Cl color centers [2] in deuterated single crystals. If these crystals are exposed to the atmosphere for short periods of time, proton hyperfine interactions from hydrogen which has exchanged with deuterium atoms in the ammonium group become pronounced in the spectra. These measurements may, in fact, be used to determine the rate of hydrogen diffusion in ammonium halide crystals. The mechanism of such a rapid diffusion is still in doubt, however. A likely explanation is that this mechanism is the same as that proposed to explain electrical conductivity in the ammonium halides, which is also dependent on motion of hydrogen atoms. Diffusion and conductivity are then related by the Nernst-Einstein equation.

Electrical conductivity measurements on the ammonium halides were obtained first by Herrington and Staveley[3]. They found that ammonium chloride, in particular, is a significantly better intrinsic conductor than any of the alkali halides. Since conductivity in this material is due entirely to ionic motion, as it is in the alkali halides, they were lead to consider processes peculiar to the ammonium halides which might lead to lower activation energies for ion migration. When single crystals were doped with either divalent cation or divalent anion substitutional impurities the conductivity was enhanced by about the same factor, implying that anions and cations make comparable contributions to the conductivity. By contrast, cation motion predominates in the alkali halides. Several other properties of NH_4Cl single crystals seemed of special relevance: (1) the heat capacity is larger than can be explained by lattice and molecular harmonic motions, (2) the thermal expansion coefficient is anomalously high and (3) the vapor pressure is high, measurable even at room temperature. These suggest that at room temperature and below there is a significant amount of dissociation within the crystal matrix, of the form $NH_4^+ + Cl^- \rightarrow NH_3 + HCl$. Herrington and Staveley finally proposed a three-stage mechanism for ionic conduction (Fig. 1) based on this ease of dissociation: (1) NH_3 and HCl are formed by a proton transfer, adjacent to either a positive or negative ion vacancy; (2) either NH_3 or HCl moves into the vacancy; (3) a reverse proton transfer occurs forming NH4+ and Cl^- again, one of which has exchanged its position with the vacancy. A succession of these ex-

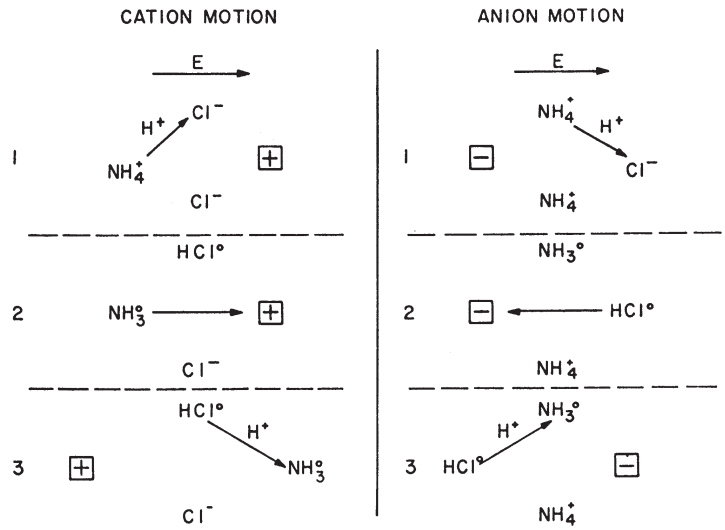

Fig. 1. Mechanism for ionic conduction in NH_4Cl (Shown in 110 plane.)

changes, under the influence of the applied electric field, results in a net transfer of charge.

A test of this hypothesis could be achieved by measuring the conductivities of both normal and deuterated ammonium chloride over some temperature interval. If a proton exchange is the controlling process in the above mechanism, in the sense that it has the highest activation energy (excluding the activation energy for vacancy production), then the attack frequency of the moving particle and hence the preexponential factor in the conductivity equation will be affected greatly upon deuteration of the crystal. The results of such measurements, reported in the following sections, show unambiguously that electrical conductivity in NH_4Cl is dependent on motion of hydrogen ions, in agreement with the mechanism proposed by Herrington and Staveley.

2. THEORY

Electrical conductivity may be expressed as the sum of the individual contributions of the different charge carriers in the material:

$$\sigma = \sum_i N_i z_i e \mu_i \tag{1}$$

where σ is the conductivity and where N_i, $z_i e$ and μ_i are the number, charge and mobility of the ith type of carrier, respectively. If, as in the alkali halides, the charge carriers are anions and cations, their contributions to the conductivity are determined by the concentrations of vacant lattice sites as well as the ion mobilities [4]. The equation for the conductivity can be written as

$$\sigma = \sigma_a + \sigma_c = N_a e \mu_a + N_c e \mu_c, \tag{2}$$

where N_a and N_c are the numbers of anion and cation vacancies per unit volume and where μ_a and μ_c are the anion and cation mobilities. The equations for the vacancy concentrations and ion mobilities are well known [5], and in our notation are:

$$N_a N_c = N_0^2 = N^2 \exp(-g/kT), \tag{3}$$

$$\mu_a = \frac{4a^2 e \nu_a}{kT} \exp(-\Delta g_a/kT), \tag{4}$$

$$\mu_c = \frac{4a^2 e \nu_c}{kT} \exp(-\Delta g_c/kT), \tag{5}$$

where N is the number of ions, either anions or cations, per unit volume, g is the Gibbs energy of Schottky defect formation, a is the anion-cation distance, ν_a and ν_c are the anion and cation

jump attempt frequencies. and Δg_a and Δg_c are the Gibbs energies of anion and cation migration. The Gibbs energy can be expressed as the enthalpy minus the product of absolute temperature and entropy, $g = h - Ts$.

In an Arrhenius plot of log (σT) vs. $1/T$ one would interpret curvature as an indication that both anions and cations make contributions to the conductivity. This is the case for alkali halides [6, 7]. On the other hand, barring the unlikely coincidence of equal activation energies, a linear Arrhenius plot would indicate that one charge carrier predominates and that the conductivity can be expressed as a single exponential,

$$\sigma T = \frac{4Na^2e^2\nu}{k}\exp\left[\frac{-g/2-\Delta g}{kT}\right] = A_0\exp\left(-[h/2+\Delta h]/kT\right). \quad (6)$$

This appears to be the situation for NH_4Cl. According to classical rate theory, the jump attempt frequency is proportional to the inverse square root of the mass of the vibrating ion [5]. In the case of NH_4Cl and ND_4Cl this means that if the mechanism for conduction is the motion of the anions, the conductivity of NH_4Cl and ND_4Cl would be the same; if the mechanism is cation motion, the ratio of NH_4Cl conductivity to ND_4Cl conductivity would be $\sqrt{11/9}$; if the mechanism for conduction is dominated by motion of a hydrogen ion, then the above ratio takes on the value $\sqrt{2}$.

In vacancy controlled mechanisms it is possible to separate the formation and migration energies from one another by putting a known amount of divalent cation impurity into the crystal. The cation vacancy concentration is then enhanced and the anion vacancy concentration is depressed. Then the equations for vacancy concentration are

$$N_c = N_a + N_i \quad (7)$$

where N_i is the number of impurity ions per unit volume, while equation (3) still holds for the product of the vacancy concentrations [5]. Consequently, the activation enthalpy for conduction changes from $h/2 + \Delta h_c$ to Δh_c, and the conductivity can be expressed as

$$\sigma T = \frac{4a^2e\nu_c}{k}N_i\exp\left(-\Delta g_c/kT\right) = C_0\exp\left(-\Delta h_c/kT\right). \quad (8)$$

3. EXPERIMENTAL PROCEDURE

NH_4Cl single crystals have the CsCl crystal structure in the temperature region from 184.3 to –30.5°C, which encompasses the interval of experimental investigation. Crystals, very nearly cubic in habit, were grown from saturated aqueous solution with urea added to suppress dendritic growth. Starting materials were either Fisher or Mallinckrodt analytic reagent grade materials. Some crystals were grown by slow evaporation of the solution in a temperature controlled chamber. Larger (up to 1 cm^3), and more perfect, crystals were grown by starting with a saturated solution at about 40°C in a closed vessel which was immersed in a water bath regulated to within 0.01°C/day. The temperature was then lowered by about 0.2°C/day over a period of weeks. The resulting crystals were colorless, perfect cubes. It was not possible to detect the presence of any urea impurity by using NMR and i.r. absorption techniques.

Deuterated single crystals were prepared by dissolving analytic grade NH_4Cl and urea in 99.85 mole-% D_2O and evaporating to dryness four times before growing crystals in a temperature-regulated solution; it is expected that 99.0 per cent deuteration was achieved for the freshly grown crystals. While handling the crystals in preparation for the conductivity measurements, they were exposed to the atmosphere with some consequent exchange of hydrogen for deuterium. An NMR analysis of some of these samples showed that the level of deuteration was 90 ± 5 per cent during measurements of the conductivity.

The samples were cut to about 1 × 7 × 7 mm size, polished, and painted with dag electrodes before being installed between the platinum contacts of the conductivity sample holder. The samples were kept in a dry argon atmosphere during the measurements of the conductivity. The conductivity measurements were made using standard a.c. bridge techniques.

4. RESULTS

A plot of log (σT) vs. 1000/T for NH_4Cl, $NH_4Cl{:}SrCl_2$ and ND_4Cl is shown for the temperature interval 180–60°C in Fig. 2. The concentration of Sr in the doped material was found to be about 55 ppm, using the flame emission spectroscopy analysis technique. There is good linearity observed for both the NH_4Cl and ND_4Cl curves over two decades of values on the ordinate within the high temperature, intrinsic region from 180 to 130°C. This implies that there is only one value for the activation enthalpy within the exponential of the conductivity equation, equation (6), and hence there is only one mechanism for conduction within this temperature interval. This contrasts with the situation for the alkali halides. whose conductivity plots show definite curvature in the high temperature regime. It should be remarked that when measurements were attempted

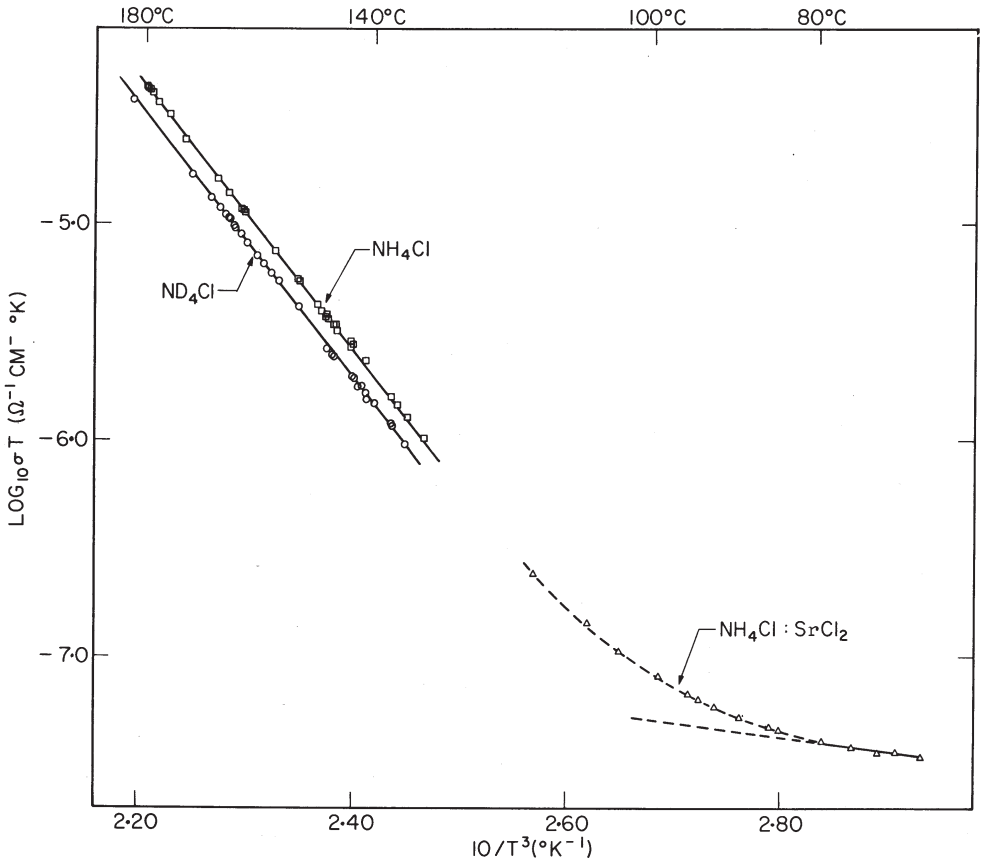

Fig. 2. The conductivity-absolute temperature product as a function of reciprocal temperature for NH_4Cl, ND_4Cl and $NH_4Cl{:}SrCl_2$ single crystals. The solid lines are a result of a least squares computer fit of a first degree polynomial to the data (only the five data points in the low temperature extreme of $NH_4Cl{:}SrCl_2$ were fitted).

at temperatures higher than about 180°C, the increased vapor pressure of NH_4Cl caused a boiloff of material to occur, degrading the sample and preventing further measurements.

The low temperature, impurity dominated or extrinsic conductivity region, is represented by the temperature interval from 130 to 60°C in the figure. Within this region, the doped material, $NH_4Cl:SrCl_2$, has conductivity values higher than those for the extrapolated linear plot of data in the intrinsic region. This shows that cation vacancies, induced by charge compensation of the substitutional Sr_2+ ions, are an essential part of the conductivity mechanism at these temperatures. In the linear portion of this region at the low temperature extreme, the conductivity equation again may be simplified to a single exponential, of the form of equation (8). There is now a single contribution to the activation enthalpy, that of the migration enthalpy of the charge carrier. This value is given in Table 1, along with the activation enthalpy for the intrinsic region.

The linear fit to the NH_4Cl data in the figure has the same slope as the NH_4Cl data in the intrinsic region, leading to the same value for the activation enthalpy within this temperature interval. In all of the above cases, a linear relation was computer-fitted to the data points using a least-squares routine.

Table 1

Material	Conductivity* (Ω^{-1} cm^{-1})	Activation enthalpy (eV)
NH_4Cl	$8{\cdot}14 \times 10^{-9}$	1·26
ND_4Cl	$6{\cdot}07 \times 10^{-9}$	1·26
$NH_4Cl:SrCl_2$	—	0·15

*At 420°K.

5. DISCUSSION

The differences in conductivity for NH_4Cl and ND_4Cl single crystals in the intrinsic region cannot be ascribed to differences in impurity concentrations since the same starting materials were used for both crystals, except that the deuterated crystals were grown from a D_2O solution. Also, the excellent fit of a single exponential to both sets of data implies that the conductivity measurement is dominated by the motion of a single charged particle across a potential barrier which is identical in both crystals. We conclude that the conductivity mechanism either is a single charge transfer process, or it is a sequence of charge transfers in which one jump (the controlling process) is associated with a significantly higher activation enthalpy than the others.

In either case, the parallel displacement of the two conductivity curves in the intrinsic region is due to a different preexponential constant in equation (6), and therefore there must be a difference in the jump attempt frequency, ν, of the charge carrier for the normal and deuterated material. Since this quantity is inversely proportional to the square root of the mass of the charge carrier, the ratio of conductivities for any particular temperature in the intrinsic region is

$$(\sigma T)_H/(\sigma T)_D = \nu_H/\nu_D = (m_D/m_H)^{1/2}, \quad (9)$$

where the subscripts H and D refer to the NH_4Cl and ND_4Cl cases, respectively. From the data of Fig. 2 we find that $(\sigma T)_H/(\sigma T)_D = 1.34$, evaluated within the linear region. Of the limited number of charge carriers which could exist in this material, only the bare proton/deuteron has a sufficiently high value for the mass ratio to fit the data: $(m_D/m_h)^{1/2} = 1.414$. The discrepancy between these two numbers is easily explained by the fact that the ND_4Cl crystals were not completely deuterated. Letting x represent the fraction of the total charge carriers in ND_4Cl crystals which result from hydrogen substitution, then

$$(\sigma T)_H/(\sigma T)_D = \sqrt{2}/[1+(\sqrt{2}-1)x]. \quad (10)$$

When equation (10) is evaluated for the value of the conductivity ratio given above, it is found that $x = 0.14$. Thus the experimental result can be accounted for by assuming only 86 per cent deu-

teration of the ND_4Cl crystals, which is in excellent agreement with the result of the NMR analysis given in Section 3.

It appears very likely, from this evidence, that the charge carrier controlling the process of charge transport in NH_4Cl is a proton. The results of divalent cation impurity substitution indicate that vacancies, of either polarity, are also required within the mechanism. These ingredients are both contained within the Herrington-Staveley model, pictorially represented in Fig. 1. Processes 1 and 3 in the dual picture are a forward and reverse proton switch. Process 2, the intermediate charge-transfer process, results in a displacement of the cation/anion vacancy by one lattice spacing along a ‹100› direction. Each step is aided by the applied electric field and contributes a portion of the total motion of the charge. Our results are consistent with this model. Furthermore, if the initial proton transfer is the controlling process of the mechanism, process 2 must have a much lower activation enthalpy.

The measured activation enthalpy (Δh_c) for conduction in strontium doped ammonium chloride in the impurity-dominated region is, from Table 1, 0.15 eV. This value represents, from equation (8), the migration enthalpy of the charge carrier, equal to that of the controlling process, step 1 of Fig. 1. The measured activation enthalpy ($h/2+ \Delta h_c$) of 1.26 eV in the intrinsic region of the conductivity curve leads to a value of 2.22 eV for the enthalpy (h) of formation of vacancy-pairs (Schottky defects) in pure NH_4Cl. These may be compared with the values for CsCl[8] of 0.6 and 0.3 eV for the enthalpies of cation and anion vacancy mobility, respectively, and 1.8 eV for the enthalpy of Schottky defect formation.

The above values for NH_4Cl differ from those reported by Herrington and Staveley, which are $\Delta h_c = 0.75$ eV and $h/2 + \Delta h_c = 1.15$ eV, so that $h = 0.80$ eV. Our disagreement principally is with the measurement of activation enthalpy in the extrinsic region of the conductivity curve. On examining their data, we observed an intermediate temperature region in their conductivity curves for doped samples in which the measurements seem to correspond very well to those of our extrinsic region. Their measurement of an activation enthalpy at even lower temperatures, which they attribute to the motion of the charge carrier of the high temperature mechanism, may, in fact, be associated with some form of charged aggregate.

Thus the energy of Schottky defect formation in NH_4Cl is in substantial agreement with the value quoted for isomorphous CsCl. The low value found for the activation enthalpy for migration of the charge carrier, compared to ionic mobilities in CsCl or alkali halides, is what one might intuitively expect for a mechanism dominated by a proton exchange. The identical process has recently been examined theoretically by Clementi [9], in his study of the transitional states in the $NH_3 + HCl \rightarrow NH_4Cl$ reaction. From his potential diagrams [10], we estimate a barrier height of about 0.5 eV for the gas phase reaction, using an interatomic distance appropriate to the solid. However, the problem is modified greatly by the presence of the Madelung potential in the solid. It would be desirable to calculate the effect of this contribution on Clementi's potential energy diagram for the free space reaction, though this appears to be a very difficult problem.

6. CONCLUSION

Conductivity in ammonium chloride seems to be dependent on formation of Schottky defects as in the alkali halides. However, the conductivity mechanism is not the simple ion motion found in alkali halides, but is a process which is apparently dominated by a proton transfer. Such a mechanism has been suggested by Herrington and Staveley and our results, based on measurements of normal and deuterated ammonium chloride single crystals, are in agreement with this model. Our conductivity data are somewhat different from those reported previously. In particular, the activation enthalpy for conduction in the extrinsic region is considerably smaller than was indicated. It is asserted that this value is essentially the activation enthalpy of the proton transfer.

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