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On the Mechanism of Conductivity of Ammonium Salts

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The conductivities of HSO_4^--doped $(NH_4)_2SO_4$ (AS) and $NH_4H_2PO_4$ (ADP) crystals are investigated in the temperature range 25°–180°C. The mobility of the charge carriers (protons) is thermally activated and is expressed in accordance with the relation $\mu = 0.16 \exp(-0.49)$ eV$/kT$ and $\mu = 0.80 \exp(-0.54\ \text{eV}/kT)\ \text{cm}^2\ \text{V}^{-1}\ \text{sec}^{-1}$ for AS and ADP crystals, respectively. Three-stage mechanism of proton transport in the lattice of ammonium salt is suggested: (1) formation of the charge carrier $NH_4^+ + X^- \rightarrow NH_3 + HX$, (2) reorientation of the protonated anion $HX \rightarrow XH$, and (3) proton jump to the neighbor anion $XH + X^- \rightarrow X^- + HX$. The activation energy for mobility is close to that for dielectric relaxation process, i.e., the only thermally activated stage in the mobility process is reorientation of the protonated anion. This very stage is also the rate-determining in the mobility as it is seen from the comparison of the correlation time for proton diffusion and the dielectric relaxation time. These experimental results are in good agreement with the known proton dynamic data in KDP-type ferroelectric crystals.

It is known that specific conductivity of ammonium salts is much higher than one for the corresponding alkali metal salts. For example, in the case of ammonium and alkali halides crystals this difference amounts to 5–6 orders of magnitude (*1*). The reason for this high conductivity was not clearly understood. The conductivity mechanism, proposed by Herrington et al. (*1*), in the best case would explain the anomalously high mobility of the charge carriers in ammonium salts. But the conductivities of alkali halides and ammonium halides crystals, containing equal quantities of aliovalent impurities, are nearly equal (*1*, *2*), so the mobilities of charge carriers in ammonium and alkali salts cannot differ markedly. Then the mechanism, proposed by Herrington et al. (*1*), as in the case of alkali halides conductivity, is reduced to the motion of cation vacancies, that is ammonium ions, although the most probable charge carriers in ammonium salts are protons (*3*, *4*).

This work suggests the mechanism of the charge transport in the ammonium salts lattice.

Ammonium sulfate (AS) and ammonium dihydrophosphate (ADP) were chosen as the initial object of this investigation due to the simplicity of the crystal growth and relatively high conductivity (*3*, *5*). Single crystals were grown from aqueous solutions by slow (0.5°C/day) cooling from 40°C down to room temperature. The quantities of additives in the crystals were determined by titration of the solutions obtained after dissolving in water the crystals measured. The direct current conductivity was measured using conventional three-electrode system. Vacuum-evaporated silver electrodes were used. Dielectric measurements were carried out in TR-9701 type bridge set.

Experimental Results

According to supposition of Schmidt (*5*), AS is a proton conductor. If so its conductivity must be sensitive to the presence in AS lattice of proton donoring impurities. The experimental values plotted in Fig. 1 represent the temperature dependence for some AS crystals

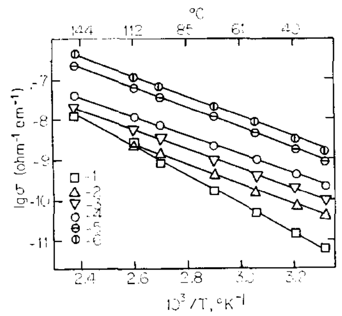

FIG. 1. Temperature dependence of conductivity for pure (1) AS crystal and ones with HSO_4^- additive (in mole%): 5×10^{-3} (2); 1.2×10^{-2} (3); 2.7×10^{-2} (4); 1.40×10^{-1} (5); 3.14×10^{-1} (6).

containing various concentrations of HSO_4^- additives. Activation energies for d.c. conductivity have the values 0.76 ± 0.02 eV and 0.49 ± 0.03 eV in intrinsic and extrinsic regions respectively. The magnitudes of the intrinsic conductivity and its activation energy are close to those obtained by Schmidt (*5*). The concentration dependence of the AS conductivity is plotted in Fig. 2 in logarithmic scale. As it is seen, the conductivity is the linear function of HSO_4^- concentration.

The charge carriers concentration factor entering the expression for the intrinsic conductivity of ionic crystals $\sigma = n\mu q$ may be written as (*2*)

$$n = \sqrt{NN'}\exp(-E_0/kT), \qquad (1)$$

where N and N' are concentrations of lattice sites and interstitials, respectively, and E_0 is the activation energy for creation of the "free" charge carriers. The mobility of the charge carriers in ionic crystals is a thermally activated process and corresponding equation may be expressed as (*2*):

$$\mu = \frac{q\nabla^2 \nu\gamma}{kT}\exp(-E_t/kT), \qquad (2)$$

where q is the charge of the carriers, ν a jump attempt frequency, ∇ the jump distance, and γ the geometric factor depending upon the type of crystal symmetry. Investigation of the extrinsic conductivity of an ionic crystal makes it possible to determine E_t values (*6*) and consequently E_0. From the known concentrations of the impurity in the crystal it is possible to determine the mobility of the charge carriers in accordance with the theory of impurity conduction, proposed by Koch and Wagner (*6*). From the data plotted in Figs. 1 and 2 the mobility can be expressed as

$$\mu = 0.16\exp(-0.49/kT)\,\text{cm}^2/\text{V sec}.$$

There seems to be an additional experimental fact proving the reliability of E_t value determined in such a way. After heating the pure AS crystals for some hours in the temperature range 160–190°C in a vacuum of 10^{-4} torr, the volume conductivity of the crystals increases 2–4 orders of magnitude, the activation energy being 0.5 eV (Fig. 3a). Under such experimental conditions AS decomposes* according to equation

$$(NH_4)_2SO_4 \rightarrow NH_3 + NH_4HSO_4,$$

so it was natural to suppose that extra conductivity as in the case of deliberate incorporation of the additive could be associated with the increase in concentration of HSO_4^- ions in the crystal lattice. The homogeneous decomposition of solids, however, occurs extremely rarely. Further investigation showed that AS crystals after heat treatment had nonohmic behavior. The current through the crystal is proportional to the square of the applied voltage (Fig. 3b). As may be seen by inspection of run 2 in Fig. 4, the increase in "conductivity" is the larger when the applied voltage is larger. The conductivity restored its initial value when the crystal was polished, that is after removing the surface, decomposed

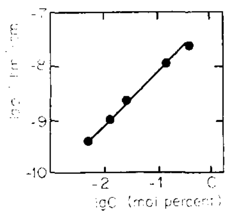

FIG. 2. Conductivity versus HSO_4^- content for doped AS crystals at 72°C.

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* The extent of decomposition in some experiments amounted to 1%.

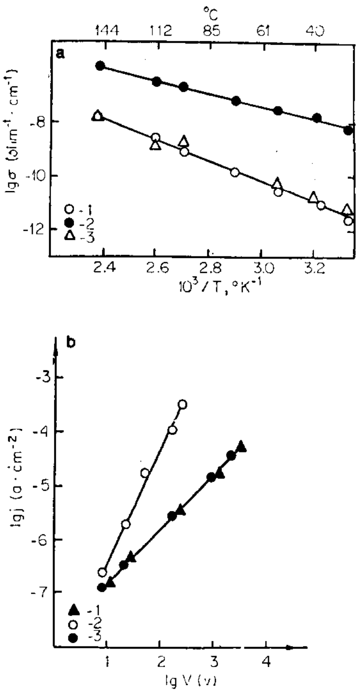

FIG. 3. Effect of heat treatment on conductivity of pure AS crystal (a) Temperature dependence: (1) initial conductivity; (2) after the heat treatment; (3) after removing the surface layer. (b) Current density versus field strength. Notations are the same as in (a).

regions of the crystal and this time had ohmic behavior (Fig. 3b, run 3).

This experimental data may be explained in terms of space charge limited currents (SCLC). As it is well known, expression for the SCLC in ionic crystals has the form (*7*)

$$j = \tfrac{9}{8}\mu\mathscr{E}(V^2/l^3), \tag{3}$$

where j is the current density, μ mobility, $\mathscr{E}$ dielectric constant, V applied voltage, and l length of the sample. SCLC due to protons injected from H_2-saturated palladium electrodes was observed (*7*, *8*, *9*). In our case injection takes place from NH_4HSO_4 layer formed during the mentioned thermal decomposition of AS. Really, the crystal of pure AS coated with NH_4HSO_4 electrodes after prolonged heating in closed vessel at 150°C shows nonohmic behavior characteristic for SCLC, just as the electrical properties of the crystal coated with usual Ag electrodes have not changed after such treatment.

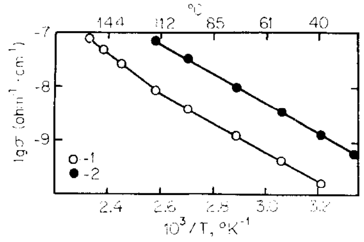

FIG. 4. Plot of $\log\sigma$ against $1/T$ for pure (1) ADP crystal and for one containing 9×10^{-2} mole% HSO_4^- additive.

As may be seen from Eq. (3) the temperature dependence of SCLC for ionic crystals is determined by the energy of activation for mobility of charge carriers, and that is the most probable reason for coincidence of the E_t and of the activation energy for "conductivity" in SCLC region.

It is interesting to compare electrical properties of HSO_4^--doped AS crystals with those of KH_2PO_4 (KDP) crystals doped as in our case with HSO_4^- impurity (*10*). According to O'Keeffe et al. (*10*) proton conductivity of KDP crystals increased linearly with impurity concentration. The values of extrinsic conductivities and their activation energies for AS and KDP crystals are nearly equal. It may be the result of identical mechanisms of the proton conductivity in both cases.

Similar data are obtained in the case of $NH_4H_2PO_4$ (ADP) crystals containing HSO_4^- impurity. As it is seen from Figs. 4 and 5 ADP conductivity is proportional to the content of HSO_4^- impurity in the crystal and the mobility may be expressed as

$$\mu = 0.8\exp(-0.54/kT)\,\mathrm{cm}^2/V\,\mathrm{sec}.$$

It is well known (*10*) that conductivities and their activation energies for ADP and

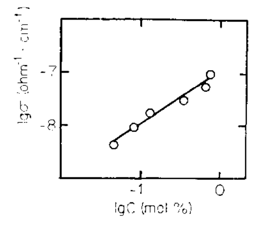

FIG. 5. Conductivity versus HSO_4^- content for doped ADP crystals at 72°C.

KDP crystals are equal so it is natural that effects of doping with the same impurity are identical in both cases.

According to Murphy's (*3*) suggestion the mechanism of the proton transport in ADP crystal consists of 2 stages:

a. Self-ionization according to equation

$$2H_2PO_4^- \rightarrow H_3PO_4 + HPO_4^{2-}$$

b. Proton transfer to the nearest anion

$$H_3PO_4 + H_2PO_4^- \rightarrow H_2PO_4^- + H_3PO_4$$

Having this in mind as well as the mechanism of proton transport in water (*11*) the following mechanism for the charge transfer in the ammonium salts lattice may be suggested, e.g., for AS:

1. Proton transfer from cation to anion:

$$NH_4^+ + SO_4^{2-} \rightarrow NH_3 + HSO_4^-$$

2. Reorientation of protonated anion

$$HSO_4^- \rightarrow SO_4H^-$$

3. Proton jump to the neighbor anion

$$SO_4H^- + SO_4^{2-} \rightarrow SO_4^{2-} + HSO_4^-$$

The first stage corresponds to formation of the "free" charge carriers, the second and third to the mobility process.

Occurrence of the first stage of this mechanism is rather probable, since this very process takes place in thermal decomposition of ammonium salts. Let us analyze more precisely the mobility process.

In tetragonal structure of ADP crystal (*12*) each anion is placed in the center of tetrahedra whose corners are formed with nearest anions. The distance between the centers of neighbor anions equals 4.3 Å while the distance covered with proton when it jumps along OH—O bond between neighbor anions (interbond jump) is no more than 0.4 Å if the favorable orientation exists.

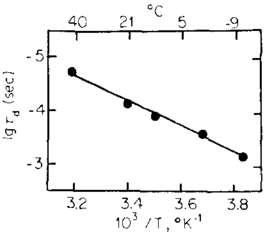

FIG. 7. τ_d versus $1/T$ for ADP crystal.

AS crystals in the temperature range investigated have the point symmetry Pnam (*13*). Each anion has in anion sublattice 6 nearest neighbors. The distance between the neighbor anions does not exceed 5.3 Å. The radius of SO_4^{2-} ion is 2.3 Å so the distance the proton passes in interbond jump between neighbor anions does not exceed 1 Å when the favorable orientation exists. Taking into consideration the length of O—H bond there may be assumed that this distance like in the case of ADP lattice does not exceed 0.3–0.4 Å that is just the same as exists in ice lattice, the typical proton conductor (*11*).

According to Schmidt et al. (*14*) the activation energy of proton intrabond jumping in KDP lattice coincides with that for extrinsic conductivity of these crystals. Following the analogy mentioned above it may be assumed that in the case of ammonium salts AS and ADP the activation energy of reorientation will coincide with that for mobility that is from the two stages of mobility process

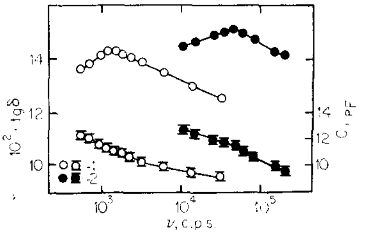

FIG. 6. Dielectric spectra of HSO_4^--doped ADP crystal at −10°C (1) and 48°C (2).

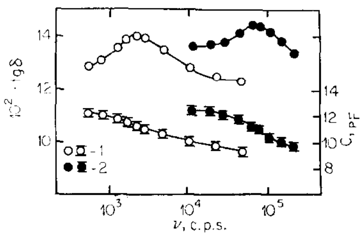

FIG. 8. Dielectric spectra of AS crystals.

TABLE I

SUMMARY OF MOBILITY AND DIELECTRIC MEASUREMENTS RESULTS FOR AS AND ADP CRYSTALS

Ammonium salt	E_t (eV)	E_d (eV)	γ^a	α^b (10^{-8} cm)	τ_c (10^{-5} sec)	τ_d (10^{-5} sec)
$(NH_4)_2SO_4$	0.49 ± 0.03	0.51 ± 0.04	1/6	6.0	3.3	5.5
$NH_4H_2PO_4$	0.54 ± 0.03	0.50 ± 0.04	1/4	7.4	8.3	4.6

[a] This choice of the γ factor, taking into consideration only the number of nearest neighbors, is determined with exponential decay of the tunneling probability as the interbond jump distance increases.

[b] Proton mobility was measured along crystalline *c* axis for AS crystals and along *a* axis for ADP.

reorientation stage only is activated. In an attempt to examine this suggestion we investigated temperature dependence of dielectric spectra of AS and ADP crystals containing HSO_4^- impurity. As is well known, the dielectric measurements can serve as the test for reorientation process of the permanent dielectric dipoles (*15*). Fig. 6 represents the frequency dependence of capacity and loss factor of ADP crystals containing 0.3 mole % of NH_4HSO_4 impurity. Dielectric spectra have the usual Debye form. Figure 7 represents in Arrhenius coordinates the temperature dependence of τ_d, i.e., the dielectric relaxation time. Similar results are obtained for AS crystals (Figs. 8 and 9). Calculated from these data activation energies are represented in Table I. It is evident that the activation energies for reorientation process and for mobility are equal for substances investigated. This made us conclude that the only thermally activated stage in the proton mobility process is reorientation of protonated anion.

The same stage apparently is limiting in the mobility process. This could be seen from comparison of the τ_d and τ_c that is the correlation time for the proton diffusion process determined from mobility values according to Nernst–Einstein relation written in the form

$$\tau_c = \frac{q\gamma p a^2}{\mu k T}, \qquad (4)$$

where p probability of interbond jump of the proton and its fixation at a neighbor anion, a lattice parameter. It is evident that for values $\tau_d \ll \tau_c$ interbond jump process will determine the mobility values, but for $\tau_d \simeq \tau_c$ the rate determining process is reorientation of the protonated anion.

Table I represents τ_c values calculated according Eq. (4) in assumption that $p = \frac{1}{2}$ and corresponding τ_d values obtained at 23°C.

It may be seen that $\tau_d \simeq \tau_c$, and this is the reason for assumption that the rate-determining stage of the mobility is reorientation of the protonated anion as it was stated above.

These results allow us to draw the conclusion that interbond jump of a proton is inactivated process and probably takes place through proton tunneling. This inference is confirmed by the results obtained by direct investigation of the proton dynamics in the lattice of ferroelectrics of KDP group. Acording to Blinc et al. (*16*, *17*) in paraelectric phase of KDP crystal protons tunnel between neighbor anions at the rate $\sim 10^{13}$ Hz. This frequency is much more than $1/\tau_c$ value in the temperature range investigated. This means that at the time of the existence of the favorable orientation for the interbond transfer proton will

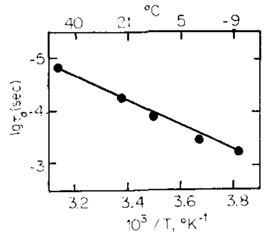

FIG. 9. Plot of $\log \tau_d$ against $1/T$ for AS crystals.

repeatedly jump from anion to anion, i.e., the proton is statistically distributed between two anions.

Thus ours and known data in literature are in good agreement with a suggested mechanism of conductivity of the ammonium salts crystals. More detailed mechanism may be suggested after investigation of some other ammonium salts including deuterated ones and will be published later.

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