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Protonic Conduction in Totally Deuterated Ammonium Dihydrogen Phosphate

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The conductivity of deuterated ammonium dihydrogen phosphate single crystals was measured as a function of temperature. Crystals doped with deuterated NH_4HSO_4 were also studied. The results parallel those for $NH_4H_2PO_4$ to the extent that defects in the hydrogen-bond network give rise to the conductivity. One difference in the results for the two crystals is the temperature which marks the onset of a high temperature conductivity distinguished by plotting log σT versus $1/T$ and observing a break in the straight line. This break temperature is different for the hydrogen versus the deuterated crystal in $NH_4H_2PO_4$ as it is for other isomorphous salts.

Introduction

Ionic conduction in $NH_4H_2PO_4$ has been discussed along with the isomorphic crystals KH_2PO_4 and KH_2AsO_4 in a review article by Glasser (*1*) which covers the entire field of proton conduction in solids. The article summarizes experimental work on solids which have three-dimensional hydrogen-bonded networks and considers conduction in $NH_4H_2PO_4$ at length, reporting the most recent work (*2–4*) on the subject. The conclusion is that this compound falls into the category of protonic conductors whose prototype is KH_2PO_4, a much studied crystal, especially from the point of view of conductivity (*5*). One remaining uncertainty in the study is whether there is a phase transition or some type of conductivity transition at higher temperatures which can be determined from a plot of log σT versus $1/T$ usually made for ionic conductors. This transition to a region where the conductivity increases more rapidly with temperature than at lower temperatures is well-documented for KH_2PO_4 (*5*) and its deuterated analog KD_2PO_4 (*6*). However, some conflicting reports have been made (*2, 3*) regarding whether the conductivity of $NH_4H_2PO_4$ shows such a break or knee in the conductivity plots. Harris and Vella (*3*) claim that the knee only appears because of surface conduction and disappears whenever surface current is shunted to ground. Our studies (*2*; and those of others, *4*) have shown that the break appears despite any attempt to shunt surface current. We have now added to the information by completing work on deuterated ammonium dihydrogen phosphate, $ND_4D_2PO_4$. This is an important part of the overall study since the transition temperature is shifted considerably by the substitution of deuterium for hydrogen (*6*), analogous to the shift in the Curie temperature when the same substitution is made.

Experimental

Our experimental work has proceeded in a fashion similar to the study of $NH_4H_2PO_4$ (*2*). Pure and DSO_4^- doped single crystals of $ND_4D_2PO_4$ were grown from supersaturated solutions and cut to a nearly cubic shape. Their d-c conductivity as a function of temperature was then measured using previous methods (*5*). An additional electrode was utilized in order to shunt any surface current to ground.

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TABLE I

CONDUCTIVITY PARAMETERS

	$ND_4D_2PO_4$	$NH_4H_2PO_4$	KD_2PO_4	KH_2PO_4
$10^{10} \times \sigma$	1.3	2.9	0.28	0.70
E_a	13.0	12.7	12.3	12.6
T_c	242	148	213	123
T_b	236	360	375	453

Results

The pertinent results are shown in Fig. 1 and demonstrate typical findings for the dihydrogen phosphate crystals. The results for $NH_4H_2PO_4$ have been included for comparison. These best straight lines have been constructed from more than 30 individual data points. The most important new result which we wish to focus on is the very distinct break in the conductivity plot at 63°C found for two crystals of $ND_4D_2PO_4$. Thus, the break occurs in $NH_4H_2PO_4$ and $ND_4D_2PO_4$ and is not the result of surface phenomena of any sort. In addition, the break temperature is lower than that found for $NH_4H_2PO_4$ by some 24°. This parallels exactly the results found for the KH_2PO_4-KD_2PO_4 isomorphous pair where the deuterated crystal has a break temperature 78° lower than KH_2PO_4.

The doped crystals show that increasing the number of defects in the hydrogen-bonded network of the deuterated crystal increases the conductivity as it did with $NH_4H_2PO_4$ (*2*).

Table I compares the room temperature conductivity σ, activation energy for conduction E_a, curie temperature T_c, and break temperature T_b for both pairs of crystals.

We cannot say whether this break in the conductivity found for the $NH_4H_2PO_4$-$ND_4D_2PO_4$ pair corresponds to a true phase transition, as has been proposed (*1*) for the potassium crystals, but we do feel that the break is real and is in some way related to the motion of protons, as is the ferroelectric transition temperature. It is after all the motion of the protons, via the defect mechanism which forms the basis for protonic conduction in all of these crystals. Additional experimental techniques should be employed to further investigate the nature of this break or transition.

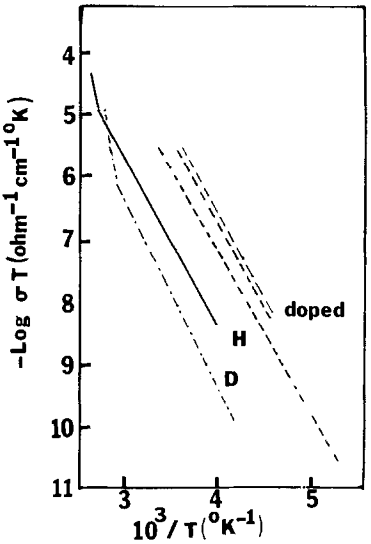

FIG. 1. The conductivity of pure and doped $ND_4D_2PO_4$.

Acknowledgments

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References

1. L. GLASSER, *Chem. Rev.* **75**, No. 1, 21 (1975).
2. C. T. PERRINO AND P. WENTRCEK, *J. Solid State Chem.* **10**, 36 (1974).
3. L. B. HARRIS AND G. J. VELLA, *J. Chem. Phys.* **58**, 4550 (1973).
4. E. J. MURPHY, *J. Appl. Phys.* **35**, 2609 (1964).
5. M. O'KEEFFE AND C. T. PERRINO, *J. Phys. Chem. Solids* **28**, 211 (1967).
6. M. O'KEEFFE AND C. T. PERRINO, *J. Phys. Chem. Solids* **28**, 1068 (1967).