JOURNAL OF SOLID STATE CHEMISTRY **10**, 36–38 (1974)

Protonic Conduction in $NH_4H_2PO_4$

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Received August 9, 1973

The conductivity of ammonium dihydrogen phosphate has been measured as a function of temperature and dopant concentration. A previously disputed break in the log conductivity vs reciprocal temperature plots has been observed. The activation energy is in agreement with previous work on $NH_4H_2PO_4$. In addition, the conductivity vs concentration of NH_4HSO_4 plot is linear, permitting the calculation of the L defect mobility and indicating that the proton is the conducting species. It is concluded that the mechanism of conduction is the same as previously proposed for KH_2PO_4 and KH_2AsO_4.

Introduction

Ionic conduction in $NH_4H_2PO_4$ has been studied by Murphy (*1*) and Pollock and Sharan (*2*). They report electrolysis experiments on single crystals which indicate that proton migration takes place under the influence of an electrical bias. In addition, they have measured proton conduction as a function of temperature and, to a degree, studied the effects of doping. Their conclusions are similar to the extent that both papers describe a mechanism of proton migration along the hydrogen-bond network. Disagreement occurs over the existence of a break or "knee" in the log σ vs $1/T$ plots and, more surprisingly, over the value of the conductivity at 298°K. In this latter instance, their results differ by a factor of 10,000.

We have undertaken a conductivity study of $NH_4H_2PO_4$, including 3 sulfate-doped crystals. It was our intention to provide additional data which would resolve the discrepancies noted above and to more clearly characterize the effect of doping. By doping these crystals with NH_4HSO_4, L defects (*2, 3*) are built into the hydrogen-bond network and a corresponding conductivity increase should be realized. An L defect is described elsewhere (*3*) as the vacancy of a proton between two oxygens on neighboring phosphate tetrahedra. We seek explicitly a conductivity dependence on the concentration of HSO_4^-, assuming that a substitution occurs on an $H_2PO_4^-$ lattice site producing one L defect each. Such a procedure has been followed for KH_2PO_4[3] and KH_2AsO_4[4] showing protonic conduction, and similar behavior is expected for $NH_4H_2PO_4$. Murphy studied two crystals, one doped with Ba^{2+} and one doped with SO_4^{2-}. Both showed an increase in conductivity but with extremely low dopant levels.

The specific mechanism of proton migration will be mentioned only briefly here, since it is amply described elsewhere (*2–4*). Protons move along the hydrogen-bond network by a series of two different types of jumps: interbond jumps, across the edge of a tetrahedron, and intrabond jumps, along the $O–H \cdots O$ hydrogen bond from one tetrahedron to another.

Experimental

Single crystals of pure and HSO_4^--doped $NH_4H_2PO_4$ were grown from supersaturated solutions and their direct-current conductivity

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Printed in Great Britain

determined by previous methods (*4*). The crystals were analyzed for sulfate by dissolving them in an acidic solution, adding $BaCl_2$ and Triton X-100 detergent suspending the $BaSO_4$ thus formed. The optical absorbance of the suspension was then compared to a calibration curve of absorbance vs known SO_4^{2-} concentration in suspension.

Results

Pure $NH_4H_2PO_4$

The experimental results obtained on the pure crystal are shown in Fig. 1 as solid lines, constructed from numerous data points. We confirm the break in the curve as reported by Murphy. We have observed this break on two crystals after slow heating and cooling with reproducible results. The break occurs at 87°C compared to 84°C found by Murphy with many fewer data points. The conductivity at 298°K is 2.0×10^{-10} ohm^{-1} cm^{-1} which compares favorably to Murphy's result and to previous data on $KH_2PO_4{}^3$, $KH_2AsO_4{}^4$, and $KD_2PO_4{}^5$. We cannot explain the results of Pollock and Sharan unless it is due to some effect of alternating-current measurements. The low temperature activation energy, which is the proton migration energy for the inter-bond jump, is 12.1 kcal/mole and compares favorably to the results of Murphy and Pollock and Sharan and to values for the other isomorphous crystals.

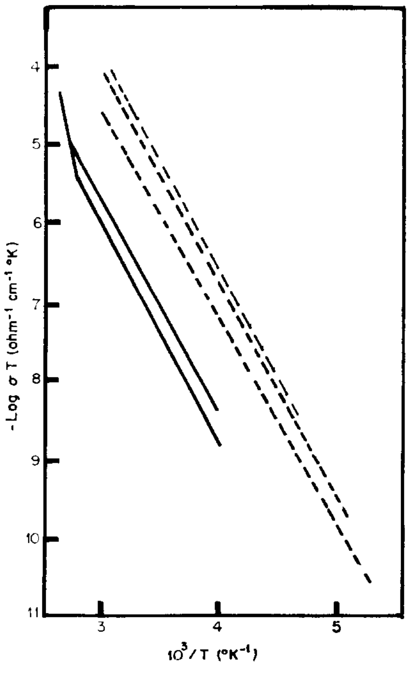

FIG. 1. The conductivity of pure and doped $NH_4H_2PO_4$. The solid lines are for the pure $NH_4H_2PO_4$ and the results of the doped crystals are indicated by the dashed lines. All of the curves are least-square fits to the numerous data points.

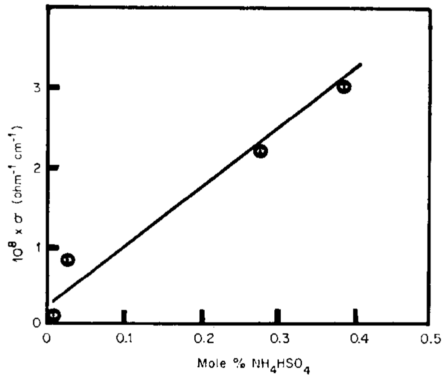

FIG. 2. The conductivity vs concentration data for $NH_4H_2PO_4$ doped with NH_4SO_4 at 298°K. The circles are the data points for the three doped crystals.

Doped $NH_4H_2PO_4$

The three dashed curves on Fig. 1 represent the doped crystals which all show an increased conductivity and nearly the same slope as the pure crystal.

Figure 2 shows the conductivity vs concentration of HSO_4^- at 298°K. If we assume, as previously indicated, one L defect for each HSO_4^-, then the nearly linear increase in conductivity proves protonic conduction when supplemented by the electrolysis experiments previously mentioned. The mobility, μ, of the L defect can be calculated from these results using $\sigma = ne\mu$, where n is the density of L defects. This procedure yields a value of 5.3×10^{-11} cm^2 V^{-1} sec^{-1} and is a realistic value when compared to other hydrogen phosphates (*3*, *4*).

Conclusion

With very little data Murphy appears to have made justifiable conclusions regarding proton conduction in $NH_4H_2PO_4$. However, the data of Pollock and Sharan are not reinforced by our results. The data verifies that $NH_4H_2PO_4$ fits the model of protonic conduction in hydrogen-bonded phosphate crystals proposed by O'Keeffe and Perrino (*3*). That paper and another on KH_2AsO_4 (*4*) provide a detailed mechanism and a complete discussion of proton migration which our data fit.

Note added in proof. A recent article (*6*) also reports results on pure $NH_4H_2PO_4$ and disputes the existence of the "knee."

Acknowledgments

This work was supported by a grant from the Research Corporation.

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