JOURNAL OF SOLID STATE CHEMISTRY 27, 263–265 (1979)

Electrical Conduction in Deuterated Hydrogen Bonded Crystals

M. SHARON

Department of Chemistry, I.I.T. Bombay-400076

Received August 25, 1978

Alternating current conduction of pellets of KH_2PO_4, KD_2PO_4, KH_2AsO_4, and KD_sAsO_4 have been studied. In all these crystals protons are the main carrier of the current. It is observed that with all the deuterated crystals, the enthalpy for the conduction is higher than for the normally hydrogen bonded crystal. The results are explained on the basis of the synchronous rotation mechanism proposed by the author in his earlier publications.

Introduction

Sharon and Kalia (*1*) have studied the dc electrical conduction of $NH_4H_2PO_4$ and KH_2PO_4 single crystals and have proposed a new mechanism of synchronous rotation of the H_2PO_4 group. They have concluded that the enthalpy for the conduction process obtained from the experimental results is related to the enthalpy for the rotation of the phosphate group rather than to the enthalpy for the formation of the defect (Frenkel type). If this hypothesis is to be taken as correct then the deuteration of the hydrogen bonded crystal should always result in higher enthalpy values irrespective of whether there is any contraction or expansion in the deuterated hydrogen bond, because the deuterated phosphate group (i.e. D_2PO_4) would always be heavier and bulkier to rotate than simple H_2PO_4 and therefore the deuterated crystal would need a higher enthalpy value. On the other hand, if a defect mechanism operates with these hydrogen bonded crystals, then the deuterated crystal where there is expansion of O–H···O bond would show a lower enthalpy value for the conduction whereas when there is a contraction in O–H···O bond due to the deuteration, it should show a higher enthalpy for the conduction process. Pollock and Sharon (*2, 3*) have shown that the KHF_2 crystal [where there is contraction of bond length on deuteration (*4*)] gives on deuteration a higher enthalpy value for the conduction than does the normal KHF_2 crystal, whereas $NH_4H_2PO_4$ also shows a higher enthalpy value for the conduction in spite of the fact that there is an expansion of the O···D–O bond (*5*).

However, there is no report about the electrical conductance in KH_2AsO_4, KD_2AsO_4 and KD_2PO_4. Ubbelohde (*4, 6*) has reported that there is a small expansion in the bond length for these crystals. It would therefore be interesting to observe whether KH_2PO_4 and KH_2AsO_4 would also behave in similar manner to what has been observed with KHF_2 and $NH_2H_2PO_4$ crystals.

Experimental

The purification of crystals was carried out in the usual manner (*1, 2*). Deuterium substitution was performed by the method

0022-4596/79/020263-03$02.00/0

discussed in (*2, 3*). A.c. conductance and d.c. conductance (to determine the transport number of current carrier in KH_2AsO_4) measurements were made by the method discussed earlier (*1, 3*). Wyne Kerr bridge (1100 Kcs) a.c. bridge was used for the electrical conductance measurements.

Results and Discussions

Direct Current Electrolysis

When d.c. voltage was applied to the pellets of KH_2AsO_4 in the electrolysis cell (*2*) at 35°C, with 60 volts across the sample, evolution of hydrogen was observed in the cathode compartment. From the comparison of a coulomb of electricity passed through the crystal and the amount of hydrogen evolved in the cathode compartment, it was found that the proton is the main carrier of the current with a transport number 0.98.

Alternating Current Conduction Results

Alternating current conduction was measured with the Wyne Kerr bridge with pellets of KH_2PO_4, KD_2PO_4, KH_2AsO_4 and KD_2AsO_4. These measurements were made in the temperature range of 20–200°C. Log of specific conductance versus $1/T$ plots for these pellets were made and are shown in Figs. 1–3. From the slopes of these linear plots, the enthalpy values for the conduction process were calculated and are shown in Table 1.

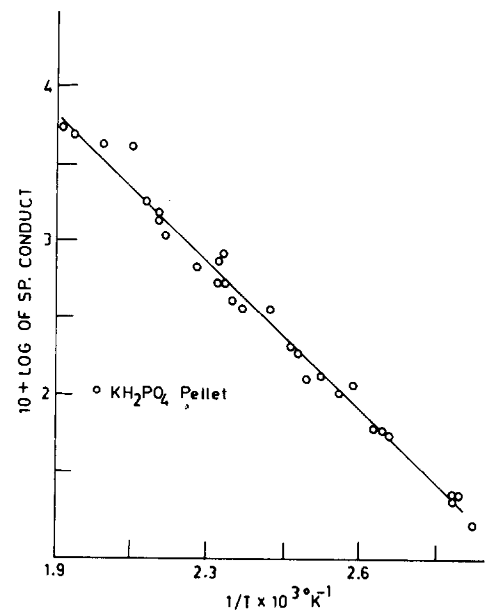

FIG. 1. Alternating current conductor of KH_2PO_4 pellet.

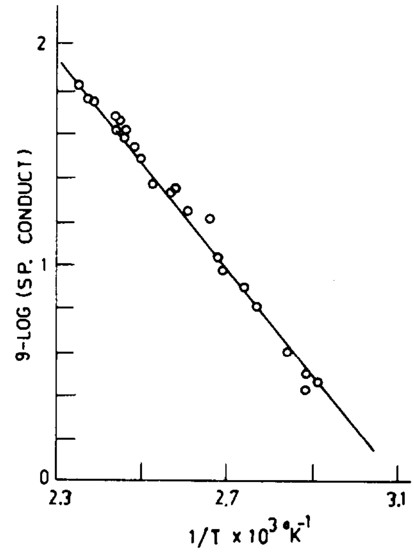

FIG. 2. Alternating current conductor of KD_2PO_4 pellet.

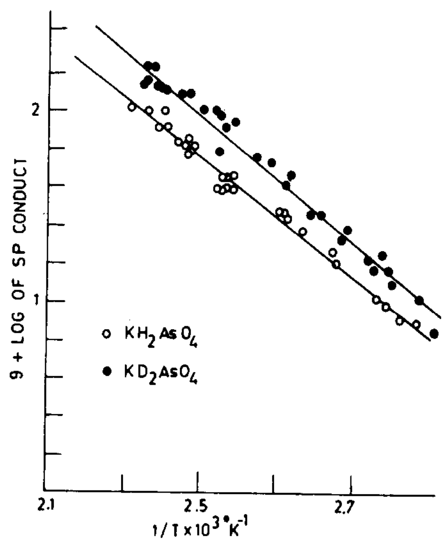

FIG. 3. Alternating current conductor of KH_2AsO_4 and KD_2AsO_4.

TABLE I

ENTHALPY VALUES FOR THE CONDUCTION PROCESS IN THE DEUTERATED CRYSTALS

Compounds	Enthalpy (eV)
KH_2PO_4	0.768 ± 0.03
KD_2PO_4	0.92 ± 0.04
KH_2AsO_4	0.62 ± 0.02
KD_2AsO_4	0.70 ± 0.03

From the values of the enthalpy for the conduction it is clear that the deuterated compound invariably takes more enthalpy value for the conduction than does the normal hydrogen bonded crystals. The conductivity plots also show the absence of any break in the conductivity data, which also confirms our previous results (*1–3*).

Conclusion

It can therefore be concluded that in acid arsenate or acid phosphate salts, the conduction occurs through the proton migration, but the mechanism for the conduction does not follow the classical defect mechanism as proposed by others. Instead the synchronous rotation mechanism is operative in these crystals.

Acknowledgments

The author is thankful to the Leicester Polytechnic and the Head of the Department for providing the fellowship to carry out this work. Author is also thankful to Dr. J. M. Pollock to provide the assistantship and for giving many encouragements for carrying out this experiment.

References

1. M. SHARON AND A. K. KALIA, *J. Solid State Chem.* **21**, 171 (1977).
2. J. M. POLLOCK AND M. SHARON, *J. Chem. Phys.* **47**, 4064 (1967).
3. J. M. POLLOCK AND M. SHARON, *J. Chem. Phys.* **51**, 3604 (1969).
4. A. R. UBBELOHDE, *Proc. Roy. Soc. Ser. A* (London) **222**, 193 (1954).
5. A. R. UBBELHODE AND I. WOODWARD, *Proc. Roy. Soc. Ser. A* (London) **179**, 117 (1939).
6. A. R. UBBELHODE AND D. H. W. DICKSON, *Proc. Roy. Soc. Ser. A* (London) **179**, 399 (1942).