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NOTE

Protonic Conduction and the Néel Temperature in Deuterated Ammonium Dihydrogen Arsenate

The conductivity of antiferroelectric $ND_4D_2AsO_4$ single crystals has been measured as a function of temperature, especially near the Néel temperature. At the Néel temperature the conductivity shows a vertical decrease to a lower value indicating that the mechanism of conduction is connected to the shift of the protons during the phase transition. This conductivity mechanism in potassium and ammonium dihydrogen phosphates and arsenates has been previously proposed to include proton motion along hydrogen bonds and proton jumps across the phosphate or arsenate tetrahedra. The jump activation energy for proton mobility in $ND_4D_2AsO_4$ is found to be 10.5 kcal/mole and the room temperature conductivity is 9.91×10^{-10} ohm^{-1} cm^{-1}.

Introduction

Ionic conduction in crystals isomorphous to $ND_4D_2AsO_4$ has been discussed in many recent papers (*1–3*). Appropriate experiments have been accomplished on KH_2PO_4, $NH_4H_2PO_4$, $ND_4D_2PO_4$ (*4*), and $NH_4H_2AsO_4$ (*5*), which include electrolysis, temperature coefficients, and doping. We report here the work on deuterated ammonium dihydrogen arsenate, $ND_4D_2AsO_4$. This is a particularly important crystal in the series to study since the Néel temperature, marking the change from an antiferroelectric to a paraelectric phase, is near room temperature so that a thorough study of the temperature coefficient at the phase transition is facilitated. Attempts to accomplish this in the other crystals have not been successful since the low temperatures involved are accompanied by extremely low conductivity values. We will not repeat here the extensive discussion on the nature of the mechanism of conduction in these crystals but refer the interested reader to the literature cited above.

Experimental

$ND_4D_2AsO_4$ powder was prepared by mixing D_2O, and As_2O_5 in stoichiometric amounts to form deuterated arsenic acid and the acid was then mixed with ND_4OD to yield the salt. When sufficient material was prepared, single crystals were grown from supersaturated solutions using a thermal convection method. Sufficiently large single crystals were prepared by this method so that they could be clamped between two platinum electrodes after gold had been evaporated onto parallel surfaces. The dc conductivity was calculated by measuring the current through the crystals with an electrometer. The temperature was varied using slush baths and a small noninductively wound heater. X-Ray diffractometer measurements were also made on the powder and, after the conductivity measurements, on the crushed single crystals.

Results

Figure 1 shows the plot of $\log \sigma T$ versus reciprocal temperature for single-crystal

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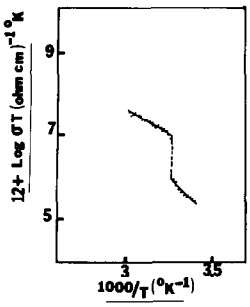

FIG. 1. The conductivity and transition temperature of $ND_4D_2AsO_4$.

$ND_4D_2AsO_4$ prepared for this study. The conductivity run was usually made by starting just below room temperature and gradually raising the temperature until some visible change occurred in the crystal or the desired higher temperature was reached. The significant result we wish to point out is the sharp increase in the conductivity plot at the Néel temperature of $ND_4D_2AsO_4$, namely, 304°K. We are able to trace the same curve with cooling except that some crystals become opaque during this operation, thus losing their singularity. Since it is well known that the phase transition at the Néel temperature involves relocation of the protons to certain positions on the arsenate tetrahedra, (*6, 7*), the 20-fold increase found in heating the crystal through 304°K gives added proof that proton motion and location determine the mechanism of conduction (*8*). This is the first time that such conductivity measurements have been taken in the region of the Néel temperature in this type of crystal, although this phenomenon has been found in other proton conductors such as $HUO_2PO_4 \cdot 4H_2O$ (*9*).

The results of the diffraction experiments show that the phase change did indeed take place since we found that the spectrum for the low-temperature orthorhombic phase disappeared as the crystal was heated above 304°K. This of course is also a guarantee that the crystal was completely deuterated since the transition for a mixed hydrogen–deuterium crystal would have been lower than 304°K by an amount proportional to the hydrogen content.

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