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Studies of Layered Uranium(VI) Compounds. IV. Proton Conductivity in Single-Crystal Hydrogen Uranyl Phosphate Tetrahydrate (HUP) and in Polycrystalline Hydrogen Uranyl Arsenate Tetrahydrate (HUAs)

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Single-crystal measurements on hydrogen uranyl phosphate tetrahydrate, $HUO_2PO_4{\cdot}4H_2O$ (HUP), have confirmed that the high proton conductivity is a bulk characteristic. The conductivity values were in substantial agreement with those previously reported for polycrystalline disks. A conductivity of 0.6 $ohm^{-1}\,m^{-1}$ at 290°K and an activation energy of 30 ± 1 kJ $mole^{-1}$ were measured parallel to the structural layers of the crystal. The conductivity was at least 100 times lower when measured in the perpendicular direction. A reasonable attempt frequency ω_0 of approximately 10^{15} Hz could be derived from the parallel conductivity on the assumption that the charge carrier concentration was equal to that of the H_3O^+ ions. This implies a low proton mobility, of the order of $10^{-9}\,m^2\,V^{-1}\,sec^{-1}$ at 290°K, in support of previous estimates. We have also shown that polycrystalline hydrogen uranyl arsenate tetrahydrate, $HUO_2AsO_4.4H_2O$ (HUAs), has a high conductivity of 0.6 $ohm^{-1}\,cm^{-1}$ at 310°K, with an activation energy of 31 ± 2 kJ $mole^{-1}$. Below the respective dielectric ordering transition temperatures of HUP and HUAs of 274 and 301°K, the lower conductivity values show a marked frequency dependence, which may be due to dispersion effects caused by water reorientations.

Introduction

Since our initial report of the unusually high H^+ conductivity in hydrogen uranyl phosphate tetrahydrate, $HUO_2PO_4{\cdot}4H_2O$ (HUP) (*1*), a more detailed study of the conductivity above the dielectric ordering transition has been presented (*2*), and a mechanism of conduction proposed (*2, 3*). The tetrahydrate phase of both HUP and the arsenate analog HUAs have been shown to be slightly nonstoichiometric with respect to water loss (*4*), and further water loss to the subhydrates has been investigated (*4*). The transitions, which occur at 274°K for HUP, and 301°K for HUAs, are variously evidenced in the H^+ conductivity (*1, 2*), in the NMR behavior (*3*), in the change from paraelectric to antiferroelectric behavior at lower temperatures (*5*), and in the onset of birefringence and complex twinning (*4, 6*). We have recently shown, from detailed X-ray studies, that the transitions in both HUP and HUAs are displacive (*7*), and have proposed ordered H-bond structures (*7, 8*) which can account for the conductivity transition and the antiferroelectric behavior. The structural nature of the transitions has therefore been considerably clarified, and we now report in more detail on the behaviour of the conductivity both above and below the transitions for HUP and HUAs. In the case of HUP, we report for the first time

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measurements made on single crystals. In the case of HUAs, there have been no previous reports concerning the conductivity.

Experimental

HUP, of type I modification, and the isostructural HUAs, were prepared by solution precipitation as previously described (*4*). The conductivities were measured either on pressed disks of 99.5±0.5% of theoretical density (*4*), or on a single crystal (*4*) about 2×2×0.2 mm in size, set in Araldite epoxy resin so as to form a separator between two solutions of phosphoric or arsenic acids, usually of pH 2.2. The experimental set up was the same as that described previously (Ref. (*4*), fig. 5). Palladium-blacked stainless-steel electrodes were spring loaded onto the sample faces, against which the unblacked electrodes had been previously rotated so as to ensure even surface contact between the electrodes and the sample faces. The temperature was controlled to within 0.1°K above 273°K and to within 1°K below 273°K, for which temperatures the solutions were replaced by methanol–acidic water mixtures. The methanol was not added until 273°K to limit possible intercalation into the layered structures. The conductivity values were always found to be reproducible upon warming to just above 273°K after the low-temperature runs. The pH probes were excluded from the solutions to prevent KCl leakage, since K^+ substitutes strongly for H_3O^+ in HUP. The ac conductivities were measured with a Wayne Kerr B 221 bridge, using a Wayne Kerr S121 generator, and either the bridge, or, for frequencies up to 100 kHz, a sensitive oscilloscope, as the detector.

Results and Discussion

Conductivities above the Transition Temperatures

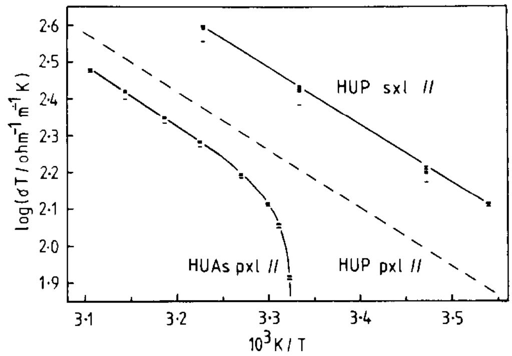

FIG. 1. log(σT) vs $1/T$ for a HUP single crystal and a HUAs polycrystalline disk. All conductivities were measured parallel to the crystal or disk faces. The range of values at each temperature represents a small frequency dependence between 46.4 Hz and 46.4 kHz for the HUP single crystal, and between 215 Hz and 46.4 kHz for the HUAs sample. The previously reported data for polycrystalline HUP (*1, 2*) are shown for comparison.

Figure 1 shows the log(σT) vs $1/T$ plot for the ac conductivities, σ, measured parallel to the faces of a plate-like HUP single crystal, and HUP and HUAs polycrystalline disks. The similarity of the conductivities of single-crystal and polycrystalline HUP can clearly be been, confirming the bulk nature of the conductivity, as also previously inferred (*2*). Moreover, the comparison also reveals that the contribution from intrinsic grain boundary conduction in the polycrystalline disks is not appreciable, and that the conductivity is a genuine bulk property. The conductivity measured in the perpendicular direction, between the faces of the crystal, was at least 100 times lower than the parallel value, reflecting the expected conduction anisotropy.

We shall now discuss in more detail the quantitative assessment of the single-crystal results. Unlike measurements on polycrystalline disks, the single-crystal conductivities were found to be very dependent on the freshness and thickness of the electrodeposited palladium black electrode coatings. Thin coatings produced a frequency dependence, between 46.4 Hz and 46.4 kHz, of typically a factor of 5, with even the high-frequency values being lower, by up to a factor of 2, than the best results. These were obtained with thick, very black-looking palladium black coatings. In addition, for the best results, more acidic solutions were used (pH 0.7), and the solubility of the crystal was suppressed by using a solution taken from above a HUP precipitate. The measurements, taken in a repetitive sequence over the entire temperature range, were performed quickly, otherwise electrode deterioration occurred. The results shown in Fig. 1 represent reproducible values showing typically only a 10% conductivity increase in going from 46.4 Hz to 46.4 kHz, and for which the high-frequency values have converged to the frequency-independent limit.

We were thus able to almost eliminate frequency dependences by using thick palladium black deposits and acidic solutions. Both of these factors enable, through adsorption of H^+, a high space charge to be established across the sample during each cycle (*9*). The small size of the single crystal compared to that of the disk sections meant that the electrodes had to cope with a higher current density compared to those used with the polycrystalline disks, which showed smaller polarization effects.

The activation energy for the single-crystal conductivity was found to be 30 ± 1 kJ mole^{-1}, which affords a slight refinement of the value of 31 ± 3 kJ mole^{-1} found for the polycrystalline sample (*2*). The same activation energy for conductivity in the single crystal was obtained even at low frequencies, for less efficient electrodes, or for solution acidities ranging from pH 0.7 to 2.2.

The absolute value of the single-crystal conductivity of 0.6 ohm^{-1} m^{-1} at 290°K appears to be about 50% higher than that determined from polycrystalline disks, of 0.4 ohm^{-1} m^{-1} at 290°K. However, both measurements have an absolute error of approximately ±20%, mainly arising from the difficulty of obtaining accurate sample dimensions, especially after leveling the surfaces against the electrodes *in situ*. In addition, a line imperfection, which appeared only to be surface deep, was visible in the crystal. Calculations showed that if this provided a pathway for solution-type conductivity, any significant increase in the conductivity would also be reflected in a decrease in the activation energy, since the activation energy for proton conduction in solution is only 12 kJ mole^{-1}. That the activation energy was 30 ± 1 kJ mole^{-1} over the large pH range of 0.7 to 2.2 argues for the absence of any effect from the imperfection in the crystal. The higher conductivity values found for the single crystal compared to the pressed disk may in fact, therefore, reflect the effects of grain boundary conduction if these exhibited a slightly lower conductivity than the bulk.

Previous measurements using HUP as a fuel cell electrolyte (*2*) have established that the transport number for protons is greater than 0.8, and is most likely close to unity. Furthermore, dc measurements (*1*) have confirmed the interpretation of the ac results. We are now, therefore, in a position to consider the parameters of bulk H^+ conduction in HUP.

The conductivity can be expressed as $\sigma = \sigma_0 \exp(-E/RT)$, where for HUP single crystals, $\sigma_0 = (1.5 \pm 0.3) \times 10^5$ ohm^{-1} m^{-1}, as calculated from σ at 290°K and E, where $E = 30 \pm 1$ kJ mole^{-1}.

Now for two-dimensional diffusion the diffusion coefficient D is related to the average time between jumps, τ, by the formula (*10*)

$$D = f\lambda^2/4\tau,$$

where f is the correlation factor, here assumed to be 1, and λ is the jump distance, taken as the distance of an interbond jump of approximately 1.5×10^{-10} m. Using the relationship (*10*)

$$\sigma = \frac{ne^2}{kT} D$$

and

$$\sigma_0 = \frac{ne^2 f\lambda^2}{4kT\tau_0}.$$

Assuming the concentrations of charge carriers n to be equal to the concentration of H_3O^+ ions (*2*) of $5 \times 10^{27}\,m^{-3}$ gives $\tau_0 = 1 \times 10^{-15}$ sec, where $\tau = \tau_0 \exp(E/RT)$. It was found that this value was increased by a factor of approximately 2 if it were assumed that rapid molecular reorientation occurred only if an H-bond vacancy was involved, and a vacancy-type mechanism was assumed, as previously discussed (*2*). The inverse of τ gives ω, the jump frequency, and $\omega = \omega_0 \exp(-E/RT)$. The barrier attempt frequency ω_0 is typically of the order of 10^{14} Hz in ionic solids (*10*). Our value for ω_0 of approximately 10^{15} Hz is therefore reasonable, and supports the evidence (*2*) that all the H_3O^+ ions act as charge carriers, since a smaller value of n would result in an even larger value for ω_0. Such evidence adds further weight to the value of the H^+ mobility, calculated using the expression $\sigma = ne\mu$, of approximately $10^{-9}\,m^2\,V^{-1}\,sec^{-1}$ at 290°K (*2*). This mobility is only one-thousandth of that found in acidic solutions (*2*), and is consistent with a solid-like water lattice rather than a liquid-like lattice, as also inferred from differential scanning calorimetry evidence (*7*). It is interesting to note that the values for τ_0 for both HUP and HUAs for the NMR relaxation processes in phase I (*3*) above the transition are 2×10^{-13} sec, which show reasonable agreement with the values obtained from the conductivity results.

Figure 1 also shows the conductivity of a polycrystalline HUAs disk, which has not been previously reported. The disk was immersed in arsenic acid of pH 2.2. The conductivity values showed typically only an increase of 10% in going from 215 Hz to 46.4 kHz. The activation energy was found to be $31 \pm 2\,kJ\,mole^{-1}$, which is similar to *that* of HUP. The conductivity, $0.6\,ohm^{-1}\,m^{-1}$ at 310°K, is slightly lower than that of HUP. In general, however, the values are very similar to those of HUP, and confirm that HUAs also has an unusually high conductivity, which by analogy with HUP, is inferred to be protonic in nature.

Conductivities below the Transition Temperatures

Let us turn now to the behavior of the conductivity through the transition, and at temperatures below the transition. Figure 2

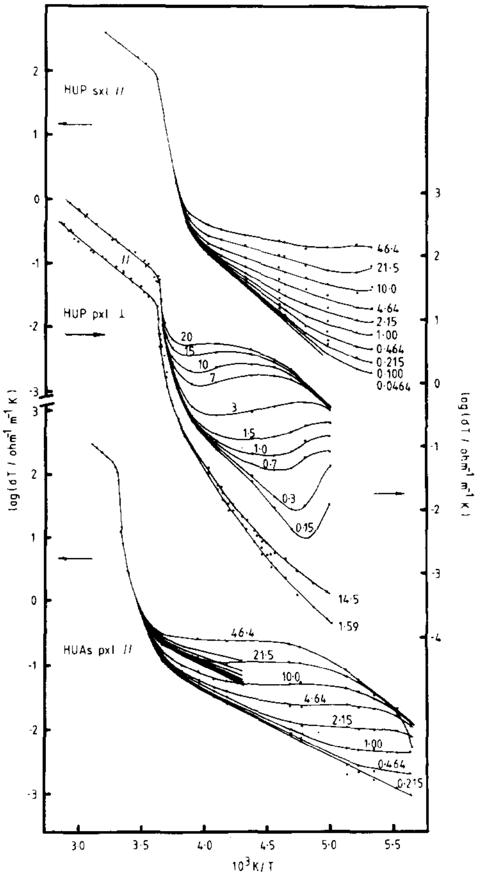

FIG. 2. $\log(\sigma T)$ vs $1/T$ for a HUP single crystal and for HUP and HUAs polycrystalline disks. The families of points represent measurements at the indicated frequencies, in kHz. The results of two runs are shown for the polycrystalline HUAs disk. The short compact family of curves was obtained over the same frequency range as shown for the other set of curves.

shows the conductivity data, plotted as log(σT) vs $1/T$, for the complete runs, for which Fig. 1 displayed just the higher-temperature portions. The full data for the HUP disk measured in the parallel direction are now shown for comparison and are the same data as those previously presented (*1, 2*). In addition, new data, typical of a HUP disk measured in the perpendicular direction, are shown. The absolute magnitude of the conductivity measured in this direction is somewhat dependent on the extent of pressing of the disk, as previously discussed (*2*).

In all cases the conductivity is seen to drop below between 274 and 276°K for HUP, and below 302°K for HUAs. The conductivity transitions therefore occur, to within experimental error, at the same temperatures as do the transitions in the other properties. The conductivity transition is therefore a consequence of the small structural and ordering changes which also cause the displacive transition (*7*) and the onset of antiferroelectricity (*5*).

Below the transition temperatures the conductivities are seen to show a pronounced frequency dependence. In all cases where a wide frequency range was employed, the values in the range 46.4 to 500 Hz were found to converge to a low-frequency limit at all temperatures below the transition, whilst the values at the high-frequency end (10 to 46.4 kHz) showed evidence of convergence only at the lowest temperatures used. Complex impedance plots did not reveal more than one arc, which was usually incomplete, and the plots did not provide any additional information.

Although a marked frequency dependence was always observed below the transition temperature, both the low-frequency limit of the conductivity and the frequency dependence often showed substantial differences from run to run, or between heating and cooling the samples. For example, Fig. 2 shows two sets of data for HUAs below the transition. Both sets gave the same, essentially frequency-independent, conductivity values above the transition, but upon cooling, one run, seen as the shorter more compact family of curves in Fig. 2, showed higher conductivity values at low frequencies and lower conductivity values at high frequencies than the second run. A different effect was observed upon temperature cycling. The data shown in Fig. 2 below the transition for polycrystalline HUP, measured in the parallel direction, were taken during warming the sample up from the lowest temperature. The data taken during the initial cooling cycle, which are not shown, were similar to those for polycrystalline HUAs, as shown in Fig. 2, in that the high-frequency values represented much lower conductivity values. The various condition-dependent results possibly arise from thermal hysteresis effects and differential rates of cooling through the transition, and will be considered in more detail later.

Nature of the Conductivity Transitions

In view of the coincidence of the conductivity transitions with the transitions observed in the other properties (*7*), we attribute the conductivity transitions to a lowering of the bulk conductivity within the crystallites, rather than the freezing or possible solution-type grain boundaries, as was initially suggested for HUP (*1*) on the grounds that the transition temperature in HUP appeared to coincide with the freezing point of water. However, the occurrence of the transition in HUAs at 301°K rules out this explanation.

Infrared evidence (*7*) has shown that the numbers of charge carriers, evident as H_3O^+ ions, do not change through the transition for either HUP or HUAs. The conductivity transition therefore indicates a change in the bulk H^+ mobility. Unfortunately, the unusual conductivity behavior below the transition prevents a reliable estimate of the activation energy for conduction in the low-temperature phase from being made. Nevertheless, one can estimate that an increase in the activation energy of approximately 10 kJ mole^{-1} would be needed to account for a typical drop of two orders of magnitude in the conductivity provided that there were no changes in the preexponential factors. Such an increase in the activation energy would be consistent with the inhibition caused by H-bond ordering of both H^+ hopping along an H bond, and molecular rotation or reorientation of water molecules. Both processes are necessary for H^+ conduction, as previously discussed in detail (*2*), and both would cause local disordering in an H-bond ordered structure. This can be seen by considering the diagrams of the proposed ordered structures shown in Part III (*7*) In addition to such an order–disorder energy term, the water network in the low-temperature, phase II, structure may distort through the displacive transition sufficiently to significantly alter the O–O distances, which may then be less favorable for H^+ conduction. It is worth noting that the NMR spin–lattice relaxation times changed from 20 kJ mole^{-1} for both HUP and HUAs in phase I, to 28 kJ mole^{-1} for both HUP and HUAs in phase II (*3*). Although such values may relate to different rotations or motions as determine the conductivities, the increases are nevertheless compatible with those anticipated for the conductivities.

The changes in the conductivity through the antiferroelectric transition of the proton conductor copper formate tetrahydrate (CFT) (*11*) are of the same kind, although less pronounced, than those found in HUP and HUAs. The conductivity of CFT is 6×10^{-5} ohm^{-1} m^{-1} at 270°K, and falls by a factor of approximately 4 at the antiferroelectric transition temperature of 235°K. The activation energy increases below the transition, from 54 to 62 kJ mole^{-1} (*11*).

Frequency-Dependent Behavior

Turning to the frequency-dependent behavior shown below the transition, we suggest that this may be due to resonant dielectric absorption arising from reorientation of water molecules and/or H_3O^+ ions at a rate comparable to the applied ac field. If the water molecules have a large spread of reorientation rates at any one temperature, a broad dielectric loss peak should result (*12*). Some evidence for a broad peak is to be seen in the downturn of the high-frequency conductivities at the lowest temperatures, as can be seen in Fig. 2. The very broad spread of the peaks at the higher temperatures would be consistent with a large range of water reorientation times, as indeed would be expected from the possible range of local environments of the water molecules provided by the distribution of H_3O^+ ions and H-bond vacancies (*7*). The thermal hysteresis effects referred to above may result from different degrees of H-bond ordering caused by the different thermal histories. A rough calculation, taking the resonant frequency to be 20 kHz at 200°K, a typical peak maximum (see Fig. 2), gives a rotational correlation time of 5×10^{-5} sec. This is a likely figure, in view of the fact that the estimated spin–lattice correlation times T_1 for both HUP and HUAs are 1×10^{-6} sec at 200°K (*3*), and are likely to also reflect rotational properties. We also considered the possibility of the frequency dependence arising from dimensionally limited conduction pathways, such as grain or domain boundaries. However, using previous estimates of the H^+ mobility (*2*), it can be shown that the average H^+ conduction pathlength at 20 kHz and 200°K is less than 1 Å, ruling out this possibility.

In conclusion, the spectrum of results has now enabled many of the detailed conduction parameters to be determined for HUP and HUAs, and these further support the

Grotthus-type mechanism for H^+ conduction previously proposed for these compounds (*2*).

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