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American Physical Society

Physical Review B, Comments and Addenda, v.8, no. 7, October 1, 1973, pp. 3475-3478

<http://hdl.handle.net/10945/47560>



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COMMENTS AND ADDENDA

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Electrical Conductivity of KH_2AsO_4 and KD_2AsO_4

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(Received 22 January 1973)

Measurements of the electrical conductivity of KH_2AsO_4 and its deuterated isomorph have been performed from room temperatures to the temperature of their respective ferroelectric transitions. Activation energies of 0.66 and 0.64 eV have been found to characterize the temperature dependence of the conductivity for KH_2AsO_4 and KD_2AsO_4 , respectively. Further evidence that these materials display anomalously long polarization relaxation times near the temperature of their ferroelectric transition is presented and discussed. The nature of this behavior remains unexplained.

I. INTRODUCTION

Potassium dihydrogen arsenate (KDA) and its deuterated isomorph (KD^*A) belong to a family of hydrogen-bonded, order-disorder ferroelectrics frequently identified by the name of the primal member, potassium dihydrogen phosphate (KDP). In a recent study¹ of the thermodynamic properties of KDA and KD^*A our efforts to measure polarization by electrocaloric techniques were thwarted by long-term charge drifts which were due either to polarization relaxation with anomalously long time constants or to anomalously high electrical conductivity (σ). These measurements were undertaken in an effort to resolve this question, and demonstrated that the conductivity does not behave anomalously. Additional evidence of anomalously long dielectric relaxation is also presented.

Previously there have been a number of studies of the conductivity of KDP ² and KD^*P ^{3,4} covering a broad range of temperatures. There exists a set of measurements, limited to the vicinity of room temperature, of the conductivity of KDA and KD^*A ,⁵ and also measurements of the conductivity of KDA from 270 to 460 K⁶ which include a study of impurity doping effects.

The electrical conductivity of this class of materials has been demonstrated by Coulometric measurements on KDP ^{7,8} to be protonic (or deuteronic) and is dependent on the ability of the proton to jump between hydrogen bonds. This conduction mechanism

has been substantiated by NMR measurements of the activation energy for interbond jump times for deuterons in KD^*P .³ Since the conduction mechanism in the KDP family is dominated by the behavior of the special hydrogen bond configuration,^{2,3} at the outset it was considered possible that there could be an anomalous enhancement of the conductivity in the vicinity of the ferroelectric transition which was associated with the establishment of order within the hydrogen bond system. No such behavior was observed.

II. EXPERIMENTAL TECHNIQUES

The experiments were performed using a vacuum calorimeter previously described by Reese and May⁹ and used for the thermodynamic measurements.¹ The temperature control and measurement process were identical to those described previously.^{1,9}

The conductivity was determined by applying a known voltage and measuring the current. The voltage was generated by a Keithly model-241 power supply and the current was determined using a Keithly model-640 vibrating capacitor electrometer. The electrometer was connected in such a manner that it acted as a unity-voltage-gain operation amplifier and drove a digital voltmeter for display of the current. A simultaneous recording of the current was made using a strip chart recorder. Voltages up to 500 V were used. The minimum detectable current was 10^{-16} A. The measurements were made with current flow parallel to the c axis

on rectangular single crystals. The KDA sample ($0.5 \times 0.5 \times 0.25$ cm) was obtained from Gould Laboratories¹⁰ and the KD*A sample ($1.0 \times 1.4 \times 1.0$ cm) was obtained from Quantum Technology Ltd.¹¹ Gold electrodes applied by vacuum evaporation were utilized.

Following the application of voltage to the sample, the current was observed to decrease for periods too long to be associated with the RC time constant of the measuring system (which is too short to be seen in Fig. 1 except at 220 K). This effect can be ascribed to either of two independent processes: (a) development of a blocking voltage by charges trapped on the surface of the crystal and (b) decay of residual current associated with slow polarization response in the crystal. The conductivity is determined from the initial value of the current-voltage ratio in the case of the latter mechanism. Thus, meaningful values for σ can only be obtained if the relative importance of these two effects is evaluated.

A series of current measurements at various voltages and temperatures were undertaken to distinguish between the charge trapping and polarization relaxation mechanism. In Fig. 1 the current-voltage ratio for several voltages and temperatures is displayed. At 296 K, the ratio determined with low applied voltages shows considerable time dependence, but little time dependence is shown when 100 V is applied. This latter determination is considered a reliable measurement of σ . Since the charge trapping mechanism results in a blocking voltage, this mechanism will be most significant at low applied voltages. Consequently

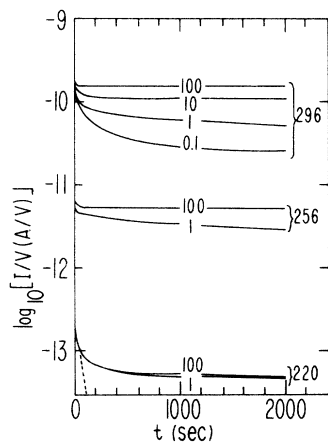


FIG. 1. Ratio of current to applied voltage for KDA as a function of elapsed time. Each curve is labeled by the applied voltage (in V) and the bracket indicates the temperature (K) of the measurement. The dashed line $T = 220$ K represents the RC-time-constant exponential decay.

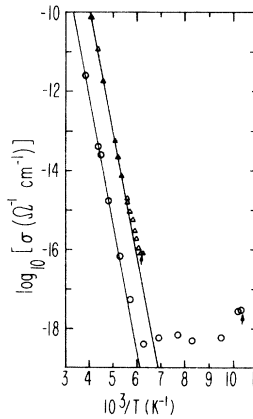


FIG. 2. Conductivity versus inverse temperature for KDA (circles) and KD*A (triangles).

it can be concluded that charge trapping is significant at 296 K but is negligible at 220 K, where the current-voltage ratio is substantially independent of applied voltage. In this latter case the time dependence of the current-voltage ratio must be ascribed to relaxation effects which are expected to be independent of applied voltage.

The conductivity values were obtained after the sample was judged fully polarized, as signaled by the time-independent behavior of the current-voltage ratio. This requires a longer time as the temperature of the ferroelectric transition is approached. Under conditions where the temperature is close to the transition temperature and long waiting times are required, great care must be taken to minimize temperature drifts. Because of the temperature dependence of the dielectric constant, temperature drifts are reflected by a polarization current proportional to $(T - \theta)^{-2} \dot{T}$, where θ is the Weiss temperature and \dot{T} is the temperature drift rate. As an example of the severity of this problem, in KDA at 97 K a temperature drift of 1 mK/h will generate a polarization current approximately equal to the real current (about 10^{-14} A at 500 V).

III. DISCUSSION

The conductivity of KDA and KD*A is shown in Fig. 2. Above 160 K, σ can be represented by

$$\sigma = \sigma_0 e^{-\epsilon/kT}.$$

The activation energy found by these experiments is associated with proton (deuteron) interbond jumps, since studies of the variation of ϵ with doping⁶ indicate that contributions to ϵ from defect formation are small. The appropriate parameters are given in Table I and a comparison with similar parameters for KDP and KD*P is also given. Only measurements taken above the temperatures of the ferroelectric transition are shown, as measurements taken below T_c were difficult to interpret

TABLE I. Experimental parameters and a comparison with similar parameters for KDP and KD*P.

	ϵ (eV)	σ_0 ($\Omega^{-1} \text{cm}^{-1}$)	T_c (K)
KDP (Ref. 4)	0.54	0.13	122
KD*P (Refs. 3 and 4)	0.58, 0.53	0.79, 0.06	220
KDA (Ref. 6)	0.66	3.2	96.2
KDA (this work)	0.66	24	96.2
KD*A (this work)	0.64	1200	161

owing to complicated relaxation behavior associated with spontaneous polarization and domains.

At room temperature we find $\sigma_{\text{KDA}} = 1.3 \times 10^{-10} \Omega^{-1} \text{cm}^{-1}$ and $\sigma_{\text{K}^*\text{DA}} = 1.8 \times 10^{-8} \Omega^{-1} \text{cm}^{-1}$. Adhav reports conductivity for KDA approximately 25 times larger and conductivity for KD*A approximately 6.3 times smaller at the same temperature. Perrino *et al.*⁶ report a room-temperature conductivity for KDA of $1.0 \times 10^{-11} \Omega^{-1} \text{cm}^{-1}$. These large discrepancies indicate the extreme sensitivity of the conductivity to impurities; for example, a factor of 100 increase in σ_{KDA} was found⁶ for 0.1% doping with KHSO_4 .

The measurements show a temperature-independent conductivity for KDA below 160 K. It is our opinion that this is an experimental artifact, since other interpretations would do violence to our understanding of the conduction processes in these materials. Further, the conditions of the experiment were such as to make this likely. Although the resolution of the equipment would permit a conductivity about a factor of 50 smaller than the minimum value in Fig. 2 to be determined, problems with temperature drifts previously discussed made reliable determinations of σ nearly impossible below 160 K. Further, since the sample resistance is on the order of $10^{18} \Omega$ at this temperature the possibility of leakage currents should not be dismissed.

In addition to providing conductivity data, the measurements indicate that the anomalous current-time behavior observed previously^{1,12} cannot be ascribed to anomalies in the electrical conductivity. The observations made in this study are entirely consistent with the previous observations. Thus, it seems appropriate to review this behavior since some of it was only alluded to in the previous report. When an electrocaloric measurement was attempted a two-stage behavior was ob-

served. Charge flow corresponding to approximately 90% of the equilibrium polarization occurred with a short time constant (instrumental). Following this there was a secondary charge flow of small magnitude and very long duration (sometimes thousands of seconds). Similar behavior occurred both above and below T_c . The most noticeable temperature effects were that the time required for the secondary process was much greater near T_c than otherwise and the fraction of the polarization involved increased somewhat near T_c .

The anomalous behavior is considered to be polarization relaxation rather than a conduction effect for the following reasons: (i) Previous electrocaloric determinations of the polarization in KDA¹² could only be brought into harmony with calorimetric data when allowance was made for the anomalous polarization behavior; (ii) some electrocaloric measurements indicated reversible temperature behavior associated with the relaxation behavior; (iii) detailed examination of the dependence of the polarization on electric field near T_c is most easily interpretable by assuming that the relaxation behavior is characteristic of the bulk polarization.

Schmidt³ has reported long-time constant (1-min) relaxation behavior observed in the measurement of the conductivity of KD*P and speculated that it may be due to electrode blockage effects. Our measurements demonstrate that electrode blockage effects are significant above 200 K, a temperature region which encompasses Schmidt's measurements. The effect discussed here, which occurs below 200 K, has a strong temperature dependence near T_c , unlike the effect reported by Schmidt.

In assessing this peculiar polarization behavior it should be emphasized that the fast process, which was associated with the largest fraction of the polarization, did not appear anomalous. High-frequency determinations of polarization relaxation, such as by ultrasonic^{13, 14} methods, would only characterize the fast process. Thus, we believe that we have observed a different manifestation of polarization relaxation than previously reported. Although one is tempted to speculate by associating it with a hindered reorientation of chains of ordered hydrogen bond configurations near the end of the polarization process, it seems best, at present, to leave this effect in the category of an intriguing mystery.

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