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DEUTERATION AND PRESSURE EFFECTS ON LANDAU FREE ENERGY EXPANSION COEFFICENTS IN $RbD_xH_{2-x}PO_4$

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Abstract-Results are presented for undeuterated, 30% deuterated and 97% deuterated monocrystals of rubidium dihydrogen phosphate (RDP) for which the polarization was measured at various applied fields and accurately controlled temperatures within a degree above the ferroelectric transition temperature. The ferroelectric transition was found to be of second order at all deuterations. Some of these results were presented earlier.[1-3]

INTRODUCTION

Rubidium dihydrogen phosphate is one of the isomorphs of the KDP family known to have a second order ferroelectric transition at zero pressure and deuteration. It was hoped that upon deuteration the transition would become first order, implying that for some critical deuteration the transition would occur at a "tri-critical" point at zero pressure. It was found, however, that upon partial and full (97%) deuteration the transition remained second order in agreement with the conclusion extrapolated from an 80% deuterated crystal by Strukov *et al.*[4]

EXPERIMENTAL

We grew undeuterated and partially deuterated samples by cooling saturated aqueous solutions of zero and 30% deuteration respectively. The 97% deuterated sample was cut from a large single crystal purchased from Interactive Radiation Inc. Faces normal to the c-axis of each sample were polished and provided with evaporated gold electrodes.

These samples were placed in our high pressure cryostat which has been described elsewhere.[5] The pressure of the helium pressurizing medium was measured with a calibrated manganin cell to an accuracy of one bar. Temperatures were measured to within 3 mK using the temperature controller capacitance sensor which was calibrated against a copper-constantan thermocouple with liquid nitrogen reference. Barometric pressure changes were taken into account for the liquid nitrogen reference.

The sample was placed in series with a low leakage polystyrene 1.00 μf capacitor (Fig. 1). Various voltages (0-225V) were applied to the series combination and the resulting buildup of charge in the capacitor due to the polarization of the sample was measured with a Cary Model 401 vibrating reed electrometer (input impedance $>10^{16}$ ohm).

In the case of the undeuterated and 30% deuterated samples, charge leakages around the sample and the capacitor were determined to be negligible. However, the 97% DRDP sample conducted significantly and a modified procedure for taking the polarization data was necessary.

Data were taken on the undeuterated and 30% deuterated crystals after the

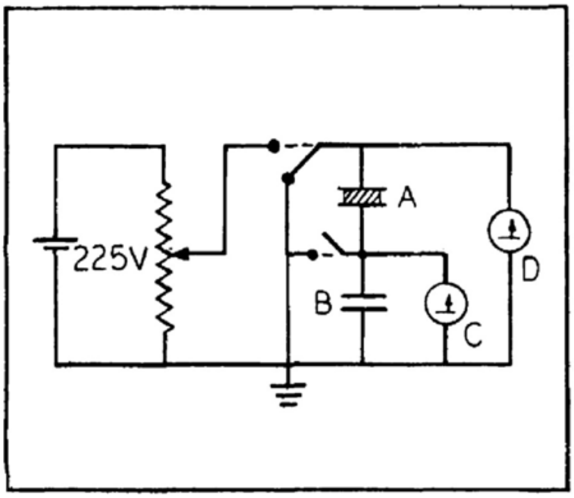

FIGURE 1. Dielectric measurement circuit. (A) sample, (B) 1 μf capacitor, (C) electrometer, (D) DVM.

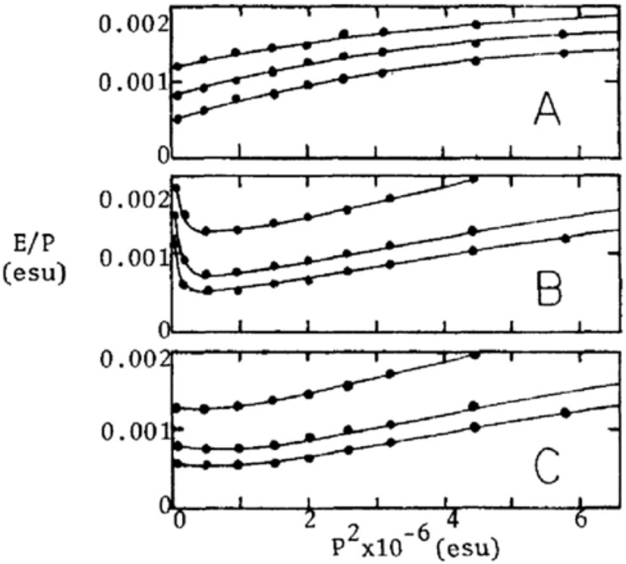

FIGURE 2. Typical isothermal plots of E/P versus P^2 for (A) undeuterated, 97%, (B) 30% (uncorrected) and (C) 30% (corrected)samples.

temperature of the sample was stabilized to better than 3 mK drift over the period of the measurements. Various voltages were applied to bring the crystal to a predetermined set of polarizations and adjusted to maintain those polarizations until equilibrium was reached. After each such measurement the crystal and capacitor were shorted to allow the crystal to depolarize.

The small but non-zero conductivity (10^{-13} ohm^{-1}cm.$^{-1}$)of the 97% deuterated sample prevented use of the above measurement method. The conductivity and polarization of this sample were measured by applying a fixed voltage to the crystal and periodically measuring the accumulated charge on the standard capacitor (Fig. 3A). When it appeared that the accumulating charge was due to conduction alone (charge vs. time plot became a straight line) enough measurements were made to allow a good determination of the conductivity, and then the crystal and the capacitor were shorted to depolarize the crystal in preparation for the next measurement. Due to the time required for the above procedure (about five hours or more near T_0) only measurements of one polarity were made. The temperature was maintained constant to within 5 mK for each set of these measurements.

DATA ANALYSIS

The calculation of the coefficients for the Landau free energy expansion

$$F = -EP + A_0(T-T_0)P^2/2 + B_0(T-T_1)P^4/4 + CP^6/6 \quad (1)$$

for each sample presented unique difficulties. However, once the raw data were reduced to plots of field versus polarization and temperature the Landau coefficients and their temperature dependence were extracted in the following manner.

Minimization of the free energy with respect to P gives

$$E = A_0(T-T_0)P + B_0(T-T_1)P^3 + CP^5 \quad (2)$$

Division by P then gives the working equation

$$E/P = A_0(T-T_0) + B_0(T-T_1)(P^2) + C(P^2)^2 \tag{3}$$

which shows E/P to be a polynomial of (P^2). In our analysis the first three terms were sufficient to fit our data. A quadratic least squares fit was performed on plots of E/P vs. P^2 at constant T for the data from each sample (see Fig. 2A) yielding the coefficients and their temperature dependences. A linear least squares fit to plots of $A_0(T-T_0)$ vs.T and $B_0(T-T_1)$vs.T gave A_0, T_0, B_0, and T_1 for each sample. These values are reported in the last four columns of table 1.

For the undeuterated crystal the E versus P measurements from the raw data were used for the above analysis. For the 97% deuterated crystal the conductivity of the sample at each temperature and applied field was the slope calculated by a linear least squares fits of the straight portion of the accumulated charge versus time plot which comprised the raw data of each polarization measurement (Fig. 3A). The time=0 intercept of this line was the charge due to the polarization of the sample (point Q of Fig. 3A). The E/P vs. P^2 plots of these are qualitatively the same as for the undeuterated sample (Fig. 2A). A least squares fit of $-\log_e\sigma$ versus 1/kT (Fig. 4B) gives a conductivity activation energy of 1.2±0.2ev.

Isothermal plots of our 30% deuterated crystal showed unusually large values of E/P for small values of P near the transition (Fig. 2B). We attribute this to a distribution of T_0 within the crystal due to the nonuniform deuteration of our homegrown crystal. Because of this spread in the transition temperature parts of the crystal were in the ferroelectric phase at temperatures above the average transition temperature of the crystal. Consequently, a P versus E plot for the crystal should show hysteresis (Fig. 4). However, due to our measurement technique of shorting the crystal and capacitor between measurements our polarization measurements (A, B, C Fig. 4) were offset from the correct values by an amount $P_0/2$ as indicated in Fig. 4. We calculated P_0 by extrapolating the steep linear portion of the raw P versus E plot to the E = 0 intercept (point D in Fig. 4). The resulting value of $P_0/2$ was added to each value of P for that isotherm before the Landau coefficients were calculated from the E/P versus P^2 plots (Fig. 2C). Typical values of the offset polarization $P_0/2$ were from 50 to 150 statcoul./cm^2.

TABLE 1. LANDAU EXPANSION COEFFICIENTS FOR RDP AT VARIOUS DEUTERATIONS AND PRESSURES

%deut.	0 (run 1)	0 (run 2)	30	30	97.7
p,kbar	0	0	0	2.5	0
A_0,esu	3.87x10^{-3}	4.73x10^{-3}	3.69x10^{-3}	3.33x10^{-3}	7.47x10^{-3}
T_0,K	146.61	145.56	175.76	162.65	209.00
B_0,esu	*	-5.8x10^{-10}	4.8x10^{-11}	*	-1.3x10^{-10}
T_1,K	*	146.14	174.26	*	209.23
$B_0(T_0-T_1)$ esu	1.4x10^{-11}	3.4x10^{-10}	7.3x10^{-11}	9.5x10^{-11}	3.0x10^{-11}
C, esu	@2x10^{-17}	-1.7x10^{-17}	@1x10^{-17}	@1x10^{-18}	@2x10^{-19}

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*Data quality did not permit determination of temperature dependence of B.

@These are error limits on the magnitude of C; its sign cannot be specified.

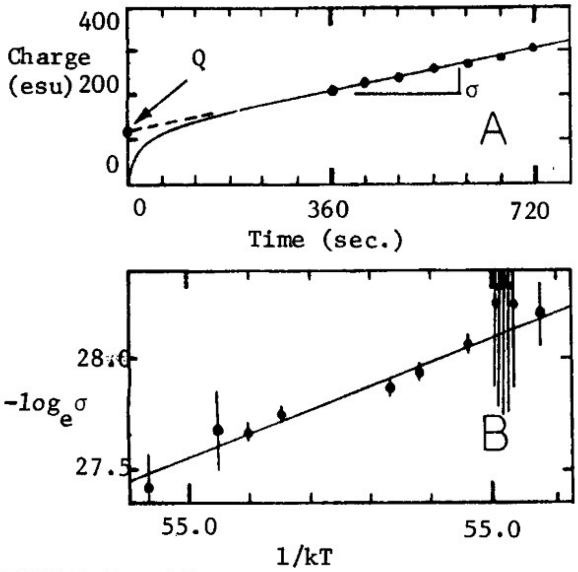

FIGURE 3. (A) A representative accumulated charge vs. time plot for 97% deuterated sample (B) $-\log_e \sigma$ vs. 1/kT plot for 97% sample.

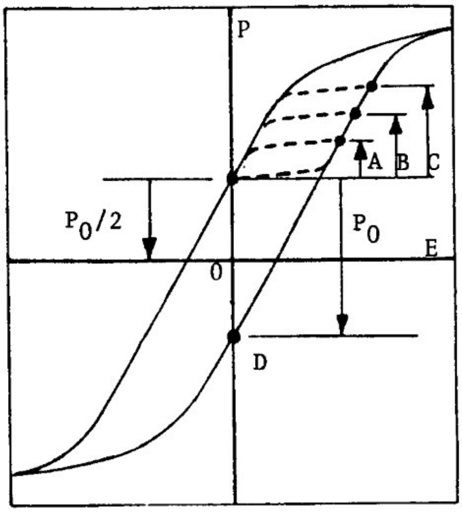

FIGURE 4. Hysteresis of 30% deuterated sample. A, B, and C are measured values of P offset from their correct values by an amount $P_0/2$ due to discharging the capacitor and shorting the crystal before each measurement.

DISCUSSION

For each of our RDP samples the value of $B_0(T_0-T_1)$ (see Table 1) was found to be positive which indicates that the ferroelectric transition is of second order for all deuterations. With increase in deuteration from zero to 97%, $B_0(T_0-T_1)$ decreased an order of magnitude. The results in column one of table 1 were analyzed in the manner described by Western.[5] This method does not allow for temperature dependence in the fourth order term in equation 1. This may be the cause of the apparent discrepancies with column 2.

ACKNOWLEDGEMENTS

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