Proton-glass dielectric behavior of a $Rb_{0.52}(ND_4)_{0.48}D_2PO_4$ crystal

V. Hugo Schmidt, Stefan Waplak,* Stuart Hutton, and Paul Schnackenberg

Department of Physics, Montana State University, Bozeman, Montana 59717

(Received 22 March 1984; revised manuscript received 23 May 1984)

The c axis dielectric permittivity at 1 kHz was measured for a 71.4 at. % deuterated crystal of $Rb_{0.52}(ND_4)_{0.48}D_2PO_4$ from 4 to 300 K. The permittivity follows, down to 150 K, a Curie-Weiss law with a Curie temperature of 0 K. Below this temperature the susceptibility rounds off to a broad maximum at 80 K, and below 50 K, starts decreasing rapidly. Between 25 and 40 K, the inverse susceptibility obeys a Curie-Weiss law which extrapolates to zero at 43 K. At 4 K, the relative permittivity flattens out to a value of 11.5. The results show general agreement with predictions of a Landau model giving a second-order transition to an antiferroelectric state at 43 K, but the rounding of the susceptibility peak over a very wide temperature range agrees better with predictions of a model which considers the asymmetry of the typical hydrogen bond caused by the crystal being only partly ammoniated. Permittivity results of Courtens and of Iida and Terauchi for undeuterated crystals with 35% and 60% ammonium, respectively, are also compared with predictions of this second model.

INTRODUCTION

Recently, there has been considerable interest in the glassy state. The definition of this state includes structural (or ordinary) glasses as well as magnetic spin glasses in which the atomic structure is crystalline but the spin arrangement is frozen into a disordered state at absolute zero. Courtens[1] and Iida and Terauchi[2] have reported on the mixed ferroelectric-antiferroelectric crystal system $Rb_{1-x}(NH_4)_xH_2PO_4$ (RADP), which is intermediate between the structural and spin glasses because there is still a basic regular structure, but within it there is random substitution of ammonium ions for rubidium ions. This affects the tendency of the hydrogens to order at low temperature, because one constituent, ammonium dihydrogen phosphate (ADP), tries to attain antiferroelectric (AFE) order while the other, rubidium dihydrogen phosphate (RDP), wants to achieve ferroelectric (FE) order. For values of x between about 0.2 and 0.8 it appears that no ordering occurs at least down to 9 K,[3] and the protons remain disordered as in ice. Courtens[4] terms this as "proton-glass" behavior. We are investigating this problem using deuterated crystals (DRADP) of this same mixed system, because deuteration tends to make phenomena occur at higher temperatures throughout the KH_2PO_4 (KDP) family and has a strong effect on the dynamic behavior also, changing the hydrogen intrabond motion from cooperative tunneling to stochastic jumps of Takagi groups.[5]

EXPERIMENTAL METHOD

Single crystals were grown from a 99.8% D_2O solution of equal molar amounts of Rb_2CO_3 and $(NH_4)_2CO_3$ with the stoichiometric quantity of P_2O_5. The crystals were grown by evaporation in an argon atmosphere. They exhibit low-angle twinning, but the tips are clear and monocrystalline with the characteristic KDP pyramid shape.

Mass spectrometry of the ammonia- and water-type fragments showed $(71.4\pm0.2)\%$ deuteration, compared to 79.7% calculated. We ascribe the difference to moisture in the P_2O_5. The Kjeldahl ammonium analysis showed $(48\pm3)\%$ ammonium replacing rubidium.

Our sample was cut from a clear crystal tip, polished, and faces perpendicular to c were covered with evaporated aluminum which serves as electrodes. Fine copper leads were attached by small dabs of Ecobond 57-C conducting epoxy. The sample was mounted on a glass tube which was inserted into an Oxford Instruments Model ESR-900 continuous flow cryostat controlled by their Model DTC2 digital temperature controller. Estimated accuracy is 0.5 K over the temperature range 300–4 K investigated.

Permittivity was measured with a bridge consisting of the sample in series with a capacitor box, paralleled by a ratio arm transformer, with source and detector provided by a Princeton Applied Research Model 124A lock-in amplifier with a Model 117 differential preamplifier operating at 1 kHz and 0° phase setting. Bridge accuracy was within 1% after correcting for stray capacitance. We did not vary frequency or measure the lossy component in these first runs.

EXPERIMENTAL RESULTS

We report here the results of two runs. In the first, the portion of one electrode under the epoxy broke off when the temperature reached 50 K. In the second, we cooled from room temperature to 4 K and returned to room temperature. There is a small amount of discrepancy between the cooling and warming curves, as shown in Fig. 1. Part of this results from the sample not being in complete thermal equilibrium, and the rest we attribute to inaccuracy in the temperature measurement system. It is possible, especially at the lower temperatures, that the sample has inherent thermal hysteresis in its electrical properties. Courtens[6] observed thermal hysteresis in the spontaneous
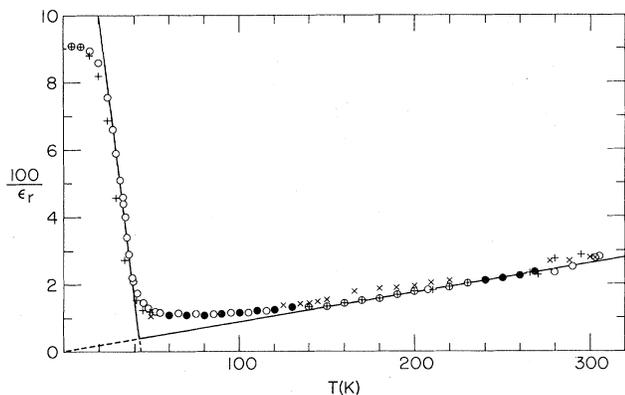
FIG. 1. Inverse dielectric permittivity for our crystal, showing comparison with prediction of Landau model for antiferroelectric phase transition. $\times$ is the cooling run for first sample (contact broke off at 50 K). Crosses and open circles show cooling and heating runs, respectively, for the second sample. Solid circles are data for all three runs. Solid line with kink is prediction of Landau theory with second-order AFE transition discussed in text.

polarization in 17% ammoniated RDP, which still has a FE transition at that ammonium concentration.

For some interval below room temperature, the crystal obeys a Curie-Weiss law with a T_0 near 0 K. Then there is a broad region in which the susceptibility rounds off, starting near 150 K, continuing to a broad peak near 80 K, and decreasing very rapidly from 45 to 15 K. It levels out near 4 K to a value of 11.5, which we attribute to local ionic motion and electronic polarizability, with the contribution from hydrogen-bond rearrangements frozen out. This is more than twice as large as the low-temperature value of the relative permittivity for KDP found by Holste et al.[7] This added permittivity probably comes from the ammonium ions, but the possibility of some residual H-bond rearrangements must be considered.

DISCUSSION

We consider two models in explaining these results. The first is a phenomenological model which predicts a second-order transition to an AFE state. Because an AFE phase appears unlikely for our crystal composition, we pass quickly on to the second model which reflects the fact that short-range interactions in this mixed crystal cause most of the hydrogen bonds to be biased even in the time average. This model, in its simplest form as presented here, predicts no phase transition.

In the first model we use a Landau free-energy expansion out to fourth-order terms in a FE order parameter P and an AFE order parameter Q. We write the free energy at constant field E as

$$F = -EP + \frac{A_p(T-T_p)P^2}{2} + \frac{B_pP^4}{4} + \frac{A_q(T-T_q)Q^2}{2}$$
$$+ \frac{B_qQ^4}{4} + \frac{DP^2Q^2}{2} . \tag{1}$$

We assume that $T_p < T_q$, and by minimizing the free ener-

gy with respect to Q when $P=0$ we obtain $Q=0$ for $T \geq T_q$, while for $T \leq T_q$ we have

$$Q^2 = A_q(T_q - T)/B_q . \tag{2}$$

Minimizing the free energy with respect to P yields, for small P,

$$E = A_p(T-T_p)P + DQ^2P , \tag{3}$$

which yields two straight lines in an inverse-permittivity plot as shown in Fig. 1, because different expressions for Q^2 must be substituted in the temperature ranges above and below T_q.

A reasonable fit to the data is made by choosing $T_q = 43$ K, as shown in Fig. 1, but this model fails to predict the rounding of the permittivity peak which extends over a 100-K temperature range. Also, at least for undeuterated RADP with 35% ammonium, Courtens et al.[3] see no evidence for an AFE state down to 9 K. For these reasons we prefer the second model, described below.

Our second model recognizes that many of the potential wells for the "acid" (O—H $\cdots$ O bond) hydrogens are asymmetric even in the time average, and that the various rules governing hydrogen configurations require a ground state (or group of lowest-energy states) with little or no order. We assume a specific hierarchy of rules and examine the nature of the ground state that they predict.

(1) The strongest rule (requiring the most energy to break it) is that there is one and only one hydrogen atom in each hydrogen bond. Violation of this rule leads to the observed small, thermally activated protonic conductivity observed in KDP (Ref. 8) and most other H—bonded crystals.[9] No measured effect of violation of this rule on ferroelectric behavior has been reported, though Takagi[10] showed that relaxing this rule for the Slater[11] KDP model would round off the spontaneous polarization curve, making the transition definitely of second order.

(2) We assume that the next strongest rule is the requirement that exactly two hydrogens be close to a given phosphate group, in the four hydrogen bonds connecting each group to its neighbors. Violation of this rule gives Takagi[12] HPO_4 and H_3PO_4 groups and modifies the predictions of the Slater model in the same way as described above. Effective motion of Takagi groups is necessary for hydrogen rearrangement to occur. These first two rules are the "ice rules" which allow much freedom for the hydrogen arrangements.

(3) The third strongest rule, in the context of the KDP-type structures, applies only to mixed FE-AFE crystals. It requires, as assumed by Courtens,[4] that if an O—H $\cdots$ O bond is asymmetric because one of its two oxygens is H—bonded to an ammonium ion, the acid hydrogen must avoid that oxygen which is H—bonded to the ammonium. This rule is based only on lack of symmetry, and there are yet no data to indicate its strength. This rule is inapplicable to pure ADP because in that crystal every oxygen is H—bonded to an ammonium ion. When, in a mixed crystal, this rule conflicts with the first two rules for certain N—H $\cdots$ O bond arrangements near a given PO_4 ion, we assume that this third rule is relaxed.

(4) We assume that the weakest rule is that associated

with the Slater H_2PO_4 energies, so this rule need be considered only if the first three do not uniquely determine the H_2PO_4 configurations. We further assume that the Slater energy of an H_2PO_4 group depends on the number of ammonium ions bonded to that phosphate ion. Because RDP and ADP order at comparable temperatures, we assume for simplicity that (a) if 0 or 1 ammoniums are bonded, the polar (FE) configurations are preferred, (b) if 3 or 4 ammoniums are bonded, the AFE configurations are preferred, and (c) if 2 ammoniums are bonded, all configurations allowed by the first three rules have equal energy.

To study the effect of these rules, we consider a given phosphate ion and the state of both of the oxygens terminating each of its four acid H bonds. Here "state" means whether or not oxygen bonds to an ammonium ion. There are $2^4 = 16$ state combinations for the four oxygens of the given phosphate ion and 16 independent combinations for the other four oxygens. We constructed a 16×16 matrix and filled in the lowest-energy hydrogen configuration(s) for each of the 256 overall states for a given phosphate ion. To keep the problem tractable, we

did not consider whether a lowest-energy configuration for a given phosphate is consistent with the lowest-energy states of its four neighbors.

The results of this analysis are shown in Table I. When the lowest-energy hydrogen configurations are added for the 256 possible phosphate states, 37 each have polarization along the positive and negative c axis, respectively, 130 have one of the four configurations which occur in AFE domains, 6 have equal energies for the two polar configurations, 20 each have equal energies for one of the two polar configurations and one or more AFE configurations, and 6 have equal energies for all configurations. Of the latter 52 configurations, a weak positive (negative) field along c will result in 32 (out of 256) configurations polarized in the positive (negative) c direction. Accordingly, the FE order parameter P in the ground state, which is the difference in fractions of aligned and antialigned polar groups, cannot exceed $\frac{1}{8}$. With such a small possible order parameter, we expect that the FE transition would occur at such a low temperature that the Takagi group motion required for the associated hydrogen rearrangement would be frozen out. Similar considera-

TABLE I. Probabilities (for $x = 0.5$) of ground-state Slater H configurations in the four O—H $\cdots$ O bonds attached to a PO_4 group participating in zero to four N—H $\cdots$ O bonds. Probabilities are based on the energy hierarchy described in the text, taking into account the 256 possible ways in which N—H $\cdots$ O bonds can attach to both ends of the four O—H $\cdots$ O bonds. Hydrogen correlations are considered only among the four O—H $\cdots$ O bonds attached to the PO_4. The N's shown by the squares representing PO_4 ions typify four equivalent arrangements for the second, fourth, and fifth squares, and two arrangements (N's at top or at bottom) for the third square.

Type of N—H $\cdots$ O ($=N$) arrangement around PO_4							Totals
N arr. probability	$\frac{1}{16}$	$\frac{1}{4}$	$\frac{1}{8}$	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{16}$	1
H arrangement around PO_4 (below) and its probability (right) (multiplied by 256)							
General arrangements:							
U (H's close at top)	5	20	7	0	4	1	37
D (close at bottom)	5	20	7	0	4	1	37
N (1 top, 1 bottom)	4	20	0	36	56	14	130
U,D	2	4	0	0	0	0	6
U,N	0	0	8	12	0	0	20
D,N	0	0	8	12	0	0	20
U,D,N	0	0	2	4	0	0	6
Totals	16	64	32	64	64	16	256
AFE arr. (N above):							
R (bot. left, top rt.)	1	4	0	7	5	1	18
L (top left, bot. rt.)	1	4	0	7	5	1	18
A (H's close at left)	1	4	0	7	5	1	18
B (H's close at right)	1	4	0	7	5	1	18
R,A	0	1	0	2	8	2	13
R,B	0	1	0	2	8	2	13
L,A	0	1	0	2	8	2	13
L,B	0	1	0	2	8	2	13
R,L,A,B	0	0	0	0	4	2	6
Totals	4	20	0	36	56	14	130

tions inhibit a transition to an AFE state for a mixed crystal with x near 0.5.

With this interaction hierarchy and the assumption that hydrogen jumps are thermally activated and uncorrelated (this assumption is valid for deuterated KDP-type crystals[5]), a Monte Carlo simulation of such hydrogen jumps could predict static and dynamic response to dc and ac applied fields. Comparison with experiment could determine the one unknown interaction strength, that between the ammonium and the acid hydrogen. We are now developing the computer program for this simulation. Meanwhile, it is instructive to approximate the fact that most bonds are asymmetric with a model in which all bonds have the same asymmetry. We neglect interactions between bonds and apply a dc field E to calculate the dc susceptibility.

This second model assumes an energy difference u between the two potential minima for all acid hydrogen bonds, as shown in Fig. 2. The minima are separated by a distance d and the applied field E is directed along the bond. The hydrogen carries effective charge q. (We measured permittivity with E along c which is perpendicular to the H bonds, and the c-axis polarization arises in KDP-type crystals by coupling of the H bonds to the heavy ions which carry the dipole moment. Our model accommodates this actual situation by making qd an adjustable parameter.) Because the electrical energy qEd is much less than the thermal energy kT, the change in dipole moment caused by E is

$$\Delta p = q^2 E d^2 / 4kT \cosh^2(u/2kT) . \tag{4}$$

The inverse polarizability α^{-1} then is given by

$$\alpha^{-1} = (4kT/q^2 d^2)\cosh^2(u/2kT) . \tag{5}$$

Because both coefficients of T can be treated as adjustable parameters, we can express the relative permittivity as

$$\epsilon_r = \epsilon_\infty + (C/T)\cosh^{-2}(u/2kT) , \tag{6}$$

where C is the Curie-Weiss constant governing the susceptibility at high temperature where the $\cosh^2(u/2kT)$ factor is near unity. Here ϵ_∞ is the so-called infinite-frequency susceptibility associated with the ionic and electronic polarizability remaining at temperatures at which most hydrogen rearrangement is frozen out. From our results at 4 K, $\epsilon_\infty = 11.5$. Treating both C and u as adjust-
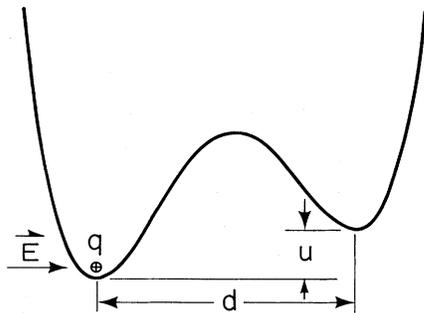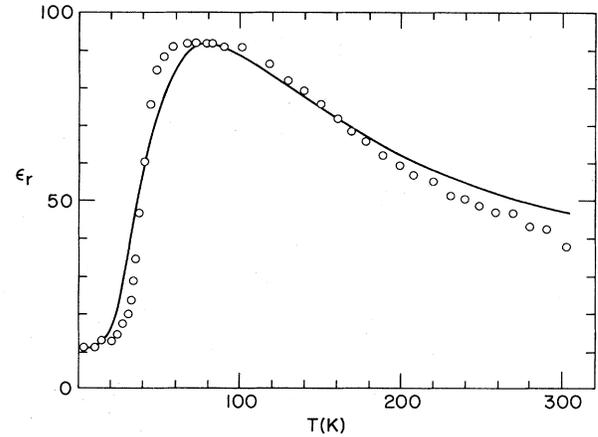

FIG. 3. Comparison of dielectric permittivity for our crystal ($x=0.48$, deuteration fraction $D=0.714$) with prediction of asymmetric-bond model. Experimental points (open circles) are the averages of our cooling and heating data for our second run.

able parameters, we analyzed our results, those of Courtens[1] which were earlier, and those of Iida and Terauchi.[2] The latter two results do not extend down to the temperature at which the permittivity levels out to the infinite-frequency value, so this value was chosen as 11.5 for the analysis of their data also. The results are presented graphically in Figs. 3—5 and the parameters obtained are presented in Table II.

We note that Courtens's data[1] for undeuterated, 35% ammoniated RADP obey a similar expression, but with u about $\frac{1}{3}$ as large in accord with the fact that short-range energy parameters in undeuterated crystals are roughly half those in deuterated KDP-type crystals.[13] These data only extend down in temperature a little past the dielectric peak, but his recent results[4] extend into the region of rapid drop of permittivity with decreasing temperature and into the nearly temperature-independent region near 4 K. From Fig. 4 one sees that above 40 K the deviation of the data from our prediction indicates a positive Curie-Weiss temperature T_0 consistent with a tendency for FE
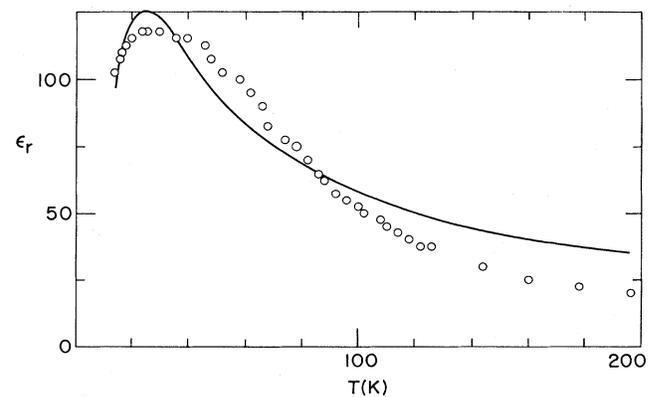

FIG. 2. Potential well for asymmetric-bond model for permittivity of mixed FE-AFE KDP-type crystals.

FIG. 4. Comparison of Courtens's dielectric permittivity data (crystal with $x=0.35$, $D=0$, Ref. 1) with prediction (solid curve) of our asymmetric-bond model.
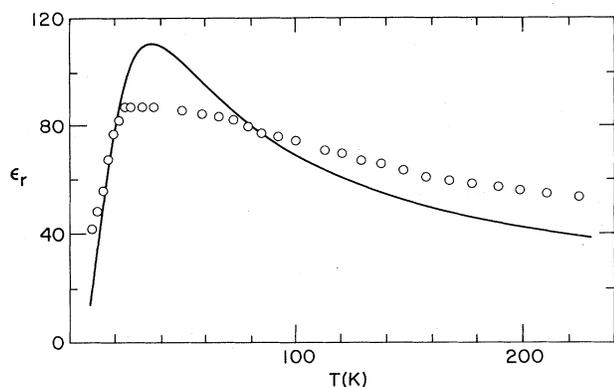
FIG. 5. Comparison of the dielectric permittivity data of Iida and Terauchi (crystal with $x=0.6$, $D=0$, Ref. 2) with prediction (solid curve) of our asymmetric-bond model.

TABLE II. Biased-bond model values for mixed RDP-ADP crystals.

Crystal	C, K	$u/2k$, K
Our crystal, T decreasing	$10\,740\pm250$	59.1 ± 1.2
Our crystal, T increasing	$11\,380\pm350$	63.8 ± 1.3
Our crystal, all data	$11\,160\pm240$	62.6 ± 0.9
$x=0.35$, $D=0$ (Ref. 1)	4780 ± 150	18.8 ± 0.5
$x=0.6$, $D=0$ (Ref. 2)	6270 ± 240	28.3 ± 0.8

order in this crystal which is only 35% ammoniated. The data of Iida and Terauchi[2] above 40 K deviate in the opposite manner from predictions of our independent-biased-bond model, consistent with an AFE ordering tendency in their 60% ammoniated crystal.

In relating our biased-bond model to Courtens's Vogel-Fulcher scaling analysis,[4] we note that our model fits the general features of the real part of the permittivity from 300 down to 4 K, while his analysis covers only the region from his dielectric peak at 33 down to 2 K but fits both the real and imaginary parts of the permittivity well over the frequency range investigated. His analysis employs a spread of energies E which govern the spread in relaxation times according to an empirical formula. In terms of our energy hierarchy, E could be identified with energies ranging from 650 K for the Takagi groups in RbH_2PO_4 as given by Fairall and Reese,[13] down to a fraction of the Slater energy of 75 K. The fraction represents the weakening of the FE ordering tendency of H_2PO_4 groups to which an ammonium ion is attached. Our model predicts dc permittivity so it overestimates the permittivity at 1000 Hz in the region [shown for Courtens's crystal in Fig. 1(a) of Ref. 4] in which permittivity both drops rapidly with temperature and exhibits dispersion.

CONCLUSION

We have presented a simple model based on noninteracting asymmetric hydrogen bonds which qualitatively explains in the dc limit the unusual dielectric behavior of mixed RDP-ADP crystals for ammonium fractional concentration x near 0.5. To better explain results for x farther from 0.5 and to predict frequency dependence, the various interactions between hydrogen bonds discussed above must be taken into account. We are developing a program for Monte Carlo simulation of hydrogen intrabond jumps governed by these interactions.

Our data for a crystal with $x=0.48$ show no indication of a phase transition down to 4 K. The onset of proton-glass behavior occurs gradually as kT becomes smaller than the bond asymmetry energy and the hydrogens are frozen into one of their lowest-free-energy configurations. We expect that there is a broad range of ammonium concentration over which such mixed crystals will exhibit no transition out of the paraelectric phase as temperature decreases toward 0 K.

ACKNOWLEDGMENTS

*On leave from Institute for Molecular Physics, Polish Academy of Sciences, Poznań, Poland.

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