Phase coexistence in the mixed crystal Rb1-x(NH4)xH2AsO4
by Nicholas Joaquim Pinto

A thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Physics
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Abstract:
A study of the coexistence phenomenon in mixed crystals of rubidium ammonium dihydrogen arsenate has been done. Coexistence in this study refers to the simultaneous presence of ferroelectric and proton glass phases as temperature is lowered below the ferroelectric phase transition temperature Tc. Such coexistence is found to exist in these mixed crystals only for small ammonium concentrations. Our results show that coexistence exists for lower ammonium concentration than previously suggested. A study was also done on crystals with larger ammonium concentrations that show pure proton glass behavior and the results compared with the coexistence phenomenon.

Dielectric, spontaneous polarization and nuclear magnetic resonance experiments on mixed crystals with small ammonium concentrations show that at low temperatures there exists intimate coexistence of ferroelectric clusters with proton glass clusters below the glass transition temperature Tg. In the proton glass phase, we observe a spread of relaxation times due to the creation and annihilation of $HAsO_4$ and H_3AsO_4 pairs as they diffuse through the crystal. Spin lattice relaxation times for the acid deuterons in a 10% ammoniated sample show a broad T1 minimum near the glass transition temperature which is characteristic of proton glasses. Field-cooling experiments were also done on the pure proton glass. The results are consistent with dielectric measurements, but the remanent polarization was found to be extremely small. This polarization was found to depend on the rate of heating and cooling the sample while performing the experiment.

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APPROVAL

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Nicholas Joaquim Pinto

This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency, and is ready for submission to the College of Graduate Studies.

Nov. 4, 1992
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ABSTRACT

A study of the coexistence phenomenon in mixed crystals of rubidium ammonium dihydrogen arsenate has been done. Coexistence in this study refers to the simultaneous presence of ferroelectric and proton glass phases as temperature is lowered below the ferroelectric phase transition temperature T_c. Such coexistence is found to exist in these mixed crystals only for small ammonium concentrations. Our results show that coexistence exists for lower ammonium concentration than previously suggested. A study was also done on crystals with larger ammonium concentrations that show pure proton glass behavior and the results compared with the coexistence phenomenon.

Dielectric, spontaneous polarization and nuclear magnetic resonance experiments on mixed crystals with small ammonium concentrations show that at low temperatures there exists intimate coexistence of ferroelectric clusters with proton glass clusters below the glass transition temperature T_g. In the proton glass phase, we observe a spread of relaxation times due to the creation and annihilation of $HAsO_4$ and H_3AsO_4 pairs as they diffuse through the crystal. Spin lattice relaxation times for the acid deuterons in a 10% ammoniated sample show a broad T_1 minimum near the glass transition temperature which is characteristic of proton glasses. Field-cooling experiments were also done on the pure proton glass. The results are consistent with dielectric measurements, but the remanent polarization was found to be extremely small. This polarization was found to depend on the rate of heating and cooling the sample while performing the experiment.

CHAPTER 1

INTRODUCTION

Investigation of the proton glass rubidium ammonium dihydrogen arsenate $(Rb_{1-x}(NH_4)_xH_2AsO_4$-RADA) and its deuterated counterpart $(Rb_{1-x}(ND_4)_xD_2AsO_4$-DRADA) has been carried out to understand the coexistence of ferroelectric and proton glass phases as temperature is lowered below the ferroelectric transition temperature T_c. Above this temperature the system is in the paraelectric phase. Below the transition temperature, for $x=0$ the system is ferroelectric below T_c and for $x=1$ the system is antiferroelectric below the Néel temperature T_N. For a range of intermediate x-values shown in the phase diagram in Fig. 1, the system makes a smooth transition to the "proton glass" phase. This "transition" to the glassy phase is <u>not</u> a thermodynamic phase transition. Rather, it is an effect seen due to competing ferroelectric and antiferroelectric interactions as a frequency dependent freezing of protons in their bond sites as temperature is lowered. The region on the phase diagram where one observes a dispersion in the
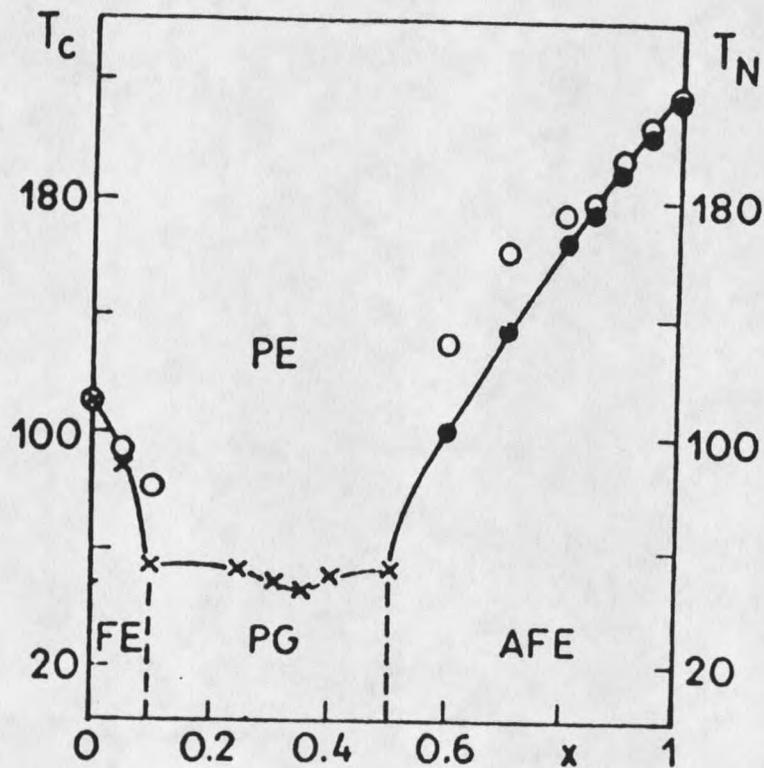
Figure 1. Phase diagram of RADA mixed crystals as a
function of ammonium concentrations (x) and
temperature. PE, FE, PG and AFE denote
paraelectric, ferroelectric, proton glass and
antiferroelectric phases respectively. [1]

dielectric response is called the "proton glass" phase. Such a phase diagram shows the boundaries between the paraelectric (PE) and ferroelectric (FE) phase for small ammonium (x) concentrations and the boundary between the PE and antiferroelectric (AFE) phase for large x values. Our experiments concentrate on crystals having ammonium concentrations (x) close to the ferroelectric side of the phase diagram.

Proton glass was first discovered by E. Courtens[2] in 1982 in the mixed crystal rubidium ammonium dihydrogen phosphate (RADP) with x=0.34. In this system, the frustration that leads to glassy behavior results from the random placement of the NH_4^+ cation. To understand the role of the NH_4^+ cation, it is important to understand the origin of ferroelectricity and antiferroelectricity in the pure crystals. The most widely studied ferroelectric crystal in this family of crystals is KH_2PO_4 (KDP). In the case of the antiferroelectric crystals it is $(NH_4)H_2PO_4$ (ADP). In the crystals studied here the following substitution must be made, Rb for K and As for P. The procedure used to grow these crystals is given in Chapter 2. These crystals are tetragonal in their structure with the ferroelectric or antiferroelectric axis along the $\underline{c}$ direction of the crystal.

Fig. 2 shows the crystal structure of KDP[3] at room

temperature and Fig. 3 is its c-axis projection in the ferroelectric ordered phase.[4] The structure consists of two interpenetrating sublattices. One is a body-centered sublattice of PO_4 tetrahedra and the other a body-centered sublattice of K^+ ions. The K^+ and P^{5+} ions are alternately arranged in chains running along the c axis and are spaced from each other by a distance c/4. Each phosphorus ion is surrounded by four oxygen ions at the corners of a tetrahedron and each PO_4 group is hydrogen bonded to four other PO_4 groups via 'acid' hydrogen bonds. Because these PO_4 neighbors in adjacent chains are c/4 higher or lower than the PO_4 in question, the linkage is such that there is an O...H-O 'acid' hydrogen bond between the one 'upper oxygen' of one PO_4 group and one 'lower oxygen' of a PO_4 group spaced c/4 above the previous one. These hydrogen bonds are nearly perpendicular to the c axis. Neutron diffraction studies show that only two hydrogen atoms are located near a PO_4 group making it as a whole an $(H_2PO_4)^-$ ion. Neutron diffraction studies also show that the hydrogen atoms are statistically distributed at the center of the O-H...O bonds in the paraelectric phase while in the ferroelectric phase the protons are statistically off center in the hydrogen bond. In this phase, the protons are ordered in such a way that in a single domain the protons are either close to the 'upper oxygen' or 'lower oxygen'
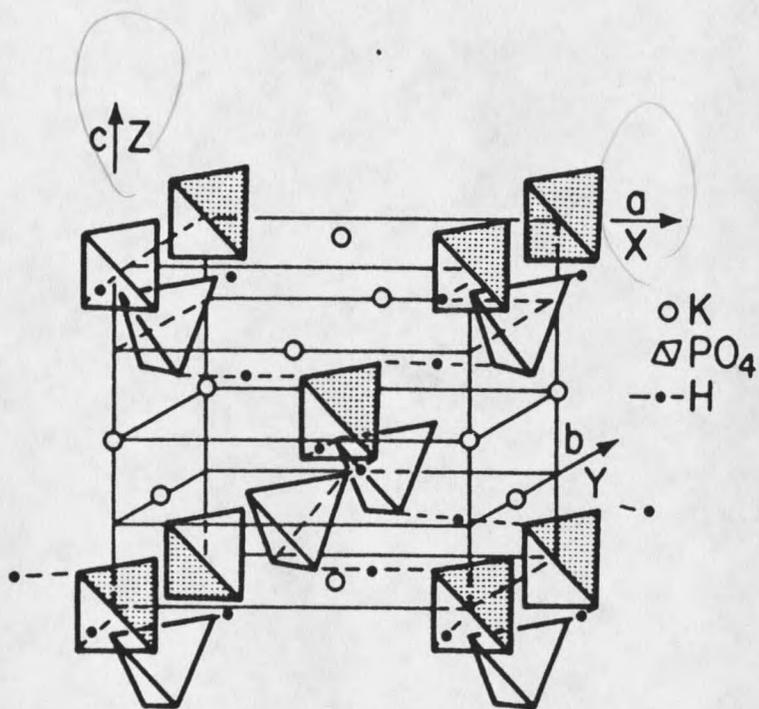
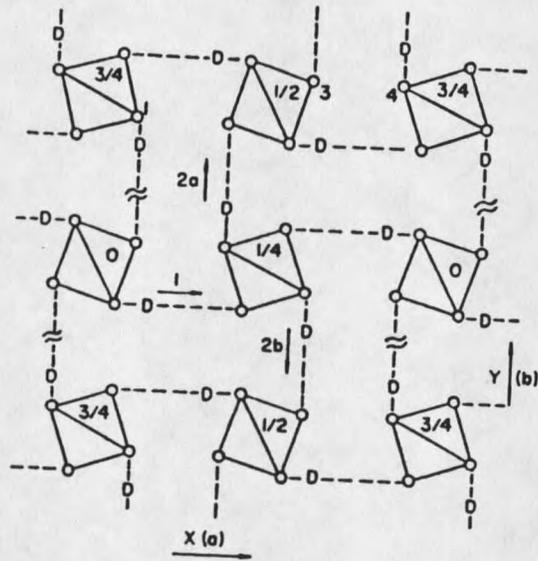Figure 2. The crystal structure of KDP at room temperature. [3]

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Figure 3. _c_-axis projection of KDP in the ferroelectric phase.[4]

depending on the polarity. This ordering effect of the protons around the PO_4 tetrahedron is the key factor responsible for ferroelectricity in these crystals. In this ordered state the polarization arises from the displacements of K^+ and P^{5+} ions in the direction of the $\underline{c}$ axis as shown in Fig.4. The direction of the spontaneous polarization is along the P^{5+} displacement. Thus, when the polarization is 'up', these protons are nearest to the 'lower oxygen' ions of each PO_4 group and vice versa.

The antiferroelectric counterpart has NH_4^+ substituted for K^+ and as a result the 'ammonium' protons are hydrogen bonded to the oxygens in addition to the 'acid' protons. Two of the 'ammonium' protons form 'short' bonds with the surrounding PO_4 tetrahedra and two 'long' as seen in Fig. 5. This has an influence on the position of the 'acid' proton in its O-H...O bond. In the antiferroelectric phase the arrangement of the 'acid' protons is such that each PO_4 tetrahedron has a proton at the upper and at the lower end unlike in KDP where in the ferroelectric phase all the 'acid' protons were attached either to the top or bottom of the PO_4 tetrahedron. Such an arrangement of the protons results in the polarization alternately pointing in the 'up' and 'down' directions as seen in Fig. 6 yielding a net polarization of zero. The arrows indicate the direction of polarization in a unit cell.
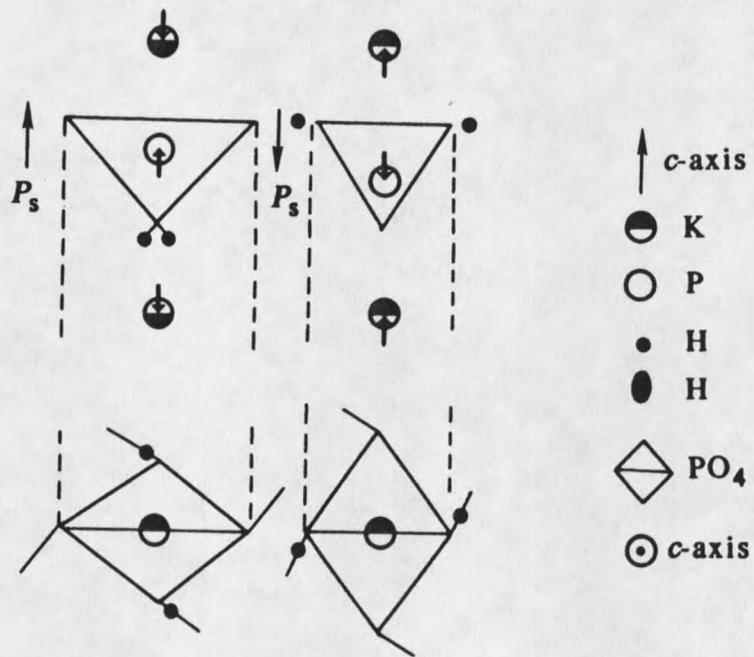
Figure 4. Schematic representation of the dipole moment in KDP. Polarization along the c axis.[5]