# Phase coexistence in the deuteron glass Rb0.9(ND4)0.1D2AsO4 proven by neutron diffraction

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# Phase Coexistence in the Deuteron Glass $Rb_{0.9}(ND_4)_{0.1}D_2AsO_4$ Proven by Neutron Diffraction

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Neutron diffraction technique has been used to study the transitions from the paraelectric (PE) phase to the ferroelectric (FE) one in the deuteron glass crystal $Rb_{0.9}(ND_4)_{0.1}D_2AsO_4$ (DRADA-10). The crystal shows PE hk0 diffraction spots splitting into spot patterns from domains, 4 spots from 4 FE domain types. A more complex phase behavior that the one corresponding to a typical PE-FE phase transition has been found. Coexistence of FE and PE features together with incommensurate correlations in the low temperature phase has been discovered. The intensity of the spots associated with the FE domains indicates the fraction of the crystal in the low-temperature phase. For DRADA-10 there is a fairly wide temperature range (7–10 K) over which these spots coexisted with spots remaining from the paraelectric phase.

*Keywords:* proton glass; coexistence; neutron diffraction; ferroelectrics

## INTRODUCTION

In the mixed ferro- (FE) and antiferroelectric (AFE) system $A_{1-x}(ND_4)_xD_2BO_4$ [A=Rb or K and B=As or P], there is competition between the FE and the

AFE orderings, each characterized by specific configurations of the acid deuterons.[1-7] The random distribution of the A and $ND_4$ ions is the main source to produce frustration which can increase local structural competition such that the long-range electric order disappears. Instead of a typical sharp FE or AFE phase transition an extremely rich x-T phase diagram appears, where phase coexistence [such as PE/FE, PE/AFE etc.] becomes a characteristic in this type of mixed compounds. In order to obtain locally a phase state which is different from the disordered host, the minimal size of the short range ordered clusters must be big enough to show typical features of the long-range ordered phases., and because of the destroyed translational invariance only microscopic investigation techniques such as e.g. NMR, x-ray and neutron scattering can detect the occurrence of such features[2].

In the present paper we show the suitability of neutron diffraction to prove and characterize phase coexistence in the example of the deuteron glass $Rb_{0.9}(ND_4)_{0.1}D_2AsO_4$.

## EXPERIMENTAL

Single crystals of $Rb_{1-x}(ND_4)_xD_2AsO_4$ with x=0.1 were grown from aqueous solutions with certain ratios of $RbD_2AsO_4$ (DRADA) and $ND_4D_2AsO_4$ (DADA) by slow evaporation of $D_2O$ in atmosphere of argon gas. The $ND_4$ concentrations determined previously[9] from the ratio of Rb and N atoms by X-ray photoelectron spectroscopy showed that the relation of $ND_4$ concentration between x' (in solution) and x (in crystal) is linear within experimental error (± 3 %).

The neutron diffraction experiment was performed at the Brookhaven High Flux Beam Reactor, using the triple axis spectrometer. Neutron parameters were λ=2.35 Å=14.7 meV and a collimation of 20'-20'-20'-40'.

The crystals were cooled by means of an APD Cryogenics Inc., Model HC-2 closed cycle He refrigerator. The temperature was controlled with a Lakeshore DRC-93CA temperature controller.

## RESULTS AND DISCUSSION

In this contribution we are focusing on the ferroelectric side of the x-T phase diagram of DRADA. All scattering was done in the hk plane of reciprocal space, perpendicular to the crystal c-axis. That means that if the crystal studied $Rb_{0.9}(ND_4)_{0.1}D_2AsO_4$ would undergo a pure ferroelectric phase transition resembling the one in the parent compound $RbD_2AsO_4$ the diffraction pattern would be as follows: In the paraelectric phase the crystal is body-centered tetragonal, so all reflections with (h+k)=odd are missing. In the ferroelectric phase, the density of Bravais lattice points does not change, so the allowed diffraction spots are the same. There are four kinds of ferroelectric domains, so each spot can break up into as many as four spots. Two of these domain types consist of sheets in the kl plane (indices refer to the tetragonal cell). These do not change the (h, $\phi$, $\phi$) spot, but they split the (0, k, 0) spot into ($\delta$, k, 0) and (-$\delta$, k, 0) spots because of the ferroelectric shear. The other two domain types are thin sheets in the hl plane. If all domain types are equally prevalent, the (h, $\phi$, $\phi$) and (0, k, 0) spot intensities will have a 1:2:1 ratio. At an h = k point (h, h, $\phi$) the four domains will give spots in a "cross" pattern, at (h, $\delta$, $\phi$), (h, -$\delta$, $\phi$), ($\delta$, h, $\phi$), (-$\delta$, h, $\phi$), with no central spot at (h, h, $\phi$). The peaks were fitted with Lorentzians. Our measurements bear out these pattern predictions but slight deviations from them helped us to identify coexistence and other microscopic features such as incommensurate correlations of this region of the phase diagram.

## Ferroelectric Domains

Typical results for scans along (2,0+η,0) and (4,0+η,0), with η small, are shown in Fig. 1. All wavevectors are expressed in reciprocal lattice units. At 168.5 K two satellite peaks appear around the Bragg reflection. This behavior is characteristic of the scattering from the ferroelectric phase, and arises from the splitting of the crystal into different ferroelectric domains when the unit cells shears to its orthorhombic structure[10]. The Bragg peak decreases drastically by entering the FE phase, the spot intensities bearing the pattern 1:2:1 predicted before.

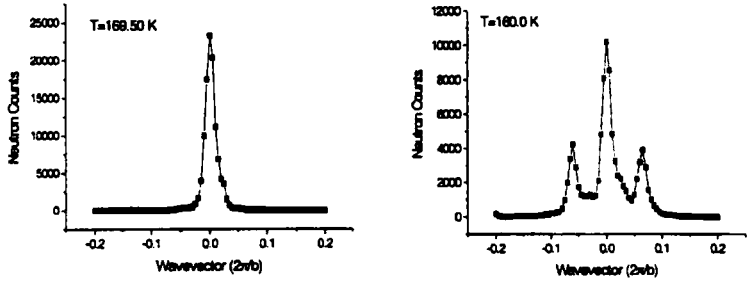


FIGURE 1 Neutron diffraction for scans along (2,0+η,0).

## Incommensurate Structure

The results of the scans along (2+ξ,0,0) and (4+ξ,0,0) shown a different pattern that the one expected form the crystallographic predictions. In this case, at T=168.5 K four satellite peaks appear around the Bragg reflection (Fig. 2). Whereas two of them correspond to the FE domains mentioned before, the peaks closer to the Bragg reflection resemble the ones observed in Ref. 10 by means of X-ray scattering in RADP. These peaks were associated with incommensurate modulations. The fact that this feature only appears along ξ indicates that the modulation only exists in this direction. The

incommensurate peaks decrease in intensity on cooling and seems to disappear below ~ 140 K. The width corresponds to the incommensurate modulations being well defined for about 80 Å.

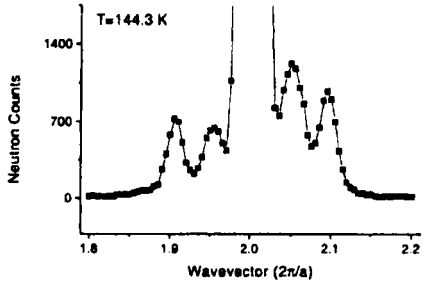


FIGURE 2 Neutron diffraction for scans along (2+ξ,0,0).

**Coexistence**

Coexistence of the paraelectric and the ferroelectric phases is undoubtedly proven by the pattern of the diffraction along (2+ξ,2,0) and (2,2+η,0) (Fig 3). By observing the scattering close to the (2,2,0) Bragg reflection, a decrease of the tetragonal paraelectric Bragg peak can be observed that coincides with the appearance of the satellite peaks corresponding to the ferroelectric domains in the orthorhombic phase. The decrease in the intensity of the tetragonal Bragg peak equals the sum of the intensities of the two ferroelectric peaks, the intensity being in this way proportional to the volume of the crystal in a given phase.

After 7-10 K of coexistence, the tetragonal component disappears and the crystal becomes pure orthorhombic-ferroelectric, the intensity of the ferroelectric peaks becoming almost constant.

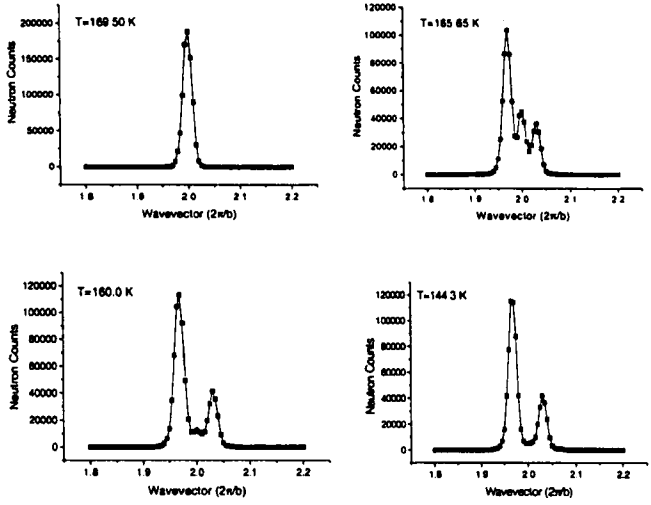


FIGURE 3 Neutron diffraction for scans along (2,2+η,0).

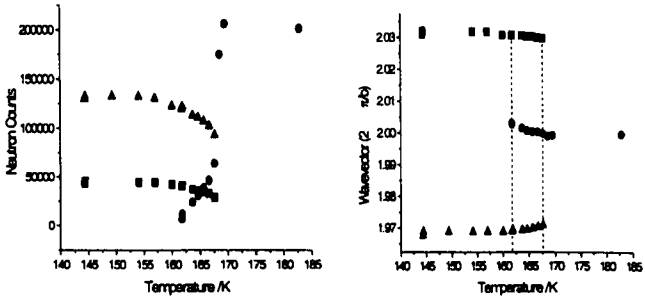


FIGURE 4 Temperature dependence of the intensity (left) and the wavevector (right) of the paraelectric and ferroelectric peaks. The lines (guides for the eyes) define the PE/FE coexistence region. Squares, circles and triangles correspond to the three peaks observed in Fig. 2 at T=165.65 K from right to left, respectively.

## CONCLUSION

Neutron diffraction provides clear evidence of the microscopic features of the phase behavior of the crystals in the ferroelectric part of the x-T phase diagram of the RADA system. The existence of incommensurate structure coexisting with the ferroelectric domains and coexistence of the paraelectric and the ferroelectric phases have been shown.

We conclude that, on cooling, $Rb_{0.9}(ND_4)_{0.1}D_2AsO_4$ undergoes the following behavior: Above 168.5 K the crystal shows an undistorted tetragonal paraelectric phase. At this temperature both ferroelectric domains, associated with an orthorhombic structure, and incommensurate correlations along the $\vec{a}$ axis appear. The coexistence of the paraelectric/ferroelectric i.e. tetragonal/orthorhombic features lasts for about 7 to 10 K; the tetragonal component vanishes at ~160 K. Below ~160 K the ferroelectric phase coexists with the incommensurate modulation down to ~140 K, the temperature at which this modulation seems to vanish.

This incommensurate modulation was associated with the glass phase[10] that appears in the x-T phase diagram at higher ammonium concentrations.

In $Rb_{0.9}(ND_4)_{0.1}D_2AsO_4$ the short-range antiferroelectric order due to the freezing-in of the $ND_4$ reorientations triggers a formation of FE/PE phase coexistence. This fact is also supported by the gradual developments in the temperature-dependent dielectric, NMR and light scattering results[3-7,9].

In the present paper we have shown the suitability of neutron diffraction for the study of phase coexistence: the presence of diffraction peaks corresponding to different phases in a given temperature range gives evidence of this fact. From the intensity of the peaks, the volume of the crystal in each phase can be calculated.

Similar measurements in the antiferroelectric part of the x-T phase diagram of DRADA have been also performed and the results will be present in the near future together with an study of the behavior of the correlation lengths of the different phases along the x-T phase diagram.

**Acknowledgments**

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