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Paraelectric-Antiferroelectric Phase Coexistence in the Deuteron Glass $Rb_{0.5}(ND_4)_{0.5}D_2AsO_4$*

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Neutron diffraction was used to study the paraelectric (PE) to antiferroelectric (AFE) phase transition in a deuteron glass crystal $Rb_{0.5}(ND_4)_{0.5}D_2AsO_4$ (DRADA-50). Coexistence of AFE and PE phases was proven in a temperature range 7-12 K wide.

Keywords Proton glass; coexistence; neutron diffraction; antiferroelectrics

PACS: 77.80.−e; 77.90.+k; 61.12.Ld; 72.80.Ng

Introduction

The mixed FE-AFE system $A_{1-x}(ND_4)_xD_2BO_4$ [A = Rb (or K, Cs) and B = As (or P)] has competition between ferroelectric (FE) and AFE ordering [1–5]. Random Rb and ND_4 distribution causes frustration that increases local structural competition and inhibits long-range electric order. Instead of a sharp FE or AFE phase transition, PE/FE and PE/AFE phase coexistence occur outside the composition region where no transition exists. Because translational invariance is destroyed, only microscopic techniques such as NMR, x-ray and neutron scattering can detect such features [3–4]. For example, PE/FE phase coexistence and incommensurate correlations were proven by neutron diffraction in $Rb_{0.9}(ND_4)_{0.1}D_2AsO_4$ [4].

In this paper we report the behavior of DRADA-50 that undergoes a PE/AFE phase transition on cooling.

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Experimental

Single crystals of $Rb_{1-x}(ND_4)_xD_2AsO_4$ with x = 0.50 were grown from aqueous solution of RbD_2AsO_4 (DRDA) and $ND_4D_2AsO_4$ (DADA) by slow evaporation under argon. The ND_4 concentrations in solution and in crystal are related linearly within experimental error (±3%) [4]. Neutron diffraction was performed on the triple axis spectrometer at the Brookhaven High Flux Beam Reactor. Neutron parameters were $\lambda = 2.35$ Å = 14.7 meV and a collimation of 20′-20′-20′-40′. The crystals were cooled with an APD Cryogenics Inc., Model HC-2 closed cycle He refrigerator controlled by a Lakeshore DRC-93CA.

Results and Discussion

All scattering was done in the hk plane, perpendicular to the crystal c-axis. The PE phase is body-centered tetragonal, so all $(h + k) =$ odd reflections are missing.

The AFE phase loses the body-center Bravais lattice point, so $(h + k) =$ odd spots appear. The four kinds of AFE domains have orthorhombic unit cells with axes parallel to the PE cell axes. Two have $a > b$ and two have $a < b$. A (h, ϕ, ϕ) spot should split into $(h + \delta, \phi, \phi)$ and $(h - \delta, 0, 0)$ spots, while a $(\phi, k, 0)$ spot should split into $(0, k + \delta, 0)$ and $(0, k - \delta, 0)$ spots. A (h, k, 0) spot should split into $(h + \delta, k - \delta, 0)$ and $(h - \delta, k + \delta, 0)$ spots. At most, a spot can double, because two domains with the same direction of cell elongation give identical spots.

We used this information to monitor the progress with decreasing temperature of the PE/AFE transition. The peaks were fitted with Lorentzians.

Antiferroelectric Domains

Typical results for scans along $(2 + \xi, 2, 0)$ with ξ small are shown in Fig. 1. All wavevectors are expressed in reciprocal lattice units. At ~170 K the original PE peak splits into two satellite peaks. The wavevector temperature dependence is presented in Fig. 2 (right).

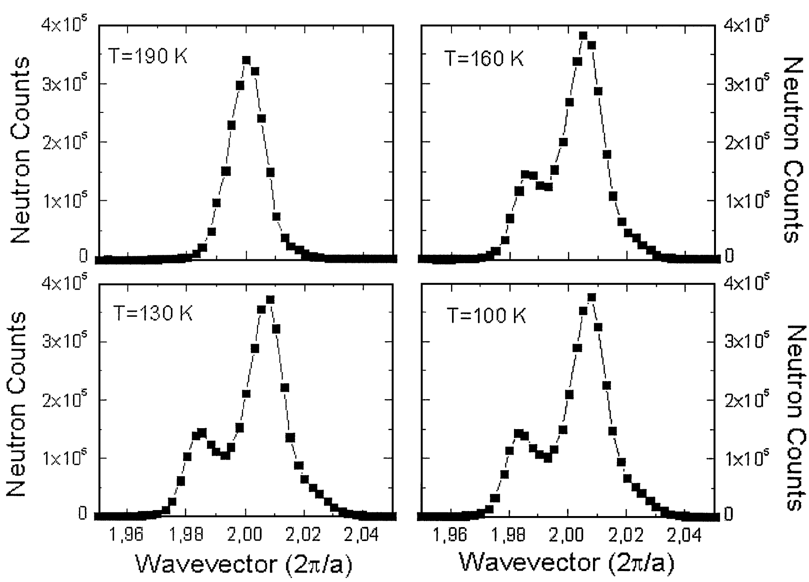

FIGURE 1 Neutron diffraction for scans along $(2 + \xi, 2, 0)$ at several temperatures.

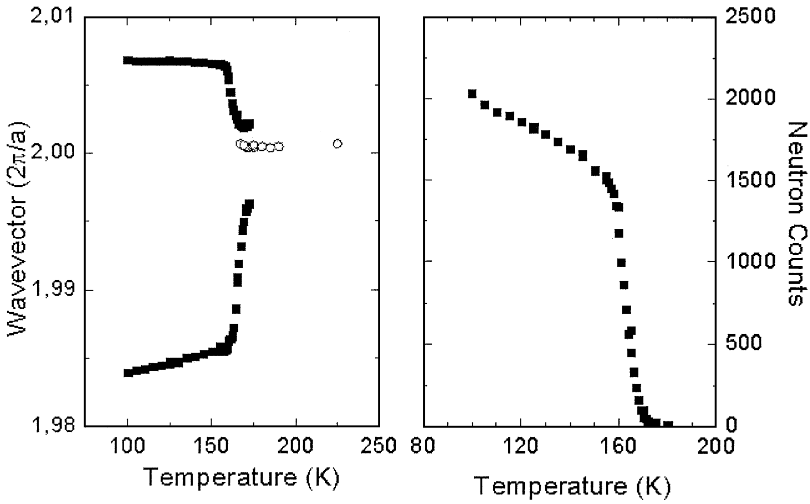

FIGURE 2 Right: Temperature dependence of the intensity of the $(0, 3 + \eta, 0)$ peaks. Left: Temperature dependence of the wavevector for the $(2 + \xi, 2, 0)$ scans. Circles correspond to a single peak fit and squares to a double peak fit.

New Peaks

The results for $(0, 3 + \eta, 0)$ scans appear in Fig. 2 (left). This peak, not allowed in the PE phase, appears in the AFE phase.

Coexistence

PE/AFE phase coexistence is proven by gradual development of the $(2 + \xi, 2, 0)$ and $(0, 3 + \eta, 0)$ diffraction patterns (Figs. 1 and 2). Both exhibit a range from 7 K to 12 K wide in which an incompletely built up AFE phase coexists with the PE phase. After 7–12 K of coexistence, the PE component disappears and the intensity of the $(2 + \xi, 2, 0)$ AFE peaks becomes constant. By comparing the intensities of the coexistence-region peaks with those in the AFE and PE phases, the crystal volume in a given phase can be calculated [6].

Conclusion

Neutron diffraction provides clear evidence for PE/AFE phase coexistence on the AFE side of the DRADA x-T phase diagram. With decreasing temperature the PE/AFE transition follows the sequence (PE ordering → PE/AFE phase coexistence → AFE ordering). This behavior is supported by gradual developments in temperature-dependent dielectric, NMR and light scattering results [1, 5].

A quantitative study of the fraction of each phase with temperature along the x-T phase diagram of DRADA will be presented soon, together with a study of the correlation lengths of the different phases [6].

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