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This is an Accepted Manuscript of an article published in [Ferroelectrics](#) in 2004, available online: <http://www.tandfonline.com/10.1080/00150190490443334>.

S. Lanceros-Mendez, V.H. Schmidt, and S.M. Shapiro, "Paraelectric-antiferroelectric phase coexistence in the deuteron glass $\text{Rb}_{0.5}(\text{ND}_4)_{0.5}\text{D}_2\text{AsO}_4$," *Ferroelectrics* 300, 117-120 (2004). doi: 10.1080/00150190490443334.

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Paraelectric-Antiferroelectric Phase Coexistence in the Deuteron Glass $\text{Rb}_{0.5}(\text{ND}_4)_{0.5}\text{D}_2\text{AsO}_4^*$

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Received in final form 15 December 2002

Neutron diffraction was used to study the paraelectric (PE) to antiferroelectric (AFE) phase transition in a deuteron glass crystal $\text{Rb}_{0.5}(\text{ND}_4)_{0.5}\text{D}_2\text{AsO}_4$ (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 $\text{A}_{1-x}(\text{ND}_4)_x\text{D}_2\text{BO}_4$ [$\text{A} = \text{Rb}$ (or K , Cs) and $\text{B} = \text{As}$ (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 $\text{Rb}_{0.9}(\text{ND}_4)_{0.1}\text{D}_2\text{AsO}_4$ [4].

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

Experimental

Single crystals of $\text{Rb}_{1-x}(\text{ND}_4)_x\text{D}_2\text{AsO}_4$ with $x = 0.50$ were grown from aqueous solution of RbD_2AsO_4 (DRDA) and $\text{ND}_4\text{D}_2\text{AsO}_4$ (DADA) by slow evaporation under argon. The ND_4 concentrations in solution and in crystal are related linearly within experimental error ($\pm 3\%$) [4]. Neutron diffraction was performed on the triple axis spectrometer at the Brookhaven High Flux Beam Reactor. Neutron parameters were $\lambda = 2.35 \text{ \AA} = 14.7 \text{ meV}$ 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 $(h+k) = \text{odd}$ reflections are missing.

The AFE phase loses the body-center Bravais lattice point, so $(h+k) = \text{odd}$ 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 $\sim 170 \text{ K}$ the original PE peak splits into two satellite peaks. The wavevector temperature dependence is presented in Fig. 2 (right).

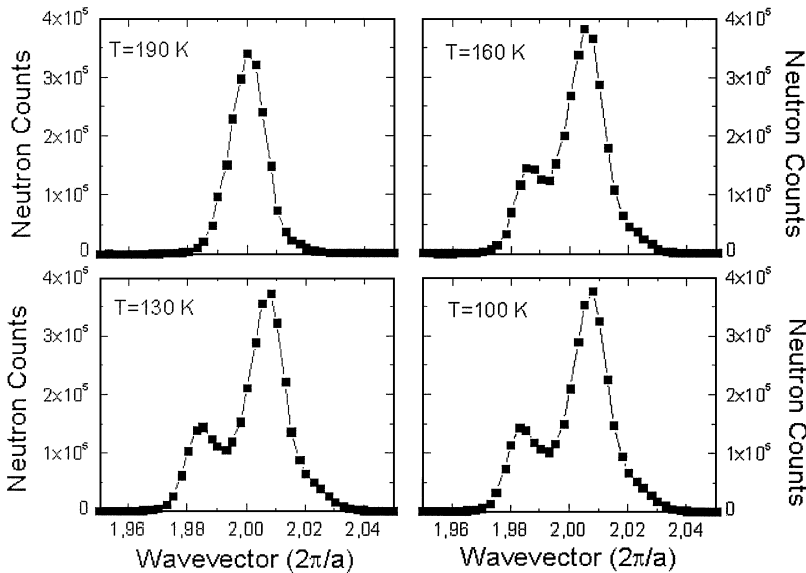


FIGURE 1 Neutron diffraction for scans along $(2 + \xi, 2, 0)$ at several temperatures.

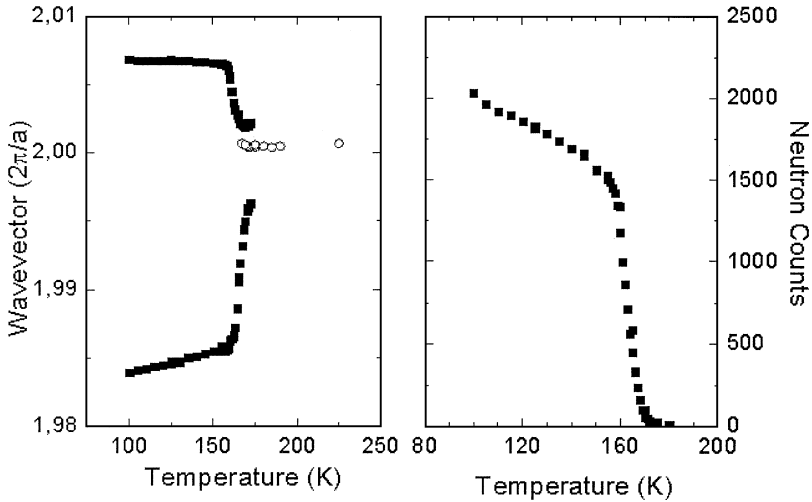


FIGURE 2 Right: Temperature dependence of the intensity of the $(0, 3 + \eta, 0)$ peaks. Left: Temperature dependence of the wavevector for the $(2 + \xi, 2, 0)$ scans. Circles correspond to a single peak fit and squares to a double peak fit.

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 \rightarrow PE/AFE phase coexistence \rightarrow 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].

Acknowledgements

Work supported in part by National Science Foundation Grant DMR-9520251 and by a BNL visitor's grant.

References

1. V. H. Schmidt, Z. Trybula, N. J. Pinto, and S. M. Shapiro, Phase coexistence in proton glass. *Phase transitions* **67**, 499–520 (1998).
2. Z. Trybula, J. Stankowski, L. Szczepanska, R. Blinc, A. Weiss, and N. S. Dalal, Proton glass state in $\text{Rb}_{1-x}(\text{NH}_4)_x\text{H}_2\text{AsO}_4$. *Physica B* **153**, 143–146 (1988).
3. R. Kind, N. Korner, Th. Koenig, and Ch. Jeitziner, Finite size effects in proton glass. *J. Kor. Phys. Soc.* **32**, S799–S802 (1998).
4. S. Lanceros-Mendez, V. H. Schmidt, and S. A. Shapiro, Phase coexistence in the deuteron glass $\text{Rb}_{0.9}(\text{ND}_4)_{0.1}\text{D}_2\text{AsO}_4$ proven by neutron diffraction. *Ferroelectrics* **223**, 203–208 (1999).
5. C. S. Tu, S. S. Gao, R. J. Jaw, Z. Q. Xue, L. G. Hwa, and V. H. Schmidt, Phases in antiferroelectric side $\text{Rb}_{1-x}(\text{ND}_4)_x\text{D}_2\text{AsO}_4$ mixed crystals by light scattering. *Phys. Rev. B* **58**, 5440–5447 (1998).
6. S. Lanceros-Mendez, V. H. Schmidt, and S. A. Shapiro, to be published.