21-Crystallography at Non-Ambient Temperatures and/or Pressures; Phase Transitions

MS-21.03.03 SUPERPROTONIC PHASE TRANSITIONS AND DELOCALIZATION OF THE HYDROGEN BOND NETWORK IN THE $Me_nH_m(AO_4)_p$ CRYSTALS. By A.I. Baranov, Institute of Crystallography RAS, Moscow, Russia.

A specific kind of dynamical proton disorder which involves orientational and positional disordering of hydrogen bonds is considered for a wide variety of crystals with general formula $Me_nH_m(AO_4)_p$, (Me = K, Rb, Cs, NH_4; A = S, Se, P, As).

This proton disorder means a delocalization of hydrogen bonds and leads to high protonic conductivity: 10^{-3}- 10^{-1} $S.cm^{-1}$, and low activation enthalpy 0.25 - 0.27 eV. The whole series of unique features is caused by interaction between a mobile proton subsystem and the immobile sublattice.

The characteristic features of the structural phase transitions between disordered (superprotonic) and ordered (low conductive) phases as well as the transitions to the proton glass state are reviewed. Particular attention is focused on the symmetry and thermodynamical properties of the superprotonic phase transitions. The connection of protonic conductivity anisotropy with the geometric features of the network of hydrogen bonds is discussed.

MS-21.03.04

EFFECTS OF ELECTRIC FIELD AND STRESS ON THE INCOMMENSURATE PHASE TRANSITIONS IN FERROELECTRIC AND FERROELASTIC CRYSTALS ON THE BASIS OF LANDAU THEORY. **By M. Suhara*, Department of Chemistry, Faculty of Science, Kanazawa University, Kanazawa, Japan and T. Kobayashi, School of Pharmacy, Hokuriku University, Kanazawa, Japan.**

The Landau theory has been applied to interpret the temperature dependence of the magnetic resonance spectrum, dielectric and elastic constants, heat anomaly, and stripple lines in the commensurate and incommensurate phases of ferroelectric and ferroelastic A_2BX_4 type crystals under stress and electric field. A free energy density function f is expanded by the complex order parameter Q belonging to the A_2 representation (Azuma,A. et al., Jpn. J. Appl. Phys., 1985, S24-2 750-752). $f=a(QQ^*)/2 +\beta(QQ^*)^2/4 +\gamma_1(QQ^*)^3/6 +\gamma_2(Q^6+Q^{*6})/6 +P^2/2\chi_0 +\xi_1 P(Q^3+Q^{*3}) +\xi_1 P^2QQ^* -PE +C_0u^2/2 +i\xi_2 u(Q^3-Q^{*3}) +\xi_2 u^2QQ^* -uS +i\delta(Q^*(dQ/dz) - Q(dQ^*/dz))/2 +\kappa(dQ/dz)(dQ^*/dz)/2$ (1), where $a = a_0(T-T_0)$. By minimizing the average thermodynamic potential derived from (1) under periodic condition, the temperature dependence of the order parameter contour on the complex plane ($Q = p+iq$) can be obtained as shown in Fig. 1 (ferroelectric case) and Fig. 2(ferroelastic case), where E is the electric field, S the stree, a_c the Curie temperature. Comparing Fig. 1 with Fig. 2, it is concluded that the modulation phase in the IC ferroelectric phase shifts 30+60×n degrees (n:integer) from that of ferroelastic one. Fig. 3 shows the phase shift along the modulation axis in ferroelectric IC phase. Under no bias, the staircase in Fig.3 is at regular intervals both in step(discommensuration) and width(commensurate region). When the electric field E(>0) is applied,+ region expands, and - one reduces. On the other hand the stress is applied to ferroelectric material, the vertical step changes alternatively as shown in Fig. 3. Similar phenomenon is obtained in ferroelastic IC phase by interchanging E and S.

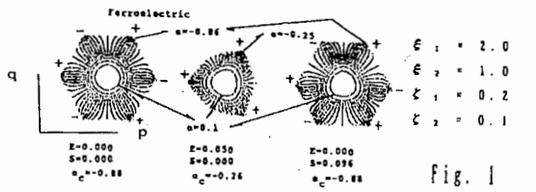

Fig. 1

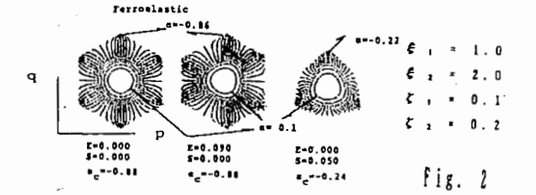

Fig. 2

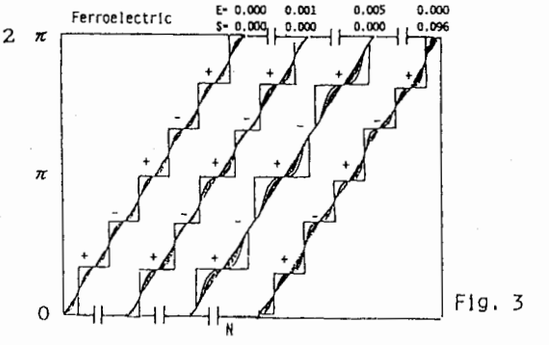

Fig. 3

MS-21.03.05

NUCLEATION MECHANISMS FOR STRAIN TRANSFORMATIONS. By P. Hong*, G. B. Olson, Department of Materials Science and Engineering, Northwestern University, Evanston, IL 60208, USA, and A. L. Roytburd, Department of Materials and Nuclear Engineering, University of Maryland, College Park, MD 20742, USA.

We present new results in the theoretical study of the homogeneous, coherent nucleation phenomenon in strain transformations considering critical nuclei of variable structure. To correctly describe interphase interfaces, where lattice deformations are highly nonuniform, dependence of the local free energy density on strain gradients [Roitburd, A. L. (1978), *Solid State Physics*, **33**, 317] must be taken into account. The strain field of a critical nucleus can then be found from a variational minimization of the free energy functional, its saddle point being identified as the homogenebus nucleation barrier. Results from two kinds of phenomenological approaches concerning the pure shear and pure dilatation cases, respectively, are discussed. One is a one-dimensional [Olson, G. B. & Cohen, M. (1982), *J. de Phys. Suppl. 12*, **43**, c4] model including both nonlinear and gradient shear strain terms. The other is a three-dimensional model [Hong, P., Roytburd, A. L. & Olson, G. B. (1993), submitted to *Phys. Rev. B*] including only harmonic terms in the dilatational strain and its gradients. Both display the disappearance of the nucleation barrier as the lattice instability point of the parent phase is approached. The strain state of the critical nucleus in both cases has been shown to vary as a function of the transformation driving force departing significantly from the classical assumption of a fixed nucleus structure. Comparisons between our model results and those of the Cahn-Hilliard theory for diffusional transformations are also made. We conclude that strong departure from classical behavior is observable only in a system which is sufficiently close to the lattice instability point of the parent phase, and when the critical nucleus size becomes comparable to the effective interfacial width.

Research is supported by the National Science Foundation under Grant DMR-9120116.

