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Some Problems of the Diffuse Ferroelectric and Antiferroelectric Phase Transitions

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The diffuse FE or AFE phase transitions are considered to be consisted of two stages: new phase accumulation and formation of the "infinite new phase clusters". The second stage can be either observed or not observed at zero external electric field or stress.

The diffuse ferroelectric (FE) or antiferroelectric (AFE) phase transitions are often observed in solid solutions (for example in Ba(Ti, Sn)O_3,[1] Ba(Ti, Zr)O_3,[2] PLZT ceramics, (Ba, Sr) (Nb, Ta)$_2O_6$,[4,5] in compounds of the complicated compositions with the perovskite and pyrochlore structure (for example in $PbMg_{1/3}Nb_{2/3}O_3$.[6], $PbFe_{2/3}W_{1/3}O_3$,[7], $Bi_2Mg_{2/3}Nb_{4/3}O_7$.[8] As a rule ferroelectric materials being used in industry are solid solutions, and have the diffuse phase transitions.

The diffuse FE phase transitions are also of scientific interest because new physical phenomena are observed in them: (1) the unusual relaxation of dielectric polarization in the phase transition region,[6,9] (2) the square dependence of the reciprocal dielectric permittivity (ε') on the temperature $1/\varepsilon = A + B(T - T_m)^2$ where T_m is the temperature of the ε' maximum,[9] (3) the unusual dependence of the maximum height of the curve $\varepsilon''(T)$ when the frequency changes[9] and (4) the absence of the apparent symmetry change as the temperature is lowering down the diffuse FE transition at zero external electric field.[10] The relaxation of dielectric polarization seems to be typical for the diffuse AFE transitions too.[8]

The "diffusion" of the FE and AFE phase transitions of the first order is explained[11,13] by the "frozen" composition fluctuations, i.e. by the concentration fluctuations of the different type ions in the equal crystal lattice sites. Because of the Curie temperature dependence on the composition, different microregions of the crystal have different transition temperatures. So the total phase transition in the crystal consists of a great number of phase transitions in microregions, and is observed in the wide temperature interval. This idea is connected with the problem whether one can apply such macroscopic conceptions as concentration, Curie temperature, or phase to the substance in microregions with size$\sim 10^6 Å^3$. The positive answer on this question is given for the case of the regions, of which size is more than the critical size of nucleus. Undoubtedly, the over-critical nuclear formation in some volume of the substance is a phase transition in this volume. So we can say of the Curie temperature of this microregion, its phase and component concentration. Then the limit of fitting of macroscopic conceptions is determined as the size of the critical nucleus, i.e. by the nature itself.

The next problem appears because of the preservation of the cubic crystal apparent symmetry as the temperature is lowering down the diffuse FE transition at zero electric field.[10,14] A birefringence appears only when the electric field is applied to the crystal at low temperature, and retains after the field is switched off. One could suppose the absence of any phase transition if the electric field is absent and there is no apparent symmetry change. One could suppose that the phase transition is observed only after the electric field application, and only this field induces the FE phase transition. But it is not so.

Really the phase transition seems to be divided into two stages. The first stage is the gradual formation of the more and more numerous nuclei of the FE phase. This stage can be named as "the stage of FE phase accumulation". However it is necessary to take into account that when forming, the FE nucleus not only polarizes and deforms its environment but also is affected by the environment which decreases the spontanneous deformation x_s and spontaneous polarization P_s of the nucleus. As a result P_s and x_s of the nucleus are less than for a single-domain crystal. So, though the phase transition is observed in the nucleus volume, quantitatively it does not reach the end.

When there are rather few polar microregions, the interaction between them is weak. When accumulating and growing, the distance between them decreases and the interaction between them increases. But the vectors of P_s and x_s of these regions are oriented along the different crystallographic axis allowed by the crystal symmetry. As a result the interfaces of the paraelectric phase between the polar regions are strongly deformed. Apparently then some charged defects migrating in the lattice neutralize partly the charge on the boundaries of the polar regions and fix the polar regions in the given orientation. Because of that the crystal remains divided into the great number of differently oriented microregions, and is macroscopically isotropic even at low temperature, and no crystal symmetry decrease is observed in the polarizing microscope.

At the X-ray investigation the pseudocubic distortion is not perceptible because of little dimension of the FE regions and different value and orientation of the spontaneous deformation in these regions. So the "isotropization" is observed.

If a sufficiently strong electric field is applied to the crystal with the great number of the polar regions, the polar regions reorientate, the electric moment vectors of all regions being aligned. Then the FE regions expanding through the paraelectric interfaces join with each other. In such a way an "infinite" cluster is formed (if the field is homogeneous, simply one FE domain is formed expanding through the whole crystal).*Then the macroscopic symmetry decreases and there is an apparent "phase transition", or to say more correctly, the next stage of the phase transition. It can be named "the stage of the "infinite" FE cluster formation". Then the counteraction of the ambience to the arise of the polar regions disappears and P_s and x_s can increase to the natural values, that is the values characteristic for a single crystal.

Since the formation of each nucleus is followed by a weak thermal effect, the effects from different nuclei is distributed through the wide temperature interval. It gives a very wide and low extreme of specific heat. When forming the "infinite" cluster, an additional (more or less sharp) thermal effect should be observed because of the P_s and x_s increase to their natural values. When the electric field is switched off the crystal state with low symmetry retains at low temperature but disappears at heating and approaching to the average temperature of the phase transition (then the "infinite" FE cluster breaks up).

The substance with the diffuse AFE transition such as $Na_{0.5}Bi_{0.5}TiO_3$ behaves in other way. Its structure is cubic above 540°C. Below 540°C the twin structure appears. This transition into pseudocubic phase is like to the high-temperature phase transitions in $NaNbO_3$. The dielectric permittivity goes at 320°C through rather diffuse maximum due to the AFE transition.[15,16)] The transition into FE phase is observed near to 200°C. There is no apparent change of twin (domain) structure at the AFE and FE transitions. But the darkening of the crystal is observed in the polarized light with the crossed polarizers in the temperature interval 222±17°C (when cooling) and 277±17°C (when heating); that is in the AFE phase interval. A considerable thermal effect[1)] and a more or less expressed decrease of ε correspond to the darkening interval and have so the temperature hysteresis (nearly 50°C), too.

The observed phenomena can be explained nearly as for the ferroelectrics with the diffuse phase transition. When cooling the crystal through the diffuse AFE transition the gradual accumulation of the AFE microregions with the different deformation orientation is observed. The interfaces of the paraelectric phase are strongly strained, and the differently oriented regions are prevented from the contact by these interfaces. Because of that the different orientation of each microregion retains, and the influence of each AFE microregion on the macroscopic birefringence is mutually extinguished. So the twins which were in the non-cubic paraelectric phase between 540 and 320°C retain in the crystal. But the birefringence in these twins seems to decrease. Indeed when there are many differently oriented AFE regions giving no total contribution in the birefringence, there is little total volume of the non-cubic

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* The conception of the infinite cluster is used here because the authors proceeded originally from the percolation theory.

paraelectric phase determining the birefringence of the apparent twins. It looks out as if the crystal becomes gradually isotropic.

The situation under consideration differs from the case of the diffuse FE transition because the large electric charges caused by the spontaneous polarization are absent here, and consequently no charged defects precipitate on the boundaries of new phase regions and do not fix them. When there is sufficiently great number of the AFE regions, a considerable mechanical energy is accumulated in the crystal causing a switching of the AFE regions, and as result their orientation becomes the same, the regions merge, and an "infinite" AFE cluster is formed. Probably the system of the clusters is already adapted to the available twins since the moment of its formation. This may be why the boundaries of twins of the high-temperature phase remains also at low temperature.

In the case mentioned above the formation of the "infinite" AFE cluster is observed without the influence of the electric field or stress. Both stages of the phase transition: the stage of the new phase accumulation and the stage of the "infinite" cluster formation are observed only as result of the temperature change.

The temperature hysteresis at the formation-disintegration of the "infinite" AFE cluster is due to the role of the paraelectric phase interfaces. When cooling, these interfaces prevent from the drowing together of the AFE regions, and themselves exist only because they separate the AFE regions with the different deformation orientation. But when the AFE cluster is formed and the paraelectric interfaces are absent for the formation of a gap in some place of the "infinite" cluster, a paraelectric phase nucleus of an over-critical size should be formed in this place. It can be at sufficiently high temperature only.

After the cluster breaking up into microscopic AFE regions they can pass under the action of thermal fluctuations from time to time into paraelectric phase and back into AFE state, and in such way may be disoriented. Then the substance becomes again pseudoisotropic until at the increasing temperature the "infinite" cluster of the paraelectric phase forms. But it is a cluster of non-cubic paraelectric phase and it shows some birefringence. So an assumption is necessary that in the same way as the system of AFE clusters fits to the twin boundaries appearing at 540°C, the new arising clusters of non-cubic paraelectric phase are also adapted to these boundaries.

Summarising we can say that the idea about breaking-up the diffuse phase transitions into two stages allows to explain a number of phenomena, which were strange earlier.

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