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Order parameter behaviour in the relaxor ferroelastic lead scandium tantalate

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Abstract. Symmetry properties and structural phase transitions of the relaxor ferroelectric $PbSc_{0.5}Ta_{0.5}O_3$ are described using Landau theory. Symmetry reductions in disordered material occur via a ferroelastic ($Pm\bar{3}m-R\bar{3}m$) and a ferroelectric transition ($R\bar{3}m-R\bar{3}m$). Ordering involves the zone boundary instabilities $Pm\bar{3}m(Z = 1)-Fm\bar{3}m(Z = 2)$ (R point), $R\bar{3}m(Z = 1)-R\bar{3}m(Z = 2)$ (Z point) and $R\bar{3}m(Z = 1)-R\bar{3}m(Z = 2)$ (Z point). The Landau potential includes the coupling between the three primary order parameters describing the cation ordering, the ferroelastic and the ferroelectric lattice distortions. Relaxor behaviour is related to the kinetic properties of order parameters with intermediate conservation lengths. Känzig domains are related to inhomogeneous solutions of the kinetic rate law.

1. Introduction

PbSc_{0.5}Ta_{0.5}O₃, PST, shows phase transformations characteristic for diffuse, relaxortype behaviour. Relaxor materials are also called dirty ferroelectrics because their transformation behaviour appears to be inhomogeneous and it is heavily influenced by lattice imperfections. The structure of these materials is based on the ABO₃ perovskite framework with ideal cubic high-temperature symmetry. In PST the B site is occupied by either scandium or tantalum. Their atomic arrangement can be controlled by isothermal annealing (Setter and Cross 1980, Stenger and Burggraaf 1980, Randall *et al* 1986) leading to different degrees of Sc,Ta order. Renewed interest in these materials has arisen because similar behaviour was observed in high- T_c superconductors (Salje 1989a, b).

Fully disordered PST shows macroscopically a diffuse phase transformation near 270 K while ordered PST undergoes a discontinuous phase transformation at about 300 K (Setter and Cross 1980, Groves 1985). Both transformations take place from a paraelectric high-temperature phase to a ferroelectric low-temperature phase. Ordering of the B cations affects the optical, thermal and dielectric properties considerably (Zimmer *et al* 1987, Cross 1987, Stenger and Burggraaf, 1980). Additionally the ordering produces a superlattice doubling of the unit cell to $2a_0 \times 2a_0 \times 2a_0$ (a_0 is about 4 Å) and yields a face-centring of the B cations on the lattice. The space group of the ordered paraelectric phase of PST is therefore Fm3m($2a_0$). The ferroelectric low-temperature phase exhibits rhombohedral symmetry. Due to the small and varying size of ferroelectric

domains and due to inhomogeneities within the crystals (Randall *et al* 1986, 1987) the space group of the ordered low-temperature modification has so far not been determined. However, geometrical descriptions of possible departures from ideal perovskite by Megaw and Darlington (1975) allow predictions of the likely space group of ferroelectric, ordered PST to be R3, R3m or R3c.

For disordered PST the atomic displacements occurring in the rhombohedral phase were described by Groves (1985). He showed that beside the influence of B-site cation order, A-site cation displacements occur below T_c which are associated with the electric dipoles. In contrast to Chang and Chen (1985) who assumed a tetragonal symmetry in the ferrophase, Grove (1985) found from x-ray diffraction a phase transformation from a cubic paraelectric phase, space group Pm3m (a_0 , Z = 1) to a ferroelastic lowtemperature modification with space group R3m or R3.

Up to now no group theoretical description of the phase transitions in relaxor materials exists which, as a prime objective, has to distinguish between the two driving transformation processes; firstly the structural ordering corresponding to the formation of a superlattice and secondly the subsequent appearance of electric dipoles accompanied by an elastic strain.

Consequently we focused our interest on a theoretical concept of the phase sequence taking into account pure supergroup–subgroup relations and correlated symmetry reductions associated with the active irreducible representations. The order parameter behaviour and their coupling is derived for ordered and disordered lead scandium tantalate. We also derive Landau–Ginzburg expressions of the free excess energy and introduce a new concept for the understanding of kinetic processes in relaxor materials. These theoretical approaches are the starting point for further experimental work which will be published separately (Bismayer *et al* 1989).

2. Group theory

Starting from the ideal cubic unit cell (Z = 1) of the disordered paraphase in PST with space group Pm $\overline{3}$ m, symmetry reductions to trigonal symmetry can theoretically be constructed using the active representations that transform as T_{1u} or Γ_4 (Janovec *et al* 1975, Stokes and Hatch 1988). The physical properties of relaxor materials are, however, not adequately described by such one-step behaviour because of the following:

(i) Relaxors represent non-equilibrium states with kinetic hindrance for some of the ordering schemes to reach the equilibrium state. Other ordering schemes may relax further in a non-homogeneous matrix. It is hence necessary to consider each ordering scheme separately, including their mutual coupling.

(ii) There is no experimental evidence in fully cation-ordered material that the phase transition $Fm\overline{3}m-R3m$ occurs in one single step. It appears plausible that the ferroelectric and the ferroelastic phase transitions take place as two coupled phenomena and should be seen as two steps of a cascade of phase transitions involving symmetry reduction to the respective maxima space groups (see Lovenc *et al* 1980).

We hence treat the system as a sequence of phase transitions each involving symmetry reductions to the maximum subgroup (*International Tables for Crystallography* 1983, Boyle and Lawrenson, 1972). Any single-step behaviour follows then automatically as special case of our general solution. An allowed *translationengleiche* maximal non-isomorphic subgroup of Pm $\overline{3}$ m is R $\overline{3}$ m (D_{3d}^5). During this transformation the unit cell



Figure 1. Brillouin zones of the cubic disordered form, space group PM3m, and the rhombohedric forms, space groups R3m and R3m. The order parameter of the ferroelastic phase transition is Q_e , its irreducible representation is T_{2g} , the critical point is the origin Γ . The critical point of the cation ordering process is $R = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ in the cubic form. The equivalent zone-boundary point in the rhombohedric Brillouin zone is called Z. Note that the Z-point notation is not identical with the nomenclature of Bradley and Cracknell (1972) which has been followed throughout the paper otherwise.

remains unchanged in size and hence the critical point of the Brillouin zone (BZ) of the paraphase is the origin (Γ) (figure 1). According to Janovec *et al* (1975) the active representation that accounts for the symmetry lowering Pm $\overline{3}m \rightarrow R\overline{3}m$ is T_{2g}. The spontaneous physical quantity that transforms according to this irreducible representation is the elastic deformation with the proper components $e_{yz} = e_{zx} = e_{xy}$, or, in Voigt notation, $2e_{yz} = e_4$, $2e_{zx} = e_5$, $2e_{xy} = e_6$. Consequently in the transition process of disordered PST the relevant order parameter is Q_e , which has the same symmetry as the spontaneous strain. In a second step the ferroelectric modification with the space group R3m is adopted as a maximal non-isomorphic *translationengleiche* subgroup of R3m. Again the size of the unit cell does not change and the critical point is again Γ (figure 1). The corresponding active representation, A_{2u} , transforms like the z-component of a polar vector giving rise to the constitution of the spontaneous polarisation parallel to z below T_c . The total phase sequence is hence Pm $\overline{3}m - R\overline{3}m$.

A hypothetical two-step phase sequence can also be described in the case of ordered lead scandium tantalate. Starting from the eightfold unit cell of the paraelectric parent phase with space group $\operatorname{Fm}\overline{3}m$ (i.e. Z = 2 for the equivalent primitive setting) a deduction to a non-cubic polar subgroup is not possible directly on the basis of the arguments given above. The first group-theoretically allowed symmetry reduction to a maximal non-isomorphic subgroup that is not accompanied by a change of the unit cell leads to $\operatorname{R}\overline{3}m$ (D_{3d}^5) (figure 2). The active representation that transforms according to the (secondary) order parameter in this transformation process in T_{2g} . The corresponding components



Figure 2. Brillouin zones of the cation-ordered phases. The cubic form has the space group $Fm\bar{3}m_{-}(top)$, the rhombohedric space groups are R3m and R3m (bottom). The ferroelastic order parameter is Q'_{e} , its irreducible representation is T_{2e} with a critical Γ point.

of the elastic deformation are the same as in disordered PST leading to the non-driving order parameter Q'_e . In a second step the point symmetry $\overline{3}m$ is lowered to $3m(C_{3v})$ by a *translationengleiche* phase transition with a critical zone-centre Γ of the paraphase (figure 2). Again the active representation for this phase transformation is A_{2u} which transforms like the spontaneous polarisation Q'_p corresponding to the formation of an electric moment parallel to the crystallographic z axis. Q'_p is the driving order parameter of the ferroelectric phase transformation in ordered PST. Due to the lowest-degree invariants of the polarisation components and of the strain ones, coupling via gradient terms to the order parameter invariant is obvious.

The symmetry change characteristic for the transformation due to the ordering of PST is accompanied by a change of the size of the unit cell. Hence, the critical point is determined by a k-vector on the surface of the Brillouin zone of each disordered modification. In order to specify the structural transformations with a breaking of translational symmetry in PST we follow the concept given by Toledano and Toledano (1982) using the notation of BZ points by Bradley and Cracknell (1972). Figure 3 shows that the representation at the R point $\frac{1}{2}$ $\frac{1}{2}$ of the BZ of disordered PST induces the transition $Pm\overline{3}m(O_{h}^{5}) \rightarrow Fm\overline{3}m(O_{3d}^{5})$ (Z = 2) induced by a critical representation at the Z point $\frac{1}{2}$ $\frac{1}{2}$ of the surface of the rhombohedral BZ of disordered PST (figure 4) (the same point Z has been called T by Cracknell *et al* (1979); we prefer to continue to use the Z-point notation to emphasise that this point is the intersection of the z axis and the Brillouin zone in the system). The polar–polar transformation is described by the space



Figure 3. Correlation between the Brillouin zones of the two cubic forms $Pm\bar{3}m$ (large zone) and $Fm\bar{3}m$ (fully included in the former zone). The order parameter which folds back the large zone into the smaller one is Q_{od} with a critical R point. The R point is the corner of the large Brillouin zone.



Figure 4. Correlation between the Brillouin zones of the rhombohedric forms. The Brillouin zone of the disordered material (R3m or R3m) encompasses the Brillouin zone of the ordered material. The order parameters are Q'_{od} for the ferroelastic forms and Q''_{od} for the ferroelastic/ferroelectric forms. The critical points are always Z, which is the intersection of the k_z axis and the Brillouin zone.



Figure 5. Correlation between the space groups involved in structural phase transitions in the relaxor material $PbSc_{0.5}Ta_{0.5}O_3$. The arrows indicate the direction in which the symmetry is reduced. At each arrow the relevant order parameter and the critical point in the Brillouin zone of the respective high-symmetry form is indicated. The active representations are shown in brackets next to the order parameters.

group change $R3m(C_{3v}^5) \rightarrow R3m(C_{3v}^5)$ with a doubling of the primitive cell corresponding to the criticality of the Z point $\frac{1}{2} \frac{1}{2} \frac{1}{2}$ of the rhombohedral BZ (figure 4).

Hence we note that group theory leads unambiguously to the space group of the ordered ferroelectric phase. The space group of this modification has not yet been identified by means of diffraction experiments. The full sequence of phase transformations disordered \rightarrow ordered, paraelectric \rightarrow ferroelectric is given in figure 5.

3. Landau potentials

The phase transitions depicted in figure 5 can be divided into two types: the zone boundary phase transitions occur at the R and Z points of the cubic and rhombohedral Brillouin zone, respectively. The irreducible representations are one-dimensional and the Landau potential takes the simple form (e.g. Landau and Lifshitz 1980)

$$G(Q_{\rm od}) = \frac{1}{2}A_{\rm od}(T - T_{\rm c}^{\rm od})Q_{\rm od}^2 + \frac{1}{4}B_{\rm od}Q_{\rm od}^4 + \frac{1}{6}C_{\rm od}Q_{\rm od}^6$$
(1)

where Q_{od} stands for all three possible order parameters of the cation ordering process, namely Q_{od} , Q'_{od} and Q''_{od} . The R and Z points are unique, so no domain structure due to the topological degeneracy of the critical point can occur. Domain boundaries can occur, however, which are related to the transformations $Z \rightarrow -Z$ in the rhombohedric system and $R \rightarrow -R$ and $R \rightarrow C_4 R$, $C_2 R$, $C_4^3 R$ in the cubic system.

The second translation-invariant phase transition is related to the order parameters Q_p and Q'_p which break the polar symmetry within the trigonal system. The Landau potential is

$$G(Q_p) = \frac{1}{2}A_p(T - T_c^p)Q_p^2 + \frac{1}{4}B_pQ_p^4 + \frac{1}{6}C_pQ_p^6 + \dots$$
(2)

We now discuss the coupling properties of Q_e and Q_p (or Q'_e, Q'_p) with respect to the

spontaneous strain $e = (e_4, e_5, e_6)$ and the spontaneous polarisation P_z . Bilinear coupling occurs between e and Q_e and, for the polar representation, between P_z and Q_p . Biquadratic coupling is symmetry allowed between $e - Q_p$ and $P_z - Q_e$; linear quadratic terms occur for all combinations of Q_e .

The ferroelastic order parameters are Q_e and Q'_e which break the cubic symmetry to rhombohedric. We assume that their irreducible representations do not change the translational symmetry which implies that these transitions are classified as proper ferroelastic ones. The active representation of Q_e (or Q'_e) is T_{2g} , the order parameter is triply degenerate with $Q_e = (Q_{e_i})$. The Landau potential is

$$G(Q_e) = {}^{\frac{1}{6}}A_e(T - T_c^e)(Q_{e_4}^2 + Q_{e_5}^2 + Q_{e_6}^2) + {}^{\frac{1}{3}}B_eQ_{e_4}Q_{e_5}Q_{e_6} + {}^{\frac{1}{12}}C_e(Q_{e_4}^4 + Q_{e_5}^4 + W_{e_6}^4) + \dots$$
(3)

A mono-domain crystal is described by a deformation along [111], for example, and we can simplify the Landau expression for $Q_{e_4} = Q_{e_5} = Q_{e_6}$ to

$$G(Q_e) = \frac{1}{2}A_e(T - T_c^e)Q_e^2 + \frac{1}{3}B_eQ_e^3 + \frac{1}{4}C_eQ_e^4 + \dots$$
(4)

This phase transition will be of first order unless the numerical value of B_e is accidentally zero. The terms of the Landau potential which are homogeneous in e and P_z are

$$G(e, P_z) = \sum_{i} \lambda_i^e Q_{e_i} e_i + \lambda^p Q_p P_z + \xi^p \sum_{i} Q_{e_i}^2 P_z^2 + \xi^e \sum_{i} Q_p^2 e_i^2 + \varphi \sum_{ikl} Q_{e_{kl}}^2 e_i + \dots + \frac{1}{2} \sum_{i} C_{ik} e_i e_k + \frac{1}{2} e P_z^2$$
(5)

where the summation has to satisfy the invariance condition. If interactions between different ferroelastic domains are ignored, the coupling term reduces to

$$G(e, P_z) = \lambda^e Q_e e + \lambda^p Q_p P_z + \xi^p Q_e^2 P_z^2 + \xi^e Q_p^2 e^2 + Q_e^2 e + \dots + \frac{1}{2} C e^2 + \frac{1}{2} e P_z^2.$$
(6)

Indirect coupling between Q_e and Q_p is introduced by minimisation of $G(e, P_z)$ with respect to e and P_z (Salje and Devarajan 1986, Bismayer et al 1986, Salje 1985). In addition direct coupling occurs between Q_e , Q_p and Q_{od} . The leading symmetry allowed terms are

$$G(\text{coupling}) = \eta_{ep} Q_e^2 Q_p^2 + \eta_{e, \text{od}} Q_e^2 Q_{\text{od}}^2 + \eta_{p, \text{od}} Q_p^2 Q_{\text{od}}^2.$$
(7)

Fluctuations and gradient coupling are described by the Ginzburg energy (Landau and Lifshitz 1980, Salje and Wruck 1988). We include non-invariant terms because we also consider inhomogeneous solutions which is necessary in order to describe the effect of chemical inhomogeneities

$$G(\text{Ginzburg}) = \frac{1}{2}g_e |\nabla Q_e|^2 + \frac{1}{2}g_p |\nabla Q_p|^2 + \frac{1}{2}g_{\text{od}} |\nabla Q_{\text{od}}|^2 + \varphi_{ep}^{\pm} (Q_e \nabla Q_p \pm Q_p \nabla Q_e) + \varphi_{e,\text{od}}^{\pm} (Q_e \nabla Q_{\text{od}} \pm Q_{\text{od}} \nabla Q_e) + \varphi_{p,\text{od}}^{\pm} (Q_p \nabla Q_{\text{od}} \pm Q_{\text{od}} \nabla Q_p).$$
(8)

The total Landau-Ginsburg energy is the sum over these energy distributions

$$G(Q_e, Q_p, Q_{od}, e, P) = G(Q_{od}) + G(Q_e) + G(Q_p) + G(e, P_z)$$

+ G(coupling) + G(Ginzburg). (9)

It represents a system with three interacting primary-order parameters and two sec-

ondary-order parameters. Analytical solutions have been obtained in case of two interacting driving-order parameters by Imry (1975), Gufan and Larin (1980) and Salje and Devarajan (1986). No systematic investigations of systems with three driving-order parameters are known to the authors and we do not want to embark in a discussion of the topology of its order-parameter vector space in this paper.

An interesting consequence of the form of the Landau–Ginzburg potential for relaxor materials is the difference of the length scale on which the various order parameters act. The longest interaction length occurs for e where strain interaction occurs over a macroscopic scale (larger than 500 Å, say), the shortest is related to Q_{od} (some 10 Å). The equivalent lattice relaxation of the elastic interaction is described on a structural level by Q_e . In the limit of strong coupling, Q_e and e follow the same pattern. If the coupling is weak, the sublattice distortion might not follow the strain field and nonlinearities of the elastic constants might develop. Salje (1985) has shown that minimisation of $G(Q_e, Q_p, Q_{od}, e, P_z)$ with respect to e or Q_e do not necessarily lead to the same minimum of the total free energy. In the case of the perovskite structure, this point might be relative if Q_{e} contains elements of octahedral rotations (in the ordered or partly ordered form) rather than pure shear distortions. The latter are the only possible components in fully disordered material. In this case we reduce the total Landau-Ginzburg energy to $G(e, Q_p, Q_{od}, P_z)$ from $(\delta/\delta Q_e)G(Q_e, Q_p, Q_{od}, e, P_z) = 0$. In a similar way we may assume strong coupling between Q_p and P_z which leads to a renormalised potential $G(e, P_z, Q_{od})$ using $(\delta/\delta Q_p)G(e, Q_p, Q_{od}, P_z) = 0$. A further reduction of the number of order parameters appears unphysical because the spontaneous strain e and the strain induced via electrostriction can be of comparable magnitude. Rescaling of e with respect to P_z is non-linear and the analytical form of $e(P_z)$ cannot be predicted from theory. Experimental determinations of the electrostriction and the piezoelectric moduli as functions of e (or P) are required to proceed further.

4. Kinetic behaviour

We finally comment on the possibility that relaxors might represent a new class of materials with respect to their kinetic behaviour. In our analysis we have constructed the Landau-Ginzburg potential of the equilibrium state. The most likely minimisation procedure leads to $G(e, P_z, Q_{od})$, where e and P_z have long interaction lengths and Q_{od} has a short interaction length. Both order parameters e and P_z relax rather rapidly and frozen-in states occur for constant values of Q_{od} . As e and P_z are non-conserved order parameters we can deduce the kinetic rate law in the limit of the Ginzburg-Landau behaviour

$$\frac{\delta Q}{\delta t} = \gamma \lambda e^{-\Delta G_{a}/kT} \frac{\delta G}{\delta Q} \bigg|_{eP_{z}Q_{\text{rd}}}$$
(10)

where we use the nomenclature of Salje (1988). The order parameter $Q(P_z, e)$ is constructed such that the slope of G with respect to the pathway of the system in e, P_z space is maximised. Fluctuation regions will then occur on a length scale which is comparable with the interaction length of e and/or P_z (i.e. some 100 Å) (Salje 1988). Experimentally, these domain structures were first observed by Känzig (1951) in BaTiO₃ where the same treatment holds as in the present case.

The typical relaxor behaviour differs from the pure relaxation of e and/or P_z in a Landau–Ginzburg mechanism, because the third order parameter, Q_{od} , may also change

kinetically. Its conservation law is, in contrast to the behaviour of e and P_z , not clear. Although it seems that Q_{od} is a conserved quantity leading to a sluggish order/disorder phase transition at temperatures above 1000 °C, its coupling with the lattice relaxation and any random field might result in a change of the length scale over which the conservation law is valid (Salje 1989b). Consequently we find that the Ginzburg–Landau kinetics has to be replaced by the more general rate law (Salje 1988)

$$\frac{\delta Q_{\rm od}}{\delta t} = \lambda \gamma e^{-\Delta G_{\rm a}/kT} \left[1 - \left(\frac{\xi_{\rm c}}{\xi}\right)^2 e^{-\xi^2 \nabla^2/2} \right] \frac{\delta G}{\delta Q_{\rm od}}$$
(11)

where the parameters ξ_c and ξ indicate the length scale of the order parameter conservation and the correlation length, respectively. If $\xi_c = \xi$, the order parameter is fully conserved and we expect exsolution features to occur (the so-called Cahn behaviour, Cook and Hilliard (1969)). In the opposite extreme, $\xi_c = 0$, this rate law is identical with that of Ginzburg-Landau kinetics. No analytical solutions have yet been described for the intermediate range $0 < (\xi_c/\xi)^2 < 1$. It appears plausible, however, that relaxor materials are related to these intermediate states because the Landau potential is very shallow with respect to an ordering process in Q_{od} . The various B atoms have very much the same size and similar chemical potentials. It is possible, therefore, that very small changes of the chemical composition, introduction of lattice imperfections etc. can turn the ordering process into an exsolution process which would then lead to clusters of slightly different chemical compositions inside a common crystallographic matrix. These local domains (Känzig domains) are then frozen in at low temperatures leading to space variations of Q_{od} and hence influence, via $G(e, P_z) + G(\text{coupling})$, the spontaneous strain and the spontaneous polarisation. With this respect, we find similarities between relaxors and metal/insulator phase transitions of the Anderson type (Anderson 1975, Schirmer and Salje 1980, Bryksin 1982). The role of the random field of the Anderson transition is now represented by Q_{od} , the electronic wavefunction is equivalent to the strain field (and/or P_2). The major difference between the two transition mechanisms is the characteristic length of the order parameters being either on the atomistic (Anderson) or the mesoscopic scale (relaxor).

Further experimental work on the relaxor $PbSc_{0.5}Ta_{0.5}O_3$ is under way.

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