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Ferroelastic Phase Transition in Pb$_3$(PO$_4$)$_2$ Studied by Computer Simulation

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Abstract. — A model of lead phosphate which describes its rhombohedral-monoclinic improper ferroelastic phase transition is proposed. It contains a reduced number of degrees of freedom but it is constructed consistently with symmetry changes at the phase transition. Potential parameters of the model are derived from available experimental data. The crystallites of $25 \times 25 \times 25$ and $121 \times 121 \times 25$ unit cells have been simulated by the molecular-dynamics technique. The results determine the phase transition at the L point of reciprocal space, the order parameter, and the temperature behavior of monoclinic lattice parameters. In the rhombohedral phase the calculated dynamical structure factor shows inelastic peaks from which a soft branch of underdamped phonons has been established. The model has been used to calculate a diffuse scattering function which shows above $T_c$ a maximum at an incommensurate wave vector located along the L–F line of the Brillouin zone. The mentioned line is parallel to the ternary symmetry axis. On the basis of the above results we were able to visualize the nature of the dynamical monoclinic microdomains persisting in the high-temperature rhombohedral phase. It has been shown that above $T_c$ the fluctuations can be treated as temporary orientational monoclinic microdomains. Each type of microdomains always contains an irregular sequence of antiphase domains.

Résumé. — Un modèle permettant de décrire la transition de phase ferroélastique impropre, rhomboédrique-monoclinique, du phosphate de plomb est proposé ci-dessous. Il est construit à partir d’un nombre réduit de degrés de liberté, tout en tenant compte des changements de symétrie caractéristique de la transition de phase. Les paramètres du modèle sont déduits quantitativement des résultats expérimentaux disponibles. La technique de dynamique moléculaire a permis de simuler le comportement des cristallites comportant $25 \times 25 \times 25$ et $121 \times 121 \times 25$ mailles. Les résultats permettent de déterminer la nature de la transition de phase (point L de la zone de Brillouin), le paramètre d’ordre, la variation avec la température des paramètres cristallins de la structure monoclinique. Dans le cas de la phase ternaire, le calcul du facteur de structure dynamique conduit à la détermination d’une branche de phonons mous sous-amortis. Le modèle a également été utilisé pour obtenir la diffusion diffuse observable le long de la ligne

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Lead phosphate, Pb$_3$(PO$_4$)$_2$, is an improper ferroelastic material that undergoes a phase transition at about 453 K. Its properties are relatively well known from X-ray and neutron diffractions, diffuse scattering and inelastic neutron scattering studies and from the optical and electron transmission microscopy. Theoretical investigations, however, have been confined to the Landau type theory of phase transition, to the derivation of simple relationship between the strain components in different crystalline phases, and to the classification of domain wall types. In this work we make an attempt to relate the microscopic static and dynamical properties of lead phosphate to a single model suitable for computer simulations.

The high-temperature phase of lead phosphate belongs to the rhombohedral symmetry with the space group R$3m$ (D$_{3h}^5$) [1, 2], and one molecular unit per unit cell ($Z = 1$). The crystal structure consists of chains of Pb atoms and PO$_4$ molecules. In each chain three subsequent Pb atoms are separated by two PO$_4$ tetrahedra. The chains are oriented along the three-fold symmetry axis of the rhombohedral system. The structure contains three types of chains with the same chain structure, but shifted with respect to each other. At low-temperature lead phosphate transforms to monoclinic C2/c (C$\overline{4}$h) space group with two molecular units ($Z = 2$) per unit cell.

The ferroelastic properties of lead phosphate should show up in measurements of the temperature dependence of the lattice parameters and spontaneous strains. Dilatometric measurements [3] showed discontinuities at the transition temperature $T_c$ in dilatation along $b$ and $c$ directions. The X-ray measurements [4] estimated the changes of lattice parameters as a function of temperature. The precise X-ray diffraction experiment [5–7] gave the temperature dependence of the $a_M$, $b_M$, $c_M$ and $\beta$ monoclinic lattice parameters below and above the phase transition and hence the variation of spontaneous strains $\epsilon_{11}$ and $\epsilon_{13}$. The ferroelastic phase transition was shown to be slightly of first order.

The Brillouin scattering measurements [8] revealed the elastic constants in the high-temperature phase in the interval of 457 – 523 K, and slight softening of $c_{11}$ and the longitudinal acoustic mode has been observed. A number of experimental studies have indicated that there exists an intermediate temperature interval from $T_c$ to about 560 K, in which the average symmetry remains rhombohedral, but the local symmetry proves to be monoclinic and it is believed that this effect is generated by the monoclinic microdomains. The diffraction X-ray scattering experiment [4] allowed to estimate the average size of the monoclinic microdomains to be of $\sim 50$ Å. The neutron scattering experiment performed above $T_c$ revealed a quasielastic nature of the supperlattice reflection and confirmed a dominantly dynamic character of the monoclinic microdomains with the characteristic relaxation time of the order of 30 ps at $T_c$ [9]. As a consequence, in this intermediate temperature range, the actual symmetry in Raman and infrared examinations is expected to be monoclinic instead of rhombohedral. Indeed, a monoclinic splitting of Raman lines above $T_c$ has been reported in references [10–12]. From the full width at half maximum of the 80 cm$^{-1}$ Raman bands the lifetime of the monoclinic microdomains was estimated again to be of the order of 30 ps [12]. The infrared spectra [13, 14] show similar behavior. Moreover, above $T_c$ anomalies related with dynamical fluctuations in Pb$_3$(PO$_4$)$_2$ have been observed in the temperature dependence of specific heat [15] and in the excess-volume strain measurements [7]. The synchrotron X-ray diffuse-scattering experiment
[16,17] shows that just above $T_c$ one sees pronounced diffuse scattering streaks close to the L-reciprocal lattice point and along the L - F direction being parallel to the ternary rhombohedral crystallographic axis. The maxima of the diffuse streaks are placed out of the high-symmetry point, but they do not lead to the formation of a regular incommensurate structure. Previous careful X-ray studies performed in the pure crystal of lead phosphate [18] have not revealed any incommensurate phase.

In the high-temperature phase the inelastic neutron scattering studies [19] have discovered a soft mode at the L-point of the Brillouin zone whose character is compatible with structural changes at the phase transition. The line shape of the soft mode shows that it is overdamped between $T_c$ and $T_c + 100$ K [9]. In addition acoustic and some optic phonon dispersion curves have been measured in principal directions.

The group theoretical analysis of symmetry reduction of the rhombohedral-monoclinic phase transition predicts three states of orientational monoclinic domains and two states of antiphase domains within each orientational monoclinic domain. These six domains may form coherent stress free domain walls along either a mirror crystallographic plane (domain wall type W), or along a specific orientation (type W') [20]. Variety of these domain walls has been observed by optical [21-24] and transmission electron [25,26] microscopy. The effective thickness of the W wall of around 10 unit cells has been determined by X-ray diffraction method [27].

The ferroelastic phase transition has been theoretically studied in terms of Landau theory [28]. The symmetry changes involve doubling of the unit cell, hence, the lead phosphate is a ferroelastic material of the improper type. The order parameter transforms according to a three-dimensional irreducible representation [29]

$$R3m \rightarrow (k = L, T^{L,2}, \eta_1 \neq 0, \eta_2 = \eta_3 = 0) \rightarrow C2/c$$

which corresponds to the L point of the Brillouin zone. It can be also induced by another distinct irreducible representations $T^{L,3}$ [28] leaving the ambiguity on the actual symmetry of the order parameter. The model used below exhibits symmetry changes given by equation (1). The free-energy expansion consists of even terms only, therefore, six-order terms have to be kept in order to describe the first order phase transition. The expansion has been used to introduce the symmetrized "flip mode" order parameter [30] and to describe the nature of the monoclinic microdomains mentioned above. This approach involves the basic ideas of the three-dimensional renormalization of the Potts model.

The aim of this work is to perform a computer simulation and to study consequences of the ferroelastic rhombohedral-monoclinic phase transition in lead phosphate. But even using the present-day most powerful supercomputers, it is not possible to simulate crystallite which contains all 13 atoms in the unit cell and which would be sufficiently large to study phenomena occurring on the intermediate scale where any interesting object spreads out at least several lattice constants.

We propose to solve this problem by the method of the reduction of degrees of freedom (RDF). It means that the unit cell of the studied crystal is simplified to a model unit cell, which possesses only very few but essential degrees of freedom. The computer time normally needed to calculate forces between many neighbors is then considerably reduced, and it is used to calculate effects over many lattice constants. Generally, the model built in the frame of the method of RDF consists of elastic and displacive subsystems. The elastic subsystem is proposed as a Bravais lattice. The displacive subsystem takes care of the changes of the crystal through the phase transition. The two subsystems interact with linear and/or bilinear terms adjusted to the crystal symmetry. In our case we require that the model preserves the following features of lead phosphate: (i) it exhibits the same symmetry changes at the phase transition; in other words the soft mode symmetries of the model and of real crystal are the same; (ii) the
soft mode frequency of both systems are similar; (iii) the elastic properties remain similar; (iv) at temperature 0 K the degree of deformation of unit cells should be comparable; (v) the transition temperatures of both systems are the same. These conditions are used to derive the numerical values of the model potential parameters.

The unit cell of the model contains five degrees of freedom only. This reduction of the complexity allows to increase the size of simulated crystallite remarkably and to derive a number of essential characteristics such as the temperature behaviour of the order parameter and the lattice parameters, the diffuse scattering, the low energy phonon modes including the temperature dependence of the soft mode, and monoclinic fluctuations in the rhombohedral phase. We show that above $T_c$ lead phosphate has a tendency to form a temporary sequence of antiphase monoclinic domains which to large extent are kept within one orientational domain due to strong coupling to the elastic deformation. Studies of annealing processes which lead to formation of domain patterns can be equally well carried on with the aim of the same model [31].

1. Model of Lead Phosphate

The rhombohedral unit cell with $a_R = 7.48$ Å and $\alpha_R = 43.4^\circ$ [1, 2], can be conveniently represented by the hexagonal one with parameters $a_h = 2a_R \sin(\alpha_R/2) = 5.53$ Å and $c_h = a_R (9 - 12 \sin^2(\alpha_R/2))^{1/2} = 20.30$ Å and with three molecular units. In Cartesian coordinates the basic vectors of the monoclinic unit cell inserted into the hexagonal lattice read: $a_M = (0, 1/\sqrt{3}, 2c)a_h$, $b_M = (1, 0, 0)a_h$ and $c_M = (0, \sqrt{3}, 0)a_h$ where $c = (1/4 \sin^2(\alpha_R/2) - 1/3)^{1/2}$, the face is centered at $(b_M + c_M)/2$, and the monoclinic angle $\beta'$ occurs between $a_M$ and $c_M$ unit cell edges. There are three orientational monoclinic domains $l = 1, 2$ and 3 and in the right-hand setting of lattice vectors the monoclinic angles are $\beta'$, $\beta$ and $\beta'$, respectively, where $\beta' = 180^\circ - \beta$. The rhombohedral phase expressed in terms of monoclinic unit cell parameters is $a_M^{(R)} = 13.896$ Å, $b_M^{(R)} = 5.53$ Å, $c_M^{(R)} = 9.58$ Å and $\beta^{(R)} = 76.72^\circ = 180^\circ - 103.28^\circ$. At room temperature the rhombohedral unit cell is deformed to the monoclinic one with parameters $a_M = 13.816$ Å, $b_M = 5.692$ Å, $c_M = 9.429$ Å, and $\beta' = 77.64^\circ = 180^\circ - 102.36^\circ$ [1].

The 39 degrees of freedom of the rhombohedral unit cell of lead phosphate can be reduced to 5 degrees of freedom by RDF. We have selected a model unit cell of the same size as the real one, but containing two objects only. The first one, placed at the corner of the unit cell $(i, j, k)$, could be considered as a combined PO$_4$ – PO$_4$ complex. Its position is specified by the Cartesian coordinates $(X_{i,j,k}, Y_{i,j,k}, Z_{i,j,k})$. The unit cell could be then identified with the elastic cage. The second object, located at the surface (generally inside) elastic cage could be treated as a complex of 3Pb atoms with two coordinates $r_{i,j,k} = (x_{i,j,k}, y_{i,j,k})$ counted from a fixed point of the unit cell $(i, j, k)$. It has been proven [4] that for describing the rhombohedral-monoclinic phase transition it is sufficient to consider the displacements of lead in the $xy$ plane only. Figure 1 shows the location of 3Pb and 2(PO$_4$) objects in the hexagonal frame. There, we have placed also the basic vectors of the non-conventional rhombohedral unit cell $a_R, b_R, c_R$ used in the simulations. Their components are: $a_R = (1, 0, 0)a_h$, $b_R = (-1/2, \sqrt{3}/2, 0)a_h$ and $c_R = (0, -1/\sqrt{3}, c)a_h$. This choice makes the three surfaces $(a_R, b_R), (a_R, c_R)$ and $(b_R, c_R)$ not equivalent but it allows to build simulation crystallites in the form of a thin plate, which is convenient when simulating domain patterns. The low-temperature monoclinic unit cell corresponding to orientational domain $l = 1$ is also indicated in Figure 1.

From the selected 5 degrees of freedom one can construct the phonon representation of modes at the wave vector $k = L$, which is $\Gamma_{\text{photon}} = 2\tau^2 + 3\tau^4$. This list contains the irreducible representation $\tau^2$, equation (1), which drives the rhombohedral monoclinic phase transition [32].
Fig. 1. — The structure of the model of lead phosphate crystal. Open and hatched circles denote 2(PO$_{4}$) and 3Pb objects, respectively. The (aR, bR, cR) and (aM, bM, cM) vectors indicate the geometrical relationships between the rhombohedral and domain $l = 1$ of monoclinic unit cells, respectively.

The potential energy of the model is written as

$$V = \frac{1}{2} \sum_{i,j,k} \left( V_{\text{displ}}^{i,j,k} + V_{\text{elast}}^{i,j,k} + V_{\text{coup}}^{i,j,k} + V_{\text{anhar}}^{i,j,k} \right), \quad (2)$$

where

$$V_{\text{displ}}^{i,j,k} = \sum_{l} r_{i,j,k} \cdot \Phi(l) \cdot r_{i(j),j(k),j(l)}; \quad (3)$$

$$V_{\text{elast}}^{i,j,k} = \sum_{n} B_n \left( R_{i,j,k; i(n),j(n),k(n)} - a_n \right)^2; \quad (4)$$

$$V_{\text{coup}}^{i,j,k} = \sum_{n} \rho_n \left( R_{i,j,k; i(n),j(n),k(n)} - a_n \right) \sum_{m} A_m (r_{i(m),j(m),k(m)}); \quad (5)$$

$$V_{\text{anhar}}^{i,j,k} = G_1 \left( x_{i,j,k}^2 + y_{i,j,k}^2 \right)^3 + G_2 \left( y_{i,j,k}^6 - 15 y_{i,j,k}^4 x_{i,j,k}^2 + 15 y_{i,j,k}^2 x_{i,j,k}^4 - x_{i,j,k}^6 \right); \quad (6)$$
Fig. 2. — Harmonic dispersion curves of the model calculated along several lines of the rhombohedral Brillouin zone and for the force constants at $T = 450$ K. The $\omega^2(k) < 0$ values are represented by negative $\omega(k)$. First three high-symmetry points $L - F - L$ on the left-hand side are located parallel to ternary symmetry axis.

and

$$A_m(r_n) = (x_n^2 + y_n^2) \cos(2\Theta_{n,m}) + 2x_n y_n \sin(2\Theta_{n,m})$$ \hspace{1cm} \text{(7)}$$

$$R_{i,j,k,i',j',k'} = [(X_{i,j,k} - X_{i',j',k'})^2 + (Y_{i,j,k} - Y_{i',j',k'})^2 + (Z_{i,j,k} - Z_{i',j',k'})^2]^{1/2}$$ \hspace{1cm} \text{(8)}$$

$$r_{i,j,k} = (x_{i,j,k}, y_{i,j,k}).$$ \hspace{1cm} \text{(9)}$$

Here, $\Phi(l)$ denotes a two-dimensional matrix of force constants, giving rise to optic phonon branches. The $\Phi(l)$ has been set up according to the symmetry of the model. The summation $l$ and $n$ run over corresponding neighboring shells, which are specified below. Summation over $m$ is limited to those displacive objects $3Pb$, which interact directly with a given pair of elastic objects $2(PO_4)$ taken into account in the $V_{i,j,k}^{elast}$ potential.

In order to indicate the method of finding the above set of parameters we discuss first the harmonic terms of the potential energy, i.e. equations (3, 4). Differentiating them, one finds the dynamical matrix whose eigenvalues and eigenvectors give the dispersion curves $\omega^2(k)$, and polarization vectors, respectively. The masses which enter the dynamical matrix have been taken as $M_{elast} = 811.5$ a.m.u. and $M_{diss} = 621.5$ a.m.u., the total mass of unit cell and mass of three lead atoms, respectively. In Figure 2 harmonic dispersion curves $\omega(k)$ are displayed for a number of lines in the rhombohedral Brillouin zone, Figure 3. A negative soft mode, responsible for the phase transition, occurs at the $L$ point. The dispersion curves have been derived under the following assumptions. The elastic forces are limited to two central forces with first ($a_1 = 5.5314$ Å) and second ($a_2 = 7.4800$ Å) nearest neighbors and with coefficients $B_1 = 9000$ a.m.u.$(THz)^2$ and $B_2 = 12000$ a.m.u.$(THz)^2$, respectively. The values of $B_1$ and $B_2$ are chosen so that they approximately reproduce the slope of the acoustic modes measured by inelastic neutron scattering [19]. The slopes are equal to $s_L = 5.14$, $s_T = 2.63$.
and \( s_L = 4.63, s_T = 2.96 \text{ THz} \) Å for longitudinal and transversal acoustic modes along \( \Gamma - Z \) and \( \Gamma - L \) directions, respectively. The displacive potential requires more parameters, since we wish that it will be able to form an incommensurate modulation as well. At \( T = 0 \text{ K} \) the soft mode is assumed to be equal to its experimental value \( \omega^2(k_L) = -0.31 \text{ (THz)}^2 \), obtained by linear extrapolation of its high-temperature experimental dependence to \( T = 0 \text{ K} \) [19]. In this assumption we simplify the soft mode picture disregarding the relaxation processes involved in it, but there seems to no other way to estimate the values of the model parameters. From the \( T = 0 \) soft mode we find that the local force constant \( \Phi_{xx}(0;0) = 8500 \text{ a.m.u.}(\text{THz})^2 \) is positive, assuring that the system is of displacive type. Two other force constants which join first nearest neighbors in \( xy \) plane are \( \Phi_{xx}(0;1,0,0) = 1500 \text{ a.m.u.}(\text{THz})^2 \) and \( \Phi_{yy}(0;1,0,0) = 4200 \text{ a.m.u.}(\text{THz})^2 \). Second nearest neighbors located along \( c_R \) lattice vector are interacting with \( \Phi_{xx}(0;0,1,0) = -1000 \text{ a.m.u.}(\text{THz})^2 \) and \( \Phi_{yy}(0;0,0,1) = -1500 \text{ a.m.u.}(\text{THz})^2 \). In order to enhance the incommensurate type of fluctuations we have included also interactions with next nearest neighbors \( \Phi_{xx}(0;0,0,2) \) and \( \Phi_{yy}(0;0,0,2) \), at the distance twice a lattice constant \( c_R \). These force constants are assumed to be temperature dependent, Figure 4. Below \( T_c \) lead phosphate produces a typical domain pattern which is possible to be reproduced by simulation only when \( \Phi_{xx}(0;0,0,2) \) and \( \Phi_{yy}(0;0,0,2) \) are negative. In contrary, to simulate at high-temperatures the effect of monoclinic microdomains built up from antiphase domains, the same force constants must be positive. Taking these facts into account we propose that

\[
\frac{8}{5} \Phi_{xx}(0;0,0,2) = \Phi_{yy}(0;0,0,2) = A_o + B_o T^2 + C_o T^4 \tag{10}
\]

with \( A_o = -800 \text{ a.m.u.}(\text{THz})^2 \), \( B_o = 5.76 \times 10^{-3} \text{ a.m.u.}(\text{THz})^2 \text{K}^{-2} \) and \( C_o = -7.74 \times 10^{-9} \text{ a.m.u.}(\text{THz})^2 \text{K}^{-4} \). Such temperature variation could be caused by other degrees of freedom of lead phosphate not taken explicitly into account in our model.

Special care has been paid to the optic dispersion curves along the \( L - F \) line, parallel to the ternary axis, since it is expected to be responsible for the existence of dynamic monoclinic microdomains occuring in lead phosphate [16]. We have noticed that the curvature of the soft mode at \( L \) point along \( L - F \) line is quite sensitive to the value of \( \Phi_{xx}(0;0,0,2) \) and \( \Phi_{yy}(0;0,0,2) \) force constants. This part of dispersion curves is shown in Figure 5 and its temperature dependence follows from the force constants, equation (10). Figure 5c indicates clearly that above \( T_c \) fluctuation of incommensurate nature could appear with energy similar to the energy of fluctuation at the \( L \)-point, since the dispersion curve is flat. Below \( T_c \), the
soft mode dispersion is steeper and incommensurate fluctuations will be less probable. The curvatures of $\omega(k)$ along directions perpendicular to the ternary axis is positive and change very little with temperature.

The anharmonic potential, equation (6), stabilizes the system, contributes to the amplitude of static displacements and defines the transition temperature. Notice that it does not contain a fourth order term, which is allowed by symmetry and will be isotropic. It could be neglected because the experimental order parameter exponent is $\beta = 1/4$, which is the typical value for a tricritical region [18,33], when the fourth order term vanishes. As a matter of fact we have been trying to generate a domain pattern during annealing using only fourth order anharmonic term, but the crystal rather quickly went to a single domain. Indeed, there is no barrier for rotation of static displacements of $3\text{Pb}$ objects, thus no barrier prevents annihilation of the domain walls. Therefore, one must use the six order local anharmonic potential. Its form, equation (6), could produce in $xy$ plane six minima which correspond to six low-symmetry domains of lead phosphate. If we set the ratio $\sigma = V_m/V_b = \sqrt{7}$, where $V_m$ and $V_b$ are the values of the potential, equation (6), at the minimum and at the barrier, respectively, then the ratio $\epsilon = G_2/G_1 = (\sigma^2 - 1)/(\sigma^2 + 1) = 3^3/4$. The choice of $G_1 = 92000$ a.m.u.$(\text{THz})^2 \text{Å}^{-4}$ and $G_2 = 69000$ a.m.u.$(\text{THz})^2 \text{Å}^{-4}$ leads to the phase transition temperature at $T_c = 470$ K.

The symmetry of the phase transition allows for the coupling of elastic and displacive degrees of freedom in the linear-quadratic form. The $V^{\text{coup}}$ term is responsible for the deformation of the elastic cage caused by the soft mode. We limit the coupling interactions to nearest and next nearest elastic objects, similarly to $B_1$ and $B_2$ parameters. We then assume that each pair of $2(\text{PO}_4)$ objects interact with two nearest $3\text{Pb}$ objects, those which are in the closest distance from the line which connects the two $2(\text{PO}_4)$ objects. From the structure of the model, one finds then the angles for the coupling function $A_m(r_n)$, equation (7), to be $\Theta_{n,m} = \pi(n + \frac{1}{2})/3$ for the six nearest neighbors in the $xy$ plane numbered anticlockwise $n = 1, 2, \ldots$ and $m = 1, 2$. The $\Theta_{n,m}$ are equal for the two nearest displacive $3\text{Pb}$ objects ($m = 1, 2$). Similarly, the six second nearest neighbors located along $c_\text{R}$ lattice constant and equivalent directions, are characterized by phases $\Theta_{n,m} = 2\pi(n + \frac{3}{4})/3$ and $\Theta_{n,m}$ are equal for two nearest
Fig. 5. — Harmonic dispersion curves along the line $L - F - L$ of rhombohedral Brillouin zone for temperatures (a) $T = 300$ K, (b) $T = 450$ K and (c) $T = 600$ K. The line $L - F - L$ is parallel to the ternary axis of the crystal.

displacive 3Pb objects. To reproduce the correct monoclinic deformation at $T = 0$ K [5] we have taken $\rho_1 = -2430$ a.m.u.(THz)$^2$Å$^{-1}$ and $\rho_2 = -850$ a.m.u.(THz)$^2$Å$^{-1}$, which involve changes of monoclinic lattice constants of the order of $\Delta a_M/a_M = 0.017$, $\Delta b_M/b_M = -0.049$, $\Delta c_M/c_M = 0.065$, and lattice angle of $\Delta \alpha_M/\alpha_M = 0.044$, where $\Delta a_M = a_M(T_c) - a_M(T = 0)$, $\Delta b_M$, $\Delta c_M$, $\Delta \alpha_M$, etc. These data are close to values obtained by extrapolating the experimental lattice parameters of reference [5] to $T = 0$ K.
For the ferroelastic materials the boundary conditions are the crucial point of simulations. To avoid additional external forces induced by the ferroelastic deformation we have used free boundary conditions. To minimize the surface problem for data analysis we have removed one layer of unit cells from each crystal surface.

2. Computer Simulation Results

The present model has been studied by molecular-dynamics technique. The calculations have been performed on the Hitachi Supercomputer S-3800/380 with 24 Gflops. The simulated crystallite had a shape of multiplicated rhombohedral unit cell of either $25 \times 25 \times 25 = 15625$, or $121 \times 121 \times 25 = 366025$ unit cells. The larger crystallite has been used to study the monoclinic microdomains. The Newton equations of motion have been solved by a simple difference scheme with time step $\Delta t = 0.025$ ps. The average kinetic energy per degree of freedom was taken as the system temperature $T$. Canonical ensemble with temperature constant was used. As referred above, the elastic and displaceable subsystems have been coupled through the linear-quadratic terms only. Such couplings do not facilitate transfer of energy between the subsystems. Therefore, to keep the temperatures of two subsystems equal, we have stabilized their temperatures to the same value by scaling the velocities independently.

2.1. Order Parameter and Lattice Parameters. — The order parameter of the monoclinic-rhombohedral phase transition has three components. They correspond to three arms of the three-dimensional irreducible star of the point $L$ of the rhombohedral Brillouin zone. The particle configuration can then be analysed in terms of local order parameter, components of which are defined as

$$
\eta_{i,j,k}^{(l)} = (x_{i,j,k} \cos \theta_l + y_{i,j,k} \sin \theta_l) \cos 2\pi(k_x^{(l)} R_{i,j,k}^x).
$$

The sum

$$
\eta^{(l)} = \frac{1}{N} \sum_{i,j,k} \eta_{i,j,k}^{(l)}
$$

(12)

where $N$ is the number of unit cells, determines the global order parameter of component $l$. Here, $l = 1, 2, 3$ numbers the orientational domains of the monoclinic phase, and $\theta_1 = 0, \theta_2 = 2\pi/3, \theta_3 = 4\pi/3$ describe the projection of displacements of $3\text{Pb}$ objects on the arms of the irreducible star $L$. The coordinates of the arms in Cartesian system are $k_x^{(1)} = (0, -1/\sqrt{3}, 1/6)(1/a_h)$. $k_x^{(2)} = (1/2, 1/2\sqrt{3}, 1/6)(1/a_h)$ and $k_x^{(3)} = (-1/2, 1/2\sqrt{3}, 1/6)(1/a_h)$ and $R_{i,j,k}$ specifies the position of $(i,j,k)$ site in the non-deformed rhombohedral lattice. The states

$$
\eta^{(1)} > 0, \ \eta^{(2)} = 0, \ \eta^{(3)} = 0,
$$

$$
\eta^{(2)} = 0, \ \eta^{(2)} > 0, \ \eta^{(3)} = 0,
$$

$$
\eta^{(3)} = 0, \ \eta^{(2)} = 0, \ \eta^{(3)} > 0,
$$

(13)

correspond to three orientational domains, respectively. Within each orientational domain one finds two antiphase domains defined respectively by the sign of a non-zero component i.e. $\eta^{(l)} > 0$ or $\eta^{(l)} < 0$.

The temperature dependence of the order parameter $\eta^{(3)}$, as resulted from our computer simulation, is shown in Figure 6. The transition temperature, where $\eta^{(3)}$ vanishes, is $T_c = 470$ K. The data of Figure 6 have been collected during heating the crystallite from a single domain $l = 3$. Similar transition temperature was obtained during heating runs which started
Fig. 6. — Calculated temperature dependence of the order parameter $\eta^{(3)}$ as simulated in the crystallite of $25 \times 25 \times 25$ unit cells. Heating rate was $dT/dt = 0.4$ K/ps.

from remaining orientational domains. Slower rates will still slightly diminish the transition temperature $T_c$, while simulation of larger system tends to increase $T_c$. The shape of the order parameter curve suggests that the phase transition is of first order. Indeed, maps of the order parameter distributions show, Figure 7, that the phase transition starts at the crystallite corner by forming nuclei of a high-temperature phase and proceeds by moving the interface between the two phases so that it decreases the volume of the monoclinic phase.

The global potential energy per model unit cell is represented in Figure 8. It increases monotonically exhibiting only a small jump in the vicinity of the transition temperature. The slope of the potential energy in the rhombohedral phase is smaller than in the monoclinic one.

The lattice constants of lead phosphate across the phase transition have already been measured [4, 5, 7] and it has been found that $a_M$ and $c_M$ lattice constants and angle $\beta$ of the monoclinic unit cell, are increasing as a function of temperature, while $b_M$ decreases. During the heating run of the simulations we have recorded the average values of the monoclinic lattice parameters of the model for the domain $l = 3$ and the lattice parameters are shown in Figures 9 and 10. These are very similar to the experimental parameters. Figure 10 shows as well two angles, which ought to remain $90^\circ$ across the phase transition and, as one sees, they stay constant with accuracy better than $\pm 0.2^\circ$. There is, however, another effect quite characteristic for the ferroelastic materials. At low temperatures the system performs large elastic vibrations corresponding to the resonance frequencies of the whole crystallite. This causes fluctuations of the lattice constants and lattice angles in the intermediate temperature range as seen in Figures 9 and 10.

2.2. DIFFUSE SCATTERING. — Systematic X-ray studies of lead phosphate [4] showed that above $T_c$ there are relatively intense spots located at the position of the superlattice peaks. This X-ray pattern could be explained by the existence of three sets of equivalent monoclinic microdomains, such that the ternary symmetry of the mean structure is restored. Recent precise synchrotron X-ray diffuse scattering measurement made above $T_c$ indicates that there are diffuse spots which do not concentrate around the L point, but are placed along lines
parallel to the ternary axis which connects the high-symmetry reciprocal lattice points L and F [16, 17]. Our model is able to reproduce the diffuse scattering anticipated by the X-ray synchrotron diffuse scattering. For that we had to assume that above $T_c$ the soft mode has a shallow minimum at the incommensurate wave vector along L – F line, but not deep enough to form a regular incommensurate phase. As we shall see in Section 2.4, this minimum at incommensurate wave vector is also responsible for the monoclinic microdomains which appear above $T_c$.

We suppose that the anomalous diffuse scattering is caused by the displacements of lead atoms. The diffuse scattering function has been calculated according to the definition

$$F(k) = \langle \rho^*(k, 0) \rho(k, 0) \rangle,$$

where the dynamical variable is simplified to

$$\rho(k, t) = \frac{1}{N} \sum_{i,j,k} \exp[2\pi i k \cdot R_{i,j,k}^{(d)}(t)] \exp[-\sum_{l=1}^{3} \epsilon_l (R_{i,j,k}^{(o)} - R_{\text{cen}})^2],$$

Here, $\langle \ldots \rangle$ denotes the time average, and

$$R_{i,j,k}^{(d)}(t) = ia_R + jb_R + kc_R + s + r_{i,j,k}(t)$$

defines the position of the $(i, j, k)$ displaceive object, and $s = 0.5(a_R + c_R)$ is the location vector of 3Pb object in the undeformed rhombohedral unit cell. To minimize the influence of crystallite surfaces we have introduced the space damping factor $\exp[-\sum_{l=1}^{3} \epsilon_l (R_{i,j,k}^{(o)} - R_{\text{cen}})^2]$ in which $R_{\text{cen}}$ describes the center of crystallite, $R_{i,j,k}^{(o)}$ is the $(i, j, k)$ site in the undeformed rhombohedral lattice, and $\epsilon_l = \epsilon'/(L_l/2)^2$ depends on the damping constant $\epsilon'$, and the linear size of the simulated crystallite $L_l$ along its $l = 1, 2, 3$ edge. The $\epsilon' = 0.8$ has been used.

Figure 11 shows the $F(k)$ function for several temperatures above $T_c$, and along the line from L to F point. In this geometry the transfer polarization vectors of the soft mode are quite parallel to the scattering vector k. The $F(k)$ has been averaged over 750 ps. Just above $T_c$ the diffuse scattering distribution is peaked at the L point. In the temperature range between 525 and 600 K the maximum of $F(k)$ shifts towards the incommensurate wave vector at about $k_\text{in} = 0.025$ Å$^{-1}$, which corresponds to average fluctuation size of $\sim 40$ Å. At still higher temperature, the incommensurate minimum of the soft mode disappears and the diffuse spot at the incommensurate wave vector merges to the diffuse peak at L.

2.3. SOFT MODE. — The soft mode of lead phosphate has been measured by the inelastic neutron scattering technique [4] above and below transition point. Much above $T_c$ it can be seen as a separate peak, which closer to $T_c$ merges to the central component. Its form can be fitted to the damped oscillator formula with square frequency $\omega^2$ increasing linearly as a function of temperature starting from zero close to $T_c$. The width of the soft mode peak, which is of order of 0.33 THz, changes only little in the whole temperature interval.

The phonon excitations of the model could be calculated by the dynamical structure factor $S(k, \omega)$

$$S(k, \omega) = \int_{-\infty}^{\infty} dt \langle \rho^*(k, 0) \rho(k, t) \rangle \exp[2\pi i \omega t] \exp[-(t/\gamma)^2],$$

where $\rho(k, t)$ is the dynamical variable, equation (15). Here, we have introduced the Gaussian damping factor $\exp[-(t/\gamma)^2]$, which is required while calculating the long-time correlations and
Fig. 7. — Maps of the domain distribution drawn during heating large simulated crystallite of 65 x 65 x 35 unit cells. The maps represent the plane perpendicular to ternary crystal axis and show monoclinic-rhombohedral phase transition mechanism. The color pairs: dark blue - light blue, dark green - light green, yellow - red denote the three orientational domains $l = 1, 2, 3$, respectively, and two colors within each pair define the antiphase domains. Red color denotes then single monoclinic domain. The color of a pixel on the maps has been chosen with the aim of equations (11, 13). Heating rate was $dT/dt = 0.4 \text{ K/ps}$. The (a) to (d) maps have been recorded at temperatures 415, 443, 470 and 486 K, respectively. For this run the transition temperature was $T_c = 495 \text{ K}$. 
which plays the same role as a Gaussian resolution function in the instrument which measures $S(k, \omega)$. The experimental frequency resolution, equation (17), is then $\Delta \omega = [2/(\pi \gamma)](\ln 2)^{1/2}$. Figure 12 shows the calculated $S(k, \omega)$ representing the phonon peaks belonging to the soft branch. The curves of Figure 12 correspond to $\Gamma - L$ line and are labelled by the wave vector $k = (2, -2q/\sqrt{3}, q/(3c))(1/a_h)$, where $q = n/12$ and $n = 1, 2, \ldots$. At $(2, 0, 0)$ $\Gamma$-point the displacements of 3Pb objects are almost parallel to the scattering wave vector $k$. The time dependent correlation function $\langle \rho^*(k, 0)\rho(k, t) \rangle$ has been calculated for $t_{\text{max}} = 20$ ps and is averaged over 730 ps. Damping factor of $\gamma = 12.5$ ps has been used, which results in energy resolution of $\Delta \omega = 0.043$ THz. As seen from Figure 12 the soft mode peak is not overdamped. This feature follows from entirely displaceable character of the model. On the other hand the widths of peaks remain finite indicating that modes are far from harmonic.

The mean frequency of the soft phonons has been collected in Figure 13 for the wave vector contour $\Gamma - L - F - \Gamma$ corresponding to points $k_\Gamma = (2, 0, 0)(1/a_h)$, $k_L = (2, -1/\sqrt{3}, 1/(6c))(1/a_h)$ and $k_F = (2, -1/\sqrt{3}, 1/(3c))(1/a_h)$ and for three temperatures above $T_c$. Most softening is observed at L and F points.

The temperature dependence of the square frequency of the soft mode is shown in Figure 14. Within accuracy of the simulations the points form a straight line which reaches zero frequency at $T = 438$ K, a little less than $T_c = 470$ K, obtained from the order parameter temperature dependence. That difference can again be an indication that the phase transition is of first order type.

2.4. ORIGIN OF DYNAMICAL MONOCLINIC MICRODOMAINS IN RHOMBOHEDRAL PHASE. — Up to now we have reproduced the phase transition, the order and lattice parameters, the diffuse scattering and soft mode. These results prove that the used model and the input data form a consistent set. Now, we shall show that within the same model, and without any additional parameters and assumptions we can demonstrate how the monoclinic microdomains look like.

Experimentally, the existence of the dynamical monoclinic microdomains has been proved on many occasions, but one does not really know the reasons why they appear. One may ask what
is the form of particle configurations within a microdomain? Why do the microdomains remain dynamical? The diffraction X-ray scattering experiment [4] showed that the superlattice reflections corresponding to the monoclinic phase, which should vanish in the rhombohedral
Fig. 10. — Calculated temperature dependence of all angles of the monoclinic unit cell of domain \( l = 3 \) as simulated in the crystallite of \( 25 \times 25 \times 25 \) unit cells. (b) shows the \( \beta = 180^\circ - \beta' \) angle since for the setting of domain \( l = 3 \) the monoclinic angle is \( \beta' < 90^\circ \). Heating rate was \( \frac{dT}{dt} = 0.4 \text{ K/ps} \).

Phase, possess above \( T_c \) non-zero intensities. The synchrotron X-ray diffuse scattering experiments [16,17] indicate a pronounced diffuse scattering streak close to the L reciprocal lattice point and along the \( L - F \) direction being parallel to the ternary rhombohedral symmetry axis.
Fig. 11. — Calculated diffuse scattering function $F(k)$ above $T_c$ and along the wave vector line from L to F point of rhombohedral Brillouin zone. The L–F line is parallel to ternary axis of the rhombohedral crystal. The wave vector is given in Å$^{-1}$ units.

A direct observations of the monoclinic microdomains by transmission electron microscopy is, of course, not possible because of their dynamical character. Better understanding of the phenomena could be achieved by combining the experimental findings with computer modelling.

The simulated crystallite consisted of $121 \times 121 \times 25$ unit cells. If filled with real atoms this crystallite would contain more than 4.7 millions of atoms. After careful equilibration at $T = 550$ K the simulations were continued during next 150 ps. The corresponding software allowed us to observe directly the fluctuations and to analyse them in terms of six domains created by the rhombohedral-monoclinic phase transition.

Due to symmetry reduction from R3m to C2/c space group, six domain states appear in the monoclinic lead phosphate. Three states are related by 120° rotation, forming orientational domains. Two other states within each orientational domain differ by translational shift. The six domain states are denoted as $D_1 = 1_1, 1_2, 2_1, 2_2, 3_1$ and $3_2$, where the first index distinguishes the orientational states and the subscript denotes the translational states. Two translational domains, i.e. $1_1$ and $1_2$ are named antiphase domains. The domain walls between orientational and antiphase domains have been directly observed by high-resolution electron microscopy [34]. The analysis of fluctuations is convenient to be performed in terms of these domains. Using equations (11, 13) and from the displacements corrected by the phase factor following from the wave vector of the order parameter at L point, we have constructed a local domain index $D_i(t, j, k)$. The $D_i(t, j, k)$ array forms a volume map in which each pixel represents one of the six
domains. We shall use the convention that six pixel values are shown as six colours. Figure 15 shows selected maps of fluctuations in terms of domain indices $D_i(i, j, k)$. No correction for crystallite deformation has been made. In Figure 15e the monoclinic domain 3 covers almost the whole map. However, the same map, Figure 15a, shown in convention which visualizes the antiphase domains, displays a pattern of antiphase domains of $3_1$ and $3_2$ types, which resembles an irregular incommensurate phase. These domains persist some time, but later they shrink.
Fig. 13. — The soft mode branches calculated along edges of the triangle $\Gamma - L - F - \Gamma$ in reciprocal space, for three temperatures $T = 475$ K, 525 K and 600 K. The reciprocal lattice point $\Gamma$, L, F in Cartesian coordinates are: $(2, 0, 0)(1/a_h)$, $(2, -1/3^{1/2}, 1/(6c))(1/a_h)$, $(2, -1/3^{1/2}, -1/(3c))(1/a_h)$, respectively.

Fig. 14. — Temperature dependence of the square frequency of the soft mode at the L point, $k_L = (2, -1/3^{1/2}, 1/(6c))(1/a_h)$. 
Fig. 15. — The maps show the evolution of monoclinic microdomains at $T = 550$ K. Their sizes along the edges are 664 Å. They represent the middle cross-section of the crystallite, and consist of $121 \times 121$ unit cells. The ternary axis is perpendicular to the maps. Maps (a, e), (b, f), (c, g) and (d, h) have been taken at time $t = 0.45, 105$ and 150 ps, respectively. Maps (a-d) are drawn in terms of orientational monoclinic and antiphase domains: (11) blue dark, (12) blue light, (21) green dark, (22) green light, (31) yellow, (32) red. Maps (e-f) represent the same events as maps (a-d), respectively, but in terms of monoclinic domains only. Color convention of domains: (1) blue, (2) green, (3) red.
and a region of another monoclinic domain 2 is created. Figure 15f. Its internal structure shows again antiphase domains \(2_1\) and \(2_2\). Our video recording of the maps confirms that the process of alternating temporary monoclinic domains is continuing. From the present simulations it can be deduced that the size of microdomains is of the order of 300 Å and their relaxation time is about 40 ps.

The understanding of the origin of the monoclinic microdomains requires to answer the following questions: (i) why each monoclinic microdomain contains an antiphase domain pattern, and (ii) why such large fluctuations of monoclinic domains may persist at all. To answer the first question we recall that the antiphase domain walls cost very little energy. Indeed, looking at Figures 2 and 5 one notices that the slope of the soft mode at the wave vector \(L\) is as a matter of fact flat. This means that the fluctuations could have forms of irregular incommensurate modulations, consisting of pairs of antiphase domains. and moreover, they do not involve lattice deformation and cost little energy.

The second question is related to the large size of the monoclinic microdomains. There are two reasons for this. First the orientational domain walls cost a lot of energy, therefore, they rarely occur. Estimates for our model lead to the value of \(10^3\) K per unit cell area. Second, the simulated crystallite, as a whole, performs macroscopic oscillations like a usual elastic body. The period of this oscillations can be estimated from acoustic dispersion phonon curves, and is of the order of 20 – 40 ps. Each oscillation, of course, deforms temporarily the simulated crystallite. Such long range dynamic deformations involve internal stresses which favor one of the monoclinic domain. Once the monoclinic domain appears the corresponding pattern of antiphase domains follows it due to strong elastic-displacive coupling characteristic for the ferroelastic crystals. The elastic oscillation continues, and the crystal transforms to another monoclinic domain in order to reduce the accompanied stresses. The dynamical character of the monoclinic microdomains is equivalent in some sense to the “flip mode” introduced in reference [30]. In the present simulations we have shown, however, that the monoclinic microdomains are always consisting of many antiphase domains of smaller sizes, which resemble an irregular incommensurate phase. These configurations lower the energy of fluctuations, produce the mentioned diffuse scattering and exploit the flatness of the soft mode around the \(L\) reciprocal lattice point.

3. Final Remarks

The results of the simulation confirm the applicability of the RDF method for finding the main features accompanying the phase transition. We could reproduce the phase transition, the temperature dependence of the order parameter, lattice parameters, diffuse scattering, the soft mode behavior above \(T_c\), and monoclinic microdomains. All that has been done using the simplified model in which only 5 degrees of freedom from 39 of the real unit cell, have been considered. The essential point, however, was that these 5 degree of freedom do transform with the same irreducible representation of the \(R\overline{3}m\) space group as the active representation of the rhombohedral-monoclinic phase transition, and that the elastic cage was able to mimic, at least approximately, the elastic properties of lead phosphate.

The model potential energy of lead phosphate has little anharmonicity. There is only local anharmonic potential and even no anharmonic coupling between the neighbors. Hence, the mode damping and relaxation processes cannot really be well simulated. In principle, the model is easy to supplement with additional anharmonic couplings. In practice, however, one would then face the problem of finding the anharmonic parameters, and this is not an easy task. Moreover, one would be forced to reduce the size of the simulated crystallite because of the limited computer time. Too weak anharmonicity involves some consequences in the
results. The soft mode peak in $S(k, \omega)$ scattering function does not become overdamped on approaching the phase transition. Also the elastic oscillations of the whole crystallite are little damped, therefore, they can drive large-size monoclinic microdomains. As a consequence our microdomains show much larger sizes ($\sim 300 \, \text{Å}$) than the experimental ones ($\sim 50 \, \text{Å}$). Enhancing the relaxation processes one would damp elastic deformations and diminish the size of monoclinic microdomains.

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