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Diffuse Scattering Analysis in the Vicinity of the M-Point in Perovskites for the Case of Intermode Interaction

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A generalization of the interacting modes model is proposed for the case of diffuse scattering (DS). The study confirms the applicability of the previously established coupled-mode model for the analysis of DS in $PbZr_{0.976}Ti_{0.024}O_3$ (PZT2.4). The model, previously used to describe inelastic scattering at individual points, can now be applied to continuously describe the change in DS intensity along an arbitrary direction in reciprocal space. The developed approach of phonon decomposition of DS in the presence of mode coupling significantly expands the opportunities of studying the critical dynamics of perovskites

Keywords: ferroelectrics, antiferroelectrics, phase transitions, lattice dynamics, critical scattering, diffuse scattering.

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1. Introduction

Intermode interaction very often occurs in different crystals subjected to phase transitions [1]; in particular, it is very important in perovskite-like crystal. Earlier major studies of the intermode interaction and associated with it diffuse scattering (DS) were made in vicinity of Γ-point of reciprocal space [2]. But many perovskite-like crystals are subjected to antiferrodistortive (AFD) phase transitions associated with condensation of soft modes at boundary Brillouin zone (BZ) in M-points ($q_M = (\frac{1}{2}\ \frac{1}{2}\ 0)$). In articles [3,4] such transitions were characterized as intrinsic to perovskite structure. Upon presence of soft mode of symmetry M_3 [5] associated with turns of oxygen octahedrons, the occurrence of intermode interaction in the vicinity of M-point turns out to be inevitable, it shall lead to unusual appearance of DS. DS of such type were many times observed [6–10], but detail analysis was not performed previously. In spite of that method of inelastic neutron scattering (INS) and X-rays (IXS) are the most direct study methods of the critical dynamics in bulk of reciprocal space, the measurements by IXS method covering large volume of reciprocal space can require long time period, and at that they can not always ensure sufficient density of obtained data. DS method, on other hand, ensures acquiring of more dense data in reciprocal space. In case of non-interacting modes of DS is widely used to study critical dynamics, however, as we know, the critical behavior of DS in the presence of intermode interaction was not analyzed in detail before, despite the existence of a large number of experimental works. We studied in detail DS of synchrotron radiation in single-crystal $PbZr_{0.976}Ti_{0.024}O_3$ (PZT2.4) in wide range of temperatures, in area of cubic phase existance. The physical conclusions from the analysis of the temperature evolution of such scattering will be considered in separate article. In present paper we describe in detail the approach used for the analysis of form of DS intensity distribution in reciprocal space.

2. Model

For DS description we used a model of intermode interaction [11], which describes low-frequency part of inelastic spectra inthe vicinity of M-points combination of three modes, namely: longitudinal and transverse „lead modes“ (TA and LA), and antiferrodistortive (AFD) „oxygen“ mode. To describe the high-frequency part of spectrum an additional high-energy optical mode (OM) was introduced. Model considers interaction of TA- and AFD-modes only. Contribution to scattering for mixed modes, according to [2], can be written as

$$I_{CM} = Sn(\omega) \sum_{i,j=1,2} F_i^*(\vec{Q}) G_{ij} F_j(\vec{Q}), \qquad (1)$$

where S — scale multiplier, $n(\omega)$ — Bose-factor, indices i and j correspond to transverse acoustic (TA) $(i, j = 1)$ or oxygen (AFD) $(i, j = 2)$ modes, F_i — inelastic structural factor for appropriate mode, and dynamic susceptibility is

provided by the expression

$$G_{ij}^{-1} = \begin{pmatrix} \omega_1^2 - \omega^2 + i\Gamma_1\omega & \Delta_{12} + i\Gamma_{12}\omega & 0 & 0 \\ \Delta_{12} + i\Gamma_{12}\omega & \omega_2^2 - \omega^2 + i\Gamma_2\omega & 0 & 0 \\ 0 & 0 & \omega_3^2 - \omega^2 + i\Gamma_3\omega & 0 \\ 0 & 0 & 0 & \omega_4^2 - \omega^2 + i\Gamma_4\omega \end{pmatrix}, \quad (2)$$

where ω_i and Γ_i — frequencies and constants of attenuation of unrenormalized modes, and Δ_{12}, $i\Gamma_{12}$ — real and imaginary parts of the complex interaction constant.

For TA-, AFD- and LA-modes the structural factor can be calculated as

$$F_i(\vec{Q}) = \sum_l \frac{f_l(Q)}{\sqrt{m_l}} \left(\vec{Q}\,\vec{e}_l^{\,j}(\vec{q})\right) \exp\left(i\vec{Q}\,\vec{r}_l\right). \quad (3)$$

Here $f_l(q)$ — atomic form-factor of ion$l$, and m_l — mass of this ion, $\vec{e}_l^{\,j}(\vec{q})$ — corresponding to ion l component of eigen vector of mode j at reduced wave vector $\vec{q}$, $\vec{r}_l$ — position of ion l in lattice cell. Summation is performed over contributions from all ions l to mode i. Inelastic structural factor for high-energy mode F_{OM} is considered as adjustment parameter independent of q and temperature T. DS intensity in point $\vec{Q}$ can be calculated based on expression (1) by integration over entire range of energies:

$$I_{\mathrm{DS}}(\vec{Q}) = \int I_{\mathrm{IXS}}(\vec{Q}, E)dE. \quad (4)$$

For such DS description in bulk of reciprocal space it is necessary to interpolate the parameters obtained from analysis of inelastic scattering for large set of values $\vec{Q}$.

3. Parameterization of model for diffuse scattering analysis

3.1. Permanent parameters

In studied range of temperatures and points of q-space the parameters Γ_1, Γ_2, Γ_3, Γ_4, responsible for attenuation of each of considered modes, as well as imaginary part of the complex attenuation constant $i\Gamma_{12}$, were considered permanent together with inelastic structural factor for high-energy mode F_{OM}. During the data analysis of experiment on DS the contribution of background into scattering intensity shall be considered. The background was described by a linear function $I_{\mathrm{BG}} = A\vec{q} + B$. Hereinafter values $\vec{q}$ are taken from M-point.

3.2. Description of TA-, LA- and OM-modes

Initially we can suppose that in direction of $\Gamma-\mathrm{M}$ the dispersion of TA-mode behaves like $\sin q$, but, as in studied crystals significant anomaly of dispersion is observed in point $q = 0.25$, where at more lower temperatures the antiferroelectric order parameter occurs, dispersion of this mode in the vicinity of M-point was described by square equatiuon $\omega_1(q) = P_1q^2 + \omega_1(q = 0)$ with negative coefficient P_1. In M-point TA and LA become degenerate $M_{5'}$-mode, this means equality of energies of both modes in this point; to describe LA-mode same representation was selected, like for TA-mode, but with positive coefficient P_3: $\omega_3(q) = P_3q^2 + \omega_1(q = 0)$, this guarantees meeting of the equality $\omega_1(0) = \omega_3(0)$ irrespective of values of coefficients P_1 and P_3. Such expressions for parameters also guarantee simple execution of requirements for presence of zero gradient of frequency at BZ boundary, existing for symmorphic structures. Values $\omega_1(q = 0)$ and $\omega_3(q = 0)$ were taken from paper [12], where they were determined from a simultaneous data customization of inelastic scattering exactly at the M-point for the symmetric and asymmetric points of the reciprocal space. To describe high-energy mode same expression was used: $\omega_4(q) = P_4q^2 + \omega_4(q = 0)$.

3.3. Description of AFD-mode

The only temperature-dependent parameter of the model is the frequency of the „oxygen“ mode, which can be written as

$$\omega_2^2(\vec{q}, T) = \omega_{\mathrm{M}}^2(0, T) + D\vec{q}^2 = \omega_{\mathrm{M}}^2(0, T)\left(1 + \frac{P_2\vec{q}^2}{\omega_{\mathrm{M}}^2(0, T)}\right). \quad (5)$$

Here $\frac{P_2\vec{q}^2}{\omega_{\mathrm{M}}^2(0,T)}$ has dimension of length and determines correlation radius of critical AFD-excitation. Parameter $\omega_{\mathrm{M}}(0, T)$ can be determined from the analysis of inelastic data directly in M-point, where intermode interaction is prohibited [12]. Eigen vectors M_3, completely determined by offsets of oxygen, away from M-point are supposed to be complex. Thus, eigen vector for O_1 and O_2, included in expression (3), were written as $\vec{e}_{O1} = (\frac{1}{\sqrt{2}}00)e^{i\phi}$ and $\vec{e}_{O2} = (0\frac{-1}{\sqrt{2}}0)e^{i\phi}$, where $\phi(\vec{q})$— phase multiplier. To describe $\phi(\vec{q})$ the following function was selected

$$\phi(-q) = P_5 \tanh(P_6q) + P_7q, \quad (6)$$

it complies with the following conditions: $\phi_2(0) = 0$ and $\phi_2(q) = -\phi_2(q)$. P_5 determines amplitude of value ϕ_2 in section, P_6 — its behavior in the vicinity of zero, and P_7 — at interval boundaries.

3.4. Description of intermode interaction

To describe q-dependence of the real part of intermode interaction the following expression was used:

$$\Delta_{12}(\vec{q}) = P_8\left(1 - \left(\frac{P_9^2}{\vec{q}^2 + P_9^2}\right)^{P_{10}}\right), \qquad (7)$$

where P_8 determines height of overturned „peak“, and combination P_9 and P_10 determine its width and concavity, upon keeping the requirement for absence of interaction exactly in M-point $\Delta_{12}(0) = 0$. This choice of function also ensures continuity at zero for the function and its first derivative.

4. Extraction and symmetrization of diffuse scattering data

Data of DS experiment are three-dimension array, where each element (voxel) corresponds to point in space. In each point the value of intensity of scattered radiation is stored. To extract the DS intensity along a certain direction, a „puncture“ (a virtual line passing through three-dimensional array of voxels in given direction) is made in the reciprocal space.

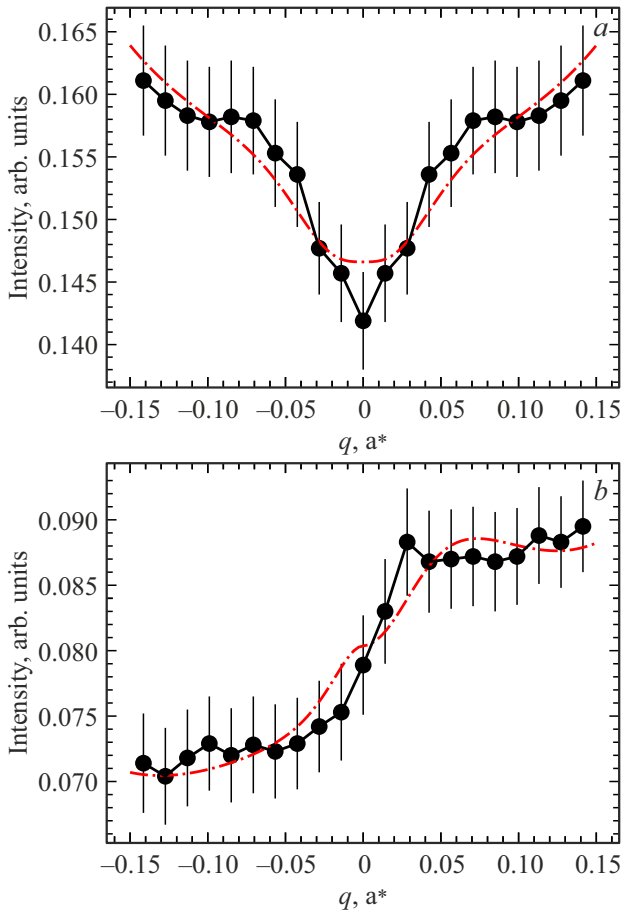
Scattering intensity for each point in selected direction is taken as sum of intensities of all voxels, entering inside some cylindrical volume with center in this point. Splitting step s and radius r determine size of volume, in which integration will be performed. To mitigate the influence of instrumental parameters and potential contributions of higher-order Bragg reflections at certain angles, the collected data are symmetrized. In this process crystallographic symmetry of crystal is used. Points of data from reciprocal space sequences, that use same symmetry operation, are summed. For example, data, acquired around $(1, 5, 0, 5, 0)$ in direction $[1, -1, 0]$, ill be added to data acquired around $(1, 5, -0, 5, 0)$ in direction $[1, 1, 0]$, as these points are interrelated by mirror symmetry.

5. Discussion

To check applicability of the above approach to processing of the experimental data the points were selected with zero and non-zero structural factor for unperturbed mode $Q_{\text{sym}} = (1.5, 1.5, 0)$ and $Q_{\text{asym}} = (3.5, 0.5, 0)$ in direction $[1, -1, 0]$. To implement possibility of customization the diffusion scattering, we need to take n points in considered interval, and calculate in each point the integral of inelastic scattering over energy. So, the problem was reduced to minimization of functional of the form

$$I_{D_{\text{exp}}}(\vec{q}, T) - \int I_{\text{IXS}}\left(\vec{q}, Q, T, \Gamma_{1-4}, P_{1-10}, \Gamma_{12}, \Delta_{12}, \phi\right) dE. \qquad (8)$$

For data approximation by formula (8) the variable-metric method MIGRAD was used [13] from package MINUIT



Results of approximation for a) Q_{sym} (symmetrical M-point) and b) Q_{asym} (asymmetrical M-point). Black symbols — experimental data for temperature 570 K with errors. Red dashed-dotted line — customization results.

C++ via interface iminuit Python [14]. To check applicability of model and developed method simultaneous customization was performed of q-dependences of DS intensities in symmetrical and asymmetrical points at $T = 570$ K. Model calculation results, presented in Figure, show good agreement with experimental data. It was determined that form of parameter $\Delta_{12}(q)$ makes significant contribution to final scattering form, tis once more emphasizes the importance of function selection for its description. Especially note the model agreement with experiment in vicinity of symmetrical M-point. Previously observed drop in q-dependence of intensity was not discussed on the whole, and was not reproduced during modeling by Monte Carlo method [6]. At value $q \approx |0.07|$, corresponding to point of crossing unrenormalized AFD- and TA-modes, in experimental curves the clear break is observed, which in model is described qualitatively only. This is associated with that in anticrossing point additional contribution shall occur into $\Delta_{12}(q)$. Such additional contribution with in principle depend on temperature, and will strong correlation with curvature of AFD- and TA-modes will occur. At same time, physically valuable parameters, dispersion and eigen

vectors of unrenormalized modes will remain practically unchanged. Due to this for $\Delta_{12}(q)$ description we limited to expression (7).

6. Conclusion

The interacting modes model, previously used to describe inelastic scattering, is modified to continuously describe the diffuse scattering intensity. The obtained approach is rather general, applicable to all perovskite-like crystals with unstability M_3 of AFD-mode. The developed approach to the phonon decomposition of DS in the presence of intermode interaction significantly expands the possibilities of studying the critical dynamics of perovskites. Previously such approach for DS analysis was not applied in perovskites.

The adequacy of the developed method is demonstrated using the example of PZT2.4, which has instability of M_3-mode. Model ensures successful description of DS in vicinity of both symmetrical, and asymmetrical M-points, this confirms efficiency of its application to study same materials.

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Conflict of interest

The authors declare that they have no conflict of interest.

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