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Second-order central peak in the Raman spectra of disordered ferroelectrics

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A theory of the central peak line shape in Raman scattering in ferroelectrics above T_c is developed. Off-center ions are considered as a possible source of the local symmetry breaking. We argue that in order to properly describe the features of the central peak line shape above T_c one should take into account the second-order invariants in the modulation of the electronic polarizability by polarization fluctuations. The theory is in excellent agreement with the Raman-scattering experiment in $KTa_{1-x}Nb_xO_3$ [J. P. Sokoloff, L. L. Chase, and L. A. Boatner, Phys. Rev. B **41**, 2398 (1990)]. [S0163-1829(99)11213-X]

I. INTRODUCTION

The appearance of a central peak in the Raman spectra of disordered crystals near second-order structural phase transitions is a precursor effect which indicates a crossover from displacive to an order-disorder type of behavior. This phenomenon has attracted considerable attention from both theorists and experimentalists.[1] It is well established that, near T_c, the central peak narrows critically and increases in height, reflecting the increase in size of precursor clusters and the slowing down the cluster dynamics.

The width of the central peak is too narrow to be explained by intrinsic mechanisms such as soft-mode anharmonicity or the interaction of the soft mode with other phonon modes. Therefore it is commonly accepted that the main mechanism of the central peak originates from the interaction of the soft mode with some relaxational degrees of freedom. These may be the symmetry-breaking defects linearly interacting with the order parameter.[2] In ferroelectrics symmetry-breaking defects have been detected in the form of off-center impurity ions. The most studied systems have been $K_{1-x}Li_xTaO_3$ (KLT) and $KTa_{1-x}Nb_xO_3$ (KTN).[3–8]

It has been proposed[9] that off-center ions are responsible for the central peak in undoped materials as well. This assumption is based on XAFS measurements which indicate that, in crystals undergoing ferroelectric phase transitions [e.g., $KNbO_3$, $PbTiO_3$, and $BaTiO_3$ (Refs. 11 and 12)], there also exists off-center displacements of atoms even far above the phase-transition temperature. Recently[10] the central peak in Raman scattering has been investigated in relaxor ferroelectrics $PbMg_{1/3}Nb_{2/3}O_3$ (PMN) caused apparently by the off-center displacement of lead above T_c.

Raman scattering is a powerful technique to analyze the low-frequency fluctuations of the order parameter in oxide perovskites since, in these materials, the polarization fluctuations modulate an already large oxygen electronic polarizability providing large scattered intensities. This technique has been successfully applied to analyze the central peak in doped and undoped materials.[1]

Usually it is assumed that the central peak line shape reproduces the shape of the dynamical structure factor of polar fluctuations which, under general circumstances, are of Lorentzian shape. In the case of Raman scattering this is only true if the change in electronic polarizability due to the polarization fluctuations is a linear function of the polarization amplitude. The latter selection rule is satisfied in the ferroelectric phase below T_c. In the cubic phase above T_c, the symmetry allows only invariants of even power in an expansion of the electronic polarizability in terms of polar fluctuations. The most significant term is obviously the second-order invariant which leads to a second-order Raman central peak. Although the possibility of the second-order central peak in Raman spectra in ferroelectrics has been noted in the literature[13,14] neither the analysis of the central peak line shape nor the manifestation of this mechanism in the experiment has been analyzed. Moreover, in the studies[15,18] of the central peak in KTN it was assumed that Nb reorientation frequency directly relates to the width of the central peak, which is not true in the case of the second-order central peak.

Thus, the purpose of the present paper is to develop a theory of the line shape of the second-order central peak in the Raman spectra in ferroelectrics.

II. MODEL

The scattered Raman intensity can be written in the form

$$I(\omega)\propto\langle\delta\hat{\alpha}(\mathbf{r},t)\,\delta\hat{\alpha}(0,0)\rangle_{q\approx 0,\omega}, \tag{1}$$

where $\langle\delta\hat{\alpha}(\mathbf{r},t)\,\delta\hat{\alpha}(0,0)\rangle_{\mathbf{q},\omega}$ denotes the spatial and temporal Fourier component of the correlation function of the electronic polarizability. In the cubic phase, the change in the electronic polarizability α due to fluctuations of the lattice polarization $\mathbf{P}(\mathbf{r},t)$ can be written in the form

$$\delta\hat{\alpha}(\mathbf{r},t)=\mathbf{P}(\mathbf{r},t)\cdot\hat{\Lambda}\cdot\mathbf{P}(\mathbf{r},t), \tag{2}$$

where $\hat{\Lambda}$ is a forth-rank tensor and where we have taken into account the lower-order term with respect to $\mathbf{P}(\mathbf{r},t)$. We assume that the polarization $\mathbf{P}(\mathbf{r},t)$ contains the contribution from optical phonon modes $\mathbf{P}^h$ and the contribution from slow relaxing polar nanoregions $\mathbf{P}^\mu$ induced by off-center ions, i.e.,

$$\mathbf{P}=\mathbf{P}^\mu+\sum_h \mathbf{P}^h. \tag{3}$$

Accordingly, three different types of terms appear in Eq. (2). Namely, the terms P^hP^h, which are responsible for the second-order Raman scattering by hard and soft optical phonons, the terms $P^\mu P^h$ which describe the first-order Raman scattering induced by polar nanoregions, and, finally, the term $P^\mu P^\mu$ which is responsible for the second-order central peak. The first two have been discussed in Refs. 7 and 8 and the last one is the subject of the present paper.

It follows from Eqs. (1) and (2) that the central peak intensity can be represented as a spatial and temporal Fourier component of the square of the correlation function of the low-frequency polar fluctuations. A further simplification is possible with the use of the decoupling approximation $\langle P^\mu(r,t)^2P^\mu(r',t')^2\rangle\propto\langle P^\mu(r,t)P^\mu(r',t')\rangle^2$. Note that such a decoupling is exact under the conditions of the validity of mean-field theory leading to the Gaussian character of the polar fluctuations. Therefore, the scattering intensity reduces to the form

$$I(\omega)\propto\int dq'\int d\omega'\langle P^\mu(r,t)P^\mu(0,0)\rangle_{q'\omega'} \times\langle P^\mu(r,t)P^\mu(0,0)\rangle_{-q'\omega-\omega'}. \tag{4}$$

The model proposed here suggests that, without the off-center ions, the crystal would undergo a second-order ferroelectric phase transition of the displacive type (or remains an incipient ferroelectric at all temperatures) with the soft optical-phonon mode ω_0 providing the high amplitude of the transverse fluctuations of the lattice polarization. We consider the following conventional form of the dispersion law of the transverse soft phonon branch

$$\omega_q^2=\omega_0^2+v^2q^2, \tag{5}$$

where q is the phonon wave vector. Since the fluctuations of the lattice polarization induce local fields at the sites of the off-center ions, the lattice polarization interacts with the off-center ion dipole moments $\mathbf{d}_i(i=1.2,\dots N)$. In order to find the slow reorienting part of the polarization induced by off-center ions, we utilize the model suggested in Ref. 5. According to this model, which is valid when the soft mode frequency ω_0 is larger than the orientation frequency ν of the off-center ions, we can obtain the polarization $\mathbf{P}^\mu(\mathbf{r},\mathbf{t})$ from the following quasistatic Hamiltonian:

$$H=2\pi V_0\sum_{\mathbf{q}s}\frac{1}{\epsilon_{0,q}}\mathbf{P}_{qs}\mathbf{P}_{-qs}-\frac{4\pi}{3}\gamma\sum_{is}\mathbf{d}_i\mathbf{P}_\mathbf{s}(\mathbf{r}_i). \tag{6}$$

Here $\mathbf{P}_{qs}$ is the q-Fourier component of the polarization $\mathbf{P}_\mathbf{s}(\mathbf{r})$ corresponding to the transverse optical-phonon branch, and s designates either one of the two transverse phonon branches. $\epsilon_{0,q}$ is the q-dependent static dielectric constant of the lattice without off-center ions related to the frequency ω_q via the Lyddane-Sachs-Teller relation. In Eq. (6) we neglected the kinetic energy of the polarization which is justified in the limit $\nu\ll\omega_0$. The second term in Eq. (6) is responsible for the interaction between the lattice polarization and the dipole moments $\mathbf{d}_i$, and γ is the parameter describing the strength of this interaction. In fact, the validity of the Hamiltonian (6) implies the adiabatic approximation, meaning that polarization fluctuations adiabatically follow the instantaneous value of the dipoles [which are treated as stochastic variables in Eq. (6)]. Accordingly, the instantaneous values of the polarization can be determined from a minimization of the Hamiltonian (6) with respect to P_{qs}. Setting $(\partial H/\partial P_{qs})=0$, we find the polarization induced by the off-center ions in the form

$$P_\alpha^\mu(\mathbf{r}_i)=\frac{\epsilon_0}{4\pi}\sum_{j\beta}K_{ij}^{\alpha\beta}(\mathbf{r}_{ij})d_{j\beta}^*, \tag{7}$$

where $\epsilon_0\equiv\epsilon_{0,q=0}$, and $r_c=v/\omega_0$ is the polarization correlation length of the crystal in the absence of off-center ions; $d_j^*=\gamma\epsilon_0d_j/3$ is the effective dipole moment which takes into account the polarization cloud surrounding each off-center ion; $\alpha,\beta=x,y,z$. The Fourier components $\hat{K}_q$ of the matrix $\hat{K}_{ij}=\hat{K}(\mathbf{r}_i-\mathbf{r}_j)$ are given by[5]

$$K_q^{\alpha\beta}=\frac{4\pi}{\epsilon_0V_0(1+r_c^2q^2)}\left(\delta_{\alpha\beta}-\frac{q_\alpha q_\beta}{q^2}\right), \tag{8}$$

where $\delta_{\alpha\beta}$ is a Kronecker δ symbol, and $r_c=v/\omega_0$.

Substitution of the polarization given by Eq. (7) back into Eq. (6) gives, according to the general concept of the adiabatic approximation, the following Hamiltonian of the dipole-dipole interaction:

$$V_{dd}=-\frac{1}{2}\sum_{ij}\mathbf{d}_i^*\cdot\hat{K}_{ij}\cdot\mathbf{d}_j^*. \tag{9}$$

Equations (7) and (9) allow us to describe the polarization dynamics in crystals with off-center ions in terms of the dynamics of the effective dipole moments $\mathbf{d}^*$. For example, the correlation function of the polarization $\langle P(r,t)P\rangle_{q,\omega}$, in (q,ω) space, which determines the features of the central peak in Raman scattering, is given by

$$\langle P^\mu(r,t)P^\mu\rangle_{q,\omega}=\langle P^\mu(r)P^\mu\rangle_q\cdot\frac{\nu_q}{\nu_q^2+\omega^2}, \tag{10}$$

where

$$\langle P^\mu(r)P^\mu\rangle_q\propto\frac{1}{(R_c^{-2}+q^2)(r_c^{-2}+q^2)},\quad T\geq T_c, \tag{11}$$

$$\nu_q=\nu\frac{R_c^{-2}+q^2}{r_c^{-2}+q^2}. \tag{12}$$

In Eqs. (11) and (12) we have used the isotropic approximation and have designated the critical correlation length by R_c. R_c diverges at the transition temperature T_c and may be expressed in terms of the dielectric constant ϵ renormalized by the off-center ion contribution

$$\frac{R_c^2}{r_c^2}=\frac{\epsilon}{\epsilon_0}, \tag{13}$$

where, near T_c, one has[5,9]

$$\frac{\epsilon}{\epsilon_0}=\frac{T_c}{2(T-T_c)}, \quad T\rightarrow T_c, \tag{14}$$

and we assumed $T_c \gg T_0$, T_0 being the phase transition temperature in the crystal without off-center ions. Equation (11) represents, for a given q, the integrated intensity of the low-frequency fluctuation spectrum of polarization. The major difference between this spectrum and the full static spectrum of the polarization is the additional factor of $(r_c^{-2}+q^2)^{-1}$ in Eq. (11). In particular due to this factor at $T \gg T_c$ $(R_c \approx r_c)$ the q dependence of the spectrum (11) has a form of the square of Lorentzian. Note that this result has been arrived at in Ref. 16 using a different formalism in an analysis of the central peak in neutron scattering.

In the next section we will apply the approach developed above to the analysis of the shape of the Raman central peak above T_c.

III. SHAPE OF THE SECOND-ORDER CENTRAL PEAK: COMPARISON WITH THE EXPERIMENT

Performing in Eq. (4) the integration over ω' and taking into account Eqs. (10) and (12), we present the central peak intensity in the following form:

$$\nu I(\omega)\propto\int_0^\infty dx x^2 \frac{1}{\left[\left(\frac{\epsilon_0}{\epsilon}+x^2\right)^2+\left(\frac{\omega}{2\nu}\right)^2(1+x^2)^2\right]\left(\frac{\epsilon_0}{\epsilon}+x^2\right)(1+x^2)}, \tag{15}$$

where $x=qr_c$.

Using Eq. (15) one can calculate the central peak line shape which changes dramatically as T approaches T_c. It follows from Eq. (15) that the line shape as a function of frequency is Lorentzian far above T_c:

$$I(\omega)\propto\frac{\nu}{\omega^2+\nu^2}, \quad \epsilon_0/\epsilon\rightarrow 1, \tag{16}$$

however, the line shape narrows and deviates significantly from the Lorentzian at $T\rightarrow T_c$. The temperature evolution of the central peak line shape is shown in Fig. 1. The values of the ϵ_0/ϵ used in the calculations are the experimental values obtained for KTN at $T=253$, 254, and 256 K for curves 1, 2, and 3, respectively with $T_0=0$ and $T_c=252$ K.

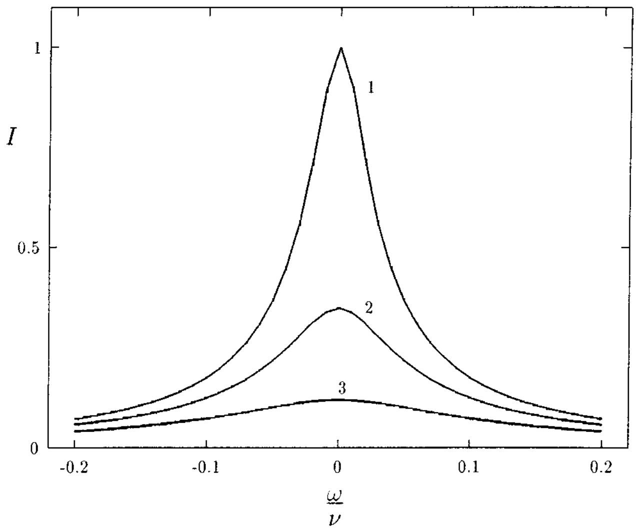

FIG. 1. Second-order central peak line shape given by Eq. (15) for the values of ϵ_0/ϵ equal to 0.008 (curve 1), 0.016 (curve 2), and 0.032 (curve 3).

Integral intensity of the center peak can be obtained by integrating Eq. (15) over ω. As $T\rightarrow T_c$, we obtain

$$I_{\mathrm{int}}(\omega)\propto\sqrt{\frac{\epsilon}{\epsilon_0}}\propto\frac{1}{\sqrt{T-T_c}}, \tag{17}$$

compared with $I_{\mathrm{int}}\propto(T-T_c)^{-1}$ for the first-order central peak integral intensity.

Note that an attempt to calculate the integral intensity of the second-order second peak has been performed in Ref. 17. However, these authors did not reproduce the critical dependence of I_{int} given by Eq. (17).

The most detailed study of the central peak line shape and intensity near a ferroelectric phase transition has been performed by Sokoloff *et al.*[18] using a KTN crystal with a Nb concentration $x=0.28$. Due to disorder effects, probably the result of random strains,[18] long-range order in KTN with a domain size larger than the wavelength of light does not develop in the absence of an applied E field. In Ref. 18 a small poling field was applied while the crystal was cooled down below the phase-transition temperature. Under these conditions the cubic symmetry of the crystal is already broken in the high-temperature phase and the Raman spectra contain two different components (A and E) which correspond to $X(ZZ)Y$ and $X(ZX)Y$ geometries, respectively (Z is the polar axis).

Note that off-center Nb ions are involved in critical and noncritical dynamics related to Nb hopping along the polar axis and perpendicular to it, respectively. Correspondingly, the central peak contains both critical and noncritical contributions. The noncritical contribution is characterized by a

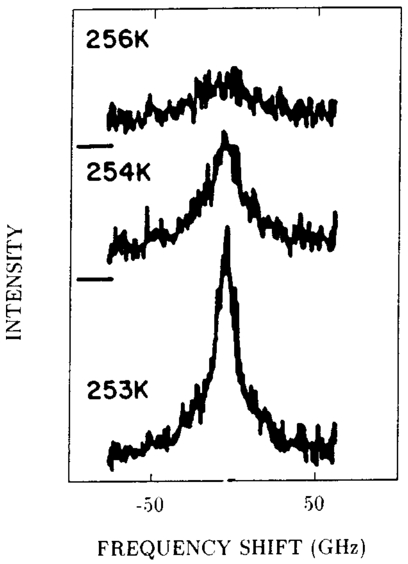

FIG. 2. Experimental low-frequency spectra of *A* symmetry in KTN (Ref. 18).

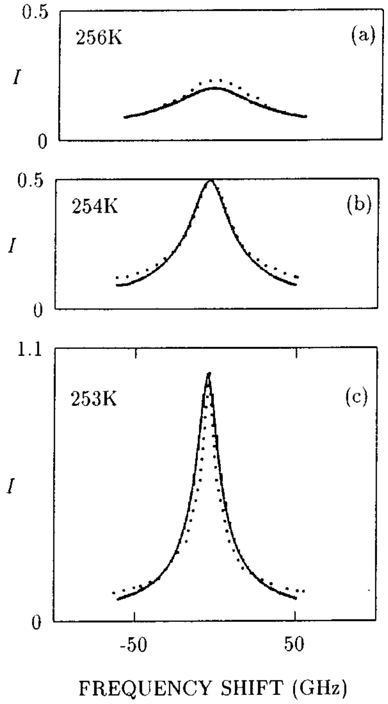

FIG. 3. Comparison of the theory (solid lines) with the experiment. Dotted lines represent the sketch of experimental data shown in Fig. 2.

low intensity broad line, which was explained in Ref. 18 using a model with one-exponential Debye relaxation. No attempts have been made to explain the narrow critical contribution which was detected in higher resolution experiments using a Fabry-Perot interferometer in the close vicinity of T_c. We will show that the critical component of the central peak is consistent with the theory developed above.

Experimental spectra for three temperatures in the vicinity of $T_c = 252$ K are reproduced in Fig. 2. One can see that the line shape narrows in width and increases in height as in Fig. 1. Also, the ratio of the peak intensities observed in the experiment, 1:0.5:0.1, is very close to the theoretical result 1:0.35:0.12. In order to compare quantitatively the theory with the experiment, we present in Fig. 3 the theoretical curves with their scale adjusted to fit the scale of the experimental ones. A sketch of the experimental data is shown by dotted lines in Fig. 3. The best fit between the theory and the experiment is obtained for a Nb hopping frequency $\nu = 140$ GHz, which compares favorably with the value $\nu \approx 120$ GHz ($3.9\ \mathrm{cm}^{-1}$) at $T = 255$ K obtained in Ref. 18.

IV. CONCLUSION

In the present paper we have developed a theory for the central peak line shape in Raman scattering in the high-symmetry phase of disordered ferroelectrics. The peculiarities in the line shape originate from second-order invariants of low-frequency polar fluctuations which modulate the electronic polarizability of the crystal. The line shape deviates significantly from the conventional Lorentzian shape, which is a characteristic of the central peak only in the low-temperature ferroelectrics phase.

The proposed mechanism reproduces quantitatively the central peak anomalies observed in the paraelectric phase of KTN at high Nb concentrations. At low Nb concentrations the experimental situation[15] is more complicated due to the coexistence of critical and noncritical Nb dynamics.[8] We expect that the proposed mechanism will be confirmed as well in future studies of the low-frequency polar fluctuations in disordered ferroelectrics, in particular in relaxor ferroelectrics which are currently under intensive investigations.

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[1] A. D. Bruce and R. A. Cowley, Adv. Phys. **29**, 219 (1980).

[2] B. I. Halperin and C. M. Varma, Phys. Rev. B **14**, 4030 (1976).

[3] Y. Yacoby, Z. Phys. B **31**, 275 (1978); **41**, 269 (1981).

[4] U. T. Hochli, K. Knorr, and A. Loidl, Adv. Phys. **39**, 405 (1990).

[5] B. E. Vugmeister and M. D. Glinchuk, Rev. Mod. Phys. **62**, 993 (1990).

[6] O. Hanske-Petitpierre, Y. Yacoby, J. Mustre-deLeon, E. A. Stern, and J. J. Rehr, Phys. Rev. B **44**, 6700 (1991).

[7] P. DiAntonio, B. E. Vugmeister, J. Toulouse, and L. A. Boatner, Phys. Rev. B **47**, 5629 (1993).

[8] B. E. Vugmeister, P. DiAntonio, and J. Toulouse, Phys. Rev. Lett. **75**, 1646 (1995).

[9] Y. Girshberg and Y. Yacoby, Solid State Commun. **103**, 425 (1997).

[10] I. G. Siny, S. G. Lushnikov, R. S. Katiyar, and E. A. Rogacheva, Phys. Rev. B **56**, 7962 (1997).

[11] N. Sicron, B. Ravel, Y. Yacoby, E. A. Stern, F. Dogan, and J. J. Rehr, Phys. Rev. B **50**, 13 168 (1994).

[12] K. H. Kim, W. T. Elam, and E. F. Skelton, in *Optical Fiber Materials and Processing*, edited by J. W. Fleming, G. H. Sigel, S. Takahashi, and P. W. France, MRS Symposia Proceedings No. **172** (Materials Research Society, Pittsburgh, 1990), p. 291.

[13] A. D. Bruce, W. Taylor, and A. F. Murray, J. Phys. C **13**, 483 (1980).

[14] V. L. Ginzburg and A. P. Levanyuk, in *Light Scattering near Phase Transitions* (North-Holland, New York, 1983).

[15] K. B. Lyons, P. A. Fleury, and D. Rytz, Phys. Rev. Lett. **57**, 2207 (1986).

[16] G. Shirane, R. A. Cowley, M. Matsuda, and S. M. Shapiro, Phys. Rev. B **48**, 15 595 (1993).

[17] L. Foussadier and M. D. Fontana, Ferroelectrics **153**, 183 (1994).

[18] J. P. Sokoloff, L. L. Chase, and L. A. Boatner, Phys. Rev. B **41**, 2398 (1990).