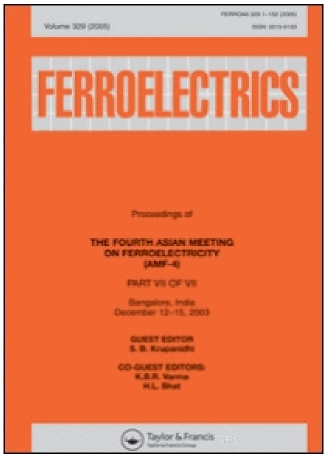

Ferroelectrics
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713617887

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First Published on: 01 February 2000
To cite this Article: Kužel, Petr, Dvořák, Vladimír and Moch, Philippe (2000) 'Phase transitions in Cs_2CdBr_4: Dynamic study of the coupling of the elastic strains to the order parameter', Ferroelectrics, 239:1, 71 - 78
To link to this article: DOI: 10.1080/00150190008213307
URL: http://dx.doi.org/10.1080/00150190008213307

Ferroelectrics, 2000, Vol. 239, pp. 71-78
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Phase Transitions in Cs_2CdBr_4: Dynamic Study of the Coupling of the Elastic Strains to the Order Parameter

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(Received July 12, 1999)

Previously published Brillouin and ultrasonic data are interpreted using a dynamical model which couples the order parameter to the shear (ε_4) and longitudinal (ε_2) strains. The model takes into account the contribution of the nonlinear fluctuations of the order parameter and provides a good quantitative agreement with the experiments.

Keywords: Ferroelastic; incommensurate; phase transition; Cs_2CdBr_4

INTRODUCTION

The compounds of A_2MX_4 family often show sequences of phase transitions with one or several incommensurate phases and ferroelastic or ferroelectric lock-in phases. In general, these transitions are driven by librations or re-orientations of the MX_4 tetrahedra.

The compound Cs_2CdBr_4 is a very interesting material from the point of view of the order parameter dynamics. It undergoes a sequence of phase transitions which includes an incommensurate phase and two pseudo-proper ferroelastic phases [1,2,3,4]. Namely, it presents a paraelastic *Pnma* ↔ incommensurate (IC) phase transition at $T_i = 252$ K with an incommensurate wave vector $\boldsymbol{q} \approx 0.16\, \boldsymbol{a}^*$, and an IC ↔ ferroelastic commensurate (C) $P2_1/n11$ lock-in transition (without unit cell multiplication) at $T_C = 235$ K. The dynamics of these transitions was studied by means of Raman [5,6] and Brillouin [7] light scattering and ultrasonic propagation experiments [5,7,8]. The whole sequence of the two transitions was shown to be governed by a relaxational mode belonging to the B_{3g} (*yz*) representation at the Γ point. This mode was directly observed in the Raman [5] and Brillouin [7,9] spectra. Its dynamics was found to be very slow: its characteristic frequency (reciprocal value of the relaxation time) softens down to the GHz frequency range where the mode strongly couples with the acoustic phonons related to the elastic stifnesses C_{22} and C_{44}.

The difficulty in the theoretical description of these transitions comes from the locking of the IC phase into a ferroelastic one at the Brillouin zone center: a careful analysis of the couplings between the order parameter and the strain components shows that while the shear strains represented by ε_4 are coupled to the zone-center B_{3g} mode (denoted as Q_0), the longitudinal strains represented by ε_2 couple most strongly to the same branch at the IC wave vectors $\boldsymbol{q}$ and $-\boldsymbol{q}$ (more specifically to the amplitudon in the IC phase) [9]. Thus, a simultaneous knowledge of the mode characteristics and of their temperature behavior at $\boldsymbol{k} = 0$ and at $\boldsymbol{k} = \boldsymbol{q}$ is required in order to describe satisfactorily the sequence of transitions.

The neutron scattering data are not available for this material. Other experimental techniques which give information about the dynamics of the system (Raman and Brillouin scattering, ultrasounds) only concern the near neighborhood of the Γ-point. Consequently, it is necessary to investigate the vicinity of the IC wave vector indirectly through non-linear couplings between the order parameter and the Γ-point modes.

A good candidate for such an analysis is the acoustic mode related to the strain component ε_2 which is characterized through the elastic constant C_{22}: in fact a quantitative discussion of the behavior of this mode is still lacking. In this paper we study the coupled equations of motion for Q, ε_4 and ε_2. The dynamics of ε_4 has already been thoroughly described [9]; we show below that the behavior of ε_2 can be described on the same footing taking into account the contribution of the nonlinear fluctuations of the order parameter and we obtain a quantitative agreement with the experiment.

PRESENTATION OF THE MODEL

Since the principal elastic anomalies connected with the phase transitions under study concern only the elastic stifnesses C_{22} and C_{44} we restrict from the beginning the discussion to the relevant strains ε_2 and ε_4, and consequently to the direction of propagation of the acoustic phonons along the ***b*** orthorhombic crystallographic axis (***k//b***). The Landau free energy development up to the 4th order can then be written as [9]:

$$\begin{aligned}\Phi = {} & \tfrac{1}{2}\sum_{k}\omega_k^2 Q_k Q_{-k} + \tfrac{1}{4}B\sum_{k,k',k''} Q_k Q_{k'} Q_{k''} Q_{-k-k'-k''} + \sum_{k} f Q_{-k}\varepsilon_{4,k} \\ & + \lambda \sum_{k,k',k''} Q_k Q_{k'} Q_{-k-k'-k''}\varepsilon_{4,k''} + g\sum_{k,k'} Q_k Q_{-k-k'}\varepsilon_{2,k'} \\ & + \tfrac{1}{2}\sum_{k}\left(C_{22}^0 \varepsilon_{2,k}\varepsilon_{2,-k} + C_{44}^0 \varepsilon_{4,k}\varepsilon_{4,-k}\right)\end{aligned} \qquad (1)$$

where ω_k^2 characterizes the relaxation time of the order parameter and shows a *minimum for* $\boldsymbol{k} = \boldsymbol{q}$; one additionaly assumes that ω_k^2 linearly softens with a slope denoted by $\underline{a}$ when the phase transitions are approached from above. The dynamic variables should then satisfy the equations of motion, which in the paraelastic phase take the form:

$$\begin{aligned}
\chi_k^{-1}(\omega)Q_k(\omega)+f\,\varepsilon_{4,k}(\omega)+2g\sum_{k',\omega'}\varepsilon_{2,k'}(\omega')Q_{k-k'}(\omega-\omega') &= h_k(\omega)\\
\chi_{2,k}^{-1}(\omega)\varepsilon_{2,k}(\omega)+g\sum_{k',\omega'}Q_{k'}(\omega')Q_{k-k'}(\omega-\omega') &= \sigma_{2,k}(\omega)\\
\chi_{4,k}^{-1}(\omega)\varepsilon_{4,k}(\omega)+f\,Q_k(\omega) &= \sigma_{4,k}(\omega)
\end{aligned} \tag{2}$$

where $\chi_k^{-1}(\omega)=\Gamma(1/\tau_k-i\omega)$, $\chi_{i,k}^{-1}(\omega)=C_{ii}^0-\rho\omega^2/k^2\ (i=2,4)$ are the susceptibilities of the uncoupled modes, ρ is the mass density, σ_i are the appropriate stress components, h_k is the random force conjugated to Q_k, and Γ is a damping constant ($\omega_k^2=\Gamma/\tau_k$, where τ_k is *interpreted* as the relaxation time).

We have already solved the problem concerning the Q–ε_4 coupling [9]. The main conclusions about the corresponding dynamics can be summarized as follows: (*i*) the order parameter is a relaxator, (*ii*) it significantly contributes to the observed spectra in the allowed scattering geometries (its coupling to the optical permittivity is even much stronger than the coupling of ε_4 through the elasto-optic coefficient p_{44}) (*iii*) the temperature dependence of the τ_k in the vicinity of the Γ-point ($\boldsymbol{k}\approx 0$) could be represented by:

$$\tau_k^{-1}(T)=\beta(T-T_i)+\tau_k^{-1}(T_i) \tag{3}$$

with $\beta\ (=a/\Gamma)\approx 2.2\times 10^9\ \mathrm{K^{-1}\ s^{-1}}$, and $\tau_k^{-1}(T_i)\approx 3.6\times 10^{10}\ \mathrm{s^{-1}}$. These results together allowed us to explain the origin of the high asymmetry of the spectral lines related to the ε_4-acoustic phonons and to give account of the significative difference between the Brillouin and the ultrasonic determination of C_{44}.

The experimental variation of C_{22} is shown in Fig. 1. Our interpretation is based on the coupling of Q and ε_2 through eq. (2). Developing these coupled equations up to the first order with respect to the perturbation one obtains [10]:

$$\sigma_{2,\boldsymbol{k}}(\omega)=\tilde{\chi}_{2,\boldsymbol{k}}^{-1}(\omega)\varepsilon_{2,\boldsymbol{k}}(\omega)$$

with

$$\tilde{\chi}_{2,\boldsymbol{k}}^{-1}(\omega)=\chi_{2,\boldsymbol{k}}^{-1}(\omega)-4g^2\sum_{\boldsymbol{k}',\omega'}\chi_{\boldsymbol{k}-\boldsymbol{k}'}(\omega-\omega')\left\langle Q_{\boldsymbol{k}'}^0(\omega')Q_{-\boldsymbol{k}'}^0(-\omega')\right\rangle,$$

where $Q_{\boldsymbol{k},\omega}^0=\chi_Q(\boldsymbol{k},\omega)h_Q(\boldsymbol{k},\omega)$ represents the uncoupled order parameter value, and $\langle\ldots\rangle$ stands for the statistical mean value. Using the fluctuation-dissipation theorem the modified elastic constant can be expressed as [10]:

$$\tilde{C}_{22}(\boldsymbol{k},\omega)=C_{22}^0-\frac{4g^2k_BT}{(2\pi)^4}\iiint d\boldsymbol{k}'\int d\omega'\frac{\chi_{\boldsymbol{k}-\boldsymbol{k}'}(\omega-\omega')\chi_{\boldsymbol{k}'}''(\omega')}{\omega'},$$

$\chi_{\boldsymbol{k}}''(\omega')$ stands for the imaginary part of the order parameter susceptibility. The integral is evaluated under the following additional assumptions: (*i*) the acoustic modes of interest have very small wave vectors ($\boldsymbol{k}\approx 0$), i.e. $\tilde{C}_{22}(\boldsymbol{k},\omega)\approx\tilde{C}_{22}(0,\omega)$ and $\tau_{\boldsymbol{k}'+\boldsymbol{k}}\approx\tau_{\boldsymbol{k}'}$, (*ii*) since the most important contribution of the integral comes from the vicinity of the maxima of the relaxation time ($\boldsymbol{k}'\approx\pm\boldsymbol{q}$), the dispersion relation is written as a quadratic development:

$$\Gamma/\tau_{\boldsymbol{k}'=\boldsymbol{q}+\Delta\boldsymbol{k}}=a(T-T_i)+d_j\,(\Delta k)_j^2,\quad j=1..3.$$

This second approximation in fact implies that the dynamics of ε_2 is driven only by the modes in the neighborhood of the IC wave vector: the comparison of the results of the model with the experimental data will allow us to validate this hypothesis.

Within the above approximations the result of the integration is:

$$\tilde{C}_{22}(\omega) = C_{22}^{0} - \frac{2i\alpha\beta}{\omega}\left[\sqrt{(T-T_i) - \frac{i\omega}{2\beta}} - \sqrt{(T-T_i)}\right] \tag{4}$$

with

$$\alpha = \frac{g^2 k_B T}{\pi\sqrt{a\, d_1 d_2 d_3}}.$$

The parameter β describes the slowing down of the order parameter dynamics versus temperature [cf. eq. (3)]: its value at wave vectors near the Γ-point was determined from the Q–ε_4 coupling: it is used in order to evaluate the anomaly of C_{22} near the phase transition. Thus, only one fitting constant α is needed. The frequency is given by the experiment: $\omega \approx 6.5 \times 10^7\ \mathrm{s}^{-1}$ for the ultrasonic measurements, and $\omega \approx 7.5 \times 10^{10}\ \mathrm{s}^{-1}$ for the Brillouin scattering data.

The results of the fit are shown in Fig. 1. It is obvious that the theoretical curve fits well the Brillouin results and that it overestimates the magnitude of the ultrasonic anomaly near T_i. However, it should be emphasized that equation (4) was deduced using the first order perturbation model. It means that when the correction of the bare elastic constant becomes too large the approximation is no more valid: this happens namely at low frequencies near T_i [10], which correspond to the discussed ultrasonic measurements.

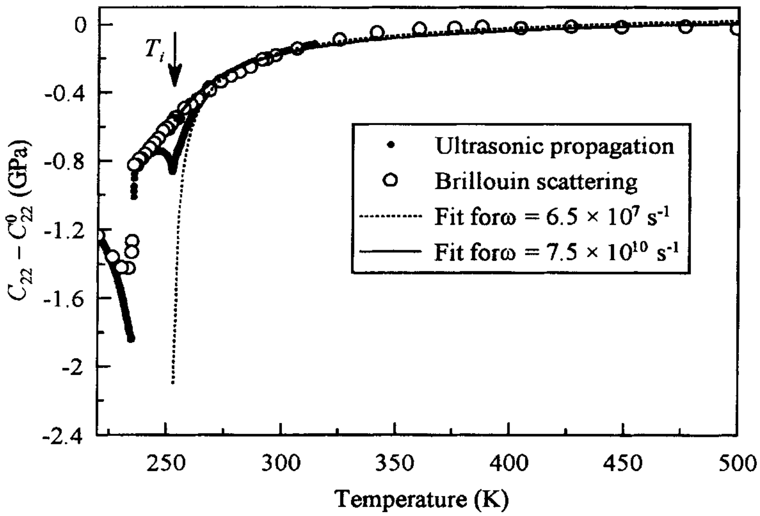

FIGURE 1 C_{22} versus temperature (taken from Ref. 7) after removing its regular variation (C^0_{22}) obtained by a linear extrapolation of the high-temperature values (T > 350 K) to the whole studied temperature interval.

CONCLUSION

The study of the dynamics of the longitudinal strain ε_2 in the paraelastic phase near the IC phase transition has clearly shown that this strain component is mainly coupled to the order parameter components with wave vectors in the neighborhood of the IC modulation. The results of the model are quantitatively compatible with the previously published conclusions concerning the coupling at the Γ-point between the order parameter and the shear strain ε_4. Finaly, the calculation has shown that the sequence of phase transitions is monitored by a linear softening of the whole soft branch which is independent of the wave vector.

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