Brillouin and ultrasonic studies of phase transitions in Cs_2CdBr_4. II. Phenomenological interpretation

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(Received 12 July 1993)

The Brillouin and ultrasonic results are interpreted using a phenomenological free-energy development. The ferroelastic phase transition at 156 K is of a displacive type and is well described by a static model: the variation of the elastic constants bilinearly coupled to the order parameter is in quantitative agreement with recent Raman data. It is shown that the order parameter Q_1 of the sequence $Pnma(\mathrm{I}) \overset{252\ \mathrm{K}}{\leftrightarrow}$ *incommensurate* (IC) $\overset{235\ \mathrm{K}}{\leftrightarrow} P2_1/n11$ (C) is a relaxator which significantly contributes to the scattering in the Brillouin frequency range. The differences between the ultrasonic and the Brillouin results are well understood. (i) A qualitative interpretation of the behavior of C_{22} is given: it is strongly influenced by the fluctuations of the order parameter and, concerning the Brillouin scattering, by a significant Landau-Khalatnikov contribution below T_i. (ii) In the vicinity of the $Pnma\leftrightarrow$ IC transition, the ultrasonic data concerning C_{44} are well interpreted in terms of a static model with a bilinear $Q_1\varepsilon_4$ coupling, while the Brillouin scattering, in the geometry which usually gives access to C_{44} through the dynamics of the strain ε_4, is interpreted as resulting from the cumulative contribution of three terms involving three pair correlation functions of the order parameter Q_1 and the strain ε_4 which allow to fit the characteristic strongly asymmetric shape of the spectra and which explain the considerable shift of the Brillouin maxima below the "static" ultrasonic curve. Finally, we show that an improved interpretation of the Brillouin and ultrasonic data is found assuming that the virtual $Pnma\leftrightarrow P2_1/n11$ transition is of the first order.

I. INTRODUCTION

In the preceding paper[1] (hereafter referred to as Paper I) we have performed a comparative experimental study of the features of the Brillouin and ultrasonic data of Cs_2CdBr_4 related to the phase transitions of this compound. A brief qualitative analysis was performed: it was based on an evaluation of the anomalies of the static elastic constants derived from a Landau development of the free energy, taking into account the appropriate coupling of the order parameter to the strains. Such a model revealed itself to be reasonably successful in interpreting the low-temperature behaviors related to the III [commensurate (C)]↔IV phase transition (at T_C) and, to a lesser extent, to the II [incommensurate (IC)]↔III (C) phase transition (at T_L): this calculation will be described with more details in the present paper. However, in the vicinity of the I↔II (IC) phase transition (at T_i), we found severe discrepancies between our experimental data and the predictions of the above-mentioned static treatment; they mainly, but not only, concern the results connected with the C_{44} shear elastic constant: the shape of the corresponding Brillouin spectra varies with temperature in a very unexpected way, while the ultrasonic measurements allow for a conventional interpretation of the C_{44} anomaly around T_i. It is clear that proper account of the dynamic effects has to be taken, in order to explain the observed differences. We show in this paper that the order parameter Q_1 (see Paper I) has to be assigned to a Debye relaxator bilinearly coupled with the strain ε_4; in addition, besides the autocorrelation function of ε_4, there are significant contributions of the autocorrelation function of Q_1 and of the cross-correlation function between Q_1 and ε_4 in the measured Brillouin-scattering intensity. Further, some peculiarities related to the variations of the longitudinal constants will be discussed and tentatively attributed to the influence of fluctuations.

In Sec. II, after recalling the form of the free-energy density assumed in Paper I we introduce an equivalent presentation in reciprocal space; then we briefly deduce the conditions for the occurrence of the IC phase. Section III is devoted to the derivation of the static elastic

constants deduced from this free-energy density and to the discussion of their adequacy to give account of the experimental results. Section IV deals with the coupled dynamics of ε_4 and Q_1 and with its observed effects upon the Brillouin spectra. Finally, in Sec. V, we comment on the remaining discrepancies and their plausible causes.

II. CONDITIONS FOR THE EXISTENCE OF THE INCOMMENSURATE PHASE

Our description of the phase sequence (see Paper I) and of the elastic properties of Cs_2CdBr_4 will be based on the following form of the free-energy density $F(x)$:

$$F(x)=\frac{1}{2}a_1(T-T_1)Q_1^2+\frac{1}{4}B_1Q_1^4+\frac{1}{2}C_x\left[\frac{dQ_1}{dx}\right]^2+\frac{1}{2}D_x\left[\frac{d^2Q_1}{dx^2}\right]^2+\frac{1}{2}C_y\left[\frac{dQ_1}{dy}\right]^2+\frac{1}{2}D_y\left[\frac{d^2Q_1}{dy^2}\right]^2$$
$$+\frac{1}{2}a_2(T-T_2)Q_2^2+\frac{1}{4}B_2Q_2^4+\sum_{i=1}^{3}(F_iQ_1^2+H_iQ_2^2)\varepsilon_i+fQ_1\varepsilon_4+\lambda_1Q_1^3\varepsilon_4+gQ_1Q_2\varepsilon_5+hQ_2\varepsilon_6$$
$$+\frac{1}{2}\sum_{i,j=1}^{3}C_{ij}^0\varepsilon_i\varepsilon_j+\frac{1}{2}\sum_{i=4}^{6}C_{ii}^0\varepsilon_i^2,\quad C_x<0,\ D_x>0,\ D_y>0\ , \tag{1}$$

where Q_1 and Q_2 are soft modes of B_{3g} (yz) and B_{1g} (xy) symmetry, respectively, and where ε_i denotes a strain component. This form of $F(x)$ is essentially the same as in Ref. 2 except that our Q_2 mode is rather of B_{1g} than of B_{2g} (xz) symmetry. We have omitted gradient terms of Q_1 in the z direction which will not be needed for our discussion. Sometimes it is more convenient to express the part of the free energy $\Phi=\int F(x)dx$ corresponding to the order parameter Q_1 in terms of the Fourier transforms of the variables Q_1, ε_i:

$$\Phi_{Q_1}=\frac{1}{2}\sum_k\omega_1^2(k)Q_1(k)Q_1(-k)+\frac{1}{4}B_1\sum_{k,k',k''}Q_1(k)Q_1(k')Q_1(k'')Q_1(-k-k'-k'')$$
$$+\sum_{i=1}^{3}F_i\sum_{k,k'}Q_1(k)Q_1(k')\varepsilon_i(-k-k')+f\sum_kQ_1(k)\varepsilon_4(-k)$$
$$+\lambda_1\sum_{k,k',k''}Q_1(k)Q_1(k')Q_1(k'')\varepsilon_4(-k-k'-k'')+\frac{1}{2}\sum_{i,j=1}^{3}C_{ij}^0\sum_k\varepsilon_i(k)\varepsilon_j(-k)$$
$$+\frac{1}{2}\sum_{i=4}^{6}C_{ii}^0\sum_k\varepsilon_i(k)\varepsilon_i(-k)\ , \tag{2}$$

where $\omega_1^2(k)=a_1(T-T_1)+C_xk_x^2+C_yk_y^2+D_xk_x^4+D_yk_y^4$ and with $Q_1^*(k)=Q_1(-k)$, $\varepsilon_i^*(k)=\varepsilon_i(-k)$. For simplicity we have omitted the term $gQ_1Q_2\varepsilon_5$. Its contribution will be studied when discussing the behavior of C_{55} in Sec. III A.

Since the wave vector k_0 of the incommensurate (IC) modulation is not too far from the Γ point we need not consider the umklapp terms in Eq. (2). The temperature T_i of the I↔II (IC) phase transition and k_0 are determined by the conditions $d\omega_1^2/dk_x=0$, $\omega_1(k_x=k_0,k_y=0;T_i)=0$ as

$$k_0^2=-\frac{C_x}{2D_x},\quad T_i=T_1+\frac{C_x^2}{4a_1D_x}\ . \tag{3}$$

It should be pointed out that the soft modes $Q_1(k_x)$ are not coupled to the strain ε_4 because the structure is modulated along the x direction: the nonlinear-displacement field components u_i are functions of x only and hence $\varepsilon_4(k_x\neq0)$ is identically equal to zero. Consequently the IC wave does not produce any local spontaneous strain $\varepsilon_4(x)$; actually it is easy to show from Eq. (1) (after introducing u_i instead of ε_i and solving the Lagrange-Euler equations) that $\varepsilon_1(x)$ is the only nonzero x-dependent spontaneous strain and that it is proportional to the spontaneous value of $Q_1(x)$ squared (note that ε_5 and ε_6 are not coupled to Q_1). Therefore the IC phase cannot be looked upon as a precursor of the monoclinic lock-in phase with the homogeneous strain ε_4; consequently, the lock-in transition is necessarily discontinuous. In this sense, Cs_2CdBr_4 is qualitatively different from other modulated ferroelastics, such as $[N(CH_3)_4]_2CuCl_4$,[3] for example, in which the IC phase near the lock-in transition consists of a periodic sequence of ferroelastic domains, which in the commensurate (C) phase continuously transforms into a real domain structure.

On the other hand, the modes $Q_1(k_y)$ are bilinearly coupled to $\varepsilon_4(k_y)=ik_yu_z(+ik_zu_y)$ which represents a transverse acoustic wave. Obviously, we should consider the stability of the parent phase with respect not only to the $Q_1(k_x)$ modes but also the $Q_1(k_y)$ modes. An analogous situation is found in the piezoelectric KH_2PO_4, for example; there is a bilinear coupling proportional to k_y between a soft optic mode and a transverse acoustic mode. It is well known that in such a case the optic-mode instability always drives the mixed acousticlike mode unstable first.[4] The instability may occur at $k_y\neq0$,

or the slope of the acousticlike branch at $k_y=0$ may fall to zero, making the system mechanically unstable. It is easy to show that, if C_y in (2) is negative, the acousticlike mode with $k_0'^2=-C_y/2D_y$ reaches zero frequency at the temperature

$$T_i'=T_1+\frac{f^2}{a_1C_{44}^0}+\frac{C_y^2}{4a_1D_y}\equiv T_1'+\frac{C_y^2}{4a_1D_y}\ . \tag{4}$$

If, however, C_y is positive, the stability of the crystal is violated when the static elastic constant $C_{44}=C_{44}^0-f^2/a_1(T-T_1)$ goes to zero at the temperature T_1'.[2] As a matter of fact, the phase modulated in the k_x direction sets in; therefore for C_y positive we should have

$$T_i>T_1'=T_1+\frac{f^2}{a_1C_{44}^0}\ ,$$

while for C_y negative a stronger inequality, i.e.,

$$T_i>T_1'+\frac{C_y^2}{4a_1D_y}\ ,$$

should be satisfied. (Obviously, the same arguments apply to the transverse acoustic modes propagating in the z direction, too.)

III. DISCUSSION OF THE STATIC ELASTIC CONSTANTS

In this section we derive and discuss the expressions for the elastic constants in the static approximation. Our theoretical results are qualitatively different in the IC phase from those reported previously.[2] Therefore we show the calculations concerning this phase in more detail. The general expression which gives the variation of the elastic constants in the IC phase using the free-energy expansion in real space is derived in the Appendix. The elastic constants calculated with the aid of this expression have to be, of course, the same as those derived in reciprocal space by the standard method (see below).

The difference with Ref. 2 concerns the variation of the three "longitudinal" constants C_{ii} $(i=1,2,3)$ which are given in the Appendix. It is clear from these expressions that all the C_{ii} $(i=1,2,3)$ have to undergo three downward jumps not only at T_L and T_C but also at T_i.

A. Transition at T_C

We start with a quantitative discussion concerning the transition at T_C. The frequency of the soft mode which governs this transition (denoted as ω_2) is about 4 cm^{-1} at T_C.[2] This is between 9 and 40 times greater than the frequency of the acoustic phonons measured by Brillouin scattering.[1] Moreover, no significant broadening was measured either in Brillouin or in Raman scattering. This means that the measured elastic constants are not influenced by the dynamics of the order parameter. The temperature dependence of ω_2^2 above and below T_C (in Ref. 2) can be approximated by two straight lines from which the following quantities are obtained: $T_2\approx 110$ K; $a_2\approx 1.2\times 10^{22}\ s^{-2}K^{-1}$; and

$$\theta=-\left.\frac{d\omega_2^2}{dT}\right|_{T<T_C}\Big/\left.\frac{d\omega_2^2}{dT}\right|_{T>T_C}\approx 3\ .$$

θ differs from 2 (the usual Curie-Weiss behavior) because of the renormalization of the slope of ω_2^2 in phase IV due to the terms $\frac{3}{2}B_2(Q_2^s)^2Q_2^2$ and $\sum H_i\varepsilon_i^sQ_2^2$ (the exponent s stands for the "static" value throughout the paper). More precisely, to be consistent with a development of the free energy up to the fourth order with respect to Q_1 and Q_2, one would have to add several terms to Eq. (1) which also renormalize ω_2^2, namely, $\zeta Q_2^3\varepsilon_6$ and $Q_2^2(\varphi_1Q_1^2+\varphi_2Q_1\varepsilon_4+\varphi_3\varepsilon_4^2)$.

Coming back to the elastic constants: using the coefficient θ, the expressions for C_{66} are found as usual:

$$C_{66}=C_{66}^0-\frac{h^2}{a_2(T-T_2)}\quad \text{for } T>T_C\ , \tag{5a}$$

$$C_{66}=C_{66}^0-\frac{h^2}{a_2(T_C-T_2)+\theta a_2(T_C-T)}\quad \text{for } T<T_C\ , \tag{5b}$$

where the renormalization of the coupling constant h due to the term $3\zeta(Q_2^s)^2Q_2\varepsilon_6$ has been neglected. In the absence of the coupling term $gQ_1Q_2\varepsilon_5$, C_{66} would vanish at $T_2'=T_2+h^2/a_2C_{66}^0$. In reality, when this coupling is present, the system becomes mechanically unstable at T_C with respect to a combination of C_{55}, C_{66}, and C_{56} which vanish at T_C. The coupling between Q_2 and ε_5 can be considered as bilinear in phases III and IV for a nonzero value of Q_1^s. To obtain the variation of C_{55} due to this coupling, one has to replace the coupling constant h in Eqs. (5a) and (5b) by gQ_1^s:

$$C_{55}=C_{55}^0-\frac{(gQ_1^s)^2}{a_2(T-T_2)}\quad \text{for } T_C<T<T_L\ , \tag{6a}$$

$$C_{55}=C_{55}^0-\frac{(gQ_1^s)^2}{a_2(T_C-T_2)+\theta a_2(T_C-T)}\quad \text{for } T<T_C\ . \tag{6b}$$

The difference between the two types of coupling acting on C_{66} and C_{55} can be observed in phases I and II. C_{66} softens already in the high-temperature phases [Fig. 12(c) in Paper I] and is not influenced by the transitions at T_i and T_L (the very small jump observed at T_L can be explained by a weak coupling between Q_1 and Q_2 which was neglected in the above calculations). On the other hand, C_{55} [Fig. 12(b) in Paper I] slightly hardens in phase I: this regular variation is due to the contraction of the unit cell and is not related to the PT sequence. In the IC phase the coupling term related to C_{55} takes the form $gQ_1^s(k_0)Q_2(-k_0)\varepsilon_5(k=0)$ (where k_0 is the frozen-in wave vector): its contribution to the elastic constant is always negative and can explain the very small softening of C_{55} in the IC phase near T_L. The effect is, however, much smaller than in the C phase because the frequency $\omega_2(k_0)$ should be higher than $\omega_2(0)$.

The fit of C_{55} and C_{66} is very satisfactory (see Fig. 1) with the following values of the parameters:

$$h^2/a_2 \approx 125 \text{ GPa K} \quad (|h| \approx 1.2\times 10^{12} \text{ GPa}^{1/2}\text{s}^{-1}) ;$$

$$T_2 \approx 111 \text{ K} \quad (T_2' \approx 142 \text{ K}); \quad \theta \approx 3.0 ;$$

$$[gQ_1^s(T_C)]^2/a_2 \approx 45 \text{GPa K}$$

{with $[Q_1^s(T)]^2$ linear versus temperature}, which agree very well with the fit of the soft-mode temperature dependence. However, it is difficult to interpret quantitatively the origins of the increase of the slope of the soft-mode frequency below T_C. The constants H_i $(i=1,2,3)$ are limited by the magnitudes of the jumps of C_{22} and C_{33} (see Figs. 5 and 8 in Paper I); a large value of ζ would renormalize the coupling constant h and would slow down the increase of C_{66} below T_C when going away from the transition. Therefore these two terms are probably not the leading ones, but they cannot be completely neglected. Unfortunately there is no other reliable information about the strength of the coupling between Q_1 and Q_2. Moreover, one generally observes a nonlinear variation of $(Q_2^s)^2$ versus temperature; this, indeed, can deeply modify the behavior of the elastic constants. Consequently we did not attempt to improve the quantitative fit with our experimental results using such additional unknown parameters.

Coming back to the longitudinal constants derived from Brillouin spectra, C_{22} and C_{33} show downward jumps around T_C as expected. This allows a rough evaluation of H_2^2/B_2 and H_3^2/B_2 (both values equal approximately 0.15 GPa). The value of H_1^2/B_2 has to be significantly smaller. The C_{22} and C_{33} jumps are rather smooth, due to the renormalizing terms arising from the bilinear coupling of the order parameter with the shear strains (see the Appendix); however, a complete quantitative interpretation of the behavior of C_{22} and C_{33} below T_C cannot be performed since, in the discussed model, fluctuations have been neglected. Notice that C_{22} was also measured by ultrasonic propagation: at T_C, it suffers an abrupt downstep, significantly larger than the one observed through Brillouin measurements. It is well known that the contribution of the fluctuations increases when the frequency decreases. However, we cannot provide a full interpretation of the measured differences, since, below T_C, the ultrasonic data show a strong attenuation of the propagating longitudinal waves, probably related to the domain walls appearing in phase IV. This prevented us from finding a satisfactory fit to the experimentally observed behavior.

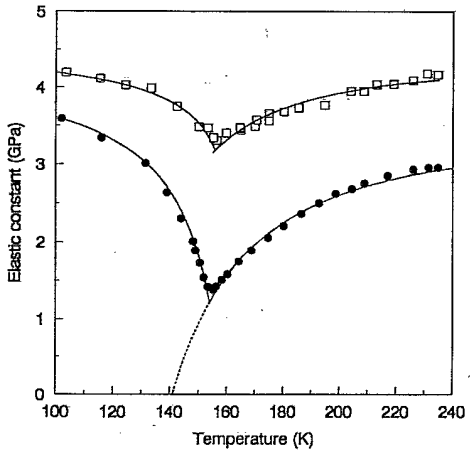

FIG. 1. Fits of the elastic constants C_{66} and C_{55} based on formulas (5a), (5b) and (6a), (6b). (●) and (□) are the Brillouin data corresponding to $\gamma_6(\mathbf{b})$ and $\gamma_5(\mathbf{c})$, respectively (the notation is defined in Paper I). We have taken $\gamma_6(\mathbf{b})=C_{66}$ and $\gamma_5(\mathbf{c})=C_{55}$ even in the triclinic phase when adjusting the fits. The intersection of the dashed line with the temperature axis gives the temperature T_2'.

B. Transitions at T_i and T_L

1. *Longitudinal elastic constants*

It is illustrative to calculate the elastic constants in the IC phase using expression (2) for the free energy in the reciprocal space. The frozen IC wave $Q_1^s(k_0)\equiv Q_{\rm IC}$ (the higher harmonics are neglected in this paper; note that $Q_{\rm IC}$ can be always chosen real[5]) produces new bilinear coupling terms between homogeneous strains $\varepsilon_i(k=0)\equiv\varepsilon_i$ and the soft-branch modes. Replacing in each F_i term one of the $Q_1(k)$ by its spontaneous value Q_1^s we get the coupling term

$$2F_i[Q_1^s(-k_0)Q_1(k_0)\varepsilon_i + \text{c.c}] = 2F_iQ_{\rm IC}[Q_1(k_0)\varepsilon_i + \text{c.c.}] , \quad (7)$$

where c.c. means the complex-conjugate expression. It is well known (see Ref. 5, for example) that the $Q_1(k)$ modes are no longer normal modes of the IC phase since they become coupled to $Q_1(k\pm 2k_0)$ modes. The true normal modes (near $\pm k_0$) are the amplitudon

$$a_q = \frac{1}{\sqrt{2}}[Q_1(k_0+q)+Q_1(-k_0+q)] = a_{-q}^* ,$$

and the phason

$$\varphi_q = \frac{1}{\sqrt{2}}[Q_1(k_0+q)-Q_1(-k_0+q)] = -\varphi_{-q}^* .$$

Expressing $Q_1(k_0)$ in terms of a_0, φ_0 the coupling term (7) is written as

$$2\sqrt{2}F_iQ_{\rm IC}a_0\varepsilon_i . \quad (8)$$

In general (Worlock's theorem[6]) the diagonal strains ε_i $(i=1,2,3)$ are coupled to amplitudons only.

At this point the question of which strains are coupled to phasons arises. Since the phason is directly related to the Lifshitz invariant, which, however, does not exist at $k=0$, we have to look for a coupling between Lifshitz terms at $k\neq 0$ and strains.[7] From symmetry arguments the following invariants can be derived:

$$-i\gamma_x\left[\frac{dQ_1(k)}{dx}Q_1(-k)-\text{c.c.}\right]\varepsilon_1 ,$$

$$-i\gamma_y\left[\frac{dQ_1(k)}{dy}Q_1(-k)-\text{c.c.}\right]\varepsilon_6 ,$$

$$-i\gamma_z\left[\frac{dQ_1(k)}{dz}Q_1(-k)-\text{c.c.}\right]\varepsilon_5 .$$

From these terms we finally get

$$\sqrt{2}\gamma_x Q_{\text{IC}} q_x[\varphi_{q_x}\varepsilon_1(-q_x)+\text{c.c.}] ,$$

$$\sqrt{2}\gamma_y Q_{\text{IC}} q_y[\varphi_{q_y}\varepsilon_6(-q_y)+\text{c.c.}] ,$$

$$\sqrt{2}\gamma_z Q_{\text{IC}} q_z[\varphi_{q_z}\varepsilon_5(-q_z)+\text{c.c.}] .$$

Since no important anomalies of C_{11}, C_{55}, C_{66} have been observed in the IC phase (see Paper I), we shall not consider these terms any more.

Using the coupling term (7) we can calculate C_{ii} in the IC phase and we get the usual formula by linearizing the equation of equilibrium in the presence of a stress σ_i:

$$C_{ii}=C_{ii}^0-\frac{(2\sqrt{2}F_i Q_{\text{IC}})^2}{\omega_a^2(q=0)} \quad (i=1,2,3) , \tag{9}$$

where the amplitudon frequency at $q=0$ is given by

$$\omega_a^2=6B_1 Q_{\text{IC}}^2 \tag{10}$$

and the static value of the Fourier component of the order parameter in the IC phase is found as

$$Q_{\text{IC}}^2=\frac{a_1(T_i-T)}{3B_1-4K} \tag{11}$$

[see (A8) for the definition of K]. Clearly, expression (9) is the same as the one obtained using the continuous model in real space [see (A7b)].

For the transition at T_L, the elastic constant C_{22} (Fig. 2), as measured by ultrasonic propagation, satisfactorily fits the model: one observes a jump which provides a rough evaluation of F_2^2/B_1 ($\approx$0.8–1.0 GPa). Concerning ε_1, it is very weakly coupled to the order parameter. The behavior of C_{33}, as discussed in Paper I, is less clearly understood. The linear quadratic coupling term is negligible; there is a change of slope below T_L but, due to morphic monoclinic effects, its value cannot be precisely derived from the experimental data; anyway, we think that there is a significant contribution of an additional biquadratic term ($GQ_1^2\varepsilon_3^2$) which was not considered in expression (1). In spite of the low frequency involved in ultrasonic experiments, the static treatment does not hold around T_i, mainly due to the fluctuations which will be discussed in Sec. IV. Concerning the Brillouin spectra, which are related to significantly higher frequencies, they have to be described, around T_L as well as around T_i, within the frame of a dynamic model, as presented in Sec. IV.

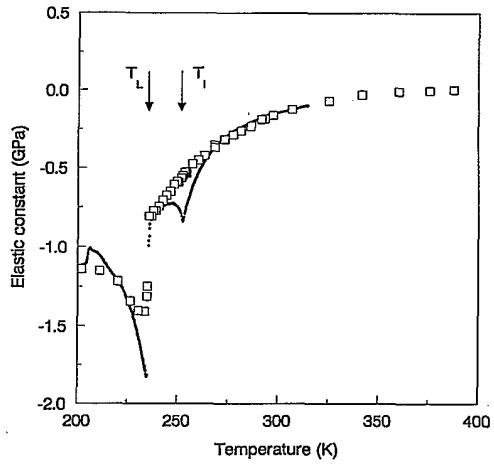

FIG. 2. γ_2 ($=C_{22}$ above T_L) versus temperature after removing its regular variation. We suppose that this variation can be obtained by a linear extrapolation of C_{22} ($T>350$ K) to the whole temperature interval studied. (●) Ultrasonic data. (□) Brillouin data.

2. C_{44}

In order to calculate C_{44} the bilinear coupling terms are found from (2) in a similar way as for C_{22}. Above T_i they reduce to $fQ_1(k=0)\varepsilon_4$, which provides for C_{44} in phase I,

$$C_{44}=C_{44}^0-\frac{f^2}{a_1(T_1-T)} . \tag{12}$$

In the IC phase the bilinear coupling is written as

$$(f+6\lambda_1 Q_{\text{IC}}^2)Q_1(k=0)\varepsilon_4+3\lambda_1 Q_{\text{IC}}^2[Q_1(2k_0)\varepsilon_4+\text{c.c.}] . \tag{13}$$

It should be pointed out that the modes $Q_1(k=0)$ and $Q_1(2k_0)$ are coupled in the IC phase. However, we shall neglect this coupling, assuming that these modes are well frequency separated (see Fig. 3). In other words we do not introduce phasons and amplitudons for such large q as $\pm k_0$. Using (13) we get for C_{44} the formula

$$C_{44}^{\text{IC}}=C_{44}^0-\frac{(f+6\lambda_1 Q_{\text{IC}}^2)^2}{\omega_{\text{IC}}^2(k=0)}-2\frac{(3\lambda_1 Q_{\text{IC}}^2)^2}{\omega_{\text{IC}}^2(2k_0)} , \tag{14}$$

where the ω_{IC} are renormalized Q_1-mode frequencies in the IC phase. They are equal to

$$\omega_{\text{IC}}^2(k)=\omega_1^2(k)+(6B_1-4K)Q_{\text{IC}}^2 . \tag{15}$$

Let us note that this expression is derived from a development of $\omega_1^2(k)$ around $k=0$ and consequently its validity for $\omega_1^2(2k_0)$ is questionable. Nevertheless, it is reasonable to suppose [as Eq. (15) suggests] that the second term in (14) is more important than the third one. Just below T_i this term decreases since $|f|$ is significantly larger than $6|\lambda_1|Q_{\text{IC}}^2$ and since $\omega_{\text{IC}}^2(k=0)$ increases; it reaches a minimum in the temperature range when $6\lambda_1 Q_{\text{IC}}^2$ becomes comparable with f and then it may

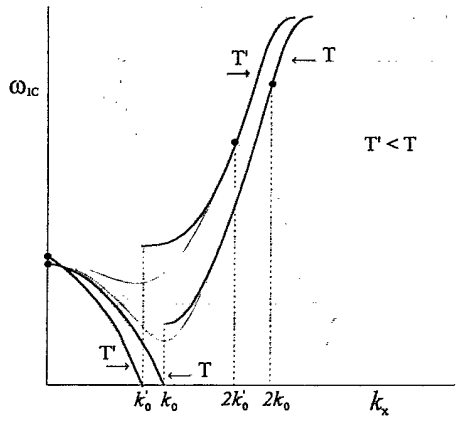

FIG. 3. Schematic illustration of amplitudon and phason dispersion curves (solid lines) at two different temperatures T and T' ($T_L < T' < T < T_i$). The dotted lines represent the soft branch $Q_1(k)$ without coupling between modes due to the frozen IC wave. Note that the frequency of the $Q_1(2k_0)$ mode decreases with decreasing temperature.

cause a decrease of C_{44}. Note that a term of this type persists in the monoclinic phase below T_L.

The third term in (14) represents the "amplitudon" contribution and could contribute to the decrease of C_{44} since $\omega_{IC}^2(2k_0)$ may decrease:[8] one observes[9] experimentally that the incommensurate wave vector k_0 decreases when the temperature decreases; the result is that ω_{IC} decreases due to the decrease of k_0 when approaching T_L (see Fig. 3). The temperature dependence does not follow from our model and we take it as an experimental fact.

There is no such third term below T_L. In fact C_{44} in the C phase is given by the formula

$$C_{44}^C = C_{44}^0 - \frac{(f+3\lambda_1 Q_C^2)^2}{\omega_C^2(k=0)}, \qquad (16)$$

where the renormalized frequency ω_C and the spontaneous value of $Q_1^s \equiv Q_C$ in the C phase are equal to

$$\omega_C^2 = \omega_1^2 + (3B_1 - 2K - 6\Lambda)Q_C^2; \quad Q_C^2 = \frac{a_1(T_1' - T)}{B_1 - 2K - 4\Lambda}, \qquad (17)$$

where $\Lambda = \lambda_1 f / C_{44}^0$. The second- and higher-order terms in λ_1 were neglected. Like the second term in (14), expression (16) explains the decrease of C_{44} in the monoclinic phase.

Since the Brillouin data deeply differ from the ultrasonic results, we assume that a comparison of the experimental measurements with the above model has to be restricted to the ultrasonic properties which are expected to correspond to the static approximation; the Brillouin spectra will be interpreted in Sec. IV within the framework of a dynamic treatment. Qualitatively the ultrasonic data follow the predictions of the static model: in the IC phase one has to take into account the λ_1 contribution in (14) which can explain the observed maximum of C_{44} between T_L and T_i. The vanishing of the third term in (14) in the C phase is presumably responsible for the upward jump at T_L.

Quantitatively, if one assumes that the static behavior of C_{44} can be deduced from the ultrasonic data, it is possible to fit its temperature variation with a value of T_1' lying between T_L and T_i [as expected in the absence of additional terms in (1) which will be discussed in Sec. IV]. Namely, satisfactory agreement [see Fig. 4(a)] is obtained for $T_1' \lesssim 236$ K and consequently $(K+2\Lambda)/B_1 \gtrsim 0.495$, a value very near the upper limit (0.5) above which the monoclinic phase is unstable [in the absence of additional terms in (1)]; on the other hand, assuming that K is the leading term, a strong linear-quadratic coupling between ε_2 and Q_1 would result and, consequently, this would induce at T_L a jump in C_{22} slightly larger than the one observed through ultrasonic measurements. However, one cannot expect a quantitative agreement for the value of this jump since the influence of fluctuations has been neglected.

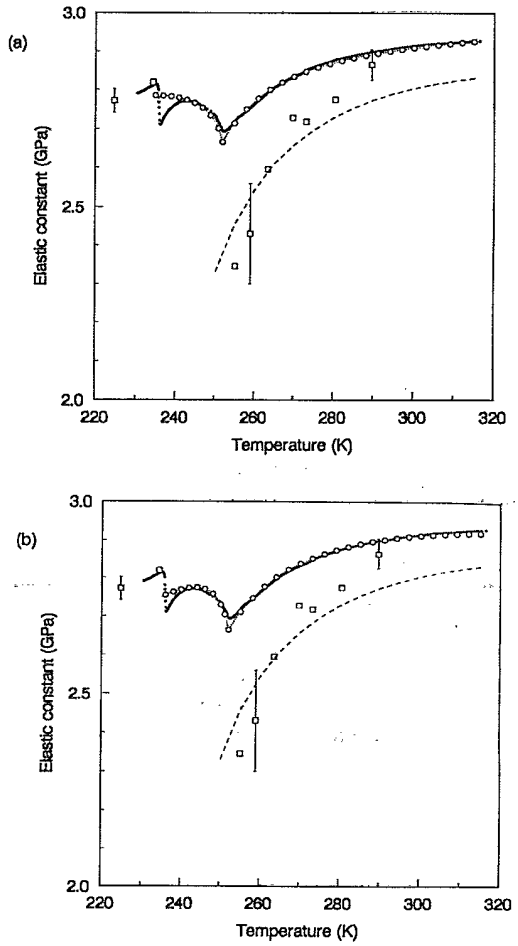

FIG. 4. Fits of the ultrasonic and Brillouin data related to γ_4(**b**). (●) ultrasonic data; (○) Fit derived from the static model; (□) Brillouin data; the dashed line corresponds to the maxima of the Brillouin lines derived from the dynamic model. The list of the "static" (T_1', f^2/a_1) and the "dynamic" (α, τ_0) parameters corresponding to (a) and (b) is given in Fig. 5.

In Fig. 4 the simulation of the variation of C_{44} versus temperature in the IC phase is given only as an example to illustrate the above qualitative interpretation. The fit is based on expression (14) without the last term and is then poorer than in phase I, especially near T_L. In fact, the contribution of this term is not known because we have no experimental information about $\omega_{IC}(2k_0)$. In addition, in order to be able to make quantitative conclusions concerning the IC phase, a more complicated treatment taking into account the experimentally observed hysteresis[8] should be employed.

Before discussing an alternative interpretation concerning the behavior of C_{44} (see at the end of Sec. IV), let us notice that in K_2SeO_4 ultrasonic data concerning the appropriate elastic constant also show less pronounced softenings than the corresponding Brillouin spectra.[14] The authors of Ref. 14 suggest that this is due to misorientations of microdomains, which would lead to a modified effective ultrasonic velocity (averaged over the whole sample studied) while the local Brillouin spectra are less sensitive to these misorientations. In our case such an explanation cannot be retained: the local disorientations do not exceed 1° and, then, it can be easily shown that the velocities do not suffer significant variations due to misorientations. However, the ultrasonic results can be affected by various defects, including domain walls between domains showing slightly different orientations.

IV. FREQUENCY DEPENDENCE OF THE ELASTIC CONSTANTS

In order to explain the large differences of the elastic constants C_{22}, C_{44} deduced from ultrasonic and Brillouin measurements in the incommensurate sequence, the dynamics of the order parameter Q_1 should be taken into account. We start with C_{44} in the parent phase above T_i. The form of the Brillouin line (see Fig. 9 in Paper I) suggests that the soft mode Q_1 is of the relaxation type, owing to a dynamic orientational disorder of $CdBr_4$ tetrahedra.[2] Using (2) we can write down two coupled equations of motion [Landau-Khalatnikov theory (LK)[10]]. As an example, for a propagation along y in phase I one writes:

$$\frac{\rho}{k_y^2}\ddot{\varepsilon}_4(k_y)+C_{44}^0\varepsilon_4(k_y)+fQ_1(k_y)=\sigma(k_y,t)\ , \tag{18a}$$

$$\Gamma\dot{Q}_1(k_y)+\frac{\Gamma}{\tau_1(k_y)}Q_1(k_y)+f\varepsilon_4(k_y)=0\ , \tag{18b}$$

where ρ is the mass density, $\sigma(k_y)$ is the Fourier component of the stress conjugate to ε_4, Γ is a damping constant, and the relaxation time $\tau_1(k_y)$ is equal to $\Gamma/\omega_1^2(k_y)$. The damping constant of the acoustic wave has been neglected. The effective "ultrasonic" elastic constant $C_{44}(k_y,\omega)\equiv C'_{44}-iC''_{44}$ is given by the well-known[11] Debye-type relaxation formulas:

$$\begin{aligned} C'_{44}&=C_{44}^0-\frac{\Delta C(k_y)}{1+\tau_1^2(k_y)\omega^2}\cong C_{44}^0-\frac{\Delta C}{1+\tau_1^2\omega^2}\ ,\\ C''_{44}&=\frac{\Delta C(k_y)\tau_1(k_y)}{1+\tau_1^2(k_y)\omega^2}\omega\cong\frac{\Delta C\tau_1}{1+\tau_1^2\omega^2}\omega\ , \end{aligned} \tag{19}$$

where $\tau_1(k_y)\cong\tau_1=\Gamma/\omega_1^2(0)$, and $\Delta C(k_y)=(f^2/\Gamma)\tau_1(k_y)\cong\Delta C=(f^2/\Gamma)\tau_1$. Below T_i obviously the same dynamic factor $(1+i\tau\omega)^{-1}$ appears in the second and in the third term of (14) with a corresponding renormalized relaxation time $\tau_{IC}=\Gamma/\omega_{IC}^2$. We do not present these formulas explicitly since the ultrasonic data can be understood qualitatively within the static approximation. As for the interpretation of the light scattering by the shear wave ε_4, a more careful analysis will be presented below.

Coming back to C_{22}, the LK theory leads to the usual result for the incommensurate sequence:

$$C_{22}=C_{22}^0,\quad T>T_i\ , \tag{20a}$$

$$C_{22}=C_{22}^0-\frac{(2F_2Q_{IC})^2}{\omega_a^2(1+i\omega\tau_a)},\quad T_L<T<T_i\ , \tag{20b}$$

$$C_{22}=C_{22}^0-\frac{(2F_2Q_C)^2}{\omega_C^2(1+i\omega\tau_C)},\quad T<T_L\ , \tag{20c}$$

where $\tau_a=\Gamma/\omega_a^2$, $\tau_C=\Gamma/\omega_C^2$ [see formulas (10) and (17) for ω_a^2 and ω_C^2, respectively]. Focusing at the transition into the IC phase, the absence of any pronounced anomaly in the Brillouin-scattering data (see Fig. 2) can be explained if one assumes that at Brillouin frequencies $\omega\tau_a\gg1$ over a wide temperature interval below T_i (10 K or more). However, the shape of the anomaly observed using ultrasonic measurements does not show the steplike jump expected in the static limit. On the other hand, the Brillouin spectra as well as the ultrasonic results show a pretransitional softening of C_{22} above T_i. As usual, a satisfactory interpretation has to include fluctuations. Recently, a consistent perturbation theory of elastic anomalies due to the order-parameter fluctuations has been worked out.[12] Using the results of this theory, we find for $C_{22}(\omega,k\cong0)$ above T_i (in the low-frequency limit):

$$\begin{aligned} C_{22}(\omega)\cong C_{22}^0&-\frac{F_2^2k_BT_i}{16\pi|C_x|^{3/2}[a_1(T-T_i)]^{1/2}}\\ &\times\left\{1-\frac{1}{32}\frac{\Gamma^2\omega^2}{[a_1(T-T_i)]^2}\right.\\ &\left.+i\frac{1}{8}\frac{\Gamma\omega}{a_1(T-T_i)}+\cdots\right\}. \end{aligned} \tag{21}$$

According to this formula C'_{22} should decrease when approaching T_i, as observed. The decrease has to be more pronounced for ultrasonic data (which essentially correspond to $\omega=0$) than for Brillouin results, as experimentally verified.

Below T_i, for an order-disorder system, the fluctuations can be accounted for simply by taking in the LK formula (20b) a non-mean-field temperature dependence of the order parameter, i.e.,

$$Q_{IC}^2\to\tilde{Q}^2=\frac{a_1(\tilde{T}_i-T)}{3B_1-4K}+\kappa\sqrt{\tilde{T}_i-T}\ ,$$

where the renormalized (experimental) phase-transition temperature is $\tilde{T}_i = T_i - \Delta$ (Δ and κ are some positive constants).[12] This does not disagree with the smearing of the jump observed by Brillouin scattering, which only results from the large value of $\omega\bar{\tau}_a$ (where $\bar{\tau}_a$ is the appropriately renormalized relaxation time). However, the C_{22} behavior derived from ultrasonic propagation is not completely understood: on the one hand, the remaining discrepancies can be due to the fact that the above model does not take into account the critical fluctuations and, consequently, cannot hold very near T_i; these critical fluctuations could be responsible for the absence of a jump of C_{22} at T_i in ultrasonic studies. On the other hand, below $\tilde{T}_i$ the "ultrasonic" C_{22} slightly increases (see Fig. 11 in Paper I). It is well known[13] that such an increase might be due to the sixth-order term $\frac{1}{6}DQ_1^6$ which should be added to (1).

The absence of any pronounced anomaly of C_{22} in the Brillouin scattering (see Fig. 6 in Paper I) throughout the IC phase suggests that the dynamics of the order parameter is very slow, i.e., $\omega\tau_a = \omega\Gamma/\omega_a^2(q=0) \gg 1$ [see (20b)]. On the other hand, concerning the behavior of C_{22} near T_L, the Brillouin results markedly differ from the ultrasonic data (see Figs. 6 and 11 in Paper I): (i) the downward jump of the static C'_{22} is significantly smaller when measured by Brillouin scattering than by ultrasonic propagation; (ii) in a large temperature interval below T_L, an increase of the Brillouin linewidth is observed, while there is no enhancement of the damping for the ultrasonic propagation. A natural explanation of these observations would be that below T_L the relaxation frequency τ_C^{-1} of the order parameter $Q_1(k=0)$ is already much greater than the ultrasonic frequency but still comparable with the Brillouin frequency (we recall that the C phase would set in at $T'_1 > T_L$ if there were no IC phase). The full width at half maximum (FWHM) of the Brillouin lines related to C_{22} is significantly larger just below T_L than just above: in the LK approximation this suggests that, at T_L, $\tau_C \ll \tau_a$. To allow this conclusion it can be shown that the value of $(K+2\Lambda)/B_1$ has to be very close to 0.5, in agreement with the evaluation derived from the C_{44} behavior in the preceding section.

An alternative hypothesis allowing $\tau_C \ll \tau_a$ assumes that the virtual ferroelastic phase transition is of the first order and takes place at a temperature $T_{tr} > T'_1$. Obviously, in such a case, the spontaneous value Q_C at T_L will be larger, leading thus to a further decrease of $\tau_C(T_L)$. In addition such a hypothesis would provide a very good fit for the static variation of C_{44} versus temperature measured by ultrasonic propagation (see Sec. III) allowing T'_1 to be smaller than T_L. Moreover, a first-order transition at T_{tr} induced by the above-mentioned $\frac{1}{6}DQ_1^6$ ($D>0$) term, is expected to give rise at T_L to an upward jump for any diagonal elastic constant related to a strain bilinearly coupled to the order parameter, which is the case for C_{44}: such a jump is indeed observed experimentally.

There is indirect experimental evidence that the ferroelastic phase transition is of first order. If the temperature dependence of C_{55} in the monoclinic phase is extrapolated into the region of the IC phase [see Fig. 12(b) of I], C_{55} is found to reach its value C_{55}^0 above T_i. This disagrees with the fact that the temperature anomaly of C_{55} is governed by the morphic coupling constant gQ_C, which is zero above T_i (otherwise the ferroelastic phase would set in at higher temperature than the IC phase, which is not the case). Clearly, this discrepancy would be removed if the hypothetical ferroelastic phase transition were of first order.

In order to get a first-order phase transition in our model we need B_1 in (1) to be negative. More precisely, various coupling terms renormalize B_1 into B_{1IC} and B_{1C} in the incommensurate and commensurate phase, respectively. To ensure a first-order (virtual) phase transition at T_{tr} and a second-order phase transition at T_i, B_{1C} has to be negative and B_{1IC} has to be positive. B_{1C} and B_{1IC} respectively are expressed as:

$$B_{1C} = B_1 - 2K - 4\Lambda \ ,$$

$$B_{1IC} = B_1 - \tfrac{4}{3}K \ .$$

There are still two fourth-order terms ($\lambda_2 Q_1^2\varepsilon_4^2$, $\lambda_3 Q_1\varepsilon_4^3$) which have not been written in expression (1) and which, in the same way as $\lambda_1 Q_1^3\varepsilon_4$, can contribute in the C phase but do not contribute in the IC phase because $\varepsilon_4(k_x)\equiv 0$. These terms and the difference between the contributions of K in the IC and the C phases may allow the conditions $B_{1C}<0$ and $B_{1IC}>0$ to be realized.

Shape of the C_{44} Brillouin line

We shall now investigate the spectral density of the scattered light $S(k,\omega)$ due to the strain wave ε_4 propagating in the **k** direction (for example along the **b** axis as discussed in Sec. III, but in order to simplify the expressions we omit the index y of the wave vector). It is well known (see Ref. 15, for example) that

$$S(k,\omega) \propto \langle |\Delta\epsilon_{ij}(k,\omega) e_{I,i} e_{S,j}|^2 \rangle \ ,$$

where $\mathbf{e}_I, \mathbf{e}_S$ are the unit polarization vectors of incident and scattered light, respectively, $\mathbf{k} = \mathbf{k}_I - \mathbf{k}_S$, $\langle \cdots \rangle$ denotes a thermal average, and $\Delta\epsilon_{ij}$ is the change of the high-frequency permittivity induced by $\delta Q_1(k,\omega)$ and $\delta\epsilon_4(k,\omega)$, i.e.,

$$\Delta\epsilon_{yz}(k,\omega) = \eta\delta Q_1(k,\omega) + \xi\delta\varepsilon_4(k,\omega) \ . \tag{22}$$

Hence

$$\begin{aligned}\langle |\Delta\epsilon_{yz}(k,\omega)|^2 \rangle = {} & \eta^2 \langle |\delta Q_1(k,\omega)|^2 \rangle \\ & + \xi^2 \langle |\delta\varepsilon_4(k,\omega)|^2 \rangle \\ & + \eta\xi \langle \delta Q_1(-k,\omega)\delta\varepsilon_4(k,\omega) + \text{c.c.} \rangle \ .\end{aligned}$$

The spectral densities of the fluctuations can be found in a usual way,[15] i.e., by solving (18a) and (18b) with a random force acting on $\delta Q_1(k)$ added to (18b) and using the fluctuation-dissipation theorem:

$$\langle|\Delta\epsilon_{yz}(k,\omega)|^2\rangle=\frac{k_BT}{\pi V}\left\{\xi^2\frac{C''_{44}\omega}{(-\rho\omega^2/k^2+C'_{44})^2+C''^2_{44}}+\eta^2\frac{\tau_1^2(k)/\Gamma}{[1+(f^2\tau_1(k)/\Gamma)(\rho\omega^2/k^2-C^0_{44})^{-1}]^2+\tau_1^2(k)\omega^2}\right.$$
$$\left.+2\eta\xi\frac{(f\tau_1^2(k)/\Gamma)}{(\rho\omega^2/k^2-C^0_{44})\{[1+(f^2\tau_1(k)/\Gamma)(\rho\omega^2/k^2-C^0_{44})^{-1}]^2+\tau_1^2(k)\omega^2\}}\right\}. \quad (23)$$

In (23), $\tau_1(k)=\Gamma/\omega_1^2(k)$ can be replaced by $\tau_1=\Gamma/\omega_1^2(0)$. The spectral density can be now rewritten into a compact form which is more convenient for further calculations:

$$S(k,\Omega)\propto k_BT\frac{\tau_0}{\Gamma}\left[\frac{\xi f}{C^0_{44}}\right]^2\frac{[1-\alpha(1-\Omega^2)]^2}{[\tau_0/\tau_1(T)(1-\Omega^2)-1]^2+\omega_B^2\tau_0^2\Omega^2(1-\Omega^2)^2}. \quad (24)$$

Here, $\Omega^2=\omega^2/\omega_B^2$ (where $\omega_B^2=k^2C^0_{44}/\rho$ is the squared frequency of the acoustic phonon far above the transition temperature), $\tau_0^{-1}=a_1\Delta T_1/\Gamma$, $\Delta T_1=T'_1-T_1=f^2/(a_1C^0_{44})$, and $\alpha=\eta C^0_{44}/\xi f$. Expression (24) holds for phases I and III but, indeed, some parameters have to be renormalized in the monoclinic phase: $\tau_1(T)\rightarrow\tau_C(T)=\Gamma/\omega_C^2$, $f\rightarrow f+3\lambda_1Q_C^2$. It can also be used in the IC phase with $\Gamma/\tau_{IC}=\omega_{IC}^2$, if one neglects the $\lambda_1Q^3\varepsilon_4$ coupling term. A more complicated expression would be obtained when taking into account λ_1; however, the main effect of λ_1 is supposed to renormalize f in (24) ($f\rightarrow f+6\lambda_1Q_{IC}^2$).

Usually, only the first term in (23) is taken into account;[16] it corresponds to the $\alpha\rightarrow 0$ limit in (24). However, the case $\alpha\neq 0$ which describes two interfering contributions has been previously considered in analogous situations of coupled variables: this is the case for instance for the analysis of the Brillouin scattering in KH_2PO_4 near its ferroelectric-paraelectric transition.[17,18]

Thus, the predicted variation of the shape of the Brillouin spectrum in phase I is completely defined by five independent parameters which, for instance, may be chosen as T_1, T'_1, ω_B, τ_0, and α. As discussed in Sec. III, the ultrasonic data give access to ω_B, T_1, and T'_1.

Coming back to our Brillouin results in phase I, the observed spectra satisfactorily agree with the above model (see Fig. 5), if one excludes from their analysis the very low frequency range where the experimental conditions do not allow us to subtract precisely the contribution of the elastically scattered light. Using $T_1=234$ K, $T'_1=236$ K, and $C^0_{44}=3.0$ GPa, which give a good account of ultrasonic results, the best fit for Brillouin scattering is obtained for $\tau_0=2.4\times10^{-10}$ s, which provides a value of $\omega_B\tau_1$ equal to 0.66 at T_i [Fig. 5(a)]. With these conditions and taking $1/\alpha\approx-0.01$, the spectra are reasonably reproduced by expression (24) convoluted with the instrumental function. An attempt to fit the spectra with $\alpha=0$ would provide a significantly poorer fit, as illustrated in Fig. 6: taking into account only the strain autocorrelation function always gives rise to a broadening of the high-frequency wing of the Brillouin line, which is not observed in our experiments; the Q-Q and the Q-ε correlation functions can delete this broadening and even give rise to a minimum of $S(k,\omega)$, at a frequency above the maximum of the line, as experimentally observed below about 265 K in our spectra (see Fig. 5).

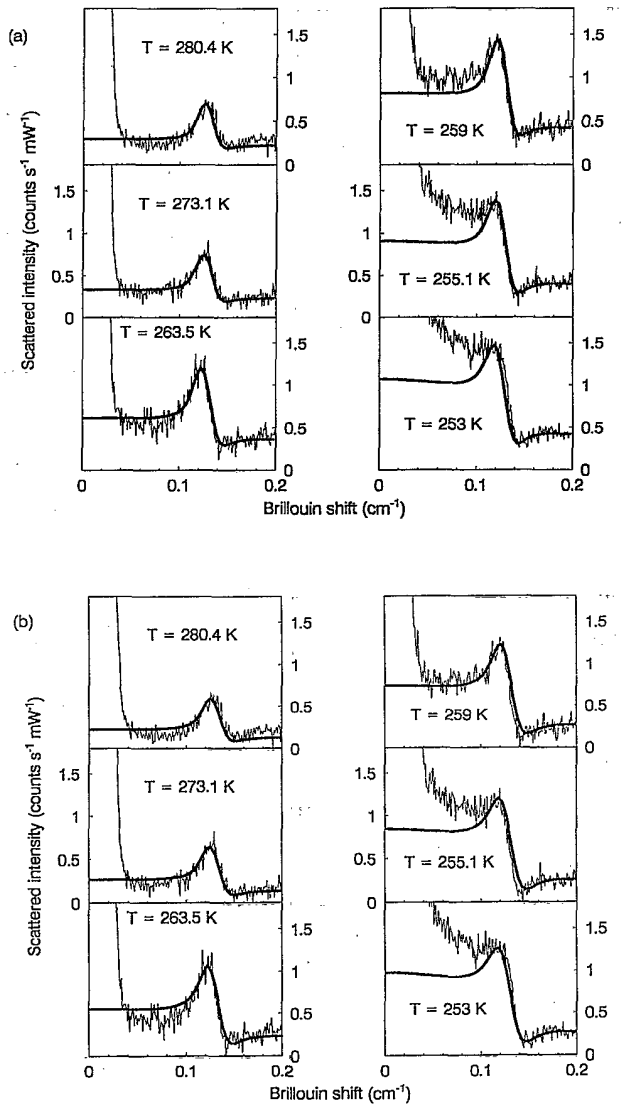

FIG. 5. Thin lines: Brillouin spectra corresponding to $\gamma_4(\mathbf{b})$ in the *Pnma* phase; bold lines: fits obtained using formula (24) convoluted with the instrumental function (Gaussian function, FWHM=0.018 cm^{-1}). The "static" parameters (T'_1, f^2/a_1) of (a) and (b) correspond to the parameters of Figs. 4(a) and 4(b), respectively. Parameters of fits: (a) $T'_1=236$ K, $f^2/a_1=6.0$ GPa K, $1/\alpha\approx-0.01$, $\tau_0=2.4\times10^{-10}$ s; (b) $T'_1=230$ K, $f^2/a_1=13.5$ GPa K, $1/\alpha\approx-0.01$, $\tau_0=1.8\times10^{-10}$ s.

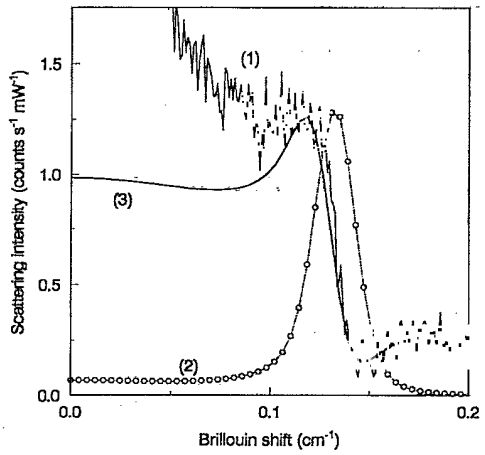

FIG. 6. Comparison of the fits of the asymmetric Brillouin spectrum near the $Pnma \leftrightarrow$IC phase transition ($T=253$ K). (1) experimental; (2) curve obtained when taking into account the ε_4-ε_4 autocorrelation function only ($\alpha=0$); (3) fit involving the contribution of the order parameter to the light scattering ($1/\alpha=-0.01$, $\tau_0=1.8\times10^{-10}$ s). Both fits are based on the static parameters which are obtained from the ultrasonic data ($T_1'=230$ K, $T_1=225.5$ K).

Moreover, the hypothesis of a non-negligible contribution of the relaxator is enforced by an independent experiment: this relaxator is observed in the geometry $x\,(yz)\bar{x}$ (see Fig. 4 in I), a configuration where the propagating phonons are not related to ε_4, and where, consequently, only an η-like term can contribute to the light scattering. There is a large uncertainty in determining T_1' from ultrasonic data, and equivalently good fits may be obtained for any value of T_1' lying in the (230, 236) K interval. We have shown that a virtual first-order ferroelastic phase transition can exist at T_{tr} between T_L and T_i, and consequently T_1' can be smaller than T_L. This last hypothesis was supported in the preceding subsection by various features of the behavior of C_{22} and C_{55}. Using $T_1'=230$ and $T_1=226$ K, the best fit for the Brillouin spectra is obtained for $\tau_0=1.8\times10^{-10}$ s (and consequently $\omega_B\tau_1=0.73$ at T_i) and $1/\alpha\approx-0.01$. Figure 5(b) shows that the agreement is about the same as in the case where T_1' exceeds T_L. In conclusion, it is not possible to decide whether the virtual I$\leftrightarrow$III transition is of first or of second order in view of the C_{44} Brillouin-line behavior, but, in both cases, the orders of magnitude of τ_0 are the same and the contributions of the relaxator to the scattering do not differ much.

Below T_L, in the C phase, $1/\tau_C$ is large enough to give rise to a symmetric sharp Brillouin line, the frequency of which is simply given by the static model used for the analysis of the ultrasonic data. In the IC phase $\omega_B\tau_{IC}$ remains in the vicinity of 1: between T_L and T_i, the shape of the Brillouin spectra does not qualitatively vary; the spectra extend over a broad frequency range and their intensity is rather low; this prevented us from precise determination of the parameters involved in (24) and from a quantitative interpretation of the small temperature variation of $\omega_B\tau_{IC}$ in this temperature range.

Finally, the high scattered intensity in the very low frequency range near T_i still needs to be interpreted but, in our opinion, owing to the experimental difficulties, quantitative data cannot be easily obtained.

V. CONCLUSION

Through a detailed comparative discussion of the Brillouin and of the ultrasonic data concerning Cs_2CdBr_4 in the vicinity of its phase transitions, we have shown that most of the results can be interpreted with the aid of the previously proposed free-energy density after some minor modifications. One has to take carefully into account the two following points. (i) The coupled dynamics of the order parameter and of the strain can deeply modify the predictions of the static model, which often becomes inappropriate when analyzing the Brillouin scattering. This is the case for the incommensurate sequence in Cs_2CdBr_4 monitored by an order parameter Q_1, which appears to be a relaxator with a characteristic temperature-dependent relaxation time lying around the inverse of the Brillouin frequency in the vicinity of the I$\leftrightarrow$II transition: it strongly affects the Brillouin spectra related to the strain ε_4, which is bilinearly coupled to Q_1. (ii) The modulation of the high-frequency permittivity does not only result from the variations of the strains but can also derive from the motion of the order parameter, which gives rise to an additional contribution to the light scattering in the studied frequency range. We have shown that this happens in Cs_2CdBr_4, where the high-frequency permittivity linearly depends upon Q_1. As a result, the above-mentioned spectra (Fig. 5) depend upon three correlation functions (shortly labeled Q_1-Q_1, ε_4-ε_4, and Q_1-ε_4) and we have found expressions which reasonably fit our experimental data.

Throughout this paper, we have been able to derive the order of magnitude of a number of parameters which appear in the free-energy density. However, it is clear that only semiquantitative evaluations can be made, since the expression for the free energy is necessarily truncated. We have shown that the influence of terms neglected in a first approach can be significant but also that nearly equivalent fits can be obtained with slightly different manifolds of parameters when many terms are retained in the free energy. As an example, we demonstrated that one cannot unambiguously decide if the virtual $Pnma \leftrightarrow P2_1/n\,11$ phase transition is a first-order one or a second-order one, but that in any case the pertinent terms have values near the limits separating these two situations. To improve the overall understanding of the phase transitions in Cs_2CdBr_4 ultrasonic and Brillouin studies under hydrostatic pressure or uniaxial stress would indeed be helpful.

Another limitation for a complete quantitative interpretation is related to the fluctuations. On one hand, it has been shown in this paper that they deeply influence the experimental results but, on the other hand, their predicted effects can be treated only by using very simplifying approximations.

Finally, some parts remain to be elucidated, for which,

up to now, we have only qualitative proposals. They concern the hysteresis effects, which are mainly observed through ultrasonic measurements, and the low-frequency quasielastic scattering in the temperature range extending over the IC phase and just above. These are probably due to defects, which were not considered in our theoretical approach, since we have only rather indirect experimental evidence of their presence in the crystals studied.

ACKNOWLEDGMENTS

We thank Dr. J. Raphanel of Laboratoire PMTM who suggested improvements for the manuscript. One of us (V.D.) thanks Université Paris-Nord for providing him a stay in the Laboratoire PMTM.

APPENDIX

We denote by Q_1^s and ε_i^s the static equilibrium values of the order parameter and of the strains ($Q_2^s=0$ in the IC phase). Applying a homogeneous constraint σ_i (or, more precisely, when dealing with the elastic waves: σ_i is constant in a volume Ω much greater than the primitive cell volume but the characteristic dimensions of Ω are much smaller than the wavelength of the elastic wave), the static values of Q_1, Q_2, and ε_i change:

$$\begin{aligned}
&\tilde{\varepsilon}_i=\varepsilon_i^s+\delta\varepsilon_i \\
&\tilde{Q}_1=Q_1^s+\delta Q_1 \\
&\quad=\tilde{q}_{0,1}+\tilde{q}_{1,1}\cos kx+\tilde{q}_{2,1}\cos 2kx+\tilde{q}_{3,1}\cos 3kx+\cdots \\
&\quad=\delta q_{0,1}+(q_1^s+\delta q_{1,1})\cos kx+\cdots \\
&\tilde{Q}_2=\delta Q_2=\tilde{q}_{0,2}+\tilde{q}_{1,2}\cos kx+\cdots \\
&\quad=\delta q_{0,2}+\delta q_{1,2}\cos kx+\cdots .
\end{aligned} \tag{A1}$$

$\tilde{q}_{i,n}$ are x independent. The values $\delta\varepsilon_i$ and δq_i are chosen to minimize the free energy of the crystal. C_{ij} is defined as

$$C_{ij}=\frac{d\sigma_i}{d(\delta\varepsilon_j)} ,$$

where the derivatives are calculated for vanishing values of the strains $\delta\varepsilon_\alpha$ ($1\le\alpha\le 6$). Using the relation between σ_i and the strains,

$$\begin{aligned}
\sigma_i&=\frac{1}{\Omega}\int_\Omega\frac{\partial F(\tilde{\varepsilon}_\alpha,\tilde{q}_{\beta,n})}{\partial\tilde{\varepsilon}_i}dV \\
&=\frac{1}{\Omega}\int_\Omega\frac{\partial F(\varepsilon_\alpha^s+\delta\varepsilon_\alpha,q_{\beta,n}^s+\delta q_{\beta,n})}{\partial(\delta\varepsilon_i)}dV ,
\end{aligned} \tag{A2}$$

C_{ij} is written as

$$\begin{aligned}
C_{ij}=&\frac{1}{\Omega}\int_\Omega\frac{\partial^2F(\tilde{\varepsilon}_\alpha,\tilde{q}_{\beta,n})}{\partial(\delta\varepsilon_i)\partial(\delta\varepsilon_j)}dV \\
&+\sum_k\frac{\partial(\delta q_{k,n})}{\partial(\delta\varepsilon_j)}\frac{1}{\Omega}\int_\Omega\frac{\partial^2F(\tilde{\varepsilon}_\alpha,\tilde{q}_{\beta,n})}{\partial(\delta\varepsilon_i)\partial(\delta q_{k,n})}dV .
\end{aligned} \tag{A3}$$

At equilibrium, where $[\partial/\partial(\delta q_{l,n})]\langle F(\tilde{\varepsilon}_\alpha,\tilde{q}_{\beta,n})\rangle=0$,

$$\begin{aligned}
&\left\langle\frac{\partial^2F(\tilde{\varepsilon}_\alpha,\tilde{q}_{\beta,n})}{\partial(\delta q_{l,n})\partial(\delta\varepsilon_j)}\right\rangle \\
&\qquad+\sum_k\left\langle\frac{\partial^2F(\tilde{\varepsilon}_\alpha,\tilde{q}_{\beta,n})}{\partial(\delta q_{l,n})\partial(\delta q_{k,n})}\right\rangle\frac{\partial(\delta q_{k,n})}{\partial(\delta\varepsilon_j)}=0 .
\end{aligned} \tag{A4}$$

Putting (A4) into (A3) one can obtain the general expression

$$C_{ij}=\left\langle\frac{\partial^2F}{\partial\tilde{\varepsilon}_i\partial\tilde{\varepsilon}_j}\right|_s\rangle-\sum_{\substack{k,l\\m,n=1,2}}\left\langle\frac{\partial^2F}{\partial\tilde{q}_{k,n}\partial\tilde{\varepsilon}_i}\right|_s\rangle\chi_{kl}_{mn}\left\langle\frac{\partial^2F}{\partial\tilde{q}_{l,m}\partial\tilde{\varepsilon}_j}\right|_s\rangle \tag{A5}$$

$$\chi_{kl}^{-1}{}_{mn}=\left\langle\frac{\partial^2F}{\partial\tilde{q}_{l,m}\partial\tilde{q}_{k,n}}\right|_s\rangle , \tag{A6}$$

where $\langle X\rangle$ denotes the mean value of X in volume Ω. The index s indicates that the second derivative is calculated in the equilibrium values of Q_1, Q_2, and ε_i.

As an example, we give here the variations of the C_{ii} ($i=1,2,3$) calculated using the above formulas (we have neglected the second and higher harmonics). For phase I ($T>T_i$):

$$C_{ii}^0 , \tag{A7a}$$

phase II (IC) ($T_L<T<T_i$):

$$C_{ii}^{IC}=C_{ii}^0-\frac{4F_i^2}{3B_1} , \tag{A7b}$$

phase III (C) ($T_C<T<T_L$):

$$C_{ii}^C=C_{ii}^0-\frac{2F_i^2}{B_1}\frac{(T_1'-T)}{(T_1'-T)(1-\Lambda/B_1)+[1/2-(K+2\Lambda)/B_1](T_1'-T_1)} , \tag{A7c}$$

phase IV ($T<T_C$):

$$C_{ii}^{IV}=C_{ii}^C-\frac{2H_i^2}{B_2}\frac{(T_C-T)}{(T_C-T)+(1/2-L/B_2)(T_C-T_2)} , \tag{A7d}$$

where

$$K=\sum_{i,j=1}^{3}F_i\{C_{ij}^0\}^{-1}F_j,\quad L=\sum_{i,j=1}^{3}H_i\{C_{ij}^0\}^{-1}H_j$$

($\{C_{ij}^0\}^{-1}$ are the elements of the inverted matrix of the

elastic constants); and

$$T_C = T_2 + \frac{h^2}{a_2 C_{66}^0} + \frac{(gQ_1^s)^2}{a_2 C_{55}^0}$$

is the renormalized temperature of the transition.

It is clear that all the C_{ii} $(i=1,2,3)$ have to undergo two downward jumps at T_i, T_L, and a more or less abrupt softening at T_C [it can be regarded as a jump for small $(T_C - T_2)$]. The coupling constants F_1, F_3, and H_1 can be neglected because all the observed jumps of C_{11} and C_{33} are very small (see Figs. 3 and 8 in I). In this way the expressions for K and L can be simplified. This means, for example,

$$K = F_2^2 \{C_{22}^0\}^{-1} . \tag{A8}$$

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