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# Brillouin scattering study of transverse elastic waves in the $\alpha$, incommensurate and $\beta$ phases of $AlPO_4$

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**Abstract.** Transverse and pseudo-transverse elastic waves have been studied in several scattering geometries in order to investigate the temperature dependences of $C_{66}^E$ and $C_{14}^E$ over the range 300-1100 K, including the transitions near 860 K. These results complete those on $C_{44}^E$ we have obtained in a previous work. All these constants display discontinuities at the lock-in transition. In the $\alpha$ phase, the results are analysed in term of lowest order couplings between strains ($e$) and the order parameter ($Q$). The main features are described by the lowest order biquadratic $e^2Q^2$ coupling, in particular for $C_{44}^E$ in a large temperature range. However, it appears that a contribution of the next coupling term arises for $C_{66}^E$ below $\sim$ 710 K and that the first two lowest order terms have to be taken into account even just below the lock-in transition in the case of $C_{14}^E$. The temperature dependence of $Q$ has been deduced and it can be well described in the framework of Landau's theory.

**PACS.** 64.70.Rh Commensurate-incommensurate transitions – 62.20.-x Mechanical properties of solids – 78.35.+c Brillouin and Rayleigh scattering; other light scattering

## 1 Introduction

Crystalline $SiO_2$ (quartz at room temperature) has been widely studied since it is one of the most important crystals used in industry. The ternary aluminium phosphate $AlPO_4$ (berlinite) is an interesting compound since it displays a polymorphism closely related to that of crystalline $SiO_2$. On heating, the same successive phases (quartz $\alpha$, incommensurate, quartz $\beta$, tridymite $\beta$ and cristobalite $\beta$) can be observed in both compounds [1]. At room temperature, the mechanical and electromechanical properties of $AlPO_4$ have been investigated by ultrasonic methods [2–4] and it was concluded that its performance is expected to be better than that of quartz in ultrasonic device applications [2].

Unlike the case of quartz, the elastic properties of $AlPO_4$ have been little studied above room temperature. Only a Brillouin determination of the elastic constant $C_{33}$ has been made up to the $\beta$ phase, but serious difficulties were encountered as a result of an important deterioration of the optical quality of the samples during heating [5].

Recently, we have reported a Brillouin investigation over the range 300-1100 K, including the $\alpha$-incommensurate-$\beta$ transitions near 860 K [6]. The excellent optical quality of our samples at room temperature was only slightly affected by heating. In this study, we have first focused on the elastic constants $C_{11}^D$ and $C_{33}$ for two reasons: (i) these constants can be directly obtained from the velocities of longitudinal waves, (ii) the related Brillouin lines are intense ones. We have also determined the elastic constant $C_{44}^E$, which is directly related to the velocity of a transverse wave, although the cross-section of the related line was much lower than that obtained for the longitudinal waves.

In this paper, we present further investigations mainly focused on transverse or pseudo-transverse waves in order to complete the results previously reported [6]. In spite of small cross-sections and small frequency shifts of the related lines, we have succeeded in obtaining experimental data in the same temperature range 300-1100 K. In particular, the elastic constants $C_{66}^E$ and $C_{14}^E$, which were the aim of this new study, have been measured; they are of great importance since, as $C_{44}^E$, they are expected to yield information about the order parameter.

## 2 Experimental and crystal data

Brillouin scattering experiments were performed with a pressure scanned, triple passed plane Fabry Perot interferometer (effective finesse 70, resolving power 760 000).

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The spectra are frequency checked by a Michelson interferometer in parallel. The light source is the $\lambda_0 = 514.5$ nm line of a single frequency Ar-ion laser, the frequency of which is controlled by an iodine cell.

The samples were cut from monocrystals, which were grown by the hydrothermal method as explained in [6].

At room temperature ($\alpha$ phase), $AlPO_4$ belongs to the same space group $P3_121$ as quartz. The parameters of the primitive hexagonal cell are $a = b = 4.942$ Å and $c = 10.97$ Å [2,7]. There are three formula units per unit cell, as in quartz, but the $c$-parameter is doubled due to the inequivalence of Al and P atoms.

Near 860 K, $AlPO_4$ undergoes an "$\alpha$–$\beta$" structural transition to a hexagonal phase with space group $P6_222$, which is similar to that occurring in quartz. As in this last compound [8,9], between $\alpha$ and $\beta$ phases, an inhomogeneous state was observed [10] which can be identified as an incommensurate phase [11]. This incommensurate phase extends on a wider temperature range $T_i - T_c = 3$ K than that observed in quartz (1.3 K), $T_i$ and $T_c$ being the $\beta \rightarrow$ inc. and lock-in transition temperatures respectively. The $\beta \rightarrow$ inc. transition is induced by the condensation of soft modes with wave vector $\mathbf{k}_i = \pm 0.03\mathbf{a}^*$ and equivalent by symmetry.

At room temperature, we have measured the refractive indices at $\lambda_0$ and obtained the value $n_a = 1.5276$ and $n_c = 1.5369$. The mass density, deduced from cell parameters at room temperature is $\rho = 2.618$ g cm$^{-3}$.

The elastic constants have been referred to a set of orthogonal $X$, $Y$ and $Z$ axes with $X$ and $Z$ parallel to a binary and the ternary crystallographic axes of the $\alpha$ phase, respectively.

To compute elastic constants from Brillouin shifts at any temperature, we used the room temperature values of both mass density and refractive indices. There are no data on the temperature dependences of indices and the data on lattice parameters are not sufficiently detailed in the vicinity of the transitions.

Brillouin spectra have been performed only on heating the samples in order to avoid eventual hysteresis at the transitions and optical degradation after a first heating run. Some samples break in the vicinity of the lock-in transition $T_c$ but the blocks are large enough in order that the spectra remain unaltered. The optical quality of the samples is preserved up to the highest investigated temperature. However, after cooling down to room temperature, an increase of the Rayleigh peak is generally observed together with a decrease of the Brillouin lines. Therefore, the same sample was not used in more than one heating run.

## 3 Brillouin experiments and results

### 3.1 Brillouin experiments

We used right angle scattering geometry for the experiments; in this case the velocity $V$ of an acoustic wave is related to the corresponding Brillouin frequency shift $\nu$ by:

$$V = \lambda_0 \nu / (n_i^2 + n_s^2)^{1/2}$$

where $n_i$ and $n_s$ are the refractive indices for the incident and scattered light beams respectively. The scattering geometries which have been investigated are reported in Table 1.

As recalled in reference [6], the piezoelectricity of the $\alpha$ phase introduces distinctions between elastic constants at constant electric displacement $C_{ij}^D$ and elastic constants at constant electric field $C_{ij}^E$, except for $C_{33}$. In the $\beta$ phase, this distinction only exists for $C_{44}$.

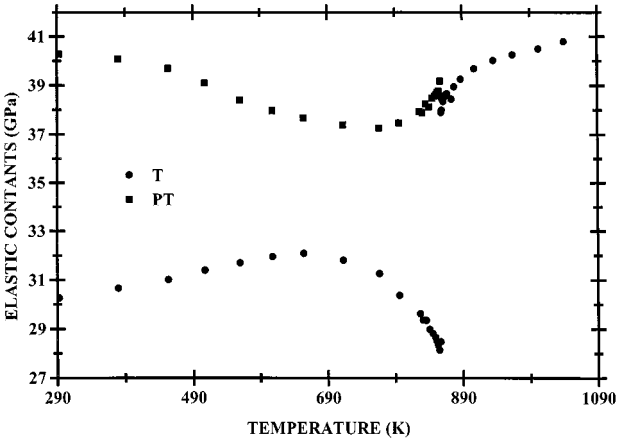



**Fig. 1.** Temperature dependence of $\rho V^2$ related to the transverse (T) and pseudotransverse (PT) waves in scattering geometries 1 and 2. The wave natures PT and T are exact in the incommensurate and $\beta$ phases; in the $\alpha$ phase, they can be considered as exact only in the vicinity of room temperature, as explained in the text.

### 3.2 Scattering geometries with acoustic wave vector parallel to Y-axis

Within harmonic elasticity, the elastic constant $C_{66}^D$ is expected to be directly obtained from the velocity of the transverse (T) wave in scattering geometry 1. In scattering geometries 1 and 2, the study of line polarizations at room temperature, which were found to agree with the expected selection rules in the $\alpha$ phase, unambiguously allows the assignment of the two weak lines which are recorded beside the intense line related to the pseudo-longitudinal (PL) wave. The T wave related to $C_{66}^D$ have the lowest frequency shift.

The temperature dependences of the "effective" elastic constants $\rho V^2$ for the T and PT (pseudo-transverse) waves are reported in Figure 1. During heating in the $\alpha$ phase, a progressive depolarization of both lines is observed. At a temperature which corresponds to $T_c$ (857 K), a result obtained by the simultaneous recording of the PL wave, the lowest frequency line abruptly disappears. Above $T_c$, the single line is found to be again full polarized and, according to the selection rules in the incommensurate and $\beta$ phases, its velocity is related to $C_{66}$.

**Table 1.** Characteristics of the investigated scattering geometries. The usual convention for wave vector and polarization direction of the incident and scattered light beams has been used. **q** is the acoustic wave vector. L, T, PL, PT are related to the nature of acoustic wave: longitudinal, transverse, pseudo-longitudinal, pseudo-transverse respectively. ($^*$) As explain in text, the line polarizations at room temperature are not preserved on heating. ($^{**}$) Within the harmonic approximation for elastic properties (no anticrossing induced by anharmonic interactions).

| | | | $\alpha$-phase | | incommensurate and $\beta$-phase | |
|---|---|---|---|---|---|---|
| scattering geometries | | Acoustic wave vector direction | Acoustic wave nature | Expression of $\rho V^2$ | Acoustic wave nature | Expression of $\rho V^2$ |
| 1 | $(-y+z)[x,-y+z](y+z)^*$ | [010] | $T^{*,**}$ | $C_{66}^{D\,**}$ | T | $C_{66}$ |
| 2 | $(-y+z)[x,x](y+z)^*$ | [010] | $\begin{cases} PL^{**} \\ PT^{*,**} \end{cases}$ | $\{C_{11}^E+C_{44}^E+ [(C_{11}^E-C_{44}^E)^2+4C_{14}^{E2}]^{1/2}\}/2^{**}$ <br> $\{C_{11}^E+C_{44}^E- [(C_{11}^E-C_{44}^E)^2+4C_{14}^{E2}]^{1/2}\}/2^{**}$ | L | $C_{11}$ |
| 3 | $(-x+y)[x+y,z](x+y)$ | [100] | $\begin{cases} T_1 \\ T_2 \end{cases}$ | $\{C_{44}^E+C_{66}^E+ [(C_{44}^E-C_{66}^E)^2+4C_{14}^{E2}]^{1/2}\}/2$ <br> $\{C_{44}^E+C_{66}^E- [(C_{44}^E-C_{66}^E)^2+4C_{14}^{E2}]^{1/2}\}/2$ | T | $C_{44}^E$ |
| 4 | $(-x+z)[(x+z),y](x+z)$ | [100] | $\begin{cases} T_1 \\ T_2 \end{cases}$ | $\{C_{44}^E+C_{66}^E+ [(C_{44}^E-C_{66}^E)^2+4C_{14}^{E2}]^{1/2}\}/2$ <br> $\{C_{44}^E+C_{66}^E- [(C_{44}^E-C_{66}^E)^2+4C_{14}^{E2}]^{1/2}\}/2$ | T | $C_{66}$ |

In the $\beta$ phase, the other T wave corresponds to $C_{44}^E$ (inactive in Brillouin scattering for this geometry) which has lower values than those of $C_{66}$ (the results for $C_{44}^E$ [6] are recalled in Figs. 3a and 3b). Therefore, it can be expected that the two modes would cross at some temperature in the $\alpha$ phase, within harmonic elasticity.

Experimentally, however, it turns out that the minimum and the maximum, occurring for $\rho V^2$(PT) and $\rho V^2$(T) respectively, obviously indicate an anticrossing-like behaviour between the two modes below $T_c$. Hereafter, the term anticrossing will be used for sake of simplicity. In fact, such an anticrossing is possible since both modes have the same irreducible representation (E) in common.

In the incommensurate and $\beta$ phases, the morphic constant $C_{14}^E$ being equal to zero (see Sect. 4), the two modes belong to different irreducible representations ($A_2$ and $E_1$). Therefore the anticrossing must disappear, the line must be full polarized (as observed) and $\rho V^2$(T) is expected to be equal to $C_{66}$. The curve obtained for $C_{66}$ above $T_c$ shows that pretransitionnal features appear over about 30 K above $T_c$ and then a linear increase with a positive slope takes place at higher temperature.

It is convenient to briefly discuss the possibility of a slight misalignment of the sample. In the $\alpha$ phase it can yield a possible explanation for the existence of a phenomenon similar to an anticrossing, *via* the appearance of non diagonal terms instead of zero ones in the Christoffel equations. In the $\beta$ phase, such a misalignment must lead to a systematic error in the measurement of elastic constant $C_{66}$; however, as emphasized in next Section 3.3, the results are in excellent agreement with those obtained in scattering geometry 4 in which another crystal cut is used. Furthermore, this hypothesis is inconsistent with the abrupt changes in line polarizations at $T_c$; above $T_c$, these polarizations agree with those which are expected in the incommensurate and $\beta$ phases in absence of any coupling. Therefore, it can be concluded that such a misalignment, which is always present even when it is small, does not give a significant contribution to the observed anticrossing.

As conclusion, it can be emphasized that scattering geometry 1 does not allow the determination of $C_{66}^D$ in the $\alpha$ phase, probably even at room temperature, owing to the anticrossing. It is interesting to note that this negative point can be avoided in the resonance methods of vibrating plates of parallelepipeds. In quartz for example [12,13], by working with high order harmonics, $C_{66}^D$ has been directly measured from the T mode which is involved in scattering geometry 1. In the same way, the constant $C_{14}^E$ cannot be obtained from the PT wave in scattering geometry 2. It can be thought that the PL wave (scattering geometry 2) would be less affected by an anticrossing with the PT and (or) T waves and then can allow the determination of $C_{14}^E$. However, this determination needs the knowledge of $C_{11}^E$, whereas only $C_{11}^D$ is directly measured [6], and the piezoelectricity correction is sufficiently significant to introduce a systematic error in $C_{14}^E$ determination.

### 3.3 Elastic constants $C_{66}^E$ and $C_{14}^E$

To determine these constants, the scattering geometries 3 and 4 have been investigated (Tab. 1). They are expected

to give the same results in the $\alpha$ phase and complementary ones in the incommensurate and $\beta$ phases. The $T_2$ line in scattering geometry 3 cannot be detected at room temperature but it appears during heating above 690 K. Then, the scattering geometries are also complementary in the $\alpha$ phase. The lines are fully polarized at room temperature, in agreement with the selection rules and no depolarization occurs during heating. The temperature dependences of $\rho V^2$ for the four lines are reported in Figure 2. An excellent agreement can be observed in the $\alpha$ phase between the results of both scattering geometries. At a temperature corresponding to the lock-in transition temperature $T_c$, as checked by the simultaneous recording of the longitudinal line associated with $C_{11}^D$, one of the two lines disappears in each scattering geometry, as expected by the selection rules if there is a vanishing of $C_{14}^E$. In fact, these disappearances can be considered as an experimental proof that $C_{14}^E$ cancels at the lock-in transition. At $T_c$, discontinuities are observed for the remaining lines. Above $T_c$, we have $\rho V^2(\mathrm{T}) = C_{44}^E$ and $\rho V^2(\mathrm{T}) = C_{66}$ in scattering geometries 3 and 4 respectively; the results for these constants are in excellent agreement with those obtained for $C_{44}^E$ in [6] and for $C_{66}$ in scattering geometry 1 as shown in Figure 3a.

In the $\alpha$ phase, the elastic constants $C_{66}^E$ and $C_{14}^E$ can be successively obtained from experimental results by:

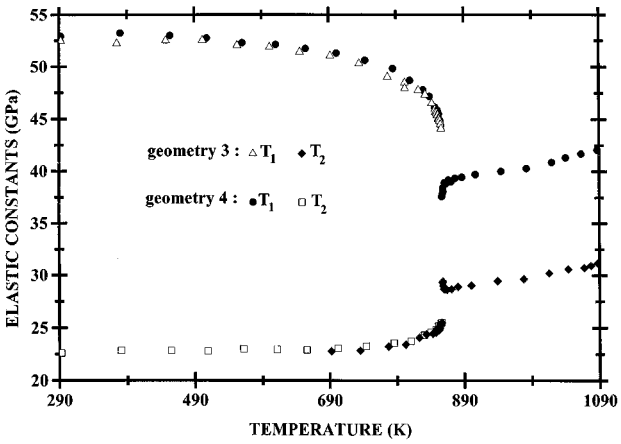
$$C_{66}^E = \rho V^2(\mathrm{T}_1) + \rho V^2(\mathrm{T}_2) - C_{44}^E$$
$$C_{14}^E = \left[(\rho V^2(\mathrm{T}_1) - \rho V^2(\mathrm{T}_2))^2 - (C_{44}^E - C_{66}^E)^2\right]^{1/2}/2$$

making use of values of $C_{44}^E$ determined in [6]. The accuracies are estimated to 5% for $C_{66}^E$ and 7% for $C_{14}^E$.

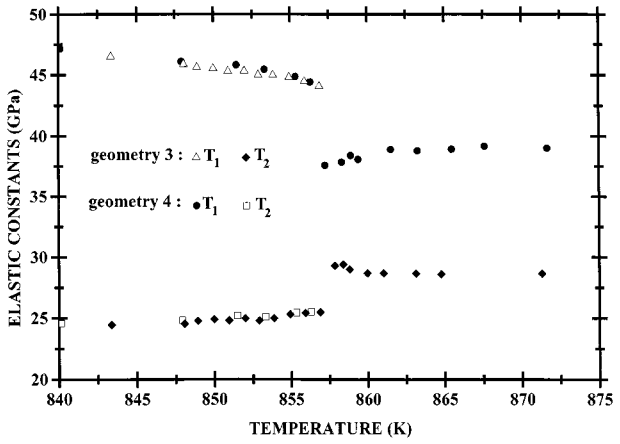
The complete results for $C_{66}^E$ over the temperature range 290-1100 K and the results for $C_{14}^E$ in the $\alpha$ phase are reported in Figures 3 and 4. In Figure 3, we have also reported the curved obtained for $C_{44}^E$ in [6]. In the $\alpha$ phase, $C_{66}^E$ exhibits a non-linear increase up to $T_c$, where a slight discontinuity occurs. This behaviour of $C_{66}^E$ in the $\alpha$ phase qualitatively resembles that of quartz [12,14]. In this compound, the investigations have been generally made either only in the $\alpha$ phase, or only above $T_c$. To our knowledge, only one recent investigation has been performed through $T_c$ [15]; a small discontinuity is observed but the evolution below $T_c$ disagrees with previous results [12,14].

In $AlPO_4$, above $T_c$, a pretransitionnal evolution appears near $T_c$ followed by a linear increase, as already described. It is difficult to compare with the case of quartz since very few results are available in the $\beta$ phase. A non-linear increase over more than 200 K above $T_c$ has been obtained by Kammer *et al.* [16], whereas more recent results are only given over 8 K above $T_c$ [15,17].

For $C_{14}^E$, an important decrease of 40% is observed between room temperature and $T_c$; at $T_c$, the constant discontinuously drops to zero. This evolution qualitatively looks like that of $C_{14}^E$ obtained in quartz [8,12,13,18].




(a)




(b)

**Fig. 2.** (a) Temperature dependence of elastic constants related to transverse waves in scattering geometries 3 and 4. (b) Expanded temperature scale near the transitions.

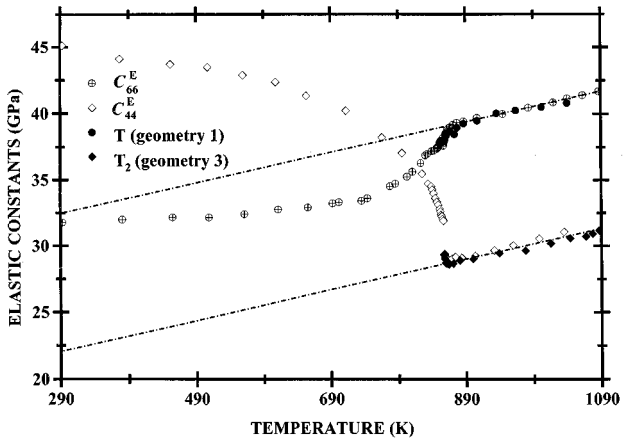
## 4 Discussion

### 4.1 Elastic constants $C_{44}^E$ and $C_{66}^E$

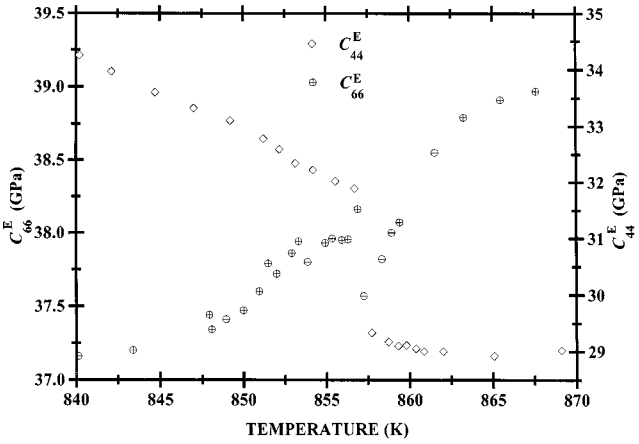
The elastic anomalies near a displacive phase transition are due to interactions between strains, induced by elastic waves, and modes belonging to the soft branch which drives the transition [19], the order parameter $Q$ being related to the modulus of the soft mode amplitude.

The strain $e_4$ and $e_6$ being not totally symmetric, the lowest order coupling terms are of the biquadratic type $He^2Q^2$ and can be written as follows:

$$\sum_{\mathbf{q},\mathbf{k}} H_j(\mathbf{q},-\mathbf{q},\mathbf{k},-\mathbf{k}) e_j(\mathbf{q}) e_j(-\mathbf{q}) Q(\mathbf{k}) Q(-\mathbf{k}) \text{ with } j=4,6 \quad (1)$$




(a)




(b)

**Fig. 3.** (a) Temperature dependence of elastic constants $C_{66}^E$ and $C_{44}^E$. For $C_{44}^E$ the results are those of reference [6]. The extrapolations of the linear variations which hold in the $\beta$ phase allow the determination of $\Delta C_{66}^E$ and $\Delta C_{44}^E$ below $T_c$. Above $T_c$, the results related to the (T) wave (scattering geometry 1) and ($T_2$) wave (scattering geometry 3) are also reported for comparison. (b) Expanded temperature scale near the transitions.

where $Q(\mathbf{k})$, which are normal coordinates of modes on the soft branch, are to be taken into account only in the vicinity of the critical wave vectors $\pm\mathbf{k}_i$; $e_j(\mathbf{q})$ is the strain induced by an elastic wave with wave vector $\mathbf{q}$. As usually, one can consider that $\mathbf{q} \cong 0$.

In the incommensurate phase and below $T_c$, term (1) gives a static contribution [19] to the anomaly of $C_{44}^E$ and $C_{66}^E$ which is proportional to the order parameter modulus squared:

$$C_{jj}^E = (C_{jj}^E)_0 + 2H_j \sum_i |Q(\pm\mathbf{k}_i)|^2 \text{ with } i = 1, 2, 3$$

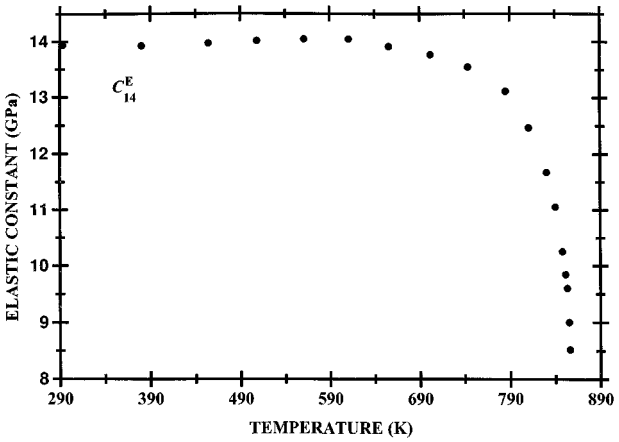



**Fig. 4.** Temperature dependence of elastic constant $C_{14}^E$.

where $(C_{jj}^E)_0$ are the bare elastic constants.

In the locked $\alpha$ phase, $\mathbf{k}_i$ is equal to zero. Considering the triple-**k** solution adapted for quartz and $AlPO_4$ [20], there is a common value $Q$ for $|Q(\pm\mathbf{k}_i)|$ which represents the order parameter. Therefore we have:

$$C_{jj}^E = (C_{jj}^E)_0 + h_j Q^2 \text{ with } h_j = 6H_j. \quad (2)$$

Above $T_i$, in the $\beta$ phase, we have $Q = 0$ and the elastic constants reduce to the bare ones $(C_{jj}^E)_0$, with $(C_{66}^E)_0 = (C_{66})_0$ since $C_{66}^E = C_{66}^D = C_{66}$. However, it has to be recalled that term (1) can also induce another contribution to elastic constant anomalies which takes place on both sides of the transition at $T_i$ and which are confined on a more or less important temperature range [21]. This contribution can be labelled fluctuation contribution since it only results from fluctuations of the order parameter. In the $\beta$ phase, near $T_i$, it can explain, at least partially, the small departure of $C_{44}^E$ and $C_{66}$ from the linear variations which hold at higher temperature. A similar contribution may occur below $T_i$.

To obtain the anomalous part of $C_{44}^E$ and $C_{66}$ below $T_i$, the linear variations of the elastic constants in the $\beta$ phase have been extrapolated below $T_i$ and identified with those of the bare ones. Then, considering only the coupling (1) and neglecting the fluctuation contributions, the anomalous parts $\Delta C_{jj}^E = C_{jj}^E - (C_{jj}^E)_0$ are expected to be given by:

$$\Delta C_{jj}^E = h_j Q^2. \quad (3)$$

From experimental results, it is obvious that $h_4$ is positive and $h_6$ negative. If $h_4$ and $h_6$ are considered to be quasi temperature independent, $\Delta C_{44}^E$ and $\Delta C_{66}^E$ would be proportional to one another. Unlike $\Delta C_{44}^E$, $|\Delta C_{66}^E|$ exhibits a broad maximum near 720 K, as can be observed in Figure 3a. For the constant $C_{66}^E$, this fact implies that (3) cannot be satisfied far from the $\alpha$–$\beta$ transition, since a normal order parameter has a monotonous variation below the transition temperature [24].

To check the validity of (3) near the transition, a plot of $|\Delta C_{66}^E|$ as function of $\Delta C_{44}^E$ is reported in Figure 5.

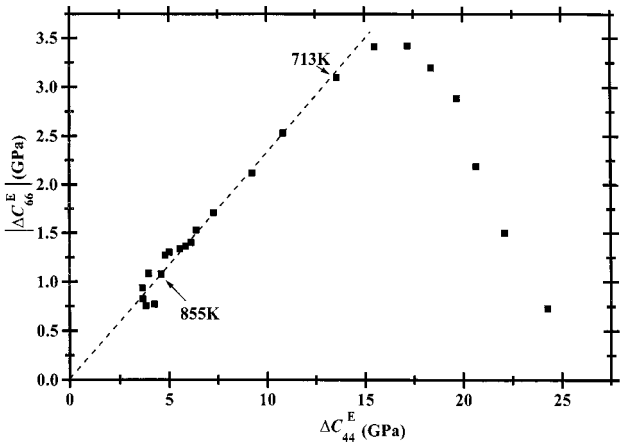



**Fig. 5.** Plot of $|\Delta C_{66}^E|$ as function of $\Delta C_{44}^E$ in the $\alpha$ phase.

Over a temperature range of about 140 K below $T_c$, a linear portion, whose extrapolation goes through the origin, is effectively observed. This result shows that $\Delta C_{44}^E$ and $\Delta C_{66}^E$ can be considered as proportional to the order parameter squared in this temperature range. Unlike the case of $\Delta C_{66}^E$, this proportionality may be valid in a wider temperature range for $\Delta C_{44}^E$. Below around 720 K a large deviation from the linear variation occurs. To explain this deviation, we think that it is necessary to put forward higher order coupling terms, allowed by symmetry, such as $M_j e_j^2 Q^4 + \cdots$ Below $T_i$, these terms give additional static contributions to the elastic anomalies which then can be written as:

$$\Delta C_{jj}^E = h_j Q^2 + m_j Q^4 \cdots \tag{4}$$

The experimental results for $\Delta C_{66}^E$ obviously suggest at least the existence of the first following term $m_6 Q^4$ with a positive coefficient $m_6$.

In the $\beta$ phase, the slopes of the linear variations of $C_{44}^E$ and $C_{66}$ are positive, a result which may be considered as exceptional, since, out of the critical region of a phase transition, the general anharmonicity gives rise to a linear decrease of the elastic constants in most compounds.

Above $T_i$, it has been pointed out in quartz [17] that the soft branch would interact with the transverse acoustic branch (corresponding to polarization in the (001) plane) for wave vectors in the vicinity of $\pm\mathbf{k}_i$ (along $\mathbf{a}^*$) and equivalently, leading to a velocity anisotropy for transverse elastic waves with $\mathbf{q}$ small but different from zero. These considerations are also valid in $AlPO_4$. Therefore, it is expected that $C_{66}$, measured for $\mathbf{q}$ along [100] and for $\mathbf{q}$ along [010] (parallel to $\mathbf{a}^*$), would exhibit different values. The experimental results (scattering geometries 4 and 1 respectively) do not corroborate these predictions, within experimental uncertainties, as it was also concluded in quartz [17]. This can be explain by the low value ($\sim 0.07$) of the $q/k_i$ ratio.

### 4.2 Elastic constant $C_{14}^E$

Before the discovery of the incommensurate phase [22], the $\alpha$–$\beta$ transition in quartz was attributed to a soft mode at the Brillouin zone centre [23] with $B_1$ symmetry (or $B_2$ depending on the choice of the binary axes label). It has been pointed out [19] that a coupling term of the form $Q[(e_1 - e_2)e_4 + e_5 e_6]$ is allowed by symmetry in the $\beta$ phase. In the $\alpha$ phase, it gives rise to the morphic constants $C_{14}$, $C_{24} = -C_{14}$ and $C_{56} = C_{14}$ which are proportional to the order parameter.

However, in quartz and quartz-like compounds among which $AlPO_4$, the wave vector of the soft modes $\mathbf{k}_i$ being indeed different from zero, such a coupling involving $Q(\mathbf{k}_i)$ is not allowed, the law of wave vectors conservation being not satisfied. Nevertheless, it can be emphasized that the following coupling term:

$$a_{14} Q(\mathbf{k} = 0)[(e_1 - e_2)e_4 + e_5 e_6] \tag{5}$$

where $Q(\mathbf{k} = 0)$ is the normal coordinate of the $\mathbf{k} = 0$ mode belonging to the soft optical branch is allowed. In the $\alpha$ phase this mode coincides with the soft mode, giving the result:

$$C_{14}^E = a_{14} Q \tag{6}$$

in this phase whereas $C_{14}^E = 0$ in the $\beta$ phase, as obtained in the earlier consideration. In the incommensurate phase of $AlPO_4$, the point symmetry of the $\beta$ phase being preserved, we have also $C_{14}^E = 0$. These predictions about $C_{14}^E$ at and above $T_c$ are corroborated by the experimental results, as noted in Section 3.3.

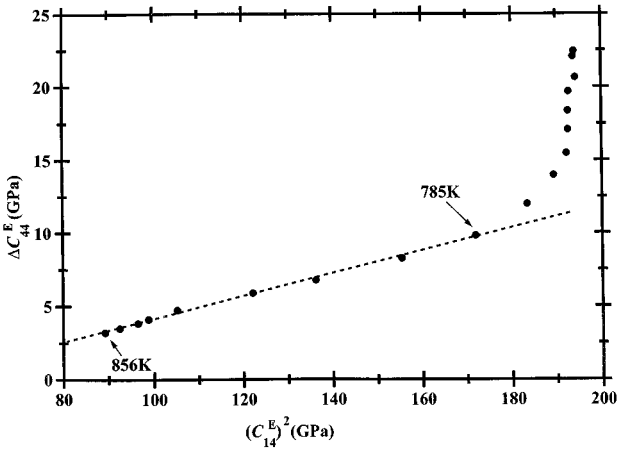
To check the validity of relation (6), we have reported $\Delta C_{44}^E$ as function of $(C_{14}^E)^2$ in the $\alpha$ phase (Fig. 6a). Over a temperature range of 70 K below $T_c$, a linear portion is obtained but its extrapolation does not go through the origin, in conflict with the expectation. To explain this discrepancy we think that it is necessary to put forward higher order coupling terms even near $T_c$. The next one, allowed by symmetry, can be written as:

$$b_{14} \sum_{\mathbf{k},\mathbf{k}'} Q(\mathbf{k}) Q(\mathbf{k}') Q(-\mathbf{k} - \mathbf{k}')[(e_1 - e_2)e_4 + e_5 e_6]. \tag{7}$$

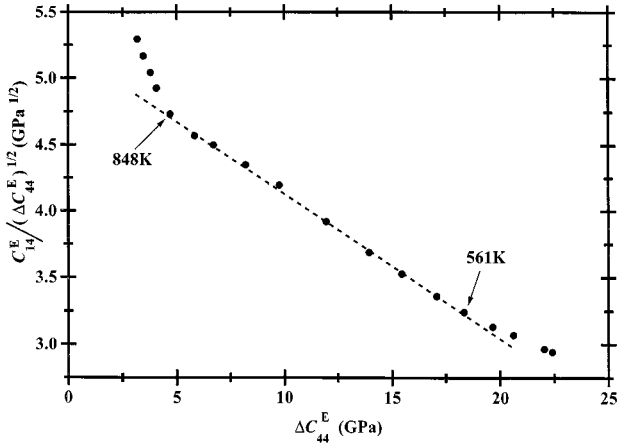
Hence, relation (6) is written as

$$C_{14}^E = a_{14} Q + b_{14} Q^3. \tag{8}$$

Considering that $\Delta C_{44}^E$ is proportional to $Q^2$ over at least 140 K below $T_c$, as obtained in Section 4.1, relation (8) can be checked by plotting $C_{14}^E/(\Delta C_{44}^E)^{1/2}$ as function of $\Delta C_{44}^E$ as shown in Figure 6b. Over $\sim$ 300 K below $T_c$, a linear part with a negative slope (implying $b_{14} < 0$) is obtained, except in a narrow range of 8 K just below the lock-in transition. This small deviation may be attributed to an additional contribution of coupling (7) coming from fluctuations of $Q(\mathbf{k})$ near $\mathbf{k} = 0$. Then, over about 300 K below $T_c$, it appears that the experimental results are well fitted by (8), together with (3) for $C_{44}^E$; this result also implies that the proportionality of $\Delta C_{44}^E$ to $Q^2$ holds on




(a)




(b)

**Fig. 6.** (a) Plot of $\Delta C_{44}^E$ as function of $(C_{14}^E)^2$ in the $\alpha$ phase. (b) Plot of $C_{14}^E/(\Delta C_{44}^E)^{1/2}$ as function of $\Delta C_{44}^E$ in the $\alpha$ phase.

a more extended range than 140 K. An equivalent conclusion has been drawn about $C_{14}^E$ in quartz in which this constant cannot be fitted to others quantities which are expected to be proportional to $Q^2$, such as the birefringence variation or a coefficient of second harmonic generation [24]. The progressive deviation from the straight line below 650 K indicates that higher order terms have to be taken into account in (8) and, possibly, in (3).

### 4.3 Anticrossing in scattering geometries with acoustic wave vector along [010]

The knowledge of $C_{66}^E(T)$, $C_{14}^E(T)$, $C_{44}^E(T)$ and $C_{11}^E(T)$ in the $\alpha$ phase allows a quantitative analysis of the anticrossing which has been observed in scattering geometries 1 and 2. Following the usual procedure, a coupling constant $K = q^2K'$, reflecting dynamic anharmonic interactions is

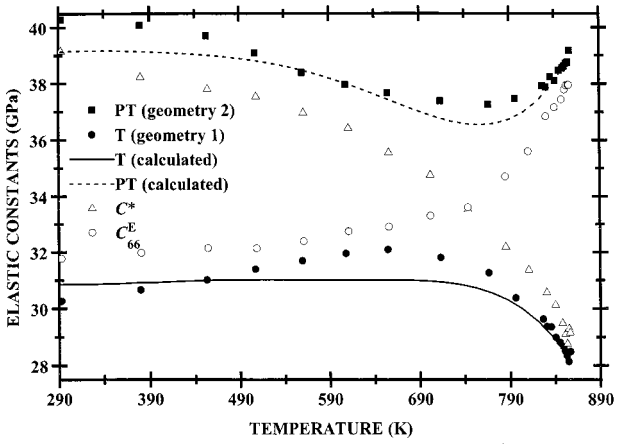



**Fig. 7.** Plot of experimental and calculated values of $\rho V_-^2$ and $\rho V_+^2$ (in scattering geometries 1 and 2) and of calculated $C^*$ and $C_{66}^E$, in the $\alpha$ phase.

introduced in the eigenvalues equation for the two modes:

$$\begin{vmatrix} C^* - \rho\frac{\omega^2}{q^2} & K \\ K & C_{66}^D - \rho\frac{\omega^2}{q^2} \end{vmatrix} = 0 \qquad (9)$$

where $C^* = [C_{11}^E + C_{44}^E - \sqrt{(C_{11}^E - C_{44}^E)^2 + 4(C_{14}^E)^2)}]/2$. The coupling constant $K$, expressed as $q^2K'$, reflects a fourth order interaction. It disappears when $\mathbf{q} \to 0$, preserving the usual set of elastic constants in the static limit. The velocities $V_+$ and $V_-$ of the coupled modes are given by:

$$\rho V_\pm^2 = \frac{C^* + C_{66}^D \pm \sqrt{(C^* - C_{66}^D)^2 + 4K^2}}{2}\,. \qquad (10)$$

The temperature dependences of $C_{11}^D$ and $C_{44}^E$ have been previously measured in the scattering geometries $(-x+y)[z,z](x+y)$ and $(y-z)[x,(y-z)](y+z)$ respectively [6]. Making use of these data, together with the present data on $C_{14}^E(T)$ and $C_{66}^E(T)$ and assuming, in the first approximation, that $C_{11}^E \cong C_{11}^D$ and $C_{66}^E \cong C_{66}^D$, $\rho V_+^2$ and $\rho V_-^2$ have been computed with $K$ as a free parameter, and fitted to experimental results (scattering geometries 1 and 2). The best fit is shown in Figure 7 and corresponds to $K = 3.0 \pm 0.5$ GPa. The agreement between calculated and experimental values can be considered satisfactory, specially near $T_c$, taking into account (i) the uncertainties on $C^*$ (estimated to 3.5%) and on $C_{66}^E$ and (ii) the assumptions concerning the use of $C_{11}^D$ and $C_{66}^E$ instead of $C_{11}^E$ and $C_{66}^D$ respectively. More precisely, a qualitative analysis of this assumption shows that an increase of $C_{66}^E$ and a decrease of $C_{11}^E$ (to simulate the value of $C_{66}^D$ and the real value of $C_{11}^E$, respectively) leads to an increase of $\rho V_-^2$ and to an insignificant variation of $\rho V_+^2$, due to almost cancelling terms. Hence, the fit to experimental results would be improved. The widespread results on the piezoelectric moduli [2–4] prevent a more quantitative analysis.

As conclusion, it can be emphasized that, due to the anticrossing, the scattering geometry 1 is not adequate for

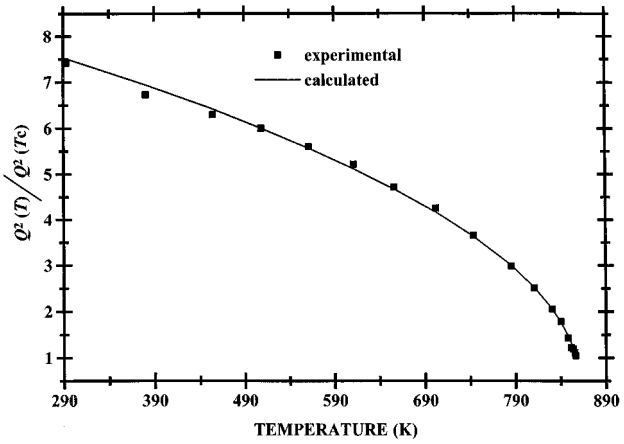



**Fig. 8.** Temperature dependence of experimental and calculated $Q^2(T)/Q^2(T_c)$.

a precise measurement of $C_{66}^D$, even at room temperature, as it was anticipated in Section 3.2.

### 4.4 Temperature dependence of the order parameter

The preceding results, particularly $\Delta C_{44}^E$, allow the determination of the temperature dependence of $Q$ and its comparison to predictions of existing theories. This comparison has been substantially discussed in quartz [24], within the framework of Landau theory and within the renormalization theory by using a power law with a critical exponent $\beta \neq 1/2$. It has been found that $Q(T)$ can be equally fitted to the Landau law and to a power law with $\beta = 1/3$. In that discussion, the transition was considered as an ordinary one, the existence of the incommensurate phase being not known.

In the framework of Landau's theory, incommensurate transitions have been investigated as a special case of continuous structural transitions adjacent to a high-symmetry crystalline phase, with more or less refinements [25]. The various theoretical schemes focus essentially on the specific features of the incommensurate phase. Taking into account only the lowest order terms in the free energy required for the occurrence of a transition, it is generally predicted that, in the locked phase, the order parameter squared varies as $T_0 - T$, with $T_0$ between $T_c$ and $T_i$. This law does not fit with our results in $AlPO_4$ since the extrapolation of the linear part of $\Delta C_{44}^E$, which holds just below $T_c$, intersects the temperature axis well above $T_i$ ($\sim 15$ K).

This discrepancy may originate in an insufficient number of terms taken into account in the power-series expansion of the free energy with respect to the order parameter. When more than two terms are taken into account, they are known to give a saturation of $Q^2(T)$ on cooling. The presence of the sixth degree term leads to the usual law:

$$Q^2(T) = \frac{-B + \sqrt{B^2 - 4AC}}{2C} \qquad (11)$$

where $A$, $B$, $C$ are the coefficients of the successive terms with $A = A_0(T - T_0)$, $C > 0$, and $B > 0$ or $< 0$ for a second or first order transition, respectively. For positive values of $B$, the experimental results for $\Delta C_{44}^E$ cannot be fitted to this law below $T_c$, with $T_0$ between $T_c$ and $T_i$, as a consequence of the large amplitude of the discontinuity at $T_c$. Therefore, we think that it is necessary to consider that this coefficient would be negative (as in a first order ordinary transition). In this case, from (3) and (11) the following relation can be obtained:

$$\Delta C_{44}^E(T)/\Delta C_{44}^E(T_c) = Q^2(T)/Q^2(T_c) = \frac{1 + \sqrt{1 + D(T_0 - T)}}{1 + \sqrt{1 + D(T_0 - T_c)}} \qquad (12)$$

where $D$ is a temperature independent constant related to $A_0$, $B$ and $C$; it is worthy of notice that $T_c$ has not to be identified with the transition temperature $T_t$ which would be associated with $T_0$ in the case of an ordinary first order transition and, therefore $T_0 < T_c$ is not imposed.

The best fit of experimental results to (12) is obtained for $T_0 = (859 \pm 0.5)$ K and $D = (0.525 \pm 0.005)$ K$^{-1}$ and reported in Figure 8. As can be verified, the temperature dependence of $Q^2(T)$ can be well described by (12), over about 400 K in the $\alpha$ phase, within experimental uncertainty. A similar conclusion has been drawn in quartz [25]. It can be noted that such fits to a Landau law over a large temperature range are always questionable and of small interest; they only give analytical temperature laws which agree with experimental points. As emphasized in this last paper [25], fits to a power law involving a critical exponent are questionable in the case of a first order transition; therefore, such fits have not been undertaken in $AlPO_4$.

In the incommensurate phase, no attempt has been made to analyse $Q(T)$. Different types of difficulties arise, among which (i) the narrowness of its temperature range, (ii) the fact that several contributions are likely added in $\Delta C_{44}^E$ .

## 5 Conclusion

The present Brillouin investigation reports, for the first time in $AlPO_4$, a study of the transverse and pseudo-transverse elastic waves in several scattering geometries over the temperature range 300 K-1100 K. These scattering geometries allow the determination of the temperature dependences of $C_{66}^E$ and $C_{14}^E$ which completes that of $C_{44}^E$, already reported in one of our previous work. The analysis of the results has shown that the lowest order coupling term between strains and order parameter is sufficient to account for the anomaly of $C_{44}^E$ in a large temperature range below $T_c$ (at least 300 K), whereas additional coupling term(s) have to be taken into account in the case of $C_{66}^E$ at temperature lower than 140 K below $T_c$, reflecting a greater anharmonicity for that constant. In the case of $C_{14}^E$, the first two lowest order terms must be taken into account even just below $T_c$. Such a detailed analysis has never been performed in quartz. However, taking into

account the similarity of experimental data about elastic constants in $AlPO_4$ and quartz, when avalaible, it is likely that the same conclusions also hold in this last material. In $AlPO_4$, our data also allow the determination of the order parameter temperature dependence in the $\alpha$ phase, which can be successfully described within the framework of Landau's theory.

All these results, which have been obtained from significant pretransitional features occurring over a large temperature range around the $\alpha-\beta$ transition, show that compounds such as $AlPO_4$ and, more generally quartz-like materials, yield an important investigation field of the anharmonicity in a solid. Some of their properties still remain not understood as, for example, the anomalous increase of some bare elastic constants on heating, as can be directly observed in the $\beta$ phase.

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