Investigation of AlPO4 by Brillouin Spectroscopy from 300 to 1100 K

N. Magneron, Y. Luspin, G. Hauret, E. Philippot

To cite this version:
N. Magneron, Y. Luspin, G. Hauret, E. Philippot. Investigation of AlPO4 by Brillouin Spectroscopy from 300 to 1100 K. Journal de Physique I, EDP Sciences, 1997, 7 (4), pp.569-580. <10.1051/jp1:1997176>. <jpa-00247345>

HAL Id: jpa-00247345
https://hal.archives-ouvertes.fr/jpa-00247345
Submitted on 1 Jan 1997

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
Investigation of AlPO$_4$ by Brillouin Spectroscopy from 300 to 1 100 K

N. Magneron (1,2,*), Y. Luspin (1,2), G. Hauret (1,2) and E. Philippot (3)

(1) Centre de Recherche sur la Physique des Hautes Températures, CNRS, 45071 Orléans Cedex 2, France
(2) Université d’Orléans, 45067 Orléans Cedex 2, France
(3) Laboratoire de Physicochimie des Matériaux Solides, CNRS. Université de Montpellier II, 34095 Montpellier Cedex 5, France

(Received 9 October 1996. received in final form 17 December 1996, accepted 24 December 1996)

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

Abstract. — The elastic constants of AlPO$_4$ (berlinite) have been measured at room temperature. The longitudinal and transverse acoustic waves related to $C^E_{11}$, $C_{33}$ and $C^E_{44}$ have been investigated over the temperature range 300-1100 K which includes the $\alpha \rightarrow \text{inc.} \rightarrow \beta$ transitions near 860 K. Large anomalies of $C^E_{11}$ and $C_{33}$, together with broadening of lines, are observed near the transitions, with a significant temperature range of pretransitional features. The $C^E_{44}$ constant exhibits a discontinuous drop at the lock-in transition. The results concerning the longitudinal modes can be qualitatively interpreted in term of a third order anharmonic coupling between the acoustic modes and the soft modes. The range of the incommensurate phase is found to be $T_1 - T_c \sim 3$ K, in agreement with previus data. The broadening of lines related to longitudinal modes allowed the determination of the constant $A$ of the relaxation time for the amplitudon $\tau_n = A/(T_1 - T)$; we obtained $A = 1.1 \times 10^{-11}$ K s.

Résumé. — Une étude par diffusion Brillouin nous a permis de mesurer les constantes élastiques de AlPO$_4$ (berlinite) à température ambiante. Les ondes acoustiques longitudinales et transverses correspondant aux constantes $C^E_{11}$, $C_{33}$ et $C^E_{44}$, ont été suivies sur un intervalle de température 300-1100 K qui inclut les transitions $\alpha \rightarrow \text{inc.} \rightarrow \beta$ proches de 860 K. Près de ces transitions, des anomalies ont été observées pour les constantes $C^E_{11}$, $C_{33}$, ainsi qu’un élargissement des raies Brillouin. La constante $C^E_{44}$ montre une discontinuité à la transition de “lock-in”. Les résultats correspondant aux modes longitudinaux peuvent être interprétés qualitativement en termes de couplage du troisième ordre entre les modes acoustiques et les modes mous. Cette étude nous a également permis de vérifier que la phase incommensurable s’étend sur 3 K. Une étude plus approfondie des largeurs de raies Brillouin, correspondant aux ondes longitudinales, permet la détermination de la constante $A$ du temps de relaxation de l’amplitudon $\tau_n = A/(T_1 - T)$ ; on obtient $A = 1.1 \times 10^{-11}$ K s.

(*) Author for correspondence (e-mail: mageron@admin.cnrs-orleans.fr)

© Les Éditions de Physique 1997
1. Introduction

Aluminium phosphate AlPO₄ (berlinitic) belongs to the family of quartz-like materials. It is known that a strong analogy exists between its physical properties and those of quartz [1]. Several investigations have been performed in order to assess the potential of AlPO₄ as an alternative to quartz in ultrasonic device applications with a larger electromechanical coupling [2–4].

AlPO₄ undergoes an $\alpha \to \beta$ transition near 860 K [5]. Between the $\alpha$ and $\beta$ phases, an intermediate incommensurate phase exists over a narrow temperature range of 3 K [6]. This sequence of phases is quite similar to that in quartz [7], corroborating the analogy between the two compounds.

At room temperature, the elastic properties of AlPO₄ have been determined by ultrasonic methods [2–4] and Brillouin scattering [8]. Unlike those of quartz, these properties have not generally been investigated over a temperature range which includes the transitions. Only the elastic constant $C_{33}$ has been studied by Brillouin scattering [8]. However, measurements in the $\beta$ phase have been limited to 12 K above the transitions, due to the appearance of opalescence in samples. This deterioration of the sample has also been observed in other experiments [6,9] and it is a likely reason for the lack of experiments by light scattering.

In the present paper, we report new results of Brillouin scattering investigations in AlPO₄. We have been supplied with samples having an excellent optical quality at room temperature which is only slightly affected by heating significantly above the transitions. Thus, the measurements have been performed from 300 K to 1100 K.

2. Experimental and Crystal Data

Brillouin scattering experiments were performed with a spectrometer which is a pressure scanned, triple passed plane Fabry Perot interferometer (effective finesse 70, resolving power 760 000). 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 of AlPO₄ which were grown by the hydrothermal method. This method has required preliminary studies of berlinitic solubility in different media with different concentrations. These studies have shown a retrograde solubility which is much higher in sulphuric acid than in the other ones [10]. All the experiments were conducted through the reverse temperature gradient method [11] using 375 cm³ platinum-lined autoclaves with baffle apertures of 8% and a filling of 80%. Systematic investigations into crystal growth conditions [11,12] have emphasized that the sulfuric acid medium is the best one to obtain crystals with the lowest OH impurity concentration. Then, both crystals used in this study have been obtained from X-seed in $\text{H}_2\text{SO}_4$ 4.5 mol. solvent for a growth temperature of $T_c = 240 \degree \text{C}$.

At room temperature, the dextrogyre crystals of AlPO₄ show the trigonal symmetry (class 32) with space group P3₁21 (α phase). The parameters of the primitive hexagonal cell are $a = b = 4.942$ Å and $c = 10.97$ Å [2,13]; this cell contains three AlPO₄ groups. The structure, close to that of quartz, is derived from that of the latter by replacing two Si atoms with one Al atom and one P atom, which results in a doubling of the cell along the c axis.

Near 860 K, AlPO₄ undergoes an "$\alpha \to \beta$" transition. Evidence for an intermediate phase came from several experiments [9,14–16]. Neutron scattering experiments [6] have given a direct verification of the incommensurable structure of this phase, which lies over a narrow range $T_i - T_c \approx 3$ K. $T_i$ and $T_c$ being the $\beta \to \text{inc.}$ and lock-in transition temperatures respectively. The $\beta \to \text{inc.}$ transition is induced by the condensation of soft modes with wave
vector $\mathbf{k}_i = \pm 0.03\mathbf{a}^*$ and equivalent by symmetry, which corresponds to the vicinity of the Brillouin zone centre. The temperature range of the incommensurate phase is greater than twice that in quartz [17]. The structure of the $\beta$ phase is hexagonal, class 622, with space group P6$_3$22.

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$^{-3}$.

We have computed the elastic constants from Brillouin shifts at any temperature, we used the room temperature values of both mass density and refractive indices. No data on indices versus temperature are available. An investigation of the lattice parameters has been made from 200 K to 1100 K [2], but the data are not sufficiently detailed in the vicinity of the transitions. It is also to be noticed that the variations in temperature of the density and of the indices may partially compensate in the calculation.

The 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 without any consequences on spectrum collecting since large regions keep their optical quality; on further heating, this quality is practically unchanged up to the highest investigated temperature. After cooling down to room temperature, a slight opacity can be observed; the initial spectra are recovered but with a decreased cross-section of the Brillouin line by a factor 2 and an increase of the elastic Rayleigh peak (factor ~10). Thus the same sample was not used in more than one heating run.

3. 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. For the measurements of elastic constants at room temperature, we used the scattering geometries which are reported in Table I.

The piezoelectricity of the trigonal phase introduces no distinction between elastic constants at constant electric displacement $C'^D_{ij}$ and elastic constants at electric field $C'^E_{ij}$ for $C_{33}$. On the contrary, the distinction holds for all other constants. In the $\beta$ phase, which is also piezoelectric, this distinction only holds for $C_{44}$.

The piezoelectric moduli $e_{11}$ and $e_{14}$ have been measured by several authors at room temperature [2–4] with widespread results, probably due to a different origin of the samples [3]. Therefore, we will give below the results for the elastic constants, $C'^D_{ij}$ or $C'^E_{ij}$, which are the most directly obtained from the Brillouin shifts, except when not possible.

4. Results

4.1. Elastic Constants at Room Temperature. — We have obtained the following values in (GPa):

$$C'^D_{11} = 71.7, C_{33} = 91.1, C'^E_{14} = 44.6, C'^D_{66} = 29.2, C'^D_{12} = 13.3, C'^E_{13} = 19.4, C'^E_{14} = -12.7$$

with an accuracy of 1% for the first four constants, 3% for $C'^D_{12}$ and 10% for $C'^E_{13}$ and $C'^E_{14}$. The calculation of $C'^E_{13}$ and $C'^E_{14}$ requires the values of $C'^E_{11}$; we have estimated the piezoelectric
Table I. — 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. \( \mathbf{q} \) is the acoustic wave vector. \( L, T, PL, PT \) are related to the nature of acoustic wave: longitudinal, transverse, pseudo-longitudinal, pseudo-transverse respectively.

<table>
<thead>
<tr>
<th>Scattering geometries</th>
<th>Acoustic wave ( \mathbf{q} ) direction</th>
<th>Acoustic wave nature</th>
<th>Expression of ( \rho V^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 ((-x+y)<a href="x+y">z,z</a>)</td>
<td>[100]</td>
<td>L</td>
<td>( C_{11}^D )</td>
</tr>
<tr>
<td>2 ((y-z)<a href="y+z">x,z</a>)</td>
<td>[001]</td>
<td>L</td>
<td>( C_{33} )</td>
</tr>
<tr>
<td>3 ((y-z)<a href="z+y">x,(y+z)</a>)</td>
<td>[001]</td>
<td>T</td>
<td>( C_{44}^E )</td>
</tr>
<tr>
<td>4 ((-y+z)<a href="y+z">(y+z),x</a>)</td>
<td>[010]</td>
<td>T</td>
<td>( C_{66}^D = (C_{11}^D - C_{12}^D)/2 )</td>
</tr>
<tr>
<td>5 ((-y+z)<a href="y+z">x,x</a>)</td>
<td>[010]</td>
<td>PL</td>
<td>( {C_{11}^E + C_{44}^E + [(C_{11}^E - C_{44}^E)^2 + 4(C_{14}^E)^2]^{1/2}}/2 )</td>
</tr>
<tr>
<td>6 ((-y+z)<a href="y+z">x,x</a>)</td>
<td>[010]</td>
<td>PT</td>
<td>( {C_{11}^E + C_{44}^E - [(C_{11}^E - C_{44}^E)^2 + 4(C_{14}^E)^2]^{1/2}}/2 )</td>
</tr>
</tbody>
</table>
| 7 \((y)[x,x](z)\) | [011] | PL | \( 1/4 \{ C_{11}^E + C_{33}^E + 2(C_{24}^E - C_{14}^E) \\
+[(C_{11}^E - C_{33}^E - 2C_{14}^E)^2 \\
+4(C_{13}^E + C_{44}^E - C_{14}^E)^2]^{1/2}\} \) |
| 8 \((y)[x,x](z)\) | [011] | PT | \( 1/4 \{ C_{11}^E + C_{33}^E + 2(C_{24}^E - C_{14}^E) \\
-[(C_{11}^E - C_{33}^E - 2C_{14}^E)^2 \\
+4(C_{13}^E + C_{44}^E - C_{14}^E)^2]^{1/2}\} \) |

correction \( C_{11}^D - C_{11}^E = \varepsilon_{11}^2/\varepsilon_{11} \) with the data of Bailey et al. [3], since those authors give the values which are the closest to ours among the different sets of results available about elastic constants. The sign of \( C_{14}^E \) has been attributed following a previous result for which the IRE standard on piezoelectric crystals has been taken into account [2].

Our results agree satisfactorily with previous ones obtained by Brillouin scattering [8] and ultrasonic methods [2-4].

4.2. Investigations with Temperature. — The Brillouin lines related to the elastic waves of cases 1, 2 and 3 (Tab. I) have been investigated versus temperature, from room temperature up to \( \sim 100 \) K. The results for \( C_{11}^D, C_{33} \) and the full widths at half maximum (FWHM) \( \Gamma_1 \) and \( \Gamma_3 \) of the related lines, after deconvolution, are reported in Figures 1, 2 and 3.

Large anomalies are to be found for the elastic constants (Fig. 1). Considerable dips occur on both sides of the temperature range of the \( \alpha \to \text{inc.} \to \beta \) transitions. Pretransitional effects are present at temperatures as low as 300 K and still exist at 1100 K. The result for \( C_{33} \) agrees with a previous study [8]. As shown on an expanded scale (Fig. 3), the bottoms of dips correspond to a continuous change which shows a rounded upward step on heating. It is to be remarked, that a change in the evolution of the increase of both elastic constants takes place in the vicinity of 860 K which will be interpreted as the temperature \( T_1 \) of the inc. \( \to \beta \) transition.

The linewidths \( \Gamma_1 \) and \( \Gamma_3 \) also show a continuous evolution in the vicinity of the transition (Fig. 3). \( \Gamma_1 \) and \( \Gamma_3 \) take a maximum value at a temperature \( T_M \), the same for both curves. \( T_M \) is 1.5 K below the value 860 K which has been noted above.
Fig. 1. — Temperature dependence of elastic constants $C_{11}^D$, $C_{33}$.

The general behaviours for $C_{11}^D$ and $C_{33}$ are consistent with those found in quartz [18]. On an expanded scale, the temperature dependence of $C_{11}^D$ and of $C_{33}$ [18, 19] is qualitatively similar to the results we have obtained in AlPO$_4$. The linewidths $\Gamma_1$ and $\Gamma_3$ in quartz [19, 20] also show a maximum below $T_c$; however, discontinuities of these linewidths are observed at $T_c$ by further cooling, contrary to the case of AlPO$_4$. There is another difference between quartz and AlPO$_4$ [18–20]. In quartz, the elastic anomalies which are like those we have observed in AlPO$_4$ in the vicinity of the transition, still when heating as specified in Section 2, are obtained when cooling from the $\beta$ phase and also when heating, but only if the sample temperature is kept above $T_c$ [19]; when quartz is heated from the $\alpha$ phase, a direct transition into the $\beta$ phase occurs, implying that both the continuous increase of the elastic constants and the broadenings with their maxima cannot be observed. Taking into account the first order character of the lock-in transition, this second fact can be explained by the narrowness ($\sim$1.3 K) of the incommensurate phase in quartz, with respect to the hysteresis amplitude at the lock-in transition.

The temperature dependence of $C_{44}^E$ is reported in Figure 4. This constant decreases from room temperature up to $T_j = 857$ K where a sharp fall occurs. Above 890 K, a linear increase is obtained up to 1100 K. It can be remarked that if a discontinuous decrease of the mass density existed at the same temperature and was taken into account (according to the data of [2] which unfortunately are incomplete in the vicinity of the transition), the fall of $C_{44}^E$ would be enhanced; thus the recorded fall should not be considered as an artefact. No broadening of the corresponding line can be observed throughout the temperature range. A similar fall of $C_{44}^E$ has also been observed in quartz [21].

5. Discussion

5.1. Elastic Constants $C_{11}^D$, $C_{33}$ and Related Broadenings. — The changes in those quantities with temperature are not unusual: they have been observed in many other structural transitions of variable types such as improper ferroelastic or incommensurate ones.
Fig. 2. — Temperature dependence of linewidth $\Gamma_1$ (a) and $\Gamma_3$ (b) related to elastic constants $C_{11}^0$ and $C_{33}$ respectively.

In particular, the results for AlPO$_4$ are very much like those of $C_{33}(T)$ and related broadening occurring near the normal-incommensurate transition in K$_2$SeO$_4$ [22–25], which has been among the most thoroughly studied crystals with an incommensurate phase.

These anomalies of elastic constants and linewidths are induced by the coupling $geQ^2$ which is linear in strain $e$ and quadratic to the order parameter $Q$: this coupling is generally the lowest order one when the bilinear coupling is forbidden by symmetry.

In AlPO$_4$, the star of the wave vector related to the soft mode in the $\beta$ phase has six arms $\pm k_1, \pm k_2$ and $\pm k_3$ [6]. The coupling $geQ^2$ is effectively the lowest order one allowed by symmetry [26]. This coupling has been widely analysed [22, 24, 25, 27, 28]. Therefore, we will only recall here the salient features and apply them to our results in AlPO$_4$. In the $\beta$ phase.
this coupling can be written as follows:

\[
\sum_{q,k,k'} g(q,k,k') e(q) Q(k) Q(k') \delta(q + k + k')
\]

where \(e(q)\) is one of the elastic strains \(e_{ij}(q)\) with \(i, j = 1\) to \(3\). \(Q(k)\) and \(Q(k')\), which are normal coordinates of modes on the soft branch, are to be taken into account only in the vicinity of \(\pm k_i\). Above \(T_1\), this term induces anomalies for both elastic constants \((C_{ij}, i\) and \(j = 1\) to \(3\)) and linewidths [29] which are given by the often designated fluctuation integrals. The quantitative calculation of these anomalies requires the knowledge of the soft branch in the vicinity of the critical points \(\pm k_i\); unfortunately those data are not available yet as far as \(\text{AlPO}_4\) is concerned.
Fig. 4. — a) Temperature dependence of elastic constant $C^{E}_{44}$. b) Expanded temperature scale near the transitions. The extrapolation of the linear variation of the $\beta$ phase allows the determination of $\Delta C^{E}_{44}$ (dashed lines).

For $T < T_1$, in the incommensurate phase, the situation is more complex, since the thermal mean values of $Q(\pm k_i)$ become different from zero. Therefore there are two different coupling terms. A first one, which can be written as follows:

$$\sum_{q,k} g(q, \pm k_i + k, \mp k_i - k - q) e(q) Q(\pm k_i + k) Q(\mp k_i - k - q)$$

is similar to the unique term above $T_1$; it gives a first contribution to elastic anomalies which are similar to those which occur above $T_1$.

The second coupling term can be written as follows:

$$2 \sum_{q,k} g(q, \pm k_i, \mp k_i - q) e(q) Q(\pm k_i) Q(\mp k_i - q).$$
Through the usual transformation into amplitudon and phason, it can fall into two parts: a part related to the amplitudon and, if allowed by symmetry [25], a part related to the phason. These two parts induce anomalies for elastic constants and broadenings of lines, \( \Delta C_{\text{LK}} \) and \( \Gamma_{\text{LK}} \) which are described by the usually called Landau-Khalatnikov (LK) terms. The terms related to the amplitudon can be written in the form [19,25]:

\[
\Delta C_{\text{LK}} \sim \frac{|Q(\pm k_i)|^2}{\Omega_a^2(\pm k_i)} \frac{1}{1 + \omega^2 \tau_a^2} \\
\Gamma_{\text{LK}} \sim \frac{|Q(\pm k_i)|^2}{\Omega_a^2(\pm k_i)} \frac{\tau_a}{1 + \omega^2 \tau_a^2}
\]

with \( \tau_a = \Gamma_a/\Omega_a^2(\pm k_i) \), \( \Gamma_a \) and \( \Omega_a \) being the damping and the frequency of the amplitudon: \( \omega \) is the angular frequency of the appropriate Brillouin line. For \( T < T_c \), the amplitudon is to be replaced by the usual soft mode.

In the simplified framework of mean field approximation, one has \( |Q(\pm k_i)|^2 \sim (T_1 - T) \), \( \Omega_a^2(\pm k_i) \sim (T_1 - T) \) and therefore \( \tau_a = A/(T_1 - T) \), if \( \Gamma_a \) is taken as temperature independent. \( \Delta C_{\text{LK}} \) describes an upward step at \( T_1 \), when \( T \) increases, which can be more or less rounded, depending on \( \Gamma_a \). The simultaneous broadening \( \Gamma_{\text{LK}} \) is expected to show a maximum at a temperature \( T_M \), below \( T_1 \), when \( \omega \tau_a(T_M) = 1 \).

The existence of such a maximum, at a temperature in the vicinity of which the elastic constant sharply increases, unambiguously indicates a significant contribution of the LK terms.

Below \( T_1 \), the various contributions to elastic anomalies have to be added. An examination of the experimental results shows that they are in qualitative agreement with the above predictions. Therefore, a few consequences can be drawn.

A first consequence of the above considerations is the precise localization of \( T_1 \) on the curve \( C_{11}^0(T) \) and \( C_{33}^0(T) \). The steep rises of \( C_{11}^0 \) and \( C_{33}^0 \) between 857 K and 860 K obviously have to be identified with the increase of the rounded step described above. Therefore, the temperature at which the change of slope occurs would coincide with \( T_1 \). Both curves give \( T_1 = 860 \pm 0.25 \) K. This result agrees with the fact that \( T_1 \) must be above the temperature at which the maximum of the broadening can be observed.

A second consequence is the determination of the constant \( A \) in \( \tau_a \) which can be obtained by:

\[
A = (T_1 - T_M)/\omega.
\]

If we assume that the maximum of the total broadening (including each contribution) is only slightly displaced with respect to \( T_M \) (relative to \( \Gamma_{\text{LK}} \)), taking into account the monotonic variations of other contributions, we obtain, from both curves \( \Gamma_1 \) and \( \Gamma_3 \), \( T_1 - T_M = 1.5 \pm 0.25 \) K. For both longitudinal modes we have practically the same value \( \omega/2\pi = 20.9 \) GHz which gives \( A = 1.1 \times 10^{-11} \) K s with an accuracy of 16% in which the major contribution comes from \( T_1 \).

5.2. ELASTIC CONSTANT \( C_{44}^E \). — The strain \( e_4 \) being not totally symmetric, the lowest order coupling terms with modes of the soft branch are biquadratic:

\[
\sum_{q,k} h_4(q,-q,\pm k)e_4(q)e_4(-q)Q(\pm k)Q(\mp k).
\]

The effect of this term upon the elastic constant \( C_{44}^E \) has also been widely analysed [22,24,25]. Below \( T_1 \), it gives a static contribution to the anomaly of \( C_{44}^E \), with respect to the bare constant \( (C_{44}^E)_0 \), which is proportional to the order parameter modulus squared:

\[
\Delta C_{44}^E = C_{44}^E - (C_{44}^E)_0 \sim |Q(\pm k_i)|^2.
\]
If the linear variation of $C_{44}^E$ in the $\beta$ phase is extrapolated below $T_i$, we can obtain $\Delta C_{44}^E$ and, consequently, information about $|Q(\pm k_i)|^2$ in the incommensurate and $\alpha$ phases. The sharp drop for $C_{44}^E$ occurs at $T_i = 857$ K which is $\sim 3$ K below $T_i$. Then, between both these temperatures, we found experimentally that the order parameter keeps a low value with respect to its values just below the discontinuity. This result strongly differs from that obtained in $K_2SeO_4$ for which, below $T_i$, a continuous decrease of $C_{44}^E$ is obtained up to $T_1$ [22]. The non zero value of $\Delta C_{44}^E$ above $T_i$ (860 K) may be attributed to the fourth order anharmonic contribution involved in the biquadratic coupling term for $k \neq k_i$.

It might well be thought that the drop of $C_{44}^E$, which is the sign of a transition, corresponds to the lock-in transition at $T_c$, since this drop occurs unambiguously below $T_i$ and that only the lock-in transition exists below $T_1$. This can be justified by the following remarks.

In $AIP_4$, our result for $C_{44}^E$ strongly resembles that obtained about the birefringence [9], for which the anomaly is also expected to be proportional to the order parameter squared. The curve for the birefringence shows a drop to a low value, more or less marked depending on the sample; above the temperature of this drop, a temperature range of also 3 K. corresponding to the irreversible behaviour of birefringence, has been identified as the incommensurate phase. It is worth noting that this temperature range of 3 K is also in agreement with the results of heat capacity measurements [6]. Therefore, it can be considered that the drop of $C_{44}^E$ takes place at the lock-in transition, whose temperature $T_c$ is thus available from Brillouin measurements.

5.3. REMARKS. — As a first remark, we will emphasize that, within experimental accuracy, no discontinuities appear at $T_c$ for $C_{11}^D$, $C_{33}$ and their related broadenings, in spite of the discontinuity of the order parameter modulus. The following arguments can be proposed.

In the simplified mean field theory, we have below $T_i$ [25]: $\Omega_a^2 = 2b|Q(\pm k_i)|^2 + 4c|Q(\pm k_i)|^4 + ...$, where $b$ and $c$ are the coefficients of the expansion of the free energy related to fourth and sixth power of $|Q(\pm k_i)|$. Keeping only the $b$ term, the LK contribution to $C_{11}^D$ or $C_{33}$ becomes:

$$\Delta C_{LK} \sim -\frac{1}{2b} \frac{1}{1 + \omega^2 \tau_a^2} \text{ with } \tau_a = \frac{\Gamma_a}{2b|Q(\pm k_i)|^2}.$$  

At $T = T_c$, one has $T_i - T_c \approx 2(T_i - T_M)$ and $\omega^2 \tau_a^2 \approx 1/4$, that reduces the effect of the discontinuity of $|Q(\pm k_i)|$ upon $\Delta C_{LK}$. Furthermore, if the $c$ term is taken into account, we have:

$$\Delta C_{LK} \sim -\frac{1}{2b + 4c|Q(\pm k_i)|^2} \frac{1}{1 + \omega^2 \tau_a^2} \text{ with } \tau_a = \frac{\Gamma_a}{2b|Q(\pm k_i)|^2 + 4c|Q(\pm k_i)|^4}.$$  

The two terms in the denominator have a tendency to compensate for a change of $|Q(\pm k_i)|$. Similar arguments can be developed for the broadenings.

An additional possibility is that the different contributions, namely the fluctuation integral and the LK terms for the amplitudon and for the phason, have compensate variations at $T_c$.

A second remark deals with the order of the transitions. From the Brillouin data, it can be deduced that the $\beta \rightarrow \text{inc.}(T_i)$ and lock-in ($T_c$) transitions are of second and first order respectively. These results agree with other experiments [6,9]. Similar conclusions have been drawn with quartz [7], corroborating the analogy of both compounds.

A last remark is about the temperature dependence of the order parameter at $T_i$ and its particularly low value in the incommensurate phase. obtained from the constant $C_{44}^E$. We have seen that this behaviour is consistent with the birefringence measurements [9]. In quartz, similar results are obtained for the birefringence [19] and for $C_{44}^E$ [21]; moreover, in a recent Raman study [30], the intensity of a line, expected to vary as the fourth power of the order
parameter, shows a temperature dependence which is strikingly similar to that of $\Delta C_{44}^E$ in AlPO$_4$. Thus, this particular behaviour of the order parameter appears to be common to this family of incommensurate materials.

6. Conclusion

In the present Brillouin scattering study of AlPO$_4$, we report for the first time an investigation of the elastic properties over a large temperature range (300-1100 K) which includes the incommensurate phase. We have focused on two longitudinal and one transverse elastic waves related to $C_{11}^P$, $C_{33}$, and $C_{44}^E$ respectively.

Large anomalies of both elastic constants and line broadenings related to the longitudinal waves are observed in the vicinity of the transitions with pretransitional features which are present up to both ends of the studied temperature range. The results can be qualitatively interpreted as the consequence of a third order anharmonic coupling between strains and the soft modes. The transverse wave, related to the $C_{44}^E$ elastic constant, yields data about the order parameter.

The results corroborate the temperature extension of the incommensurate phase over $\sim$3 K, in agreement with the results of other types of investigations. They also confirm the first and second order character of the lock-in and normal incommensurate transitions respectively. The broadening of lines allows a determination of the relaxation time related to the amplitudon.

Many of these results are similar to those obtained in quartz, when available. The interest of AlPO$_4$ is that the temperature range of the incommensurate phase is more than twice that of quartz. Therefore experimental investigations of this phase are easier in AlPO$_4$.

A quantitative analysis of the Brillouin data about the longitudinal modes requires data on the soft phonons in each phase. More generally, we think that a widened study of the lattices dynamics by other spectroscopies (IR, Raman and neutrons scattering) is suitable to get a better knowledge of the transitions.

References


