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Discontinuities in Elastic Properties of CsH₂PO₄ at the Superionic Transition

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Abstract. — An investigation of the elastic properties of CsH₂PO₄ has been performed by Brillouin spectroscopy throughout a temperature range which includes the superionic transition at \( T_s \approx 233 \, ^\circ\text{C} \). At \( T_s \), discontinuities have been observed for elastic constants \( C_{11}, C_{22}, C_{33} \) and \( C^* = (C_{11} + C_{22} + 2C_{66})/4 + [(C_{11} - C_{22})^2 + 4(C_{12} + C_{66})^2]^1/2]/4 \). Above \( T_s \), the corresponding Brillouin lines show a broadening without pretransitional features. In the conducting phase, a domain structure is revealed by the spectra. The observed elastic anomalies are similar to those obtained in other hydrogen-bonded crystals, such MHSeO₄ (with M = NH₄, Rb, Cs) or CsH₂AsO₄. In the conducting phase, it has been shown that a bilinear coupling between strains and mobile protons neither contribute to a significant variation of the elastic constants nor can explain the values of the observed broadenings. It is concluded that the experimental results could reflect a strong general anharmonicity of the lattice dynamics in the conducting phase.

Résumé. — Une étude des propriétés élastiques de CsH₂PO₄ a été faite par spectroscopie Brillouin sur un intervalle de température qui inclut la transition superionique à \( T_S \approx 233 \, ^\circ\text{C} \). À \( T_S \), des discontinuités sont observées pour les constantes élastiques \( C_{11}, C_{22}, C_{33} \) et \( C^* = (C_{11} + C_{22} + 2C_{66})/4 + [(C_{11} - C_{22})^2 + 4(C_{12} + C_{66})^2]^1/2]/4 \). Au-dessus de \( T_S \), les raies Brillouin correspondantes présentent un élargissement sans effet prétransitionnel. Dans la phase conductrice, une structure en domaines est mise en évidence par les spectres. Ces anomalies élastiques ressemblent à celles qui ont été observées dans d’autres cristaux à liaisons hydrogène tels que MHSeO₄ (avec M = NH₄, Rb, Cs) ou CsH₂AsO₄. Dans la phase conductrice, nous avons montré qu’un couplage bilinéaire entre les déformations et les protons mobiles ne pouvait pas contribuer à une variation significative des constantes élastiques ni rendre compte des valeurs obtenues pour les élargissements. Il a été conclu que les résultats expérimentaux pourraient refléter une forte anharmonicité générale de la dynamique de réseau dans la phase conductrice.

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1. Introduction

Potassium dihydrogen phosphate, KH$_2$PO$_4$ (abbreviated KDP), and its alkali phosphate and arsenate isomorphs form an important group of hydrogen-bonded crystals. In the last decades, these substances have been extensively studied with respect to their ferroelectric-paraelectric transition, which occurs at low temperature. Above room temperature, many crystals of this KDP group undergo other phase transitions [1] but they have seldom been studied.

Cesium dihydrogen phosphate CsH$_2$PO$_4$, hereafter abbreviated CDP, is generally considered as a compound of this group, although its paraelectric phase does not exhibit the tetragonal structure of the prototype KDP. This paraelectric phase is monoclinic as is that of RbD$_2$PO$_4$ [2] and CsD$_2$PO$_4$ [3]; therefore, CDP is considered as a low-symmetry representative of the KDP group. The low temperature ferroelectric transition in CDP, which occurs at 153 K, has been intensively studied due to the unusual pseudo one-dimensional character of the properties [4]. Above room temperature, two phase transitions have been reported [1, 5, 6], but a controversy still remains about the existence and the temperature of the lower one [7, 8]. It has been shown [9] that the highest temperature phase is a protonic superionic one. Among the alkali phosphate and arsenate compounds belonging to the KDP group which exhibit a phase transition above room temperature, only CDP and CDA (CsH$_2$AsO$_4$) have been found to become superionic conductors [10].

The properties of both these compounds above room temperature, particularly in the vicinity of the superionic transition, have been scarcely studied to date. Therefore, we have planned to investigate their elastic properties by Brillouin spectroscopy and have recently reported the results obtained in CDA [11]. We present here a similar study on CDP. Such a study is a priori justified by the structure difference of these compounds. The room temperature paraelectric (PE) phase of CDA is tetragonal, like that of KDP, with the same space group I42d while the room temperature PE phase of CDP is monoclinic with space group P2$_1$/m. The PE phase of CDP is isomorphic to the one of TiH$_2$PO$_4$ (TDP) which has however a slightly different space group (P2$_1$/a). This last compound, also belonging to the KDP group, undergoes a ferroelastic transition above room temperature which has been recently refined by neutron diffraction [12].

2. Experimental and Brillouin Data

Brillouin scattering spectra have been obtained with a spectrometer which is a pressure scanned, triple passed Fabry-Perot interferometer (effective finesse 70, resolving power 760000). The spectra are frequency checked by a Michelson interferometer in parallel. We worked with the $\lambda_0 = 514.5$ nm line of a single frequency Ar ion laser and the stability of the line is controlled by an iodine cell.

The samples have been cut from monocrystals obtained by seed growth from aqueous solution by very slow cooling.

As noted in the introduction, the room temperature structure of CDP is monoclinic, not piezoelectric, with space group P2$_1$/m (C$_{2h}$) [13]. The latest measurements of the cell parameters [14] give $a = 7.9072$ Å, $b = 6.3869$ Å, $c = 4.8792$ Å and $\beta = 107.712^\circ$. There are two formula units per cell. It has been pointed out that the structure is quasi-orthorhombic with the choice $a' = 2a + c$, $b' = b$ and $c' = c$ since it gives $\beta' = 90.22^\circ$ [15].

Unlike the case of KDP, for which all hydrogen bonds are symmetry related, there are two crystallographically non equivalent hydrogen bonds in the structure at room temperature related to H(1) and H(2) atoms [13, 15]. The stronger bonds, involving H(1) atoms, form chains of PO$_4$ tetrahedrons along the c axis and they are ordered at that temperature. The other H(2) hydrogen bonds make zigzag chains running along the b axis and the corresponding protons
are found to be disordered on two off-centre sites with significant correlations [3] and to become ordered below the ferroelectric transition. These two kinds of connected chains make layers parallel to (100) planes which correspond to the observed cleavage plane [16]. This structure strongly resembles that of TDP at room temperature [17].

Above room temperature two phase transitions have been found near 149 °C and 230 °C by differential scanning calorimetry [1, 5]. However, contradictory results exist for the lower transition. In a recent study [18], this transition did not appear in DSC but a broad heat capacity anomaly has been detected near 149 °C. An X-ray diffraction investigation [19] has revealed that no change of the space group occurs at 149 °C; only a weak feature in one of the thermal expansion coefficients has been observed. In an earlier work [6], it was reported that a monoclinic-tetragonal change near 150–160 °C is possible as a result of prolonged heating in this temperature range. In other experiments performed above room temperature, such as conductivity measurements [9, 10] or Raman spectroscopy [20], the lower transition has not been detected. It has been also claimed [7, 8] that, by appropriate pretreatments of the samples, a transition can occur at 107 °C which is much lower than the temperature 149 °C cited above. Thus, it can be considered up to date that no definitive conclusion is available about the existence of that transition.

The second transition near $T_S \sim 230$ °C is well marked in every experiment. The high temperature phase has been identified as a protonic superionic one [9, 10], but contradictory data exist about its structure. From polarization microscopic observations Baranov et al. [10] concluded to a cubic structure. In an X-ray investigation performed on samples in air, Bronowska et al. [19] obtained a monoclinic structure 7 °C above $T_S$ which is found to coexist with other phases coming from the decomposition of CDP by successive water losses; but in new experiments performed in a H$_2$O atmosphere by the powder method, a cubic structure has been found with Pm3m ($O_\text{h}^3$) space group [21].

At room temperature, we have verified that, in the (010) plane, the angle between one axis of the refractive index ellipsoid and the $c$ axis is $\sim 4.5^\circ$ as previously reported [22]. The small value of that angle shows that, in this plane, the ellipsoid axes almost coincide with the crystallographic axes $a'$ and $c$. At room temperature, we have measured the indices at $l_0$ with light polarized along $a'$, $b$ and $c$; the following values have been obtained: $n_{a'} = 1.518$, $n_b = 1.512$ and $n_c = 1.537$.

For all the phases above room temperature, the elastic constants have been referred to a set of orthogonal $x$, $y$ and $z$ axes with $y \parallel b$, $z \parallel c$, $x \perp y$ and $z$ (Fig. 1). It can be remarked that $x$, $y$ and $z$ axes almost coincide with the crystallographic axes of the quasi-orthorhombic cell.
Table I. — Characteristics of the investigated scattering geometries. The usual convention depicting wavevector and polarization directions of the incident and scattered light beams has been used.

<table>
<thead>
<tr>
<th>Scattering geometries</th>
<th>Direction of ( \mathbf{q} )</th>
<th>( \rho V^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 ((-x + z)[y, y](x + z))</td>
<td>[100]</td>
<td>( C_{11} )</td>
</tr>
<tr>
<td>2 ((x - y)[z, z](x + y))</td>
<td>[010]</td>
<td>( C_{22} )</td>
</tr>
<tr>
<td>3 ((x - z)[y, y](x + y))</td>
<td>[001]</td>
<td>( C_{33} )</td>
</tr>
<tr>
<td>4 ((-y)<a href="x">z, z</a>)</td>
<td>[110]</td>
<td>( C^* )</td>
</tr>
</tbody>
</table>

The mass density \( \rho = 3.254 \text{ g cm}^{-3} \) has been deduced from cell parameters \([14]\). Due to the weak change of unit cell volume between 20 °C and 207 °C \([19]\), the lack of data about the mass density above 207 °C and about the temperature dependence of refractive indices, we used the room temperature values of both density and refractive indices in computing the elastic constants from Brillouin shifts at any temperature. It is usually considered that the variations versus temperature of these two quantities may partially compensate.

During measurements, the samples were immersed in silicon oil as index matching liquid to decrease the stray light; another advantage is a better homogeneity of the temperature in the sample.

To avoid hysteresis effects, all measurements have only been performed on heating. Above \( T_5 \), the samples keep their optical quality; but an irreversibl deterioration can be observed when temperature decreases through \( T_3 \) from the conducting phase. Due probably to the appearance of numerous microcracks, the samples become milky, retaining the integrity of their external shapes, but the laser beam can no longer enter them. These results agree with previous observations \([10]\). After cooling down to room temperature, if the samples are heated for a second time, the opacity does not disappear above \( T_5 \).

Contradictory data exist about the onset of decomposition of CDP in experiments performed in air. It has been reported that a thermal decomposition starts in the range 175–225 °C \([19,23]\), in contradiction with others observations made up to 250 °C \([5,18]\); Romain et al. \([20]\), which worked with samples in sealed glass tubes, did not detect any decomposition compounds up to \( \sim 250 \) °C. For our samples, heated in oil up to 260 °C, no start of bubble has been observed; that would indicate that no obvious loss of water occured below that temperature. To ensure this result, we have performed an X-ray diffraction analysis on a sample which has been heated up to 260 °C, after it was cooled down to room temperature, and we have checked that the recorded spectrum is identical to the standard one of CDP at room temperature \([14]\).

3. Brillouin Experiments

In the right angle scattering geometry, which has been used, the velocity \( V \) of an acoustic wave is related to the corresponding Brillouin frequency shift \( \nu \) by:

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

where \( n_i \) and \( n_s \) are the refractive indices for the incident and scattered light beams respectively.

Parallelepipedic samples have been cut and oriented so that the acoustic wave vector \( \mathbf{q} \) lies along \( x, y \) and \( z \) axes. Investigations versus temperature have been focused on Brillouin lines which correspond to longitudinal or pseudo-longitudinal (pL) acoustic waves (see Tab. I).
For these waves, $\rho V^2$ is related to elastic constants by:

$$
\begin{align*}
q \parallel x & : \quad \rho V_x^2 = [C_{11} + C_{55} + (C_{11} - C_{55})^2 + 4C_{15}^2]^{1/2}/2 \\
q \parallel y & : \quad \rho V_y^2 = C_{22} \\
q \parallel z & : \quad \rho V_z^2 = [C_{33} + C_{55} + (C_{33} - C_{55})^2 + 4C_{35}^2]^{1/2}/2.
\end{align*}
$$

If we assume that $C_{15}$ and $C_{35}$ are small with respect to $C_{11} - C_{55}$ and $C_{33} - C_{55}$, we have:

$$\rho V_x^2 \cong C_{11}, \quad \rho V_y^2 = C_{22}, \quad \rho V_z^2 \cong C_{33}.$$ 

This assumption can be justified by the fact that the chosen axes $x$, $y$ and $z$ almost coincide with the directions of the pseudo-orthorhombic axes $a'$, $b$ and $c$. Nevertheless, to check it more quantitatively at room temperature, we have made additional measurements on pseudo-transverse (pT) acoustic waves in the samples described above and in another sample cut with edges along $x$, $y$ and $z$. We have measured the values of $\rho V_p^2$ and $\rho V_T^2$ along [100], [001], [101] and [101] (among which $\rho V_p^2 = 32.8$ GPa and $\rho V_T^2 = 67.2$ GPa). From these values, those related to the last two directions being only used in the relation $\rho(V_p^2[101] + V_T^2[101] - V_p^2[101] - V_T^2[101]) = 2(C_{15} + C_{35})$, the following results have been obtained (in GPa):

$$C_{11} = 32.4, \quad C_{22} = 29.6, \quad C_{33} = 67.0, \quad C_{55} = 4.73, \quad C_{15} = 3.3, \quad C_{35} = 3.2$$

with an accuracy estimated to 2%, except for $C_{15}$ and $C_{35}$ for which it is equal to 20%. It can be concluded that $\rho V_x^2$ and $\rho V_z^2$ coincide with $C_{11}$ and $C_{33}$ within the measurement accuracy.

We have also performed a temperature investigation of the pseudo-longitudinal wave with $q$ along [110]. The related expression of $\rho V^2$ is very cumbersome; within the assumption of a quasi-orthorhombic symmetry (i.e. if we consider that $C_{15}$, $C_{35}$ and $C_{46}$ are $\cong 0$), we have:

$$\rho V^2 = C^* \cong (C_{11} + C_{22} + 2C_{66})/4 + [(C_{11} - C_{22})^2 + 4(C_{12} + C_{66})^2]^{1/2}/4.$$ 

It is be emphasized that, in the high temperature phases, we have named the elastic constants $C_{11}$, $C_{22}$, $C_{33}$ and $C^*$ in keeping with the nomenclature used in the room temperature phase. Indeed, they represent the values of $\rho V^2$ corresponding to acoustic waves which propagate along the directions [100], [010], [001] and [110] defined with respect to the chosen frame at room temperature, because neither the structure nor the crystallographic axes are known.

4. Results

4.1. Elastic Constants. — The temperature dependences of $C_{11}$, $C_{22}$, $C_{33}$ and $C^*$ are reported in Figures 2 and 3. No obvious features are detected around 107 °C or 149 °C corresponding to the uncertain transition discussed above. On the contrary, discontinuities occur in every elastic constant at the superionic transition which we have found to occur at $T_S = 233.1 \pm 0.1$ °C. Between 20 °C and $T_S$, the four curves exhibit a downward bending which is more or less marked, depending on the constant.

Above $T_S$, unexpected results are obtained for $C_{11}$, $C_{22}$, and $C^*$. In a given scattering geometry, when the sample is translated to modify the position of the scattering volume (cylindrical shape with a diameter of 0.1 mm and a length of 0.2 mm), the spectrum, involving initially a given Brilliouin doublet, may change quasi-discontinuously, exhibiting a new doublet with a different value for the frequency shift, the broadening and the intensity. The spatial extension of the regions related to a given doublet can be very different, depending on both the doublet and the sample; therefore it is difficult to perform a complete exploration of the samples.
Fig. 2. — Temperature dependence of the elastic constants $C_{11}$, $C_{22}$ and $C^*$. $D_1$, $D_2$ and $D'$ refer to the different doublets observed in the conducting phase. $D_1$ ($D_2$) corresponds to the highest (lowest) frequency shift.

Fig. 3. — Temperature dependence of the elastic constant $C_{33}$.

and we are never sure to have detected all the possible different regions. The number of observed doublets depends on the direction of $q$: two ($D_1$, $D_2$) for [100] and [010], three ($D_1$, $D'$, $D_2$) for [110], but a single one for [001] in spite of a careful exploration, within the reserve noted above. The lines of every doublet have been found to be polarized with the same polarization (VV) as the corresponding doublet below $T_S$. Taking into account the polarization and the cross-section of the lines, we think that they have to be attributed to longitudinal or pseudo-longitudinal elastic waves. The corresponding elastic constants show linear decreases versus temperature in the conducting phase.
Table II. — Characteristics of the Brillouin spectra just above the superionic transition. Polar. is the polarization of the light beams (V, H stand for vertical and horizontal respectively, the scattering plane being horizontal). r is the ratio i/I where i and I are the recorded lines integrated intensities of the additional doublet and main doublets respectively.

<table>
<thead>
<tr>
<th>Scattering geometries</th>
<th>Main doublet</th>
<th>Additional doublet</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ρV² (GPa)</td>
<td>Γ (GHz)</td>
<td>existence</td>
<td>polar.</td>
</tr>
<tr>
<td>1</td>
<td>D₁</td>
<td>26.0</td>
<td>1.8</td>
<td>yes</td>
</tr>
<tr>
<td></td>
<td>D₂</td>
<td>20.7</td>
<td>0.55</td>
<td>no</td>
</tr>
<tr>
<td>2</td>
<td>D₁</td>
<td>25.2</td>
<td>1.75</td>
<td>yes</td>
</tr>
<tr>
<td></td>
<td>D₂</td>
<td>20.1</td>
<td>0.58</td>
<td>no</td>
</tr>
<tr>
<td>3</td>
<td>26.3</td>
<td>1.63</td>
<td>yes</td>
<td>VV</td>
</tr>
<tr>
<td>4</td>
<td>D₁</td>
<td>24.64</td>
<td>1.75</td>
<td>yes</td>
</tr>
<tr>
<td></td>
<td>D’</td>
<td>21.76</td>
<td>1.0</td>
<td>no</td>
</tr>
<tr>
<td></td>
<td>D₂</td>
<td>19.94</td>
<td>0.61</td>
<td>yes</td>
</tr>
</tbody>
</table>

In some spectra, besides the main doublet, an additional doublet is unambiguously detected with a very small intensity and with the same polarization as that of the main doublet, except for D₂ of C*, for which it appears in crossed polarization (VH). The characteristics of the spectra just above T₅ are reported in Table II.

4.2. BRILLOUIN LINEWIDTHS. — Below T₅, no broadening of Brillouin lines can be detected; but above T₅, every line related to a main doublet exhibits a broadening. The full widths at half maximum (FWHM) Γ₁, Γ₂, Γ₃ and Γ* of the lines corresponding to C₁₁, C₂₂, C₃₃ and C* are reported in Figure 4, after deconvolution. The uncertainty is estimated to 0.2 GHz and the instrumental width is 0.9 GHz.

The broadening of a line significantly depends on the type of doublet (D₁, D₂ or D’), but for a given doublet, D₁ or D₂, similar values are obtained whatever the elastic constant C₁₁, C₂₂ or C*. No pretransitional features appear near the transition, but a smooth increase of Γ₁(D₁), Γ₂(D₁), Γ*(D₁) and Γ₃ takes place on heating, while Γ₁(D₂), Γ₂(D₂) and Γ*(D₂) keep nearly constant values.

4.3. ELASTIC AND QUASI-ELASTIC SCATTERING. — The unshifted Rayleigh peak has been recorded in every spectrum by mean of calibrated attenuators. At T₅, its intensity generally shows an abrupt increase in most of the scattering geometries, except in the case of C₁₁(D₂), for which a small decrease is observed. Figure 5 shows typical variations of the Rayleigh peak intensity. In spite of an almost very same behaviour consisting of an increase of the intensity, at T₅, to a value which remains nearly unchanged with further heating, it seems difficult to draw any conclusions about the existence of an additional contribution to the elastic scattering in the conducting phase, having in mind the major role played by the static defects and the difficulty to predict its temperature dependence.
Fig. 4. — Temperature dependence of $\Gamma_1$, $\Gamma_2$, $\Gamma_3$ and $\Gamma^*$, FWHM of the Brillouin lines related to elastic constants $C_{11}$, $C_{22}$, $C_{33}$ and $C^*$ respectively. For $D_1$, $D_2$ and $D'$: as in Figure 2.

Fig. 5. — Examples of temperature dependence of the Rayleigh line intensity. $R_1$ and $R_3$ correspond to the spectra related to $C_{11}$ and $C_{33}$ respectively. For $D_1$ and $D_2$: as in Figure 2.

We also observed that the Rayleigh peak profile does not change at $T_S$ and that no obvious background appears in the spectra above $T_S$. So, it can be concluded that there is no evidence for the occurrence of a quasi-elastic scattering in the conducting phase.

5. Discussion

5.1. Existence of Domains in the Conducting Phase. — As in CDA [11], the observation of more than one doublet in some scattering geometries above $T_S$ obviously suggests
the existence of domains in the conducting phase. In that phase, we recall that $C_{11}, C_{22}, C_{33}$ and $C^*$ represent “effective” elastic constants, equal to $\rho V^2$, related to elastic waves propagating along directions which have been defined with respect to the crystallographic axes of the room temperature phase. We must take into account that, above $T_S$, the symmetry class may have changed and that, for a given domain, the crystallographic axes may have rotated. A relation between the cubic and the monoclinic structures has been proposed in the latest X-ray investigation [21], in which two axes of the cubic phase are rotated by $\sim 45^\circ$ in the (001) plane, but no possibility of a domain structure has been suggested.

When $\mathbf{q}$ lies along [001], the fact that a single doublet is observed implies that the [001] direction is common to the different domains or that the values of $\rho V^2$ are very similar in the different domains. When $\mathbf{q}$ lies along [100] or [010], the close values of $C_{11}$ and $C_{22}$ for $D_1$ and $D_2$ and of the corresponding linewidths are consistent with the assumption that the crystallographic axes are oriented as described in [21] in one type of domain, while they are rotated by $45^\circ$ around an axis perpendicular to the (001) plane in the other type.

Within the latter assumption, in the case 4 of Table I, the observation of two doublets is expected with values of $\rho V^2$ which should be close to those obtained for $C_{11}$ and $C_{22}$. The doublets $D_1$ and $D_2$ for $C^*$ are consistent with that prediction. However, another doublet $D'$ has also been detected with intermediate values for $\rho V^2$ and linewidth. This implies the existence of a third type of domain which should also be observed in cases 1 and 2. This fact shows the difficulty in detecting all the types of domain. From the Brillouin results, the domain structure appears to be not simple, since three types of domain at least have been revealed.

The existence of an additional doublet in some spectra is also compatible with a cubic structure. Such a doublet is expected when $\mathbf{q}$ is not parallel to a face of the cubic cell, a situation which exists in the possible domains described above.

In conclusion, we will emphasize that a domain structure is unambiguously established by the Brillouin spectra. These spectra are compatible with a cubic structure of the domains but they cannot corroborate this structure. We think that there is only a few domain types, although the exact number cannot be given. The crystallographic orientations of the domains cannot be determined, but they appear well defined with respect to the monoclinic axes. We have verified that the same doublets are still recorded, whatever the investigated sample in a given scattering geometry.

5.2. ELASTIC ANOMALIES. — The elastic behaviour of CDP strongly resemble that of CDA [11]. At $T_S$, the abrupt jumps of elastic constants and the simultaneous appearance of significant broadening of the lines indicate a sharp first order transition in both compounds. Such a similarity was a priori not expected, owing to the difference of the structures at room temperature, even in the presence of an intermediate phase. A comparison of the results shows that the anisotropy of elastic properties is reduced at $T_S$ in both compounds, with the same range of values (20-26 GPa) for the elastic constants just above $T_S$. For the linewidths, the range appears greater in CDP than in CDA: 0.5–1.9 GHz and 0.5–1 GHz just above $T_S$, respectively. It can be pointed out that such an elastic behaviour has been also observed in the MHSeO$_4$ compounds (with $M = \text{NH}_4$, Rb, Cs) [24–26]. A downward jump of elastic constants is generally observed in all these protonic superconductors on heating through $T_S$; however, it can be pointed out that the present result for $C_{22}$ ($D_1$ doublet) shows that this type of jump does not systematically occur.

This common elastic behaviour is in keeping with a similarity of the conductive properties which appears in all these compounds [10, 27–30]. Such a similarity was also unexpected since in the MHSeO$_4$ family the number of protons is half that of their possible equivalent sites, whilst in the KDP family the number of possible sites is just equal to that of protons.
Whatever the domain, the jumps of elastic constants have to be related to the break of hydrogen bonds at $T_S$ which would probably occur with a simultaneous modification of the structure. Such a transition may either be induced primarily by the protons, as proposed in CsHSeO$_4$ type crystals [31], or be of the structural type related to a loss of stability of the rigid sublattice, as suggested for the superionic transition in Rb$_2$H(SeO$_4$)$_2$ [32], the disappearance of the protons mobility below $T_S$ being a consequence of the structural modification.

An analysis of the transition first requires an examination of the symmetry change. In CDP, the room temperature space group $P2_1/m$ is a subgroup of the cubic group $Pm3m$. However, there is a difficulty due to the possible existence of an intermediate phase between the monoclinic room temperature phase and $T_S$. This phase has been clearly evidenced in the study of the phase diagram [1], although not detected in the latest X-ray analysis [21]. A detailed study of the symmetry change is beyond the scope of this paper and we think that such a study might be undertaken when the structure data will be refined and confirmed. Nevertheless, it can be emphasized that, if a group-subgroup relation holds for the superionic transition, it is difficult to understand the existence of domains in the high temperature phase, which is the most symmetric one. Conversely, if there is no such relation, it is difficult to understand why the crystallographic orientations of the domains appear well defined with respect to the monoclinic room temperature phase structure.

Among the compounds MHSSeO$_4$ (with M = NH$_4$, Rb, Cs) and CsH$_2$AsO$_4$ (with A = As, P), it can be remarked that, below $T_S$, a non linear temperature dependence for elastic constants only appears in CDP. If an order parameter exists for the transition, a possible explanation of these evolutions with temperature is the biquadratic coupling $he^2Q^2$ between a strain $e$ ($e_1$, $e_2$ and $e_3$) and the order parameter $Q$, which is generally allowed whatever the symmetry of the prototype phase. In the low symmetry phase, this coupling gives a static contribution $\Delta C$ to the anomaly of an elastic constant $C$, which is proportional to the square of the average value $Q_0$ of the order parameter:

$$\Delta C = C - C_0 = 2hQ_0^2$$

where $C_0$ is the bare elastic constant. Thus, the temperature dependence of elastic constants would reflect, at least partially, the evolution of $Q_0^2$ far from the stability limit of the low temperature phase, taking into account the first order character of the transition.

In the conducting phase, couplings between elastic waves and mobile protons are expected to take place. A general study of couplings between these waves and mobile atoms has been given by Huberman et al. [33]. From that study, it can be deduced that a bilinear coupling $\lambda'\varepsilon s$ between a strain $e$, related to an acoustic wave, and a pseudospin variable $s$, describing the mean values of proton occupation numbers on their possible sites, leads to a complex frequency $\omega - i\beta$ for the acoustic wave, i.e. to a damped wave. If the damping is weak: $\beta \ll \omega$, the elastic constant $C(\omega)$ and the linewidth $\Gamma(\omega)$ can be written as follows:

$$\begin{align*}
C(\omega) &= \rho\omega^2/q^2 = C_0 - \lambda'^2\gamma_s^2/((\gamma_s - \beta)^2 + \omega^2) \\
\Gamma(\omega) &= 2\beta = (\lambda'^2/\rho)q^2\gamma_s/((\gamma_s - \beta)^2 + \omega^2)
\end{align*}$$

(1)

where $C_0$ is the bare elastic constant, $\lambda'$ a constant related to $\lambda$, $\gamma_s$ the relaxational frequency for the variable $s$. When $\omega \rightarrow 0$, we have also $q \rightarrow 0$ and $\beta \rightarrow 0$; therefore the static variation $\Delta C_0$ of the elastic constant is $\Delta C_0 = C_0 - C(0) = \lambda^2$ and (1) can be expressed as follows:

$$\begin{align*}
\begin{align*}
C'(\omega) &= C_0 - \Delta C_0\gamma_s^2/((\gamma_s - \beta)^2 + \omega^2) \\
\Gamma(\omega) &= \gamma_s(\Delta C_0/C(\omega))\omega^2/((\gamma_s - \beta)^2 + \omega^2)
\end{align*}
\end{align*}$$

(2)

No measurement of $\gamma_s$ by RMN investigation of the protons has been made in CDP. An estimation of $\gamma_s$ can be obtained by comparison with CsHSeO$_4$ [29, 34], taking into account
the similarity of the conducting characteristics; the order of magnitude is $\gamma_s \sim 0.5$ GHz. If several broadening mechanisms simultaneously occur, the experimental linewidth $\Gamma_{\text{exp}}$ verifies $\Gamma_{\text{exp}} \geq \Gamma = 2\beta$ with $\Gamma_{\text{exp}} = a\gamma_s$, $a$ being a factor between 1 and 4; therefore we have $0 < \beta \leq 2\gamma_s$ and $0 \leq (\gamma_s - \beta)^2 \leq \gamma_s^2$. Since $\omega$ is $\sim 10$ GHz for every line, we have consequently $(\gamma_s - \beta)^2 \ll \omega^2$ and the relations (2), adapted to the present results become:

$$
\begin{cases}
C(\omega) = C_0 - \Delta C_0 \gamma_s^2 / \omega^2 \approx C_0 \\
\Gamma(\omega) = \gamma_s (\Delta C_0 / C_0)
\end{cases}
$$

The first relation (3) shows that the influence of the coupling on the elastic constant is relaxed. If we assume that $\Gamma_{\text{exp}} = \Gamma$, i.e. if there is only the contribution of the coupling $\lambda'\varepsilon_s$, the second relation (3) gives for $\Delta C_0 / C_0$ a value between 1 and 4. Consequently, the static elastic constant $C(0) = C_0 - \Delta C_0$, obtained from the first relation (2) takes a null or negative value, a result which must be rejected. The conclusion is that the experimental linewidth $\Gamma_{\text{exp}}$ must be greater than $\Gamma$, which implies the presence of other broadening mechanism(s).

The observed broadenings are temperature independent or only slightly increased by heating, without pretransitional evolutions near $T_S$. This might be an argument in favour of a strong general anharmonicity of the lattice dynamics in the conducting phase, as one possible other mechanism. This assumption is consistent with a Raman study in CDP [20], which concluded in favour the existence of an important structural disorder in this phase.

The mobile protons are expected to give a contribution to the unshifted peak with a width of the order of $\gamma_s$, which is slightly lower than the apparatus width. This explains why no quasi-elastic scattering can be detected in the Brillouin spectra, even in the case of a significant contribution. Experimentally, this contribution cannot be distinguished from the elastic peak and is hidden by it as discussed in Section 4.3.

6. Conclusion

In this Brillouin investigation, we have observed a sharp modification of the lattice dynamics for the acoustic modes in the vicinity of the Brillouin zone centre, at the superionic transition. At $T_S$, the elastic constants $C_{11}$, $C_{22}$, $C_{33}$ and $C^*$ show discontinuities and broadenings of the related Brillouin lines abruptly take place. These anomalies of the elastic properties strongly resemble those of compounds of the MHSSeO$_4$ family ($M =$ NH$_4$, Rb, Cs) and those of CsH$_2$AsO$_4$, which belongs to the KDP family as CDP does. In the conducting phase, the spectra have revealed the existence of a domain structure which is difficult to understand with respect to the structure data available to date.

In the conducting phase, we have shown that a bilinear coupling between strains and mobile protons cannot contribute significantly to a modification of the elastic wave characteristics. We have proposed a strong general anharmonicity of the lattice dynamics as a possible explanation of the line broadenings. Therefore, we think that further investigations in CDP, such as structure refinements and lattice dynamics studies by other vibrational spectroscopies, will improve the knowledge of the transition mechanism in that compound and, possibly, in the other compounds above cited.
References