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Abstract. — A Brillouin scattering investigation in CsH$_2$AsO$_4$ has been performed over a temperature range $20 - 200$ °C which includes the superionic transition at $T_S \sim 167$ °C. At T_S, large discontinuities are observed for elastic constants C_{11}, C_{33} and $C^* = (C_{11} + C_{12} + 2C_{66}^E)/2$ and, above T_S, a broadening of the corresponding lines takes place. In the conducting phase above T_S, the spectra reveal a domain structure. The results are discussed by comparison with compounds of CsHSeO$_4$ type. It is shown that a linear coupling between strains and mobile protons in the conducting phase can neither contribute to modification of elastic constants nor to broadening of lines. The experimental results reflect a strong general anharmonicity of the lattice dynamics in the conducting phase.

Résumé. — Une étude par diffusion Brillouin de CsH$_2$AsO$_4$ a été faite sur l'intervalle de température $20 - 200$ °C qui contient la transition superionique à $T_S \sim 167$ °C. À T_S, d'importantes discontinuités sont observées pour les constantes C_{11}, C_{33} et $C^* = (C_{11} + C_{12} + 2C_{66}^E)/2$ et, au-dessus de T_S, un élargissement des raies correspondantes apparaît. Dans la phase conductrice au-dessus de T_S, les spectres révèlent une structure en domaines. Les résultats sont discutés par comparaison avec les composés du type CsHSeO$_4$. On montre qu'un couplage linéaire entre une déformation et les protons mobiles dans la phase conductrice ne peut pas contribuer à la modification des constantes élastiques ni à l'élargissement des raies. Les résultats expérimentaux révèlent plutôt une forte anharmonicité générale pour la dynamique de réseau dans la phase conductrice.

1. Introduction

Cesium dihydrogen arsenate CsH$_2$AsO$_4$, hereafter abbreviated CDA, belongs to the KDP (KH$_2$PO$_4$) family which has been the object of intense research for generally focused on the low temperature ferroelectric-paraelectric transition, over three decades.

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Above room temperature, two phase transitions have been detected near 123 °C and 165 °C respectively [1–5]. The lower transition appears only in X-ray and some DTA investigations, while the upper one is systematically detected whatever the type of investigation. It has been recently established [6] that the highest temperature phase is a protonic superionic conductive one. CDA and cesium dihydrogen phosphate (CDP) are the only two compounds in the KDP family which are known, to date, to exhibit such a conductive phase [6].

The properties of CDA above room temperature have only been scarcely investigated. We report here an investigation of the elastic behaviour by Brillouin spectroscopy over a temperature range which includes the two transitions cited above. The interest of such a study is enhanced by the fact that conductive phases also exist in other, but structurally different, families of hydrogen bonded compounds such as $MHSeO_4$ (with M = NH_4, Rb and Cs) that we have recently investigated by Brillouin scattering [7–9].

2. Experimental and Crystal Data

The Brillouin scattering experiments were performed with a spectrometer which is a pressure scanned, triple passed plane Fabry-Perot interferometer (effective finesse 70, resolving power 760000). 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 samples were cut from monocrystals which were obtained by seed growth from aqueous solution by slow evaporation.

At room temperature, the structure is tetragonal with space group $I\bar{4}2d$ (the same as KDP at room temperature). The most recent measurements of cell parameters give $a = b = 7.9865$ Å and $c = 7.8979$ Å [10].

The first transition near 123 °C has been observed by DTA in some experiments [2,3], but not systematically [4], and by X-ray diffraction [3,4]. The structure of the phase above 123 °C is given as monoclinic but without data about parameters [4].

It has been suggested that the superionic phase, which takes place above the second transition near $T_S = 165$ °C, has a monoclinic structure [2]. However, in an X-ray investigation [4], the structure has been found to be orthorhombic with parameters which are different from those at room temperature. Recently, Baranov et al. have claimed a cubic structure on the basis of optical observations [6]. Thus, we think that no definitive data are now available about that structure.

At room temperature, we have measured the refractive indices at λ_0 and obtained the values $n_a = 1.5749$ and $n_c = 1.5525$ which are in excellent agreement with those cited in [11]. The mass density $\rho = 3.610$ g cm^{-3} has been deduced from cell parameters at room temperature [10].

In computing the elastic constants from Brillouin frequency shifts, we have used the room temperature values of mass density and refractive indices at any temperature. No data are available about their temperature dependences and it is usually considered that their evolution with temperature may partially compensate one another.

In every measurement, the sample was immersed in silicon oil as index matching liquid; the advantages being a reduction in the amount of stray light and a more homogeneous temperature of the sample.

To avoid hysteresis effects, all measurements were performed by heating the crystals. Above T_S, the samples still have a good optical quality (identical to that between room temperature and T_S), but an irreversible deterioration takes place when temperature decreases through T_S from the conducting phase. The samples become milky, retaining the integrity of their external shapes, but the laser beam can no longer enter them.

Table I. — *Characteristics of the investigated scattering geometries. The usual convention* $x\|a, y\|b(=a)$ *and* $z\|c$ *and that depicting wave vector and polarization directions of the incident and scattered light beams have been used.*

	Scattering geometry	direction of **q**	expression of ρV^2
1	$(x+y)[y,y](-x+z)$	[100]	C_{11}
2	$(x+y)[z,z](-x+y)$	[100]	C_{11}
3	$(-z-y)[x,x](-y+z)$	[001]	C_{33}
4	$-x[z,z]y$	[110]	$C^* = (C_{11} + C_{12} + 2C_{66}^E)/2$
5	$(x+z)[(-x+z),y](-x+z)$	[100]	C_{66}^E

Above T_S, for sample immersed in oil, we observed in oil no bubble starting from the samples. That would indicate that no obvious water loss occurs in the studied temperature range. It is to be noted that for experiments performed in air, there are significant disparities about the temperature of the onset of water elimination , which is found between 150 and 250 °C [2,4]. In order to corroborate our observations, we have performed an X-ray diffraction analysis on a sample which has been used in Brillouin investigations, after cooling down to room temperature and verified that the obtained spectrum is identical to the standard one of CDA [10].

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 ν 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 are reported in Table I along with the direction of the acoustic wave vector **q** and the expression of ρV^2 in terms of elastic constants in the tetragonal room temperature phase.

The piezoelectricity of the tetragonal phase introduces no distinction between elastic constants at constant electric displacement C_{ij}^D and elastic constants at constant electric field C_{ij}^E for C_{11}, C_{33}, and C_{12}. On the contrary, C_{66}^D and C_{66}^E have to be distinguished; the values of the piezoelectric modulus d_{36} [12] and of the dielectric constant ε_{33} lead to a relative difference of 15% between them at room temperature.

We have focused on Brillouin lines corresponding to longitudinal elastic waves which are intense lines, as usual, and for which ρV^2 is a simple expression in terms of elastic constants (the four first scattering geometries). C_{11} has been investigated in two scattering geometries in order to detect a possible splitting in the high temperature phase. We have also studied the Brillouin line corresponding to the transverse elastic wave related to C_{66}^E for two reasons; firstly, its intensity appears to be as large as that of a longitudinal wave and secondly, it is the constant C_{66}^E which exhibits the famous decrease to zero at the low temperature ferroelectric phase transition, common to all the KDP family compounds. It must be pointed out that, in the superionic phase, the elastic constants have been named C_{11}, C_{33} and C^* in keeping with the nomenclature at room temperature. The structure of this phase is not clearly established and our data only represent the values of ρV^2 corresponding to acoustic waves propagating along the directions [100], [001] and [110] defined at room temperature.
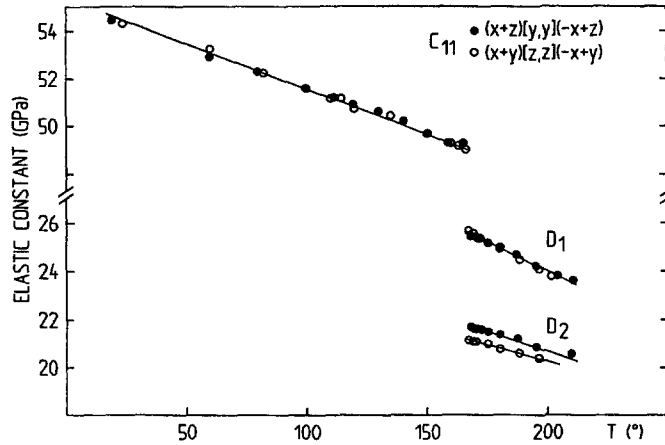
Fig. 1. — Temperature dependence of elastic constant C_{11}. D_1 and D_2 refer to the two observed doublets (see text). Lines are guides for the eye.

4. Results

4.1. ELASTIC CONSTANTS. — At room temperature, the following values have been obtained (in GPa) :

$$C_{11} = 54.5 \quad C_{33} = 41.8 \quad C_{66}^E = 1.82 \quad C^* = 29.7 \quad C_{12} = 1.3$$

with an accuracy estimated to 1%, except for C_{12} for which the accuracy drops to 100%, due to its indirect determination. These values agree satisfactorily with previous results [13], although they are systematically higher. This fact can be explained by the lower value of the mass density which has been taken in [13].

The temperature dependences of C_{11}, C_{33}, C_{66}^E and C^* are reported in Figures 1 and 2. They show no obvious feature around the first transition near 123 °C. Abrupt and relative large downward jumps for each elastic constant appear at the superionic transition, which we have found to occur at $T_S = 167.3 \pm 0.1$ °C, without pretransitional evolution below T_S.

Above T_S, unexpected results are obtained. In a given scattering geometry, if the sample is translated in order to change the position of the scattering volume (of cylindrical shape with a diameter of 0.1 mm and a length of 0.2 mm) the spectrum, involving initially a given Brillouin doublet, may change quasi-discontinuously, exhibiting a new doublet with a different frequency shift and a different cross section. Such an exploration of the samples is tedious because the spatial extensions of regions giving different spectra can be very different, depending on the samples. In the sample cut to measure C^*, only one type of spectrum has been detected, while for every other scattering geometry two types of doublet have been observed which we have named D_1 and D_2 (D_1 being the doublet with the highest frequency shift). The lines for D_1 and D_2 have been found to be well polarized with the same polarization as that of the corresponding doublet below T_S. Taking into account their intensities, it is reasonable to associate them with longitudinal acoustic waves. In some spectra, an additional doublet with very small intensity and small frequency shift is unambiguously observed, with a polarization which is the same as that of the main doublet. The characteristics of the spectra obtained just above T_S are reported in Table II.
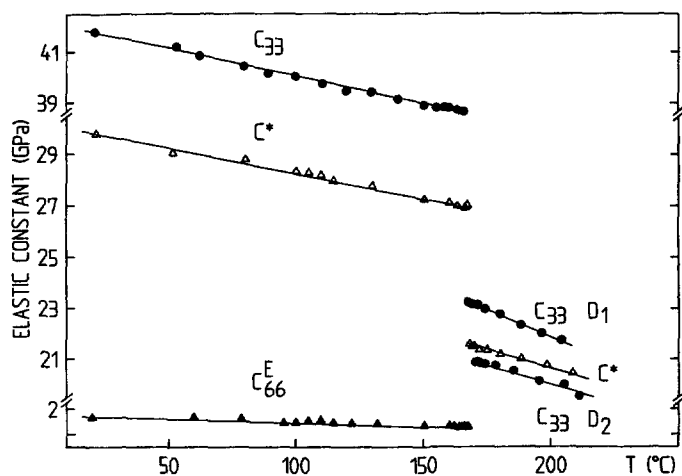
Fig. 2. — Temperature dependence of elastic constants C_{33}, C^*, and C_{66}^E. For D₁ and D₂: as in Figure 1. Lines are guides for the eye.

Table II. — *Characteristics of Brillouin spectra just above T_S. R is the ratio of the recorded line height H with respect to that of the corresponding line just below T_S; r is the ratio h/H, h being the recorded line height of the additional weak doublet.*

Scattering geometry	Main doublet		Additional doublet		
	ρV^2 (GPa)	R	existence	ρV^2 (GPa)	r
1	D₁ 25.7	unchanged	yes	3.5	2.6×10^{-2}
	D₂ 21.7	enhanced by ~ 2	yes (v. weak)	4.0	2.2×10^{-2}
2	D₁ 25.7	unchanged	yes	3.9	3.6×10^{-2}
	D₂ 21.2	enhanced by ~ 2	yes (v. weak)	4.7	2.0×10^{-2}
3	D₁ 23.3	unchanged	yes	4.0	4.0×10^{-2}
	D₂ 20.9	enhanced by ~ 2	no		
4	21.6	enhanced by ~ 2	no		

When the temperature increases, the doublet related to C_{66}^E disappears abruptly at T_S. Above T_S no line with the same polarization can be detected in spite of careful research. This result shows that either the line height is reduced by a factor greater than 100 or the frequency shift (at constant height) is lower than 1.10 GHz, corresponding to a value of ρV^2 equal to 0.25 GPa.

4.2. BRILLOUIN LINEWIDTHS. — Below T_S, no broadening of lines has been detected. But above T_S, every line related to a main doublet exhibits a broadening. The full widths at half maximum (FWHM) Γ_1, Γ_3 and Γ^* of lines corresponding to elastic constants C_{11}, C_{33} and C^* are reported in Figure 3, after deconvolution. No critical behaviour appears near the superionic transition, but smooth increases take place when temperature increases.
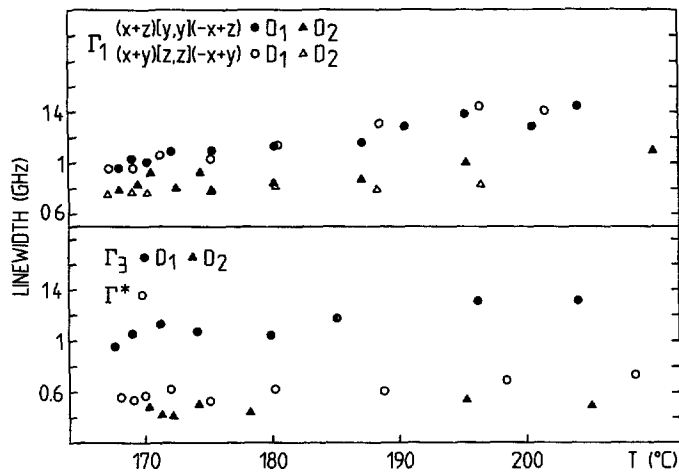
Fig. 3. — Temperature dependence of line broadenings Γ_1, Γ_3 and Γ^* in the conducting phase, respectively related to elastic constants C_{11}, C_{33} and C^*. For D_1 and D_2: as in Figure 1.

4.3. ELASTIC AND QUASI-ELASTIC SCATTERING. — When temperature increases through T_S, the intensity of the unshifted Rayleigh line is generally found to increase by a factor which varies from 1.6 to 40 depending on the sample, except in the case of scattering geometry n°4 for which a decrease is observed by a factor $\sim 10^{-1}$ These results largely reflect the role played by static defects in elastic scattering and do not allow any conclusions about the appearance of an additional elastic contribution in the conducting phase. Furthermore. the shape of the Rayleigh line does not change at T_S and no obvious background is evident above T_S. Taking into account the value of the FWHM of the recorded Rayleigh line (0.77 GHz) and the fact that the apparatus works with a ± 600 GHz (± 20 cm^{-1}) filter centered on λ_0 to remove the Raman spectra, we can conclude that no evidence is obtained for quasi-elastic scattering within this range, in the conducting phase.

5. Discussion

5.1. DOMAINS IN THE CONDUCTING PHASE. — The appearance of doublets above T_S obviously suggests the existence of domains in the conducting phase. In that phase, we recall that C_{11}, C_{33}, and C^* represent "effective" elastic constants equal to ρV^2 related to elastic waves propagating along directions which are defined with respect to the crystallographic axes of the tetragonal phase, because the crystal system may have changed and the crystallographic axes may have rotated. Similarly, as indicated above, we have used in the conducting phase the same index as below T_S for a given scattering geometry. Then, these indices are not, a priori, appropriate. However, we can reasonably assume that the influence of their changes upon the computation of the velocities is weak. This point is supported by the results for the constant C_{11}, for which a unique curve is obtained for D_1 when the indices n_a and n_b are used as below T_S while two curves appear slightly but unambiguously split for D_2. If n_a and n_b are exchanged in the computing, the splitting is doubled. Nevertheless, the two curves can be reasonably related to the same effective elastic constant, taking into account the similar cross section of the lines.

The set of results show that the directions of the crystallographic axes in the domains are not related in a simple way to those of the tetragonal phase since it appears that neither of them remains common to the various domains. Furthermore, the existence of an additional weak doublet with the same polarization as the main doublet, in almost all the scattering geometries, would indicate that the acoustic wave vector **q** never lies along a crystallographic axis in an orthorhombic, tetragonal or cubic structure or that **q** lies along a non-binary axis of a monoclinic or triclinic structure. On the basis of the Brillouin results only, we think that no definitive conclusion can be obtained about the number of domain types and about the orientation of their crystallographic axes.

The domain structure revealed by Brillouin scattering can be related to the changes which have been reported in visual observation [2] and can explain the fact that, apparently, the crystal becomes optically isotropic [2,6].

5.2. ELASTIC ANOMALIES. — The abrupt jumps of elastic constants at T_S and the simultaneous broadening of lines indicate a sharp first order transition. From that point of view, the elastic behaviour of CDA strongly resembles that of the compounds NH$_4$-, Rb- and CsHSeO$_4$ of the MHSeO$_4$ family [7-9]. These results are in keeping with the similarity of conductive characteristics between the KDP family and the MHSO$_4$ closed to the MHSeO$_4$ one, which has been previously emphasized [6]. Such a similarity was *a priori* 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 equivalent sites is just equal to that of protons.

The abrupt jumps of elastic constants, whatever the domain, have to be related to the break of hydrogen bonds at T_S which would reduce the lattice cohesion. However, a complete understanding of the results first requires the symmetry analysis of the transition and therefore the knowledge of the structure above T_S. If a group-subgroup relation holds, the presence of domains in the conducting phase would indicate that the low symmetry phase is the high temperature phase, a situation which has been rather scarcely observed. Another possibility is that the symmetry groups of the low and high temperature phases are subgroups of the same parent group. In this case, the transition would occur between two phases which may or may not be related by a group-subgroup relation. No definitive conclusion can be drawn about the connection between the existence of domains and the symmetry change, since the structure of the conducting phase is not known at present.

In the conducting phase, couplings between elastic waves and mobile protons are expected to take place. A general study of these couplings has been given by Huberman *et al.* [14]. From that study, it can be deduced that a linear coupling λes between a strain e and a pseudospin variable s, related to the mean values of proton occupation numbers on their possible sites, leads to a frequency dependent elastic constant $C(\omega)$ and Brillouin linewidth $\Gamma(\omega)$ which are given by [9]:

$$C(\omega) = \rho\omega^2/q^2 = C_0 - \Delta C_0\gamma_s(\gamma_s - \beta)/(\gamma_s^2 + \omega^2)$$
$$\Gamma(\omega) = 2\beta = (\Delta C_0/C(\omega))\omega^2\gamma_s/(\gamma_s^2 + \omega^2)$$

where γ_s is the relaxation frequency for fluctuations of s, C_0 the bare elastic constant, β the damping of elastic wave and $\Delta C_0 = C_0 - C(0) = \lambda^2$.

No NMR investigation about the measurement of γ_s has been performed till now. Taking into account the similarity of the conducting characteristics [6,15], if we assume that the value of γ_s for CDA is of the same order of magnitude as that for CsHSeO$_4$, namely $\gamma_s \sim 0.5$ GHz, the same conclusion as in that compound can be reached for CDA as well since $\gamma_s^2 \ll \omega^2$ holds. On one hand, the influence of the coupling on the elastic constant is relaxed and, consequently,

no decrease of that constant will occur; on the other hand, the expected broadening is much smaller than the experimental one. Therefore, the observed broadening would reflect other mechanism(s). From this point of view, investigations of lattice modes other than acoustic modes are suitable. The fact that no critical behaviour of the broadening appears near T_S might be an argument in favour of a strong general anharmonicity of the lattice dynamics in the conducting phase.

5.3. QUASI-ELASTIC SCATTERING. — The estimated value for γ_s would explain why no quasi-elastic scattering appears in the Brillouin spectra. The contribution of the mobile protons is expected to give an unshifted peak with a width similar to that of the apparatus. Therefore this contribution, if it takes place with detectable intensity, would be hidden by the elastic Rayleigh peak.

6. Conclusion

Our Brillouin investigations have shown that important discontinuities of elastic constants hold at the superionic transition in CsH_2AsO_4, without pretransitional features. In the conducting phase, a broadening is observed for each investigated Brillouin line, without critical evolution near the transition. All these results strongly resemble those of the $MHSeO_4$ family of compounds, although these compounds are structurally different from CDA. In the conducting phase, the results show the existence of a domain structure, a result which, unfortunately, cannot be discussed in relation to the structure change, due to the lack of data on the conducting phase. It seems that the broadening of lines above the transition would reflect a strong anharmonicity of the lattice dynamics, a suggestion that needs to be corroborated by a widened study of the lattice dynamics.

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