The Room Temperature Elastic Behaviour of CsH$_2$PO$_4$

S. Prawer, T. F. Smith and T. R. Finlayson

Department of Physics, Monash University, Clayton, Vic. 3168.

Abstract

The components of the elastic constant matrix of monoclinic caesium dihydrogen phosphate (CDP) have been determined using ultrasonic velocity measurements to be $C_{11} = 28.83 \pm 0.43$, $C_{22} = 26.67 \pm 0.37$, $C_{33} = 65.45 \pm 0.48$, $C_{44} = 8.10 \pm 0.15$, $C_{55} = 5.20 \pm 0.24$, $C_{66} = 9.17 \pm 0.22$, $C_{12} = 11.4 \pm 3.6$, $C_{13} = 42.87 \pm 1.58$, $C_{15} = 5.13 \pm 0.67$, $C_{23} = 14.5 \pm 4.4$, $C_{25} = 8.4 \pm 4.3$, $C_{35} = 7.50 \pm 0.81$ and $C_{46} = -2.25 \pm 0.31$ GPa. Calculations of the velocity surfaces, ray directions, Young's modulus surfaces and linear compressibility show marked elastic anisotropy, which has been correlated with the chain and layer-like structure of CDP.

1. Introduction

The crystal structure of ferroelectric CsH$_2$PO$_4$ ($T_c = 154$ K) was unambiguously determined to be monoclinic $P2_1/m$ by Usu and Kobayashi (1976) rather than the orthorhombic structure earlier reported by Fellner-Feildeg (1952). On the basis of the oxygen–oxygen bond distances they suggested that the structure consists of PO$_4$ groups, hydrogen bonded approximately along the $a$ and $c$ axes as shown in Fig. 1. The hydrogen bonds along the $a$ axis link the PO$_4$ groups into chains running along the $b$ axis. These chains are cross linked by the hydrogen bond along the $c$ axis. Thus (100) layers are formed which are bonded to each other by ionic forces involving the Cs$^+$ ion (see also Fig. 6a). The relative weakness of the interlayer forces is evident from the perfect cleavage that occurs along the (100) plane.

The structure was further refined by Matsunaga et al. (1980) who also determined the position of the hydrogen atoms. They found that the sites for the two hydrogen ions were inequivalent. The hydrogen ions associated with hydrogen bonding along the $c$ axis were ordered at room temperature, whereas the ions along the $a$ axis were disordered at room temperature. At $T_c$ the ordering of this hydrogen linked the chains of PO$_4$ tetrahedra together along the ferroelectric $b$ axis. Since one hydrogen is already ordered in the paraelectric state, the ferroelectric transition has been described as pseudo-one-dimensional, unlike the three-dimensional behaviour observed in the case of KH$_2$PO$_4$ (KDP) (Frazer et al. 1979). This one-dimensionality has been the focus to date of many of the studies on CsH$_2$PO$_4$ (CDP) (see e.g. Youngblood et al. 1980; Iwata et al. 1980; Yakushkin et al. 1981; Kanda et al. 1982, 1983).
The present paper does not specifically address the problem of the elastic behaviour in the vicinity of the transition but is restricted to a report of the room temperature elastic behaviour and its relationship to the crystal structure. As such, this work represents a first step in the overall understanding of the lattice dynamics of CDP.

The nature of the chain and layer like bonding can be expected to be reflected in the elastic properties of the crystal, as the elastic constants are given by the second derivative with respect to strain of the free energy. Here we report a complete determination of the elastic constant matrix of CDP, via measurements of the ultrasonic phase velocities along different crystallographic directions. There are 13 independent nonzero elastic constants $C_{11}$, $C_{22}$, $C_{33}$, $C_{44}$, $C_{55}$, $C_{66}$, $C_{12}$, $C_{13}$, $C_{15}$, $C_{23}$, $C_{25}$, $C_{35}$ and $C_{46}$ (Nye 1967) for monoclinic symmetry. Direct and simple relationships between measured velocities and elastic constants are only possible for $C_{22}$, $C_{66}$ and $C_{44}$. All the other constants occur coupled together in more complicated relationships. Also, only measurements along the $b$ axis yield pure elastic waves (i.e. purely transverse or purely longitudinal particle motion). Hence, the determination of all 13 elastic constants of a monoclinic system is demanding both experimentally and computationally.

The elastic constants are usually referred to an orthonormal set of axes $x, y, z$ which have a standard orientation with respect to the crystallographic axes $a, b, c$ (see 'Standards on Piezoelectric Crystals' 1949). The conventional arrangement is shown in Fig. 2. In order to avoid confusion, the normal notation $[x, \beta, \gamma]$ will refer to directions with respect to the monoclinic axes $a, b, c$, and the primed notation $[l, m, n]$ will refer to directions with respect to the orthonormal set.

Fig. 1. Crystal structure of CsH$_2$PO$_4$. Disorder in the hydrogen bonds along the $a$ axis involved in chain formation is indicated by the neighbouring solid and dotted circles used to represent the proton positions. Note that adjacent PO$_4$ groups in the $b$-axis chain are not in the same cell. [From Frazer et al. (1979).]
Once the $C_{ij}$ matrix is known it is possible to calculate the Debye temperature, bulk modulus, linear compressibility and Young's modulus, as well as constant phase and group velocity surfaces. The dependence of the last four quantities on crystal orientation must be related to the crystal structure, although this relationship is very complex.

Finally, as previously mentioned, the ferroelectric ordering in CDP is essentially of a one-dimensional nature. The elastic constants, particularly the off-diagonal elements, provide information about the cross compliance between the principal ferroelectric axis and directions at right angles to it. A knowledge of the cross compliance is essential for the description of anomalies which appear in these off-principal-axis directions.

2. Theory: Elastic Waves in Crystals

The equation of motion for particles in a crystal with displacements $u_i$ from their mean positions is given in the index-summation convention used throughout this paper by (Brown 1967)

$$
p \frac{\partial^2 u_i}{\partial t^2} = C_{ijkl} \frac{\partial^2 u_k}{\partial x_j \partial x_l},
$$

(1)

where $\rho$ is the density and $C_{ijkl}$ is the elastic constant tensor.

Representing a travelling wave in a crystal by the form

$$
u_i = A_i \sin(\omega t - k_j x_j),
$$

(2)

where $\omega$ is the frequency, $k$ is the wave vector and $A$ is the polarization vector, and substituting this into equation (1) yields

$$
p \omega^2 A_i = C_{ijkl} k_i k_j A_k.
$$

(3)
As dispersion effects are negligible in the long wavelength region of the ultrasonic measurements, the ultrasonic velocity \( V \) is \( \omega |k|^{-1} \), where \( |k| = (k_1^2 + k_2^2 + k_3^2)^{\frac{1}{2}} \).

Equation (3) may then be written as

\[
\lambda A = \rho V^2 A,
\]

where \( \lambda \) is a real symmetric matrix whose components are quadratic functions of the direction cosines \( l, m, n \) of the propagation vector \( k \). Specifically, if

\[
Q = \begin{bmatrix}
C_{11} & C_{66} & C_{55} & C_{56} & C_{15} & C_{16} \\
C_{66} & C_{22} & C_{44} & C_{24} & C_{46} & C_{26} \\
C_{55} & C_{44} & C_{33} & C_{34} & C_{35} & C_{45} \\
C_{56} & C_{24} & C_{34} & \frac{1}{2}(C_{23} + C_{44}) & \frac{1}{2}(C_{36} + C_{45}) & \frac{1}{2}(C_{46} + C_{25}) \\
C_{15} & C_{46} & C_{35} & \frac{1}{2}(C_{36} + C_{45}) & \frac{1}{2}(C_{13} + C_{55}) & \frac{1}{2}(C_{14} + C_{56}) \\
C_{16} & C_{26} & C_{45} & \frac{1}{2}(C_{46} + C_{25}) & \frac{1}{2}(C_{14} + C_{56}) & \frac{1}{2}(C_{12} + C_{66})
\end{bmatrix},
\]

\[
L = \begin{bmatrix}
il^2 \\
m^2 \\
n^2 \\
2mn \\
2ln \\
2lm
\end{bmatrix},
\]

then

\[
\lambda_{11} = Q_{1j} L_{j}, \quad \lambda_{22} = Q_{2j} L_{j}, \quad \lambda_{33} = Q_{3j} L_{j},
\]

\[
\lambda_{23} = Q_{4j} L_{j}, \quad \lambda_{13} = Q_{5j} L_{j}, \quad \lambda_{12} = Q_{6j} L_{j},
\]

where the Voigt notation has been used (Nye 1967) and \( j = 1-6 \).

Equation (4) indicates that \( \rho V^2 \) are the eigenvalues of the matrix \( \lambda \), whilst \( A \) (the polarizations) are the corresponding eigenvectors. For (4) to have non-trivial solutions it is required that

\[
|\lambda_{ik} - \rho V^2 \delta_{ik}| = 0.
\]

Hence, measurements of the three velocities (two transverse and one longitudinal) for a given propagation direction \( l, m, n \) were used to establish relationships between the elastic constants. To obtain sufficient relationships to determine all 13 elastic constants for a monoclinic material, measurements of all three velocities were required in at least six different directions (i.e. \([100]^\prime\), \([010]^\prime\), \([001]^\prime\), \([10n]^\prime\), \([110]^\prime\) and \([011]^\prime\)). Some of the relationships were redundant and were used as internal consistency checks on the data. The procedure adopted is outlined in Section 4.

The direction of energy flow \( R \) in a crystal is, in general, not parallel to the propagation vector. Often called the ray vector, \( R \) is given by the tensor product of stress and particle velocity (Musgrave 1970) and, by assuming Hooke’s law that strain is linearly proportional to stress (Nye 1967), it has been shown that its components are given by

\[
R_j = C_{ijkl} \hat{u}_i \partial u_k / \partial x_i.
\]

By assuming a wave solution of the form (2) exists, equation (6) can be written as

\[
\bar{R}_j = \frac{1}{2} C_{ijkl} A_i A_k k_i \omega,
\]
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where \( \bar{R}_j \) is the time average over one period \((2\pi/\omega)\) of the energy vector. As only the direction of \( R_j \) is of interest, (7) may be rewritten as

\[
r_j = 2\bar{R}_j |k|^{-1} \omega^{-1} = C_{ijkl} A_i A_j p_l,
\]

where \( p_l = k_l |k|^{-1} \) are the direction cosines of the propagation vector. Then, expanding (8) and using the Voigt notation we get

\[
r_1 = lQ_{1j} S_j + mQ_{6j} S_j + nQ_{5j} S_j,
\]
\[
r_2 = lQ_{6j} S_j + mQ_{2j} S_j + nQ_{4j} S_j,
\]
\[
r_3 = lQ_{5j} S_j + mQ_{4j} S_j + nQ_{3j} S_j,
\]

where \( j = 1-6 \), and \( S \) is the column matrix

\[
S = \begin{bmatrix}
A_1^2 \\
A_2^2 \\
A_3^2 \\
2A_2 A_3 \\
2A_3 A_1 \\
2A_1 A_2
\end{bmatrix}
\]

Hence for a given propagation direction \([lmn]\) the \( \lambda \) matrix was calculated and equation (4) was solved to obtain the eigenvalues (i.e. the values of \( \rho V^2 \)) and the eigenvectors (i.e. the polarization vector \( A \)).

Since \( \lambda \) is real and symmetric it has three real positive eigenvalues and three independent eigenvectors which are mutually perpendicular. In general the eigenvectors do not constitute purely transverse or purely longitudinal particle motion. In the special case that the longitudinal mode is pure, the two transverse modes are also pure. However, if only one transverse mode is pure, the remaining transverse and the longitudinal eigenvectors are not pure but are constrained to lie in a plane perpendicular to the pure transverse mode and are therefore referred to as semi-pure modes of vibration.

Once the polarization vector \( A \) was determined the matrix \( S \) could be calculated and using equation (9) the components of the ray direction \( r \) calculated.

3. Experimental

Sample Preparation

The CDP crystals used in this investigation were produced by the solvent evaporation method. The saturated solution was produced by reacting stoichiometric quantities of CsOH and H₃PO₄ which gave a saturated solution with a pH of approximately 4. The resulting crystals sometimes showed evidence of mixed growth habits which were revealed by examining the samples between crossed polarizers. In these cases, the offending section of crystal was removed before measurements were performed. It was found that lowering the pH to 2–2.5 by addition of excess H₃PO₄
eliminated this problem and gave crystals of excellent quality. Frazer et al. (1979) have also reported that in order to obtain good crystal growth, it was necessary to add a slight excess of H₃PO₄ to produce a starting solution with a pH of about 2·5. The crystals used for the elastic measurements varied in size and quality, but in all cases were at least 3 mm thick and the faces to which the transducers were bonded had diameters of at least 3·2 mm.

The crystals were aligned using Laue back reflection photographs with the aid of a computer program that produced simulations of Laue patterns for any given orientation (Cornelius 1981). These simulations enabled the Laue spots to be indexed, and using the actual indexed spot positions from the photograph, an estimate of the error in alignment could be calculated. This was found to be a maximum of one degree, but along the main symmetry directions the error was closer to $\pm 0·5^\circ$.

The ultrasonic measurements require two opposite faces to be polished flat and parallel to each other and perpendicular to a given crystallographic direction. CDP is brittle, heat sensitive and extremely water soluble making polishing a difficult task. However, samples were polished with faces parallel to within a tolerance of 10' of arc, with each surface flat to within 10 interference fringes per cm, and surface scratches less than 5 $\mu$m deep.

**Velocity Measurements**

The ultrasonic velocity was measured by the pulse echo overlap technique described by Papadakis (1967). A 3·18 mm (0·125 in.) diameter quartz transducer was bonded to one face of the specimen, and was excited by a 50–100 V peak-to-peak 10 MHz r.f. pulse. The returning echoes were picked up by this same transducer and displayed on a CRO. The pulse echo overlap technique involves triggering the CRO with a signal, the period of which is equal to the round trip travel time between the echoes of interest and hence overlapping the two echoes r.f. cycle for r.f. cycle on the oscilloscope screen. This enables the round trip travel time $T$ to be determined accurately from the triggering frequency and hence, from the pathlength of the specimen between the parallel faces, the velocity $V$ of the particular mode may be calculated.

The major source of error in this technique is the choice of the correct r.f. cycle for overlap. We have used, with some success, the criterion suggested by McSkimin (1961) for the determination of the correct overlap condition. However, whereas he applied the technique to homogeneous samples such as fused silica, which gave excellent quality echo trains, not only did the present samples contain defects which resulted in poor echo train quality, but the inherent monoclinic symmetry of the system also gave rise to mixed modes which produced an echo train composed of a superposition of separate modes, each with a different velocity. In these cases determination of the correct echo for overlap was difficult and in some cases there was an ambiguity of $\pm 1$ r.f. cycle in the overlap which gave rise to errors of the order of $\pm 1\%$ in the determined velocity.

The echo train quality, and hence the ability to determine the correct echo for overlap, is also very dependent on the quality of the bond between transducer and sample. In general, the thinner the bond the better the echo train quality. We found that Dow Corning 276-V9 resin (a thick and very viscous alpha methyl styrene fluid) was a satisfactory bonding agent for both longitudinal and transverse waves. Less
viscous bonding agents, such as silicone greases, whilst satisfactory for longitudinal waves, lacked sufficient acoustic coupling for the transverse waves. The Dow Corning 276-V9 resin has the important advantage over solid bonds (such as salol) that the crystal may be rotated in situ with respect to the transverse transducer to excite each one of the two transverse modes separately. This is essential in the case of a monclinic system, because for some propagation directions the polarization of the transverse mode with respect to the crystal axes is a function of the elastic constants which are yet to be determined.

### Table 1. Ultrasonic sound velocities in CsH₂PO₄

<table>
<thead>
<tr>
<th>No.</th>
<th>Direction of wave propagation¹</th>
<th>Approximate wave displacement direction</th>
<th>Velocity (10⁴ m s⁻¹)</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>V₁</td>
<td>100</td>
<td>100</td>
<td>3·047±0·005</td>
<td>SPL</td>
</tr>
<tr>
<td>V₂</td>
<td>100</td>
<td>010</td>
<td>1·688±0·02</td>
<td>PT</td>
</tr>
<tr>
<td>V₃</td>
<td>100</td>
<td>001</td>
<td>1·133±0·01</td>
<td>SPT</td>
</tr>
<tr>
<td>V₄</td>
<td>010</td>
<td>010</td>
<td>2·878±0·02</td>
<td>PL</td>
</tr>
<tr>
<td>V₅</td>
<td>010</td>
<td>100</td>
<td>1·788±0·02</td>
<td>PT</td>
</tr>
<tr>
<td>V₆</td>
<td>010</td>
<td>001</td>
<td>1·416±0·002</td>
<td>PT</td>
</tr>
<tr>
<td>V₇</td>
<td>001</td>
<td>001</td>
<td>4·540±0·01</td>
<td>SPL</td>
</tr>
<tr>
<td>V₈</td>
<td>011</td>
<td>010</td>
<td>1·586±0·015</td>
<td>PT</td>
</tr>
<tr>
<td>V₉</td>
<td>001</td>
<td>100</td>
<td>1·153±0·003</td>
<td>SPT</td>
</tr>
<tr>
<td>V₁₀</td>
<td>0·520, 0, −0·854</td>
<td>0·520, 0, −0·854</td>
<td>3·847±0·006</td>
<td>SPL</td>
</tr>
<tr>
<td>V₁₁</td>
<td>0·520, 0, −0·854</td>
<td>010</td>
<td>1·796±0·004</td>
<td>PT</td>
</tr>
<tr>
<td>V₁₂</td>
<td>0·520, 0, −0·854</td>
<td>0·854, 0, −0·520</td>
<td>0·7605±0·006</td>
<td>SPT</td>
</tr>
<tr>
<td>V₁₃</td>
<td>110</td>
<td>110</td>
<td>2·982±0·006</td>
<td>QL</td>
</tr>
<tr>
<td>V₁₄</td>
<td>110</td>
<td>001</td>
<td>1·683±0·003</td>
<td>QT</td>
</tr>
<tr>
<td>V₁₅</td>
<td>110</td>
<td>110</td>
<td>1·307±0·013</td>
<td>QT</td>
</tr>
<tr>
<td>V₁₆</td>
<td>011</td>
<td>011</td>
<td>3·622±0·008</td>
<td>QL</td>
</tr>
<tr>
<td>V₁₇</td>
<td>011</td>
<td>011</td>
<td>1·980±0·008</td>
<td>QT</td>
</tr>
<tr>
<td>V₁₈</td>
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<td>100</td>
<td>1·409±0·007</td>
<td>QT</td>
</tr>
<tr>
<td>V₁₉</td>
<td>0·252, 0·588, −0·769</td>
<td>0·252, 0·588, −0·769</td>
<td>3·686±0·008</td>
<td>QL</td>
</tr>
<tr>
<td>V₂₀</td>
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<td>Trans 1</td>
<td>2·014±0·01</td>
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</tr>
<tr>
<td>V₂₁</td>
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<td>1·219±0·009</td>
<td>QT</td>
</tr>
<tr>
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<td>0·698, 0, −0·716</td>
<td>3·217±0·13</td>
<td>SPL</td>
</tr>
<tr>
<td>V₂₃</td>
<td>0·698, 0, −0·716</td>
<td>010</td>
<td>1·796±0·004</td>
<td>PT</td>
</tr>
<tr>
<td>V₂₄</td>
<td>0·698, 0, −0·716</td>
<td>0·716, 0·698</td>
<td>3·151±0·004</td>
<td>SPL</td>
</tr>
<tr>
<td>V₂₅</td>
<td>0·925, 0·395</td>
<td>0·925, 0·395</td>
<td>3·151±0·004</td>
<td>SPL</td>
</tr>
<tr>
<td>V₂₆</td>
<td>0·925, 0·395</td>
<td>010</td>
<td>1·520±0·004</td>
<td>PT</td>
</tr>
<tr>
<td>V₂₇</td>
<td>0·925, 0·395</td>
<td>0·395, 0, −0·925</td>
<td>0·83±0·03</td>
<td>SPT</td>
</tr>
</tbody>
</table>

¹ Direction is with respect to xyz axes.

### 4. Results

The measured velocities are shown in Table 1. The wave displacement directions are approximate only, because in most instances the waves are not pure and their true displacement vectors can only be determined by calculation from the determined elastic constants. Nevertheless, experience has shown that most waves are either predominantly longitudinal or transverse in character and hence one may assume that the polarization of the exciting transducer (which is the basis for the approximate
wave displacement directions given in Table 1) is a reasonable first approximation to the actual eigenvector.

The measurement of the velocity was repeated at least twice for each mode using different specimens. An exception to this was for propagation along [011]' for which the measurement was repeated by repolishing the sample to reduce its pathlength and examining a different section of the crystal. In general the consistency in the velocity between the different measurements was within ±1 r.f. cycle (~1–2%). However, in some cases, particularly for semi-pure modes, the velocity data between measurements were consistent to between 0·2–0·6%.

The density used in the calculation was obtained by hydrostatic weighing in chloroform at 20°C and found to be \( \rho = 3·22 \pm 0·04 \) g cm\(^{-3} \), which corresponds well to the value given by Rashkovich et al. (1977) of 3·24±0·01 g cm\(^{-3} \). The X-ray density, computed from the unit cell data given by Uesu and Kobayashi (1976), is 3·27 g cm\(^{-3} \) which also agrees well with our results.

It is possible to find \( C_{22}, C_{66} \) and \( C_{44} \) directly using pure modes. The necessary relationships are

\[
C_{22} = \rho V_4^2 = 26·67 \pm 0·37 \text{ GPa}, \quad (10)
\]

\[
C_{66} = \rho V_2^2 = 9·17 \pm 0·22 \text{ GPa}, \quad (11)
\]

\[
C_{44} = \rho V_8^2 = 8·10 \pm 0·15 \text{ GPa}. \quad (12)
\]

The velocities corresponding to the remaining pure modes with propagation vector along the \( b \) axis are related to the above constants by the relationship

\[
\rho V_5^2 + \rho V_6^2 = C_{44} + C_{66}. \quad (13)
\]

On substituting the numerical values the left- and right-hand sides of (13) agree to 3%, which is well within experimental error.

The value of \( C_{46} \) may be determined from the velocity of the last remaining pure mode propagating along the [010]' direction in the \( xz \) plane. Here, the relationship is

\[
C_{46} = (\rho V_{11}^2 - \rho V_{12}^2 - n^2 C_{44})/2n = -2·25 \pm 0·31 \text{ GPa}. \quad (14)
\]

A consistency check may be obtained by using the relationship

\[
C_{46}^2 = C_{44} C_{66} - \rho V_5^2 \rho V_6^2. \quad (15)
\]

Here, the numerical agreement of the left- and right-hand sides is within 24%, which is still within experimental error. The error is large because the small value of \( C_{46} \) corresponds to subtracting nearly equal terms on the right-hand side of (15).

The relationships necessary for the determination of the remaining diagonal elastic constants and \( C_{15} \) and \( C_{35} \) are

\[
C_{11} + C_{55} = \rho (V_1^2 + V_3^2) = 34·03 \pm 0·19 \text{ GPa}, \quad (16)
\]

\[
C_{11} C_{55} - C_{15}^2 = \rho V_1^2 \rho V_3^2 = 123·6 \pm 2·7 \text{ (GPa)}^2, \quad (17)
\]

\[
C_{33} + C_{55} = \rho (V_1^3 + V_3^3) = 70·65 \pm 0·29 \text{ GPa}, \quad (18)
\]
\[ C_{33} C_{55} - C_{35}^2 = \rho V_3^2 V_9^2 = 284.1 \pm 2.8 \text{(GPa)}^2, \]  
\[ l^2 C_{11} + C_{55} + n^2 C_{33} + 2ln(C_{15} + C_{55}) = \rho V_{10}^2 + \rho V_{12}^2 \]
\[ = 49.51 \pm 0.18 \text{ GPa}, \]

where \( l^2 + n^2 = 1 \).

Whilst it is possible (but tedious) to solve (16)–(20) analytically it is more convenient to solve these equations numerically using a generalized Newton–Raphson algorithm (Carnahan et al. 1969). The system converges to two separate solutions, depending on the starting values of the variables. One solution may be rejected as unphysical as, on substituting this set of elastic constants back into equation (4), it is found that the eigenvector corresponding to the fastest mode (i.e. the quasi-longitudinal wave) is polarized close to 90° to the propagation direction.

The errors in \( C_{11}, C_{55}, C_{33}, C_{15} \) and \( C_{35} \) were calculated by varying the right-hand sides of (16)–(20) by plus or minus the quoted error for all possible permutations and noting the maximum and minimum values of the constants which emerge when the equations are solved. This is considered to be a more realistic estimate of the error than would be obtained by solving (16)–(20) analytically and summing all possible maximum errors. In the latter case the errors calculated are unreasonably large, as no account is taken of the self-consistency requirements which do not allow worst case errors to occur independently of one another.

The value of \( C_{13} \) may then be obtained from the calculated constants above by the equation

\[ \{l^2 C_{15} + n^2 C_{35} + ln(C_{13} + C_{55})\}^2 \]
\[ -(l^2 C_{11} + n^2 C_{55} + 2nlC_{15})(l^2 C_{55} + n^2 C_{33} + 2nlC_{35}) \]
\[ -\rho V_{10}^2 \rho V_{12}^2 = 88.75 \pm 0.84 \text{ (GPa)}^2. \]  

There will be two solutions for \( C_{13} \) depending on whether the positive or negative square root is taken in (21). Once again one solution has been rejected as unphysical on the criterion that the quasi-longitudinal wave travels faster than the quasi-transverse wave and is polarized closer to the propagation direction.

To obtain \( C_{12}, C_{25} \) and \( C_{23}, \) the velocities in the [110]' and [011]' directions were measured. The solution to the eigenvalue equation requires for the [110]' direction

\[
\begin{vmatrix}
C_{11} + C_{66} - 2\rho V^2 & C_{12} + C_{66} & C_{15} + C_{46} \\
C_{12} + C_{66} & C_{22} + C_{66} - 2\rho V^2 & C_{25} + C_{46} \\
C_{15} + C_{46} & C_{25} + C_{46} & C_{55} + C_{44} - 2\rho V^2
\end{vmatrix} = 0, \tag{22}
\]

and for the [011]' direction

\[
\begin{vmatrix}
C_{66} + C_{55} - 2\rho V^2 & C_{46} + C_{25} & C_{46} + C_{35} \\
C_{46} + C_{25} & C_{22} + C_{44} - 2\rho V^2 & C_{44} + C_{23} \\
C_{46} + C_{35} & C_{44} + C_{23} & C_{44} + C_{33} - 2\rho V^2
\end{vmatrix} = 0. \tag{23}
\]
The properties of the roots of the cubic equations (22) and (23) give us relations that may be used as consistency checks on the measured velocities. These relations are for the [110]' direction

\[ 2\rho(V_{13}^2 + V_{14}^2 + V_{15}^2) = C_{11} + C_{22} + 2C_{66} + C_{55} + C_{44}, \] (24)

and for the [011]' direction

\[ 2\rho(V_{16}^2 + V_{17}^2 + V_{18}^2) = C_{66} + C_{55} + 2C_{44} + C_{22} + C_{33}. \] (25)

On substituting the values of the constants so far determined the left- and right-hand sides of (24) and (25) agree to within 0.7\% and 0.2\% respectively, which is well within experimental error. The properties of the cube roots of (22) and (23) also yield, for the [110]' direction,

\[
(C_{12} + C_{66})^2 + (C_{55} + C_{44})^2 - (C_{15} + C_{46})^2 - (2\rho)^2(V_{13}^2 V_{14}^2 + V_{14}^2 V_{15}^2 + V_{13}^2 V_{15}^2),
\]

(26)

\[
(C_{55} + C_{44})(C_{12} + C_{66})^2 + (C_{11} + C_{66})(C_{25} + C_{46})^2 - 2(C_{12} + C_{66})(C_{15} + C_{46})(C_{25} + C_{46}) = (C_{11} + C_{66})(C_{22} + C_{66})(C_{55} + C_{44}) - (2\rho V_{13}^2)(2\rho V_{14}^2)(2\rho V_{15}^2)
\]

(27)

For the [011]' direction the corresponding relationships are

\[
(C_{23} + C_{44})^2 + (C_{25} + C_{46})^2 = (C_{66} + C_{55})(C_{22} + C_{44}) + (C_{66} + C_{55})(C_{44} + C_{33}) + (C_{22} + C_{44})(C_{44} + C_{33}) - (C_{46} + C_{35})^2 - (2\rho)^2(V_{16}^2 V_{17}^2 + V_{17}^2 V_{18}^2 + V_{16}^2 V_{18}^2),
\]

(28)

\[
(C_{66} + C_{55})(C_{23} + C_{44})^2 + (C_{44} + C_{33})(C_{46} + C_{25})^2 - 2(C_{46} + C_{25})(C_{46} + C_{35})(C_{44} + C_{23}) = (C_{66} + C_{55})(C_{22} + C_{44})(C_{44} + C_{33}) - (2\rho V_{16}^2)(2\rho V_{17}^2)(2\rho V_{18}^2)
\]

(29)

Equations (26), (27) and (28) were solved for the unknowns \(C_{12} + C_{66}, C_{25} + C_{46}\) and \(C_{23} + C_{44}\) simultaneously by a generalized Newton–Raphson algorithm. The solutions were checked by substitution into equation (29) which yielded consistency between right- and left-hand sides of better than 0.7\%. The solution to (26)–(28) involves the intersection between two circles (26) and (28), and an ellipse or hyperbola (27). As such there are two sets of distinct solutions:

\[
(C_{12}, C_{25}, C_{23}) = \pm (11.4 \pm 3.6, 8.4 \pm 4.3, 14.5 \pm 4.4) \text{ GPa}
\]

\[
= \pm (12.2 \pm 2.9, 0.95 \pm 4.2, 15.3 \pm 4.0) \text{ GPa}.
\]

An attempt to calculate the errors in \(C_{12}, C_{25}\) and \(C_{23}\) by solving the equations for all the possible permutations of plus or minus the quoted errors in \(C_{11}, C_{22}, C_{33}, C_{44},\)
$C_{55}$, $C_{66}$, $C_{13}$, $C_{15}$, $C_{35}$, $C_{46}$ and the measured velocities $V_{13}, \ldots, V_{18}$ was unsuccessful. For most permutations of the errors the system of equations (26)–(28) no longer converged, as the internal consistency requirements of (24) and (25) were no longer satisfied. The uncertainties in $C_{12}$, $C_{25}$ and $C_{23}$ quoted above were calculated by restricting the errors in the velocities so that the left- and right-hand sides of (24) and (25) agreed to within $1\%$ for all permutations of the errors in the velocities. In this case the system of equations (26)–(28) converged for most error permutations, except those extreme cases for which all the errors were either added or subtracted.

Two of the above solutions (the negative of each pair) may be rejected as unphysical by a consideration of the eigenvectors as described above. This still leaves two distinct solutions, and although the eigenvectors corresponding to each solution are different, both are physically quite reasonable. Clearly, the choice of solution has little effect on the value of $C_{12}$ and $C_{23}$, but the value of $C_{25}$ is radically changed. In order to differentiate between these solutions the velocity in a further general direction $[0\cdot252, 0\cdot588, -0\cdot769]$ was measured. The criterion

$$R_{19-21} = \sum_{i=1}^{21} (V_{\text{calc}} - V_i)^2 / V_i^2,$$

where $V_{\text{calc}}$, are the velocities calculated for the $[0\cdot252, 0\cdot588, -0\cdot769]$ direction from the elastic constants, was used as a measure of the goodness of fit of the data. The first solution gives an $R$ value three times smaller than for the second solution and has therefore been adopted.

The criterion

$$R_{1-18} = \sum_{i=1}^{18} (V_{\text{calc}} - V_i)^2 / V_i^2$$

has been calculated and a value of $1\cdot8 \times 10^{-3}$ obtained. This compares very favourably with the value of $R$ obtained by Krupnyi et al. (1972) in their calculations for some monoclinic organic crystals. However, they found it necessary to employ a least squares error function to refine the elastic constants in order to reduce their value of $R$ to less than $10^{-2}$. This procedure resulted in their final value for $C_{22}$ being lower than the directly measured value. No physical justification was offered by them for modifying a directly measured quantity as a result of numerical calculation.

Table 2. Elastic constants of CsH$_2$PO$_4$

The $C_{ij}$ were calculated using a density of $3\cdot22$ g cm$^{-3}$ at 20°C

<table>
<thead>
<tr>
<th>$ij$</th>
<th>$C_{ij}$ (GPa)</th>
<th>$S_{ij}$ (GPa)$^{-1}$</th>
<th>$ij$</th>
<th>$C_{ij}$ (GPa)</th>
<th>$S_{ij}$ (GPa)$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>11</td>
<td>28.83±0.43</td>
<td>1.82</td>
<td>12</td>
<td>11.4±0.13</td>
<td>-0.219</td>
</tr>
<tr>
<td>22</td>
<td>26.67±0.37</td>
<td>0.103</td>
<td>13</td>
<td>42.87±1.58</td>
<td>-1.17</td>
</tr>
<tr>
<td>33</td>
<td>65.45±0.48</td>
<td>0.772</td>
<td>15</td>
<td>5.13±0.67</td>
<td>0.249</td>
</tr>
<tr>
<td>44</td>
<td>8.10±0.15</td>
<td>0.133</td>
<td>23</td>
<td>14.5±4.4</td>
<td>0.138</td>
</tr>
<tr>
<td>55</td>
<td>5.20±0.24</td>
<td>0.450</td>
<td>25</td>
<td>8.4±4.3</td>
<td>-0.150</td>
</tr>
<tr>
<td>66</td>
<td>9.17±0.22</td>
<td>0.117</td>
<td>35</td>
<td>7.50±0.81</td>
<td>-0.181</td>
</tr>
<tr>
<td></td>
<td></td>
<td>46</td>
<td></td>
<td>-2.25±0.31</td>
<td>0.033</td>
</tr>
</tbody>
</table>

The complete elastic constant matrix $C_{ij}$ is given in Table 2. The inverse of the elastic constant matrix was calculated to give the elastic compliance matrix $S_{ij}$ which is also listed in Table 2. Quantities discussed in the following section, such as bulk modulus and linear compressibility are calculated in terms of these $S_{ij}$.
5. Discussion

Velocity Surfaces

Using the values of the $C_{ij}$ matrix in Table 2, the wave velocity for any propagation direction can be calculated via equations (4) and (5). Figs 3a, 3b and 3c are polar plots of velocity versus propagation direction for propagation vectors in the $xy$, $xz$ and $yz$ planes respectively.

Fig. 3. Polar plots of the calculated phase velocity for the (a) $xy$, (b) $xz$ and (c) $yz$ planes, together with the absolute value $\Phi$ of the deviation angle between the ray and propagation vectors (d)-(f), where $\theta$ is measured in the sense given in the corresponding polar plot. The solid circles show the measured velocities actually used in the calculations. The triangles represent the measured velocities for the two pure transverse (PT) waves travelling parallel to the $b$ axis and are used as a cross-check. The open circles show other measured velocities in the $xz$ plane.
It is immediately obvious that, for propagation directions in the \(xy\) and \(yz\) planes, the wave velocity is quite isotropic. This stands in very marked contrast to the plot for the \(xz\) plane (Fig. 3b), which displays very marked anisotropy, particularly for the semi-pure transverse (SPT) mode with the smallest velocity. The calculations predict a minimum in the velocity of this mode of \(0.290 \times 10^3 \text{ m s}^{-1}\) for propagation directions making angles of 38° and 140° to the \(x\) axis. This is a remarkably low value. For comparison, Sil’vestrova \textit{et al.} (1975) have reported a value of \(0.347 \times 10^3 \text{ m s}^{-1}\) for the velocity of a transverse wave propagating in the \(yz\) plane in Calomel, which they claimed to be the ‘lowest value’ measured for crystals at that time. It should be pointed out, however, that Sil’vestrova \textit{et al.} actually determined this value experimentally whilst our value is calculated from the determined elastic constants.

In an effort to check the unusual predictions arrived at from the calculations we attempted to measure the velocity of each of the three modes for other propagation directions in the \(xz\) plane. For all propagation directions in this plane, one mode is pure transverse (PT) having a polarization vector parallel to \([010]’\). The other two modes are semi-pure having polarization vectors of the form \([n0-1]\)’ and \([10n]\)’. For propagation at 134° to the \(x\) axis the measured PT velocity agrees very well with the predicted value. The SPT mode, with a predicted velocity of \(0.363 \times 10^3 \text{ m s}^{-1}\), could not be generated at all. It was found that, on rotating the crystal with respect to the transverse exciting transducer, the pure mode decreased in amplitude as expected, but that no other mode could be detected. Similar difficulties were encountered for the measurements of \(V_{12}\) (see Table 1), although in that case a weak mode could be detected. It was also noted that this SPT mode could be generated by a longitudinal transducer.

The failure to observe the very low velocity mode is not unexpected as such a mode would be expected to be heavily damped compared with the faster modes. However, as can be seen from Fig. 3b, the measured velocity of the semi-pure longitudinal (SPL) mode, which is strongly propagated, is significantly smaller than the predicted value in this direction. Similar results were obtained for propagation at 23° to the \(x\) axis, in that the measured pure mode velocity is very close to the predicted value and that the SPL wave velocity was significantly less than the predicted value. In this case, the SPT wave could be detected, but it was very weakly propagated and only a rough estimate of its velocity could be obtained (\(V = 0.83 \times 10^3 \text{ m s}^{-1}\)).

The discrepancy between the measured and calculated values of this SPL mode suggests that the severe damping of the SPT mode influences the longitudinal mode as well. The formulation of the equation of motion assumes an infinite lossless medium and therefore does not include any damping term. Normally, the introduction of such a term should have little or no influence on the velocities. However, if the damping is sufficiently severe so as to almost stop one mode from propagating at all, the nature of the eigenvalue equation can be expected to change, since the dimensionality of the problem would effectively be reduced from 3 to 2. We are currently investigating the effect that a severe damping term for one mode will have on the other measured velocities.

\textit{Ray Directions}

For each direction of propagation there are three associated wave modes, each with a different velocity, polarization and ray energy propagation direction. Figs 3d,
3e and 3f show plots of the magnitude of the absolute angle between the ray direction and the propagation direction, calculated via equation (9), for the xy, xz and yz planes respectively.

Deviation angles of up to 70° are not unusual (see e.g. Neighbours 1973). The plots for the xy and yz planes show that there are no accidental pure modes of propagation, since the deviation angle only goes to zero for propagation along the b axis, which is demanded by symmetry. Once again the plot for the xz plane is very peculiar. The deviation angle for the SPT mode increases rapidly for propagation off the x axis, reaching a value of 73° at 30° from the x axis. With further displacement, the deviation angle decreases abruptly to a value of 14° at 38° from the x axis and then abruptly increases. Similar behaviour occurs for propagation directions about 140° to the x axis.* Note that the minima in the calculated velocities of this mode occur for the same propagation directions. The sharpness of the dip is striking. In the region of the anomalies the deviation angle changes by about 38° for a 1° change in propagation direction. Calomel (Sil'vestrova et al. 1975) displays similar behaviour for the transverse mode, the velocity of which has a minimum value of 0.347 × 10^3 m s⁻¹ for propagation at 45° to the x axis in the xy plane.

The deviation angles for the measured velocities (V_{22} - V_{27}) in the xz plane can be read from Fig. 3e. It can be seen that the mode propagating at 134° to the x axis has a deviation angle of 76°. It is therefore not unexpected that this ray was unobserved since it must reflect off the sides of the crystal many times during its round trip. The mode at 23° has a smaller deviation angle, namely 69°, and was weakly observed. The mode at 121.3° (V_{12}) has a deviation angle of 64° and was clearly observed.†

In order to test these conclusions, measurements of the velocity for propagation at the angles in the xz plane at which the minima in velocity and deviation angle occur (namely 38° and 140°) would be desirable. However, such measurements would require the crystal to be aligned very precisely as even small errors in alignment will lead to large changes in the deviation angle. The crystal would also have to be of excellent quality as a mosaic spread of even 1° will lead to a gross divergence of the beam. Finally, even if the beam were propagated without a large divergence, the very low value of velocity for this mode will probably be accompanied by a high value of attenuation, making the mode difficult or impossible to observe experimentally.

**Bulk Modulus, Linear Compressibility and Young’s Modulus**

The bulk modulus of CsH₂PO₄ was calculated via the relationship (Nye 1967)

\[ B = \frac{1}{S_{11} + S_{22} + S_{33} + 2(S_{12} + S_{23} + S_{13})} \]

A value of 5.28 GPa was obtained using the S_{ij} matrix calculated by taking the inverse of the C_{ij} matrix in Table 2. An attempt was made to calculate the error in the bulk modulus by adding all possible permutations of the errors to the values of C_{ij} before inverting the matrix. However, for most permutations of the errors, especially those involving extreme cases where

* The eigenvectors in the xz plane are well behaved and do not deviate from pure mode behaviour by more than 17°.

† It should be recalled that the number of reflections off the side walls of the crystal will depend on the tangent of the deviation angle. Thus a deviation angle of 76° (tan 76° = 4.01) will result in about twice as many side wall reflections as a deviation of 64° (tan 64° = 2.05).
Elastic Behaviour of CsH₂PO₄

all the errors were either added or subtracted, the $C_{ij}$ matrix ceased to be positive definite. Positive definiteness is the mathematical consequence of demanding a positive strain energy for lattice stability. Thus a $C_{ij}$ matrix which is not positive definite cannot describe the elastic properties of any real material. Hence we may reject those error permutations for which the $C_{ij}$ matrix is not positive definite as unphysical.

When the calculation was performed using only those error combinations for which the $C_{ij}$ matrix was positive definite, the bulk modulus was found to lie in the range 0.9–16.5 GPa. This large uncertainty is due to ignoring the fact that constants are coupled in such complicated ways that the quoted errors cannot occur independently. A more sophisticated error calculation system is required—possibly a Monte Carlo method of assigning the value of $C_{ij}$ to be used as a normally distributed variable with mean and standard deviation equal to the values and errors respectively given in Table 2.

<table>
<thead>
<tr>
<th>Crystal</th>
<th>Class</th>
<th>$B$ (GPa)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>CsH₂PO₄</td>
<td>Monoclinic</td>
<td>5.28</td>
<td>This paper</td>
</tr>
<tr>
<td>KH₂PO₄</td>
<td>Tetragonal</td>
<td>27.3</td>
<td>Fritz (1976)</td>
</tr>
<tr>
<td>Potassium tartrate</td>
<td>Monoclinic</td>
<td>16.8</td>
<td>Aleksandrov (1958)</td>
</tr>
<tr>
<td>NH₄H₂PO₄</td>
<td>Tetragonal</td>
<td>20.1</td>
<td>Fritz (1976)</td>
</tr>
<tr>
<td>CsSCN</td>
<td>Orthorhombic</td>
<td>13.2</td>
<td>Irving et al. (1983)</td>
</tr>
<tr>
<td>Calomel</td>
<td>Tetragonal</td>
<td>18.0</td>
<td>Sil'vestrova et al. (1975)</td>
</tr>
</tbody>
</table>

The value of $B$ is remarkably small. For comparison, $B$ for some other materials is shown in Table 3. These values have been calculated via the elastic constants given in the references listed. Note that Calomel, whilst displaying some similar anisotropic features to CDP in the behaviour of the velocity and ray directions, nevertheless has a value of bulk modulus comparable with the other crystals listed.

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Since CDP displays a chain-like structure it is of interest to calculate the linear compressibility $K_{lmn}$ which is the strain response of the crystal along a given direction $[l, m, n]$ to the application of hydrostatic pressure. For a monoclinic system the expression is (Nye 1967)

$$K_{lmn} = (S_{11} + S_{12} + S_{13})l^2 + (S_{12} + S_{22} + S_{23})m^2 + (S_{13} + S_{23} + S_{33})n^2 + (S_{15} + S_{25} + S_{35})ln.$$  

A plot of linear compressibility versus direction in the $xy$, $xz$ and $yz$ planes is given in Fig. 4. Note how the compressibility along the $x$ axis is twenty times larger than that along the $y$ axis, and that the compressibility along the $z$ axis is negative. Thus when hydrostatic pressure is applied to CsH$_2$PO$_4$ the crystal responds by contracting along the $x$ axis and expanding along the $z$ axis. By comparison the length change along the $y$ axis is small. This further demonstrates the marked elastic anisotropy of CDP.

Finally, the central sections of the Young’s modulus surface on the $xy$, $xz$ and $yz$ planes were calculated and are shown in Figs 5a, 5b and 5c respectively. In Fig. 5
the radius vector is proportional to the value of Young's modulus \( Y \) for that direction. The curves were calculated from the expression (Nye 1967)

\[
Y^{-1} = l^4S_{11} + 2l^2m^2S_{12} + 2l^2n^2S_{13} + 2l^3nS_{15} \\
+ m^4S_{22} + 2m^2n^2S_{23} + 2mn^2S_{25} \\
+ n^4S_{33} + 2hn^3S_{35} + mn^2S_{44} + 2lhn^2S_{46} \\
+ l^2n^2S_{55} + l^2m^2S_{66}.
\]

Young's modulus gives a measure of the 'stiffness' of the crystal to a uniaxial stress applied along the direction of interest. Once again the elastic behaviour is clearly very anisotropic.

Using the elastic constants in Table 2, J. G. Collins (personal communication) has calculated the elastic Debye temperature to be 134·5 K for Avogadro's number of ions. This value is consistent with an estimate from thermal conductivity data of 140 ± 10 K (Spörl et al. 1984).

**Relationship to Crystal Structure**

Much of the elastic anisotropy in CDP originates from the extremely low velocity predicted for the SPT mode for propagation in the \( xz \) plane at 38° and 140° to the \( x \) axis. This anomaly results in the sharp dip for the deviation angle between ray and wave normals for these propagation directions. It also results in the very low value for the bulk modulus, and the large anisotropies in Young's modulus and the linear compressibility. We suggest the following qualitative explanation, in terms of the known crystal structure of CDP, as to why this mode should behave anomalously.

As previously noted, CDP consists of (100) layers of hydrogen bonded \( \text{PO}_4 \) groups, the layers being held together by electrostatic attraction to the \( \text{Cs}^+ \) ions. A projection of the structure onto the (010) plane is given in Fig. 6a based on the atomic positions given by Uesu and Kobayashi (1976) and Matsunaga et al. (1980). The \( \text{H}_2 \) hydrogen links 03-03 and 04-04 groups to form the \( \text{PO}_4 \) chains along the \( b \) axis. The \( \text{H}_1 \) hydrogen cross links the chains to form the (100) layers.

Uesu and Kobayashi (1976) pointed out that nearly linear chains of \( \text{Cs} \) and \( \text{P} \) ions are formed along the [10\(\bar{1} \)] direction with an interatomic distance of 4·03 Å (≈4·03 × 10^{-10} m). However, it is evident from Fig. 6a that this is an error and that the chains with close to this interatomic distance lie along the [10\(\bar{1} \)] direction. It is also seen in Fig. 6a that there are nearly linear chains of \( \text{P}-01, \text{Cs}^+, \text{P}-01 \) groups along the [10\(\bar{1} \)] direction where the \( \text{Cs}_1-\text{P}_1 \) separation is 5·46 Å (with an oxygen intervening) and the \( \text{Cs}_1-\text{P}_2 \) separation is 5·01 Å (with no intervening atoms). Uesu and Kobayashi (1976) also pointed out that these distances are considerably longer than the \( \text{K}-\text{P} \) distance of 3·49 Å in KDP.

If we consider a wave propagating in the \( xz \) plane at 38° to the \( x \) axis, the eigenvectors for this direction can be calculated by solving the eigenvalue equation (4). The eigenvectors lie in the \( xz \) plane and make angles of 39·9° (SPT) and 50·1° (SPL) to the \( x \) axis as shown in Fig. 6b. The third mode is PT and has polarization parallel to [010]. The SPT polarization is approximately parallel to the [10\(\bar{1} \)] direction and makes an angle of only 1·4° with the direction joining \( \text{Cs}_1 \) and \( \text{P}_2 \).

Since there are no intervening atoms between \( \text{Cs}_1 \) and \( \text{P}_2 \) and since the eigenvectors are constrained to lie in the \( xz \) plane, the force constants associated with this mode
Fig. 6. (a) Projection of the structure of CDP onto the ac plane. The disordered hydrogen H2 forms the chains of PO₄ tetrahedra up the b axis, whilst the ordered H1 cross links the chains. The nearly linear chains of Cs and P atoms can be seen along the [101] and [101] directions. (b) Direction of transverse and longitudinal polarization for a mode propagating at 38° to the x axis in the ac plane.

may be expected to be small due to the comparatively very large nearest neighbour separation. We also note that the particle vibration direction shown in Fig. 6b is roughly (to within 5°) parallel to the projection of the 03–H2–03 hydrogen bond onto the xz plane. This bond is expected to be quite compliant as this hydrogen is
disordered in the room temperature phase. As a consequence of both these factors we may expect the velocity to be correspondingly small for this mode.

Irrespective of the above explanation, the correspondence of the transverse polarization for the mode propagating at 38° to the axis to the linear Cs–P arrays and the 03–H2–03 hydrogen bond direction seems unlikely to be coincidental. It is unfortunate that this mode is not more easily observed experimentally, for the response of the velocity of this mode to temperature through the ferroelectric ordering would be very interesting.

It has also been observed by Uesu and Kobayashi (1976) that nearly linear arrays of Cs and P atoms also occur along the [0, ±1, 1] directions with a comparatively large Cs–P separation. However, we observed that in the yz plane the velocity of all modes is very isotropic, showing none of the peculiar effects of the xz plane. We may account for this difference by recalling that for propagation in the xz plane the eigenvectors are constrained by symmetry to lie in that plane, whereas for propagation in the yz plane no such restriction applies and in fact the eigenvectors lie considerably out of the plane. Thus the force constants for this mode will not necessarily be determined by the comparatively large Cs–P interatomic distance within the yz plane.

The anisotropy of the linear compressibility and of Young’s modulus is related to the layer and chain structure of CDP. The maximum in the value of the linear compressibility and the corresponding minimum in the value of Young’s modulus for the x-axis direction correspond to the weak bonding between the (100) layers. Under hydrostatic pressure these layers are forced closer together. The corresponding expansion along the c axis may be explained by a small rotation of the PO4 tetrahedron (possibly caused by repulsion between the 01 and 02 atoms of adjacent layers), which results in an elongation of the hydrogen bonded c-axis chain. Selenium and tellurium are examples of other chain-like materials which have negative linear compressibility parallel to the chain axis (Munn 1972). Under uniaxial stress, however, the bonding in the c-axis chain is only about as strong as the interlayer bonding (see Fig. 5b).

It is surprising that the b-axis bonding is so much stronger than for the c axis (see Fig. 5c), especially in view of the disordered state of the hydrogen bonds linking this chain. This may be explained by noting that these hydrogen bonds lie nearly parallel to the a axis, so that compression of the b-axis chain would involve a bending of the bond, rather than a compression of the double well potential along its axis. The strength of the b-axis bonding is consistent with the findings of Frazer et al. (1979) that the correlation length along the b axis is much longer than those along the a and c axes.

The very strong anisotropy for Young’s modulus in the xz plane (Fig. 5b) is correlated to the anomalous SPT mode discussed above. The maxima in Young’s modulus (at 54° and 131° to the x axis) occur for directions which are almost parallel to the SPL polarization for wave propagation directions for which the SPT mode has its minimum velocity. Thus the crystal is stiffest at right angles to the [101] Cs–P chains (see Fig. 6).

Finally, as mentioned in the Introduction, most of the studies on CDP to date have focussed on the comparison between the transition mechanism in pseudo-one-dimensional CDP, and the more familiar three-dimensional K2HPO4. The plots
of Young’s modulus for KH$_2$PO$_4$ (calculated from the elastic constants quoted by Fritz 1976) for the $xy$ and $yz$ ($\equiv xz$) planes (see Fig. 7) indicate clearly that the very anisotropic elastic behaviour in CDP is absent in the case of KH$_2$PO$_4$. In particular, it is obvious that the elastic behaviour for the ferroelectric $z$ axis in KH$_2$PO$_4$ is not very different from that for the other axes, in contrast to CDP for which the ferroelectric $b$ axis is much stiffer than the $a$ or $c$ axes.

![Young's modulus surface](image_url)

Fig. 7. Central sections of the Young’s modulus surface for the (a) $xy$ and (b) $yz$ planes in KH$_2$PO$_4$. The magnitude of the radius vector is proportional to the value of Young’s modulus.

6. Conclusions

The elastic constant matrix of CsH$_2$PO$_4$ has been determined via ultrasonic velocity measurements. Significant anisotropy in the elastic constants was found. In particular, calculations using the matrix determined predict a very low velocity of sound ($0.290 \times 10^3$ m s$^{-1}$) for the semi-pure transverse mode propagating in the $xz$ plane at 38° to the $x$ axis. This could not be confirmed experimentally due to the failure to propagate the mode. As the polarization direction for this mode is almost parallel to the linear Cs–P chains with a large (5.01 Å) nearest neighbour separation and to the direction of the disordered hydrogen bond, its low velocity is attributed to the relatively weak forces acting in this direction.

The significant anisotropy found in Young’s modulus and the linear compressibility reflect the weak forces between the (100) layers and show clearly that even in the paraelectric state the bonding along the $b$-axis chain is different to that along the $c$ axis. Hence, the one-dimensional chain-like structure of CDP reveals itself, not only in the critical phenomena, but also in the static elastic behaviour at room temperature. These observations of the elastic anisotropy must be added to the differences in the nature of the ferroelectric transition mechanism in setting CDP apart from other members of the KH$_2$PO$_4$ family.

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