

The Room Temperature Elastic Constants of Caesium Thiocyanate

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Abstract

The velocities of propagation of elastic waves in caesium thiocyanate have been measured along the three orthorhombic axes and normal to the (110), (011) and (101) planes using a double-transducer technique at 10 MHz. The velocities are found to be consistent with the orthorhombic crystal symmetry, and in favourable agreement with a recently published rigid-ion model calculation. The calculated elastic stiffness constants have values $c_{11} = 18.9 \pm 0.7$, $c_{22} = 20.6 \pm 1.0$, $c_{33} = 28.1 \pm 1.6$, $c_{44} = 1.96 \pm 0.05$, $c_{55} = 7.30 \pm 0.2$, $c_{66} = 3.04 \pm 0.07$, $c_{12} = 7.8 \pm 4.3$, $c_{13} = 14.8 \pm 4$ and $c_{23} = 6.3 \pm 4$ GPa. The calculated values for the adiabatic bulk modulus and the low temperature limiting value of the Debye temperature are 13.2 ± 3.5 GPa and 132 K respectively.

1. Introduction

The alkali metal thiocyanates have crystal structures consisting of spherical cations and rod-shaped anions. These substances are of interest because of order-disorder type phase transitions involving the orientation of the anions which occur just below their melting points.

Potassium thiocyanate has been extensively studied by X-ray diffraction (Klug 1933; Yamada and Watanabe 1963; Akers *et al.* 1968), thermal expansion (Sakiyama *et al.* 1963), heat capacity (Vanderzee and Westrum 1970; Kinsho *et al.* 1979), differential thermal analysis (Sakiyama *et al.* 1963; Braghetti *et al.* 1969) and spectroscopic investigations (Jones 1958; Iqbal *et al.* 1972; Dao and Wilkinson 1973; Ti *et al.* 1976; Owens 1979).

By comparison caesium thiocyanate has received little attention, as only the crystal structure for the room temperature phase (Manolatos *et al.* 1973) and a differential thermal analysis investigation of the transition under pressure (Klement 1976) have been reported.

Recently, lattice dynamical calculations based upon a rigid-ion model have been made for both potassium and caesium thiocyanate (Ti *et al.* 1978; Ti and Ra 1980*a*, 1980*b*). The model potential parameters were determined from lattice stability and static equilibrium conditions. The calculated zone centre energies for the optic modes agreed favourably with the available Raman data (Ti *et al.* 1977).

In the present paper measurements of the elastic constants for caesium thiocyanate using ultrasonic techniques are reported. These are the initial results in a more extensive study to determine the dispersion relations for this crystal using

inelastic neutron scattering. The results so far compare favourably with the initial slopes of the dispersion curves derived from the model calculations of Ti and Ra.

2. Experiment

The room temperature phase of caesium thiocyanate is orthorhombic with space group $Pnma$. Plate-like single crystals were grown from water solution by evaporation. Growth was predominantly in the plane normal to $[001]$. The crystals were aligned from Laue back-reflection X-ray photographs with a maximum error in orientation of one degree. Faces on opposite sides of the crystals, normal to the required propagation directions, were ground and polished using grinding papers down to 1200 grade and then $6\text{ }\mu\text{m}$ diamond grit. The final samples had thicknesses between 5 and 10 mm.

Ultrasonic velocities were measured using a double-transducer technique as described by Papadakis (1967). One transducer was excited by a 50–100 V peak-to-peak 10 MHz r.f. pulse train, and the resulting echo train was detected by a similar transducer bonded to the opposite face. The received signal was displayed on an oscilloscope which was triggered by an external oscillator with a period comparable with the round-trip travel time of the pulse in the crystal. Additional electronics made it possible to intensity-modulate the display and to trigger the transmitter coherently. The frequency of the external oscillator was then adjusted to overlap the r.f. cycles of two successive echoes displayed on the oscilloscope, and from the measured frequency the round-trip travel time was determined.

There is not one unique overlap condition, but several displaced from each other by whole r.f. cycles. The choice of the correct overlap corresponding to the true round-trip travel time was determined using McSkimin's criterion (Papadakis 1967). We believe that the cyclic mismatch of these results could be up to one r.f. cycle, because of the small acoustic impedance of the crystal and unknown bond thicknesses, which could introduce large phase delays on reflection from the transducer interface.

The transducers used were fine-ground X - and Y -cut quartz, 0.125 in (3.17 mm) in diameter and coaxially gold plated. The nominal resonance frequency of each transducer was 10 MHz. The bonding materials used were a commercially available epoxy-resin glue, '5 minute Araldite', and 'Apiezon' vacuum grease. It was found that in the case of the transverse vibrating Y -cut transducers only the solid bond obtained with Araldite provided enough mechanical coupling to generate a pulse of sufficient amplitude for the velocity to be measured. However, in the case of the longitudinal vibrating X -cut transducers, the Apiezon grease could be used.

The alignment of the transducers for the transverse measurements was done by eye relative to the appropriate crystallographic directions. Consequently, the polarization for the transverse measurements could have been in error by up to 5° from the desired direction. Such an error should only affect the amplitude of the echo signal and should not alter the measured velocity. Furthermore, this type of misalignment should result in the appearance of an echo train corresponding to the transverse mode at right angles to that being measured. This was not observed and so it was assumed that any misalignment was not significant. For all modes measured, echo trains consisting of two or more echoes were observed.

In an orthorhombic system there are nine nonzero elastic constants (Nye 1967). The six diagonal terms c_{ij} can most easily be measured along the principal crystallographic directions while the off-diagonal terms can only be measured along non-

Table 1. Ultrasonic velocities and associated elastic stiffness constants for CsSCN at 293 K
 ρ is the density; l , m and n are the direction cosines for the appropriate direction; (av.) denotes that the average velocity was used in determining c_{ij}

V (kms ⁻¹)		Elastic constant (GPa)
V_{xx}	2.52 ± 0.04	$c_{11} = 18.9 \pm 0.7 = \rho V^2$
V_{yy}	2.63 ± 0.06	$c_{22} = 20.6 \pm 1.0$
V_{zz}	3.07 ± 0.08	$c_{33} = 28.1 \pm 1.6$
V_{yz}	0.81 ± 0.01	$c_{44} = 1.96 \pm 0.05$
V_{zy}	0.81 ± 0.01	
V_{xz}	1.56 ± 0.02	$c_{55} = 7.30 \pm 0.21$ (av.)
V_{zx}	1.57 ± 0.02	
V_{xy}	1.00 ± 0.01	$c_{66} = 3.04 \pm 0.07$ (av.)
V_{yx}	1.02 ± 0.01	
$V_{(110)l}$	2.40 ± 0.04	$c_{12} = 7.9 \pm 4.1$ $= [(l^2 c_{11} + m^2 c_{66} - \rho V^2)(l^2 c_{66} + m^2 c_{22} - \rho V^2)/l^2 m^2]^{1/2} - c_{66}$
$V_{(110)t}$	1.39 ± 0.02	$c_{12} = 7.6 \pm 3.5$ $= [(l^2 c_{11} + m^2 c_{66} - \rho V^2)(l^2 c_{66} + m^2 c_{22} - \rho V^2)/l^2 m^2]^{1/2} - c_{66}$
$V_{(011)l}$	2.38 ± 0.06	$c_{23} = 6.4 \pm 4.8$ $= [(m^2 c_{22} + n^2 c_{44} - \rho V^2)(m^2 c_{44} + n^2 c_{33} - \rho V^2)/n^2 m^2]^{1/2} - c_{44}$
$V_{(011)t}$	1.70 ± 0.03	$c_{23} = 6.1 \pm 2.7$ $= [(m^2 c_{22} + n^2 c_{44} - \rho V^2)(m^2 c_{44} + n^2 c_{33} - \rho V^2)/n^2 m^2]^{1/2} - c_{44}$
$V_{(101)l}$	2.96 ± 0.09	$c_{13} = 14.3 \pm 7.3$ $= [(l^2 c_{11} + n^2 c_{55} - \rho V^2)(l^2 c_{55} + n^2 c_{33} - \rho V^2)/l^2 n^2]^{1/2} - c_{55}$
$V_{(101)t}$	1.14 ± 0.02	$c_{13} = 15.2 \pm 3.9$ $= [(l^2 c_{11} + n^2 c_{55} - \rho V^2)(l^2 c_{55} + n^2 c_{33} - \rho V^2)/l^2 n^2]^{1/2} - c_{55}$

principal directions. The velocities of a longitudinal and two transverse modes were measured along each of the orthorhombic axes. These are denoted by V_{ij} where i and j indicate the directions of propagation and displacement vectors respectively (Manolatos *et al.* 1973). The velocities and the six directly derivable stiffness constants (McSkimin 1964) are listed in Table 1.

The off-diagonal constants were derived from quasi-longitudinal and quasi-transverse modes along crystal directions chosen for ease of alignment and for the partial diagonalization of the secular equation (Neighbours and Schacher 1967). These directions were normal to the crystal planes (110), (011) and (101). The velocities are labelled by these planes and a suffix, either l (longitudinal) or t (transverse), to indicate the nature of the transducer employed. The polarization of the transverse measurements was aligned parallel to the [110], [011] and [101] crystal directions respectively. Two of the modes along any off-diagonal direction are not pure, in that the displacements are neither parallel nor perpendicular to the propagation direction. These are denoted as being 'quasi-longitudinal' or 'quasi-transverse' because the deviation from pure mode behaviour was subsequently calculated to be small. The remaining mode is pure transverse with displacements perpendicular to the plane of interest. It was not measured because the velocity is only dependent on previously measured diagonal constants. The off-diagonal velocities and their functional dependence on the elastic constants (McSkimin 1964) are listed in Table 1.

To calculate the elastic constants the density of the material was measured to be 2.98 ± 0.01 g cm⁻³ at 293 K by the displacement method using chloroform. This may be compared with the X-ray value of 3.025 g cm⁻³ calculated from the lattice parameters (Manolatos *et al.* 1973).

3. Results

The ultrasonic velocities and associated elastic constants at 293 K are summarized in Table 1. The errors in the velocities are predominantly due to the one r.f. cycle uncertainty in the correct overlap condition. More velocities than needed for determining the elastic constants were measured to check the consistency of the velocity measurements. The transverse velocities V_{ij} and V_{ji} must be identical by symmetry and experimentally are equal within the quoted errors. The quasi-longitudinal and quasi-transverse velocities for the off-diagonal measurements represent the two roots of the quadratic secular equation. The off-diagonal elastic constants derived from the measurement of both roots agree, which again indicates the consistency of the data.

The quoted errors in the off-diagonal elastic constants are large, firstly because of the dependence of these constants on other moduli, and secondly on account of a significant uncertainty in the alignment of the propagation direction. It should be noted that the quoted error represents the worst possible error, and the concordance of the longitudinal and transverse off-diagonal measurements indicates a greater accuracy than shown by the quoted errors.

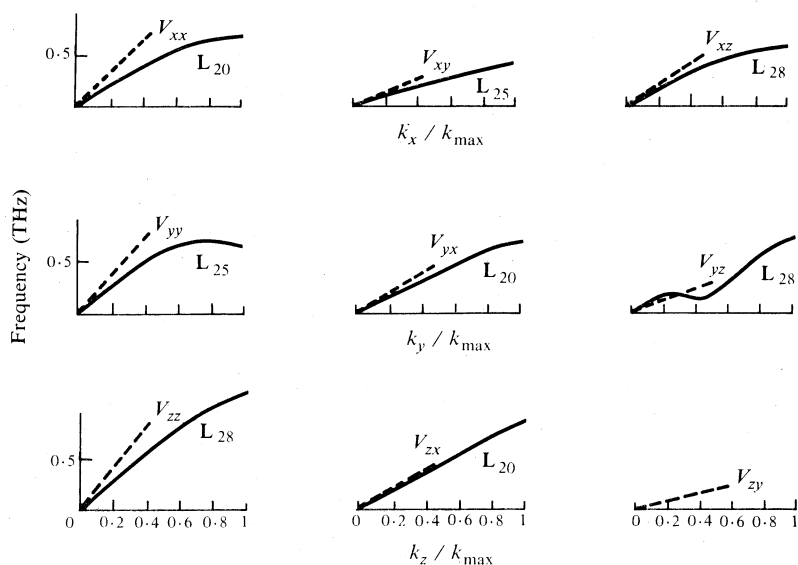


Fig. 1. Dispersion curves for the acoustic modes of CsSCN calculated by Ti and Ra (1980a). The broken line indicates the initial slopes as determined from the measured velocities.

For comparison, the ultrasonic velocities along the orthorhombic axes, together with the dispersion curves by Ti and Ra (1980a) for the acoustic modes, are presented in Fig. 1. The labelling, L_m , of the curves follows the notation adopted by Ti and Ra.

The elastic constants fully describe the elastic behaviour of the crystal. The eigenvalue problem for propagating an elastic wave can be solved using the measured constants for any arbitrary direction. Figs 2a–c show the dependence of the calculated velocities of the three modes of propagation for directions in the xz , xy and yz planes respectively. The measured velocities are also shown. These plots readily illustrate

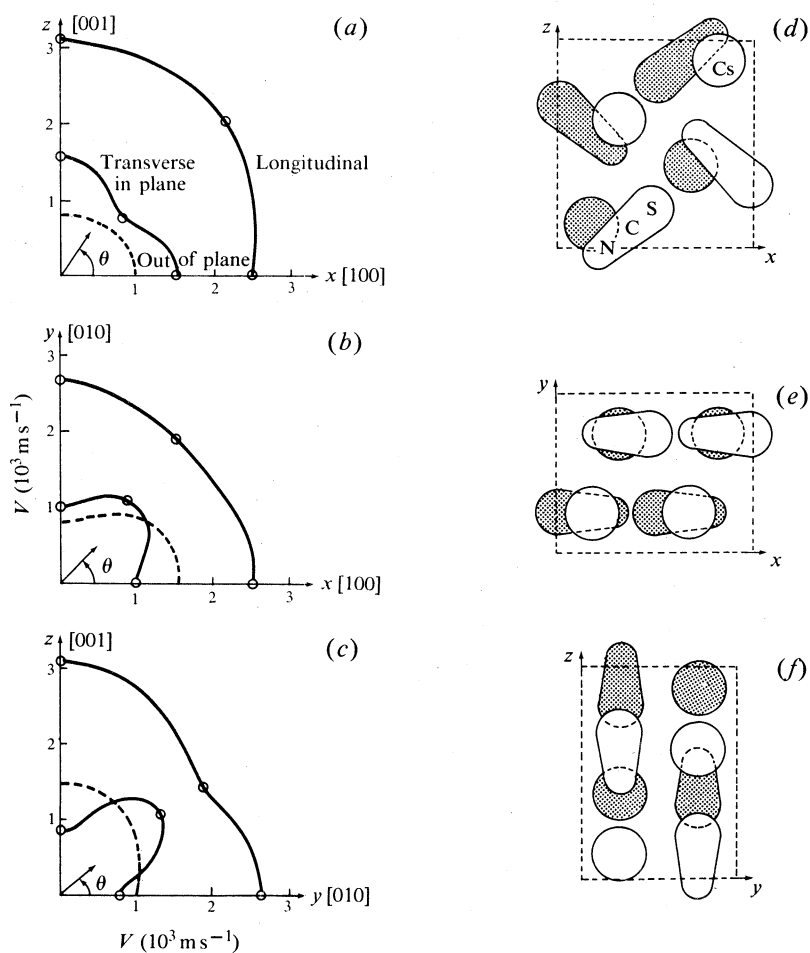


Fig. 2. Calculated velocities of propagation for acoustic modes in the xz , xy and yz planes (a-c); projections of the unit cell on the respective planes with atomic radii not drawn to scale (d-f). The actual measured velocities are shown by the open circles and the sense of θ in each plane is indicated.

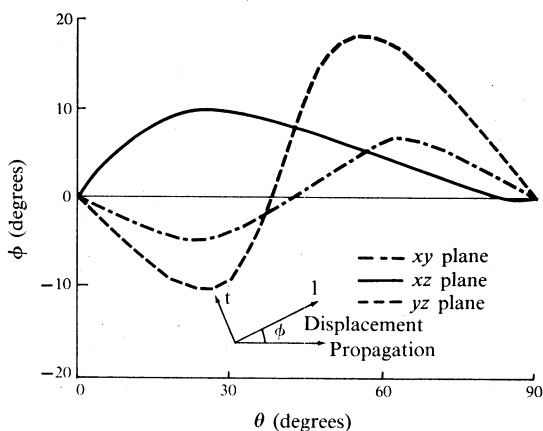


Fig. 3. Deviation from pure mode behaviour ϕ plotted against polar angle θ for the xy , xz and yz planes. The sense of ϕ is shown in the insert.

the anisotropy of the elastic behaviour. The velocity for the longitudinal mode, which is relatively isotropic, has a maximum value along the [001] direction. The minimum longitudinal and the maximum transverse velocity both occur close to the [011] direction.

Only for propagation along the principal crystallographic directions do all three elastic waves have pure modes of vibration. In any arbitrary direction within a principal plane, only the transverse wave, with polarization out of the plane, is a mode of pure vibration. The velocity for this wave is denoted by a broken curve in Figs 2*a-c*. The other two modes may be excited to be predominantly longitudinal or transverse in character, but the displacement vectors for such quasi-longitudinal and quasi-transverse modes will be directed at angles of ϕ and $90^\circ + \phi$ to the propagation direction respectively.

It is possible, for suitable combinations of direction cosines and elastic constants, that directions can occur for which $\phi = 0$, resulting in 'accidental' pure modes. The dependence of ϕ on the propagation direction, described by θ (see Fig. 2) in the principal planes is shown in Fig. 3, from which it is seen that 'accidental' pure modes occur in all three planes. However, whereas these pure modes occur close to the [011] and [110] directions for the *xy* and *yz* planes, the pure mode in the *xz* plane lies close to the *z*-axis.

The adiabatic bulk modulus B_s was determined from the expression

$$B_s = 1/(s_{11} + s_{22} + s_{33} + 2s_{13} + 2s_{23} + 2s_{12}),$$

where s_{ij} are the elastic compliances which were determined by inverting the c_{ij} matrix. An estimate of the worst error in B_s was determined by inverting all permutations of the various extreme values of c_{ij} , obtained by adding or subtracting the error from the value. The calculated value is 13.2 ± 3.5 GPa.

Finally, an estimate for the value of the elastic Debye temperature Θ_0^{el} was determined from the elastic constants by integrating over 5868 directions in one-quarter of the unit sphere. The result is 132 K.

4. Discussion

From Fig. 1, it can be seen that there is generally good agreement between the initial slopes of the calculated dispersion curves and the experimental velocities. These measurements represent the first experimental test of the wave-vector dependence of the calculated acoustic phonon dispersion curves for caesium thiocyanate. While the agreement lends support to the rigid-ion model and the stability criteria adopted, the acoustic modes close to the zone centre do not provide a severe test of the model. For such modes the relative changes in the positions of the atoms within the unit cell are small and therefore the effects of electronic polarization, which are not catered for in the model, will not be significant. A more rigorous test of the model requires a wider exploration of both the acoustic and optic mode branches away from the zone centre.

Major discrepancies do occur for those modes corresponding to the velocities V_{xx} and V_{zy} . In the latter case the calculated mode has negative energies. In view of the relatively low energies for this mode, the failure of the model may be due to numerical rounding errors in the eigenvalue problem for that particular symmetry group and propagation direction or, alternatively, the residual forces acting on the atoms may not be small enough to produce a valid prediction for this mode.

We note also that the mode denoted by L_{28} corresponding to V_{yz} has a pronounced dip at $k = 0.5k_{\max}$. Since the elastic constant appropriate to this mode is identical to the mode for which the model gave negative energies, it is probable that the dip merely reflects the numerical limitations of the model. However, it is interesting to speculate that such a softening of the L_{28} mode may be responsible for the phase transition which occurs at 197°C. This transition in the related potassium compound is associated with the librational fluctuation of the NCS^- anion (Owens 1979). The calculated librational component for the L_{28} mode at $k = 0.5k_{\max}$ is only 3% for caesium thiocyanate at room temperature. However, it is possible that this may increase as the temperature increases.

The values for the bulk modulus and Debye temperature fall within the range of values for the same parameters for other caesium ionic crystals, i.e. the caesium halides have bulk moduli which range from 14 to 26 GPa and elastic Debye temperatures from 130 to 175 K. Specific heat data for CsSCN have not been reported, however, measurements have been made by Vanderzee and Westrum (1970) for KSCN and NH_4SCN . Their values for Θ_0° are 210 and 238 K respectively where these correspond to Avogadro's number of molecular units per mole. As the value of Θ_0^{el} corresponds to Avogadro's number of *atoms* it is necessary to divide the values of Θ_0° by the cube root of 4 and 8 respectively for comparison with Θ_0^{el} . This gives values of 132 K (KSCN) and 119 K (NH_4SCN) which are close to the elastic value for CsSCN.

While there is marked anisotropy in the stiffness of the crystal for the propagation of transverse vibrations, the similarity of the elastic behaviour for the xy and yz planes is striking. Ultimately, the anisotropy of the elastic properties of the crystal must be related to the symmetry of the bonding within the crystal. Projections of the unit cell onto the three principal planes are shown in Figs 2*d-f*. From these, the planar-like stacking of the atoms along the [010] direction and the similarity of the xy and yz planes are clearly seen. A detailed theoretical description of the connection between the crystal structure and the elastic properties is currently being investigated.

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