# Neutron Diffraction Studies of CsSCN above Room Temperature

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#### Abstract

Neutron diffraction studies have been made on the orthorhombic phase of caesium thiocyanate for temperatures below the order-disorder phase transition at 470 K. The structure, as determined at 453 K by elastic neutron diffraction, is found to be very similar to that at room temperature. This behaviour is contrasted with that of potassium thiocyanate. The temperature dependences of the acoustic phonon dispersion branches, as determined by inelastic neutron diffraction, are also presented for temperatures up to 463 K. No evidence of significant mode softening was observed.

## 1. Introduction

Caesium thiocyanate is an ionic crystal consisting of spherical metal cations and rod-shaped molecular anions. The room temperature phase is orthorhombic and transforms at 470 K to a disordered cubic structure (Manolatos *et al.* 1973). Several room temperature investigations of the lattice dynamics have been reported (Ti *et al.* 1977; Ra *et al.* 1978; Ti and Ra 1980*a*, 1980*b*; Irving *et al.* 1983, 1984). However, prior to this study only the determination of the molecular volume as a function of temperature (Manolatos *et al.* 1973) and differential thermal analysis investigations (Klement 1976) have been reported above room temperature.

Considerably more work has been reported on potassium thiocyanate and its order-disorder phase transition. The phase transition has been determined to be high order in character with a small first order component (Klement 1976). X-ray and thermal investigations (Sakiyama *et al.* 1963; Yamada and Watanabe 1963) have determined that at the transition the thiocyanate ions become disordered between two orientations. The heat capacity as a function of temperature and several spectroscopic investigations (Iqbal *et al.* 1972; Owens 1979) reveal changes in behaviour related to the transition at least ten degrees below the transition.

The transition in CsSCN is not identical to that in KSCN, as thermal investigations have identified the transition to be first order in nature. The cubic symmetry of the high temperature phase also indicates that there must be considerably more disorder present in CsSCN than in KSCN. The behaviour of CsSCN reported to date suggests that the transition may be more closely related to the orthorhombic/cubic transitions in KCN and NaCN.

The atomic positions and anisotropic thermal parameters of CsSCN were measured at 453 K with the aim of contrasting the room temperature structure with the structure

at 453 K. It was hoped that such a contrast could give some indication, either in the atomic positions or in the thermal parameters, as to how the structure changes at the transition. Selected portions of the dispersion relations were measured at 393, 453 and 463 K in an attempt to determine whether a 'soft' phonon mode could be associated with the phase transition. The search was concentrated on the acoustic modes because of the similarity of CsSCN with potassium cyanide, which displays a softening of the transverse acoustic modes (Rowe *et al.* 1978).

### 2. Experimental

The room temperature structure of caesium thiocyanate is orthorhombic with space group *Pnma*. Single crystals were grown from water solution by evaporation. The structure determination was made by using the 2TANB single-crystal four-circle diffractometer attached to the HIFAR reactor at the Australian Atomic Energy Commission Lucas Heights Laboratories. A single crystal of CsSCN with dimensions  $5 \times 5 \times 5$  mm<sup>3</sup> was mounted with a high temperature cement in a simple furnace. The temperature immediately below the sample was measured with a copper-constantan thermocouple. A simple temperature controller switched the heater current off and on as the temperature crossed a set point. The thermocouple voltage was also measured with a digital voltmeter and the variation in temperature over a heating cycle was at most  $\pm 1.5$  K at 453 K.

The comparatively crude temperature controller and furnace arrangement prevented the measurement at temperatures in the immediate region of the transition. A point 17 K below the transition was selected so as to minimize the danger of heating the crystal above the transition temperature, which may have damaged the crystal, and also to prevent softening of the cement bond. Subsequent to the measurements at 453 K for the structure determination, the crystal was heated above the transition and was found to melt at 484 K. This compares favourably with the actual value of 479 K which indicates that the difference between the crystal temperature and thermocouple temperature was not large.

Measurements were made at a wavelength of 1.238 Å. The data consisted of 727 reflections with the standard (022) reflection measured 30 times during the course of the data collection. These data were reduced to 392 independent reflections by the collection of equivalents, and the discarding of several reflections because of the occulting effect of the furnace leads for some orientations of the furnace. All data reduction was performed at Lucas Heights with the standard single-crystal dataset reduction programs (Elcombe *et al.* 1971). No absorption correction was made. The structure factors were found to be consistent with the room temperature space group. The structure was refined by means of the LINUS program with the room temperature parameters of Manolatos *et al.* (1973) as a starting point.

The effect of thermal vibrations on the structure factors was incorporated by using the anisotropic thermal parameters  $\beta_{ij}$ , with  $\beta_{12}$  and  $\beta_{23}$  constrained to be zero because all of the atoms lie on mirror planes normal to [010]. A reasonable unweighted disagreement factor between the calculated and observed structure factors of

$$R = \sum |F_{calc}| - |F_{obs}| / |F_{obs}| = 9.2\%$$

was obtained.

The phonon dispersion measurements were made with the 10H triple-axis neutron spectrometer attached to the HIFAR reactor. Incident wavelength selection was obtained by Bragg reflection from the (111) planes of a single crystal of copper. Scattered wavelength selection was obtained from (0004) reflection from a pyrolitic graphite crystal. The collimation before the sample was  $0.7^{\circ}$  FWHM and  $1.3^{\circ}$ FWHM before the analyser. The detector had an acceptance angle of  $3^{\circ}$ . The majority of measurements were made by using the 'constant Q' method with a fixed scattered neutron wavevector of  $2.6 \text{ Å}^{-1}$ . The energy resolution, as determined from a 'constant Q' scan by using the elastic incoherent scatterer vanadium, was 0.16THz for a scattered wavevector of  $2.6 \text{ Å}^{-1}$ . The calibration of the instrument and the alignment of the sample was such that the energy mismatch between analyser and monochromator was at most 0.01 THz, and the error in phonon q was  $\pm 0.5\%$ .



A cross-sectional view of the furnace showing the aluminium sample block and the arrangement of heating coils is presented in Fig. 1. The nichrome wire heating coils were placed both above and below the sample in order to minimize the thermal gradient across the sample. The temperature difference between the top and bottom thermocouples was 1 K at 473 K.

Two type 'T' copper-constantan thermocouples were used to monitor the temperature just above and below the sample position. A temperature controller varied the heater current about a fixed value in proportion to the difference between the thermocouple voltage and a reference voltage. The controller held the thermocouple voltage constant to within  $\pm 5 \,\mu$ V which corresponds to a temperature variation of  $\pm 0.1$  K. A heater current of 0.26 A was required to reach 463 K.

Measurements were made along the three orthorhombic axes and in the [110] direction. This required three settings of the crystal corresponding to each of the orthorhombic axes mounted vertically and therefore perpendicular to the scattering

plane. The samples were flat discs approximately 3 cm in diameter with a thickness of 1 cm. It was possible to mount both the [100] and [010] directions vertical in the furnace shown in Fig. 1. A slightly modified furnace sample block, in conjunction with a slightly (20%) larger crystal, was used for the measurements with [001] vertical. In both cases the samples were held in place by small aluminium clamps with aluminium foil placed between the samples and mounting block to wedge them into position and to aid the heat transfer. It was apparent from the measurements that the crystal did not move during the course of the experiment.

No significant damage to the samples occurred during the normal course of the experiment, although the first crystal was destroyed when the temperature controller broke down. The small inclusions of saturated solution trapped in the crystals during their growth increased in size as the temperature was increased. Above 373 K most of the trapped solution escaped from the sample leaving a small amount of powdery residue on the surface of the crystal.

The measurement of the phonon branches at various temperatures is an extension of a previous room temperature investigation (Irving *et al.* 1984), and measurements were made at the same positions in reciprocal space as for the room temperature measurements.

#### 3. Results

The lattice parameters at 453 K were determined to be

$$a = 8.093 \pm 0.007$$
,  $b = 6.432 \pm 0.005$ ,  $c = 8.480 \pm 0.007$  Å,

and at room temperature

$$a = 8.032 \pm 0.040$$
,  $b = 6.331 \pm 0.020$ ,  $c = 8.429 \pm 0.030$  Å.

The indicated limits are the standard deviations obtained during the orientation refinement. The room temperature lattice parameters are of a lower precision because only a few Bragg reflections were used for the orientation refinement. These can be compared with the values

$$a = 7.978 \pm 0.003$$
,  $b = 6.332 \pm 0.002$ ,  $c = 8.332 \pm 0.003$  Å,

obtained by Manolatos et al. (1973) from X-ray measurements at room temperature.

Table 1.	Atomic	positions and	thermal	parameters	at 453 K	
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Values in parentheses denote the standard deviation in the last decimal place;  $\beta_{12}$  and  $\beta_{23}$  are zero by symmetry

Atom	x	y <sup>A</sup>	Ζ	$\beta_{11}$	β22	$\beta_{33}$	$\beta_{13}$
Cs S C N	0.1806(2) 0.0250(4) 0.1738(1) 0.2836(1)	$ \begin{array}{c} 0 \cdot 25 \\ 0 \cdot 25 \\ 0 \cdot 25 \\ 0 \cdot 25 \\ 0 \cdot 25 \end{array} $	$0.1048(2) \\ 0.6868(3) \\ 0.5585(1) \\ 0.4689(1)$	0.0179(3) 0.0191(6) 0.0167(2) 0.0217(2)	$\begin{array}{c} 0.0293(4) \\ 0.047(1) \\ 0.0263(3) \\ 0.0425(3) \end{array}$	$\begin{array}{c} 0.0153(2) \\ 0.0180(4) \\ 0.0140(2) \\ 0.0187(2) \end{array}$	$ \begin{array}{c} -0.0016(2) \\ 0.0009(4) \\ -0.0022(2) \\ 0.0024(2) \end{array} $

<sup>A</sup> Fixed by symmetry.

The atomic positions and thermal parameters are presented in Table 1. The C-S and C-N bond lengths at 453 K were determined to be  $1.618\pm0.007$  and

(a)

 $(\hat{\mathbf{z}})$ 



Fig. 2. Thermal ellipsoids at from the X-ray measurements by Manolatos *et al.* (1973), and (b) 453 K from the present work. (a) room temperature (293 K),

ΰ

a

q

 $1 \cdot 165 \pm 0 \cdot 003$  Å. The S-C-N bond angle was determined to be  $178 \cdot 4 \pm 0 \cdot 5^{\circ}$ . The anisotropic thermal parameters give the r.m.s. thermal displacements detailed in Table 2. The atoms are situated on mirror planes which requires that  $\beta_{12} = \beta_{23} = 0$ . Thus, one of the principal directions of the thermal ellipsoids is always parallel to the [010] direction. The other two principal directions lie in the *a*-*c* plane. The angle that these directions make with the *a* axis is given by the direction cosine,  $\cos \alpha$ , in Table 2. The cosines quoted in Table 2 refer to the Cs, S, C and N atoms whose positions are given in Table 1, and for clarity are shaded in Fig. 2. The positions

[010]		Components in $a-c$ plane			
(Å)	(Å)	cosα	(Å)	$\cos \alpha$	
0.247	0.251	0.8099	0.227	0.5866	
0.313	0.247	-0.8161	0.260	0.5778	
0.234	0.247	0·7990	0.212	0.6014	
0.298	0.280	-0.7830	0.247	-0.6221	
	[010] (Å) 0 · 247 0 · 313 0 · 234 0 · 298	[[[010]]         (Å)           0.247         0.251           0.313         0.247           0.234         0.247           0.298         0.280	$\begin{array}{c c} \hline \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ $	Imposits at 425 K           Imposits at 425 K           Imposits at 425 K           Imposits at 425 K           Components in $a-c$ plane           (Å)         Cos $\alpha$ 0.247         0.251         0.8099         0.227           0.313         0.247         -0.8161         0.260           0.234         0.247         0.7990         0.212           0.298         0.280         -0.7830         0.247	

Table 2. The r.m.s. components of thermal motions along principal axes of the thermal<br/>ellipsoids at 453 K

Phonon	Temp. (K)	Q	q	Energy (THz)
LA [100]	463	$(5 \cdot 2 \ 0 \ -2) \\ (5 \cdot 3 \ 0 \ -2) \\ (5 \cdot 4 \ 0 \ -2)$	$\begin{bmatrix} 0 \cdot 2 & 0 & 0 \end{bmatrix} \\ \begin{bmatrix} 0 \cdot 3 & 0 & 0 \end{bmatrix} \\ \begin{bmatrix} 0 \cdot 4 & 0 & 0 \end{bmatrix}$	$ \begin{array}{r} 0.631 \pm 0.018 \\ 0.922 \pm 0.026 \\ 1.056 \pm 0.014 \end{array} $
	393	$(5 \cdot 4 \cdot 0 - 2)$ $(5 \cdot 5 \cdot 0 - 2)$ $(5 \cdot 2 \cdot 0 - 2)$	[0 + 0 0] $[0 \cdot 5 0 0]$ $[0 \cdot 2 0 0]$	$1 \cdot 0.05 \pm 0 \cdot 0.14$ $1 \cdot 300 \pm 0 \cdot 0.29$ $0 \cdot 676 \pm 0 \cdot 0.11$
		$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	$\begin{bmatrix} 0 \cdot 3 & 0 & 0 \end{bmatrix} \\ \begin{bmatrix} 0 \cdot 4 & 0 & 0 \end{bmatrix} \\ \begin{bmatrix} 0 \cdot 5 & 0 & 0 \end{bmatrix}$	$0.995 \pm 0.034$ $1.144 \pm 0.024$ $1.298 \pm 0.039$
TA [100]/[010]	453	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	$\begin{bmatrix} 0 \cdot 2 & 0 & 0 \end{bmatrix} \\ \begin{bmatrix} 0 \cdot 3 & 0 & 0 \end{bmatrix} \\ \begin{bmatrix} 0 \cdot 4 & 0 & 0 \end{bmatrix} \\ \begin{bmatrix} 0 \cdot 5 & 0 & 0 \end{bmatrix}$	$0.266 \pm 0.009 \\ 0.382 \pm 0.011 \\ 0.510 \pm 0.012 \\ 0.627 \pm 0.013$
	393	$(-0.2 \ 4 \ 0) \\ (-0.3 \ 4 \ 0) \\ (-0.4 \ 4 \ 0) \\ (-0.5 \ 4 \ 0)$	$\begin{bmatrix} 0 \cdot 2 & 0 & 0 \\ 0 \cdot 3 & 0 & 0 \end{bmatrix}$ $\begin{bmatrix} 0 \cdot 4 & 0 & 0 \\ 0 \cdot 5 & 0 & 0 \end{bmatrix}$	$0.274 \pm 0.009 \\ 0.392 \pm 0.011 \\ 0.519 \pm 0.011 \\ 0.637 \pm 0.013$
TA [100]/[001]	463	$\begin{array}{ccc} (-2 \cdot 2 & 0 & 5) \\ (-2 \cdot 3 & 0 & 5) \\ (-2 \cdot 4 & 0 & 5) \\ (-2 \cdot 5 & 0 & 5) \end{array}$	$\begin{bmatrix} 0 \cdot 2 & 0 & 0 \end{bmatrix} \\ \begin{bmatrix} 0 \cdot 3 & 0 & 0 \end{bmatrix} \\ \begin{bmatrix} 0 \cdot 4 & 0 & 0 \end{bmatrix} \\ \begin{bmatrix} 0 \cdot 5 & 0 & 0 \end{bmatrix}$	$\begin{array}{c} 0.337 \pm 0.013 \\ 0.513 \pm 0.016 \\ 0.675 \pm 0.018 \\ 0.833 \pm 0.013 \end{array}$
	393	$\begin{array}{rrrr} (-2 \cdot 2 & 0 & 5) \\ (-2 \cdot 3 & 0 & 5) \\ (-2 \cdot 4 & 0 & 5) \\ (-2 \cdot 5 & 0 & 5) \end{array}$	$\begin{bmatrix} 0 \cdot 2 & 0 & 0 \end{bmatrix} \\ \begin{bmatrix} 0 \cdot 3 & 0 & 0 \end{bmatrix} \\ \begin{bmatrix} 0 \cdot 4 & 0 & 0 \end{bmatrix} \\ \begin{bmatrix} 0 \cdot 5 & 0 & 0 \end{bmatrix}$	$\begin{array}{c} 0.369 \pm 0.011 \\ 0.548 \pm 0.012 \\ 0.735 \pm 0.014 \\ 0.880 \pm 0.009 \end{array}$
Optic 7	453	(0.9 4 0) (-1.2 4 0) (-0.7 4 0)	$\begin{bmatrix} 0 \cdot 1 & 0 & 0 \end{bmatrix} \\ \begin{bmatrix} 0 \cdot 2 & 0 & 0 \end{bmatrix} \\ \begin{bmatrix} 0 \cdot 3 & 0 & 0 \end{bmatrix}$	$1.059 \pm 0.034$ $1.016 \pm 0.036$ $0.848 \pm 0.025$
	393	(-0.7 4 0)	$[0 \cdot 3 \ 0 \ 0]$	$0.858 \pm 0.020$

 Table 3. Phonon resonances along the [100] direction

of the other atoms within the unit cell, for each atom type, can be calculated from those positions in Table 1 by using the 4c equivalent positions for the *Pnma* space group.

The anisotropic thermal parameters have been used to calculate the thermal ellipsoids for each atom. The thermal ellipsoids define the volume inside which an atom has a 0.5 probability of being found and have principal axes, the magnitude of which are proportional to the corresponding r.m.s. displacement (Willis and Pryor 1975). Fig. 2 displays cross sections of the unit cell of CsSCN for the *a*-*c* and *b*-*c* planes showing the cross sections of the thermal ellipsoids at room temperature, as determined in the X-ray study by Manolatos *et al.* (1973) (Fig. 2*a*), and at 453 K (Fig. 2*b*).

Phonon	Temp. (K)	Q	· q	Energy (THz)
LA [010]	463	(0 4.2 0)	[0 0.2 0]	$0.704 \pm 0.018$
		(0 4.3 0)	[0 0 · 3 0]	$0.80 \pm 0.1$
		(0 4.4 0)	[0 0 • 4 0]	$0.734 \pm 0.032$
	453	(0 4.2 0)	[0 0 2 0]	$0.723 \pm 0.021$
		(0 3.6 0)	[0 0 • 4 0]	$0.802 \pm 0.021$
		(0  3.5  0)	[0 0 · 5 0]	$0.754 \pm 0.011$
	393	$(0  4 \cdot 2  0)$	[0 0 • 2 0]	$0.725 \pm 0.023$
		$(0  3 \cdot 6  0)$	[0 0 • 4 0]	$0.846 \pm 0.027$
		(0  3.5  0)	[0 0.5 0]	$0.705 \pm 0.029$
TA [010]/[100]	453	$(2  2 \cdot 2  0)$	[0 0 · 2 0]	$0.307 \pm 0.011$
		(2 2.3 0)	[0 0 · 3 0]	$0.445 \pm 0.013$
		$(2  2 \cdot 4  0)$	[0 0 • 4 0]	$0.587 \pm 0.014$
		(2 2.5 0)	[0 0.5 0]	$0.700 \pm 0.009$
	393	$(2  2 \cdot 2  0)$	[0 0 • 2 0]	$0.310 \pm 0.010$
		$(2  2 \cdot 3  0)$	[0 0.3 0]	$0.455 \pm 0.013$
		$(2  2 \cdot 4  0)$	[0 0 • 4 0]	$0.593 \pm 0.018$
		(2 2.5 0)	[0 0.5 0]	$0.732 \pm 0.028$
TA [010]/[001]	463	$(0 - 2 \cdot 15 \ 0)$	[0 0.15 0]	$0.209 \pm 0.011$
		$(0 - 2 \cdot 2  0)$	[0 0 · 2 0]	$0.287 \pm 0.013$
		$(0 - 2 \cdot 3  0)$	[0 0.3 0]	$0.422 \pm 0.030$
		$(0 - 2 \cdot 4  0)$	[0 0 · 4 0]	$0.569 \pm 0.018$
		$(0 - 2 \cdot 5  0)$	[0 0 • 5 0]	$0.700 \pm 0.015$
	453	$(0 - 2 \cdot 15 \ 0)$	[0 0.15 0]	$0.219 \pm 0.013$
		$(0 - 2 \cdot 2  0)$	[0 0 • 2 0]	$0.282 \pm 0.012$
		$(0 - 2 \cdot 3  0)$	[0 0.3 0]	$0.433 \pm 0.017$
		$(0 - 2 \cdot 4  0)$	[0 0 • 4 0]	$0.571 \pm 0.012$
		$(0 - 2 \cdot 5  0)$	[0 0 · 5 0]	$0.704 \pm 0.015$
	393	$(0 - 2 \cdot 15 \ 0)$	[0 0.15 0]	$0.223 \pm 0.016$
		$(0 - 2 \cdot 2  0)$	[0 0 · 2 0]	$0\cdot 308\pm 0\cdot 013$
		$(0 - 2 \cdot 3  0)$	[0 0.3 0]	$0.478 \pm 0.015$
		$(0 - 2 \cdot 4  0)$	[0 0 • 4 0]	$0.593 \pm 0.013$
		$(0 - 2 \cdot 5  0)$	[0 0.5 0]	$0.717 \pm 0.015$

Table 4. Phonon resonances along the [010] direction

The measured phonon resonances at 393, 453 and 463 K are collected in Tables 3–6. The notation for the transverse acoustic modes indicates the propagation direction and the polarization of the atomic displacements respectively. The phonon resonances

Phonon	Temp. (K)	Q	q	Energy (THz)
LA [001]	463	$\begin{array}{c} (0 \ 2 \ 2 \cdot 2) \\ (0 \ 2 \ 2 \cdot 4) \end{array}$	$\begin{bmatrix} 0 & 0 & 0 \cdot 2 \end{bmatrix} \\ \begin{bmatrix} 0 & 0 & 0 \cdot 4 \end{bmatrix}$	$0.651 \pm 0.019$ $1.215 \pm 0.011$
	453	$\begin{array}{cccc} (0 & 2 & 2 \cdot 2) \\ (0 & 2 & 2 \cdot 3) \\ (0 & 2 & 2 \cdot 4) \end{array}$	$\begin{bmatrix} 0 & 0 & 0 \cdot 2 \\ 0 & 0 & 0 \cdot 3 \end{bmatrix}$ $\begin{bmatrix} 0 & 0 & 0 \cdot 4 \end{bmatrix}$	$ \begin{array}{r} 0 \cdot 724 \pm 0 \cdot 027 \\ 1 \cdot 123 \pm 0 \cdot 043 \\ 1 \cdot 237 \pm 0 \cdot 027 \end{array} $
	393	$(0 2 2 \cdot 2) (0 2 2 \cdot 3) (0 2 2 \cdot 4) (0 2 2 \cdot 5)$	$\begin{bmatrix} 0 & 0 & 0 \cdot 2 \\ [0 & 0 & 0 \cdot 3 ] \\ [0 & 0 & 0 \cdot 4 ] \\ [0 & 0 & 0 \cdot 5 ] \end{bmatrix}$	$ \begin{array}{c} 0 \cdot 688 \pm 0 \cdot 029 \\ 0 \cdot 999 \pm 0 \cdot 020 \\ 1 \cdot 091 \pm 0 \cdot 040 \\ 1 \cdot 132 \pm 0 \cdot 016 \end{array} $
TA [001]/[100]	463	$(5 0 2 \cdot 2) (5 0 2 \cdot 3) (5 0 2 \cdot 4) (5 0 2 \cdot 5)$	$\begin{bmatrix} 0 & 0 & 0 \cdot 2 \\ [0 & 0 & 0 \cdot 3 ] \\ [0 & 0 & 0 \cdot 4 ] \\ [0 & 0 & 0 \cdot 5 ] \end{bmatrix}$	$0.368 \pm 0.013 \\ 0.502 \pm 0.013 \\ 0.701 \pm 0.010 \\ 0.855 \pm 0.008$
	393	$(5 0 2 \cdot 2) (5 0 2 \cdot 3) (5 0 2 \cdot 4) (5 0 2 \cdot 5)$	$\begin{bmatrix} 0 & 0 & 0 \cdot 2 \\ 0 & 0 & 0 \cdot 3 \end{bmatrix}$ $\begin{bmatrix} 0 & 0 & 0 \cdot 4 \end{bmatrix}$ $\begin{bmatrix} 0 & 0 & 0 \cdot 5 \end{bmatrix}$	$\begin{array}{c} 0 \cdot 402 \pm 0 \cdot 014 \\ 0 \cdot 539 \pm 0 \cdot 009 \\ 0 \cdot 751 \pm 0 \cdot 016 \\ 0 \cdot 904 \pm 0 \cdot 010 \end{array}$
TA [001]/[010]	463	$(0 \ 4 \ 2 \cdot 15) (0 \ 4 \ 2 \cdot 2) (0 \ 4 \ 2 \cdot 3) (0 \ 4 \ 2 \cdot 4) (0 \ 4 \ 2 \cdot 5)$	$\begin{bmatrix} 0 & 0 & 0 \cdot 15 \end{bmatrix} \\ \begin{bmatrix} 0 & 0 & 0 \cdot 2 \end{bmatrix} \\ \begin{bmatrix} 0 & 0 & 0 \cdot 3 \end{bmatrix} \\ \begin{bmatrix} 0 & 0 & 0 \cdot 4 \end{bmatrix} \\ \begin{bmatrix} 0 & 0 & 0 \cdot 5 \end{bmatrix}$	$0.192 \pm 0.014 \\ 0.228 \pm 0.013 \\ 0.309 \pm 0.016 \\ 0.416 \pm 0.016 \\ 0.525 \pm 0.011$
	453	$\begin{array}{c} (0 \ 4 \ 2 \cdot 15) \\ (0 \ 4 \ 2 \cdot 2) \\ (0 \ 4 \ 2 \cdot 2) \\ (0 \ 4 \ 2 \cdot 4) \\ (0 \ 4 \ 2 \cdot 5) \end{array}$	$\begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 15 \end{bmatrix}$ $\begin{bmatrix} 0 & 0 & 0 & 2 \end{bmatrix}$ $\begin{bmatrix} 0 & 0 & 0 & 3 \end{bmatrix}$ $\begin{bmatrix} 0 & 0 & 0 & 4 \end{bmatrix}$ $\begin{bmatrix} 0 & 0 & 0 & 5 \end{bmatrix}$	$0.202 \pm 0.013 \\ 0.202 \pm 0.013 \\ 0.241 \pm 0.014 \\ 0.325 \pm 0.016 \\ 0.433 \pm 0.016 \\ 0.535 \pm 0.011 \\ 0.555 \pm 0.01$
	393	$\begin{array}{c} (0 \ 4 \ 2 \cdot 15) \\ (0 \ 4 \ 2 \cdot 2) \\ (0 \ 4 \ 2 \cdot 3) \\ (0 \ 4 \ 2 \cdot 4) \\ (0 \ 4 \ 2 \cdot 5) \end{array}$	$\begin{bmatrix} 0 & 0 & 0 \cdot 15 \\ [0 & 0 & 0 \cdot 2] \\ [0 & 0 & 0 \cdot 3] \\ [0 & 0 & 0 \cdot 4] \\ [0 & 0 & 0 \cdot 5] \end{bmatrix}$	$0.217 \pm 0.014 \\ 0.257 \pm 0.014 \\ 0.339 \pm 0.014 \\ 0.459 \pm 0.014 \\ 0.561 \pm 0.016$
Optic 1	463 453	$\begin{array}{c} (0 \ 4 \ 2 \cdot 75) \\ (0 \ 4 \ 2 \cdot 75) \end{array}$	$\begin{bmatrix} 0 & 0 & 0 \cdot 25 \end{bmatrix} \\ \begin{bmatrix} 0 & 0 & 0 \cdot 25 \end{bmatrix}$	$0.778 \pm 0.095$ $0.766 \pm 0.028$

Table 5. Phonon resonances along the [001] direction

Table 6. Zone centre and [110	phonon resonance
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Temp. (K)	Q		Energy (THz)
463	$(0 \ 4 \ 1)$ $(0 \ 0 \ 5)$		$0.888 \pm 0.014$ $1.718 \pm 0.036$
453	$\begin{array}{ccc} (0 & 4 & 1) \\ (1 & 4 & 0) \\ (2 \cdot 1 & 2 \cdot 1 & 0) \\ (2 \cdot 2 & 2 \cdot 2 & 0) \end{array}$	q = 0.1 [110] q = 0.2 [110]	$ \begin{array}{c} 0.861 \pm 0.029 \\ 1.115 \pm 0.030 \\ 0.400 \pm 0.016 \\ 0.033 \pm 0.045 \end{array} $
393	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	q = 0.1 [110]	$0.933 \pm 0.043$ $0.884 \pm 0.024$ $1.755 \pm 0.008$ $1.117 \pm 0.032$ $0.411 \pm 0.020$

were fitted by a simple gaussian and linear background to obtain the energy centre in a similar manner to previous measurements (Irving *et al.* 1984). Only some branches were measured at 463 K. The intensity and half-widths of the resonances did not change greatly over the temperature range. A typical set of resonances for a transverse acoustic mode is shown in Fig. 3. The temperature dependence of the acoustic dispersion curves is shown in Fig. 4. For clarity, only the highest temperature measurements and the corresponding room temperature measurements (Irving *et al.* 1984) are shown in Fig. 4. The standard deviation obtained from the fitting procedure for the high temperature data is shown as error bars on the data points, or where smaller than the symbol plotted, a typical error bar is shown.



**Fig. 3.** Phonon resonances at 293, 393, 453 and 463 K for TA [0 0 0.3]/[010].



#### 4. Discussion

The structure of CsSCN at 453 K is very similar to that at room temperature. The structure above the transition is thought to be cubic, and therefore in this structure the caesium atoms should reside at sites of cubic symmetry within the unit cell. At 453 K there is no evidence for a substantial movement in the positions of the caesium atoms, which suggests there is little change in the structure until the transition temperature is reached. This is further evidence of the discontinuous first order nature of the transition as suggested by the thermodynamical studies.

There are several features of the thermal ellipsoids (Fig. 2) that should be noted:

- (i) the SCN molecular axis is co-linear with one of the C, S and N ellipsoidal axes;
- (ii) the r.m.s. thermal displacements for the C, S and N atoms parallel to the molecular axis are approximately equal;
- (iii) there are relatively large r.m.s. displacement values for the S and N atoms perpendicular to the molecular axis both in and out of the a-c plane, with the out-of-plane values being approximately 20% larger than the in-plane values;
- (iv) the thermal displacements are larger at 453 K, but there is no evidence that the ratio of the out-of-plane r.m.s. displacements to the in-plane displacements changes significantly with temperature.

Observations (i)–(iii) are indicative of rigid body behaviour for the SCN ion with rotation occurring about the centre of gravity. Although the out-of-plane rotation is more pronounced than the in-plane rotation, the feature (iv) would indicate that there is no evidence of any relative softening of the former below 453 K. This behaviour contrasts with the softening of the out-of-plane motion which ultimately leads to the disordering of the SCN ion in KSCN (Yamada *et al.* 1963; Owens 1979).

The dispersion behaviour of the phonon branches at higher temperatures is very similar to that at room temperature. In general the changes are small with the frequencies decreasing with increasing temperature. The changes in the transverse acoustic branches, apart from TA [100]/[001] and TA [001]/[100], are less than 7%. The TA [100]/[001] branch on the other hand softens by up to 15%. It is interesting to note that of the transverse acoustic branches, the TA [100]/[001] and TA [001]/[100], which propagate and have displacements in the plane containing the thiocyanate ions, soften to the greatest extent.

The longitudinal modes have considerably more error and scatter associated with their measurement. Some of the measured frequencies of the LA [001] branch increase with temperature; however, the relatively large errors may be the major source of the apparent upward energy shift. The longitudinal mode along the [110] direction displays the largest softening of 12% at 453 K. The measured optic resonances show small decreases at higher temperature.

The changes observed in the dispersion curves are not large and the overall shape of the branches does not change. This result is consistent with the measured structure at 453 K. Together they indicate that there is little change up to 453 K from the room temperature structure and lattice dynamics. The similarity in the intensity, half-width, and background of the phonon resonances at 463 K and room temperature suggests that the lattice is still well behaved. This indicates that in contrast to KSCN (Yamada and Watanabe 1963), the motions of the thiocyanate ions immediately below the transition do not include gross rotations.

No search was undertaken at 453 or 463 K for new phonon resonances, and not all the reported room temperature optic modes were measured at these temperatures. It is therefore possible that a mode, not necessarily along a principal direction, may

be associated with the phase transition and display a far greater softening than those measured so far. However, in view of the conclusions drawn from the thermal displacements this is not considered likely.

## 5. Conclusions

The measured atomic structure at 453 K is not very different to that at room temperature. In KSCN the phase transition is attributed to the flipping of the orientation of the SCN ions out of the plane in which they are situated. The anisotropic thermal parameters for CsSCN indicate preferred out-of-plane rotation, but the measurements at 453 K do not provide any evidence of a softening of this librational mode. This is further evidence of the first order nature of the transition, and is in contrast to the behaviour of KSCN which displays a variety of pre-transition phenomena.

Measurements of the dispersion of the acoustic branches and some optic modes along the orthorhombic directions up to 463 K do not show that a single mode is softening. All modes soften to varying extents with the TA [100]/[001] and TA [001]/[100] branches showing the largest softening. This is consistent with the small changes in the atomic positions and the expansion of the lattice.

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