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Polymorphism in Cesium Thiocyanate*

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The crystal structure of the orthorhombic modification and the high temperature cubic form of CsSCN have been investigated by X ray diffraction, differential calorimetry, and microscopy.

The orthorhombic phase contains four molecules per unit cell; the space group is *Pnma*; $a = 7.978$ Å, $b = 6.332$ Å, $c = 8.332$ Å. The structure is layered. In each unit cell, two Cs^+ ions and two SCN^- ions lie on planes perpendicular to the b axis at $y = 1/4$ and $3/4$.

Between 197°C and the melting point (at 206°C), CsSCN crystallizes in a cubic structure similar to CsCl: $a_0 = 4.83$ Å, $Z = 1$. The symmetry of the monomolecular cubic unit cell requires that the SCN^- orientation be disordered. Reasonably good agreement between F_{obsd} and F_{calcd} is achieved by postulating 24-fold orientational disorder of the SCN^- ion.

Introduction

In the course of a high temperature optical examination of single crystals of cesium thiocyanate, we noted that the crystals transformed at about 197°C from an optically birefringent to an optically isotropic form. The latter melted at 206 ± 2°C.

Subsequent studies using X ray diffraction and differential scanning calorimetry revealed that the room temperature modification is orthorhombic while the form stable above 197°C crystallizes in the cesium chloride structure type [$a_0 = 4.83(2)$].

Of the alkali thiocyanates, only potassium thiocyanate has been studied extensively (*1–3*); an orthorhombic to tetragonal transformation has been reported; two-fold disorder involving the SCN^- ion appears to be present in the high temperature tetragonal modification (*4*).

In this work we have undertaken a study of structural and related aspects of the orthorhombic to cubic transformation in CsSCN. Single crystal platelets of the orthorhombic modification were obtained by slow evaporation of saturated methanol solutions. Precession photographs established that the crystal system is orthorhombic at room temperature and that

$$a = 7.978(3), \qquad b = 6.332(2), \qquad c = 8.332(3).$$

There are four molecules per unit cell ($d_{calcd} = 2.99$ g/cc; the density determined by flotation in methylene iodide diluted with carbon tetrachloride is 2.98 g/cc).

Two space groups are consistent with the observed reflections: *Pnma* and $Pn2_1a$. Piezoelectric measurements of several crystals gave no detectable signal. The most probable space group therefore appeared to be the centrosymmetric *Pnma*. This was corroborated in the course of the crystal structure determination.

Experimental

Selected crystals were ground to spherical form; the crystal used for intensity measurements was a sphere of 0.10 mm radius ($\mu R = 0.93$ cm^{-1} for Mo$K\alpha$ radiation). Intensity data were collected with the Pailred automatic single crystal diffractometer using crystal monochromatized Mo$K\alpha$ radiation. Reflection intensities were measured out to $\sin\theta/\lambda = 1.0$ Å^{-1}. Six hundred and twenty-seven independent reflections, out of approximately 1500 accessible in the range studied,

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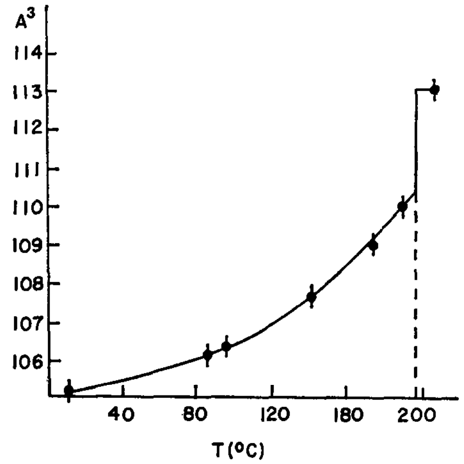

FIG. 1. Volume per "molecule" vs temperature.

were used for the structure determination. Reflection intensities were recorded using an ω scan of $\pm 2°$; backgrounds were measured for 20 sec at each end of the scan range. Corrections for absorption by spherical crystals, described by Bond (5), were applied to the measured intensities.

For the high temperature investigation, heated air was blown across small single crystals of CsSCN enclosed in thin-walled glass capillary tubes (0.2 mm i.d.). To establish the variation of the volume with temperature, the Bragg angles of several high angle reflections were measured with Cu$K\alpha$ radiation at temperature intervals of 40° between room temperature and 195°C; in addition, measurements of the volume of the cubic unit cell were made at 202 ± 2°C. A plot of "molecular" volume vs temperature is shown in Fig. 1. The slope appears to change discontinuously at the transition temperature.

A Perkin Elmer differential scanning calorimeter (DSC) was used to determine the heats of transformation and fusion, the orthorhombic-cubic transition temperature, and the melting point. Typical DSC plots are shown in Fig. 2. Repeated integrations of the areas under the curves yielded the following average values for relevant thermal quantities (estimated standard errors in parentheses):

$\Delta H_{\text{trans}} = 2670(80)$ cal/mole $T_{\text{trans}} = 196.9(2)$°C
$\Delta H_{\text{fusion}} = 1440(30)$ cal/mole $T_{\text{fusion}} = 206(2)$°C
$\Delta S_{\text{trans}} = 5.7(2)$ e.u./mole
$\Delta S_{\text{fusion}} = 3.0(1)$ e.u./mole

The discontinuous change in volume and, in particular the latent heat of transformation, indicate that the transformation is first order.

The diffraction pattern of the cubic phase was indexed on the basis of a primitive cubic unit cell with $a = 4.83$ Å. The birefringent orthorhombic crystals appeared unaffected by repeated cycling through the transition at 197°C. In several instances, a portion of a platelet showed the vivid colors characteristic of orthorhombic CsSCN when viewed through crossed polaroids, while the remainder of the crystal was optically isotropic.

The cubic crystal used for intensity measurements grew in the form of a cylinder, 0.22 mm diam ($\mu R = 9.0$ cm^{-1} for CuKα). Intensities were measured with a scintillation counter using filtered CuKα radiation. A theta-two-theta scan at 1° (2θ)/min was used to record reflection

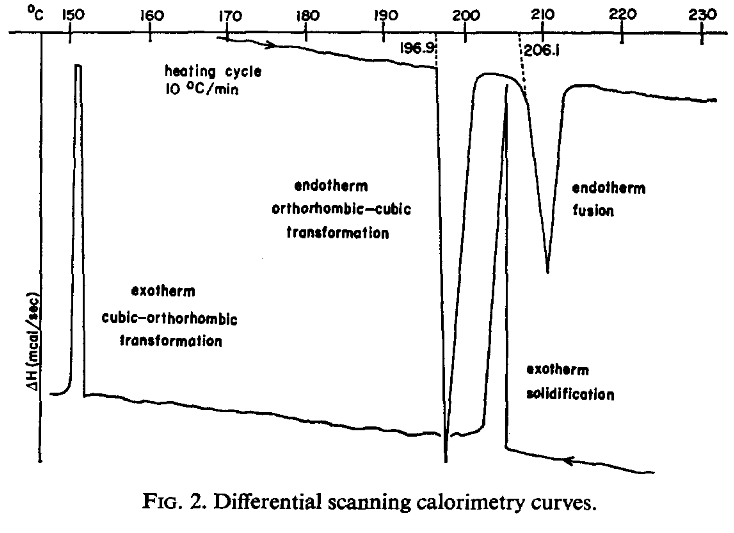

FIG. 2. Differential scanning calorimetry curves.

TABLE I

Shortest Interatomic Distances (see Fig. 3)

Atoms	Distance (Å)
Cs(1)–S(3)	4.039
Cs(1)–S(5)	3.667
Cs(3)–S(2)	4.295
Cs(1)–S(1)	5.021
Cs(2)–S(1)	5.804
Cs(1)–C(3)	3.407
Cs(1)–C(1)	3.772
Cs(2)–C(1)	4.269
Cs(1)–N(3)	3.374
Cs(1)–N(1)	3.153
Cs(2)–N(1)	3.242
S(1)–C(1)	1.64
C(1)–N(1)	1.13

intensities. At least four equivalent reflections were measured for each *hkl*. Only ten independent reflections were detected. The diffraction symmetry was *m*3*m*.

The Structure of the Orthorhombic Modification

The positions of the Cs atoms were readily determined from a Patterson (*u*, *o*, *w*) map. All the atoms in the unit cell lie in positions 4*c* of space group *Pnma*. Approximate positions of the sulfur, carbon, and nitrogen atoms were obtained from a difference electron density map. The atomic positions and thermal parameters were refined by least squares methods using a local version of the Busing and Levy Crystallographic Least Squares Program (*6*). Atomic scattering factors were taken from the International Tables for X Ray Crystallography (*7*). Anomalous scattering corrections were applied to the cesium form factors. Extinction appeared to be minor and no corrections were made. Weights were assigned according to the method outlined by Evans (*8*).

TABLE III

RMS Components of Thermal Displacements Along the Principal Axes of the Thermal Ellipsoids

Atom	RMS Displacements (Å)		
Cs	0.172(1)	0.186(3)	0.190(2)
S	0.174(4)	0.190(3)	0.231(4)
C	0.143(13)	0.155(12)	0.183(13)
N	0.178(12)	0.212(14)	0.216(11)

After five cycles, the disagreement factor was

$$R=(\sum W\|F_0|-|F_c\|)/\sum|F_0| \text{ was } 3.7\%.$$

Unobserved reflections were not included in the above. Results of the analysis obtained from the crystallographic function and error program (ORFFE) are listed in Tables I, II, and III.

The atomic arrangement is shown in Fig. 3. Adjacent thiocyanate ions in any one level (at $y=1/4$ or $3/4$) are almost perpendicular to one another. The nitrogen and sulfur atoms closest to the cesium ions lie within the same level as the latter. The SCN^- ion angle is 178.1(9)°. The indicated deviation from linearity is probably not significant.

The bond distances are: sulfur to carbon, 1.64(1) Å, and carbon to nitrogen, 1.13(1) Å. Observed and calculated structure factors are available.[1]

TABLE II

Atomic Position and Thermal Parameters

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cs	0.1784(1)	0.250[a]	0.1060(1)	0.0107(1)	0.0169(2)	0.0088(1)	0	−0.0008(1)	0
S	0.0194(3)	0.250[a]	0.6890(3)	0.0102(3)	0.0263(8)	0.0095(3)	0	0.0008(3)	0
C	0.172(1)	0.250[a]	0.559(1)	0.009(1)	0.012(2)	0.007(1)	0	−0.002(1)	0
N	0.280(1)	0.250[a]	0.472(1)	0.014(2)	0.022(3)	0.009(1)	0	−0.001(1)	0

[a] Fixed by symmetry.

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[1] A table of structure factors has been deposited as Document No. NAPS-01938 with the ASIS National Auxiliary Publications Service, c/o CCM Information Corp., 909 Third Avenue, New York, N.Y. 10022. A copy may be secured by citing the document number and remitting $5.00 for photocopies or $1.50 for microfiche. Advance payment is required. Make check or money order payable to ASIS-NAPS.

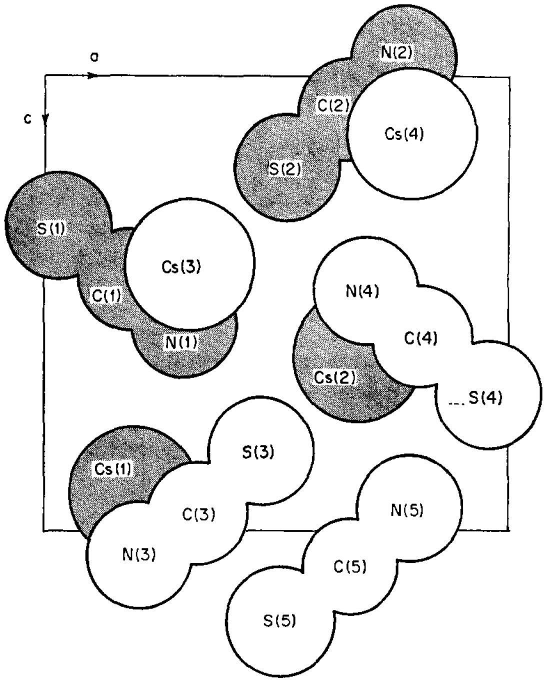

FIG. 3. Arrangement of thiocyanate ions in the orthorhombic unit cell; shaded and unshaded atoms are at $y = 1/4$ and $y = 3/4$, respectively.

The Orthorhombic to Cubic Transition

The arrangement of cesium ions in the orthorhombic phase is shown in Fig. 5. When these atoms are connected as shown, a parallelepiped with edge lengths of 4.66, 5.36, and 5.36 Å is formed. The angles among edges are 54.3, 102.13, and 102.60°.

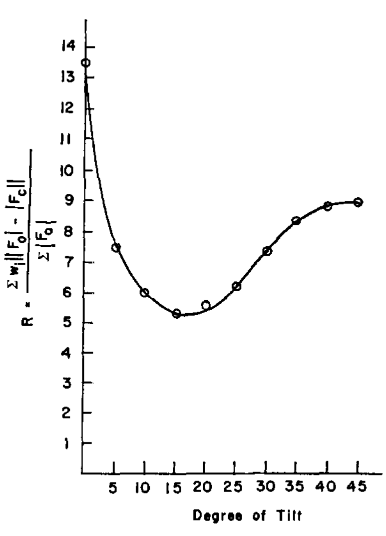

FIG. 4. R vs degree of tilt of SCN^-.

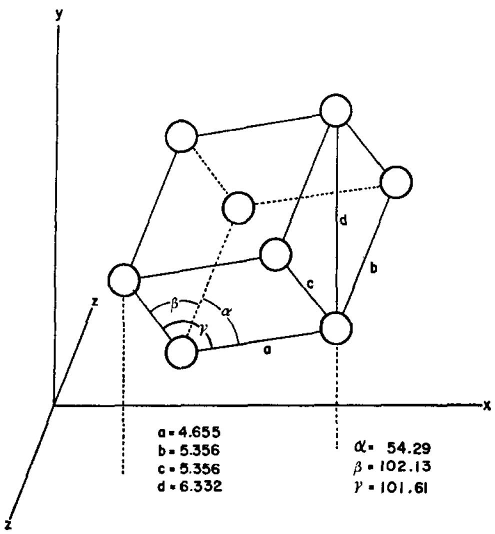

FIG. 5. The "primitive cube" in orthorhombic CsSCN.

It appears likely that this parallelepiped is progressively distorted as the temperature is raised until, just below 197°C, it approximates a cube. The orthorhombic [010] orientation would then transform to the cubic [110]. On several occasions, orthorhombic single crystals oriented along [010] did transform to the cubic modification oriented within a few degrees of the cubic [110]. Similarly, cubic crystals, grown from the melt and aligned along [110], usually transformed to orthorhombic crystals along [010].

The Cubic Modification

The diffraction data for the cubic phase and the Laue symmetry ($m3m$) indicate that $Pm3m$ is the most probable space group. $P43m$ and $P432$ are also possible, but no reasonable model consistent with the observed data could be placed in the positions available in these two space groups, and they were not considered further. Simple symmetry considerations indicate that only a disordered arrangement of the SCN^- ions is compatible with the cubic symmetry. In $Pm3m$ the point symmetry of one-fold positions is $m3m$. It was clear that no ordered arrangement of one SCN^- ion per unit cell could satisfy the requirements of point symmetry $m3m$. Disordered arrangements of the SCN^- ion had to be considered.

The disorder was investigated primarily by generating a series of models in which the SCN^- ion was placed as follows: the long dimension

TABLE IV

F_{obsd} AND F_{calcd} (FOR SCN$^-$ TILTED 15°) CUBIC MODIFICATION

$h\,k\,l$	F_{obsd}	F_{calcd}
1 0 0	55.8	52.9
1 1 0	52.3	55.4
1 1 1	38.0	37.9
2 0 0	32.8	33.4
2 1 0	20.2	18.9
2 1 1	15.8	15.9
2 2 0	9.0	9.6
2 2 1	9.4	6.6
3 0 0	5.0	5.4
2 2 2	6.9	5.9
R		5.3%
Scale factor		0.89
Crystal temperature factor	($B = 8\pi^2\overline{\mu^2}$)	23.6(1.4) Å^2

of the SCN$^-$ ion was initially set parallel to [100] and then rotated in discrete increments about an axis parallel to [010] passing through its center of mass (placed at 1/2, 1/2, 1/2). The angle between [100] and the line through the SCN$^-$ ion is referred to as the 'angle of tilt'. Structure factors were calculated for settings between 0° and 45° at intervals of 5°. Other postulated models were ruled out on either steric grounds or because of poor agreement between F_{obsd} and F_{calcd}.

At 0° tilt (i.e., SCN^{-1} along [100]) the S, C, and N atoms are in six-fold, 1/2, 1/2, x, positions of $Pm3m$. For tilts between 0° and 45°, the atoms are in 24-fold x, y, 1/2 positions. In the 45° orientation the atoms are along the [110] direction and are located in 12-fold, x, x, 1/2 positions.

Since only ten independent reflections were observed, the refinement was restricted to efforts to minimize R by varying a scale factor and one crystal temperature factor (in addition to rotation of SCN$^-$).

The results summarized in Fig. 4 show a broad minimum in R near a tilt angle of 15°. R decreases from 13.5% at 0° tilt to 5.3% at 15°. Observed and calculated structure factors are shown in Table IV.

The 24-fold disorder indicated by the above would involve an entropy increase of approximately 6.3 e.u. at the transition (using $\Delta S = k \ln W$) compared with the 5.7 e.u. measured. It appeared that though the general forms of the transition and the disorder in the cubic phase are indicated by the above, the available data do not make it possible to present a satisfactorily detailed picture of the SCN$^-$ disorder in the cubic phase.

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