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Die Kristallstruktur von Sn_2S_3 , einer dritten Phase im System Zinn-Schwefel. Von D. MOOTZ und R. KUNZMANN, *Institut für Anorganische Chemie der Technischen Hochschule, Braunschweig, Germany.*

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Entsprechend Angaben von Wolynski & Ssewrjukow (1955) gelang es, durch vorsichtigen thermischen Abbau von SnS_2 eine schwarz — gepulvert tiefbraun — gefärbte Phase der Zusammensetzung Sn_2S_3 mit eigenem Debye-Scherrer-Diagramm zu erhalten.

Versuche einer rhombischen Indizierung mit dem analytischen Verfahren von Lipson (1949) versprachen Erfolg, brauchten aber nicht fortgesetzt zu werden, da es gelang, durch Erhitzen eines Gemisches von SnS_2 und SnS — desgleichen auch von SnS_2 und Sn , SnS und S sowie Sn und S — in stöchiometrischen Mengen in abgeschmolzenen Quarzampullen die Phase Sn_2S_3 in Form von für Röntgenaufnahmen brauchbaren nadelförmigen Einkristallen zu gewinnen. Die Nadelachse liegt parallel zu [001], senkrecht zu [010] besteht gute Spaltbarkeit.

Mit $\text{Cu } K\alpha$ -Strahlung in grosser Zahl angefertigte Drehkristall-, Weissenberg- und Precessionaufnahmen ergaben rhombische Symmetrie und die Gitterkonstanten

$$a = 8,864, \quad b = 14,020 \quad \text{und} \quad c = 3,747 \text{ \AA}.$$

Die von uns zu $d = 4,87 \text{ g.cm.}^{-3}$ bestimmte Dichte führt zu vier (4,10) Formeleinheiten in der Elementarzelle. Die beobachteten Auslöschungen sind charakteristisch für die Raumgruppen $D_{2h}^6\text{-Pnam}$ und $C_{2v}^9\text{-Pna}2_1$. Weissenbergaufnahmen um [001] lassen für $hk0$ die gleiche Intensitätsverteilung erkennen wie für $hk2$.

Alle diese Tatsachen machen das Vorliegen des Strukturtyps $E2_4$ wahrscheinlich. In diesem Typ kristallisieren die Substanzen NH_4CdCl_3 , KCl_3 und RbCdCl_3 mit der Raumgruppe $D_{2h}^6\text{-Pnam}$ (Brasseur & Pauling, 1938; MacGillavry, Nijveld, Dierdorp & Karsten, 1939; Brandenberger, 1947). Zum Beispiel hat die Ammoniumverbindung die Gitterkonstanten

$$a = 8,96, \quad b = 14,87 \quad \text{und} \quad c = 3,97 \text{ \AA}.$$

Auffallende Unterschiede im Gange der ($hk0$)-Intensitäten

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The crystal and molecular structure of α -thiophenic acid; a refinement at -170°C . By P. HUDSON and J. H. ROBERTSON, *Department of Inorganic and Structural Chemistry, The University, Leeds 2*

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The crystal structure of thiophene-2-carboxylic acid, or α -thiophenic acid, has been studied by Care (1952), determined by Nardelli, Fava & Armellini (1958) and refined by Nardelli, Fava & Giraldo (1962). As part of a study of heterocyclic five-membered-ring carboxylic acids, we have collected new data and confirmed the structure of Nardelli *et al.*

Whereas Care measured only (010) and (100) projections, failing to solve the (100) projection correctly, Nardelli *et al.* recorded data for the b axis layer lines 0 to 4, solving the structure by comparison with the isostructural α -selenophenic acid. We have collected hkl

zwischen Sn_2S_3 und NH_4CdCl_3 liessen sich bei Annahme gleicher Atomlagen durch die verschiedenen Atomformfaktoren, also im wesentlichen durch den Ersatz von NH_4 durch Sn , erklären.

Der Typ $E2_4$ erfordert aus strukturellen Gründen eine Formulierung des Sn_2S_3 als $\text{Sn}^{\text{II}}[\text{Sn}^{\text{IV}}\text{S}_3]$, Zinn (II)-thiostannat (IV), was auch vom chemischen Standpunkt aus wahrscheinlich ist. Interessant ist, dass auch die Komponenten der komplexen Verbindungen, die Alkalihalogenide und SnS einerseits und CdCl_2 und SnS_2 andererseits jeweils untereinander verwandte Strukturtypen ausbilden.

Sn_2S_3 besitzt dieselbe Raumgruppe wie SnS (Hofmann, 1935), und auch die Gitterkonstanten beider Phasen sind bis auf eine ungefähre Verdoppelung in einer Richtung ähnlich. Die Symmetrieeigenschaften der Achsen folgen aber dieser Analogie nicht, sondern sind umgruppiert ($Pmcn$ für SnS mit $a = 3,98$, $b = 4,33$ und $c = 11,18 \text{ \AA}$).

Zur Sicherung des für Sn_2S_3 vorgeschlagenen Strukturtyps ist eine Atomlagenbestimmung mit Fouriersynthesen vorgesehen. Ein orientierender Versuch, mit der gleichen präparativen Technik das von Spandau & Klanberg (1958) erwähnte Ge_2S_3 kristallin darzustellen, brachte noch keinen Erfolg.

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data about a and b axes at a temperature of -170°C . and refined the structure by least-squares techniques, using anisotropic temperature factors, corrections being applied for molecular vibration. At the low temperature the cell dimensions are

$$a = 5.665, \quad b = 5.018, \quad c = 19.551 \text{ \AA}, \\ \pm 0.005 \text{ \AA}; \quad \beta = 98.2^\circ.$$

The space group is $P2_1/c$. The axial lengths are all systematically less than those reported by Nardelli *et al.* for room temperature, although only the change in c

(0.02 Å) is greater than the standard deviations. There are significant changes in the atomic co-ordinates, due to the cooling; these are recorded in Table 1. Despite these changes, however, the molecular dimensions show no significant differences from those of the molecule at room temperature. The hydrogen-bonding distance of the dimers is also unaffected.

Table 1. Differences in atomic coordinates (Å)

The authors' values are subtracted from those of Nardelli *et al.* The final column contains the estimated standard deviations

	<i>x</i>	<i>y</i>	<i>z</i>	
S	0.028	-0.007	-0.036	0.002
O ₁	0.048	-0.012	-0.037	0.006
O ₂	0.046	0.008	0.011	0.006
C ₁	0.044	-0.009	-0.028	0.008
C ₂	0.025	-0.021	-0.022	0.007
C ₃	0.045	-0.045	-0.008	0.008
C ₄	0.038	-0.101	-0.019	0.007
C ₅	0.036	-0.026	-0.008	0.007

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The structure of poly-L-proline II. By R. E. BURGE, P. M. HARRISON* and S. MCGAVIN,† *Wheatstone Physics Laboratory, University of London King's College, Strand, W. C. 2, England*

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Poly-L-proline has been shown (for references see Downie & Randall, 1959; Steinberg, Harrington, Berger, Sela & Katchalski, 1960) to exist in solution in two configurations characterized respectively by a small positive (I) or a large negative (II) optical rotation. It was shown (Cowan & McGavin, 1955) by X-ray diffraction methods that poly-L-proline II in the solid state consists of three-fold left-handed spirals, the peptide groups having the *trans* configuration.

A three-fold (or nearly three-fold) spiral structure for poly-L-proline I has also been proposed (Cowan & Burge, 1957) but the screw sense is right-handed and the imide groups have the *cis* configuration.

Cowan & McGavin (1955) found a trigonal unit cell for poly-L-proline II, space group $P3_2$, with $a = 6.62$, $c = 9.36$ Å. A similar structure has been published by Sasisekharan (1959) with some modification of co-ordinates and unit-cell dimensions ($a = 6.68$, $c = 9.36$ Å). Sasisekharan found, from stereochemical considerations and by a comparison of optical diffraction patterns and the X-ray powder pattern, the range of the possible orientations of the chain axis of the polymer in the *c* plane.

It is proposed here to present the results of a comparison between calculated intensities and measured X-ray intensities giving more specifically the orientation of the poly-L-proline II helix.

The polar co-ordinates for the poly-L-proline II chain used in these calculations are the previously published values (Cowan & McGavin, 1955). The atoms in the imide group and proline ring are planar except for the β -carbon atom which is 0.4 Å out of the plane. Bond lengths and angles are respectively within ± 0.02 Å and $\pm 3^\circ$ of the values for the amide groups published by

A three dimensional difference map computed with our data enabled three of the hydrogen atoms to be satisfactorily identified, but the carboxyl group hydrogen could not be adequately sited. Our work confirms the displacement of the sulphur atom from the plane of the ring, by 0.02 Å at the low temperature.

We should like to record our thanks to Dr E. G. Cox for his initiation of the problem and to Prof. Challenger for his interest and instructive discussions, and also to the Department of Scientific and Industrial Research for a maintenance grant to one of us (P. H.).

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Corey & Pauling (1953) and of those found for hydroxy-L-proline by Donohue & Trueblood (1952). The configuration of the prolyl residue is also close to that occurring in L-leucyl-L-prolyl-glycine subsequently published by Leung & Marsh (1958).

The orientation of the polymer chain was fixed with

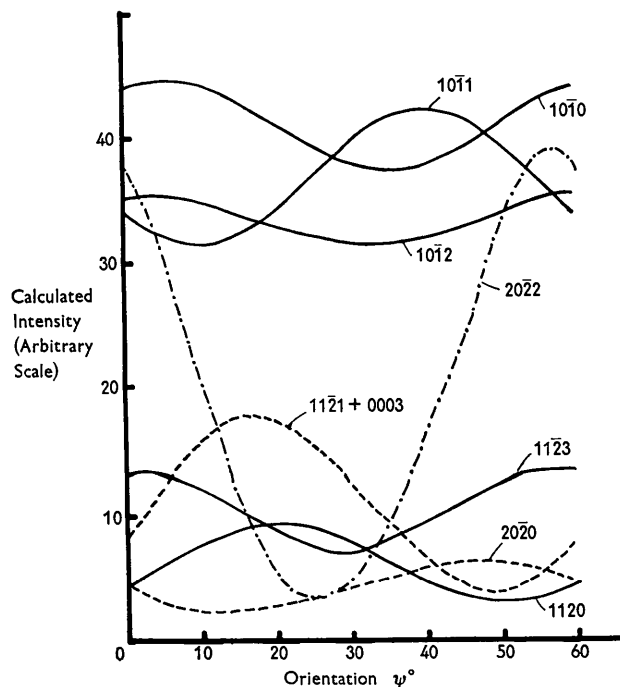


Fig. 1. The calculated variation, with orientation ψ of the poly-L-proline II helix in the unit cell, of the intensities of reflections corresponding to those observed in the X-ray powder diagram. A graph corresponding to $I_{hkl} + I_{h\bar{k}l}$ is marked with the hkl indices. Ordinate: Calculated intensity (arbitrary scale). Abscissa: Orientation ψ° .

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