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The crystal structure of $Cu_{0.65}NbS_2$ and some related compounds.

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Introduction

It has been shown (Crevecœur, 1961) that Cu and Ag are soluble in NbS_2. The structure of the phase Cu_xNbS_2 ($\sim 0{\cdot}6 \leq x \leq 0{\cdot}8$) has been determined. The phase Ag_yNbS_2 ($\sim 0{\cdot}6 \leq y \leq 0{\cdot}8$) shows a similar powder diffraction pattern, likewise the compound $Cu_{0{\cdot}65}NbSe_2$, but $Ag_{0{\cdot}65}NbSe_2$ shows extra diffraction lines, which could not be indexed.

Preparation

The sulphides were prepared by heating weighed quantities of the components Cu and NbS_2 in evacuated quartz tubes at 800 °C for a few days and subsequently cooled slowly. Single crystals could not be isolated.

Crystallographic investigations

For the structure determination the phase with composition $Cu_{0{\cdot}65}NbS_2$ was chosen. Powder photographs, taken with a Guinier–de Wolff camera, could be indexed on a hexagonal lattice. To measure the unit-cell dimensions accurately the photographs were calibrated with KCl. The cell constants are:

		a	*c*	
	$Cu_{0{\cdot}65}NbS_2$	3·35 Å	13·13 Å	
	$Ag_{0{\cdot}7}NbS_2$	3·35	14·46	
	$Cu_{0{\cdot}65}NbSe_2$	3·47	13·53	
Cf.	NbS_2	3·31 Å	11·89 Å	(Jellinek, 1960)
	$NbSe_2$	3·43	12·51	

The pycnometrically measured density of $Cu_{0{\cdot}65}NbS_2$ was found to be 4·7 g.cm^{-3} with 2 molecules per unit-cell. A density of 5·1 g.cm^{-3} is calculated.

Since these compounds show strong preferred orientation, although less than MoS_2 and NbS_2, the Guinier–de Wolff method could not be used for intensity measurements for the structure determination. The intensity was therefore measured with a Philips diffractometer. In order to avoid the preferred orientation the powdered samples were allowed to fall through a very fine sieve on a thin layer of petrolatum in the sample holder. Cu *Kα* radiation was used.

Calculations

The diffraction pattern of $Cu_{0{\cdot}65}NbS_2$ strongly resembles that of hexagonal MoS_2 (Dickinson & Pauling, 1923). The calculations were therefore started on the assumption that the space group might be the same and the Nb atoms might occupy the positions of the Mo atoms in MoS_2 (Fig. 1(*b*)). This position differs from that in hexagonal NbS_2 (Jellinek, 1960) (Fig. 1(*a*)). 4/3 Cu was assumed to be statistically distributed in tetrahedral interstices. Calculations were also carried out with the Nb position as in the NbS_2 structure. The results showed this to be incorrect. An alternative possibility for the Cu atoms might be a statistical distribution in octahedral surroundings on the twofold position 0, 0, 0; 0, 0, $\frac{1}{2}$. However in this case Cu would not contribute to reflexions with l = odd and so these should have the same intensities as in the NbS_2 and MoS_2 structure respec-

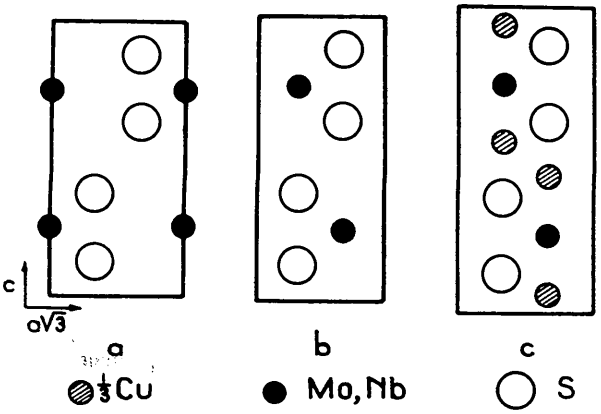

Fig. 1. Section parallel to (11$\bar{2}$0) in the structures of (*a*) NbS_2, (*b*) MoS_2, (*c*) $Cu_{0{\cdot}65}NbS_2$.

Table 1. *Comparison of observed and calculated intensities*

hkl	$\sin^3 \theta_o$	$\sin^2 \theta_c$	I_o	I_c
002	0·0137	0·0137	50	55
004	0·0551	0·0550	14	2
100	0·0703	0·0704	57	59
101	0·0737	0·0738	25	31
102	0·0842	0·0842	11	8
103	0·1012	0·1014	60	47
006	0·1241	0·1238	8	12
104	0·1254	0·1254		—
105	0·1564	0·1564	87	80
106	0·1942	0·1942	3	9
110	0·2113	0·2112	30	40
008	0·2201	0·2201	15	12
112	0·2249	0·2250	5	7
107	0·2392	0·2390	—	1
114	0·2661	0·2662	3	1
200	0·2816	0·2816	3	6
201	0·2851	0·2850	2	4
108	0·2909	0·2906	7	11
202	0·2954	0·2954	1	1
203	0·3126	0·3126	6	7
116	0·3354	0·3350	5	14
204	—	0·3366		—
0,0,10	0·3443	0·3440	5	1
109	0·3490	0·3490	4	—
205	0·3674	0·3676	14	17
206	0·4052	0·4054	1	2
1,0,10	0·4151	0·4144	4	—
118	0·4315	0·4314	9	23

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tively. It was evident that this is not so. The calculated intensities, listed in Table 1, were corrected with the appropriate *LP* factor and scaled to the observed intensities. No correction for temperature movement was applied. The atom positions used in the calculation are:

Space group $P6_3mmc$

4 S in *f* $\frac{1}{3}, \frac{2}{3}, z; \ldots; z=\frac{1}{8}$ (assumed);
2 Nb in *d* $\frac{1}{3}, \frac{2}{3}, \frac{3}{4}; \frac{2}{3}, \frac{1}{3}, \frac{1}{4};$
4/3 Cu in *f* $\frac{1}{3}, \frac{2}{3}, z; \ldots; z=0{\cdot}563$ (assumed).

As stated above, for z_S the value $\frac{1}{8}$ has been assumed. For z_{Cu} the above-mentioned value is calculated by assuming equal distances from Cu to the corners of the S tetrahedron. A better fit would probably be obtained by slight shifts in these parameters. However, for such a refinement the study of the isomorphous Se compound seems to be more suited. On the basis of the chosen parameters, atomic distances are as follows:

Nb–S	2·5 Å
Cu–S	2·5
Nb–Cu	2·5
Cu–Cu	2·5

Discussion

The structures of NbS_2, MoS_2 and $Cu_{0\cdot65}NbS_2$ are compared in Fig. 1(*a*), (*b*) and (*c*) respectively. The shift of the Nb from its positions in NbS_2 to those in $Cu_{0\cdot65}NbS_2$ is the more remarkable since we were unable to prepare an analogous compound Cu_xMoS_2 ($\sim 0{\cdot}6 \le x \le 0{\cdot}8$). The distance Nb–Cu is comparable to the sum of the metallic atomic radii.

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Crystal symmetry of the dimer of cyclobutene-1,2-dicarboxylic acid dimethyl ester.

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In a review article on small ring compounds, Vogel (1960) mentions several interesting tricyclic dimers of various derivatives of cyclobutene and cyclobutadiene. Although all of these compounds possess the same basic eight-membered 3-ring skeleton, there is considerable uncertainty about the configuration of individual members of this series. Criegee (1958) has shown from chemical evidence and dipole moment measurements that in the dimer of tetramethylcyclobutadiene the two cyclobutene rings are in a *syn* configuration. Kitahara, Caserio, Scardiglia & Roberts (1960) suggest that the dimer of fluorotriphenyl cyclobutadiene is *anti*-1,2-difluoro-3,4,5,6,7,8-hexaphenyltricyclo[4.2.0.$0^{2,5}$]octa-3,7-diene. In an X-ray diffraction investigation of this compound Fritchie & Hughes (1962) confirm this structure. Vogel & Roos (1962) have recently prepared the dimer of cyclobutene-1,2-dicarboxylic acid dimethyl ester. Although the gross structure resembles that of the above compounds there is no conclusive evidence of whether the compound is *syn* or *anti*. We have therefore undertaken an X-ray diffraction study of this compound.

The material was recrystallized from methanol as thin tetragonal blocks. Small single crystals were chosen for X-ray examination. Rotation and Weissenberg photographs around the *a* and *c* axes showed the substance to be tetragonal, with

$$a=7{\cdot}11\pm0{\cdot}01,\ c=33{\cdot}37\pm0{\cdot}03\ \text{Å}$$
$$(\lambda\ \text{Cu}\ K\alpha=1{\cdot}5418\ \text{Å})\ .$$

The density, as measured pycnometrically with t-butanol, is 1·29 g.cm^{-3}; the density calculated for four molecules of the dimer per unit cell is 1·33 g.cm^{-3}. The systematic conditions limiting possible reflections on the Weissenberg photographs, namely (h00) with $h=2n$ and (00l) with $l=4n$, indicate that the space group is the noncentric space group $P4_12_12(D_4^4)$ or the related $P4_32_12(D_4^8)$.

The general equivalent positions of these space groups are eightfold. Placing the atoms in the special fourfold positions would lead to a chemically unrealistic structure; therefore each molecule must contain two halves related by one of the symmetry elements of the space group. The only symmetry element leading to discrete molecules is the diagonal twofold axis. Unfortunately, the presence of a twofold axis in the molecule will not lead to a distinction between the *syn* and *anti* forms, nor does it lead to a choice from packing considerations. No further work is planned on this structure.

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