Stunden bis auf 600 °C und tempert es über Nacht bei der gleichen Temperatur. Das überschüssige Li_2O lässt sich mit kaltem Wasser leicht auswaschen.

Die Kristalldaten von α-$LiEuO_2$ wurden ebenso wie diejenigen der früher beschriebenen rhombischen Modifikation β-$LiEuO_2$ (Bärnighausen, 1963) ausschliesslich aus Guinieraufnahmen mit Cu $K\alpha_1$-Strahlung abgeleitet (wegen methodischer Einzelheiten vgl. die β-$LiEuO_2$-Arbeit).

α-$LiEuO_2$ kristallisiert in der monoklinen Raumgruppe $P2_1/c$ mit den Gitterkonstanten

$$a = 5{,}6815 \pm 0{,}0005\ , \quad b = 5{,}9885 \pm 0{,}0005\ ,$$
$$c = 5{,}6221 \pm 0{,}0005\ \text{Å} \quad \text{und} \quad \beta = 103°\,10' \pm 3'\ .$$

Unter der Annahme von 4 Formeleinheiten in der Elementarzelle ergibt sich die berechnete Dichte zu 6,807 $g.cm^{-3}$. Die Dichte der bei höheren Temperaturen dargestellten, dem Diaspor-Typ zugehörigen β-Form (Gondrand & Bertaut, 1963) beträgt 6,004 $g.cm^{-3}$ (Berichtigung des früher angegebenen Wertes). Tabelle 1 enthält zur näheren Charakterisierung des α-$LiEuO_2$-Gitters die Interferenzdaten der ersten 33 Linien einer Guinieraufnahme.

Vorläufige Studien zur Polymorphie von $LiEuO_2$ machen es wahrscheinlich, dass kein definierter Umwandlungspunkt existiert; vielmehr scheinen geringfügige Unterschiede im Li-Gehalt für das Auftreten der einen oder anderen Modifikation massgebend zu sein. Dabei besitzt weder die α- noch die β-Form eine merkliche Phasenbreite. Die Strukturbestimmung ist vorerst nicht beabsichtigt.

Durch ein Programm zur Berechnung der theoretischen Linienabfolge auf Röntgen-Pulverdiagrammen, das Herr A. von Plehwe für die Rechenanlage SIEMENS 2002 schrieb, wurde die Ableitung der Kristalldaten sehr erleichtert.

Tabelle 1. *Indizes, gemessene Netzebenenabstände d_0 und grob geschätzte Intensitäten I_0 einer Guinieraufnahme von* α-$LiEuO_2$.

Intensitätsskala: *ss* = sehr schwach, *s* = schwach, *m* = mittel, *st* = stark, *sst* = sehr stark.

hkl	d_0	I_0	*hkl*	d_0	I_0
100	5,53 Å	*m*	$\bar{2}12$	2,077 Å	*s*
110	4,062	*m–st*	220	2,032	*s–m*
011	4,040	*m–st*	022	2,021	*m*
$\bar{1}11$	3,562	*sst*	$\bar{2}21$	2,018	*s–m*
111	3,029	*sst*	$\bar{1}22$	2,010	*m*
020	2,995	*s–m*	130	1,878	*st*
200	2,766	*s–m*	031		
002	2,738	*m*	300	1,845	*s*
$\bar{1}02$	2,711	*s–m*	$\bar{1}31$	1,820	*ss*
021	2,627	*m–st*	221	1,809	*m*
012	2,487	*st*	122	1,803	*ss*
$\bar{2}11$			$\bar{3}11$	1,796	*ss*
$\bar{1}21$	2,481	*m–st*	$\bar{2}22$	1,780	*ss*
$\bar{1}12$	2,469	*ss*	$\bar{1}13$		
102	2,257	*s*	310	1,762	*ss*
$\bar{2}02$	2,215	*ss*	202	1,756	*s*
211	2,123	*ss*	013	1,746	*m*
112	2,112	*s–m*	131	1,736	*ss*

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An X-ray study of Cu_3Si*.

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(*Received* 8 *March* 1965 *and in revised form* 28 *May* 1965)

An X-ray study of zone-melted Cu_3Si crystals was undertaken in order to determine the unit cell of this intermetallic compound. To a certain extent similar diffraction patterns have been described for the case of CuSe (Taylor & Underwood, 1960) and interpreted as due to a particular kind of twinning. The geometrical interpretation of the Cu_3Si patterns is possible if we suppose that similar twins are present in this case. On the other hand Cu_3Si differs from CuSe, both with regard to the intensity distribution of the X-ray reflexions and to the unit cell. This latter is rhombohedral and not primitive hexagonal as in the case of CuSe. The powder diagram of Cu_3Si, showing many lines, can be indexed on this cell. The complete structure analysis is still under investigation.

Results

An oscillation photograph of a Cu_3Si crystal, showing definite layer lines, is given in Fig. 1. From what follows it can be deduced that the rotation axis is either a hexagonal or a trigonal axis. The numbering of the layer lines is based on the smallest distance between two lines. Evidently some layer lines are missing. After recording each layer line in the Weissenberg-camera, rather complicated photographs were obtained.

The layer lines *hkl* with $l = 3n$ (n is an integer) give the same kind of Weissenberg photograph. A representative example is given in Fig. 2. The reciprocal vectors deduced from this photograph end in a number of points, which can be considered as belonging to one of two superposed reciprocal nets. The superposition of the two nets can be obtained by rotating two identical hexagonal nets with respect to each other about an axis perpendicular to the net plane and passing through the origin (O in Fig. 3), the angle of rotation being $\pm(2\,\text{arc tg}\,\sqrt{3}/7)°$. From the resulting pattern

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* This work is part of the research programme of the Metals Research Group 'F.O.M.–T.N.O.', sponsored by Z.W.O.

† Research associate of the Foundation for Fundamental Research on Matter (F.O.M.).

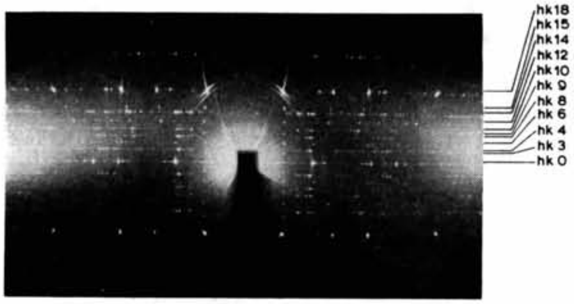

Fig. 1. Oscillation photograph of Cu_3Si. The intense layer lines are indicated.

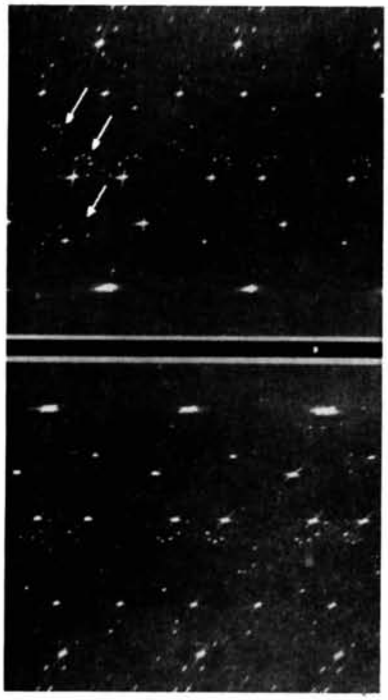

Fig. 2. Weissenberg photograph of the eighteenth layer line. The reflexions are arranged mainly on circles, some of which are indicated by arrows.

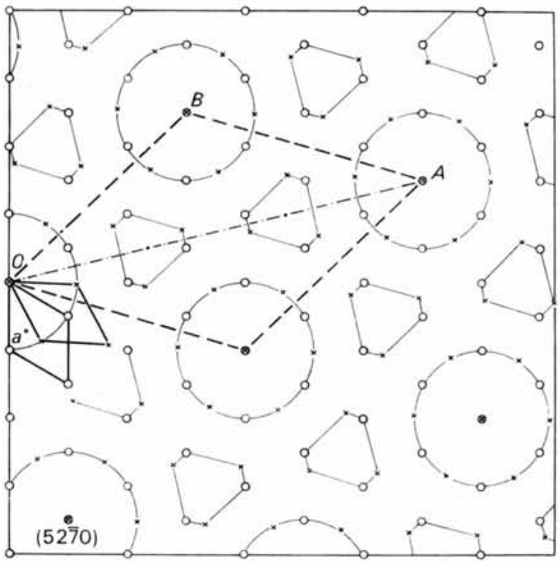

Fig. 3. Composite net resulting from two reciprocal hexagonal nets (circles and crosses). The cell sides a^* of the true reciprocal unit cells (full lines) are enlarged to $\sqrt{13}a^*$ in the reciprocal unit rhomb of the resulting net (dotted lines).

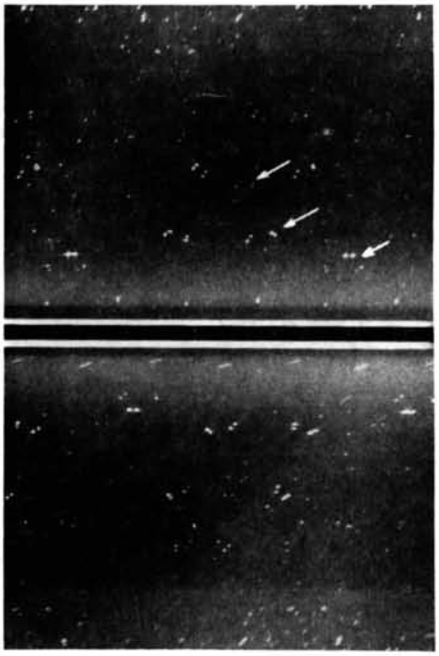

Fig. 4. Weissenberg photograph of the tenth layer line. The reflexions are arranged mainly on hexagons, some of which are indicated by arrows.

in Fig. 3 it is clear that the symmetry of the composite net is hexagonal again with a cell constant in reciprocal space equal to $\sqrt{13}$ times the side of the two component nets. This follows from the fact that one in every thirteen points coincide (for example the $\{310\}$ points of one component net coincide with the $\{4\bar{1}0\}$ points of the other). As in the case of CuSe, around these the other 24 points can be arranged on two concentric circles. However, for reasons that will be obvious later on, we prefer to divide the whole pattern into circles and hexagons.

Examining Fig. 2 in detail (for instance the reflexions on a circle) we see two sets of reflexions, differing in intensity and shape, which are related by the rotation mentioned above. Therefore it seems reasonable to suppose that the two sets belong to different components (twins), unequal in volume and shape. The reciprocal $h,k,3n$ sections of these twins are related by the mirror line OA or OB in Fig. 3.

The layer lines with $l=3n+1$ and $l=3n+2$ show a Weissenberg photograph according to Fig. 4. The reciprocal nets of these layer lines are as complicated as the $h,k,3n$ nets, but different with respect to symmetry and pattern of diffracted spots: their nets show trigonal symmetry and their diffraction pattern consists mainly of the hexagons, whereas the $h,k,3n$ patterns show the circles.

From the intensity and shape of the reflexions in Fig. 4 it may be deduced again that there exist two sets of reflexions. Each set of a certain relative intensity and shape evidently belongs to the component which produces $h,k,3n$ reflexions with the same relative intensity and shape.

The reflexions of each component lie on a rhombohedral reciprocal lattice. The two lattices are related by the mirror plane passing through OA in Fig. 3 and the axis of rotation. In real space this plane has the indices $\{52\bar{7}0\}$ with respect to the hexagonal axes of one component. The components being twins the twin law is $\{52\bar{7}0\}$. Considering one twin component in real space, the lattice constants of the hexagonal triple primitive unit cell may be calculated: $c=44{\cdot}2$, $a=25{\cdot}4$ Å. The rhombohedral lattice constants are: $a=20{\cdot}8$ Å, $\alpha=75{\cdot}3°$. The hexagonal unit cell contains approximately 2000 atoms. The lines present on a powder diagram can be satisfactorily indexed with reference to this cell.

Symmetry considerations for one twin give hexagonal symmetry for the weighted $h,k,3n$ sections and trigonal symmetry for the weighted sections with $l \neq 3n$. Symmetry planes are absent and hence the Laue symmetry of the whole weighted reciprocal lattice for one twin is $\bar{3}$.

Discussion

As our samples are prepared from the melt and as at least one transformation takes place during cooling (Sanfourche, 1919; Smith, 1929) the conditions for growth twinning as well as transformation twinning are present. By microscopic research transformation twins could be demonstrated by Mima & Hasegawa (1960). These authors and Iokibe (1931) have described the existence of two transformations in the composition range of Cu_3Si, which could be verified by our experiments.

The presence of definite strong lines on the powder diagram makes it probable that the calculated unit cell contains a number of small units. It is conceivable that the large cell is built up from the smaller units in a number of ways, producing twins. In that case an uncommon twin law like $\{52\bar{7}0\}$ seems not unlikely. This approach may be helpful for the solution of the remaining problems, *viz.* the remarkable distribution of the reflexions and the uncommon twin law.

The author is indebted to Prof. W. G. Burgers, in whose laboratory this investigation was carried out, for his constant interest and valuable discussions. He wishes to thank Prof. P. M. de Wolff from the Department of Technical Physics for calling his attention to the paper on CuSe by Taylor & Underwood, and Dr Ir J. H. Palm for his assistance in the first stage of the X-ray experiments.

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Acta Cryst. (1965). **19**, 1051

A reinvestigation of the crystal structure of dialuric acid monohydrate.

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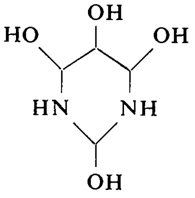
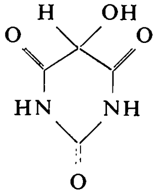
(*Received* 4 *May* 1965)

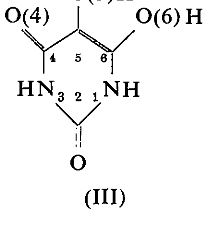
Different lines of evidence for the formula of the dialuric acid molecule seem to be at variance. Tipson & Cretcher (1951) and Davol & Laney (1956) allocated it the tetrahydroxy formula (I) on the basis of infrared spectral measurements, whereas other authors (Biltz & Paetzold, 1923; Hantzsch, 1921; and most textbooks) give it the formula (II) which follows from its chemical reactions and preparation.



(I)



(II)



(III)

The crystal structure of dialuric acid monohydrate was deduced by Alexander & Pitman (1956) from projection data, but only 65 reflexions were collected in the two most badly resolved zones. They concluded that the formula is (III). However, there are some interesting features about this structure; for instance the bonds C(5)–O(5)H and C(6)–O(6)H [see (III) for numbering] differ by 0·10 Å from one another and the molecule is non-planar; moreover formula (III) is the one ascribed to isodialuric acid by Berend & Roosens in their classic synthesis of uric acid. Furthermore the structure has more close oxygen–oxygen hydrogen bonding approaches than it is possible to account for with the available hydrogen atoms. In particular there is an unusual hydrogen bonding interaction (of 2·68 Å) between two equivalent –OH groups related by a twofold screw axis.

Large crystals of dialuric acid monohydrate were grown by passing hydrogen sulphide through alloxan solution overnight, then allowing the solution to stand at 0 °C (Tipson &

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