Tabelle 1. *Gitterkonstanten von Verbindungen der Reihe* $M_2(C_2O_4)_3 . 10H_2O$ *mit* M = Nd, Pm, Sm

Angabe des Winkels β in der zweiten Zeile gibt die verschiedenen Aufstellungen an:

92,8° = zentrierte Aufstellung
119° = alte primitive Aufstellung
114,4° = neue reduzierte primitive Aufstellung

	$Nd_2(C_2O_4)_3 . 10H_2O$			$Pm_2(C_2O_4)_3 . 10H_2O$		$Sm_2(C_2O_4)_3 . 10H_2O$		
	92,8°	119°	114,4°	119°	114,4°	92,8°	119°	114,4°
a [Å]	20,36 ± 0,02	11,64 ± 0,01	11,19 ± 0,01	11,59 ± 0,02	11,14 ± 0,02	20,22 ± 0,02	11,56 ± 0,01	11,12 ± 0,01
b [Å]	9,62 ± 0,01	9,63 ± 0,01	9,63 ± 0,01	9,64 ± 0,02	9,64 ± 0,02	9,62 ± 0,01	9,63 ± 0,01	9,63 ± 0,01
c [Å]	10,24 ± 0,01	10,24 ± 0,01	10,24 ± 0,01	10,20 ± 0,02	10,19 ± 0,02	10,15 ± 0,01	10,17 ± 0,01	10,17 ± 0,01
β [°]	92,8 ± 0,2	118,9 ± 0,2	114,4 ± 0,2	118,9 ± 0,2	114,4 ± 0,2	92,8 ± 0,2	118,9 ± 0,2	114,4 ± 0,2
V [Å^3]	2003,2	1004,9	1004,5	997,7	996,5	1972,0	991,2	991,8
d [g.cm^{-3}] berechnet	2,43	2,42	2,42	2,46	2,46	2,51	2,50	2,49
d [g.cm^{-3}] gemessen	2,42 ± 0,02	2,42 ± 0,02	2,42 ± 0,02	—	—	2,51 ± 0,02	2,51 ± 0,02	2,51 ± 0,02
Z	4	2	2	2	2	4	2	2

Indizes beziehen sich auf die völlig reduzierte Zelle mit $\beta = 114{,}4°$. Die *Y*-Achse liegt parallel zur zweizähligen Drehachse und senkrecht zur Spiegelebene.

Röntgenbeugung

Auf Grund der einfacheren Justierung der Einkristalle bei Verwendung der *Z*-Achse als Rotationsachse ergab sich röntgenographisch primär eine *B*-flächenzentrierte ebenfalls monokline Zelle mit einem Winkel von $\beta = 92{,}8 \pm 0{,}2°$, die durch einfache Reduktion die bisher in der Literatur angenommene Zelle mit $\beta = 119°$ und durch völlige Reduktion nach Delaunay eine neue primitive monokline Zelle mit $\beta = 114{,}4°$ ergab (vergl. Fig. 1).

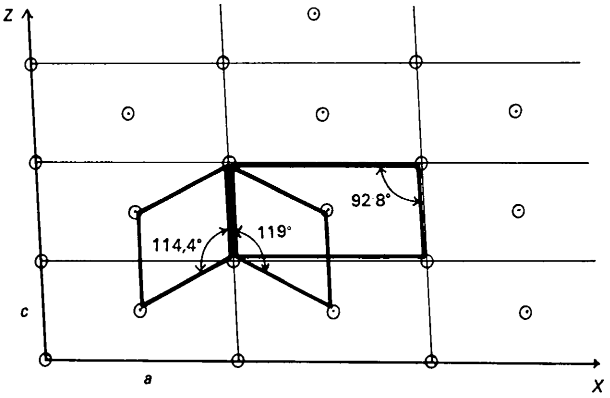

Fig. 1. Geometrische Zusammenhänge zwischen den Elementarzellen, die das Gitter der Lanthaniden(III)-oxalat-Dekahydrate beschreiben.

Die röntgenographisch ermittelten Daten sind in Tabelle 1 wiedergegeben. Die Gitterkonstanten der Promethiumverbindung erhielten wir durch Interpolation zwischen den Einkristall- bzw. Guinierdaten der Neodym- und Samariumverbindung. Diese interpolierten Gitterparameter konnten durch die Indizierung der in unserem Labor gemachten Pulveraufnahme des Promethiumsalzes bestätigt werden.

Aus den systematischen Auslöschungen auf den Buerger- bzw. Weissenbergaufnahmen ergibt sich nach der Reduktion auf die beiden primitiven Zellen *keine* integrale Bedingung, für alle $(h0l)$ $l = 2n$ und für alle $(0k0)$ $k = 2n$. Somit ist für das Neodym(III)-, Promethium(III)- und Samarium(III)-oxalat-Dekahydrat die Raumgruppe mit $P2_1/c$ (Nr. 14) eindeutig bestimmt.

Eine Strukturbestimmung dieser Verbindungen ist nicht geplant.

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Acta Cryst. (1967). **22**, 924

The refinement of the structures of the intermetallic phases $ReAl_6$ and $TcAl_6$.

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(*Received* 2 *November* 1966)

The structures of the intermetallic phases $ReAl_6$ and $TcAl_6$ have been refined using as starting point the coordinates given by Nicol (1953) for the atoms in the isomorphous structure $MnAl_6$. No evidence has been found in the present refinements of a non-centrosymmetric arrangement of aluminum atoms which Forsyth, Black & Edwards [*Acta Cryst.* **14**, 993 (1961)] and Walford [*Acta Cryst.* **18**, 287 (1965)] have suggested might occur in the isostructural group to which these phases belong.

Introduction

In an investigation of the rhenium–aluminum and technetium–aluminum phase diagrams d'Alte da Veiga (1962) reported the existence of the phases $ReAl_6$ and $TcAl_6$. These phases appeared to be isomorphous with $MnAl_6$ (Nicol, 1953) and with α-$CuFeAl_6$ (Forsyth, Black & Edwards, 1961). The present note describes the refinement of the structures of $TcAl_6$ and $ReAl_6$ and confirms that they belong to the isostructural group which includes $MnAl_6$, α-$CuFeAl_6$ and also $FeAl_6$ (Walford, 1965).

Crystals, unit cell and space group

Crystals of $ReAl_6$ and $TcAl_6$ were kindly provided by Dr d'Alte da Veiga and were acicular in form. Laue, oscillation and Weissenberg photographs showed that the unit cell is orthorhombic, with the needle axis parallel to the longest side of the cell and the prism faces {110}. The cell dimensions, which are shown in Table 1, were determined by the methods of Farquhar & Lipson (1946) and Main & Woolfson (1963).

Weissenberg photographs of the [100] and [010] projections showed that the possible space groups were *Ccmm*, *Ccm*2₁ or *Cc*2*m*, only the first of which is centrosymmetric. The structure of $MnAl_6$ was refined by Nicol using the centrosymmetrical group, and this was also adopted in the present refinements. No evidence was obtained during the course of the refinements which was in contradiction to this choice.

Table 1. *Cell dimensions of* $ReAl_6$ *and* $TcAl_6$

Cell side	$TcAl_6$	$ReAl_6$
'*a*'	6·5944 ± 0·0009†	6·6117 ± 0·0006†
	6·596 ± 0·007*	6·612 ± 0·008*
'*b*'	7·629 ± 0·009*	7·6091 ± 0·0009†
'*c*'	9·0011 ± 0·0011†	9·023 ± 0·010*

* By Main & Woolfson's method.
† By Farquhar & Lipson's method.

Collection of intensities

Zero-layer normal beam Weissenberg photographic data were collected for the [100] and [010] projections with the use of Mo *Kα* radiation. The relative intensities of reflexions were visually estimated out to $\sin\theta/\lambda = 1{\cdot}2$ and were corrected for Lorentz, polarization and absorption effects.

Refinement of the structures

The refinement of the structure of $TcAl_6$ was commenced from the atomic positions given by Nicol for $MnAl_6$. In the space group *Ccmm* these were

4 Tc or Re in 4(*c*) x_0, 0, $\frac{1}{4}$
8 Al_1 in 8(*e*) 0, y_1, 0
8 Al_2 in 8(*f*) x_2, 0, z_2
8 Al_3 in 8(*g*) x_3, y_3, $\frac{1}{4}$.

The values given by Nicol for the *x*, *y* and *z* coordinates were adopted as a starting point. After six cycles of refinement the [001] *R* index was 0·084 while the [010] *R* index was 0·104. Examination of a list of observed & calculated structure amplitudes for both projections revealed no reflexions which were obviously suffering from extinction. Fourier and difference maps of the electron-density distributions were computed.

The coordinates obtained in the refinement of $TcAl_6$ were used as trial coordinates for the [001] and [010] projections of $ReAl_6$. After two cycles of refinement the *R* indices were reduced to 0·078 and 0·105 respectively. The final atomic coordinates for $TcAl_6$ and $ReAl_6$ are given in Table 2. Bond lengths were calculated for the nearest neighbours of each type of atom and these are given in Table 3. Lists of observed and calculated structure amplitudes and Fourier and difference maps are published elsewhere (Wilkinson, 1965).

Table 2. *Atomic coordinates in* $ReAl_6$ *and* $TcAl_6$

Parameter	$TcAl_6$	$ReAl_6$
x_0	0·4555 ± 0·0002	0·4555 ± 0·0001
y_1	0·3257 ± 0·0005	0·3257 ± 0·0007
x_2	0·1338 ± 0·0009	0·1338 ± 0·0009
z_2	0·3970 ± 0·0013	0·3970 ± 0·0030
x_3	0·7120 ± 0·0006	0·7158 ± 0·0015
y_3	0·6820 ± 0·0050	0·6818 ± 0·0014

Discussion

A full discussion of this type of structure is given by Nicol (1953). The structures were found to refine successfully in the centrosymmetric space group *Ccmm*. Forsyth, Black & Edwards (1961) and Walford (1965) have reported that there are indications of a non-centrosymmetric arrangement of Al atoms in this type of structure. No evidence was found during the present work to support such a conclusion and no significant anomalies were observed at the positions of the Al atoms which would be concerned. The heavy atoms in $ReAl_6$ and $TcAl_6$, however, tend to mask small changes in the Al atomic positions. This is

Table 3. *Bond lengths in* $ReAl_6$ *and* $TcAl_6$

			Bond length	
Atom	bonded to	Number of bonds	$TcAl_6$	$ReAl_6$
Tc or Re	Al(1)	4	2·630 ± 0·004 Å	2·633 ± 0·005 Å
	Al(2)	2	2·501 ± 0·013	2·507 ± 0·028
	Al(3)	2	2·595 ± 0·038	2·598 ± 0·015
	Al(3)	2	2·668 ± 0·038	2·663 ± 0·015
Al(1)	Al(1)	1	2·660 ± 0·005	2·653 ± 0·005
	Al(2)	2	2·795 ± 0·014	2·791 ± 0·028
	Al(2)	2	2·909 ± 0·014	2·913 ± 0·028
	Al(3)	2	2·946 ± 0·038	2·953 ± 0·016
	Al(3)	2	2·867 ± 0·038	2·872 ± 0·016
Al(2)	Al(2)	1	2·646 ± 0·017	2·652 ± 0·036
	Al(2)	1	2·559 ± 0·019	2·565 ± 0·037
	Al(3)	2	2·822 ± 0·030	2·818 ± 0·032
	Al(3)	2	2·976 ± 0·030	2·980 ± 0·032
Al(3)	Al(3)	1	2·770 ± 0·053	2·763 ± 0·015

confirmed by the relatively large standard deviations in the coordinates of the Al atoms.

Statistical tests to distinguish between centrosymmetric and noncentrosymmetric structures seem inappropriate in this case. Any departures from a centrosymmetric arrangement must be small and to these the tests are relatively intensitive. The structures are also strongly layered, a feature which can significantly disturb the statistical distribution of intensities.

I wish to thank Professor N. F. Mott and Dr W. H. Taylor for provision of facilities and Dr P. J. Brown for her interest and encouragement. I am indebted to Professor V. M. Wilkes and Mr E. Mutch for permission to use the EDSAC II digital computer, and to the Department of Scientific and Industrial Research for the award of a research studentship during the tenure of which this work was performed.

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The unit-cell dimensions and space group of 2-(benzylthio)imidazoline and 2-(benzylthio)tetrahydropyrimidine hydrochlorides.

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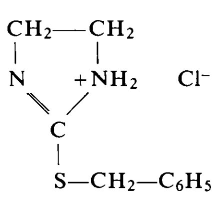
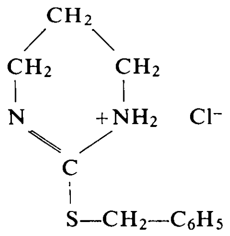
(*Received* 5 *December* 1966)

Crystals of 2-benzylthioimidazoline and of 2-benzylthiotetrahydropyrimidine hydrochlorides are isostructural. They crystallize in the orthorhombic system, space group $P2_12_12_1$, with $a = 11{\cdot}06$, $b = 10{\cdot}50$, $c = 11{\cdot}25$ Å, $Z = 4$, and $a = 10{\cdot}93$, $b = 11{\cdot}25$, $c = 10{\cdot}17$ Å, $Z = 4$, respectively.

In the course of investigations on the structure of thioamides, cyclic thioureines and related compounds (Piazzesi, Bardi, Mammi & Walter, 1964; Mammi, D'Angeli & Bezzi, 1965; Del Pra, D'Angeli & Di Bello, 1966) the hydrochlorides of 2-(benzylthio)imidazoline (I) and of 2-(benzylthio)tetrahydropyrimidine (II) (McKay & Hatton, 1956) have been examined by X-rays.


(I)


(II)

The compounds were prepared by refluxing in ethanol for some hours the corresponding thioureines with benzyl chloride.

Single crystals were grown from ethanol solution as colourless prisms, with rectangular cross section, elongated along [100].

From Weissenberg and precession photographs of zero and upper layers, the crystal symmetry and the unit-cell dimensions of the two compounds were determined. The crystal densities were measured by flotation in carbon tetrachloride–benzene.

The physical and crystallographic data are reported in Table 1.

Table 1. *Crystallographic data*

	(I)	(II)
	$C_{10}H_{13}SN_2Cl$	$C_{11}H_{15}SN_2Cl$
M.W.	228·8	242·8
m.p. (°C)	170	183
Crystal system	Orthorhombic	Orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$
a (Å)	11·06 ± 0·01	10·93 ± 0·01
b (Å)	10·50 ± 0·01	11·25 ± 0·01
c (Å)	10·04 ± 0·01	10·17 ± 0·01
V (Å^3)	1165·1	1252·0
D_x (g.cm^{-3})	1·303	1·288
D_m (g.cm^{-3})	1·310	1·281
Z	4	4
$F(000)$ (e)	480	512
$\mu_{\text{Cu}K\alpha}$ (cm^{-1})	42·3	39·2
$\mu_{\text{Mo}K\alpha}$ (cm^{-1})	4·7	4·3

It was apparent both from these data and from a straightforward comparison of diffraction intensities that compounds (I) and (II) are isostructural.

No further work is contemplated.

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