Derid, Yu. O., Kozhachenko, E. I., Radautsan, S. I. & Tiginyanu, I. M. (1989). *Phys. Status Solidi A*, **113**, K265–K266.

Eisenmann, B., Jakowski, M., Klee, W. & Schäfer, H. (1983). *Rev. Chim. Minér.* **20**, 255–263.

Gao, Y.-M., Wu, P., Kershaw, R., Dwight, K. & Wold, A. (1989). Proc. SPIE, Orlando, Florida, March 1989.

Garbato, L., Ledda, F. & Rucci, A. (1987). *Prog. Cryst. Growth Charact.* **15**, 1–41.

Gates, A. S. Jr (1976). PhD Dissertation, Univ. of Toledo, USA.

Goodyear, J. & Steigmann, G. A. (1963). *Acta Cryst.* **16**, 946–949.

Guiseinov, G. G., Mamedov, F. Kh., Amiraslanov, I. R. & Mamedov, Kh. S. (1983). *Sov. Phys. Crystallogr.* **28**(5), 513–515.

Hahn, H., Frank, G., Klingler, W., Stoerger, A. & Stoerger, G. (1955). *Z. Anorg. Allg. Chem.* **279**, 241–270.

Kipp, D. O., Lowe-Ma, C. K. & Vanderah, T. A. (1989). In *Optical Materials: Processing and Science.* MRS Proc., Vol. 152, edited by C. Ortiz & D. B. Poker. San Diego, CA, USA.

Krämer, V., Frick, B. & Siebert, D. (1983). *Z. Kristallogr.* **165**, 151–157.

Krämer, V., Hirth, H., Hofherr, W. & Trah, H.-P. (1987). *Thermochim. Acta*, **112**, 89–94.

Mazurier, A., Jaulmes, S. & Guittard, M. (1987). *Acta Cryst.* **C43**, 1859–1861.

Nitsche, R., Boelsterli, H. U. & Lichtensteiger, M. (1961). *J. Phys. Chem. Solids*, **21**, 199–205.

Razzetti, C., Lottici, P. P. & Antonioli, G. (1987). *Prog. Cryst. Growth Charact.* **15**, 43–73.

Roques, R., Rimet, R., Declercq, J.-P. & Germain, G. (1979). *Acta Cryst.* **B35**, 555–557.

Shannon, R. D. (1981). *Bond Distances in Sulfides and a Preliminary Table of Sulfide Crystal Radii.* In *Structure and Bonding in Crystals*, Vol. II, edited by M. O'Keeffe & A. Navrotsky, pp. 53–70. New York: Academic Press.

Shay, J. L. & Wernick, J. H. (1975). *Ternary Chalcopyrite Semiconductors: Growth, Electronic Properties, and Applications*, pp. 3–13. New York: Pergamon Press.

Sheldrick, G. M. (1984). *SHELXTL Users Manual.* Revision 4.1. Nicolet XRD Corporation, Madison, Wisconsin, USA.

Solans, X., Font-Altaba, M., Moreiras, D., Trobajo-Fernandez, M. C. & Otero-Arean, C. (1988). *Afinidad*, **45**(415), 277–279; taken from *Chem. Abstr.* **109**, 201988w.

Tomas, A., Pardo, M. P., Guittard, M., Guymont, M. & Famery, R. (1987). *Mater. Res. Bull.* **22**(11), 1549–1554.

Van Vechten, J. A. & Phillips, J. C. (1970). *Phys. Rev. B*, **2**(6), 2160–2167.

White, W. B. (1980). *Ternary Sulfides.* In *Advanced Optical Ceramics*, Phase II, General Electric Report for ONR Contract No. N00014-78-C-0466, DIN: 80SDR2172. August 1980.

Wu, P., He, X-C., Dwight, K. & Wold, A. (1988). *Mater. Res. Bull.* **23**, 1605–1609.

Zhang, J. M., Chen, W. W., Dunn, B. & Ardell, A. J. (1988). In Conf. on Ceramics and Inorganic Crystals for Optics, Electro-optics, and Non-linear Conversion, August 1980. Proc. SPIE, San Diego, CA, USA.

Acta Cryst. (1991). C47, 924–930

Structures of the Misfit Layer Compounds $(LaS)_{1.13}TaS_2$, '$LaTaS_3$' and $(CeS)_{1.15}TaS_2$, '$CeTaS_3$'

By J. L. de Boer, A. Meetsma, Th. J. Zeinstra, R. J. Haange and G. A. Wiegers*

Laboratory of Inorganic Chemistry, Materials Science Center of the University, Nijenborgh 16,
9747 *AG Groningen, The Netherlands*

(*Received* 7 *May* 1990; *accepted* 23 *October* 1990)

Abstract. $(LaS)_{1.13}TaS_2$ and the isostructural compound $(CeS)_{1.15}TaS_2$ are misfit layer compounds built of alternate double layers of *M*S (*M* = La, Ce), each approximately a {100} slice of NaCl-type *M*S, and sandwiches of TaS_2 with Ta surrounded by distorted trigonal prisms of S. Both structural units are described in centered orthorhombic space groups, *Cm*2*a* for the *M*S part ($Z = 4$) and *Fm*2*m* for the TaS_2 part ($Z = 4$) of the structure. $\lambda(\text{Mo } K\bar{\alpha}) = 0{\cdot}71073$ Å. For $(LaS)_{1.13}TaS_2$, $M_r = 438{\cdot}3$, $D_x = 6{\cdot}63$ g cm^{-3}, $\mu = 367{\cdot}3$ cm^{-1}; the LaS part: $a = 5{\cdot}813\,(1)$, $b = 5{\cdot}773\,(1)$, $c = 11{\cdot}526\,(1)$ Å, $V = 386{\cdot}8\,(1)$ Å^3, $F(000) = 292$, $T = 295$ K, $R_F = 0{\cdot}038$ for 255 unique reflections; the TaS_2 part: $a = 3{\cdot}295\,(1)$, $b = 5{\cdot}778\,(1)$, $c = 23{\cdot}057\,(1)$ Å, $V = 439{\cdot}0\,(2)$ Å^3, $F(000) = 420$, $T = 295$ K, $R_F = 0{\cdot}034$ for 312 unique reflections; the layer stacking direction is **c**. For $(CeS)_{1.15}TaS_2$, $M_r = 443{\cdot}1$, $D_x = 6{\cdot}78$ g cm^{-3}, $\mu = 328{\cdot}8$ cm^{-1}; the CeS part: $a = 5{\cdot}737\,(1)$, $b = 5{\cdot}749\,(1)$, $c = 11{\cdot}444\,(2)$ Å, $V = 377{\cdot}5\,(1)$ Å^3, $F(000) = 296$, $T = 295$ K, $R_F = 0{\cdot}062$ for 427 unique reflections; the TaS_2 part: $a = 3{\cdot}293\,(1)$, $b = 5{\cdot}752\,(1)$, $c = 22{\cdot}892\,(2)$ Å, $V = 433{\cdot}6\,(2)$ Å^3, $F(000) = 420$, $T = 295$ K, $R_F = 0{\cdot}035$ for 310 unique reflections. The composition is determined by the misfit along the *a* axes (the ratio $a(M\text{S})/a(\text{TaS}_2)$].

Introduction. Recent investigations (Wiegers, Meetsma, Haange & de Boer, 1988; Guemas, Rabu,

---

* Author to whom correspondence should be addressed.

0108-2701/91/050924-07$03.00

Meerschaut & Rouxel, 1988; Meetsma, Wiegers, Haange, & de Boer, 1989; Kuypers, Van Tendeloo, Van Landuyt & Amelinckx, 1989; Wiegers, Meetsma, Haange, van Smaalen, de Boer, Meerschaut, Rabu & Rouxel, 1990; Wulff, Meetsma, van Smaalen, Haange, de Boer & Wiegers, 1990) have shown that compounds formerly designated as ternary sulfides MTS_3 (M = Sn, Pb, rare-earth metals; T = Nb, Ta) (Schmidt, 1970; van Maaren, 1972; Schmidt, McCarthy & Maita, 1970; Donohue, 1975) are misfit layer compounds $(MS)_nTS_2$ (n = 1·08–1·19) built of alternate double layers of MS, each being approximately a {100} slice of NaCl-type MS, and sandwiches of TS_2 as occur in NbS_2-2H and TaS_2-2H. The diffraction patterns of the compounds are described by two centered orthorhombic lattices; the unit cells have their b axes in common while the c axes (perpendicular to the crystal platelet) are either equal or $c(TS_2)$ is twice $c(MS)$. The ratio of the lengths of the a axes (the axes being parallel) is irrational but close to $3^{1/2}$. So far three types have been found which differ in the stacking of units along **c**. The structure types are designated by the centering types C and F of the two orthorhombic sublattices. The type indicated by CC, with both the MS and the TS_2 lattice C-centered orthorhombic, is found for $(SnS)_{1\cdot17}NbS_2$ (Meetsma *et al.*, 1989; Kuypers *et al.*, 1989); the CF type with a C-centered MS lattice and an F-centered TS_2 lattice, $c(TS_2)$ being twice $c(MS)$, is found, for *e.g.* $(LaS)_{1\cdot14}NbS_2$ (Wiegers Meetsma, Haange, van Smaalen, de Boer, Meerschaut, Rabu & Rouxel, 1990) while the FF type with both lattices F-centered is found for *e.g.* $(PbS)_{1\cdot13}TaS_2$ (Wulff *et al.*, 1990). The composition of the compounds is determined by the ratio of the length of the a axes (the misfit axes) and the number of formula units per cell.

One expects reflections from the two sublattices in the crystal and also reflections (satellites) due to their mutual modulation and indeed these satellites are clearly visible using electron diffraction (Kuypers *et al.*, 1989). $(LaS)_{1\cdot13}TaS_2$ and $(CeS)_{1\cdot15}TaS_2$, described in this paper, are isostructural with $(LaS)_{1\cdot14}NbS_2$, first described by Meerschaut, Rabu & Rouxel (1989) in a large orthorhombic unit cell with space group $Bbcb$ and unit-cell dimensions a = 23·216, b = 5·806, c = 23·031 Å. The agreement between the observed and calculated structure factors was good for reflections $h = 4n$, n = 1,2,3,..., but rather poor for the $h = 7n$, n = 0,1,2,... reflections and the remaining weak reflections. A reinvestigation of these diffraction data of $(LaS)_{1\cdot14}NbS_2$ was performed in terms of a composite crystal with an LaS part with $a' = a/4$, $b' = b$, $c' = c/2$, space group $Cm2a$, and an NbS_2 part with $a' = a/7$, $b' = b$, $c' = c$, space group $Fm2m$ (Wiegers, Meetsma, Haange, van Smaalen, de Boer, Meerschaut, Rabu & Rouxel, 1990). Refinements converged to R_F = 0·048 and 0·087, respectively, for reflections of the LaS and NbS_2 parts and to 0·067 for the $0kl$ reflections which are common to both parts. The remaining reflections, which are all weak, are satellites due to the mutual modulation of the two sublattices. The symmetry of the complete structure, including the mutual modulation of the two sublattices, was analyzed in terms of a four-dimensional space group based on the theory of Janner & Janssen (1980) and van Smaalen (1989).

A review of recent studies on misfit layer compounds $(MS_n)TS_2$ (M = Sn, Pb, Bi, rare-earth metals; T = Nb, Ta) is given by Wiegers, Meetsma, van Smaalen, Haange, Wulff, Zeinstra, de Boer, Kuypers, Van Tendeloo, Van Landuyt, Amelinckx, Meerschaut, Rabu & Rouxel (1989).

Experimental. Powder samples with compositions $(LaS)_{1\cdot13}TaS_2$ and $(CeS)_{1\cdot15}TaS_2$, prepared from the elements at 1073 K, were used as starting materials for crystal growth. Their powder patterns do not correspond to those of crystals obtained by vapor transport using Cl_2 as the transport agent. $(NH_4)_2PbCl_6$ was used as a source for chlorine; about 10 mg $(NH_4)_2PbCl_6$ was added to about 300 mg of the starting material. Crystals suitable for single-crystal X-ray diffraction and electrical transport properties grew as thin platelets at the low-temperature side of a gradient of 1373 to 1123 K.

The structure determination of $(MS)_nTaS_2$, M = La, n = 1·13 (M = Ce, n = 1·15). Data for the Ce compound are given in square brackets following those for the La compound. Single-crystal X-ray diffraction with an Enraf–Nonius CAD-4F diffractometer using monochromatized Mo $K\overline{\alpha}$ (λ = 0·71073 Å) radiation on a crystal of approximate dimensions 0·066 × 0·059 × 0·006 [0·06 × 0·05 × 0·016] mm revealed that the reflections can be indexed using two orthorhombic unit cells with cell constants as given in Table 1. These two lattices have the b axis in common and the ratio in c axes is commensurate ($c_{TaS_2} = 2 \times c_{MS}$) while the lattices do not match along the a axes, the ratio of their lengths being 5·813/3·295 = 1·7642 (6) [5·737/3·293 = 1·7422 (6)]. Because this ratio is irrational, it is not possible to choose a larger unit cell which describes the complete structure. The c axes are perpendicular to the crystal platelet. The structure determination was therefore split into three different parts, *viz* the structure determination of the MS and TaS_2 parts separately, during which the common $0kl$ reflections were omitted because their intensities are determined by both lattices together, followed by determination of the relative y position of both structure parts in the complete structure, using the common $0kl$ reflections, as described for $(SnS)_{1\cdot17}NbS_2$ (Meetsma *et al.*, 1989).

Table 1. *Crystal data and details of the structure determinations of* $(LaS)_{1\cdot13}TaS_2$ *and* $(CeS)_{1\cdot15}TaS_2$

(*a*) LaS and CeS parts

	LaS	CeS
Crystal data		
Crystal system	Orthorhombic	
Space group, No.	*Cm*2*a*, 39	
a (Å)	5·813 (1)	5·737 (1)
b (Å)	5·773 (1)	5·749 (1)
c (Å)	11·526 (1)	11·444 (2)
V (Å^3)	386·8 (1)	377·5 (1)
Z	4	4
Data collection		
Diffractometer	Enraf–Nonius CAD-4F	
Radiation (Å)	Mo $K\overline{\alpha}$, 0·71073	
Monochromator	Graphite	
Temperature (K)	295	
θ range; min., max. (°)	1·77, 29·97	−10·45, 40·00
$\omega/2\theta$ scan (°)	$\Delta\omega = 0{\cdot}75 + 0{\cdot}35\tan\theta$	$\Delta\omega = 0{\cdot}08 + 0{\cdot}35\tan\theta$
Data set	h: 0→8; k: −8→8; l: −16→16	h: 0→10; k: −10→10; l: −20→20
Crystal-to-receiving-aperture distance (mm)	173	
Horizontal, vertical aperture (mm)	4·0; 4·5	4·2; 4·5
Reference reflections; r.m.s. dev. (%)	$02\underline{4}$; 0·66 $02\bar{4}$; 0·69	$02\underline{4}$; 0·42 $02\bar{4}$; 0·51
Instability constant, *P*	0·0062	0·0051
Drift correction	1·000–1·000	0·993–1·000
Min. and max. absorption correction factors	1·25–4·36	1·82–8·27
X-ray exposure time (h)	14·7	37·5
Total data	1218	2531
Unique data	336	683
$R_{\rm int}$	0·039	0·073
Refinement		
Number of reflections $h \neq 0$	255	427
Number of refined parameters	12	12
Final agreement factors		
R_F	0·038	0·062
wR	0·042	0·036
Weighting scheme	1	$1/\sigma^2(F)$
S	3·342	2·063
Min. and max. residual electron densities in final difference Fourier map (e Å^{-3})	−2·67, 3·21	−4·3, 3·6
Max. (shift/σ) final cycle	0·073	0·0009
Average (shift/σ) final cycle	0·0177	0·0003

(*b*) TaS_2 part

	$(LaS)_{1\cdot13}TaS_2$	$(CeS)_{1\cdot15}TaS_2$
Crystal data		
Crystal system	Orthorhombic	
Space group, No.	*Fm*2*m*, 42	
a (Å)	3·295 (1)	3·293 (1)
b (Å)	5·778 (1)	5·752 (1)
c (Å)	23·037 (1)	22·892 (2)
V (Å^3)	439·0 (2)	433·6 (2)
Z	4	4
Data collection		
Diffractometer	Enraf–Nonius CAD-4F	
Radiation (Å)	Mo $K\overline{\alpha}$, 0·71073	
Monochromator	Graphite	
Temperature (K)	295	
θ range; min., max. (°)	1·77, 40·00	0·89, 40·00
$\omega/2\theta$ scan (°)	$\Delta\omega = 0{\cdot}75 + 0{\cdot}35\tan\theta$	$\Delta\omega = 0{\cdot}85 + 0{\cdot}35\tan\theta$
Data set	h: 0→5; k: −10→10; l: −40→40	h: −1→5; k: −10→10; l: −40→40
Crystal-to-receiving-aperture distance (mm)	173	
Horizontal, vertical aperture (mm)	4·0; 4·5	4·2; 4·5
Reference reflections; r.m.s. dev. (%)	$20\bar{4}$; 0·42 204; 0·41	$02\bar{8}$; 0·68 $02\bar{8}$; 0·49
Instability constant, *P*	0·0062	0·0066
Drift correction	1·000–1·002	1·000–1·004
Min. and max. absorption correction factors	1·25–5·93	1·82–8·82
X-ray exposure time (h)	19·7	43·0
Total data	1506	1901
Unique data	411	408
$R_{\rm int}$	0·043	0·073

Table 1 (*cont.*)

	$(LaS)_{1\cdot13}TaS_2$	$(CeS)_{1\cdot15}TaS_2$
Refinement		
Number of reflections $h \neq 0$	312	310
Number of refined parameters	10	10
Final agreement factors		
R_F	0·034	0·035
wR	0·049	0·050
Weighting scheme	1	1
S	6·317	6·459
Min. and max. residual electron densities in final difference Fourier map (e Å^{-3})	−3·25, 7·31	−3·79, 7·69
Max. (shift/σ) final cycle	0·109	0·094
Average (shift/σ) final cycle	0·041	0·027

(*c*) Projection down [100]

	$(LaS)_{1\cdot13}TaS_2$	$(CeS)_{1\cdot15}TaS_2$
Crystal data		
Space group, No.	*P*11*m*, 6	
b (Å)	2·889 (1)	2·875 (1)
c (Å)	11·528 (1)	11·446 (1)
Refinement		
Number of reflections $h \neq 0$	98	97
Number of refined parameters	11	11
Final agreement factors		
R_F	0·055	0·042
wR	0·074	0·051
Weighting scheme	1	1
S	3·490	2·298
Min. and max. residual electron densities in final difference Fourier map (e Å^{-3})	−2·50, 1·94	−1·21, 1·61
Max. (shift/σ) final cycle	0·374	0·0106
Average (shift/σ) final cycle	0·163	0·0023

MS part: Unit-cell dimensions and their standard deviations were determined from the setting angles of 19 reflections in the range $22{\cdot}71 < \theta < 28{\cdot}00°$ [$20{\cdot}45 < \theta < 21{\cdot}80°$] in four alternate settings (de Boer & Duisenberg, 1984). All reflections were measured in one hemisphere up to $\theta = 30°$ [40°]. The two reference reflections measured every 2·0 [2·8] h showed only a small fluctuation (< 0·7%) [< 0·5%] about the mean value during the 14·7 [37·8] h of X-ray exposure time. A 360° ψ scan was made for $(CeS)_{1\cdot15}TaS_2$: the reflection 211 close to axial showed an intensity variation up to 14% about the mean value. The net intensities of the data were corrected for the scale variation, Lorentz and polarization effects and for absorption using a Gaussian integration method (Spek, 1983) (corrections in the range 1·25 to 4·36 [1·82 to 8·27]). Standard deviations in the intensities based on counting statistics were increased according to an analysis of the excess variance of the two reference reflections: $\sigma^2(I) = \sigma^2_{\rm cs}(I) + (PI)^2$ where $P = 0{\cdot}0062$ [0·0051] is the instability constant (McCandlish, Stout & Andrews, 1975). Averaging equivalent reflections resulted in 336 [683] unique reflections satisfying the $I \geq 2{\cdot}5\sigma(I)$ criterion of observability. From the systematic extinctions (hkl: $h + k = 2n + 1$; $hk0$: h, $k = 2n + 1$), the possible space groups are *Cmma*, *C*2*mb*, *Cm*2*a*. As discussed in our papers on $(SnS)_{1\cdot17}NbS_2$ (Meetsma *et al.*, 1989; van Smaalen, 1989) and $(LaS)_{1\cdot14}NbS_2$ (Wiegers, Meetsma, Haange, van Smaalen, de Boer, Meerschaut, Rabu & Rouxel, 1990), the space group of the *M*S lattice must be *Cm*2*a*, on the basis of the symmetry of the complete structure. It was not possible to discriminate between *Cmma*, *C*2*mb*, *Cm*2*a* on the basis of *R* factors. In space group *Cm*2*a* the atoms are on site 4(*c*): $\frac{1}{4}$, *y*, *z*. To define the origin, *y* of *M* was chosen equal to zero. The midplane of the *M*S double layer was put at $z = \frac{1}{2}$. Refinements on *F* by full-matrix least squares with 255 [427] unique reflections converged at $R_F = 0{\cdot}038$ [0·062]; $wR = 0{\cdot}042$ [0·036]; $S = 3{\cdot}342$ [2·063]; 12 parameters refined; the weighting scheme was $w = 1$ [$w = 1/\sigma^2(F)$]. Cell data, details of data collection and refinement are given in Table 1, final fractional coordinates are given in Table 2.

Table 2. *Atomic positions and temperature factors of* (LaS$_{1\cdot13}$)TaS$_2$ *and* (CeS)$_{1\cdot15}$TaS$_2$

Values are fractional coordinates with respect to the unit cells defined in Table 1. E.s.d.'s are given in parentheses.

$$U_{\rm eq} = (1/3)\textstyle\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j .$$

$$F(\mathbf{h}) = F_o(\mathbf{h})\exp[-8\pi^2 U_{\rm iso}(\sin^2\theta/\lambda)^2].$$

	x	y	z	$U_{\rm eq}$ (Å^2)
LaS				
La(1)	$\frac{1}{4}$	0·0	0·65272 (9)	0·0172 (3)
S(1)	$\frac{1}{4}$	−0·506 (8)	0·6005 (4)	0·012 (1)
CeS				
Ce(1)	$\frac{1}{4}$	0·0	0·65087 (9)	0·0217 (2)
S(1)	$\frac{1}{4}$	−0·512 (3)	0·5994 (3)	0·013 (1)

	x'	y'	z'	$U_{\rm eq}$ (Å^2)
TaS$_2$ of (LaS)$_{1\cdot13}$TaS$_2$				
Ta(1)	0·0	−0·079 (–)	0·0	0·0047 (2)
S(2)	0·0	0·2587 (8)	0·0679 (1)	0·072 (8)
TaS$_2$ of (CeS)$_{1\cdot15}$TaS$_2$				
Ta(1)	0·0	−0·0795 (–)	0·0	0·0047 (2)
S(2)	0·0	0·2584 (8)	0·0685 (1)	0·0070 (8)

Common part of (LaS)$_{1\cdot13}$TaS$_2$ [coordinates in a unit cell with b'' = 2·889 (1), c'' = 11·528 (1) Å]

	x''	y''	z''	s.o.f.	$U_{\rm iso}$ (Å^2)
Ta(1)	–	−0·158 (2)	0·0	1·0	0·0012 (5)
S(2)	–	−0·485 (5)	0·136 (1)	1·0	0·005 (2)
La(1)	–	0·0	0·6521 (6)	0·51 (2)	0·011 (1)
S(1)	–	−0·013	0·597 (2)	0·51 (2)	0·006 (4)

Common part of (CeS)$_{1\cdot15}$TaS$_2$ [coordinates in a unit cell with b'' = 2·875 (1), c'' = 11·446 (1) Å]

	x''	y''	z''	s.o.f.	$U_{\rm iso}$ (Å^2)
Ta(1)	–	−0·159 (2)	0·0	1·0 (0)	0·0027 (4)
S(2)	–	−0·484 (4)	0·1373 (7)	1·0 (0)	0·007 (1)
Ce(1)	–	0·0	0·6507 (4)	0·53 (1)	0·017 (1)
S(1)	–	−0·025	0·597 (2)	0·53 (1)	0·012 (4)

TaS$_2$ *part*: Unit-cell dimensions and their standard deviations were determined from the setting angles of 23 reflections in the range $25{\cdot}50 < \theta < 27{\cdot}65°$ [$25{\cdot}56 < \theta < 27{\cdot}68°$] in four alternate settings (de Boer & Duisenberg, 1984). All reflections were measured in one hemisphere up to $\theta = 40{\cdot}0°$. The two reference reflections measured every 2·0 [2·8] h showed only a small fluctuation (< 0·4%) [< 0·7%] during the 19·7 [43] h of X-ray exposure time. A 360° ψ scan for the reflection 220 of (LaS)$_{1\cdot13}$TaS$_2$ close to axial showed an intensity variation up to 40% about the mean value. The net intensities of the data were corrected for the scale variation, Lorentz and polarization effects and for absorption (Spek, 1983) (corrections in the range 1·25 to 5·93 [1·82 to 8·82]). Standard deviations in the intensities based on counting statistics were increased according to an analysis of the excess variance of the two reference reflections. Refinements by full-matrix least squares performed in space group *Fm*2*m* with Ta at 4(*a*): 0,y',0 with *y* chosen equal to zero and S at 8(*c*): 0,y',z', using 312 [310] unique reflections with $I \geq 2{\cdot}5\sigma(I)$ converged at $R_F = 0{\cdot}034$ [0·035]; $wR = 0{\cdot}049$ [0·50]; $S = 6{\cdot}317$ [6·459]; 10 parameters refined; the weighting scheme was $w = 1$. Cell data, data collection and refinement details are given in Table 1, final fractional coordinates are given in Table 2. The y' coordinates are transformed according to the results of the common projection (0*kl* reflections), see below.

The complete structure. From the size of the unit cells in the *ab* plane and the number of formula units *M*S and TaS$_2$ per cell one finds that the compositions of the compounds are (LaS)$_{1\cdot13}$TaS$_2$ and (CeS)$_{1\cdot15}$TaS$_2$, respectively. The symmetry element in the structure projected along [100] is a mirror plane perpendicular to the *c* axis. Since the 0*kl* reflections are only present for $k = 2n$ (and $l = 2n$), a smaller unit cell can be chosen for the refinement, *viz* the unit cell with $b'' = (1/2)b$ and $c'' = (1/2)c_{\rm TaS_2}$; this unit cell contains one TaS$_2$ and 1·13 [1·15] *M*S units. The two-dimensional space group is *pm* [No. 3 of the 17 two-dimensional space groups (*International Tables for Crystallography* (1983, Vol. A)]. Tantalum of the TaS$_2$ sandwich was placed at the mirror plane at $z'' = 0$; from the refinement of the TaS$_2$ lattice one finds for the z'' coordinates of the two S atoms of the TaS$_2$ unit $z'' = \pm 0{\cdot}1358$ [$\pm 0{\cdot}1370$]. The y'' coordinate of La (Ce) was fixed at zero; using the *y* coordinates of the atoms in the LaS (CeS) lattice one finds y'' of S(1) equal to −0·013 [−0·025]; this coordinate was also kept fixed. The midplane of the LaS (CeS) double layer is at $z'' = \frac{1}{2}$. Starting values for the y'' coordinates of Ta and S(2) were from the isostructural compound (LaS)$_{1\cdot14}$NbS$_2$. For the refinement using *XTAL* (Hall & Stewart, 1987), we chose the three-dimensional space group *P*11*m*, with atoms on positions 1(*a*) and 2(*c*). The full-matrix least-squares refinement on *F* with anisotropic thermal parameters converged at $R_F = 0{\cdot}055$ [0·042]; $wR = 0{\cdot}074$ [0·51]; $S = 3{\cdot}490$ [2·298]. Parameters in the refinement were coordinates, except $y''$of *M* and z'' of Ta, the site occupancy factor of *M*(1) [s.o.f. of S(1) kept equal to the s.o.f. of *M*(1)] and the isotropic thermal parameters of all atoms. It may be noted that it is useless to relate the *x* coordinates in the complete structure because of the incommensurate character of the structure along the *a* axes. It is seen that the site occupancy factor of *M*S [0·51 (2) and 0·53 (1) for LaS and CeS, respectively] is lower than expected, 0·565 and 0·575, respectively, from the ratio of the misfit axes. This lower *M*S 'content' than expected is also observed in the ratio of the experimental scale factors (0·9764:1 for LaS:TaS_2 and 0·9802:1 for CeS:TaS_2). The 'theoretical' ratios are 0·8850:1 and 0·8696:1 for $(LaS)_{1.13}TaS_2$ and $(CeS)_{1.15}TaS_2$, respectively. A possible explanation is the effect of the modulation which is strongest for the *M*S lattice (see below). The intensity of the satellites is borrowed from the main reflections, thus causing a decrease of the intensities compared to a 'rigid' *M*S lattice. Another possibility is stacking disorder, especially in the *M*S lattice, which decreases the intensities of the main reflections.

Crystal data and experimental details of this part of the structure determination are compiled in Table 1. Final fractional atomic coordinates and equivalent isotropic thermal parameters and s.o.f.'s are given in Table 2.* It is now possible to give the true y' coordinates of the TaS_2 lattice relative to LaS (CeS) with La (Ce) at $y = 0$; this is done by halving the y'' coordinates for Ta in the common projections and using these values for Ta in the TaS_2 tables. The y' coordinate of S(2) is changed accordingly, *viz* $y'[S(2)] = y'_0[S(2)] - 0{\cdot}5 \times y''[M]$ in which $y'_0[S(2)]$ is the coordinate for the refinement with $y'[Ta] = 0$.

In all our calculations scattering factors were taken from Cromer & Mann (1968). Anomalous-dispersion factors are those given by Cromer & Liberman (1970). All calculations were carried out on the CDC-Cyber 170/760 computer of the University of Groningen with the program packages *XTAL* (Hall & Stewart, 1987) and *EUCLID* (Spek, 1982; calculation of geometric data).

Discussion. $(LaS)_{1.13}TaS_2$ and $(CeS)_{1.15}TaS_2$ belong to the *CF* structure type of misfit layer compounds with centered orthorhombic lattices; the compounds are isostructural with $(LaS)_{1.14}NbS_2$ and $(PbS)_{1.14}NbS_2$, neglecting the disorder in the NbS_2 lattice in the latter compound (Wiegers, Meetsma, Haange, van Smaalen, de Boer, Meerschaut, Rabu & Rouxel, 1990). They are built of alternate double layers of *M*S (*M* = La, Ce) (Fig. 1) and sandwiches of TaS_2 (Fig. 2). The complete structure is shown in projection along the misfit *a* axes in Fig. 3.

The four-dimensional space group which describes the complete structure, including the mutual modulation of the two sublattices, $P^{Fm2m}_{\bar{1}1s}$ $(\alpha,0,0)$ [$\alpha = a(TaS_2)/a(MS) \simeq 4/7$] agrees with that of the isostructural compound $(LaS)_{1.14}NbS_2$ (Wiegers, Meetsma, Haange, van Smaalen, de Boer, Meerschaut, Rabu & Rouxel, 1990; van Smaalen, 1989).

M(= La, Ce) is coordinated in an approximate square pyramid by five S atoms from the *M*S double layer; the *M*—S distances (Table 3) are close to those found in NaCl-type *M*S: *a*(LaS) = 5·860 (Flahaut,

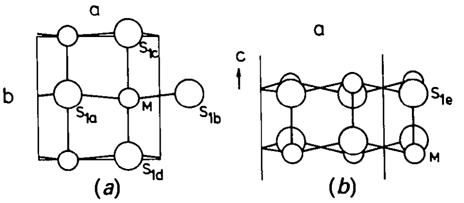

Fig. 1. Projections of the *M*S double layer: (*a*) along the *c* axis, only upper half shown; (*b*) along the *a* axis.

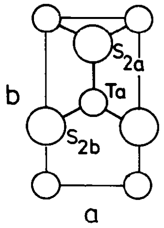

Fig. 2. Projection of the TaS_2 sandwich along the *c* axis.

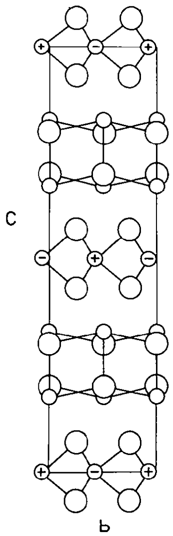

Fig. 3. Projection of the structures of $(LaS)_{1.13}TaS_2$ and $(CeS)_{1.15}TaS_2$ along the misfit *a* axes. In order to demonstrate the *F* centering of the TaS_2 lattice Ta atoms (at $z = 0$ and $z = \frac{1}{2}$) in the same plane parallel to (100) have the same symbol (+ or −); Ta atoms $\frac{1}{2}a_2$ apart have different symbols. Large circles are S atoms.

---

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53682 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Distances* (Å) *in* $(LaS)_{1\cdot13}TaS_2$ *and* $(CeS)_{1\cdot15}TaS_2$ (M = La, Ce)

	$(LaS)_{1\cdot13}TaS_2$	$(CeS)_{1\cdot15}TaS_2$
M—S_{1a}	2·968 (1)	2·929 (1)
M—S_{1b}	2·968 (1)	2·929 (1)
M—S_{1c}	2·98 (5)	3·00 (2)
M—S_{1d}	2·91 (5)	2·87 (2)
M—S_{1e}	2·919 (5)	2·865 (4)
Ta—S_{2a} (2 ×)	2·502 (3)	2·497 (5)
Ta—S_{2b} (4 ×)	2·459 (3)	2·457 (3)

Note: The numbering of the atoms refers to Figs. 1 and 2.

1960), a(CeS) = 5·779 Å (Hulliger, Natterer & Ott, 1978). NaCl-type MS may be considered to be the parent substance of the MS part since the double layer is a distorted slab with a thickness of half the cell edge of f.c.c. MS; the distortion is such that the M atoms are on the outside of the planes of S atoms. The M atoms (at $y = 0$ and $y = \frac{1}{2}$) are lying in the grooves parallel to **a** formed by rows of S atoms at $y \simeq 0{\cdot}258$ and $y \simeq 0{\cdot}758$ of the TaS_2 sandwiches. In this way each M atom is coordinated to the S atoms of the MS double layer and also to the S atoms of the neighboring TaS_2 sandwiches. Owing to the incommensurate character of the structure along the a axes, the number of coordinating S atoms ranges from two to three (Fig. 4). The total number of coordinating S atoms for each M atom is, therefore, seven or eight.

The TaS_2 sandwiches are, apart from a distortion as discussed below, the same as in TaS_2-2H. The relationship becomes visible by comparing the a and b axes of the TaS_2 part with the orthohexagonal axes of TaS_2-2H, $a = 3{\cdot}314$, $b = 5{\cdot}740$ Å [from a single-crystal X-ray diffraction study by Meetsma, Wiegers, Haange & de Boer (1990)]. On the basis of an orthohexagonal cell the space group is changed from $P6_3/mmc$ for TaS_2-2H to $Pm2c$ for the distorted structure. Owing to the different way of stacking of the sandwiches of TaS_2 in TaS_2-2H and $(LaS)_{1\cdot13}TaS_2$ and $(CeS)_{1\cdot15}TaS_2$, the translational components of each element may differ for the two compounds. It is thus found that the subsystem space group of the TaS_2 part, $Fm2m$, is compatible with the orthohexagonal space group of TaS_2-2H. Since the distortion is small, the ratio b/a being somewhat larger than $3^{1/2}$ (1·754 for the La compound and 1·747 for the Ce compound), the Ta–Ta distances in the TaS_2 units differ: 3·295 (1) (4 ×) and 3·326 (1) Å (2 ×) for the La compound and 3·293 (1) (4 ×) and 3·314 (1) Å (2 ×) for the Ce compound. There are two types of Ta—S distances in the TaS_2 sandwich (Table 3), those occurring in pairs being longer than the remaining four equal Ta—S distances. The same trend is found in $(PbS)_{1\cdot13}TaS_2$: 2·524 (4) (2 ×) and 2·443 (3) Å (4 ×) (Wulff *et al.*, 1990). The average Ta—S distances, 2·477 Å for the La compound, 2·470 Å for the Ce compound and 2·470 Å for the Pb compound, are close to the 2·468 (2) Å observed in TaS_2-2H (Meetsma *et al.*, 1990). For misfit compounds with NbS_2 sandwiches $(SnS)_{1\cdot17}NbS_2$ (Meetsma *et al.*, 1989), $(LaS)_{1\cdot14}NbS_2$ and $(PbS)_{1\cdot14}NbS_2$ (Wiegers, Meetsma, Haange, van Smaalen, de Boer, Meerschaut, Rabu & Rouxel, 1990), the Nb—S distances are close to those for undistorted trigonal-prismatic coordination.

Two factors seem to be important for considering the stability of these misfit layer compounds. (*a*) Compared to TaS_2-2H, the van der Waals interaction between neighboring sandwiches of TaS_2 is replaced by probable bonding interactions between the M(La, Ce) atoms and the S atoms of TaS_2. It may be noted that the distortion of the {100} slice in NaCl-type MS is such that the metal atoms are protruding, making these bonds possible. (*b*) Electrical transport properties (resistivity, Hall coefficient and Seebeck coefficient) and magnetic properties [for $(LaS)_{1\cdot14}NbS_2$ given by Wiegers & Haange (1990)] indicate that there is an electron donation from the MS part to the TS_2 (T = Nb, Ta) part of the structure. The electrical transport properties of $(LaS)_{1\cdot14}NbS_2$ are those of a d-band metal; the conduction is by holes in a $4d_{z^2}$ band of mainly Nb character, the band being half-filled in the case of NbS_2-2H. In the misfit compound the band contains 0·12 hole/Nb indicating a transfer of 0·88/1·14 = 0·78 electron/La. The magnetic properties indicate that the remaining electrons are in an La 4f orbital.

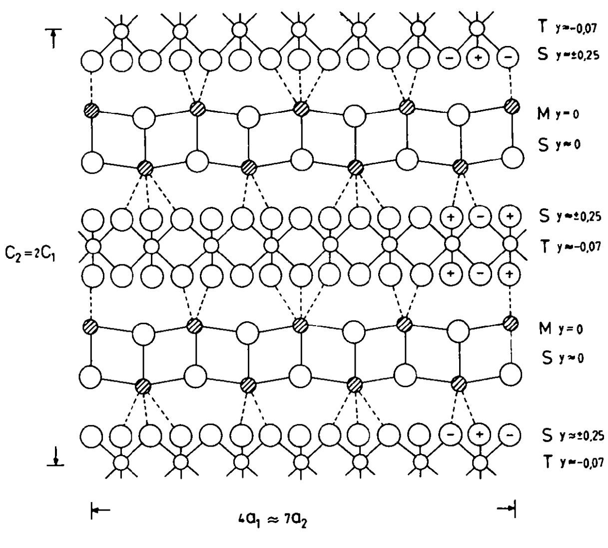

Fig. 4. Projection of the structures of $(LaS)_{1\cdot13}TaS_2$ and $(CeS)_{1\cdot15}TaS_2$ along the [010] axes. Large and small open circles are S and Ta atoms, respectively; La (Ce) atoms are indicated by dashed circles. Along the misfit axes a length corresponding to four unit cells of the LaS (CeS) part is indicated. Only the sheets of LaS (CeS) parallel to (010) with $y = 0$ for La (Ce) and $y \simeq 0$ for S(1) and the TaS_2 sandwich with Ta at $y \simeq -0{\cdot}07$ and S at $\simeq \pm 0{\cdot}25$ are shown for clarity.

References

BOER, J. L. DE & DUISENBERG, A. J. M. (1984). *Acta Cryst.* **A40**, C410.

CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.

CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321–324.

DONOHUE, P. C. (1975). *J. Solid State Chem.* **12**, 80–83.

FLAHAUT, J. (1960). *Bull. Soc. Chim. Fr.* **11**, 1282–1290.

GUEMAS, L., RABU, P., MEERSCHAUT, A. & ROUXEL, J. (1988). *Mater. Res. Bull.* **23**, 1061–1069.

HALL, S. R. & STEWART, J. M. (1987). Editors. *XTAL2.2 Users Manual.* Univs. of Western Australia, Australia, and Maryland, USA.

HULLIGER, F., NATTERER, B. & OTT, H. R. (1978). *J. Magn. Magn. Mater.* **8**, 87–89.

JANNER, A. & JANSSEN, T. (1980). *Acta Cryst.* **A36**, 399–408, 408–415.

KUYPERS, S., VAN TENDELOO, G., VAN LANDUYT, J. & AMELINCKX, S. (1989). *Acta Cryst.* **A45**, 291–296.

MAAREN, M. H. VAN (1972). *Phys. Lett.* **40**, 353–354.

MCCANDLISH, L. E., STOUT, G. H. & ANDREWS, L. C. (1975). *Acta Cryst.* **A31**, 245–249.

MEERSCHAUT, A., RABU, P. & ROUXEL, J. (1989). *J. Solid State Chem.* **78**, 35–45.

MEETSMA, A., WIEGERS, G. A., HAANGE, R. J. & DE BOER, J. L. (1989). *Acta Cryst.* **A45**, 285–291.

MEETSMA, A., WIEGERS, G. A., HAANGE, R. J. & DE BOER, J. L. (1990). *Acta Cryst.* **C46**, 1598–1599.

SCHMIDT, L. (1970). *Phys. Lett.* **31A**, 551–552.

SCHMIDT, L., MCCARTHY, S. L. & MAITA, J. D. (1970). *Solid State Commun.* **8**, 1513–1515.

SMAALEN, S. VAN (1989). *J. Phys. Condens. Matter*, **1**, 2791–2800.

SPEK, A. L. (1982). *The EUCLID package.* In *Computational Crystallography*, edited by D. SAYRE, p. 528. Oxford: Clarendon Press.

SPEK, A. L. (1983). Proc. 8th Eur. Crystallogr. Meet. Liège, Belgium.

WIEGERS, G. A. & HAANGE, R. J. (1990). *J. Phys. Condens. Matter*, **2**, 455–463.

WIEGERS, G. A., MEETSMA, A., HAANGE, R. J. & DE BOER, J. L. (1988). *Mater. Res. Bull.* **23**, 1551–1559.

WIEGERS, G. A., MEETSMA, A., HAANGE, R. J., VAN SMAALEN, S., DE BOER, J. L., MEERSCHAUT, A., RABU, P. & ROUXEL, J. (1990). *Acta Cryst.* **B46**, 324–332.

WIEGERS, G. A., MEETSMA, A., VAN SMAALEN, S., HAANGE, R. J., WULFF, J., ZEINSTRA, T., DE BOER, J. L., KUYPERS, S., VAN TENDELOO, G., VAN LANDUYT, J., AMELINCKX, S., MEERSCHAUT, A., RABU, P. & ROUXEL, J. (1989). *Solid State Commun.* **70**, 409–413.

WULFF, J., MEETSMA, A., VAN SMAALEN, S., HAANGE, R. J., DE BOER, J. L. & WIEGERS, G. A. (1990). *J. Solid State Chem.* **84**, 118–129.

Acta Cryst. (1991). C47, 930–932

Crystal Chemistry of *cyclo*-Hexaphosphates. XIV. Structure of Silver Ammonium *cyclo*-Hexaphosphate Monohydrate

BY M. T. AVERBUCH-POUCHOT

Laboratoire de Cristallographie, associé l'Université J. Fourier, CNRS, 166X, 38042 Grenoble CEDEX, France

(*Received* 16 *May* 1990; *accepted* 25 *October* 1990)

Abstract. $Ag_3(NH_4)_3P_6O_{18}.H_2O$, M_r = 869·562, trigonal, $R\bar{3}$, a = 15·172 (5), c = 13·994 (5) Å, Z = 6, V = 2790 (3) Å^3, D_x = 3·105 Mg m^{-3}, λ(Ag $K\bar{\alpha}$) = 0·5608 Å, μ = 1·873 mm^{-1}, F(000) = 2508, room temperature, final R = 0·036 for 2442 reflections. Pseudo-hexagonal rings built up by three silver atoms and three ammonium groups alternate with the P_6O_{18} groups along the ternary axes. The $Ag_3(NH_4)_3$ rings are centred by the water molecule.

Introduction. The crystal structures of ammonium *cyclo*-hexaphosphate monohydrate, $(NH_4)_3P_6O_{18}.H_2O$, and of the corresponding silver salt, $Ag_6P_6O_{18}.H_2O$, have already been described (Averbuch-Pouchot, 1989*a*,*b*). These two compounds have very similar unit cells: a = 15·445 (10), c = 7·553 (7) Å for the ammonium salt, a = 14·807 (10), c = 6·597 (7) Å for the silver salt.

Both crystallize with the space group $R\bar{3}$ and Z = 3. The title compound, $Ag_3(NH_4)_3P_6O_{18}.H_2O$, is also trigonal, $R\bar{3}$, and its unit cell is closely related to the previous ones. The observed a value is approximately halfway between the values measured for a(Ag) and $a(NH_4)$ and the value of c is close to the sum c(Ag) + $c(NH_4)$. These observations suggest that the atomic arrangement of the title compound must be very similar to those determined for the silver and ammonium salts with, in addition, an order between the associated cations to explain the doubling of the c axis.

Experimental. Crystals of the title compound have been prepared by adding a dilute aqueous solution of silver nitrate to a dilute aqueous solution of ammonium *cyclo*-hexaphosphate to obtain a ratio Ag/NH_4 = 1/2 in the resulting solution. After several weeks of evaporation at room temperature large crystals of $Ag_3(NH_4)_3P_6O_{18}.H_2O$ appeared as stout trigonal prisms. The compound is very sparingly soluble in water.

0108-2701/91/050930-03$03.00