tion that the probability that $\varphi_{200}=\pi$ is not insignificant. It seems reasonable to insist that a probabilistic argument be labelled as such, particularly when the probabilities involved cannot be evaluated readily and rough estimates are not overwhelmingly conclusive; the argument presented by Hauptman certainly falls in this category, but no indication of this was given in the original article.

References

COOPER, A., NORTON, D. A. & HAUPTMAN, H. (1969). *Acta Cryst.* B**25**, 814–828.

HAUPTMAN, H. (1972). *Acta Cryst.* B**28**, 3103.

HAUPTMAN, H., FISHER, J., HANCOCK, H. & NORTON, D. A. (1969). *Acta Cryst.* B**25**, 811–814.

Comments on Gilardi's paper '*A priori*, for estriol, $\varphi_{200}=0$ or π'. By HERBERT HAUPTMAN, *Medical Foundation of Buffalo, Buffalo, New York, U.S.A.*

Gilardi's thesis [*Acta Cryst.* (1973). B**29**, 1739–1740] is certainly correct. However, his work is based on a misunderstanding of the intent of the earlier paper which it purports to criticize so that it is, in reality, a valid criticism of his misinterpretation.

First, it is surely true that there exist *a priori* acceptable structures with E_{200} large and negative and $E_{100}=0$, as Gilardi (1973) demonstrates by his example. However, he has misconstrued the essential point of the earlier paper (Hauptman, 1972) which is not that there are no acceptable structures with $\varphi_{200}=\pi$ but that such structures are relatively rare. The proof of this contention lies in the comparison (apparently too concise in the earlier paper) of Gilardi's equations (1) and (2). First, since the ε_μ are small, it is clear that the magnitude of each contributor to (1) is, in general, significantly less than the magnitude of the corresponding contributor to (2). Next, 21 of the contributors to (1) are positive and 21 are negative, a distribution of signs most conducive to complete or nearly complete annihilation. A situation as favorable as this is quite unlikely (but admittedly not impossible) in (2) since the ε_μ are, *a priori*, just as likely to be positive as negative so that the probability of equal numbers of positive and negative signs is only 0·1, approximately. (In fact, the probability that the difference between the number of positive contributors to (2) and the number of negative contributors be less than four is still only about 0·3. A similar comparison may be made if one chooses to invoke the one-dimensional random walk.) Finally, the numerical factor in (1), $1/\sqrt{84}$, is just half the corresponding factor in (2), $2/\sqrt{84}$. For these three reasons then, while it may not have been 'clear' in the earlier paper, it is nevertheless true that the 'right-hand side of equation (1) is more consistent with a value of zero (for E_{100}) than that of equation (2)', in the probabilistic sense.

In correspondence with Professor David Templeton it has been pointed out that several factors 2π following equation (6) have been lost. This error is most easily corrected by replacing the ε_μ of equations (4) and (5) of the original paper by $\varepsilon_\mu/2\pi$. I wish to thank Professor Templeton for noting this error and also for other constructive criticism.

References

GILARDI, R. D. (1973). *Acta Cryst.* B**29**, 1739–1740.

HAUPTMAN, H. (1972). *Acta Cryst.* B**28**, 3103.

The crystal structure and X-ray diffraction data for anhydrous gadolinium bromide. By HENRY H. THOMAS, *Goodyear Atomic Corporation, P.O. Box 628, Piketon, Ohio 45661, U.S.A.* and W. A. BAKER JR, *University of Texas, Arlington, Texas, U.S.A.*

The X-ray diffraction data for $GdBr_3$ are reported. The crystal structure of $GdBr_3$ is the monoclinic $AlCl_3$ type belonging to space group $C2/m$. The unit-cell parameters are: $a=7\cdot224\pm0\cdot005$, $b=12\cdot512\pm0\cdot005$, $c=6\cdot84\pm0\cdot01$ Å, and $\beta=110\cdot6\pm0\cdot2°$. The results of pycnometer density measurements are reported.

Introduction

In the course of a general investigation of the properties of some anhydrous rare-earth halides, an X-ray study of several of the compounds was carried out and the lattice parameters determined. The result of the X-ray investigation of $GdBr_3$ is reported herein.

Though nearly all the lanthanide trifluoride, trichloride,

and triiodide series have been prepared and the crystal structures determined, only limited data on the lanthanide tribromides have been published. Previous X-ray investigations of the lanthanide halides have reported that, for a given halide, a transition occurs in crystal structure near the midpoint of the lanthanide series. Although there are some other transitions in the lanthanide halide series, only the transition at the midpoint of the series is accompanied by a large change in molecular volume. Such a transition has been observed in the trifluorides (Zalkin & Templeton, 1959), the trichlorides (Templeton & Carter, 1954; Templeton & Dauben, 1954), and the triiodides (Asprey, Keenan & Kruse, 1964). The data published for the tribromides (Zachariasen, 1948) have not been sufficient to establish whether such a change in crystal structure occurs. The only lanthanide metals for which bromide data are available are La, Ce, Pr, Nd, and Sm, which accounts for all the metals in the first half of the lanthanide group except Pm and Eu. The crystal structure of La, Ce, and Pr bromide is the hexagonal $Y(OH)_3$-type, while that of Nd and Sm is the orthorhombic $PuBr_3$-type. The bromide structures for the second half of the lanthanide metal groups have not previously been determined.

Experimental

Materials

Unless otherwise indicated, all materials employed were reagent grade and were used without further purification. The gadolinium oxide was purchased from the Lindsay Chemical Division of the American Potash and Chemical Corporation. The purity was 99·9% by manufacturer's claim.

Preparations

Anhydrous $GdBr_3$ was prepared by the method of Taylor & Carter (1962). The hydrated bromide was first prepared by dissolving the metal oxide in hydrobromic acid followed by the addition of enough water to dissolve a sixfold excess of ammonium bromide. The resulting mixture was dried to a slush on a hot plate followed by a final drying and sublimation of the excess ammonium bromide under vacuum. The sublimation was completed at 400 °C and 1×10^{-6} torr. The drying chamber containing the anhydrous product was sealed off under vacuum and removed to a dry box for handling.

The production of europium(III) bromide was also attempted. The pure dibromide, prepared by the above method, was soaked in liquid bromine for a period of two days. The gray dibromide turned to a bright yellow-orange color. However, magnetic and spectroscopic analyses showed this to be primarily the starting material.

X-ray data

X-ray diffraction patterns were obtained with a 14·3 cm diameter powder camera and Ni-filtered copper $K\alpha$ radiation. Since the compound was hygroscopic, all grinding, mixing, and filling of capillaries was done in a dry box. Intensities were visually estimated.

For the precise determination of d values, and thus, cell parameters, an internal standard, NaBr, was employed. The more common Straumanis (Cullity, 1959) method of precision d value determination was not possible because of the large amount of fluorescence which prevented any readings in the back-reflection region.

Intensity calculations were made using the equation:

$$I = F^2 p\theta$$

where F is the structure factor, p is the multiplicity, and θ represents the Lorentz–polarization factor. Temperature and absorption corrections were not made. The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1952).

Density

The density was determined by pycnometry. A 2 ml volume pycnometer was employed with ethylene dichloride at the immersion liquid. Since the samples were in powdered form, the density determined in this manner represents a lower limit for the true density. The value reported is the average of at least three determinations.

Results

The data of $GdBr_3$ are shown in Table 1. The powder data of $GdBr_3$ were originally indexed as the hexagonal $CrCl_3$-type structure, space group $P3_112$, originally described by Wooster (1930) with parameters: $a = 7·224 \pm 0·005$ and $c = 19·20 \pm 0·04$ Å. However, it was later found that the structure of $CrCl_3$ had been shown to be the monoclinic $AlCl_3$-type structure of space group $C2/m$ (Morosin & Narath, 1964). The monoclinic parameters for $GdBr_3$ were calculated from the hexagonal parameters using the relations given by Ketelaar (1935). The parameters found are: $a = 7·224 \pm 0·005$, $b = 12·512 \pm 0·005$, $c = 6·84 \pm 0·01$ Å, and $\beta = 110·6 \pm 0·2°$. The density determined with the pycnometer was 4·3 while that calculated from the monoclinic X-ray data was 4·56 g cm^{-3}. To verify which structure $GdBr_3$ did indeed possess, the relative intensities were calculated for both the monoclinic space group, $C2/m$, and the hexagonal Wooster structure, space group $P3_112$. The unrefined atomic coordinates, derived from steric considerations, assigned to the $C2/m$ structure are as follows:

$(0,0,0; \frac{1}{2},\frac{1}{2},0) +$
Gd in $4(g)$: $\pm (0,y,0)$ with $y = 0·167$
Br in $4(i)$: $\pm (x,0,z)$ with $x = 0·210$
$z = 0·210$
B in $8(j)$: $\pm (x,y,z; x,\bar{y},z)$ with $x = 0·250$
$y = 0·167$
$z = 0·750$.

The atomic coordinates assigned the hexagonal structure are:

Gd in $3a(1)$: $x,\bar{x},\frac{1}{3}; x,2x,\frac{2}{3}; 2\bar{x},\bar{x},0$ with $x = \frac{2}{3}$
Gd in $3a(2)$: $x,\bar{x},\frac{1}{3}; x,2x,\frac{2}{3}; 2\bar{x},\bar{x},0$ with $x = \frac{5}{9}$
Br in $6c(1)$: $x,y,z; \bar{y},x-y,\frac{1}{3}+z, y-x,\bar{x},\frac{2}{3}+z$
$x,x-y,\bar{z}; y-x,\frac{1}{3}-z; \bar{y},\bar{x},\frac{2}{3}-z$
with $x = \frac{2}{9}, y = \frac{4}{9}, z = 0·1740$
Br in $6c(2)$: $x,y,z; \bar{y},x-y, \frac{1}{3}+z; y-x,\bar{x},\frac{2}{3}+z$
$x,x-y,\bar{z}; y-x,\frac{1}{3}-z; \bar{y},\bar{x},\frac{2}{3}-z$
with $x = \frac{4}{9}, y = \frac{5}{9}, z = 0·1740$
Br in $6c(3)$: $x,y,z; \bar{y},x-y-\frac{1}{3}+z; y-x,\bar{x},\frac{2}{3}+z$
$x,x-y,\bar{z}; y-x,\frac{1}{3}-z; y,\bar{x},\frac{2}{3}-z$
with $x = \frac{1}{9}, y = \frac{2}{9}, z = 0·1740$.

Both structures are composed of layers of close-packed bromine atoms with the gadolinium atoms situated in octa-

Table 1. *Observed and calculated lattice spacings and intensities for* GdBr$_3$

		Monoclinic, $C2/m$			Hexagonal, $P3_112$		
d observed	I observed	d calc'd (Å)	I_o calc'd	hkl	d calc'd (Å)	I_o calc'd	hkl
		6·402	64	001	6·401	8	003
6·418	S	6·256	12	020	6·256	4	100
		5·949	34	110	5·948	7	101
(a)	–	5·242	16	$11\bar{1}$			
(b)	–	4·475	6	021			
3·547	M	3·550	19	130	3·550	11	111
		3·550	16	201			
3·381	W	3·381	10	$13\bar{1}$	3·381	0	112
		3·381	4	200			
(b)	–	3·273	8				
3·201	F	3·201	3	002	3·200	21	006
2·885	VVS	2·886	53	$20\bar{2}$	2·886	100	114
		2·887	100	131			
2·628	F	2·632	2	201	2·631	0	115
		2·631	9	$13\bar{2}$			
		2·621	3	$22\bar{2}$	2·621	1	204
2·187	VF	2·185	13	132	2·185	2	117
		2·185	5	$20\bar{3}$			
2·085	S	2·085	21	060	2·085	20	300
		2·085	39	$33\bar{1}$			
2·000	VS	2·000	15	202	1·999	0	118
		1·999	35	$13\bar{3}$			
		1·983	7	061			
1·982	M	1·983	4	$33\bar{2}$	1·983	2	303
		1·983	10	330			
1·798	VF	1·798	5	$26\bar{1}$	1·806	0	220
		1·798	1	$40\bar{1}$	1·798	0	221
					1·791	<1	217
		1·748	<1	331			
1·749	VF	1·747	1	$33\bar{3}$	1·746	0	00, 11
		1·747	1	062	1·747	22	306
		1·690	21	$26\bar{2}$	1·696	9	11, 10
1·690	W	1·690	9	400	1·690	0	224
					1·684	<1	218
1·601	F	1·601	7	004	1·600	2	00, 12
		1·443	6	$40\bar{4}$			
1·443	W	1·443	10	262	1·443	11	228
		1·438	2	114			
		1·313	8	460			
1·313	W	1·313	9	191	1·313	18	414
		1·313	9	$53\bar{3}$			

(a) The fluorescence prevented location of weaker lines in the forward reflection region.
(b) The calculated intensity of these lines are sensitive to the bromine atomic parameters which were not refined.

hedral holes between alternate layers of bromine atoms. The structures differ only in the stacking arrangement of adjacent Br–Br layers along the crystallographic c axis.

The observed and calculated lattice spacings and intensities are shown in Table 1. The calculated data for both the monoclinic and hexagonal structures are included. It can be seen that the true structure is easily identified as the monoclinic. The agreement between the observed and calculated intensities for the monoclinic structure is quite satisfactory. The choice of crystal structure is then considered substantiated and no further estimate of atomic parameters was attempted.

The change in structure near Gd found for the other halides is, therefore, also found for the bromides. Because of our inability to prepare EuBr$_3$, we are unable to determine if the structure of EuBr$_3$ follows the first or second half of the series. Further, a consideration of the molecular volumes of the bromides indicates that, as is observed for the other halides (Asprey, Keenan & Kruse, 1962), there is a large increase in volume that accompanies the change in crystal structure, the value for SmBr$_3$ being 118 (Zachariasen, 1948) and for GdBr$_3$ 143 Å^3. If the rest of the bromides of the second half of the series follows the trend of other halides, they should all possess the GdBr$_3$ structure.

References

ASPREY, L. B., KEENAN, T. K. & KRUSE, F. H. (1964). *Inorg. Chem.* **3**, 1137–1140.
CULLITY, B. D. (1959). *Elements of X-ray Diffraction*, pp. 154–155, Reading: Addison-Wesley.
International Tables for X-ray Crystallography, (1952). Vol. III, pp. 202–206. Birmingham: Kynoch Press.
KETELAAR, J. A. A. (1935). *Z. Kristallogr.* **90**, 237–255.

MOROSIN, B. & NARATH, A. (1964). *J. Chem. Phys.* **40**, 1958–1967.

TAYLOR, M. D. & CARTER, C. P. (1962). *J. Inorg. Nucl. Chem.* **24**, 387–391.

TEMPLETON, D. H. & CARTER, G. F. (1954). *J. Phys. Chem.* **58**, 940–944.

TEMPLETON, D. H. & DAUBEN, G. H. (1954). *J. Amer. Chem. Soc.* **76**, 5237–5239.

WOOSTER, N. (1930). *Z. Kristallogr.* **74**, 363–365.

ZACHARIASEN, W. H. (1948). *Acta Cryst.* **1**, 265–268.

ZALKIN, A. & TEMPLETON, D. H. (1953). *J. Amer. Chem. Soc.* **75**, 2453–2458.

Acta Cryst. (1973). B29, 1743

Refinement of the structure of CuV_2O_6.

By CRISPIN CALVO and DAN MANOLESCU, *Institute for Materials Research, McMaster University, Hamilton, Ontario, Canada*

CuV_2O_6 is triclinic, $C\bar{1}$ (an unconvential setting of $P\bar{1}$), with $a = 9.168$ (5), $b = 3.543$ (3), $c = 6.478$ (7) Å, $\alpha = 92.25$ (8), $\beta = 110.34$ (7), $\gamma = 91.88$ (6)°, $\varrho_{calc} = 4.35$, $\varrho_x = 4.30$ g cm^{-3}. Crystals were grown in an oxygen atmosphere from a melt whose composition corresponded to 0.50 mole % CuO and V_2O_5. The structure is closely related to that of the mineral brannerite, $ThTi_2O_6$ [Ruh, R. & Wadsley, A. D. (1966). *Acta Cryst.* **21**, 974–976] with the symmetry reduced from $C2/m$ because of a Jahn–Teller distortion of the CuO_6 octahedra. The VO_6 octahedra is also distorted with the vanadium ion displaced from the center towards an edge of the polyhedron.

Introduction

The intensities and cell dimensions were obtained from a crystal with average linear dimension of 0.1 mm utilizing a Syntex $P\bar{1}$ automatic diffractometer (Mo $K\alpha$, $\lambda = 0.71069$ Å, graphite-monochromated, θ–2θ scan, scintillation counter with pulse-height discrimination, one check reflexion measured every fifty with backgrounds measured 1° on either side of the peak). 1163 symmetry independent reflexions had a positive intensity, with 1060 above 3σ. Absorption corrections were applied. The systematic absences were hkl with $h + k$ odd. Trial parameters were taken from those reported by Lavaud & Galy (1972) for CuV_2O_6 with apparent $C2$ symmetry, with the Cu ion placed at the center of symmetry at the origin. Full-matrix least-squares refinement with anisotropic thermal parameters and weights chosen so that $\omega(|F_o| - |F_c|)^2$ would be independent of F_o yielded a final R value of 0.047, unobserved reflexions with F_c greater than 3σ included. The final atomic parameters are in Tables 1 and 2. The bond lengths and angles are in Table 3. Observed and calculated structure factors are in Table 4.

Table 1. *Atomic parameters for* CuV_2O_6 *with standard errors in parentheses*

	x	y	z
Cu	0	0	0
V	0.19279 (4)	0.01267 (10)	0.65463 (6)
O(1)	0.0304 (2)	0.0027 (5)	0.7239 (3)
O(2)	0.3426 (2)	0.0482 (6)	0.8896 (3)
O(3)	0.3067 (2)	−0.0028 (5)	0.4316 (3)

Discussion

CuV_2O_6 is one of a series of MV_2O_6 compounds showing nearly identical structures. Some of these, such as ZnV_2O_6

Table 2. *Thermal parameters* ($\times 10^4$) *for* CuV_2O_6 *with standard errors in parentheses*

The $U_{ij} = 2\pi^2 b_i b_j \beta_{ij}$ where the β_{ij} appear in the structure-factor expression as exp $-[h^2\beta_{11} + 2hk\beta_{12} + \dots]$ and the b_i's are reciprocal lattice vectors.

	U_{11} (Å)^2	U_{22} (Å)^2	U_{33} (Å)^2	U_{12} (Å)^2	U_{13} (Å)^2	U_{23} (Å)^2
Cu	97 (2)	103 (2)	67 (2)	0	60 (2)	0
V	64 (2)	42 (2)	51 (2)	15 (1)	46 (1)	5 (1)
O(1)	95 (7)	95 (6)	97 (7)	−0 (5)	79 (5)	−6 (5)
O(2)	103 (7)	114 (7)	79 (7)	7 (5)	38 (5)	7 (5)
O(3)	94 (7)	46 (5)	91 (7)	21 (4)	67 (5)	11 (5)

Table 3. *Interatomic distances and angles in* CuV_2O_6 *with standard errors in parentheses*

Cu–O(1)a, b	1.904 (2) Å	O(1)a–Cu–O(2)c	90.9 (1)°
Cu–O(2)c, d	2.049 (2)	O(1)a–Cu–O(2)c'	87.7 (1)
Cu–O(2)c', d'	2.438 (2)	O(2)c–Cu–O(2)c'	104.0 (1)
V–O(1)b	2.588 (2)	O(1)b–V–O(3)a	76.3 (1)
V–O(3)a	2.056 (2)	O(1)b–V–O(1)a	77.0 (1)
V–O(1)a	1.697 (2)	O(1)b–V–O(2)a	175.6 (1)
V–O(2)a	1.655 (2)	O(1)b–V–O(3)d	80.9 (1)
V–O(3)d	1.871 (2)	O(1)b–V–O(3)d'	76.0 (1)
V–O(3)d'	1.845 (2)	O(3)a–V–O(1)a	153.2 (1)
		O(3)a–V–O(2)a	100.6 (1)
		O(3)a–V–O(3)d	73.8 (1)
		O(3)a–V–O(3)d'	75.4 (1)
		O(1)a–V–O(2)a	106.2 (1)
		O(1)a–V–O(3)d	99.8 (1)
		O(1)a–V–O(3)d'	100.2 (1)
		O(2)a–V–O(3)d	101.5 (1)
		O(2)a–V–O(3)d'	100.2 (1)
		O(3)d–V–O(3)d'	144.9 (1)

Symmetry transforms (except for translations by a unit cell length)

$a = x,y,z$; $b = -x, -y, -z$; $c = \frac{1}{2} + x, \frac{1}{2} + y, z$; $d = \frac{1}{2} - x, \frac{1}{2} - y, -z$.