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**Hartree-Fock-Slater coherent scattering factors for ions\***. By H. P. HANSON and R. F. POHLER, *Department of Physics, The University of Texas, Austin 12, Texas, U.S.A.*

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Coherent scattering factors for 70 different ionic configurations have been calculated from HFS wave functions. The compilation of these results represents an extension of the work reported previously by Hanson, Herman, Lea & Skillman (1964). Form factors have been calculated for the more common ionic configurations of elements in the first three rows of the periodic table, for the 3*d* transition elements, and for Ga<sup>3+</sup>, Ga<sup>+</sup>, Ge<sup>4+</sup>, Ge<sup>2+</sup>, Br<sup>-</sup>, Rb<sup>+</sup>, Mo<sup>+</sup>, Ag<sup>+</sup>, Au<sup>+</sup>, Hg<sup>+</sup>, Tl<sup>3+</sup>, Tl<sup>+</sup>, and U<sup>6+</sup>. The list of these configurations includes essentially all of those ions which are stable within the framework of the HFS model. Thus Cl<sup>-</sup>, O<sup>-</sup>, and S<sup>-</sup> were calculable but not O<sup>2-</sup> or S<sup>2-</sup>.

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However, in view of the recent publication of Dirac-Slater scattering factors for many of these same ions (Cromer & Waber, 1965), the use of journal space for detailed HFS results does not seem justified. Nevertheless, the HFS values have a certain merit and utility; in order that they be generally accessible, they have been placed on file with the American Documentation Institute. Moreover an abridged set of these results may be obtained by writing to the authors.

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**The anti-Th<sub>3</sub>P<sub>4</sub> structure type for rare earth germanides, antimonides and bismuthides.** By D. HOHNKE and E. PARTHÉ, *School of Metallurgical Engineering and Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, Pennsylvania, U.S.A.*

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The Th<sub>3</sub>P<sub>4</sub> structure type was first described by Meisel (1939) and has been found since for numerous lanthanide and actinide compounds. Kripyakevich (1963) has shown that the structure can be represented as an arrangement of polyhedra such as [ThP<sub>8</sub>] or [PTh<sub>6</sub>] where each Th atom is surrounded with 8 P atoms and, conversely, each P atom has 6 nearly octahedral Th neighbors. Most of the early known compounds with the Th<sub>3</sub>P<sub>4</sub> structure are the homologues of Th and P. During the last few years, however, a number of isostructural rare earth sulfides, selenides and tellurides were reported (in certain cases with deviations from the ideal composition R<sub>3</sub>X<sub>4</sub>, where R denotes rare earth element and X the metalloid). (Flahaut, 1965; Holtzberg, Okaya & Stemple, 1965).

The fourteen new rare earth germanides, antimonides and bismuthides which are reported here have the composition R<sub>4</sub>X<sub>3</sub> and crystallize with the anti-Th<sub>3</sub>P<sub>4</sub> structure type. Here the rare earth elements occupy the centers of the distorted octahedra.

The rare earth elements with a stated purity of 99.9% were obtained from the Research Chemicals Division of Nuclear Corporation of America, Phoenix. All compounds were prepared by fusing the components in an arc melting furnace. Appropriate control of the operating conditions assured negligible weight losses. A homogenization annealing was performed on La<sub>4</sub>Ge<sub>3</sub>, but it was subsequently found that this procedure was unnecessary as the arc melted samples were already homogeneous and well crystallized.

All investigated germanides are stable in air, while the antimonides and bismuthides react with the moisture of

the air in varying degrees. To avoid decomposition during the diffraction experiments, those materials were enclosed in quartz capillaries filled with dried ligroin. The experiments were performed with Cu K $\alpha$  or Cr K $\alpha$  radiation.

La<sub>4</sub>Ge<sub>3</sub> gave a cubic diffraction pattern with  $a=9.3563 \pm 0.0004$  Å. The conditions for possible reflections were found to be  $hkl: h+k+l=2n$  only and  $hhl: 2h+l=4n$  only, which lead to the unique space group I43*d* ( $T_d^2$ ). Only a limited number of equipoints are available in this space group, the lowest multiplicity being twelve. Assuming the smallest possible number of formula units per unit cell,  $M=4$ , a theoretical density of 6.17 g.cm<sup>-3</sup> is obtained. The next higher number of formula units which can be accommodated in the space group,  $M=12$ , leads to an unreasonably high density of 18.8 g.cm<sup>-3</sup>. Thus only the 12-fold and one 16-fold equipoint position are available for the positioning of the atoms. A simple geometrical consideration showed that the only reasonable arrangement is:

16 La in 16 (*c*) with  $x \sim \frac{1}{6}$   
12 Ge in 12 (*a*)

Such an arrangement can be called the anti-Th<sub>3</sub>P<sub>4</sub> structure type.

The line intensities of the La<sub>4</sub>Ge<sub>3</sub> diffractometer pattern, obtained from a flat specimen, were measured with a planimeter. Owing to the many coincidences of the 44 measured diffraction lines only 30 could be used for a least-squares analysis of the adjustable parameter  $x$  of the La atoms in 16 (*c*). The least-squares refinement program of Gantzel, Sparks & Trueblood (1961) was used.  $\sum w(F_o - |F_c|)^2$  was

minimized with  $w$ , the weighting factor, unity for all  $F_o$ . Structure factors for permitted  $hkl$  lines too weak to be observed were estimated from a smallest observable intensity. The weighting of these  $F$  values was directly proportional to their magnitude. With a final  $x$  value of  $0.0645 \pm 0.0010$  the residual factor, considering observed together

Table 1. Intensity calculation for  $\text{La}_4\text{Ge}_3$  with anti- $\text{Th}_3\text{P}_4$  structure type.  $\lambda(\text{Cu } K\alpha_1) = 1.54051 \text{ \AA}$

$hkl$	$10^3 \sin^2 \theta_c$	$10^3 \sin^2 \theta_o$	$I_c$	$I_o$		
211	40.7	40.5	7.8	9.8		
220	54.2	54.2	16.3	14.0		
310	67.8	67.7	100.0	100.0		
321	94.9	94.7	57.0	55.0		
400	108.4	108.2	0.2	0.3		
420	135.5	135.4	5.3	5.9		
332	149.1	148.9	8.9	9.1		
422	162.7	162.3	16.2	16.0		
510	176.2	175.9	4.9	32.1		
431					27.2	34.0
521	203.3	203.0	4.8	4.7		
440	216.9	216.7	0.3	0.3		
530	230.4		<0.1	—		
611	257.5	257.6	8.9	19.5		
532					10.6	21.3
620	271.1	270.8	10.0	10.5		
541	284.6	284.3	12.7	12.7		
631	311.8	311.4	3.2	3.5		
444	325.3	324.9	6.4	6.5		
543	338.9	—	<0.1	0.1		
710					<0.1	—
640	352.4	352.1	1.0	1.0		
633	366.0	365.5	2.7	13.4		
721					8.2	16.0
552					2.5	—
642	379.5	379.0	6.6	7.2		
730	393.1	392.6	1.2	1.2		
732	420.2	419.9	2.2	6.1		
651					3.9	7.2
800	433.7	433.4	1.0	1.0		
741	447.3	—	<0.1	—		
653	474.4	474.0	2.6	3.0		
822	488.0	487.5	0.9	4.1		
660					3.2	5.0
743					4.9	—
750					3.8	10.5
831	501.5	501.0	1.8	11.5		
752	528.6	528.3	3.5	3.7		
840	542.2	542.0	0.3	0.3		
910	555.7	—	<0.1	—		
842	569.3	569.0	0.9	1.1		
921	582.8	582.5	5.4	7.4		
761					0.2	8.5
655					1.8	—
664	596.4	596.8	1.3	2.0		
754	610.0	609.4	3.7	10.8		
851					6.4	13.4
930			0.7	—		
932	637.1	636.6	0.9	4.1		
763					3.2	4.4
844	650.6	650.9	0.3	0.3		
941	664.2	—	<0.1	—		
853			<0.1	—		
772	691.3	690.8	0.1	2.3		
1011					2.2	2.5
1020	704.8	704.3	2.0	4.2		
862					2.2	5.1
950	718.4	718.1	3.1	7.0		
943					3.9	8.5
1031					1.1	—
952	745.5	745.0	2.1	4.4		
765					1.2	5.5

Table 1. (cont.)

$hkl$	$10^3 \sin^2 \theta_c$	$10^3 \sin^2 \theta_o$	$I_c$	$I_o$		
871	772.6	—	<0.1	—		
1040	778.2	785.9	0.4	1.3		
864					0.9	1.0
1033	799.7	799.4	1.2	1.7		
961					0.5	2.6
1042	813.3	812.9	5.6	5.5		
1110	826.8	826.5	0.8	12.2		
954					4.3	14.7
873					7.1	—
1051	853.9	853.7	3.1	7.8		
1121					1.7	9.2
963					3.0	—
880	867.5	867.1	8.1	9.6		
1130	881.1	—	<0.1	0.1		
970					<0.1	—
1053					3.5	—
972					0.5	—
1132	908.2	908.1	3.0	9.6		
776					2.6	10.3

with unobserved  $|F|$  values for all non-coinciding reflections, was calculated to be 0.05. An isotropic Debye-Waller temperature coefficient of  $0.5 \text{ \AA}^2$  was used for the calculations. Table 1 shows the agreement between observed and calculated data for  $\text{La}_4\text{Ge}_3$ . The calculated data were obtained from a computer with the use of a Fortran IV program for the intensity calculation of powder patterns by Jeitschko & Parthé (1966). Constants for the analytical expression for the atomic scattering factors are from Moore (1963).

The anti- $\text{Th}_3\text{P}_4$  structure type was also found for  $\text{Pr}_4\text{Ge}_3$  and the following rare earth antimonides and bismuthides:  $\text{La}_4\text{Sb}_3$ ,  $\text{Ce}_4\text{Sb}_3$ ,  $\text{Pr}_4\text{Sb}_3$ ,  $\text{Nd}_4\text{Sb}_3$ ,  $\text{Tb}_4\text{Sb}_3$ ,  $\text{Dy}_4\text{Sb}_3$ ,  $\text{Ho}_4\text{Sb}_3$ , and  $\text{La}_4\text{Bi}_3$ ,  $\text{Ce}_4\text{Bi}_3$ ,  $\text{Pr}_4\text{Bi}_3$ ,  $\text{Nd}_4\text{Bi}_3$ ,  $\text{Gd}_4\text{Bi}_3$ ,  $\text{Tb}_4\text{Bi}_3$ . The lattice parameters of these new phases are given in Table 2 together with data of three isotopic compounds reported earlier by Holtzberg, McGuire, Methfessel & Suits (1964) and Bodnar & Steinfink (1965). All lattice parameters and their probable errors were calculated on the computer with

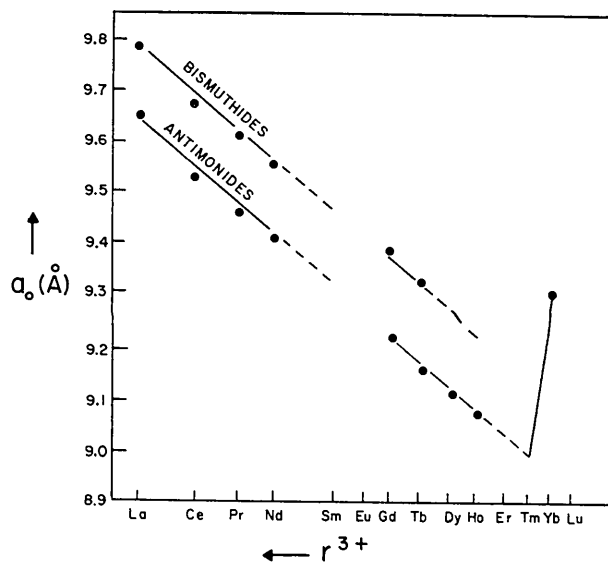


Fig. 1. Lattice constants of rare earth antimonides and bismuthides with anti- $\text{Th}_3\text{P}_4$  structure versus the ionic radius  $r^{3+}$  of the rare earth element.

Table 2. Lattice constants of rare earth germanides, antimonides and bismuthides with anti-Th<sub>3</sub>P<sub>4</sub> structure type

Germanides	
	<i>a</i>
La <sub>4</sub> Ge <sub>3</sub>	9.3563 ± 0.0004 Å
Pr <sub>4</sub> Ge <sub>3</sub>	9.153 ± 0.001
Antimonides	
La <sub>4</sub> Sb <sub>3</sub>	9.648 ± 0.003
Ce <sub>4</sub> Sb <sub>3</sub>	9.528 ± 0.002
Pr <sub>4</sub> Sb <sub>3</sub>	9.458 ± 0.001
Nd <sub>4</sub> Sb <sub>3</sub>	9.406 ± 0.001
Gd <sub>4</sub> Sb <sub>3</sub>	9.224 ± 0.005*
Tb <sub>4</sub> Sb <sub>3</sub>	9.159 ± 0.003
Dy <sub>4</sub> Sb <sub>3</sub>	9.114 ± 0.001
Ho <sub>4</sub> Sb <sub>3</sub>	9.072 ± 0.001
Yb <sub>4</sub> Sb <sub>3</sub>	9.30†
Bismuthides	
La <sub>4</sub> Bi <sub>3</sub>	9.786 ± 0.001
Ce <sub>4</sub> Bi <sub>3</sub>	9.672 ± 0.001
Pr <sub>4</sub> Bi <sub>3</sub>	9.611 ± 0.003
Nd <sub>4</sub> Bi <sub>3</sub>	9.553 ± 0.001
Gd <sub>4</sub> Bi <sub>3</sub>	9.383 ± 0.005*
	9.385 ± 0.002
Tb <sub>4</sub> Bi <sub>3</sub>	9.321 ± 0.001

\* Holtzberg, McGuire, Methfessel & Suits (1964).

† Bodnar & Steinfink (1965).

the Nelson-Riley extrapolation equation and the least-squares program by Gvildys (1965).

Fig. 1 shows a plot of the lattice constants of antimonides and bismuthides versus the trivalent ionic radii of the rare earth elements. All data except for Yb<sub>4</sub>Sb<sub>3</sub> fall essentially on two straight lines, one for antimonides and one for bis-

muthides. The deviation for Yb<sub>4</sub>Sb<sub>3</sub> may be explained by the occurrence of a partly two-valent Yb atom. Data for Eu compounds are missing, but the same deviations may be expected for these.

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**Refinement of the crystal structure of euchroite, Cu<sub>2</sub>(AsO<sub>4</sub>)(OH) · 3H<sub>2</sub>O.** By J.J. FINNEY, *Department of Geological Engineering, Colorado School of Mines, Golden, Colorado, U.S.A.*

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### Introduction

The structure of euchroite was determined by Giuseppetti (1963), using three-dimensional Patterson sections to determine the heavy atom positions, but was completed by means of electron density projections. As part of an overall study of the crystal chemistry of secondary copper minerals a three-dimensional refinement of this structure was considered necessary to portray the structure more accurately and to describe the complex hydrogen bonding which occurs in euchroite.

### Experimental

Dr L.G. Berry kindly provided a few crystals of euchroite (USNM 470456) from the sample used in his original work (Berry, 1951). The crystal fragment used in this refinement had the dimensions 0.25 × 0.20 × 0.30 mm.

Euchroite is orthorhombic, space group *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>. The unit-cell dimensions *a* = 10.063, *b* = 10.522 (both ± 0.010), *c* = 6.107 (± 0.005 Å) were obtained from precession films. The unit-cell contents are Cu<sub>8</sub>(AsO<sub>4</sub>)<sub>4</sub>(OH)<sub>4</sub> · 12H<sub>2</sub>O. The

density based on the above unit cell is calculated as 3.46 compared with the observed density of 3.389 reported by Giuseppetti.

Data were collected by means of multiple film pack equi-inclination Weissenberg photographs about the *a* and *c* axes with the use of Mo (*K*α) radiation. Intensities were estimated visually.

In each case the zero- and first-layer data were collected. Dr Giuseppetti supplied zero and unpublished upper-level data about the *b* axis taken with Cu *K*α radiation.

Both sets of data were corrected for absorption as well as Lorentz-polarization factors and were placed on an approximately equivalent relative scale by comparison of reflections common to the two sets of data. Absolute scaling was accomplished as a normal part of the least-squares refinement.

### Refinement of the structure

The structure was refined with Giuseppetti's atomic positions as a starting point. A full-matrix least-squares program was used in the refinement modified after a program