PREPARATION AND STRUCTURAL INVESTIGATIONS OF ANTI-MONIDES WITH THE LaFe₄ P_{12} STRUCTURE

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(Received January 18, 1980)

Summary

Fourteen compounds LnT_4Sb_{12} ($Ln \equiv La$, Ce, Pr, Nd, Sm, Eu; $T \equiv Fe$, Ru, Os) were prepared for the first time. Their isotypy with $LaFe_4P_{12}$ (filled CoAs₃ structure) is shown by their X-ray powder patterns. $LaFe_4Sb_{12}$ and CeFe₄Sb₁₂ show metallic conductivity. The crystal structure of $LaFe_4Sb_{12}$ was refined from single-crystal counter data to a residual value of 0.046 for 389 independent structure factors. A comparison of the structural data for $LaFe_4Sb_{12}$ with those for the previously determined $LaFe_4P_{12}$ and $LaFe_4As_{12}$ structures shows systematic trends in the positional and thermal parameters. The thermal amplitudes of the lanthanum atoms are highest in $LaFe_4Sb_{12}$, indicating that the polymeric $[Fe_4Sb_{12}]_n$ "framework" is somewhat too large for the lanthanoids. This can also be concluded from an almost non-existent lanthanoid contraction. Systematic trends of the cell volumes suggest that cerium and europium have mixed valencies in most compounds with this structure.

1. Introduction

Recently we reported on ternary phosphides and arsenides with the compositions LnT_4P_{12} and LnT_4As_{12} ($Ln \equiv light lanthanoid; T \equiv Fe, Ru, Os$) which crystallize with the filled skutterudite ($CoAs_3$) structure [1, 2]. The structure was determined and refined for $LaFe_4P_{12}$ and $LaFe_4As_{12}$. We have now prepared the corresponding antimonides and have refined the structure for $LaFe_4Sb_{12}$.

2. Preparation

The ternary antimonides were prepared in a way similar to the corresponding arsenides. The starting materials were the elemental components with stated purities of 99.9% or better. Filings of the lanthanoids were prepared under argon and were annealed with an equiatomic amount of antimony for 2 d at 900 K in evacuated sealed silica ampoules. The resulting products were mostly single-phase LnSb with the NaCl structure. The X-ray powder photographs of the Eu-Sb samples showed the diffraction patterns of Eu₁₁Sb₁₀ [3, 4] and Eu₂Sb₃ [4]. The lanthanoid antimonides were ground together with appropriate amounts of antimony and powdered transition metals. These mixtures were sealed in evacuated silica ampoules which had been annealed under vacuum to eliminate traces of water. The best results were obtained with the overall starting composition Ln:T:Sb = 1:4:20. The samples were quickly heated to 1150 K, were kept at this temperature for 3 h and were then quenched. The excess antimony was removed by treating the product for several minutes with concentrated nitric acid. The oxidation products of antimony were then dissolved in concentrated hydrochloric acid. (The treatment with nitric acid has to be watched because the ternary antimonides are also attacked.) After this procedure the ternary antimonides were about 80% single phase with binary lanthanoid and transition metal antimonides as impurities.

To check for possible contamination with silicon some samples were prepared in closed alumina containers sealed under vacuum in silica tubes. These samples showed the same diffraction lines as those prepared in silica ampoules. The deviations of the lattice constants are within the standard deviations.

3. Cell constants and properties

X-ray powder patterns of the products were recorded with a Guinier camera and α quartz (a = 4.91304 Å, c = 5.40463 Å) as the standard. The lattice constants (Table 1) were refined by least-squares calculations. Samples prepared from various starting compositions and with various heat treatments did not show marked differences in lattice constants. The evaluations of some typical powder patterns are given in Table 2.

The LnT_4Sb_{12} compounds were generally obtained as black sponges. Some small nearly cubic single crystals were also isolated. They were stable in air and could not be dissolved in half-concentrated hydrochloric acid.

For both $LaFe_4Sb_{12}$ and $CeFe_4Sb_{12}$ the electrical conductivity measured with a four-probe technique [6] between liquid helium temperature and room temperature decreased with increasing temperature, thus indicating metallic or semimetallic behaviour.

4. Structure refinement of LaFe₄Sb₁₂

Single crystals of $LaFe_4Sb_{12}$ were investigated with a Buerger precession camera. They showed Laue symmetry m3 and no other systematic extinctions apart from those characteristic of body centring. The structure refinement was carried out in space group Im3, the space group with the highest symmetry compatible with these observations.

TABLE 1

Compound	a (Å)	V (Å ³)	$D_{\rm c}({\rm g\ cm}^{-3})$
LaFe ₄ Sb ₁₂	9.1395(2)	763.4(1)	7.931(1)
CeFe ₄ Sb ₁₂	9.1350(2)	762.3(1)	7.949(1)
PrFe ₄ Sb ₁₂	9.1351(2)	762.3(1)	7.952(1)
LaRu ₄ Sb ₁₂	9.2700(2)	796.6(1)	8.355(1)
CeRu ₄ Sb ₁₂	9.2657(2)	795.5(1)	8.372(1)
PrRu ₄ Sb ₁₂	9.2648(2)	795.3(1)	8.378(1)
NdRu ₄ Sb ₁₂	9.2642(2)	795.1(1)	8,393(1)
EuRu ₄ Sb ₁₂	9.2824(2)	799.8(1)	8.376(1)
LaOs ₄ Sb ₁₂	9.3029(2)	805.1(1)	9.738(1)
CeOs ₄ Sb ₁₂	9.3011(2)	804.6(1)	9.748(1)
PrOs ₄ Sb ₁₂	9.2994(2)	804.2(1)	9.757(1)
NdOs ₄ Sb ₁₂	9.2989(2)	804.1(1)	9.772(1)
SmOs ₄ Sb ₁₂	9.3009(2)	804.6(1)	9.791(1)
$EuOs_4Sb_{12}$	9.3187(2)	809.2(1)	9.742(1)

Cell dimensions and calculated densities of $LaFe_4P_{12}$ -type antimonides

The standard deviations (given in parentheses for the least significant digits) obtained in the least-squares refinements do not reflect possible homogeneity ranges.

The single crystal used for the collection of the intensity data was approximately cubic with overall dimensions of 60 μ m × 50 μ m × 50 μ m. For the absorption correction it was approximated by a sphere with the same volume ($\mu_{Mo K\alpha} = 256 \text{ cm}^{-1}$; $\mu R = 0.8$). An automated four-circle diffractometer was used with graphite-monochromated Mo K α radiation, a scintillation counter and a pulse height discriminator. $\theta - 2\theta$ scans were taken up to 80° in 2 θ with a speed of 0.07° s⁻¹ in 2 θ and a scan angle of $\theta = 1.2 + 0.2 \times \sin \theta$. The background was counted at both ends of each scan for half the time taken for the measurement of the reflection itself. Equivalent reflections were averaged.

The structure was refined by a full matrix least-squares program [7] with lanthanum, iron and antimony in the positions 2(a), 8(c) and 24(g) respectively of space group Im3. The initial starting parameters for the antimony positions were assumed to be the same as those obtained for the phosphorus positions in LaFe₄P₁₂ [1]. Scattering factors for neutral atoms were used [8], corrected for anomalous dispersion [9]. The weighting scheme was according to counting statistics. An isotropic extinction parameter x refined to 2.44×10^{-7} where F_c is multiplied by $1 - x |F_c|^2/\sin \theta$.

The final R value is 0.046 for 389 structure factors, excluding those which were lower than six standard deviations and eight reflections which were strongly affected by secondary extinction. For all 458 unique structure factors the R value is 0.060. A final difference Fourier synthesis resulted in no peaks higher than +4.0 or lower than -3.8 electrons A^{-3} . The highest

TABLE 2

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220	958	I	1	T	932	932	7	₿	925	925	29	E
310) 130	1198	1198	1001	VS	1165	1165	1001	VB	1156	1156	1001	SV
222	1438	1	-	í	1398	I		I	1388	1388	2	M
231	1677	1678	44) 2	60	1631	1632	44 2	60	1619	1619	44 2	60
400	1917	ı		I	1864	1862	61	M.	1850	1850	7	M
411) 330 ⁵	2157	2156	 	₿	2097	2097	<u> </u>	₿	2081	2078	- 4	₿
420	2396	2395		E	2330	2330	14 14	E	2313	2315	28 28	8
332	2636	2636	9	₿	2563	I	9	₿	2544	1	9	W
422	2875	2876	21	8	2796	2797	34	60	2775	2774	62	60
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The patterns were recorded with a Guinier camera and Cu K $^{\alpha}$ radiation. The Q values are defined by Q = 10⁴/d² (Å⁻²). The calculated pattern was generated by a computer program [5] assuming the positional parameters of the antimony atoms to be as determined in the single-crystal study of LaFe₄Sb₁₂.

peaks were at or close to the sites of the atoms and there were no indications of occupancy of interstitial sites by impurity atoms. The final parameters are given in Table 3. A list of the observed and calculated structure factors is available from the authors on request. Table 4 lists the interatomic distances and selected interatomic angles.

The thermal parameters of the lanthanum atoms are relatively large and we considered the possibility of partial occupancy of the lanthanum position. We therefore refined the occupancy factor of this position in several leastsquares cycles by allowing for a simultaneous variation of the correlated thermal parameter. The resulting occupancy factor was $93.9 \pm 1.3\%$ and the thermal parameter *B* was 1.10 ± 0.05 Å². Since the lanthanum position has very high symmetry, experimental errors in the data strongly affect it and standard deviations are therefore usually underestimated. Nevertheless, there is a slight indication of some defects in this position. The thermal parameters of the lanthanum atoms, however, still remain high compared with those of the other atoms.

5. Discussion

The structure of the LaFe₄P₁₂-type compounds can be regarded as a filled skutterudite (CoAs₃) type which exists in the systems formed by the transition metals $T \equiv Co$, Rh, Ir with the pnicogens $Pn \equiv P$, As, Sb [10, 11]. The structure of skutterudite can be derived from that of ReO₃ by doubling

	La	Fe	Sb
Im3	2(a)	8(c)	24(g)
<i>x</i>	0	1/4	0
У	0	1/4	0.33696(6)
z	0	1/4	0.16042(5)
U ₁₁	0.0165(4)	0.0031(2)	0.0024(2)
$U_{22}^{}$	U ₁₁	U ₁₁	0.0057(2)
$U_{33}^{}$	$U_{11}^{}$	$U_{11}^{}$	0.0039(2)
U_{12}	0	0.0004(3)	0
U_{13}^{-}	0	U ₁₂	0
$U_{23}^{}$	0	$U_{12}^{}$	0.0007(1)
B	1.30(4)	$0.\overline{24}(2)$	0.32(2)
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TABLE 3

Positional and thermal parameters of LaFe₄Sb₁₂

The standard deviations of the least significant digits are given in parentheses. The ellipsoidal thermal parameters are defined by

 $T = \exp \left\{-2\pi^2 (U_{11}h^2a^{*2} + \ldots + 2U_{12}hka^{*}b^{*} + \ldots)\right\}$

and the equivalent isotropic parameters B are in square angströms.

Atom	Interator	nic distances	Interatomic angles			
La	12 Sb	3.411	Sb-Fe-Sb	180.0 (3×)		
Fe	6 Sb	2.554	Sb-Fe-Sb	84.8 (6×)		
\mathbf{Sb}	2 Fe	2.554	Sb-Fe-Sb	95.2 (6×)		
	1 Sb	2.932	Sb'-Sb-Sb"	90.0 (1×)		
	1 Sb	2.980	Fe-Sb-Fe	126.9 (1×)		
	1 La	3.411	Fe-Sb-Sb'	108.7 (2×)		
	4 Sb	3.443	Fe-Sb-Sb"	108.1 (2×)		

Interatomic distances (Å)	and selected interatomic	angles	(°)) in	LaFe ₄ SI	b ₁₂
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All distances shorter than 3.5 Å are listed. The standard deviations are all less than 0.002 Å for the distances and 0.1° for the angles.

the cell edge and tilting the corner-shared ReO_6 octahedra. This tilting results in a bonding approach of the pnicogen atoms which thereby form nearly quadratic rings. Moreover this procedure creates large voids which are empty in the binary skutterudites but filled with lanthanoid atoms in the LaFe₄P₁₂type compounds. The LaFe₄P₁₂ structure is also related to the structure of WAl₁₂ [12, 13] in which the octahedra which contain the iron atoms in LaFe₄P₁₂ are empty.

The tilting of the octahedra is described by the (only) two positional parameters of these structures. Only small changes in these parameters are required to go from a coordination number of 4 for the phosphorus atoms in the phosphides to a coordination number of 11 for the aluminium atoms in WAl₁₂ (Fig. 1). The gradual changes in the positional parameters towards higher coordination number of the pnicogen atoms in the sequence TP_3 , TAs_3 , TSb_3 is paralleled in the ternary compounds. Thus the differences in the Pn-Pn distances of the first (the average of the two shortest Pn-Pn distances) and second (the next four shortest Pn-Pn distances) coordination sphere become smaller. The ratios of these radii of the first and the second coordination sphere diminish from 1.28 to 1.22 to 1.16 in LaFe₄P₁₂, LaFe₄As₁₂ and LaFe₄Sb₁₂ respectively. Not only these ratios but also the absolute differences in the sphere radii decrease (0.65, 0.57 and 0.49 Å for the phosphide, arsenide and antimonide respectively) even though the atomic size increases from phosphorus to antimony.

This gradual change from low coordination with localized bonding in the phosphides to high coordination with delocalized bonding in the antimonides is reflected in the electrical conductivity. CoP_3 is a semiconductor with an optical band gap of 0.45 eV whereas $CoAs_3$ and $CoSb_3$ are semimetallic or metallic with increasing resistivity with temperature [17]. It is therefore not suprising that the conductivity of the ternary antimonides $LaFe_4Sb_{12}$ and $CeFe_4Sb_{12}$ also shows metallic behaviour. Nevertheless care must be taken in interpreting these measurements since deviations from the nominal compositions may also cause this behaviour.

TABLE 4



Fig. 1. Positional parameters for compounds with the LaFe₄P₁₂ and related structures. It can be seen that an ideal octahedral environment for the iron atoms, an ideal icosahedral environment for the lanthanum atoms and equal short P-P distances (Oftedal's relation) cannot be obtained simultaneously. In addition to the compounds discussed in the text the plot contains data for Sc(OH)₃ [14] and CaCu₃Mn₄O₁₂ [15] which recently have been recognized [16] as topologically related to skutterudite.

The positional parameters of the antimony atoms in $LaFe_4Sb_{12}$ fall on the same side of Oftedal's line (defined by $y + z = \frac{1}{2}$, the condition for equal Pn-Pn distances in the Pn₄ groups) as the parameters of the binary skutterudites. This means that the shortest Pn-Pn distances in $LaFe_4Sb_{12}$ and in the TPn₃ compounds correspond to each other but do not correspond to the shortest P-P and As-As distances in $LaFe_4P_{12}$ and $LaFe_4As_{12}$.

The voids which contain the lanthanoid atoms become smaller when the free parameters y and z become equal. Therefore these voids are (compared with the lattice constants) smallest in the antimonides with the LaFe₄P₁₂ structure. Nevertheless, because the antimonides also have the largest lattice constants (*i.e.* the largest polymeric $[Fe_4Pn_{12}]_n$ "framework"), the absolute space available for the lanthanoid atoms is greatest in the antimonides. This is supported by three observations: the high thermal parameter of the lanthanoid num atoms in LaFe₄Sb₁₂, the relatively large La–Sb distances and the almost non-existent lanthanoid contraction in the antimonides.

The absolute values of the thermal parameters obtained in X-ray structure determinations are not very reliable and are usually in error by much more than their standard deviations because they reflect systematic errors, the most frequent and serious of which is the missing or oversimplified absorption correction. The relative values, however, are much more meaningful. In our earlier structure refinements of $LaFe_4P_{12}$ and $LaFe_4As_{12}$ [1, 2] the thermal parameters of the iron atoms are practically the same as those found for the iron atoms in the present investigation. The thermal parameters of the pnicogens are also very similar. For the lanthanum atoms, however, the *B* values increase from 0.40 Å² in LaFe₄P₁₂ through 0.61 Å² in LaFe₄As₁₂ to 1.30 Å² in LaFe₄Sb₁₂ (as discussed earlier, the last value might be slightly lower). This large thermal amplitude of the lanthanum atom in the antimonide is an indication of a flat minimum in the spatial configuration of the potential energy; *i.e.* the lanthanum atoms seem to "rattle" or (in a more sophisticated and somewhat different model) they may participate in a " "soft" lattice mode [18 - 20]. It seems possible that at lower temperatures the LaFe₄P₁₂-type antimonides transform by a displacive phase transition to a crystal structure of lower symmetry.

A comparison of the La–Sb distances in $LaFe_4Sb_{12}$ with the corresponding distances in binary lanthanum antimonides is difficult because the crystal structures of most binary lanthanum antimonides have not been refined. Furthermore we have to consider the differences in coordination numbers. In $LaFe_4Sb_{12}$ the lanthanum atoms are surrounded by 12 antimony atoms at 3.41 Å. This is the highest coordination towards antimony found for lanthanum in any lanthanum antimonide and it is also the longest La–Sb bonding distance*. The La-As distances in LaFe₄As₁₂ are 3.152 Å [2]. If we add to this the difference of 0.175 Å between the near-neighbour La-Pn interactions in LaAs [24] and LaSb we obtain 3.327 Å. Thus is seems that the cage for the lanthanum atoms formed by the 12 antimony atoms in $LaFe_4Sb_{12}$ is about 0.17 Å greater in diameter than the optimal coordination sphere. The Fe–Sb distance of 2.554 Å in $LaFe_4Sb_{12}$ compares rather well with the corresponding distances of 2.575 and 2.598 Å in $FeSb_2$ [26]. The Sb–Sb distances of 2.932 and 2.980 Å in LaFe₄Sb₁₂ are somewhat longer than normal two-electron bonding distances. For instance, the Sb-Sb distances in CrSb₂, FeSb₂, NiSb₂, RuSb₂ and OsSb₂ cover the range from 2.84 to 2.89 Å [26]. The binary skutterudite $CoSb_3$ shows a similar elongation; there the Sb–Sb distances are 2.891 and 2.982 Å [11]. We have previously suggested that this elongation of the Pn-Pn bonds may be due to the filling of antibonding Pn-Pn states [2].

The most important argument for the unusual bonding situation of the lanthanoid atoms can be seen in the fact that the $LaFe_4P_{12}$ -type antimonides show almost no lanthanoid contraction (Fig. 2). This is particularly true for the osmium-containing antimonides: the difference in the cell volumes of $LaFe_4P_{12}$ and $NdFe_4P_{12}$ is 4.3 Å³ while it is only 1.0 Å³ for $LaOs_4Sb_{12}$ and $NdOs_4Sb_{12}$. EuRu₄Sb₁₂ and EuOs₄Sb₁₂ in which europium is obviously divalent have larger cell volumes than the corresponding lanthanum antimonides. In the corresponding phosphides the cell volumes of the lanthanum compounds are higher. The cerium atoms seem to be essentially trivalent in

^{*}References for the binary compounds are as follows: La₂Sb [21], La₅Sb₃ [22], La₄Sb₃ [23], LaSb [24], LaSb₂ [25].



Fig. 2. Cell volumes of $LaFe_4P_{12}$ -type compounds. The broken lines indicate the volume decreases expected from the LnP compounds with the NaCl-type structure [24].

the antimonides; in the phosphides and arsenides the cell volumes indicate cerium to be tetravalent or at least partially so. In the antimonides tetravalent cerium is apparently too small to form a stable filled skutterudite-type compound.

Acknowledgments

This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. We wish to thank Professor Dr. C. Heiden and Dipl. Ing. U. Krieger, Institut für Angewandte Physik, Universität Giessen, for the conductivity measurements and Dr. M. Jansen, Institut für Anorganische und Analytische Chemie, Universität Giessen, for collection of the single-crystal X-ray data.

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