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Ternary Arsenides with $LaFe_4P_{12}$-Type Structure

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Ten new ternary arsenides with composition LnT_4As_{12} (Ln = rare earth element, T = Fe, Ru, or Os) were synthesized by reaction of the elemental components in silica ampoules. Their X-ray powder patterns show them to crystallize with the $LaFe_4P_{12}$-type structure. Their lattice constants are reported. The crystal structure of $LaFe_4As_{12}$ was refined from single-crystal X-ray counter data to a conventional R value of 0.039 for 312 independent reflections. While the La–As and Fe–As distances are considered normal, the As–As distances of 2.57 and 2.58 Å are found to be unusually large, as compared to distances of other two-electron As–As bonds. It is suggested that this is due to filling of As–As antibonding states.

Introduction

The skutterudite ($CoAs_3$)-type structure occurs for all nine combinations of the metals Co, Rh, and Ir with the pnicogens P, As, and Sb (*1*). Recently we reported (*2*) on a series of isostructural compounds with composition LnT_4P_{12} (Ln = lanthanoid, T = Fe, Ru, and Os) and determined their structure from single-crystal data of $LaFe_4P_{12}$. It derives from the skutterudite-type structure by filling the Ln atoms in large voids formed by the pnicogens of the binary compounds. In the present paper we report on the corresponding ternary arsenides.

Sample Preparation

Starting materials were ingots of the rare earth metals (all of stated purities greater than 99.9%), powders of Fe, Ru, Os (>99.9%), and As (>99.5%). Filings of the rare earth metals were prepared and stored under argon. The As powder was kept at 510 K for several days under vacuum to drive off the As_2O_3. After no further As_2O_3 was sublimated, the elemental arsenic was purified by sublimation in a temperature gradient from 920 to 680 K under vacuum.

The coarse filings of the lanthanoids are not well suited for the preparation of the ternary compounds by reaction of the components at relatively low temperatures. Therefore rare earth arsenides with overall composition LnAs were prepared first by reaction of the elements components in sealed silica tubes, which were kept at 900 K for 2 days. The resulting sponges of the arsenides were ground under Ar together with the transition metals and As, and sealed again in evacuated silica tubes which, prior to filling, were annealed under vacuum to eliminate traces of water. The best results were obtained with the overall compositions $Ln:T:As = 1:4:20$ which were rapidly heated to 1150 K and kept at this temperature for 3 hr. Then the samples were annealed at 1000 K for 4 to 7 days.

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Thereafter the excess As was sublimated by keeping the hot end of the silica tubes at 900 K and the cold end at about 700 K. After that the samples were furnace cooled. X-Ray powder photographs showed them to be about 70 to 90% single phase with binary lanthanoid and transition metal arsenides as major impurities.

Apparently the ternary LnT_4As_{12} compounds become thermodynamically instable for the smaller lanthanoid components. Thus we were not successful in preparing the Nd compounds by this procedure. $NdOs_4As_{12}$ was prepared as described above, except that the samples were rapidly quenched after the heat treatment at 1000 K. However, the corresponding Nd–Fe and Nd–Ru arsenides were not obtained by this procedure either. To ensure that a possible contamination with silicon is not essential for the stability of these ternary arsenides, several compositions were successfully prepared in closed alumina containers sealed under vacuum in silica tubes.

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 standard. Lattice constants (Table I) were refined by least-squares calculations. In several cases the samples were prepared from different starting compositions and with different heat treatments. In all cases the resulting lattice parameters differed by no more than two standard deviations and no indications for extended homogeneity ranges were found. The evaluations of some typical powder patterns are given in Table II.

The $LaFe_4P_{12}$-type arsenides were obtained in the form of black sponges which could easily be ground to powders. They are stable in air and not dissolved in moderately diluted (1 : 1) hydrochloric acid.

TABLE I

CELL DIMENSIONS AND CALCULATED DENSITIES OF $LaFe_4P_{12}$-TYPE ARSENIDES[a]

	a (Å)	V (Å^3)	D_c (g cm^{-3})
$LaFe_4As_{12}$	8.3252(3)	577.0(1)	7.26
$CeFe_4As_{12}$	8.2959(4)	570.9(1)	7.34
$PrFe_4As_{12}$	8.3125(3)	574.4(1)	7.30
$LaRu_4As_{12}$	8.5081(3)	615.9(1)	7.77
$CeRu_4As_{12}$	8.4908(3)	612.1(1)	7.83
$PrRu_4As_{12}$	8.4963(3)	613.3(1)	7.82
$LaOs_4As_{12}$	8.5437(2)	623.6(1)	9.57
$CeOs_4As_{12}$	8.5249(3)	619.5(1)	9.64
$PrOs_4As_{12}$	8.5311(3)	620.9(1)	9.62
$NdOs_4As_{12}$	8.5291(2)	620.4(1)	9.65

[a] Standard deviations (given in parentheses for the least significant digits) obtained in the least-square refinements do not reflect possible homogeneity ranges

Structure Refinement of $LaFe_4As_{12}$

A single crystal of $LaFe_4As_{12}$ was isolated from a sample prepared as described above It had overall extensions of about 70 × 70 × 85 μm and was — for the purpose of the absorption correction — approximated by a sphere ($\mu MoK_\alpha = 415$ cm^{-1}; $\mu R = 1.9$) Diffractometer data were collected with an automated four-circle instrument with graphite-monochromatized MoK_α radiation, a scintillation counter, and a pulse-height discriminator. Omega scans were taken for all reflections within one octant of reciprocal space up to $2\theta = 84°$. The scan width was 1.2° and background counts were taken at both ends of the scans. Equivalen reflections were averaged.

The structure was refined (*4*) in space group *Im*3 with La, Fe, and As in the positions 2(*a*), 8(*c*), and 24(*g*), respectively. The initial free parameters for the As position were taken as obtained for the P positions in $LaFe_4P_{12}$ (*2*). Scattering factors for neutra atoms were used (*5*), corrected fo anomalous dispersion (*6*). An isotropi extinction parameter was refined as a least

TABLE II

TYPICAL POWDER PATTERNS OF ARSENIDES WITH $LaFe_4P_{12}$-TYPE STRUCTURE[a]

	$PrFe_4As_{12}$				$PrRu_4As_{12}$				$PrOs_4As_{12}$			
hkl	Q_c	Q_o	I_c	I_o	Q_c	Q_o	I_c	I_o	Q_c	Q_o	I_c	I_o
110	289	289	2	vw	277	-	2	vw	275	-	2	vw
200	579	-	<1	-	554	554	11	m	550	550	56	s
211	868	868	1	vw	831	-	1	-	824	-	1	-
220	1158	1159	8	w	1108	1109	33	s	1099	1100	89	vs
310 130	1447	1448	5 100	vs	1385	1384	5 100	vs	1374	1373	4 89	vs
222	1737	-	<1	-	1662	1664	2	vw	1649	1649	16	w
231 321	2026	2026	47 4	s	1939	1940	47 4	s	1924	1924	42 3	s
400	2316	2314	2	vw	2216	2216	8	w	2198	2197	20	m
411 330	2605	2605	<1 2	vw	2494	2494	<1 2	vw	2473	-	<1 2	-
420 240	2894	2896	7 7	m	2771	2771	18 19	s	2748	2748	40 40	vs
332	3184	3184	3	w	3048	3047	3	vw	3023	-	2	-
422	3473	3474	31	s	3325	3324	57	vs	3298	3297	100	vs
341 510 150 431	3763	3764	<1 <1 3 37	s	3602	3602	<1 <1 3 37	s	3572	3573	<1 <1 2 33	s
251 521	4342	4342	2 <1	w	4156	4155	2 <1	vw	4122	4121	2 <1	vw
440	4631	-	<1	-	4433	4434	3	w	4397	4397	10	w
530 350 433	4921	4919	8 <1 2	w	4710	4709	8 <1 2	w	4672	4672	7 1 4	w
442 600	5210	5209	4 9	m	4987	4987	<1 5	w	4946	4948	<1 2	w

[a] The patterns were recorded with a Guinier camera and Cu*K*α radiation. The Q values are defined by $Q = 10^4/d^2\ [\text{Å}^{-2}]$. The calculated pattern was generated by a computer program (*3*) assuming positional parameters of the As atoms as determined in the single-crystal study of $LaFe_4As_{12}$.

squares parameter. Ten reflections which were strongly affected by secondary extinction were not included in the last cycles of the refinements. Similarly very weak reflections with $F_0 < 6\sigma$ were excluded. Their observed structure factors were usually greater than their calculated structure factors, since they were affected by Laue streaks of neighboring reflections, which were not completely suppressed by the graphite monochromator. The final conventional R value is 0.039 for the 312 reflections with nonzero weight. For the total of 429 reflections (Table III) R equals 0.061. A final difference Fourier map showed no features higher than 2.9 e Å^{-3} or lower than −3.7 e Å^{-3}. Final parameters are listed in Table IV, interatomic distances and angles in Table V.

Discussion

The $LaFe_4P_{12}$-type structure (Fig. 1) consists of FeP_6 octahedra which share all corners with adjacent octahedra and thus the Fe : P ratio is 1 : 3. The octahedra are rotated in such a way that for every four octahedra one large void is formed which is empty in the binary skutterudite-type compounds and filled by the lanthanoid atoms in the ternary compounds.

TABLE III

OBSERVED AND CALCULATED STRUCTURE FACTORS[a]

H	K	L	FO	FC
0	0	2	29	-22
1	1	2	25	24
0	2	2	128	128
2	2	2	11	8
0	1	3	322	302 ••
1	0	3	116	-116
1	2	3	253	266 ••
2	1	3	78	81
0	3	3	98	-98
2	3	3	94	-95
0	0	4	131	138
0	2	4	190	-208
1	1	4	21	19
1	3	4	25	-28
2	0	4	197	-206
2	2	4	276	292 ••
3	1	4	298	318 ••
3	3	4	88	-86
0	4	4	38	38
2	4	4	122	118
4	4	4	351	356 ••
0	1	5	124	129
0	3	5	87	-90
1	0	5	22	-14
1	2	5	79	82
1	4	5	97	96
2	1	5	32	29
2	3	5	140	148
3	0	5	236	255
3	2	5	32	22
3	4	5	41	-41
4	1	5	13	3 •
4	3	5	193	193
0	5	5	57	58
2	5	5	55	54
4	5	5	52	49
0	0	6	319	344 ••
0	2	6	193	202
0	4	6	112	-115
1	1	6	19	14
1	3	6	300	317
1	5	6	96	93
2	0	6	198	203
2	2	6	124	-125
2	4	6	54	55
3	1	6	63	-62
3	3	6	80	-75
3	5	6	58	-56
4	0	6	115	-114
4	2	6	61	57
4	4	6	137	-136
5	1	6	9	-7 •
5	3	6	190	190
5	5	6	48	45
0	6	6	373	405 ••
2	6	6	18	-18
4	6	6	69	67
6	6	6	209	206
0	1	7	56	-55
0	3	7	80	-82
0	5	7	52	-54
1	0	7	33	31
1	2	7	30	-26
1	4	7	41	-39
1	6	7	21	21
2	1	7	13	5 •
2	3	7	240	244
2	5	7	66	66
3	0	7	349	374 ••
3	2	7	80	78
3	4	7	17	-12 •
3	6	7	295	300 ••
4	1	7	27	18
4	3	7	296	301 ••
4	5	7	92	90
5	0	7	123	122
5	2	7	9	2 •
5	4	7	33	-28
5	6	7	93	92
6	1	7	43	-41
6	3	7	46	-48
6	5	7	38	-36
0	7	7	37	-37
2	7	7	39	-35
4	7	7	32	-33
6	7	7	39	-31
0	0	8	266	283
0	2	8	78	-77
0	4	8	53	50
0	6	8	78	80
1	1	8	16	13 •
1	3	8	135	132
1	5	8	42	40
1	7	8	19	-9 •
2	0	8	80	-79
2	2	8	145	145
2	4	8	15	-14 •
2	6	8	87	85
3	1	8	103	101
3	3	8	64	-65
3	5	8	48	47
3	7	8	104	102
4	0	8	46	46
4	2	8	18	-14 •
4	4	8	165	163
4	6	8	92	-92
5	1	8	38	34
5	3	8	71	68
5	5	8	42	38
5	7	8	29	21
6	0	8	84	79
6	2	8	90	87
6	4	8	90	-89
6	6	8	183	180
7	1	8	16	-5 •
7	3	8	128	130
7	5	8	34	29
7	7	8	27	-25
0	8	8	113	117
2	8	8	35	-35
4	8	8	84	86
6	8	8	23	-15 •
8	8	8	88	80
0	1	9	232	245
0	3	9	60	-62
0	5	9	139	143
0	7	9	227	237
1	0	9	66	-59
1	2	9	148	149
1	4	9	187	191
1	6	9	33	-34
1	8	9	59	60
2	1	9	44	41
2	3	9	31	-29
2	5	9	26	18 •
2	7	9	50	43
3	0	9	21	-15 •
3	2	9	48	-45
3	4	9	51	-49
3	6	9	21	-14 •
3	8	9	28	-27
4	1	9	16	-14 •
4	3	9	27	-19
4	5	9	24	-15 •
4	7	9	11	-10 •
5	0	9	39	-40
5	2	9	83	84
5	4	9	110	111
5	6	9	29	-25
5	8	9	34	31
6	1	9	189	190
6	3	9	50	-49
6	5	9	112	111
6	7	9	191	189
7	0	9	54	-52
7	2	9	145	145
7	4	9	190	186
7	6	9	39	-31
7	8	9	67	62
8	1	9	79	79
8	3	9	33	-30
8	5	9	41	44
8	7	9	81	82
0	9	9	21	-15 •
2	9	9	21	-14 •
4	9	9	15	-12 •
6	9	9	14	-13 •
8	9	9	20	-12 •
0	0	10	117	-124
0	2	10	19	16 •
0	4	10	120	-124
0	6	10	19	22 •
0	8	10	99	-100
1	1	10	12	9 •
1	3	10	49	-49
1	5	10	9	-8 •
1	7	10	18	16 •
1	9	10	22	-30 •
2	0	10	22	17 •
2	2	10	53	52
2	4	10	218	224
2	6	10	99	-97
2	8	10	101	105
3	1	10	230	234
3	3	10	49	-51
3	5	10	137	140
3	7	10	226	230
3	9	10	18	-10 •
4	0	10	125	-124
4	2	10	223	224
4	4	10	143	142
4	6	10	27	28 •
4	8	10	14	14 •
5	1	10	66	66
5	3	10	40	-46
5	5	10	36	31
5	7	10	72	70
5	9	10	32	-24
6	0	10	20	21 •
6	2	10	96	-99
6	4	10	27	28 •
6	6	10	92	-92
6	8	10	28	23 •
7	1	10	29	-30
7	3	10	35	-38
7	5	10	34	-30
7	7	10	32	-23
7	9	10	35	-28
8	0	10	92	-97
8	2	10	104	105
8	4	10	16	14 •
8	6	10	34	25
8	8	10	43	-35
9	1	10	144	148
9	3	10	44	-36
9	5	10	91	89
9	7	10	156	154
9	9	10	19	-10 •
0	10	10	19	14 •
2	10	10	79	77
4	10	10	212	214
6	10	10	68	-72
8	10	10	102	106
0	1	11	126	134
0	3	11	49	-49
0	5	11	74	76
0	7	11	131	135
0	9	11	21	-19
1	0	11	30	-26
1	2	11	84	82
1	4	11	104	103
1	6	11	15	-15 •
1	8	11	40	37
1	10	11	80	84
2	1	11	31	23
2	3	11	32	32
2	5	11	28	23
2	7	11	23	16 •
2	9	11	26	21 •
3	0	11	71	70
3	2	11	20	-13 •
3	4	11	36	-33
3	6	11	55	54
3	8	11	19	11 •
3	10	11	38	-33
4	1	11	10	-6 •
4	3	11	53	51
4	5	11	14	9 •
4	7	11	18	-15 •
4	9	11	41	32
5	0	11	8	3 •
5	2	11	50	50
5	4	11	41	60
5	6	11	10	5 •
5	8	11	33	27
5	10	11	54	48
6	1	11	104	106
6	3	11	40	-35
6	5	11	63	61
6	7	11	110	110
6	9	11	25	-14 •
7	0	11	33	-37
7	2	11	82	80
7	4	11	106	105
7	6	11	32	-25
7	8	11	38	34
8	1	11	45	44
8	3	11	11	3 •
8	5	11	39	30
8	7	11	48	43
9	0	11	43	41
9	2	11	6	-2 •
9	4	11	18	-13 •
9	6	11	39	33
10	1	11	19	-16 •
10	3	11	44	45
10	5	11	19	2 •
0	11	11	29	20 •
2	11	11	24	18 •
4	11	11	18	17 •
0	0	12	252	272
0	2	12	31	-27
0	4	12	43	44
0	6	12	115	118
0	8	12	118	124
0	10	12	72	-78
1	1	12	12	7 •
1	3	12	146	149
1	5	12	41	43
1	7	12	19	-19 •
1	9	12	95	98
2	0	12	17	-25 •
2	2	12	72	69
2	4	12	59	-57
2	6	12	79	83
2	8	12	37	-37
2	10	12	44	44
3	1	12	6	3 •
3	3	12	42	-41
3	5	12	11	-8 •
3	7	12	14	9 •
3	9	12	35	-28
4	0	12	46	46
4	2	12	54	-56
4	4	12	62	60
4	6	12	65	-64
4	8	12	53	48
4	10	12	42	-43
5	1	12	6	5 •
5	3	12	86	87
5	5	12	33	26
5	7	12	14	-11 •
5	9	12	58	57
6	0	12	114	118
6	2	12	84	82
6	4	12	66	-65
6	6	12	185	190
6	8	12	19	13 •
7	1	12	11	6 •
7	3	12	156	153
7	5	12	47	44
7	7	12	22	-21
8	0	12	122	125
8	2	12	41	-38
8	4	12	48	46
8	6	12	19	14 •
9	1	12	16	3 •
9	3	12	8	-12 •
9	5	12	15	-3 •
10	0	12	73	-77
10	2	12	46	45
10	4	12	41	-42
0	1	13	39	-42
0	3	13	41	-44
0	5	13	42	-38
0	7	13	32	-35
0	9	13	45	-35
1	0	13	20	19 •
1	2	13	18	-22 •
1	4	13	33	-32
1	6	13	18	14 •
1	8	13	16	-7 •
2	1	13	12	2 •
2	3	13	144	145
2	5	13	42	38
2	7	13	33	-25
2	9	13	97	97
3	0	13	222	233
3	2	13	39	46
3	4	13	11	-6 •
3	6	13	191	192
3	8	13	87	86
4	1	13	18	11 •
4	3	13	183	186
4	5	13	55	55
4	7	13	26	-22 •
5	0	13	70	74
5	2	13	11	-4 •
5	4	13	28	-23
5	6	13	60	59
5	8	13	20	17 •
6	1	13	39	-34
6	3	13	32	-26
6	5	13	35	-29
6	7	13	35	-31
7	0	13	23	-21 •
7	2	13	31	-29 •
7	4	13	42	-31
7	6	13	28	-20 •
8	1	13	13	-11 •
8	3	13	68	67
8	5	13	14	11 •
9	0	13	154	160
9	2	13	32	29
0	0	14	97	108
0	2	14	76	77
0	4	14	51	-62
0	6	14	168	180
0	8	14	29	9 •
1	1	14	13	7 •
1	3	14	110	110
1	5	14	41	32
1	7	14	11	-13 •
2	0	14	74	75
2	2	14	46	-41
2	4	14	57	58
2	6	14	39	-30
2	8	14	53	56
3	1	14	17	12 •
3	3	14	35	-36
3	5	14	14	-3 •
3	7	14	18	17 •
4	0	14	66	-65
4	2	14	62	58
4	4	14	39	-36
4	6	14	39	36
5	1	14	16	8 •
5	3	14	66	65
5	5	14	26	22 •
6	0	14	169	179
6	2	14	28	-28 •
6	4	14	39	39
7	1	14	19	4 •
7	3	14	119	118
8	0	14	11	8 •
8	2	14	58	56
0	1	15	88	96
0	3	15	36	-35
0	5	15	55	55
1	0	15	30	-22
1	2	15	56	58
1	4	15	73	77
1	6	15	13	-14 •
2	1	15	14	17 •
2	3	15	20	12 •
2	5	15	25	14 •
3	0	15	42	33
3	2	15	14	-12 •
3	4	15	26	-22 •
4	1	15	14	-5 •
4	3	15	29	23
5	0	15	21	-7 •
5	2	15	43	35
6	1	15	74	80
0	0	16	27	19 •
0	2	16	71	-78
1	1	16	19	4 •
2	0	16	72	-77
2	2	16	105	110

LAFE4AS12

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[a] Very weak structure factors and those which were strongly affected by secondary extinction were given zero weight in the least-squares refinement and were marked with one and two dots, respectively.

The rotation of the octahedra permits a close approach of the P (As) atoms which hereby form rectangular, nearly quadratic, four-membered rings. It is remarkable that the average P–P (As–As) bond distances in the binary skutterudite-type compounds are always somewhat greater than the usual two-electron bond distances. They are still greater in the ternary "filled" skutterudite-type compounds. Thus in CoP_3 (*7*) the two different P–P distances are 2.24 and 2.34 Å; in $LaFe_4P_{12}$ (*2*) they are 2.29 and 2.36 Å as compared to the usual two-electron bond P–P distance of 2.21 Å (*8*, *18*). In $CoAs_3$ (*9*) the As–As distances are 2.46 and 2.57 Å, and in the present study of $LaFe_4As_{12}$ they

TABLE IV

POSITIONAL AND THERMAL PARAMETERS OF $LaFe_4As_{12}$[a]

*Im*3	La 2(*a*)	Fe 8(*c*)	As 24(*g*)
x	0	$\frac{1}{4}$	0
y	0	$\frac{1}{4}$	0.34556(7)
z	0	$\frac{1}{4}$	0.15474(7)
U_{11}	0.0077(2)	0.0031(2)	0.0039(2)
U_{22}	U_{11}	U_{11}	0.0044(2)
U_{33}	U_{11}	U_{11}	0.0045(2)
U_{12}	0	−0.0001(2)	0
U_{13}	0	U_{12}	0
U_{23}	0	U_{12}	0.0003(2)
B	0.61(2)	0.24(2)	0.34(2)

[a] Standard deviations in the least significant digits are given in parentheses. Ellipsoidal thermal parameters are defined by $T = \exp[-2\pi^2(U_{11}h^2a^{*2} + , \ldots, +2U_{12}hka^*b^* + , \ldots)]$; equivalent isotropic parameters B are in Å^2.

were found to be 2.57 and 2.58 Å. This compares to As–As distances of 2.43 Å in $(AsCH_3)_5$ (*10*), 2.45 Å in $(AsCF_3)_4$ (*11*), 2.46 Å in $(AsC_6H_5)_6$ (*12*), and the weighted average As–As distances of 2.43 Å in $MgAs_4$ (*13*), 2.45 Å in $SrAs_3$ (*14*), 2.46 Å in LiAs (*15*), 2.48 Å in $NdAs_2$ (*16*), 2.50 Å in Sr_3As_4 (*17*), 2.52 Å in α-As (*18*), Ca_2As_3 (*19*), and EuAs (*20*), and 2.53 Å in CaAs (*21*) and Eu_5As_4 (*22*). In various transition and post-transition metal diarsenides with pyrite (*23*), marcasite (*24, 25*), arsenopyrite (*26*), and

TABLE V

INTERATOMIC DISTANCES AND SELECTED INTERATOMIC ANGLES IN $LaFe_4As_{12}$[a]

La: 12As	3.152	As–Fe–As	180.0	(3*x*)
Fe: 6As	2.365	As–Fe–As	83.5	(6*x*)
As: 2Fe	2.365	As–Fe–As	96.5	(6*x*)
1As′	2.572	As′–As–As″	90.0	(1*x*)
1As″	2.577	Fe–As–Fe	123.3	(1*x*)
1La	3.152	Fe–As–As′	109.7	(2*x*)
4As	3.149	Fe–As–As″	109.6	(2*x*)

[a] All distances shorter than 3.5 Å are listed. Standard deviations are all less than 0.002 Å and 0.1°, respectively.

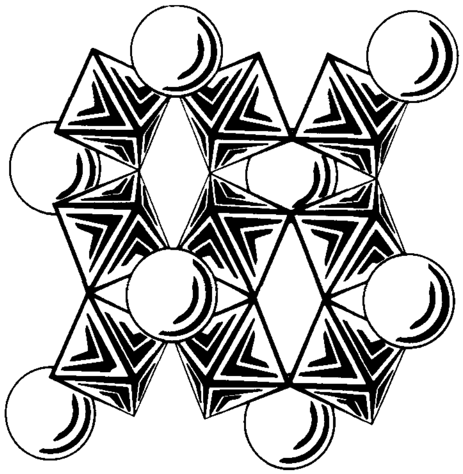

FIG. 1. Crystal structure of $LaFe_4As_{12}$. One layer of the corner-shared $FeAs_6$ octahedra is shown with the adjacent La atoms (spheres) above and below. The corners of the octahedra represent As atoms. The Fe atoms inside the octahedra are not shown.

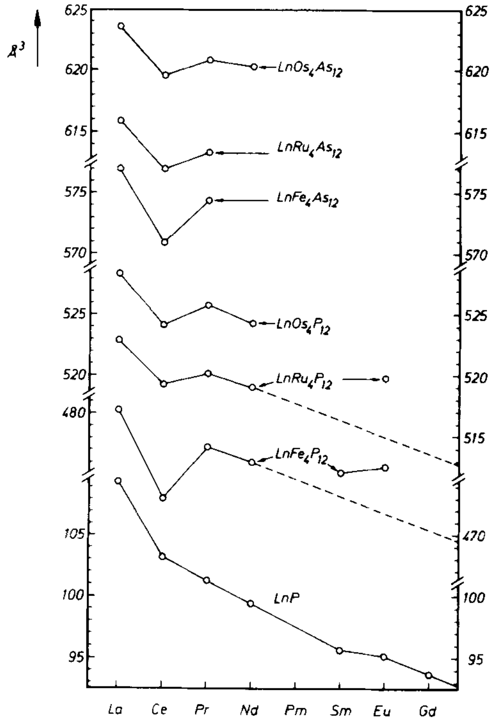

FIG. 2. Cell volumes of $LaFe_4P_{12}$-type phosphides and arsenides. For comparison the lanthanoid contraction as observed for *Ln* compounds with NaCl-type structure (*35*) is also plotted. All volumes correspond to two lanthanoid atoms.

related structures (*27–29*) and compositions (*30, 31*) the As–As distances continuously cover the range between 2.41 and 2.49 Å. Thus they are all shorter than the As–As distances in $LaFe_4As_{12}$.

On the other hand, the La–As and Fe–As distances are within the expectancy. The Fe–As distances of 2.365 Å in $LaFe_4As_{12}$ are close to the average Fe–As distances of 2.379 Å in $FeAs_2$ (*24*). For a direct comparison of La–As distances few data are available. In LaAs with NaCl-type structure (*32*) and coordination number 6 for La, the La–As distances are 3.07 Å. Since the coordination number of La in $LaFe_4As_{12}$ is 12, the somewhat larger La–As distances of 3.15 Å in $LaFe_4As_{12}$ are entirely acceptable.

Thus only the surprisingly large As–As distances remain to be rationalized. In the discussion of the structure of $LaFe_4P_{12}$ (*2*) we have used geometric arguments to account for the large P–P distances. We considered the $[Fe_4P_{12}]^{3-}$ poly-"anion" as a framework in which the P–P distances are stretched to accommodate the large La^{3+} cation, which in turn has shorter La–P distances than would be expected from the La–P distances in various La–polyphosphides. While we maintain this to be a reasonable explanation for the situation in $LaFe_4P_{12}$, we do not believe that geometric considerations of this kind can solely account for the large As–As distances in $LaFe_4As_{12}$. The reason for this is that the La–As distances in $LaFe_4As_{12}$ appear to be normal, while the La–P distances in the phosphide seem to be rather short.

As another possible explanation for the long As–As distances one might think of the possibility that the As–As interactions do not correspond to two-electron bonds. Both, less than two electrons per As–As bond (i.e., partial filling of As–As bonding states) or more than two electrons per As–As bond (i.e., partial filling of antibonding As–As states) would weaken the As–As bonds and thereby shift the As–As distances to higher values.

We have previously proposed a qualitative band structure for $CeFe_4P_{12}$ (*2*). In this diagram the valence electrons fill with increasing energy first the P–P bonding, then the Fe–P bonding states. After that comes the t_{2g} manifold with six electrons per Fe atom (formal oxidation number +2 for Fe; low-spin d^6 system) and at still higher energy come the P–P antibonding states which for $CaFe_4P_{12}$ were assumed to be unfilled. We expected the polyanion $[Fe_4P_{12}]^{4-}$ of $CeFe_4P_{12}$ to be semiconducting in analogy with isoelectronic CoP_3 (*33*), with the band gap situated between the Fe–P bonding and P–P antibonding levels. The localized t_{2g} states were assumed within the band gap. For the isostructural arsenides essentially an analogous scheme can be used. The main difference will need to be a much smaller, possibly zero band gap, since in general band gaps of isostructural compounds decrease with increasing atomic weight within homologous series. More specifically, a band gap of 0.45 eV was recently reported for skutterudite-type CoP_3 and no optical band gap was observed for the isostructural compositions $CoAs_3$ and $CoSb_3$ (*34*). With a decreasing band gap the antibonding As–As levels will overlap with the nonbonding t_{2g} states and/or with the bonding Fe–As level. In this way the antibonding As–As level will be partially filled and thereby the As–As distances will increase. We have started an investigation of the magnetic properties of these compounds to confirm and further elaborate on this model.

In Fig. 2 the cell volumes of the new $LaFe_4P_{12}$-type arsenides are plotted together with the volumes of the earlier-reported (*2*) isotypic phosphides. The small volumes of the Ce compounds indicate that the Ce atoms are at least partially tetravalent. There is a larger difference in volume between the Ruand Os-containing arsenides, than between the corresponding phospides. Only the large, more electropositive *Ln* elements seem to be able to form $LaFe_4P_{12}$-type compounds.

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