JOURNAL OF SOLID STATE CHEMISTRY **24**, 351–357 (1978)

Ternary Lanthanoid–Transition Metal Pnictides with $ThCr_2Si_2$-Type Structure

ROGER MARCHAND* AND WOLFGANG JEITSCHKO

Institut für Anorganische und Analytische Chemie, Universität Giessen, D-6300 Giessen, West Germany

Received September 13, 1977

Fifteen new compounds AB_2X_2 were synthesized where A is a lanthanoid, B = Fe, Co, or Ni, and X = P, As, or Sb. They crystallize with the $ThCr_2Si_2$ ($BaAl_4$, $CeAl_2Ga_2$) type of structure. Their lattice constants are reported. Single crystals of the ternary phosphides were obtained using tin as a flux. The crystal structure of $EuCo_2P_2$ ($ThCr_2Si_2$-type) was refined from single-crystal counter data to a conventional R value of 0.047 for 210 unique structure factors. While in most silicides with $ThCr_2Si_2$-type structure, the Si atoms form pairs, the P atoms in $EuCo_2P_2$ are isolated from each other. Thus in an extreme ionic formulation, the compound can be rationalized as $Eu^{2+}Co_2^{2+}P_2^{3-}$. Bonding in these and the Zintl compounds is briefly discussed.

Introduction

Since the first ternary silicides with $ThCr_2Si_2$-type structure were synthesized (*1*) more than 50 publications have reported on the preparation, structure, and physical properties of more than 200 isotypic silicides and germanides AB_2X_2, where A is a large metal atom (e.g., Ca, Sr, Ba, a lanthanoid or actinoid element), B is a small metal atom (late transition metals or Cu, Ag, Au, Mg, Zn, Cd), and X is silicon or germanium (*2–10*). Isotypic compounds where X is boron (*11, 12*), aluminum (*13, 14*), tin (*15*), lead (*16*), or sulfur and selenium as in $TlCo_2S_2$ and $TlCo_2Se_2$ (*17*) are also reported. Very little is known about similar ternary pnictides (X = P, As, or Sb). $LiCu_2P_2$ is reported with $ThCr_2Si_2$-type structure (*18*) and recently Mewis (*19*) prepared $CaNi_{1.95}P_2$ with that structure. In the course of our investigations on ternary pnictides (*20, 21*) we have now found this structure also in systems lanthanoid–transition metal–pnicogen.

Experimental and Results

Sample Preparation and Crystal Growth

Starting materials were the metallic components (all of stated purity >99.5%) and red P, As, or Sb (purities 99% or better). Filings of the rare earth elements were obtained from ingots under Ar. The transition metals were used in the form of freshly reduced powders. Red P was treated with boiling diluted NaOH (*22*). Stoichiometric amounts of the elemental components were sealed under Ar in silica tubes, heated at 920°K for 12 hr, followed by 4 hr at 1250°K and rapid cooling. The samples were then ground to powder, cold pressed to small pellets, resealed in silica tubes under Ar, and annealed for 15 hr at 1250°K.

Well-developed crystals of the ternary phosphides AB_2P_2 were obtained using Sn as a flux (*23*) with the atomic ratio A : B : P : Sn =

---

* On leave of absence from Laboratoire de Chimie Minérale C, Université de Rennes, 35031 Rennes Cedex, France.

0022-4596/78/2434-0351$02.00/0

Printed in Great Britain

1 : 2 : 2 : 20. The mixtures were sealed under Ar in silica tubes, annealed at 1050°K for 1 week and slowly cooled to room temperature within 2 days. The tin matrix of the samples was then dissolved with moderately diluted hydrochloric acid (1 : 1) which left the crystals of the ternary phase essentially unattacked. We were not successful in preparing the corresponding arsenides or antimonides by this method.

Phase Analysis and Cell Constants

Powder patterns of the products were recorded with a Guinier camera using α-quartz (a = 4.91304, c = 5.40463 Å) as standard. They usually showed the pattern characteristic for the $ThCr_2Si_2$-type structure and were indexed with the corresponding body-centered tetragonal cell. The evaluation of a typical pattern is shown in Table I. Least-squares refinement of the data resulted in the lattice constants listed in Table II.

TABLE I

EVALUATION OF A GUINIER PATTERN OF $EuNi_2As_2$ WITH $ThCr_2Si_2$-TYPE STRUCTURE

$h k l$	d_o (Å)	d_c (Å)	I_o^a	I_c^b
0 0 2	5.06	5.043	vw	2
1 0 1	3.811	3.810	w	7
1 1 0	2.910	2.910	m	26
1 0 3	2.605	2.604	vs	100
0 0 4	—	2.5215	—	4
1 1 2	2.520	2.5203	vs	57
2 0 0	2.057	2.0575	vs	61
1 1 4	1.906	1.9056	w	9
2 0 2	—	1.9050	—	1
1 0 5	1.812	1.8113	m	15
2 1 1	—	1.8104	—	3
0 0 6	—	1.6810	—	2
2 1 3	1.614	1.6143	s	67
2 0 4	1.594	1.5941	vw	5
1 1 6	1.455	1.4556	s	43
2 2 0		1.4549		28
2 2 2	—	1.3979	—	1
1 0 7	—	1.3599	—	1
2 1 5	1.359	1.3595	m	17
3 0 1	—	1.3592	—	1
2 0 6	—	1.3018	—	6
3 1 0	1.301	1.3013	w	11

[a] CuKα radiation.

[b] In the calculation of the powder pattern (*24*) the free parameter of the As position was assumed to equal the corresponding value in $EuCo_2P_2$.

The powder patterns frequently showed weak additional lines which could be attributed to small amounts of second- and third-phase products. To investigate any major deviations from the ideal 1 : 2 : 2 composition, samples in the system Eu–Fe–P were prepared, with the overall compositions 1 : 1.5 : 2.5 and 1 : 2.5 : 1.5. While the composition 1 : 1.5 : 2.5 did not contain the $ThCr_2Si_2$-type phase at all, the composition 1 : 2.5 : 1.5 showed that phase as a minor component. Its lattice constants were the same within the error limits, as those found for the sample 1 : 2 : 2. In different preparations of the same compound no differences in lattice constants were observed. This is also true for the ternary phosphides most of which were prepared with and without tin flux. Thus no indications were obtained for extended homogeneity ranges or for any substantial deviations from the ideal composition.

Of the 135 possible combinations *Ln*–Fe,Co,Ni–P,As,Sb, we have studied 30 and

TABLE II

CELL DIMENSIONS OF $ThCr_2Si_2$-TYPE COMPOUNDS[a]

	a (Å)	c (Å)	c/a	V (Å³)
$LaCo_2As_2$	4.054(1)	10.328(6)	2.548	169.8
$CeCo_2As_2$	4.026(1)	10.216(7)	2.538	165.6
$PrCo_2As_2$	4.017(1)	10.169(7)	2.531	164.1
$NdCo_2As_2$	4.006(1)	10.078(6)	2.516	161.7
$EuFe_2P_2$	3.818(1)	11.224(4)	2.940	163.6
$EuCo_2P_2$	3.7649(5)	11.348(2)	3.014	160.9
$EuNi_2P_2$	3.939(1)	9.482(2)	2.407	147.2
$EuFe_2As_2$	3.911(1)	12.110(4)	3.096	185.2
$EuCo_2As_2$	3.964(2)	11.111(6)	2.803	174.6
$EuNi_2As_2$	4.115(1)	10.086(2)	2.451	170.8
$EuNi_2Sb_2$	4.3834(6)	10.664(1)	2.433	204.9
$GdNi_2P_2$	3.8884(7)	9.378(2)	2.412	141.8
$GdNi_2As_2$	3.9857(8)	9.816(2)	2.463	155.9
$GdNi_2Sb_2$	4.259(1)	9.809(4)	2.303	177.9
$YbNi_2P_2$	3.8333(6)	9.325(2)	2.433	137.0

[a] Standard deviations in the last place are given in parentheses.

have obtained 15 $ThCr_2Si_2$-type compounds. Our results indicate that the $ThCr_2Si_2$-type structure may possibly be thermodynamically stable in as many ternary systems with pnicogen as the X component as there are with X = Si or Ge.

Physical Properties

Crystals of the $ThCr_2Si_2$-type phases are shiny and can easily be ground to black powders. The chemical stability of the ternary phosphides is demonstrated by their resistance

TABLE III

LIST OF STRUCTURE AMPLITUDES[a]

1	1	0	66	56	1	7	4	8	2	3	6	9	28	29	3	4	15	24	23
1	3	0	50	43	0	1	5	83	90	0	0	10	6	9	0	5	15	24	23
3	3	0	42	37	1	2	5	78	78	1	1	10	79	84	2	5	15	22	22
1	5	0	33	31	0	3	5	65	69	0	2	10	5	7	0	0	16	67	66
3	5	0	25	25	2	3	5	64	62	2	2	10	5	5	1	1	16	9	8
5	5	0	15	17	1	4	5	57	56	1	3	10	63	67	0	2	16	63	61
0	6	0	75	75	3	4	5	48	46	3	3	10	55	56	2	2	16	58	57
2	6	0	73	70	0	5	5	45	46	2	4	10	10	3	1	3	16	8	5
4	6	0	60	57	2	5	5	43	42	4	4	10	5	2	0	4	16	50	50
1	7	0	16	17	4	5	5	33	33	1	5	10	54	48	2	4	16	46	47
0	1	1	66	72	1	6	5	35	36	3	5	10	43	43	1	5	16	6	3
1	2	1	72	63	3	6	5	30	31	0	1	11	78	79	0	1	17	56	53
0	3	1	55	54	0	7	5	27	29	1	2	11	68	72	1	2	17	50	48
2	3	1	55	47	2	7	5	27	27	0	3	11	63	65	0	3	17	45	45
1	4	1	46	42	0	0	6	38	39	2	3	11	58	59	2	3	17	42	41
3	4	1	38	35	0	2	6	35	35	1	4	11	53	54	1	4	17	38	39
0	5	1	34	35	2	2	6	34	33	3	4	11	43	46	0	0	18	10	1
2	5	1	35	32	0	4	6	27	28	0	5	11	45	46	1	1	18	50	50
4	5	1	28	25	2	4	6	25	26	2	5	11	40	42	1	3	18	44	43
1	6	1	29	27	4	4	6	19	19	4	5	11	33	34	3	3	18	38	39
3	6	1	26	24	1	5	6	78	79	1	6	11	35	37	0	1	19	38	34
0	7	1	23	22	3	5	6	70	68	0	0	12	93	94	1	2	19	34	32
2	7	1	21	21	5	5	6	54	52	1	1	12	14	12	0	3	19	32	29
1	1	2	128	119	0	6	6	16	18	0	2	12	81	85	2	3	19	31	28
0	2	2	10	8	2	6	6	15	16	2	2	12	74	77	0	0	20	61	62
2	2	2	11	9	4	6	6	12	12	1	3	12	12	11	1	1	20	18	16
1	3	2	112	107	1	7	6	50	52	3	3	12	10	9	0	2	20	58	58
3	3	2	95	86	0	1	7	46	48	0	4	12	62	65	2	2	20	56	55
0	4	2	9	10	1	2	7	41	41	2	4	12	58	60	1	3	20	17	13
2	4	2	11	10	0	3	7	37	36	4	4	12	48	49	0	1	21	22	18
4	4	2	8	8	2	3	7	33	32	1	5	12	8	7	1	2	21	22	17
1	5	2	75	71	1	4	7	30	29	3	5	12	6	6	0	0	22	14	11
3	5	2	65	60	3	4	7	26	25	0	6	12	46	47	1	1	22	51	50
5	5	2	48	46	0	5	7	26	25	2	6	12	43	44	0	2	0	143	187*
0	6	2	7	7	2	5	7	24	23	0	1	13	39	38	2	2	0	154	154*
2	6	2	7	6	4	5	7	20	19	1	2	13	35	34	0	4	0	116	118*
1	7	2	46	46	1	6	7	22	20	0	3	13	32	31	2	4	0	116	106*
0	3	3	85	91	3	6	7	18	18	2	3	13	30	29	4	4	0	89	81*
2	3	3	86	81	0	7	7	17	17	1	4	13	28	27	4	6	2	3	6*
1	4	3	75	73	1	1	8	33	32	3	4	13	23	23	0	1	3	96	131*
3	4	3	67	61	1	3	8	28	28	0	5	13	24	23	1	2	3	100	105*
0	5	3	59	61	3	3	8	23	24	2	5	13	23	22	0	0	4	102	143*
2	5	3	57	55	0	4	8	87	91	1	6	13	19	19	0	2	4	97	114*
4	5	3	44	43	2	4	8	83	83	0	0	14	37	34	2	2	4	97	95*
1	6	3	46	47	4	4	8	66	66	1	1	14	96	97	5	5	4	5	1*
3	6	3	41	40	1	5	8	19	20	0	2	14	33	31	1	1	6	129	159*
0	7	3	35	37	3	5	8	16	15	2	2	14	28	28	1	3	6	111	118*
2	7	3	35	35	0	6	8.	59	61	1	3	14	79	82	3	3	6	96	94*
1	1	4	15	16	2	6	8	56	57	3	3	14	70	70	0	0	8	126	147*
1	3	4	10	8	0	1	9	70	76	0	4	14	23	23	0	2	8	114	125*
3	3	4	7	4	1	2	9	63	67	2	4	14	20	21	2	2	8	105	110*
0	4	4	71	74	0	3	9	59	61	4	4	14	14	16	0	4	10	4	1*
2	4	4	71	67	2	3	9	53	55	1	5	14	59	61	0	6	10	5	0*
4	4	4	54	52	1	4	9	47	50	3	5	14	51	54	2	6	10	4	1*
1	5	4	6	2	3	4	9	43	42	0	1	15	38	36	3	3	16	5	6*
3	5	4	6	2	0	5	9	41	42	1	2	15	34	33	0	2	18	5	3*
0	6	4	48	48	2	5	9	39	39	0	3	15	31	30	2	2	18	4	1*
2	6	4	46	45	4	5	9	31	31	2	3	15	29	28	0	4	18	3	3*
4	6	4	39	38	1	6	9	32	33	1	4	15	27	26	2	4	18	3	3*

[a] The columns contain the values *hkl*, *F*(obs), *F*(calc). Reflections where *F*(obs) was less than three standard deviations and reflections strongly affected by secondary extinction were not included in the final least-squares cycles and are marked with asterisks.

against diluted hydrochloric acid. None of the new phases was strongly attracted by a magnet at room temperature nor after cooling with liquid air.

Structure Refinement of $EuCo_2P_2$

A small single crystal of $EuCo_2P_2$ with approximately globular shape was examined in a Weissenberg camera with Mo*Kα* radiation. The body-centered tetragonal cell with high Laue symmetry was confirmed. No other extinctions were observed. Although these characteristics are common for several space groups, the successful refinement of the structure in *I*4/*mmm* and the fact that the thermal parameters of none of the atoms were higher than expected indicate that, of the possible space groups, the group with the highest symmetry, *I*4/*mmm*, is correct.

Intensity data were collected with an automated four-circle diffractometer, monochromatized Mo*Kα* radiation, scintillation counter, and pulse height discriminator. Scans were along θ, and all reflections within one octant were measured up to $(\sin \theta)/\lambda = 1.0$. After averaging equivalent reflections, an absorption correction was applied, assuming spherical crystal shape.

The structure was refined by full-matrix least-squares cycles (*25*) with starting parameters as determined for YCu_2Si_2 (*3*). Atomic scattering factors for neutral atoms (*26*) were used, corrected for anomalous dispersion (*27*). The weighting scheme was according to counting statistics. An isotropic correction for secondary extinction was applied to the calculated structure factors. The final conventional R value (on F's) is 0.047 for 210 unique reflections, excluding 31 reflections most severely affected by secondary extinction or poor counting statistics (Table III). Final parameters and interatomic distances are given in Tables IV and V.

TABLE IV

STRUCTURAL DATA FOR $EuCo_2P_2$

	*I*4/*mmm*	*x*	*y*	*z*	*B* (Å^2)
Eu	2*a*	0	0	0	0.41(2)
Co	4*d*	0	$\frac{1}{2}$	$\frac{1}{4}$	0.34(2)
P	4*e*	0	0	0.3558(2)	0.37(3)

TABLE V

INTERATOMIC DISTANCES, SITE SYMMETRY, AND SELECTED INTERATOMIC ANGLES IN $EuCo_2P_2$[a]

Eu	4/*mmm*	8P	3.125	P–Co–P	106.8(4x)
Co	$\bar{4}m2$	4P	2.233	P–Co–P	115.0(2x)
		4Co	2.662	Co–P–Co	73.2(4x)
P	4*mm*	4Co	2.233	Co–P–Co	115.0(2x)
		4Eu	3.125	Eu–P–Eu	74.1(4x)
		1P	3.272	Eu–P–Eu	116.9(2x)

[a] All distances shorter than 3.4 Å are listed. Standard deviations are all less than 0.006 Å and 0.1°, respectively.

Discussion

The $ThCr_2Si_2$-type structure occurs for compounds where all components are relatively electropositive elements, like those in the binary prototype $BaAl_4$ (*13*), or in $RbIn_4$ (*28*). It occurs also for $ThZn_4$ (*29*) and is reported for compositions like $CeAl_2Ga_2$ (*14*) where the two nonequivalent sites of the Al atoms in $BaAl_4$ are occupied by similar elements in an ordered manner. Most compounds with that structural arrangement, however, are ternary compounds where the positions 4*d* and 4*e* of space group *I*4/*mmm* are occupied by elements of entirely different character.

The new $ThCr_2Si_2$-type pnictides are best discussed together with the corresponding silicides and germanides. The cell constants and cell volumes of the silicides (*2*, *30*) and germanides (*2*, *3*, *6*) corresponding to the phosphides and arsenides reported here are very similar. (No stannides corresponding to $EuNi_2Sb_2$ and $GdNi_2Sb_2$ have been reported yet.) In most corresponding compounds, the cell volume of the pnictide is smaller by 1 to 3%. Similarly the *c*/*a* ratios of the Ni-containing compounds are smaller for both the pnictides and silicides (and germanides) when compared with the corresponding Fe and Co compounds. This probably has to do with the well-known preference of Ni for square-planar, rather than tetrahedral coordination (Fig. 1), although a perfectly square-planar Si or P coordination of the Ni atom cannot be achieved in the $ThCr_2Si_2$-type structure.

There is one important difference between the silicides and germanides with that structure, and the structure of the pnictides as refined for $EuCo_2P_2$: In those silicides and germanides, where the z parameter for the Si (Ge) position has been refined, the Si–Si (Ge–Ge) distances are short (2.3 to 2.7 Å), suggesting Si–Si (Ge–Ge) bonding. In $EuCo_2P_2$ the corresponding P–P distance is 3.27 Å and thus P–P bonding can be ruled out.

The ternary $ThCr_2Si_2$-type compounds contain relatively electropositive components (earth and rare earth metals) and metalloids (e.g., Si, Ge, P, As). In binary compounds of these elements Zintl's concept (*32*) helps to rationalize the structure of the poly-"anion." In the best-known example, LiAl, the valence electrons of the Li atoms are assumed to be transferred to the Al atoms, which then have the same number of valence electrons as Si and thus, like Si, assume the diamond structure with Li in interstitial positions. Although this concept is applicable to numerous structures (*33*), it has occasionally been criticized ((*34*) and references therein). Thus some difficulty arose because (to stay with the chosen example) the NaTl-type structure is adopted not only by LiAl, LiGa, and similar isoelectronic compounds, but also by LiZn and LiCd, where only three valence electrons are available per Zn (Cd) atom. This is, however, no difficulty in a band model, since the sp^3 valence band, made up from the atomic functions of the metalloid atoms, does not have to be completely filled. Although this fact reduces the value of Zintl's concept in predicting the structure of the poly-"anion," it does not diminish its value for the prediction of the band structure. Thus, in the present example, it predicts metallic conductivity for LiZn, while LiAl should be a semiconductor or semimetal.[1]

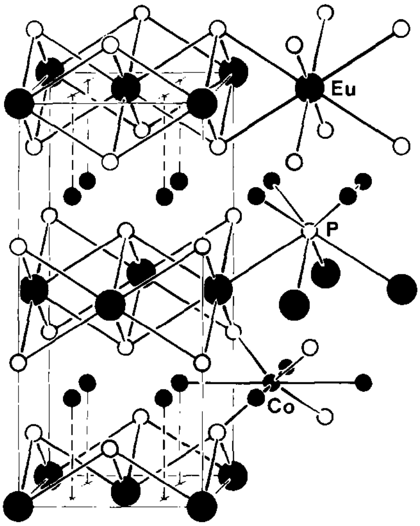

FIG. 1. Crystal structure and near-neighbor environment of $EuCo_2P_2$. The outlined cell is doubled: the *a* axis of the drawing is $2^{1/2}$ times longer than the *a* axis for the *I4/mmm* setting, to emphasize the relation of the structure to the NaCl, MgAgAs, $MnCu_2Al$, PbFCl, and ZrCuSiAs structure types (*31*).

Many of the $ThCr_2Si_2$-type silicides and germanides are readily rationalized with Zintl's concept; for instance $CaZn_2Ge_2$ (*4*). In counting all valence electrons (regardless of their partial covalent bonding character) as belonging to the most electronegative element, the Ge atoms each obtain seven valence electrons. Therefore, like the halogens in their elemental state, the Ge atoms are expected to form pairs, which is also suggested by the short Ge–Ge distance of 2.47 Å. Thus in the ionic formulation $Ca^{2+}Zn^{2+}Zn^{2+}[Ge_2]^{6-}$, the metal atoms occur in their usual oxidation state. Similarly, diamagnetic $ThCu_2Si_2$ (*39*) can be formulated as $Th^{4+}Cu^{1+}Cu^{1+}[Si_2]^{6-}$. Its

---

[1] The good electric conductivity of LiAl indicates the latter to be the case (*35*), which makes an experimental differentiation between LiZn and LiAl difficult by conductivity measurements. The high mobility of Li in LiAl (*36*) cannot prove or disprove Zintl's concept, since good ionic conductivity is known to occur not only for very electropositive ions like Li^+ (*37*), but also for more or less covalently bonded species like Cu^+ or Ag^+ (*38*).

Si–Si bonding distance is 2.39 Å (*1*). There are, however, also many $ThCr_2Si_2$-type silicides and germanides, where some difficulties arise with a straightforward application of Zintl's concept. For instance, in $NdFe_2Si_2$ the average atomic volume, in comparison with isotypic $LnFe_2Si_2$ compounds (*40*), suggests valency +3 for Nd and, on the other hand, the short Si–Si distance of 2.57 Å (*41*) indicates at least some Si–Si bonding. The formulation $Nd^{3+}Fe^{1.5+}Fe^{1.5+}[Si_2]^{6-}$, however, is probably too simplistic, especially also because some disorder between the Si and Fe atoms was found (*41*).

With the $ThCr_2Si_2$-type pnictides we face a similar situation. Most of the compounds reported in the present paper contain Eu as the most electropositive component. The plot of the cell volumes (Fig. 2) indicates Eu to be in its two-valent state. For the transition metals Fe, Co, and Ni, an oxidation state of +2 is reasonable. Accordingly the compound $EuCo_2P_2$ can be formulated as $Eu^{2+}Co^{2+}Co^{2+}P^{3-}P^{3-}$. Thus each of the P-atoms obtains an electron octet and, in agreement with Zintl's concept, the P atoms are isolated from each other. In those ternary pnictides, however, where the volume plot indicates valence +3 for the lanthanoid component, the situation is more complicated. Certainly, because of its higher electronegativity, the *s* and *p* states of the pnictide component will be filled and thus formal oxidation numbers −3 will again be obtained for these elements. Without any further physical data, it is, however, difficult to place the additional valence electron of the *Ln* component. Apparently more valence electrons are offered by the metal atoms than can be accommodated in low-energy states of the metalloid atoms. Similar situations are encountered for competing compositions like $La_6Ni_6P_{17}$ (*21*) and $Eu_2Co_{12}P_7$ (*42*).

Several derivative structures of the prototypical $ThCr_2Si_2$ ($BaAl_4$, $CeAl_2Ga_2$) type of structure are known: $LaAl_4$ (*43*), $CaBe_2Ge_2$ (*44*), and $BaMg_2Sn_2$ (*45*). It seems possible that careful studies will prove that some of the many binary or ternary compounds reported with $ThCr_2Si_2$-type structure crystallize in a lower-symmetry crystal class and/or with a larger cell (*46*).

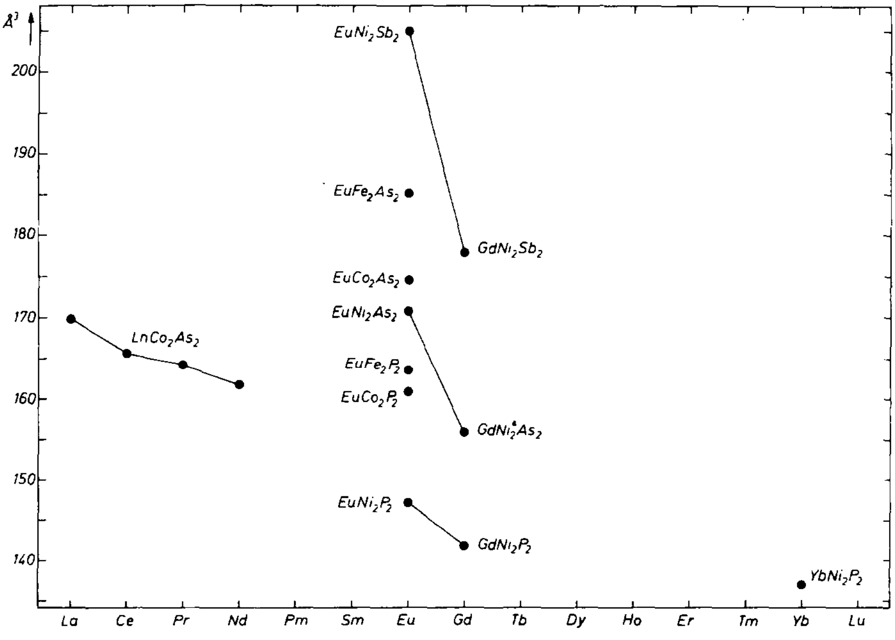

FIG. 2. Cell volumes of $ThCr_2Si_2$-type pnictides.

Acknowledgments

We wish to thank Dipl.-Chem. D. Braun for considerable competent help with the structure refinement and Dr. M. Jassen for the supervision of the single-crystal X-ray data collection. The *Deutsche Forschungsgemeinschaft* has supported this work through a travel grant (to R.M.) and a research grant (to W.J.). We also want to acknowledge the *Fonds der Chemischen Industrie* for financial support.

References

1. Z. Ban and M. Sikirica, *Acta Crystallogr.* **18**, 594 (1965).
2. O. I. Bodak, E. I. Gladyshevskii, and P. I. Kripyakevich, *Izv. Akad. Nauk. SSSR. Neorg. Mater.* **2**, 2151 (1966).
3. W. Rieger and E. Parthé, *Monatsh. Chem.* **100**, 444 (1969).
4. B. Eisenmann, N. May, W. Müller, H. Schäfer, A. Weiss, J. Winter, and G. Ziegleder, *Z. Naturforsch. B* **25**, 1350 (1970).
5. I. Mayer, J. Cohen, and I. Felner, *J. Less-Common Metals* **30**, 181 (1973).
6. W. M. McCall, K. S. V. L. Narasimhan, and R. A. Butera, *J. Appl. Crystallogr.* **6**, 301 (1973).
7. K. S. V. L. Narasimhan, V. U. S. Rao, R. L. Bergner, and W. E. Wallace, *J. Appl. Phys.* **46**, 4957 (1975).
8. R. Ballestracci, *C. R. Hebd. Seances Acad. Sci., Ser. B* **282**, 291 (1976).
9. J. Gal, M. Kroupp, Z. Hadari, and I. Nowik, *Solid State Commun.* **20**, 515 (1976).
10. R. Marazza, R. Ferro, G. Rambaldi, and G. Zanicchi, *J. Less-Common Metals* **53**, 193 (1977).
11. K. Niihara, T. Shishido, and S. Yajima, *Bull. Chem. Soc. Japan* **46**, 1137 (1973).
12. P. Rogl, *Monatsh. Chem.* **104**, 1623 (1973).
13. K. R. Andress and E. Albertini, *Z. Metallk.* **27**, 126 (1935).
14. O. S. Zarechnyuk, P. I. Kripyakevich, and E. I. Gladyshevskii, *Kristallografiya* **9**, 835 (1964).
15. W. Dörrscheidt, N. Niess, and H. Schäfer, *Z. Naturforsch. B* **31**, 890 (1976).
16. N. May and H. Schäfer, *Z. Naturforsch. B* **27**, 864 (1972).
17. H. Boller and K. Klepp, Abstracts of the Fourth European Crystallographic Meeting, Oxford (1977).
18. H. Schlenger, H. Jacobs, and R. Juza, *Z. Anorg. Allg. Chem.* **385**, 177 (1971).
19. A. Mewis, *Z. Naturforsch. B* **32**, 351 (1977).
20. W. Jeitschko and D. Braun, *Acta Crystallogr. B* **33**, 3401 (1977).
21. D. Braun and W. Jeitschko, *Acta Crystallogr. B* **34**, in press (1978).
22. G. Brauer, "Handbuch der Präparativen Anorganischen Chemie", 3rd ed., Enke, Stuttgart (1975).
23. P. Jolibois, *C. R. Hebd. Seances Akad. Sci.* **150**, 106 (1910).
24. K. Yvon, W. Jeitschko, and E. Parthé, *J. Appl. Crystallogr.* **10**, 73 (1977).
25. G. Sheldrick, SHELX-76, an unpublished program system for the determination of crystal structures (1976).
26. D. T. Cromer and J. B. Mann, *Acta Crystallogr. A* **24**, 321 (1968).
27. D. T. Cromer and D. Liberman, *J. Chem. Phys.* **53**, 1891 (1970).
28. G. Bruzzone, *Acta Crystallogr. B* **25**, 1206 (1969).
29. E. S. Makarov and L. S. Gudkov, *Kristallografiya* **1**, 650 (1956).
30. I. Felner and I. Mayer, *Mater. Res. Bull.* **8**, 1317 (1973).
31. V. Johnson and W. Jeitschko, *J. Solid State Chem.* **11**, 161 (1974).
32. W. Klemm, *Proc. Chem. Soc.* (*London*) 329 (1958).
33. H. Schäfer, B. Eisenmann, and W. Müller, *Angew. Chem. Int. Ed.* **12**, 694 (1973).
34. M. B. McNeil, W. P. Pearson, L. H. Bennett, and R. E. Watson, *J. Phys. C.* **6**, 1 (1973).
35. N. P. Yao, W. J. Walsh, H. Shimotaka, J. D. Arntzen, and P. A. Nelson, Electrochemical Society Meeting, Boston, Abstr. No. 12 (1973).
36. J. R. Willhite, N. Karnezos, P. Cristea, and J. O. Brittain, *J. Phys. Chem. Solids* **37**, 1073 (1976).
37. W. Jeitschko, T. A. Bither, and P. E. Bierstedt, *Acta Crystallogr. B* **33**, 2767 (1977).
38. R. D. Armstrong, R. S. Bulmer, and T. Dickinson, *J. Solid State Chem.* **8**, 219 (1973).
39. L. Omejec and Z. Ban, *Z. Anorg. Allg. Chem.* **380**, 111 (1971).
40. I. Felner, I. Mayer, A. Grill, and M. Schieber, *Solid State Commun.* **16**, 1005 (1975).
41. H. Pinto and H. Shaked, *Phys. Rev. B* 7, 3261 (1973).
42. W. Jeitschko, D. Braun, R. H. Ashcraft, and R. Marchand, *J. Solid State Chem.* **25**, in press (1978).
43. I. I. Zalutsky and P. I. Kripyakevich, *Dopov. Akad. Nauk. Ukr. RSR A* **29**, 362 (1967).
44. B. Eisenmann, N. May, W. Müller, and H. Schäfer, *Z. Naturforsch. B* **27**, 1155 (1972).
45. B. Eisenmann and H. Schäfer, *Z. Anorg. Allg. Chem.* **403**, 163 (1974).
46. H. Wondratschek and W. Jeitschko, *Acta Crystallogr. A* **32**, 664 (1976).