

Superconducting LaRu_2P_2 and Other Alkaline Earth and Rare Earth Metal Ruthenium and Osmium Phosphides and Arsenides with ThCr_2Si_2 Structure*

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The ThCr_2Si_2 -type compounds MRu_2P_2 ($M = \text{Ca, Sr, Ba, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb}$), MOs_2P_2 ($M = \text{Sr, Ba, Eu}$), and MRu_2As_2 ($M = \text{Ca, Sr, Ba, La, Eu}$) were prepared by sintering techniques and/or by reaction of the elemental components in a tin flux. The crystal structures of SrRu_2P_2 and LaRu_2P_2 were refined from single-crystal diffractometer data to residuals of $R = 0.019$ (224 structure factors, 11 variable parameters) and $R = 0.028$ (510 F 's, 11 variables), respectively. LaRu_2P_2 is diamagnetic and becomes superconducting at 4.1 K. No transition to a superconducting state was observed down to 1.8 K for the compounds MFe_2P_2 ($M = \text{Ca, Sr, Ba, La}$), MRu_2P_2 ($M = \text{Ca, Sr, Ba, Y}$), and MOs_2P_2 ($M = \text{Sr, Ba}$). © 1987 Academic Press, Inc.

Introduction

Ternary rare earth transition metal silicides and germanides with ThCr_2Si_2 structure (1) have been known for more than twenty years (2, 3). A recent survey (4) lists almost 200 rare earth transition metal silicides and germanides with this structure type. The first corresponding phosphides and arsenides were prepared much later (5). Up to now some 50 rare earth metal nickel (6, 8), palladium (7, 9), cobalt (10), and iron (10) phosphides and arsenides with this structure were reported.

ThCr_2Si_2 -type compounds have attracted much interest in recent years. Several of these show a variety of unusual combinations of physical properties, which are connected with the intermediate, fluctuating,

or mixed valency of cerium, europium, or ytterbium in these compounds, e.g., EuCu_2Si_2 (11-14), EuPd_2Si_2 (15, 16), YbCu_2Si_2 (12, 14), CeCu_2Si_2 (14, 17, 18), CeRh_2Si_2 (19-22), EuNi_2P_2 (6, 23-28), and EuPd_2P_2 (7, 29-32). Besides the "heavy fermion" superconductor CeCu_2Si_2 , several compounds of the nonmagnetic rare earth metals yttrium, lanthanum, and lutetium with ThCr_2Si_2 or the closely related CaBe_2Ge_2 structure were found to be superconducting, e.g., LaPd_2Ge_2 , YbPd_2Ge_2 , and LaPt_2Ge_2 (33), LaIr_2Si_2 (34), YRh_2Si_2 and LaRh_2Si_2 (35, 36), LaRu_2Si_2 and LuRu_2Si_2 (36), YIr_2Si_2 (37), and LaIr_2Ge_2 (38).

We report on new ThCr_2Si_2 -type phosphides and arsenides with ruthenium and osmium as the transition metal component. Of these LaRu_2P_2 becomes superconducting at 4.1 K, the highest superconducting

* Dedicated to Professor Albrecht Rabenau on the occasion of his 65th birthday.

transition temperature reported so far for ThCr_2Si_2 -type compounds. A preliminary account of this work was given before (39).

Sample Preparation

The starting materials were as follows. Most alkali earth and rare earth metals were purchased in the form of filings or powders (40 mesh) with nominal purities of m2N5 (Ca, Y) or m3N (all lanthanoids). Filings of strontium and barium were prepared from ingots (m2N5) under dried paraffin oil. The filings of the alkaline earth and the light lanthanoids were kept under oil. Prior to the reactions the oil was washed away by repeated treatments with *n*-hexane which had been dried with sodium. The remaining *n*-hexane was evaporated under vacuum; iron filings were removed by a magnet. During these procedures the filings were not exposed to air. Ruthenium and osmium were in the form of powders (m3N, 60 mesh), red phosphorus was "electronic grade" (Hoechst-Knapsack), and arsenic and tin were from Merck ("rein"). The arsenic was purified by fractional sublimation prior to the reactions.

The ruthenium-containing phosphides were prepared in two ways. With the exception of BaRu_2P_2 all of them could be prepared by the tin flux method. The starting ratios $M:\text{Ru}:\text{P}:\text{Sn}$ varied between 1:2:2:5, 1:2:2:20, and 3:2:2:15. The samples were slowly heated (50°C/hr) to 880°C, kept at this temperature for about 2 weeks, and quenched to room temperature. After dissolving the tin-rich matrix, binary ruthenium phosphides were frequently observed as by-products, indicating that thermodynamic equilibrium had not been obtained. This can be avoided by using prereacted finely ground RuP as a starting material. In samples with low *M* content we have observed Ru_3Sn_7 (40) as a by-product.

The other preparation procedure is the direct reaction of stoichiometric mixtures

of the elemental components in evacuated, sealed silica tubes. The samples were slowly heated (50°C/hr) to 880°C, kept at this temperature for about a week, slowly cooled (5°C/hr) to 700° or 600°C, and quenched. The resulting products frequently contained second and third phase material of which the ternary compounds with PbFCl structure are noteworthy (39). Better results were achieved by subsequently grinding the samples to a fine powder under argon and annealing the cold-pressed pellets for another week at temperatures between 800° and 1150°C. The higher temperatures were needed for the osmium-containing samples.

Properties

The products prepared by the tin flux method were well crystallized with prismatic crystals of up to 0.5-mm edge lengths. The other samples were microcrystalline. The powders were black and not sensitive to air. Energy-dispersive fluorescence analyses of several samples in a scanning electron microscope showed no foreign elements in the ThCr_2Si_2 -type crystals. The detection limits for tin and silicon were estimated to be less than 0.3 and 1.0 at.%, respectively.

The Guinier powder patterns showed the tetragonal body-centered ThCr_2Si_2 -type structure. As an example, the evaluation of the pattern of BaOs_2P_2 is shown in Table I. In no case did we observe the primitive superstructure reflections typical for the closely related CaBe_2Ge_2 structure (42). For the compounds MRu_2As_2 , where the superstructure reflections would be weak, because of the relatively small difference in the scattering power of ruthenium and arsenic, we carefully compared the observed intensities with those of the calculated patterns for the ThCr_2Si_2 - and CaBe_2Ge_2 -type structure. There was clearly better agreement for the ThCr_2Si_2 -type structure. The

TABLE I
POWDER PATTERN OF BaOs₂P₂ WITH ThCr₂Si₂
STRUCTURE^a

<i>hkl</i>	<i>Q_c</i>	<i>Q_o</i>	<i>I_c</i>	<i>I_o</i>
002	269	270	54	vs
101	684	684	10	m
004	1076	1077	33	vs
103	1222	1222	22	m
110	1233	1234	7	w
112	1502	1499	100	vs
105	2297	—	5	—
114	2309	2308	20	s
006	2421	2423	2	w
200	2465	2464	35	vs
202	2734	2734	12	m
211	3149	3149	3	w
204	3542	3539	27	s
116	3654	3653	38	vs
213	3687	3687	9	m
107	3912	3913	1	vw
008	4305	4304	7	m
215	4763	4764	4	w
206	4887	4887	3	w
220	4931	4927	14	m
222	5200	5200	5	m

^a The pattern was recorded with a Guinier camera with CuK_{α1} radiation. For the calculated pattern (41) the positional parameters of SrRu₂P₂ were assumed. The *Q* values are defined by $Q = 100/d^2$ (nm⁻²).

lattice constants were refined by a least-squares treatment using α-quartz as a standard ($a = 0.49130$, $c = 0.54046$ nm). They are listed in Table II together with those obtained in an independent study (43) of some of these compounds.

Magnetic susceptibility measurements for LaRu₂P₂ carried out with a Faraday balance at room temperature showed diamagnetism with a susceptibility of $\chi = -50 \times 10^{-6}$ cm³/mole.

Superconducting critical temperatures were determined by ac induction measurements. Several samples of LaRu₂P₂ were measured. They became superconducting with an onset temperature of 4.1 K, a transition width of 0.5 K, and the maximum at 3.9 K. No superconducting transition down

to 1.8 K was found for the ThCr₂Si₂-type compounds *M*Fe₂P₂ (*M* = Ca, Sr, Ba) (44), LaFe₂P₂ (10), *MRu*₂P₂ (*M* = Ca, Sr, Ba, Y), SrOs₂P₂, and BaOs₂P₂.

Structure Refinements of SrRu₂P₂ and LaRu₂P₂

Single crystals of SrRu₂P₂ and LaRu₂P₂, grown in the tin flux, were examined in a

TABLE II
CELL DIMENSIONS OF ThCr₂Si₂-TYPE COMPOUNDS^a

Compound	<i>a</i> (pm)	<i>c</i> (pm)	<i>c/a</i>	<i>V</i> (nm ³)
CaRu ₂ P ₂	404.8(1)	977.3(1)	2.414	0.1601
CaRu ₂ P ₂ ^b	404.6(1)	977.1(2)	2.415	0.1600
SrRu ₂ P ₂	403.2(1)	1112.2(1)	2.758	0.1808
SrRu ₂ P ₂ ^b	403.3(1)	1113.5(2)	2.761	0.1811
BaRu ₂ P ₂	403.1(1)	1206.2(2)	2.992	0.1960
BaRu ₂ P ₂ ^b	402.9(1)	1206.4(2)	2.994	0.1958
YRu ₂ P ₂	403.0(1)	954.5(1)	2.368	0.1550
LaRu ₂ P ₂	403.1(1)	1067.5(5)	2.648	0.1735
CeRu ₂ P ₂	404.2(1)	1013.4(1)	2.507	0.1656
PrRu ₂ P ₂	404.8(1)	997.4(1)	2.464	0.1634
NdRu ₂ P ₂	404.6(2)	987.4(6)	2.440	0.1616
SmRu ₂ P ₂	403.5(1)	968.2(7)	2.400	0.1576
EuRu ₂ P ₂	403.0(1)	1078.5(3)	2.676	0.1752
EuRu ₂ P ₂ ^b	402.9(1)	1077.2(2)	2.674	0.1749
GdRu ₂ P ₂	403.4(1)	963.4(2)	2.388	0.1568
TbRu ₂ P ₂	402.8(1)	957.8(2)	2.378	0.1554
DyRu ₂ P ₂	402.4(1)	953.6(3)	2.370	0.1544
HoRu ₂ P ₂	402.3(1)	949.9(2)	2.361	0.1537
ErRu ₂ P ₂	402.2(1)	946.3(2)	2.353	0.1531
YbRu ₂ P ₂	402.6(1)	946.3(2)	2.350	0.1534
SrOs ₂ P ₂	403.5(1)	1128.3(2)	2.796	0.1837
BaOs ₂ P ₂	402.8(1)	1219.3(2)	3.027	0.1978
EuOs ₂ P ₂	403.7(1)	1089.1(2)	2.698	0.1775
CaRu ₂ As ₂	417.3(1)	1029.3(3)	2.467	0.1793
CaRu ₂ As ₂ ^b	417.4(1)	1030.3(2)	2.468	0.1795
SrRu ₂ As ₂	416.8(1)	1117.9(2)	2.682	0.1942
SrRu ₂ As ₂ ^b	416.9(1)	1118.7(2)	2.683	0.1944
BaRu ₂ As ₂	415.2(1)	1223.8(3)	2.947	0.2110
BaRu ₂ As ₂ ^b	415.2(1)	1223.5(2)	2.947	0.2109
LaRu ₂ As ₂	418.0(1)	1062.3(2)	2.541	0.1856
EuRu ₂ As ₂	416.7(1)	1077.8(3)	2.587	0.1871
EuRu ₂ As ₂ ^b	417.5(1)	1077.2(2)	2.580	0.1878

^a Standard deviations in the position of the least significant digit are given in parentheses.

^b Data from Ref. (43).

TABLE III
 ATOMIC PARAMETERS OF SrRu₂P₂ AND LaRu₂P₂^a

	<i>I4/mmm</i>	Occupancy	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁ = <i>U</i> ₂₂	<i>U</i> ₃₃	<i>B</i> _{eq}
SrRu₂P₂								
Sr	2 <i>a</i>	1.018(4)	0	0	0	0.0099(2)	0.0075(3)	0.00719(7)
Ru	4 <i>d</i>	1	0	½	¼	0.00405(7)	0.0084(1)	0.00433(3)
P	4 <i>e</i>	0.994(7)	0	0	0.3529(1)	0.0059(3)	0.0073(5)	0.0050(1)
LaRu₂P₂								
La	2 <i>a</i>	0.997(2)	0	0	0	0.00688(5)	0.00537(7)	0.00518(2)
Ru	4 <i>d</i>	1	0	½	¼	0.00354(4)	0.01029(9)	0.00457(2)
P	4 <i>e</i>	0.947(7)	0	0	0.3593(1)	0.0055(2)	0.0068(3)	0.00468(9)

^a The anisotropic thermal parameters are defined by $\exp[-2\pi^2(h^2a^{*2}U_{11} + \dots)]$. In this structure the parameters *U*₁₂, *U*₁₃, and *U*₂₃ are all equal to zero. The last column contains the equivalent isotropic thermal parameter *B* (nm²). Standard deviations in the position of the last digit are listed in parentheses.

Weissenberg camera. They had the Laue symmetry *4/mmm* and the body-centered extinctions typical for the ThCr₂Si₂ structure (*I*). Intensity data for the two compounds were collected from elongated prismatic crystals with maximal extensions of about 0.2 mm in an automated four-circle diffractometer with graphite-monochromated MoK_α radiation, a scintillation counter, and a pulse-height discriminator. Background counts were measured at both ends of each θ -2 θ scan and empirical absorption corrections were applied from psi scan data. For the SrRu₂P₂ data an additional spherical absorption correction was utilized to obtain reasonable thermal parameters. For SrRu₂P₂ (with the data for LaRu₂P₂ in parentheses) a total of 1527 (6676) intensity data up to $2\theta = 90^\circ$ (140°) were recorded in one-half (all) of the reciprocal space. After averaging of equivalent reflections and omitting those with intensities less than three standard deviations, 224 (510) independent reflections remained.

For the full-matrix least-squares refinements scattering factors for neutral atoms (45) were used, corrected for anomalous dispersion (46). The weighting scheme was according to the counting statistics. An isotropic secondary extinction parameter was

refined and applied to the calculated structure factors. To check for positional disorder we have also refined the relative occupation parameters by fixing the occupation of the ruthenium atoms to the ideal value to hold the scale factor. Thus, including the ellipsoidal thermal parameters, a total of 11 variable parameters were refined for each of the two structures. The conventional residuals are *R* = 0.019 and *R* = 0.028 for the strontium and the lanthanum compounds, respectively. The atomic parameters are listed in Table III and interatomic distances in Table IV. Listings of the observed and calculated structure factors are available from the authors (47, 48).

Discussion

Various aspects of chemical bonding in ThCr₂Si₂-type pnictides were discussed in the past (5-10). More quantitative band structure calculations are also available on compounds with this structure (49-51). In a first approximation, the interaction of the electropositive *M* atoms with the two-dimensionally infinite transition metal-pnictogen "anion" (Fig. 1) may be considered as essentially ionic, i.e., La⁺³ [Ru₂P₂]⁻³. The phosphorus atoms are isolated from

each other and obtain oxidation number -3 (thus counting the electrons within the essentially covalent Ru–P bonds as belonging to the phosphorus atoms). As a consequence the ruthenium atoms obtain oxidation number $+1.5$ ($\text{La}^{+3} \text{Ru}^{+1.5} \text{Ru}^{+1.5} \text{P}^{-3}$), i.e., a $d^{6.5}$ system. The fractional oxidation numbers do not give rise to a problem in a band structure and especially not here, since considerable metal–metal bonding (Ru–Ru distances of 285.0 pm) is present in all ThCr_2Si_2 -type phosphides (7–10, 49).

The diamagnetic susceptibility of LaRu_2P_2 shows that all spins are essentially compensated. Its value of $\chi_{\text{exp}} = -50 \times 10^{-6} \text{ cm}^3/\text{mole}$, however, is not small enough to match the possible values calculated from the increments. This is true regardless of which formal charges are conjectured for the ruthenium atoms.¹ However, the superconducting transition of this compound indicates metallic conductivity and thus the weak diamagnetism of LaRu_2P_2 can be rationalized by the superimposed Pauli paramagnetism.

LaRu_2P_2 is the first superconducting phosphide with ThCr_2Si_2 structure. Of the superconducting silicides and germanides enumerated in the Introduction, LaRh_2Si_2 has the highest transition temperature with $T_c = 3.9 \text{ K}$ (35, 36). Like LaRu_2P_2 it has 29 valence electrons per formula unit and thus the two compounds could be isoelectronic. This is not necessarily the case, because the Si–Si distance in LaRh_2Si_2 has not been determined, and ThCr_2Si_2 -type compounds are known with both isolated and pair-forming metalloid atoms (6, 49). Furthermore the body-centered ThCr_2Si_2 - and the

¹ With the increments ($\times 10^{-6}$ in cm^3/mole) of -20 for La^{3+} , -36 and -29 for Ru^{1+} and Ru^{2+} , and the Pascal constant of -26 for P, a value of $\chi_{\text{calc}} = -137 \times 10^{-6} \text{ cm}^3/\text{mole}$ is obtained (52, 53). No increment for P^{3-} is available, however, its value would certainly be smaller than the Pascal constant for P and thus an even smaller total susceptibility would be calculated.

TABLE IV
INTERATOMIC DISTANCES (pm) IN MRu_2P_2
($M = \text{Sr, La}$)^a

	SrRu_2P_2	LaRu_2P_2	Ratio Sr/La
M: 8P	328.7	322.2	1.020
8Ru	343.5	334.4	1.027
Ru: 4P	231.8	232.9	0.995
4Ru	285.1	285.0	1.000
4M	343.5	334.4	1.027
P: 4Ru	231.8	232.9	0.995
1P	327.1	300.4	(1.089)
4M	328.7	322.2	1.020
(Cell volume) ^{1/3}	565.5	557.7	1.014

^a All distances shorter than 350 pm are listed. Standard deviations computed from those of the lattice constants and the positional parameters are all less or equal to 0.3 pm. In the last column the ratios of the bond lengths of the Sr and La compounds are listed.

primitive CaBe_2Ge_2 -type structures are difficult to distinguish from powder diffraction patterns. Actually in the case of LaIr_2Si_2 (34), it is the quenched high-temperature modification with CaBe_2Ge_2 structure which becomes superconducting below 1.6 K, while the carefully annealed samples with the low-temperature ThCr_2Si_2 -type

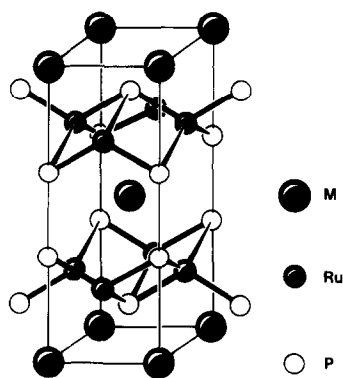


FIG. 1. Crystal structure of MRu_2P_2 compounds with the tetragonal ThCr_2Si_2 structure. The near-neighbor interactions within the essentially covalently bonded ruthenium phosphorus poly-'anion' are emphasized by thick lines.

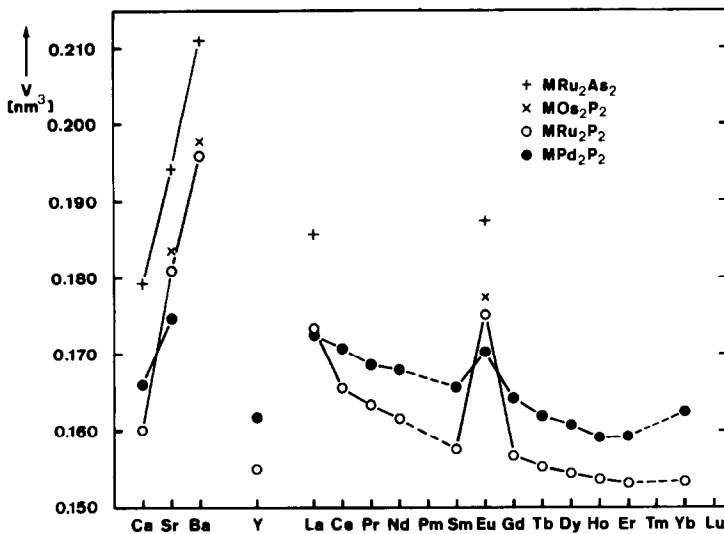


FIG. 2. Cell volumes of ruthenium and osmium compounds with ThCr_2Si_2 structure as compared to the cell volumes of the corresponding palladium compounds.

structure are not superconducting at all down to 1 K.

In Fig. 2 we have plotted the cell volumina of the ternary ruthenium and osmium phosphides and arsenides. It can be seen that the cell volume of EuRu_2P_2 far exceeds that of the other corresponding lanthanoid ruthenium phosphides. Thus, in agreement with its magnetic behavior (43), europium is probably purely divalent in the ruthenium phosphides. The situation is more complicated for EuPd_2P_2 , where the cell volume (7), the europium L_{III} -edge X-ray absorption spectrum (32), and the photoemission from the europium $3d$ core level (31) suggest mixed valence, while magnetic susceptibility measurements (29), the ^{151}Eu Mössbauer isomer shifts (29, 30), and the photoemission of the $4f$ shell (31) indicate divalent europium. The interpretation of these seemingly contradictory results is difficult and outside the scope of our paper. However, in view of the suggestion that in compounds with "divalent" europium the $4f$ states may strongly participate in the formation of the valence bands (29, 30), thus

reducing the cell volume, an unambiguous definition of the term "valency" is needed.

The volume plots (Fig. 2) suggest that cerium in CeRu_2P_2 and CePd_2P_2 is essentially trivalent. The cell volumina of LaRu_2P_2 and LaPd_2P_2 seem to be inconsistent with respect to the corresponding compounds with the heavier rare earth elements. With respect to the corresponding lanthanoid nickel phosphides (6), the cell volume of LaRu_2P_2 seems to be somewhat too large, while that of LaPd_2P_2 is somewhat too small. Such differences are well outside the error limits of the determinations of the lattice constants. They may be due to slight deviations from the ideal composition.

The cell volume of SrRu_2P_2 is larger than that of LaRu_2P_2 . A comparison of the interatomic distances shows, as expected, that the distances from the Sr atoms to its neighbors are larger than the corresponding distances of the La atoms (Table IV). The Ru-Ru distances are the same in both compounds, while the Ru-P distances are slightly larger in the La compound. This may be taken as an indication that the addi-

tional valence electron of the La atoms is filling a band which is antibonding with respect to the Ru–P interactions. The Ru–Ru (284.9 pm) and Ru–P (231.9 pm) distances of EuRu₂P₂ (43), where Eu is divalent as discussed above, are the same within 0.2 pm as those of SrRu₂P₂.

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References

1. Z. BAN AND M. SIKIRIKA, *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. E. PARTHÉ AND B. CHABOT, in *Handbook on the Physics and Chemistry of Rare Earths* (K. A. Gschneidner, Jr., and L. Eyring, Eds.), Vol. 6, pp. 113–334, North-Holland, Amsterdam (1984).
5. R. MARCHAND AND W. JEITSCHKO, *J. Solid State Chem.* **24**, 351 (1978).
6. W. JEITSCHKO AND B. JABERG, *J. Solid State Chem.* **35**, 312 (1980).
7. W. JEITSCHKO AND W. K. HOFMANN, *J. Less-Common Met.* **95**, 317 (1983).
8. W. K. HOFMANN AND W. JEITSCHKO, *J. Solid State Chem.* **51**, 152 (1984).
9. W. K. HOFMANN AND W. JEITSCHKO, *Monatsh. Chem.* **116**, 569 (1985).
10. W. JEITSCHKO, U. MEISEN, M. H. MÖLLER, AND M. REEHUIS, *Z. Anorg. Allg. Chem.* **527**, 73 (1985).
11. E. R. BAUMINGER, D. FROINDLICH, I. NOWIK, S. OFER, I. FELNER, AND I. MAYER, *Phys. Rev. Lett.* **30**, 1053 (1973).
12. A. PALENZONA, S. CIRAFICI, AND F. CANEPA, *J. Less-Common Met.* **119**, 199 (1986).
13. E. ZIRNGIEBL, S. BLUMENRÖDER, G. GÜNTHERODT, AND E. V. SAMPATHKUMARAN, *J. Magn. Magn. Mater.* **54–57**, 343 (1986).
14. G. NEUMANN, J. LANGEN, H. ZAHLE, D. PLÜMACHER, Z. KLETOWSKI, W. SCHLABITZ, AND D. WOHLLEBEN, *Z. Phys. B* **59**, 133 (1985).
15. E. V. SAMPATHKUMARAN, R. VIJAYARAGHAVAN, K. V. GOPALAKRISHNAN, R. G. PILLEY, H. G. DEVARE, L. C. GUPTA, B. POST, AND R. D. PARKS, in "Valence Fluctuations in Solids" (L. M. Falicov, W. Hanke, and M. B. Maple, Eds.), p. 193. North-Holland, Amsterdam (1981).
16. E. KEMLY, M. CROFT, V. MURGAI, L. C. GUPTA, C. GODART, R. D. PARKS, AND C. U. SEGRE, *J. Magn. Magn. Mater.* **47–48**, 403 (1985).
17. F. STEGLICH, J. AARTS, C. D. BREDL, W. LIEKE, D. MESCHEDER, W. FRANZ, AND H. SCHÄFER, *Phys. Rev. Lett.* **43**, 1892 (1979).
18. F. STEGLICH, U. AHLHEIM, J. J. M. FRANSE, N. GREWE, D. RAINER, AND U. RAUCHSCHWALBE, *J. Magn. Magn. Mater.* **52**, 54 (1985).
19. L. C. GUPTA, D. E. MACLAUGHLIN, CHENG TIEN, C. GODART, M. A. EDWARDS, AND R. D. PARKS, *Phys. Rev. B* **28**, 3673 (1983).
20. J. D. THOMPSON, J. O. WILLIS, C. GODART, D. E. MACLAUGHLIN, AND L. C. GUPTA, *Solid State Commun.* **56**, 169 (1985).
21. M. J. BESNUS, J. P. KAPPLER, P. LEHMANN, AND A. MEYER, *Solid State Commun.* **55**, 779 (1985).
22. J. FLOUQUET, P. HAEN, F. LAPIERRE, D. JACCARD, AND G. REMENYI, *J. Magn. Magn. Mater.* **54–57**, 322 (1986).
23. R. NAGARAJAN, E. V. SAMPATHKUMARAN, L. C. GUPTA, R. VIJAYARAGHAVAN, AND G. K. SHENOY, *J. Magn. Magn. Mater.* **31–34**, 757 (1983).
24. R. NAGARAJAN, G. K. SHENOY, L. C. GUPTA, AND E. V. SAMPATHKUMARAN, *J. Magn. Magn. Mater.* **47–48**, 413 (1985).
25. E. V. SAMPATHKUMARAN, I. STANG, R. VIJAYARAGHAVAN, G. KAINDL, AND K. LÜDERS, *Phys. Rev. B* **31**, 6099 (1985).
26. R. NAGARAJAN, G. K. SHENOY, L. C. GUPTA, AND E. V. SAMPATHKUMARAN, *Phys. Rev. B* **32**, 2846 (1985).
27. B. PERSCHIED, E. V. SAMPATHKUMARAN, AND G. KAINDL, *J. Magn. Magn. Mater.* **47–48**, 410 (1985).
28. E. V. SAMPATHKUMARAN, G. WORTMANN, AND G. KAINDL, *J. Magn. Magn. Mater.* **54–57**, 347 (1986).
29. E. V. SAMPATHKUMARAN, B. PERSCHIED, AND G. KAINDL, *Solid State Commun.* **51**, 701 (1984).

30. E. V. SAMPATHKUMARAN, G. KAINDL, W. KRONE, B. PERSCHIED, AND R. VIJAYARAGHAVAN, *Phys. Rev. Lett.* **54**, 1067 (1985).
31. G. K. WERTHEIM, E. V. SAMPATHKUMARAN, C. LAUSCHAT, AND G. KAINDL, *Phys. Rev. B* **31**, 6836 (1985).
32. E. V. SAMPATHKUMARAN, B. PERSCHIED, W. KRONE, AND G. KAINDL, *J. Magn. Magn. Mater.* **47-48**, 407 (1985).
33. G. W. HULL, J. H. WERNICK, T. H. GEBALLE, J. V. WASZCAK, AND J. E. BERNARDINI, *Phys. Rev. B* **24**, 6715 (1981).
34. H. F. BRAUN, N. ENGEL, AND E. PARTHÉ, *Phys. Rev. B* **28**, 1389 (1983).
35. B. CHEVALIER, P. LEJAY, J. ETOURNEAU, AND P. HAGENMULLER, *Mater. Res. Bull.* **18**, 315 (1983).
36. I. FELNER, AND I. NOWIK, *J. Phys. Chem. Solids* **45**, 419 (1984).
37. M. HIRJAK, P. LEJAY, B. CHEVALIER, J. ETOURNEAU, AND P. HAGENMULLER, *J. Less-Common Met.* **105**, 139 (1985).
38. M. FRANCOIS, G. VENTURINI, J. F. MARÉCHÉ, B. MALAMAN, AND B. ROQUES, *J. Less-Common Met.* **113**, 231 (1985).
39. R. GLAUM AND W. JEITSCHKO, in "Third European Conference on Solid State Chemistry, Regensburg, West Germany, May 29-31, 1986," abstracts p. 22.
40. O. NIAL, *Svensk. Kemi Tidskr.* **59**, 172 (1947).
41. K. YVON, W. JEITSCHKO, AND E. PARTHÉ, *J. Appl. Crystallogr.* **10**, 73 (1977).
42. B. EISENMANN, N. MAY, W. MÜLLER, AND H. SCHÄFER, *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **27**, 1155 (1972).
43. G. WENSKI AND A. MEWIS, *Z. Naturforsch. B: Anorg. Chem., Org. Chem.* **41**, 38 (1986).
44. A. MEWIS, *Z. Naturforsch. B: Anorg. Chem., Org. Chem.* **35**, 141 (1980).
45. D. T. CROMER AND J. B. MANN, *Acta Crystallogr. Sect. A* **24**, 321 (1968).
46. D. T. CROMER AND D. LIBERMAN, *J. Chem. Phys.* **53**, 1891 (1970).
47. L. BOONK, Diplomarbeit, Universität Münster, Münster, West Germany (1986).
48. R. GLAUM, Diplomarbeit, Universität Münster, Münster, West Germany (1985).
49. R. HOFFMANN AND C. ZHENG, *J. Phys. Chem.* **89**, 4175 (1985).
50. C. ZHENG AND R. HOFFMANN, private communication.
51. S. ISHIDA, S. ASANO, AND J. ISHIDA, *J. Phys. Soc. Japan.* **55**, 936 (1986).
52. W. KLEMM, *Z. Anorg. Allg. Chem.* **246**, 347 (1941).
53. LANDOLT-BÖRNSTEIN, "New Series II/2," Springer-Verlag, Berlin (1966).