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Ternary Lanthanoid Ruthenium Gallides with a High Gallium Content: $Ln_2Ru_3Ga_{10}$ (Ln = Yb, Lu) with a New Structure Type and $LnRu_2Ga_8$ (Ln = La−Nd) with $CaCo_2Al_8$-type Structure

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The title compounds were prepared by reaction of the elemental components at high temperatures. The compounds $Yb_2Ru_3Ga_{10}$ and $Lu_2Ru_3Ga_{10}$ crystallize with a new structure type, which has been determined from the single-crystal X-ray data of $Yb_2Ru_3Ga_{10}$: $P4/mbm$, $Z = 2$, $a = 881.9(1)$ pm, $c = 632.5(1)$ pm. In this structure the gallium atoms form two-dimensionally infinite double layers that extend perpendicular to the tetragonal axis. They contain two-thirds of the ruthenium atoms. The other ruthenium and the ytterbium atoms are situated between the gallium double layers. The structure is closely related to that of Mn_2Hg_5. The latter compound may be written with the formula $Mn_2Mn_2\square Hg_{10}$, thus indicating that its structure may be regarded as a defect-variant of the presently reported structure of $Yb_2Ru_3Ga_{10}$. The four gallides of the series $LnRu_2Ga_8$ (Ln = La−Nd) crystallize with the orthorhombic $CaCo_2Al_8$-type structure ($Pbam$, $Z = 4$). This structure has been refined from single-crystal X-ray data of the cerium and neodymium compounds. Slight deviations from the ideal composition for one of the two ruthenium sites resulted in the formulas $CeRu_{1.913(4)}Ga_8$ and $NdRu_{1.858(4)}Ga_8$. Magnetic susceptibility measurements with a SQUID magnetometer indicate diamagnetism for $LaRu_2Ga_8$, which is partially compensated by the expected Pauli paramagnetism. The cerium atoms in $CeRu_2Ga_8$ show mixed or intermediate valent behavior, and $PrRu_2Ga_8$ follows the Curie−Weiss law with no magnetic order down to 4 K.

Introduction

A large number of ternary intermetallics of the rare earth and transition metals with a high content of aluminum have been reported. Some recent examples are $La_4Mo_7Al_{51}$ and $La_4W_7Al_{51}$,[1] $EuCo_2Al_9$,[2] the series $LnRe_2Al_{10}$,[3] $Ln_4Pd_9Al_{24}$ and $Ln_4Pt_9Al_{24}$,[4] $GdRe_2Al_{10}$ and $TbRe_2Al_{10}$,[5] and $NdRh_4Al_{15.37}$.[6] We have started to search for corresponding gallium compounds, and we have already presented our results on the series $Ln_2Ru_3Ga_9$.[7]

We now report on gallides with the similar compositions $Ln_2Ru_3Ga_{10}$ with a new structure type and $LnRu_2Ga_8$ with $CaCo_2Al_8$-type[8] structure. Various aluminides and gallides with this latter structure type have been prepared in recent years: the calcium compounds $CaCo_2Al_8$ and $CaNi_2Al_8$,[9] the series $LnFe_2Ga_8$ and $LnCo_2Ga_8$,[10,11] the series $LnCo_2Al_8$,[12,13] and the compound $EuFe_2Al_8$.[14] Only recently the first indium-containing compound $EuRh_2In_8$ with $CaCo_2Al_8$-type structure has been reported.[15] A preliminary account on the new crystal structure of $Yb_2Ru_3Ga_{10}$ has already been presented at a conference.[16]

Experimental Section

Sample Preparation, Properties, and Lattice Constants. The compounds were prepared from the elemental components, all with nominal purities >99.9%. The rare earth elements were purchased in the form of ingots; they were cut to pieces prior to the cold-pressing. Ruthenium (Degussa) was obtained in powder form and gallium (VAW) in the form of ingots that were crushed to small pieces at liquid nitrogen temperature. The three components with a total weight of ca. 0.5 g were mixed in the ratios Ln:Ru:Ga = 1:1:10 for the compounds $LnRu_2Ga_8$ and Ln:Ru:Ga = 2:3:10 for the compounds $Ln_2Ru_3Ga_{10}$. They were cold-pressed to pellets and placed in alumina crucibiles. These crucibles were then put in a water-cooled silica sample chamber in a high-frequency furnace under argon atmosphere. The samples were heated (up to ca. 1000 °C) until an exothermic reaction was observed. They were then cooled to a temperature slightly below the melting point and kept at that temperature for 5 h. Finally the samples were cooled to room temperature within 1 min. The excess rare earth and gallium in the samples Ln:Ru:Ga = 1:1:10 was dissolved in diluted hydrochloric acid, which attacks the crystals of the ternary compounds at a much smaller rate.

All of these ternary gallides are stable on air for long periods of time and show silvery metallic luster. The powders are dark gray. One

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Table 1. Lattice Constants of Gallides with Orthorhombic $CaCo_2Al_8$-type Structure and $Ln_2Ru_3Ga_{10}$ with a New Tetragonal Structure[a]

compound	*a* (pm)	*b* (pm)	*c* (pm)	*V* (nm^3)
$LaRu_2Ga_8$	1264.7(2)	1473.3(2)	411.7(1)	0.7671
$CeRu_2Ga_8$	1260.4(2)	1471.1(2)	409.8(1)	0.7598
$PrRu_2Ga_8$	1260.7(3)	1471.1(3)	408.0(1)	0.7567
$NdRu_2Ga_8$	1259.1(3)	1470.8(3)	407.2(1)	0.7541
$Yb_2Ru_3Ga_{10}$	881.9(1)		632.5(1)	0.4919
$Lu_2Ru_3Ga_{10}$	881.7(1)		630.7(1)	0.4902

[a] These lattice constants were obtained from Guinier powder data. Standard deviations in the place values of the last listed digits are given in parentheses throughout the paper.

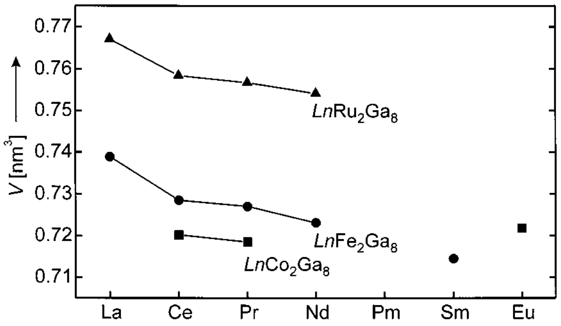

Figure 1. Cell volumes of the new gallides $LnRu_2Ga_8$ with $CaCo_2Al_8$-type structure together with those of the series $LnFe_2Ga_8$ and $LnCo_2Ga_8$ reported from a previous investigation.[11]

sample of $Yb_2Ru_3Ga_{10}$ contained well-crystallized platelets. After dissolving the matrix, the compounds $LnRu_2Ga_8$ were obtained in the form of elongated needles, frequently aggregated in the form of bundles. Energy-dispersive X-ray fluorescence analyses in a scanning electron microscope did not reveal any impurity elements heavier than sodium.

Guinier powder diagrams of the new intermetallic compounds were recorded with monochromated Cu $K\alpha_1$ radiation and α-quartz ($a = 491.30$ pm, $c = 540.46$ pm) as an internal standard. To ensure proper assignment of the indices, the observed patterns were compared with the ones calculated[17] by assuming the atomic positions obtained from the structure refinements of the cerium and ytterbium compounds. The lattice constants (Table 1) were obtained by least-squares fits. The cell volumes of the $CaCo_2Al_8$-type compounds are plotted in Figure 1 together with those of isotypic gallides found during another investigation.[11]

Structure Determinations. Single crystals of the compounds $CeRu_2Ga_8$, $NdRu_2Ga_8$, and $Yb_2Ru_3Ga_{10}$ were selected for the structure determinations on the basis of Laue patterns. X-ray intensity data were collected at room temperature on an Enraf-Nonius CAD4 diffractometer with $\theta/2\theta$ scans using graphite-monochromated Mo Kα radiation, a scintillation counter with pulse-height discrimination, and background counts at both ends of each scan. Empirical absorption corrections were made on the basis of ψ scan data. The crystal data are listed in Table 2, and more detailed information is in the Supporting Information.

The structures were determined and refined with the program package SHELX-97.[18] The positions of the rare earth atoms were located by a Patterson function, and the other atoms through difference Fourier syntheses. For the refinements, a full-matrix least-squares program was used with atomic scattering factors, corrected for anomalous dispersion as provided by the program. The weighting schemes reflected the counting statistics, and isotropic parameters correcting for secondary extinction were optimized as least-squares variables. For all three structures we refined occupancy values together with the displacement parameters. These occupancy parameters generally varied between 0.993(2) and 1.005(3) for the Yb and Ru2 positions of $Yb_2Ru_3Ga_{10}$, between 0.992(5) and 1.014(9) for the Ga6 and Ga9 positions of $CeRu_2Ga_8$, and between 0.984(8) and 1.012(8) for the Ga6 and Ga1 positions of $NdRu_2Ga_8$; for these positions, the ideal occupancies were assumed during the final refinement cycles. The only exceptions were the Ru1 positions of $CeRu_2Ga_8$ and $NdRu_2Ga_8$, where relative large deviations from the full occupancies were observed. Thus, in the final least-squares cycles these positions were refined with variable occupancies. In the final difference Fourier syntheses, the highest and lowest values were $1.6/-2.1$ e/Å^3 for $CeRu_2Ga_8$, $2.4/-2.7$ e/Å^3 for $NdRu_2Ga_8$, and $5.2/-4.3$ e/Å^3 for $Yb_2Ru_3Ga_{10}$. All of the positive peaks were in the vicinity of fully occupied atomic sites and for that reason not suited for additional atomic positions. The positional parameters of all three compounds were standardized using the program STRUCTURE TIDY.[19] The atomic parameters and interatomic distances are listed in the Tables 3−6. The anisotropic displacement parameters are given in a table of the Supporting Information.

Magnetic Properties. After dissolving the gallium-rich matrix, the Guinier powder patterns of the three compounds $LnRu_2Ga_8$ (Ln = La, Ce, Pr) showed no impurity lines. The magnetic properties of these compounds were investigated with a superconducting interference quantum device magnetometer (SQUID; Quantum Design, MPMS). About 20−30 mg of each sample was placed in a thin-walled silica tube (o.d. 2 mm) and held in place by compression with a cotton plug. The samples were cooled in zero magnetic field and their magnetic susceptibilities were recorded at the desired magnetic flux density on heating. To check for ferromagnetic impurities, the samples were examined at 300 K with variable magnetic flux densities. Only very small amounts of such impurities were detected that way. The susceptibilies measured at 3 T were practically identical with those measured at 5 T.

The magnetic susceptibility of $LaRu_2Ga_8$ (Figure 2) shows nearly temperature-independent diamagnetism We have evaluated these data with the modified Curie−Weiss law: $\chi = \chi_0 + C/(T - \Theta)$. The least-squares fit resulted in a temperature-independent term of the magnetic susceptibility of $\chi_0 = -1.6(\pm 0.1) \times 10^{-9}$ m^3 per mol of the formula unit (fu). From the temperature-dependent part a small magnetic moment of $\mu_{exp} = 0.11(\pm 0.01)$ μ_B was obtained. This corresponds to the upturn of the magnetic susceptibility at low temperatures ("Curie

Table 2. Crystal Data of $Yb_2Ru_3Ga_{10}$, $CeRu_2Ga_8$, and $NdRu_2Ga_8$[a]

compound	$Yb_2Ru_3Ga_{10}$	$CeRu_2Ga_8$	$NdRu_2Ga_8$
space group	*P*4/*mbm* (No. 127)	*Pbam* (No. 55)	*Pbam* (No. 55)
a (pm)	881.9(1) [881.8(1)]	1260.4(2) [1260.3(2)]	1259.1(3) [1258.1(1)]
b (pm)	881.9(1) [881.8(1)]	1471.1(2) [1470.7(2)]	1470.8(3) [1469.8(1)]
c (pm)	632.5(1) [632.0(1)]	409.8(1) [409.7(1)]	407.2(1) [407.1(1)]
V (nm^3)	0.4919 [0.4914]	0.7598 [0.7594]	0.7541 [0.7529]
Z	2	4	4
T (°C)	21	21	21
λ (pm)	71.07	71.07	71.07
composition	$Yb_2Ru_3Ga_{10}$	$CeRu_{1.913(4)}Ga_8$	$NdRu_{1.858(4)}Ga_8$
formula mass	1346.5	891.1	889.8
ρ_{calc} (g/cm^3)	9.09	7.79	7.84
μ (cm^{-1})	501	373	383
$R(F)$[b]	0.033	0.020	0.021
$R_w(F^2)$[b]	0.090	0.057	0.055

[a] The lattice constants were obtained from Guinier powder [single crystal] data. [b] $R = \sum||F_o - |F_c||/\sum F_o$; $R_w = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (V \cdot P)^2]$, where $P = (\max(F_o^2) + 2F_c^2)/3$ and $V = 0.0271$ for $CeRu_2Ga_8$, $V = 0.0210$ for $NdRu_2Ga_8$, and $V = 0.0580$ for $Yb_2Ru_3Ga_{10}$.

Table 3. Atomic Parameters of $Yb_2Ru_3Ga_{10}$[a]

atom	*P4/mbm*	x	y	z	B_{eq}
Yb	4*g*	0.18337(4)	$^1/_2 + x$	0	0.56(2)
Ru1	4*h*	0.17841(6)	$^1/_2 + x$	$^1/_2$	0.38(2)
Ru2	2*a*	0	0	0	0.36(2)
Ga1	16*l*	0.06093(7)	0.20684(7)	0.2925(1)	0.56(2)
Ga2	4*f*	0	$^1/_2$	0.2843(2)	0.62(2)

[a] The last column contains the equivalent isotropic B values ($\times 10^4$ pm^2).

Table 4. Interatomic Distances in the Structure of $Yb_2Ru_3Ga_{10}$[a]

Yb:	2Ga2	290.9		2Yb1	316.3		2Ga1	268.9
	4Ga1	292.4	Ru2:	8Ga1	265.3		Ga1	289.6
	4Ga1	300.0		4Yb1	322.7		Yb1	292.4
	2Ru1	316.3	Ga1:	Ga1	262.5		Yb1	300.0
	2Ru2	322.7		Ga2	264.1	Ga2:	2Ru1	261.0
Ru1:	2Ga2	261.0		Ru2	265.3		4Ga1	264.1
	4Ga1	265.9		Ru1	265.9		Ga2	272.9
	4Ga1	268.4		Ru1	268.4		2Yb1	290.9

[a] All distances <355 pm are listed. They were calculated with the lattice constants from the Guinier powder data. The standard deviations are all equal to or less than 0.1 pm for all interatomic distances, with the exception of the Ga2−Ga2 distance, where it is 0.3 pm.

Table 5. Atomic Parameters of $CeRu_2Ga_8$ and $NdRu_2Ga_8$[a]

atom	*Pbam*	x	y	z	B_{eq}
		$CeRu_{1.913(4)}Ga_8$			
Ce	4*g*	0.34381(3)	0.31907(3)	0	0.71(1)
Ru1	4*g*	0.03618(5)	0.40415(4)	0	0.48(2)
Ru2	4*g*	0.15421(4)	0.09574(4)	0	0.43(1)
Ga1	4*h*	0.02329(6)	0.13231(6)	$^1/_2$	0.62(2)
Ga2	4*h*	0.16624(6)	0.37550(6)	$^1/_2$	0.68(1)
Ga3	4*h*	0.24244(6)	0.17556(5)	$^1/_2$	0.72(1)
Ga4	4*h*	0.33052(6)	0.48638(6)	$^1/_2$	0.71(1)
Ga5	4*h*	0.45172(6)	0.18503(6)	$^1/_2$	0.66(1)
Ga6	4*g*	0.09922(7)	0.25260(6)	0	0.99(2)
Ga7	4*g*	0.34046(6)	0.04456(6)	0	0.93(2)
Ga8	2*d*	0	$^1/_2$	$^1/_2$	0.76(2)
Ga9	2*a*	0	0	0	0.81(2)
		$NdRu_{1.858(4)}Ga_8$			
Nd	4*g*	0.34438(3)	0.31914(3)	0	0.80(1)
Ru1	4*g*	0.03628(6)	0.40445(5)	0	0.48(2)
Ru2	4*g*	0.15401(5)	0.09611(4)	0	0.46(1)
Ga1	4*h*	0.02294(7)	0.13264(6)	$^1/_2$	0.63(2)
Ga2	4*h*	0.16705(7)	0.37521(6)	$^1/_2$	0.69(2)
Ga3	4*h*	0.24310(7)	0.17627(6)	$^1/_2$	0.73(2)
Ga4	4*h*	0.33034(7)	0.48604(6)	$^1/_2$	0.72(2)
Ga5	4*h*	0.45186(7)	0.18559(6)	$^1/_2$	0.67(2)
Ga6	4*g*	0.09937(8)	0.25359(7)	0	1.10(2)
Ga7	4*g*	0.34050(8)	0.04469(7)	0	0.98(2)
Ga8	2*d*	0	$^1/_2$	$^1/_2$	0.84(2)
Ga9	2*a*	0	0	0	0.85(3)

[a] For the Ru1 positions, occupancy values of 0.913(4) and 0.858(4) were obtained for the cerium and neodymium compounds, respectively. All other atomic positions were refined with the ideal occupancies (see the text). The last column contains the equivalent isotropic B values ($\times 10^4$ pm^2).

tail") and can be ascribed to minor amounts of paramagnetic impurities and surface states. For one uncompensated spin/fu a much larger magnetic moment of $\mu_{eff} = 1.73\ \mu_B$ could be expected. Thus, the ruthenium atoms of these compounds do not seem to carry magnetic moments.

The reciprocal susceptibility of $CeRu_2Ga_8$ seems to follow the Curie−Weiss law at temperatures above 100 K. However, the behavior at lower temperatures suggests a mixed or intermediate valence for the cerium atoms. This is also indicated by the extremely negative Weiss constant of $\Theta = -155(\pm 5)$ K. On the other hand, the plot of the cell volumes (Figure 1) shows no great deviation from the linear lanthanoid contraction for this compound, thus indicating that only a small fraction of the cerium atoms can be four-valent.

The praseodymium compound $PrRu_2Ga_8$ shows Curie−Weiss behavior down to very low temperatures (Figure 2). A negative Weiss constant of $\Theta = -8$ K was extrapolated from the linear $1/\chi$ vs T plot. The magnetic moment of $\mu_{exp} = 3.48(2)\ \mu_B$ calculated from the slope of this plot is in very good agreement with the theoretical moment of $\mu_{eff} = 3.58\ \mu_B$, calculated from the formula $\mu_{eff} = g(J(J+1))^{1/2}$.[20] The negative Weiss constant suggests antiferromagnetic or ferrimagnetic order, which seems to set in at 2 K, as indicated by the magnetization behavior at this temperature. The highest magnetization of $\mu_{sm(exp)} = 1.77\ \mu_B$/fu observed at a magnetic flux density of 5.5 T (the highest obtainable with our SQUID magnetometer) is well below the theoretical saturation magnetization of $\mu_{sm(calc)} = 3.20\ \mu_B/Pr^{3+}$, calculated from the relation $\mu_{sm(calc)} = gJ$.[20] The low ordering temperature of the praseodymium moments reflects the fact that the praseodymium atoms are well-separated from each other. They are coordinated only by gallium atoms, and in the corresponding neodymium compound the shortest Nd−Nd distances amount to 407.2(1) pm.

Discussion

The crystal structure and the coordination polyhedra of $Yb_2Ru_3Ga_{10}$ are shown in the Figures 3 and 4. The ytterbium atoms are situated in pentagonal prisms of gallium atoms with four additional ruthenium neighbors capping the two pentagonal and two of the rectangular faces of this prism. The Yb−Ga distances (290.9−300.0 pm) are shorter than the Yb−Ru distances (316.3 and 322.7 pm), even though the metallic radii for the coordination number (CN) 12 show the inverse relation ($r_{Ga} = 141.1$ pm, $r_{Ru} = 133.9$ pm).[21] This indicates that the Yb−Ga bonding is stronger than the Yb−Ru interactions.

Both ruthenium atoms have CN 12, however, with remarkably different environments. The Ru1 atom is situated in a pentagonal prism of gallium atoms, where the two pentagonal faces are capped by ytterbium atoms. The Ru2 atom has eight gallium neighbors in a square-prismatic arrangement with the four rectangular faces capped by ytterbium atoms. The Ru−Ga distances cover the relatively narrow range from 261.0 to 268.4 pm. These distances are considerably shorter than the sum of the CN 12 radii of these elements, which amounts to 275.0 pm, thus reflecting the strength of the Ru−Ga bonding.

The two gallium positions have less regular coordinations with CN 10 and 9 for Ga1 and Ga2, respectively. Both have five gallium neighbors with Ga−Ga distances between 262.5 and 289.6 pm and average Ga−Ga distances of 270.8 and 265.9 pm. Again, these distances are shorter than twice the radius of gallium for CN 12 (282.2 pm). However, here the gallium atoms have coordination numbers lower than 12, which are known to result in stronger bonds and shorter distances. In elemental gallium, a gallium atom has seven near neighbors at distances between 248.4 and 278.8 pm with an average Ga−Ga distance of 270.0 pm.[22]

The crystal structure of $Yb_2Ru_3Ga_{10}$ is of a new type. Because of the high gallium content of this compound, its structure is dominated by the Ga−Ga interactions (Figure 3). The gallium atoms form two-dimensionally infinite double layers that extend

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Table 6. Interatomic Distances in the Structures of $LnRu_2Ga_8$ (Ln = Ce/Nd)[a]

Ln:	2Ga1	313.5/311.5	Ga2:	Ga4	263.6/262.4		2Ga6	291.5/289.8
	2Ga2	314.6/313.2		2Ru1	265.8/265.4		2Ln	315.2/313.6
	2Ga5	315.2/313.6		Ga8	278.3/279.2		2Ga7	323.1/322.6
	2Ga4	320.7/319.4		Ga5	284.6/285.3	Ga6:	Ru1	236.7/235.7
	2Ga3	320.8/319.2		2Ga6	286.0/284.1		Ru2	241.0/241.6
	Ga6	323.4/323.2		Ga3	309.4/307.9		2Ga2	286.0/284.1
	Ga9	331.1/330.4		2Ln	314.6/313.2		2Ga1	287.2/287.0
	Ga6	338.7/338.4		2Ga7	322.3/322.0		2Ga5	291.5/289.8
Ru1:	Ga6	236.7/235.7	Ga3:	2Ru2	261.0/260.7		2Ga3	295.6/295.2
	2Ga8	252.9/251.6		Ga5	264.2/263.2		Ln	323.4/323.2
	Ga7	258.0/257.6		Ga1	283.5/284.5		Ln	338.7/338.4
	Ga7	258.5/258.1		Ga4	293.1/294.7	Ga7:	Ru2	246.5/246.7
	2Ga5	265.6/265.1		2Ga6	295.7/295.2		Ru1	258.0/257.6
	2Ga2	265.8/265.4		2Ga7	307.3/306.5		Ru1	258.5/258.1
	Ru1	296.4/295.5		Ga2	309.4/307.9		2Ga8	294.5/293.4
Ru2:	Ga9	240.0/240.0		2Ln	320.7/319.2		2Ga3	307.2/306.5
	Ga6	241.0/241.6	Ga4:	2Ru2	261.2/260.9		2Ga4	309.4/308.5
	Ga7	246.5/246.7		Ga2	263.6/262.4		2Ga2	322.3/322.0
	2Ga3	261.0/260.7		Ga1	282.9/283.9		2Ga5	323.1/322.6
	2Ga4	261.2/260.9		Ga3	293.1/294.7	Ga8:	4Ru1	252.9/251.6
	2Ga1	268.5/267.5		2Ga9	296.7/295.8		2Ga2	278.3/279.2
Ga1:	2Ru2	268.5/267.5		Ga1	299.2/298.8		2Ga5	278.9/279.6
	Ga4	282.9/283.9		2Ga7	309.4/308.5		4Ga7	294.5/293.4
	Ga5	283.4/282.0		2Ln	320.7/319.4	Ga9:	2Ru2	240.0/240.0
	Ga3	283.5/284.5	Ga5:	Ga3	264.2/263.2		4Ga1	284.1/283.5
	2Ga9	284.1/283.5		2Ru1	265.6/265.1		4Ga4	296.7/295.8
	2Ga6	287.2/287.0		Ga8	278.9/279.6		2Ln	331.1/330.4
	Ga4	299.2/298.8		Ga1	283.5/282.0			
	2Ln	313.5/311.5		Ga2	284.6/285.3			

[a] All distances shorter than 390 pm are listed. The standard deviations are all 0.1 pm or less.

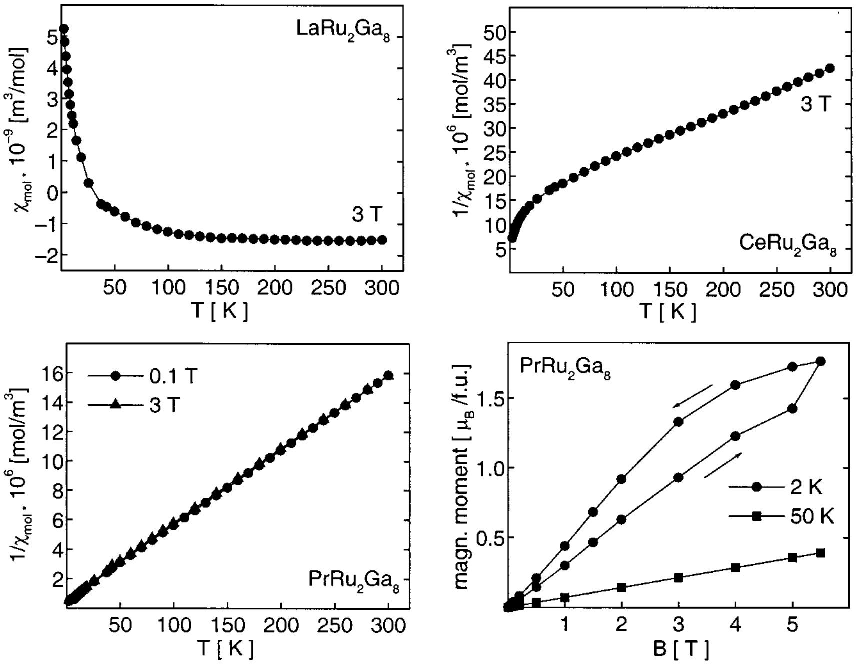

Figure 2. Magnetic properties of the three gallides $LnRu_2Ga_8$ (Ln = La, Ce, Pr). The magnetic susceptibilities χ of $LaRu_2Ga_8$ (measured with a magnetic flux density of 3 T) and the reciprocal susceptibilities of $CeRu_2Ga_8$ and $PrRu_2Ga_8$ are plotted as a function of temperature. The magnetization behavior of $PrRu_2Ga_8$, measured at temperatures of 2 and 50 K with magnetic flux densities up to 5.5 T, is also shown.

perpendicular to the tetragonal axis. Mirror planes are situated between and within the double layers. Viewed along the 4-fold axis, the layers consist of triangles, squares, and pentagons of gallium atoms, all with relatively strong Ga−Ga bonds. The tesselation of these layers can be described by the Schläfli symbol[21b,23] 3545 + 3535 (4:1), where the first and second groups of numbers correspond to the Ga1 and Ga2 sites, respectively, and the numbers indicate the sequence of adjacent triangles, squares, and pentagons for the two gallium sites. The Ga−Ga distances between the double layers are greater than 350 pm, and therefore, these distances are all very weekly bonding at best. The Ru1 atoms occupy pentagonal gallium prisms within the double layers, the Ru2 and Yb atoms are situated between the double layers in tetragonal and (distorted) pentagonal prisms of gallium atoms.

Figure 3 demonstrates the close relationship of the $Yb_2Ru_3Ga_{10}$ structure to that of Mn_2Hg_5 reported by de Wet.[24] The

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(23) (a) Frank, F. C.; Kasper, J. S. *Acta Crystallogr.* **1958**, *11*, 184. (b) Frank, F. C.; Kasper, J. S. *Acta Crystallogr.* **1959**, *12*, 483.

(24) de Wet, J. F. *Acta Crystallogr.* **1961**, *14*, 733.

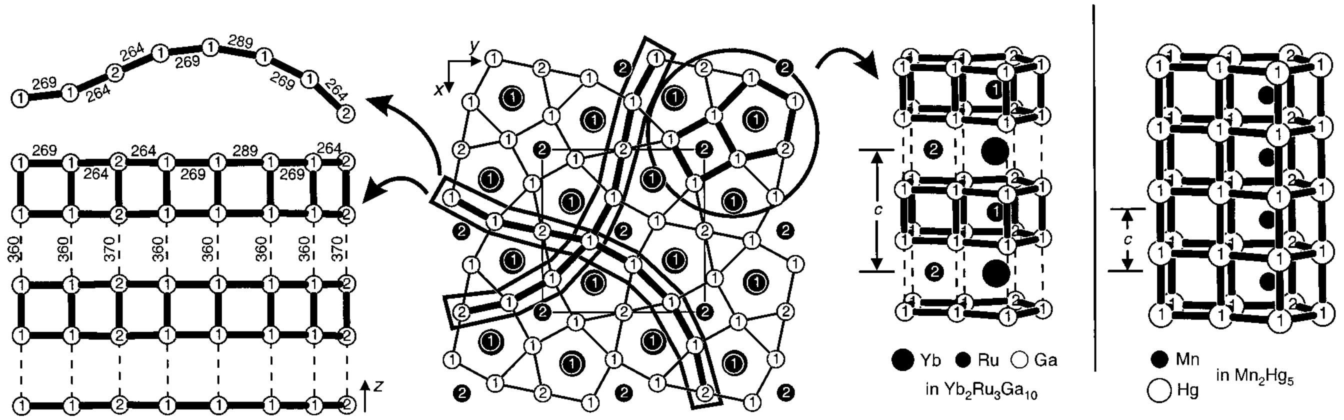
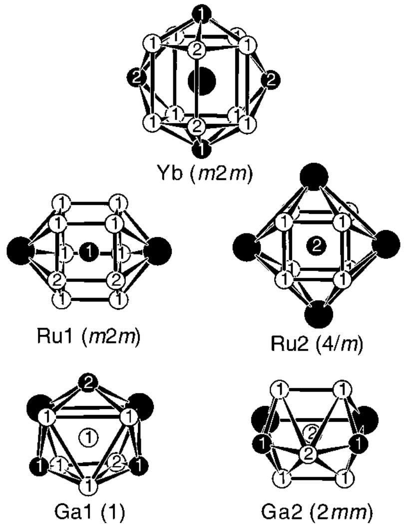


Figure 3. Crystal structure of $Yb_2Ru_3Ga_{10}$ and its relation to the structure of Mn_2Hg_5. A projection of the $Yb_2Ru_3Ga_{10}$-type structure along the tetragonal axis is shown in the center of the figure. Two condensed columns of gallium atoms with tetragonal and pentagonal cross sections are outlined in this drawing and shown at the right-hand side of the figure together with a corresponding atomic arrangement of the Mn_2Hg_5 type structure. Both structures have the same space group symmetry (*P*4/*mbm*). The difference arises through the ordered arrangement of Yb and Ru1 atoms on the Mn sites of the Mn_2Hg_5, which leads to a doubling of the translation period *c* in $Yb_2Ru_3Ga_{10}$. The positions corresponding to the Ru2 atoms are not occupied in the structure of Mn_2Hg_5 ($\sim Mn_2Mn_2\square Hg_{10}$). The gallium atoms in the structure of $Yb_2Ru_3Ga_{10}$ are all situated at two levels with $z \sim 0.29$ and ~ 0.71. They are bonded to each other, thus forming two-dimensionally infinite double layers extending perpendicular to the tetragonal *c* axis. Superimposed chains of gallium atoms can be visualized. Two of these superpositions are outlined in the center of the figure, and one of these, emphasizing the Ga−Ga bonds (pm), is shown in a projection perpendicular to the tetragonal axis at the left-hand side of the figure.


Yb (*m*2*m*)

Ru1 (*m*2*m*)

Ru2 (4/*m*)

Ga1 (1)

Ga2 (2*mm*)

Figure 4. Coordination polyhedra in the structure of $Yb_2Ru_3Ga_{10}$. All near neighbors listed in Table 4 are shown. Single-digit numbers correspond to the atom designations. The site symmetries of the central atoms are listed in parentheses.

latter structure has also been observed for the binary gallides Mn_2Ga_5,[25,26] V_2Ga_5,[25,27−30] and W_2Ga_5,[31] as well as for the indium and tin compounds Ti_2In_5[32] and Li_2Sn_5.[33] It can be seen on the right-hand part of Figure 3 that the positions of the Mn atoms of Mn_2Hg_5 are occupied by alternating Yb and Ru1 atoms in $Yb_2Ru_3Ga_{10}$. The Ru2 atoms occupy sites that are empty in Mn_2Hg_5. The translation period *c* of the ternary gallium compound is doubled (i) due to the alternating Yb and Ru1 atoms and (ii) due to the sequence of occupied Ru2 positions. The binary compound may be written with the formula $Mn_2Mn_2\square Hg_{10}$, thus indicating that its structure may be regarded as a defect-variant of the ternary compound represented by the formula $Yb_2Ru_2RuGa_{10}$. The electron counts for two formula units of the binary compounds enumerated above cover the range from 44 for Li_2Sn_5 to 58 for two formula units of Mn_2Ga_5. For $Yb_2Ru_3Ga_{10}$ the electron count is somewhat higher, with 60 electrons for the corresponding formula. It would be interesting to see how the higher electron count affects the interatomic distances. However, for a detailed comparison of Ga−Ga bonding in the binary gallides T_2Ga_5 (T = V, W, and Mn) on one hand and the ternary compound $Yb_2Ru_3Ga_{10}$ on the other, the positional parameters of the binary gallides would need to be known. It can be expected that, due to the higher electron count of the ternary compound, the Ga−Ga bonding will be weaker in the ternary compound; i.e., the orbitals coming from the gallium atoms will contain electrons with somewhat more nonbonding character. This is already indicated by the large number of relatively long Ga−Ga distances of 360−370 pm in the ternary compound (left-hand side of Figure 3), as compared to the corresponding distances in the binary compound Mn_2Hg_5 (right-hand side of Figure 3). In this respect the double layers of gallium atoms filled with the Ru1 atoms resemble the double layers of sulfur atoms in the layer structures of the early transition metal disulfides, for instance TiS_2 or MoS_2. The positions of the Yb and the Ru2 atoms would then correspond to the positions of the metal atoms resulting from an intercalation reaction of the binary disulfides with intercalating metals. For reviews about such intercalation compounds, the reader is referred to the literature and the references cited therein.[34−36]

The compounds $LnRu_2Ga_8$ (Ln = La−Nd) are isotypic with a structure first determined for $CaCo_2Al_8$.[8] This structure has also been refined for $YbCo_2Ga_8$,[10] $CaNi_2Al_8$,[9] and $EuRh_2In_8$.[15] We have refined this structure for $CeRu_2Ga_8$ and $NdRu_2Ga_8$.

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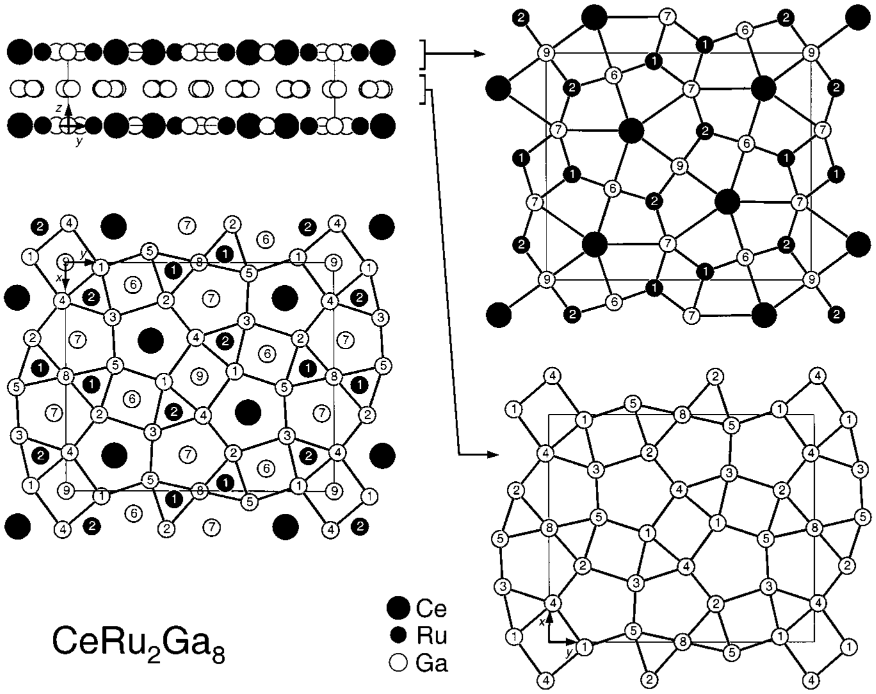

Figure 5. Crystal structure of $CeRu_2Ga_8$. All atoms are located on mirror planes at $z = 0$ and $^1/_2$. The lines connecting the atoms do not necessarily represent chemical bonds. Single-digit numbers correspond to the atom designations.

Our structure refinements are the first ones where one transition metal site was found not to be fully occupied, resulting in the compositions $CeRu_{1.913(4)}Ga_8$ and $NdRu_{1.858(4)}Ga_8$. We have considered the possibility of mixed Ru/Ga occupancies for the Ru1 positions. The corresponding least-squares refinements for these positions resulted in Ru/Ga occupancies of 64(2)/36(2) and 40(2)/60(2) for the cerium and neodymium compounds, respectively. However, such large gallium contents for these sites can be ruled out, considering that the Ru1 and Ru2 atoms have similar coordinations, quite different from those of the gallium atoms. Furthermore, the gallium atoms are much larger. With a gallium content of 60% for the Ru1 site of the neodymium compound (as compared to 36% for the Ru1 position of the cerium compound), the interatomic distances for the Ru1 atoms of the neodymium compound should be longer than those in the cerium compound. A look at Table 6 readily shows that the opposite is the case. Thus, a large amount of gallium atoms on the Ru1 sites can be ruled out.

As could be expected, the interatomic distances of the two compounds are very similar (Table 6). We will briefly discuss the structure and the near-neighbor coordinations (Figures 5 and 6) with $CeRu_2Ga_8$ as an example. All atoms are situated on two mirror planes. One of these is occupied by the cerium, ruthenium, and some gallium atoms; all other gallium atoms are situated on the other mirror plane.

The large cerium atoms are situated in a pentagonal prism of gallium atoms where all faces are capped by gallium atoms. However, there is a distinct differentiation in that the near gallium neighbors have Ce−Ga bonds of between 313.5 and 338.7 pm. The next near gallium neighbor of a cerium atom is at 403.9 pm. Thus, there is a huge gap between 338.7 and 403.9 pm, and in counting only gallium neighbors up to that gap, the cerium atoms have only 13 gallium neighbors.

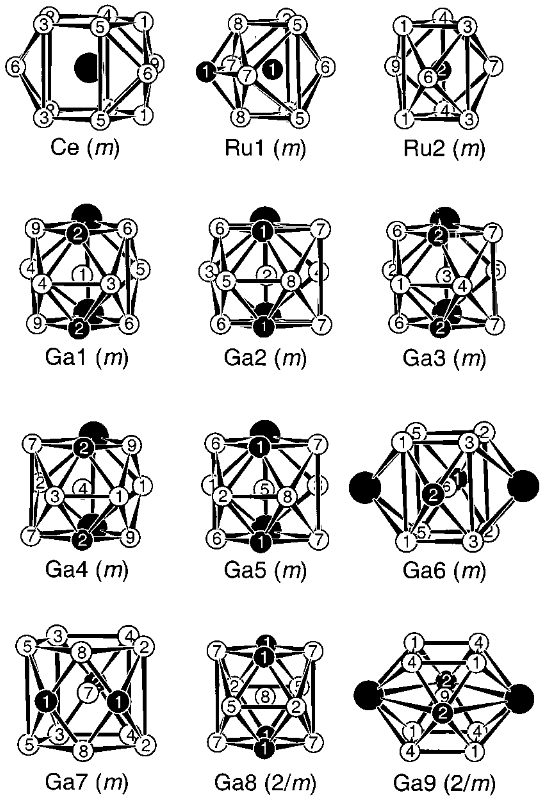
Ce (*m*) Ru1 (*m*) Ru2 (*m*)
Ga1 (*m*) Ga2 (*m*) Ga3 (*m*)
Ga4 (*m*) Ga5 (*m*) Ga6 (*m*)
Ga7 (*m*) Ga8 (2/*m*) Ga9 (2/*m*)

Figure 6. Near-neighbor environments in the gallide $CeRu_2Ga_8$. All neighbors listed in Table 6 are shown. Single-digit numbers correspond to the atom designations. The site symmetries are listed in parentheses.

There are two ruthenium positions. Both are situated in tricapped trigonal prisms of gallium atoms, resulting in CN 9. However, the Ru1 atom has another neighbor, a Ru1 atom with a Ru1−Ru1 distance of 296.4 pm. This distance may be considered as very weakly bonding, in view of the metallic radius (for CN 12) of ruthenium $r = 133.9$ pm[21] ($2r = 267.8$ pm). The Ru−Ga distances cover the range between 236.7 and 268.5 pm, with averages of 258.0 and 256.5 pm for the Ru1 and Ru2 atoms, respectively, reflecting the higher CN of the Ru1 atom. The fact that the Ru1 position is not fully occupied [occupancies of 91.3(4)% and 85.8(4)% for the cerium and neodymium compounds, respectively] should result in shorter

Ru1−Ga bonds; apparently, this is outweighed by the differences in the CNs. A small amount of Ru/Ga substitution could also account for this small difference of the average Ru−Ga distances for the two ruthenium sites. Any substantial Ru/Ga substitution, however, can be ruled out, as discussed above.

The gallium atoms occupy nine different positions, all with 8 gallium neighbors, with the exception of the Ga7 atom, which has 10 gallium neighbors. Including the ruthenium and cerium neighbors, the total CN of the gallium atoms is 12, again with the one exception for the Ga7 atom, which has a CN of 13. The five gallium positions Ga1−Ga5 have very similar coordinations (Figure 6) with 2Ce + 2Ru + 8Ga neighbors. This is also the coordination of the Ga6 and Ga9 atoms; however, the arrangement of these neighbors is different. The Ga7 and Ga8 atoms have no cerium neighbors but more ruthenium neighbors: three for Ga7 and four for Ga8. The Ga−Ga distances of all gallium atoms cover the range between 263.6 and 323.1 pm. The average Ga−Ga distances for the gallium atoms with CN 12 vary between 286.5 pm for the Ga1 atom and 294.5 pm for the Ga3 atom. For the Ga7 atom with the higher CN of 13, the average Ga−Ga distance is greater: 311.3 pm. These distances may be compared with the average Ga−Ga distance in elemental gallium of 270.0 pm.[22] It is considerably shorter than the average Ga−Ga distances enumerated above for $CeRu_2Ga_8$. However, the gallium atoms in elemental gallium have a CN of only 7, whereas in the ternary compound the gallium atoms have CNs of 12 and 13.

From the viewpoint of chemical bonding, it is interesting that the corresponding lanthanum compound $LaRu_2Ga_8$ is diamagnetic. Thus, almost all electronic spins are well-compensated. From the composition and the high coordination numbers of all atoms, one may expect these compounds to be metallic conductors and consequently Pauli paramagnetic. The fact that $LaRu_2Ga_8$ is diamagnetic suggests that the Pauli paramagnetism of the compound is small and is overcompensated by the atomic core diamagnetism. This in turn suggests a small density of states at the Fermi level. In this context it is interesting to know that elemental gallium is also diamagnetic, while molten gallium is (Pauli) paramagnetic.[37]

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Supporting Information Available: Further crystallographic details and X-ray crystallographic files of $Yb_2Ru_3Ga_{10}$, $CeRu_2Ga_8$, and $NdRu_2Ga_8$ in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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