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On new rare-earth compounds LnIrGa and LnRhGa

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Abstract

Compounds of nominal composition LnIrGa with Ln = La ⋯ Nd, Gd ⋯ Ho, Tm and some LnRhGa were found to crystallize in the orthorhombic TiNiSi-type structure (ordered Co_2Si type) whereas off-stoichiometric 'ScIrGa' was obtained in the hexagonal $MgZn_2$-type structure. Ferromagnetic and antiferromagnetic ordering was observed with ordering temperatures of 4 to 66 K. The valence of Ce in CeIrGa is between three and four at room temperature, and close to four in CeRhGa.

Keywords: Ternary rare-earth intermetallics; Rare-earth iridium and rhodium gallides; Magnetic ordering temperatures

1. Introduction

Recently, the synthesis of the aluminides LnIrAl was reported [1]. Two representatives of the corresponding gallium series LnIrGa (those with *Ln* = *Y* and Er) were already known [2] and the remaining rare-earth compounds were predicted by Hovestreydt [3] to adopt the same TiNiSi-type structure. An (only partially successful) attempt to complete the whole series and to confirm the predictions has now been made.

2. Experimental

The experimental procedure was the same as with the LnIrAl series [1] but the larger difference between the melting points of Ir and Ga caused additional difficulties. Thus, it was impossible to obtain single-phase samples by arc melting. All LnIrGa samples, with the exception of the Sc sample, contained non-negligible amounts of $LnIr_2$ which did not vanish on annealing at 850°C. In the LuIrGa sample we were unable to identify any TiNiSi-type portion. As with ScIrAl, the gallium sample 'ScIrGa' contained considerable amounts of foreign phases. The idea that the correct stoichiometry should be Sc_2Ir_3Ga, analogous to Sc_2Ni_3Si or Ta_2Ni_3Ga, etc. [4] (rather than Sc_2IrGa_3 (like Lu_2CoAl_3 [4]) since Ga was distilled off), could not be corroborated experimentally.

The valence state of Ce in CeIrAl [1] and CeIrGa made us curious about CeRhGa, and in order to demonstrate the valence of Ce in this compound, also via the lattice parameters, it was necessary to prepare the neighboring LnRhGa representatives. The preparation of these compounds was much less problematic. With the exception of GdRhGa and LuRhGa, the samples contained only small traces of foreign phases and showed good crystallinity, better than those with the heavier Ln elements, as is reflected by the standard deviations of the lattice parameters. Considering the price and our exhausted stock of Ir and Rh, we omitted the usually delicate compounds with Sm, Eu and Yb. Only at the end of the work was an attempt made to prepare YbRhGa; this was only partially successful (as the sample was not single phase).

3. Results and discussion

The crystallographic data are summarized in Table 1. The compounds with the genuine trivalent rare-earth elements adopt the orthorhombic TiNiSi-type structure, which can be considered as an ordered derivative of the Co_2Si- or anti-$PbCl_2$-type structures (as PbClBr). These compounds are genuine ternary phases, not just intermediate alloys in the systems $LnIr_2$–$LnGa_2$, since all $LnIr_2$ representatives crystallize in the cubic Laves structure of the Cu_2Mg type, while the $LnGa_2$ representatives with Ln = La to Er

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Table 1

Lattice parameters *a*, *b*, *c*; unit cell volume *V*, and X-ray density d_x at $T = 295$ K of the orthorhombic compounds LnIrGa and LnRhGa (TiNiSi type, oP12, space group *Pnma* (No. 62), all atoms in positions 4c) and hexagonal off-stoichiometric ScIrGa ($MgZn_2$ type, hP12, space group $P6_3/mmc$ (No. 194)). The standard deviations of the last figure, added in parentheses, refer to the statistical error only and do not include the error due to calibration and off-stoichiometry, which may be at least as large

LnTGa	*a* (Å)	*b* (Å)	*c* (Å)	*V* ($Å^3$)	d_x ($g\,cm^{-3}$)
LaIrGa	7.1580 (9)	4.4046 (8)	7.9308 (11)	250.04 (11)	10.65
CeIrGa	7.026 (3)	4.3829 (12)	7.8211 (13)	240.8 (2)	11.09
PrIrGa	7.048 (2)	4.363 (1)	7.839 (2)	241.0 (2)	11.10
NdIrGa	7.0129 (11)	4.3508 (7)	7.8261 (8)	238.8 (1)	11.30
NdIrGa[a]	7.073 (3)	4.393 (1)	7.7837 (12)	241.8 (2)	–
GdIrGa	6.8956 (6)	4.3173 (4)	7.7565 (6)	230.92 (6)	12.06
TbIrGa	6.8584 (9)	4.3142 (7)	7.7173 (8)	228.34 (9)	12.24
DyIrGa	6.808 (5)	4.298 (4)	7.727 (6)	226.1 (5)	12.47
HoIrGa	6.795 (2)	4.2907 (12)	7.709 (2)	224.8 (2)	12.70
ErIrGa [2]	*6.744 (5)*	*4.281 (4)*	*7.680 (7)*	*221.7 (3)*	*12.86*
TmIrGa	6.735 (2)	4.2711 (5)	7.6781 (8)	220.87 (10)	12.96
YIrGa [2]	*6.848 (7)*	*4.312 (3)*	*7.690 (6)*	*227.1 (3)*	*10.26*
ScIrGa[a]	5.2767 (4)	–	8.1625 (12)	196.82 (6)	(10.36)
LaRhGa	7.0864 (8)	4.3827 (4)	8.0079 (6)	248.70 (7)	8.32
CeRhGa	6.8559 (8)	4.3773 (4)	7.8570 (7)	235.79 (8)	8.81
PrRhGa	6.9783 (7)	4.3334 (4)	7.9255 (7)	239.67 (7)	8.69
NdRhGa	6.9514 (5)	4.3163 (3)	7.8999 (6)	237/03 (5)	8.88
GdRhGa	6.8567 (8)	4.2762 (7)	7.8237 (9)	229.4 (1)	9.55
TbRhGa	6.8121 (5)	4.2653 (3)	7.7912 (4)	226.38 (5)	9.73
ErRhGa [2]	*6.723 (2)*	*4.234 (1)*	*7.744 (4)*	*220.4 (1)*	*10.24*
TmRhGa	6.7062 (4)	4.2243 (3)	7.7391 (5)	219.24 (5)	10.35
YbRhGa	6.6985 (5)	4.2009 (3)	7.7416 (5)	217.85 (5)	10.54
LuRhGa	6.6665 (4)	4.2130 (3)	7.7188 (7)	216.79 (5)	10.65
YRhGa [2]	*6.801 (5)*	*4.290 (1)*	*7.737 (3)*	*225.7 (2)*	*7.70*

[a] Off-stoichiometric.

adopt the hexagonal AlB_2 structure. Only $TmGa_2$, $LuGa_2$ and $ScGa_2$ are reported with the orthorhombic $CeCu_2$ structure, which is a disordered higher-symmetry version of the TiNiSi structure [4].

In the TiNiSi-type structure of LnIrGa, infinite trigonal-prism slabs $[Ln_{2/2}Ir]_\infty$ (with nearly isosceles triangle cross-sections of Ln_2Ir) around the Ga atoms are linked up in a zig-zag array via the Ln atoms. Ga is thus located near the center of a trigonal prism tricapped by 1Ln + 2Ir belonging to neighboring arrays shifted by $c/2$. The structure is visualized for instance in fig. 3 of Ref. [2] and in fig. 21 of Ref. [5].

The dependence of the lattice parameters of the TiNiSi-type compounds LnIrGa and LnRhGa on the rare-earth size is depicted in Fig. 1. The slightly smaller radius of Ga with respect to Al manifests itself in only slightly smaller unit-cell volumes of the LnIrGa series, but smaller *a* and *c* values, whereas the *b* values are more than 2% larger than in the corresponding LnIrAl compounds. The anisotropic discontinuity of the lattice parameters observed in the case of CeIrAl, obviously due to the different valence electron distribution and not exclusively due to the different size of the cation Ce^{4+}, is less distinct in the case of CeIrGa where cerium is closer to trivalent, as confirmed by its magnetic susceptibility. It has to be admitted that the relatively high foreign-phase contents of the samples strongly reduce the value of magnetic measurements. However, $CeIr_2$ is non-magnetic [7] so that the weak discontinuity of $d\chi/dT$ in CeIrGa at 9 K may really indicate an antiferromagnetic transition. $CeGa_2$ has a Néel point at 4.1 K [7]. The remaining AlB_2-type $LnGa_2$ compounds are all antiferromagnetic with Néel temperatures in the range 6–18 K [7], whereas the $MgCu_2$-type $LnIr_2$ compounds order ferromagnetically with Curie temperatures that are all higher than the ordering temperatures observed in our LnIrGa samples. PrIrGa showed a susceptibility maximum near 3.8 K, while $PrIr_2$ is ferromagnetic below $T_C = 16$ K [7]. In the NdIrGa sample the main part ordered ferromagnetically below 10 K. A second, much weaker, effect was observed at 12–13 K which can be attributed to the ferromagnetic ordering of $NdIr_2$ at $T_C = 12$ K [7]. A ferromagnetic behavior was also detected in the 'GdIrGa' and 'TbIrGa' samples below $T_C \approx 66$ K and $T_C \approx 32$ K respectively. Both samples contained the $LnIr_2$ phase [4], though with a slightly larger lattice constant ($a = 7.568$ Å and $a = 7.547$ Å respectively). For the corresponding $LnIr_2$ compounds Curie temperatures of 80 K and 43 K are reported [7]. In GdIrAl (which contained distinctly less foreign phase than GdIrGa) a similar ordering temperature was observed ($T_C = 67$ K), whereas X-ray pure TbIrAl revealed a neat anti-

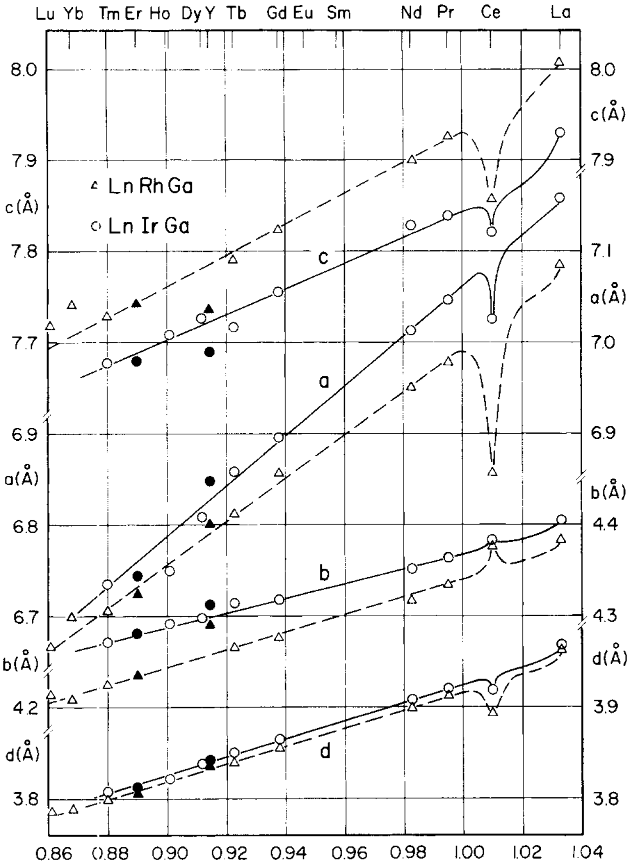

Fig. 1. Lattice parameters a, b, c and $d = (V/Z)^{1/3}$ of the LnRhGa and LnIrGa compounds plotted vs. the radii of the trivalent rare-earth ions according to Shannon [6], except the radius of yttrium. The filled symbols refer to the literature data [2].

ferromagnetic transition at $T_C = 36$ K [1]. Therefore, the possibility that the ferromagnetism of our samples might be due to $LnIr_{2-x}Ga_x$ cannot be excluded. No magnetic transition was found in TmIrGa down to 2 K, while the Al analogue is antiferromagnetic below 3.8 K [1] (for $TmIr_2$ $T_C = 1$ K [7]). Since the magneton numbers, and particularly the paramagnetic Curie temperatures, are falsified by foreign phases, we abstain from listing them, although, with the exception of CeIrGa, the Curie–Weiss law was neatly obeyed from somewhat above the ordering temperatures up to 300 K, with magneton numbers 0% (Nd) to 7% (Gd) lower than corresponding to the free-ion value.

Probably, the results are affected not only by foreign-phase contributions but also by deviations from the ideal stoichiometry. At least in the case of the Nd compound, we identified the orthorhombic structure in a definitely off-stoichiometric sample with fairly deviating lattice parameters (Table 1), although the metallic radii of Ga and Ir are nearly identical, 1.353 Å and 1.357 Å respectively [8]. This may point to negative charges on Ir and positive charges on Ga in accordance with the high electronegativity of iridium. The occurrence of a homogeneity range $LnIr_{1+x}Ga_{1-x}$ would explain the unexpected large scatter of the lattice parameter data in the plot vs. the rare-earth ion radii (Fig. 1).

On comparing the unit cells of LnIrAl [1] and LnIrGa, we see that a replacement of Al by the slightly smaller Ga (Al 1.432 Å, Ga 1.353 Å [8]) mainly affects the b-axis and the c-axis; the b-axis is enlarged whereas the length of the c-axis and, to a lesser extent, the length of the a-axis are reduced, while the volume shrinks by less than 1%, except for the Ce compound due to the different valence state.

According to Teatum and Gschneidner [8], the metallic radius of Rh is a trifle smaller than that of Ir (1.345 Å vs. 1.357 Å). As this difference is about one-sixth of that between Ga and Al, we also expect smaller variations on going from LnIrGa to LnRhGa; in this case though, an atom with another coordination is replaced (though all atoms occupy the same positions, i.e. 4c of space group *Pnma*). In fact, all three axes change (Fig. 1); however, now the a-axis and the b-axis shrink while the c-axis becomes longer, but the volume shrinks by as much as about 0.6%. This is in clear contrast to the LnCoGa series [4] where the b-axes are distinctly larger than in the LnIrGa series, although their volumes are 4–6% smaller, reflecting the smaller size of Co (−8% [8]). We concentrated our investigation around CeRhGa, in order to clarify its valence state. Based on a slightly higher electronegativity of Ir with respect to Rh [9], we expected a higher valence for Ce in CeIrGa. The same reasoning holds for Ga and Al. However, just the contrary is found experimentally: the lowest 'oxidation state' of Ce is realized in CeIrGa, although it is above trivalence as well, as follows from Fig. 1.

It may not be a rule but, nevertheless, the existence of tetravalent Ce in a series of Ln compounds makes it very likely that an isomorphous Yb compound would form with trivalent Yb (analogous to the conclusion that the occurrence of a different structure type would point to divalent Yb (and Eu)—a trivial reasoning if this structure type is known already with Ca and Sr). The lattice parameters (Table 1) demonstrate the trivalence of Yb at room temperature. Another proof is provided by the magnetic susceptibility ($T_N \approx 2.6$ K).

Magnetic measurements also confirm the non-magnetic state of Ce in CeRhGa (the slight increase of the susceptibility from the room temperature value $\chi_{mol} = 1.28 \times 10^{-3}$ emu mol^{-1} to 1.40×10^{-3} emu mol^{-1} at 100 K and 2.55×10^{-3} emu mol^{-1} at 4.2 K is certainly due to traces of foreign Ce phases, as indicated by the Guinier pattern). For the other Rh compounds the ordering temperatures were found to be lower than in the LnIrGa analogues: NdRhGa $T_C \approx 9$ K (and compared with $NdRh_2$ $T_C \approx 7$ K); GdRhGa $T_C \approx 58$ K ($GdRh_2$ $T_C \approx 73$ K), TbRhGa $T_N \approx 22$ K, with a transition to ferromagnetic order at 17 kOe at 2 K, in contrast to TbIrGa ($TbRh_2$ $T_C = 39$ K [7]).

It is noteworthy that in CeCoGa cerium is also close to tetravalent, the Curie–Weiss behavior observed between 165 and 300 K being due to magnetic Co [10]. CeCoGa, however, crystallizes in the monoclinic CeCoAl structure, an ordered version of the $PdBi_2$(r) type. The TiNiSi-type, in contrast, is met with Pr, Nd, Sm, Gd···Er, i.e. with Ln smaller than Ce^{3+} [4]. According to Shannon [6], Ce^{4+} has about the same size as Yb^{3+}. If the transition Ce^{3+} to Ce^{4+} were isotropic we could expect the CeCoAl-type structure to occur also in TmCoGa and LuCoGa.

Furthermore, if the analogy CeRhGa–YbRhGa and CeIrGa–YbIrGa holds, we can expect an intermediate-valence behavior in YbIrGa.

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