On new rare-earth iridium aluminides LnIrAl

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Abstract

The compounds LnIrAl with Ln = Ce ... Nd, Sm, Gd ... Tm, Lu, Y, were found to crystallize in the orthorhombic TiNiSi-type structure (ordered Co_2Si type), whereas ScIrAl was obtained in the hexagonal $MgZn_2$-type structure. Ferromagnetic and antiferromagnetic ordering was observed with ordering temperatures of 7 to 67 K. Ce in CeIrAl is close to tetravalent.

Keywords: Rare-earth iridium aluminides; Magnetic susceptibility

1. Introduction

Among the ternary rare-earth transition-element 'intermetallics' LnTX with X = Al, Ga, In, Tl, Si, Ge, Sn, Pb, various structure types exist. (The term 'intermetallics' is a little misleading here since Si and Ge are in fact nonmetallic under normal conditions. The ternaries Ln_xT_ySi and Ln_xT_yGe are metallic, though.) Most of them are ordered derivatives of types occurring in binary phases: EuNiGe-type (mP12; ordered $CoSb_2$-type), CeCoAl (mS12; $PdBi_2$), TiFeSi (oI36; Fe_2P), $CeCu_2$ (oI12), TiNiSi (tP12; Co_2Si), LaPtSi (tI12; $ThSi_2$), PbFCl (tP6; Cu_2Sb), $MgZn_2$ (hP12), ZrNiAl (hP9; Fe_2P), LiGaGe (hP6; $CaIn_2$), ZrBeSi (hP6; Ni_2In), AlB_2 (hP3), $MgCu_2$ (cF24), LaIrSi (cP12; $SrSi_2$), MgAgAs (cF12; CaF_2) [1–3]. The most abundant types are TiNiSi and ZrNiAl. Usually the orthorhombic TiNiSi-type changes to the hexagonal ZrNiAl-type with increasing size of the X atoms, e.g. in the series LnPtGa, LnPtAl (TiNiSi) → LnPtIn (ZrNiAl), LnNiGa (TiNiSi) → LnNiAl, LnNiIn (ZrNiAl), or from low-temperature to high-temperature modifications, as in the LnPdAl series [4]. If we leave the transition-element compounds, as in LnCuX, LnAgX, LnAuX (which are related to the binaries $LnZn_2$, $LnCd_2$, $LnHg_2$) the structure of the series with the smallest X atom is the disordered $CeCu_2$-type, e.g. LnAuGa ($CeCu_2$) → LnAuAl (TiNiSi) → LnAuIn (ZrNiAl).

YIrGa and ErIrGa [5] were known to crystallize in the TiNiSi structure, whereas for ThIrAl, ThIrGa, UIrAl and UIrGa the ZrNiAl structure was reported [1]. Based on the regularities mentioned above, the TiNiSi structure was to be expected for the LnIrAl compounds, although a transition to the ZrNiAl-type could not be excluded.

2. Experimental details

Polycrystalline samples of nominal composition LnIrAl were synthesized by reacting the constituent elements (rare-earth metals from Research Chemicals, Phoenix, nominally 99.9% grade, 99.9% iridium powder from Johnson-Matthey, London, 99.997% aluminium from Alusuisse, Neuhausen) in an argon arc furnace. The resulting buttons of about 1 g weight have a metallic lustre and are fairly brittle. Although a non-negligible weight loss was observed only in the case of SmIrAl, most samples contained traces of foreign phases. All compounds appear to melt congruently at temperatures below 1400°C.

The room temperature lattice parameters were derived from Guinier patterns taken with Cu $K\alpha_1$ radiation with silicon as internal standard (assuming $a = 5.43047$ Å at 22°C). The structure assignment was supported by intensity calculations with LAZY PULVERIX [6] using the site parameters of YbAuAl [7] for the orthorhombic compounds. Magnetic measurements on the buttons were carried out from 4.2 K to room temperature in magnetic fields of 0.2–40 kOe. Bulk samples instead of powders were used in order to

avoid oxidation. On calculating the paramagnetic magneton numbers the unknown diamagnetic and temperature-independent paramagnetic contributions were neglected (as were contributions from other rare-earth impurities, the concentration of which well may amount to 0.1%).

3. Results and discussion

The numerical results are summarized in Tables 1 and 2. All LnIrAl members with the exception of the as yet unknown EuIrAl and YbIrAl adopt the ordered TiNiSi structure. The present investigation showed that no structure change occurs within the genuine Ln series. The drastic reduction of the atomic size on going from Lu to Sc, however, leads to the $MgZn_2$ structure in ScIrAl. The same change in structure type is also observed in the LnNiAl and LnPdAl series [1]. One might be tempted to conclude that a higher valence is required to induce a change to the ZrNiAl structure since ThIrAl (Th^{4+} is similar to Gd^{3+} in

size), UIrAl and NpIrAl [8] all crystallize in the hexagonal structure. However, CeIrAl with nearly tetravalent Ce is comparable to ThIrAl but still adopts the orthorhombic structure. Thus, the stability range of the ZrNiAl-type could well fall into the missing range between Lu and Sc. The ZrNiAl-type to $MgZn_2$-type transition too is more influenced by size than by valence: ZrIrAl and HfIrAl [1], with the same number of valence electrons as ThIrAl, crystallize in the $MgZn_2$-type like ScIrAl.

The structural data are plotted vs. the 6-coordinated Ln^{3+} ionic radii of Shannon [9] in Fig. 1. Since in many other Ln–T–X series deviations occurred with yttrium this was shifted correspondingly. Whereas the upturn at the La compound may be connected with off-stoichiometry, the distinct deviations of the parameters of CeIrAl indicate a tetravalent state of Ce. The anisotropy is noteworthy, though unexplained if it is not due to off-stoichiometry. The nonmagnetic configuration of the Ce atom was confirmed by the magnetic measurements. The paramagnetic susceptibility remained nearly constant between room tem-

Table 1

Crystallographic data of the orthorhombic compounds LnIrAl, Ln = La · · · Nd, Sm, Gd · · · Tm, Lu, Y (lattice parameters a, b, c; unit cell volume V, and X-ray density d_x; $T = 295$ K); TiNiSi-type, $oP12$, space group $Pnma$ (No. 62), all atoms in positions 4c; and hexagonal ScIrAl, $MgZn_2$-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 twice as large

Ln	a (Å)	b (Å)	c (Å)	V (Å^3)	d_x (g cm^{-3})
La	7.1662 (12)	4.3010 (7)	8.1686 (10)	251.77 (11)	9.45
Ce	6.8931 (4)	4.3205 (2)	7.9361 (4)	236.35 (3)	10.10
Pr	7.0620 (5)	4.2653 (4)	8.0271 (5)	241.79 (6)	9.89
Nd	7.0327 (4)	4.2542 (3)	8.0081 (6)	239.59 (5)	10.08
Sm	6.9833 (5)	4.2271 (5)	7.9611 (5)	235.00 (7)	10.45
Gd	6.9337 (6)	4.2177 (4)	7.9340 (6)	232.02 (6)	10.78
Tb	6.8907 (4)	4.2062 (3)	7.8998 (5)	228.97 (4)	10.97
Dy	6.8592 (4)	4.1947 (2)	7.8836 (3)	226.83 (3)	11.18
Ho	6.8344 (4)	4.1878 (2)	7.8754 (4)	225.40 (4)	11.32
Er	6.8063 (5)	4.1784 (3)	7.8598 (5)	223.53 (4)	11.48
Tm	6.7774 (3)	4.1615 (3)	7.8491 (5)	221.38 (4)	11.65
Lu	6.7398 (4)	4.1590 (3)	7.8350 (5)	219.62 (4)	11.92
Y	6.8676 (3)	4.2089 (2)	7.8834 (4)	227.87 (3)	8.98
Sc[a]	5.2875 (4)		8.140 (3)	197.08 (9)	8.90

[a] Possibly off-stoichiometric.

Table 2

Preliminary magnetic data of the LnIrAl compounds; uncertainties may be caused by inclusions of foreign phases

Ln	Curie–Weiss range (K)	$g[J(J + 1)]^{1/2}$	μ_{eff} (μ_{Bohr})	Θ_p (K)	T_C (K)	T_N (K)
Pr	40–300	3.58	3.51	+2	8	
Nd	75–300	3.62	3.69	~0	~14 (?)	
Gd	90–300	7.94	7.97	+40	67 (?)	
Tb	45–300	9.72	9.9	+14		36[a]
Dy	20–300	10.65	10.5	+8	8.5	
Ho	10–300	10.61	10.5	+2		7
Er	10–300	9.58	9.50	−1		7
Tm	10–100	7.56	7.47	−3		3.8

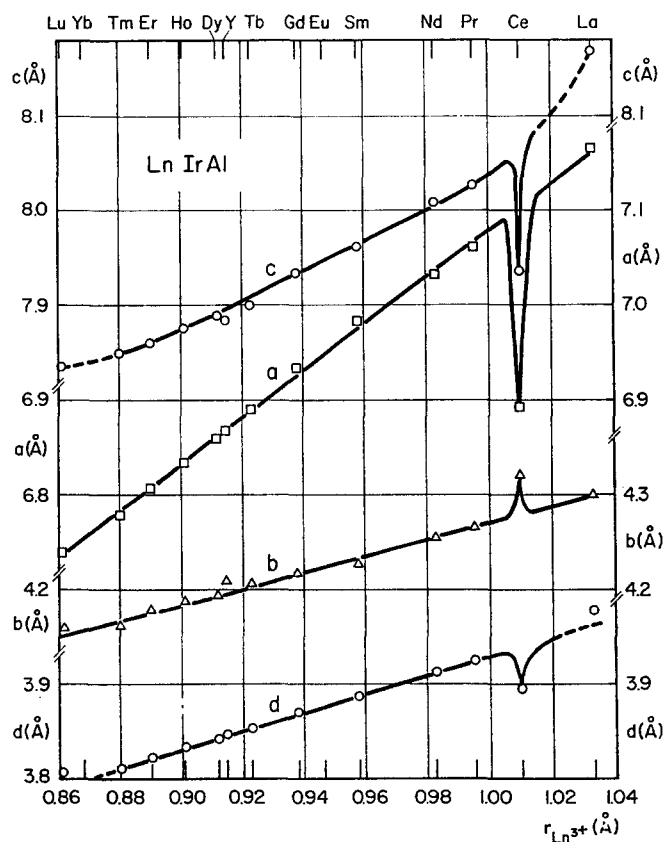[a] Transition from antiferromagnetic to ferromagnetic order near 17 kOe at 4.2 K.

Fig. 1. Lattice parameters a, b, c and $d = (V/Z)^{1/3}$ plotted vs. the radii of the trivalent rare-earth ions according to Shannon [9], except the radius of yttrium.

perature and about 100 K and then increased by a factor of four down to liquid-helium temperature. The results of the magnetic measurements on the compounds with magnetic rare-earth atoms are given in Table 2. Although the ordering temperature is a maximum in the Gd compound, no regularity is detectable in the whole series.

Based on a three-dimensional structure–stability

diagram, Hovestreydt [3] predicted the structures of the corresponding LnIrGa compounds. Since the metallic radius of Al is only slightly larger than the Ga radius [10,11] it is not surprising that, with the exception of the Sc compound, Hovestreydt's predictions apply also to the aluminides.

Acknowledgements

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