ELSEVIER

Journal of Alloys and Compounds 218 (1995) 255–258

Journal of
ALLOYS
AND COMPOUNDS

On rare earth gold aluminides $LnAuAl_3$ and related compounds

F. Hulliger

Laboratorium für Festkörperphysik ETH, CH-8093 Zürich, Switzerland

Received 3 September 1994

Abstract

The compounds $LnAuAl_3$ ($Ln \equiv La$–Tb) and $SrAuAl_3$ as well as $GdAuGa_3$, $PrCuAl_3$, $NdCuAl_3$ and $LaCuGa_3$, $PrCuGa_3$, $NdCuGa_3$ were found to crystallize in the tetragonal $BaAl_4$ structure, disordered or ordered in the $BaNiSn_3$-type or the $CeCuAl_3$-type structure. Low magnetic ordering temperatures were derived from the magnetic susceptibility.

Keywords: Rare earth gold aluminides; Magnetic ordering; Magnetic susceptibility

---

1. Introduction

In a previous paper [1] we described the compounds $LnAu_2Al_2$ which adopt the tetragonal $CaBe_2Ge_2$-type structure (tP10, space group *Pnmm*). These phases exist within a certain homogeneity range. Thus $LaAu_{1.5}Al_{2.5}$ still crystallizes in the $CaBe_2Ge_2$ structure, but for higher Al concentrations the atomic ordering becomes different and the space group changes from primitive to body centred. In the completely disordered state the structure is of the $BaAl_4$ type, whereas for the composition 1:1:3 ordered structures occur, e.g. the $BaNiSn_3$ type for $LaAuAl_3$. In the following the data for some new $LnAuAl_3$ representatives are reported.

2. Experimental details

Polycrystalline samples of nominal composition $LnAuAl_3$ were synthesized by reacting the constituent elements (rare earth metals from Research Chemicals, Phoenix, nominally 3N grade; 4N gold from Métaux Précieux, Neuchâtel, 4N7 aluminium from Alusuisse, Neuhausen) in an argon arc furnace. A non-negligible weight loss was observed only in the case of $SmAuAl_3$. $SrAuAl_3$ and $EuAuAl_3$ were prepared in a closed tantalum tube. The samples were annealed for several hours at the lowest temperature possible in the argon arc. As usual the room temperature lattice parameters were derived from X-ray patterns taken with Cu $K\alpha_1$ radiation on a Guinier–Jagodzinski camera. Silicon was used as internal standard, assuming $a/\lambda = 3.52511$ at 22 °C. The assignment of the structure types is based on the computer programme LAZY PULVERIX [2] with averaged site parameters of related compounds [3]. Preliminary magnetic measurements between 1.6 and 300 K were made on a moving-sample magnetometer in fields up to 10 T. Bulk samples instead of powder samples were used in order to avoid oxidation.

3. Results and discussion

The crystallographic results are summarized in Table 1. We have included some other compounds, the data of which were needed to complete the curves of related compounds shown for comparison. Tetragonal compounds $LnAuAl_3$ were obtained with $Ln \equiv La$–Tb. The X-ray pattern of our $DyAuAl_3$ sample was not indexable. It was definitely different from the $HoCuAl_3$-type pattern expected in analogy with the $LnCuAl_3$ compounds with $Ln \equiv Tb$–Tm which crystallize in an orthorhombic structure (whereas $YbCuAl_3$ is again tetragonal) [3]; neither was it compatible with the orthorhombic but unknown structure found in stoichiometric $DyCuGa_3$ [3]. All the known structures are derivatives of the b.c.t. $BaAl_4$ structure.

In the $BaAl_4$ structure (*I4/mmm*, No. 139) the atomic positions are as follows:

Ba in 2*a*: 0, 0, 0;
Al 1 in 4*d*: 0, $\frac{1}{2}$, $\frac{1}{4}$; $\frac{1}{2}$, 0, $\frac{1}{4}$;
Al 2 in 4*e*: $\pm(0, 0, z)$, $z \approx 0.38$; Al 2–Al 2 $= (1-2z)c$

Ba is located at the centre of a space-filling Fedorov polyhedron, CN = 18 (4 $(\mathrm{Al}\ 2)_2$ pairs + 2 × 4 Al 1 + 2Al 2 (upper and lower corners)). The most obvious and most frequent ordered derivative is the $ThCr_2Si_2$ type

0925-8388/95/$09.50
SSDI 0925-8388(94)01389-6

Table 1

Room temperature lattice parameters and X-ray densities d_X of the tetragonal $BaNiSn_3$-type and $CeCuAl_3$-type [a] compounds (the nominal compositions are given); space groups $I4mm$ (No. 107) and $I4/mmm$ (No. 139) respectively, both tP10. $T=295$ K. [b] In these cases a decision about ordering was not possible. The standard deviations given in parentheses refer to the statistical error only; the additional error due to calibration and off-stoichiometry may be at least as large

Compound	a (Å)	c (Å)	c/a	V (Å^3)	d_X (g cm^{-3})
$LaAuAl_3$	4.3660(3)	10.8445(8)	2.4839(4)	206.72(4)	6.696
$CeAuAl_3$	4.3318(2)	10.8390(7)	2.5022(3)	203.39(4)	6.826
$PrAuAl_3$	4.3101(2)	10.8552(6)	2.5185(3)	201.66(3)	6.897
$NdAuAl_3$	4.2919(2)	10.8631(9)	2.5311(3)	200.10(4)	7.006
$SmAuAl_3$	4.2516(2)	10.9162(8)	2.5676(3)	197.32(4)	7.208
$EuAuAl_3$ [a]	4.3309(3)	11.0630(11)	2.5544(4)	207.51(5)	6.880
$GdAuAl_3$ [a]	4.2167(2)	10.9900(6)	2.6063(3)	195.41(3)	7.396
$TbAuAl_3$ [a]	4.1905(3)	11.0432(11)	2.6353(4)	193.92(4)	7.481
$SrAuAl_3$ [a]	4.3564(5)	11.253(3)	2.5831(11)	213.56(10)	5.684
$PrCuAl_3$ [a]	4.2361(3)	10.6337(12)	2.5103(5)	190.82(5)	4.967
$NdCuAl_3$ [a]	4.2175(3)	10.5787(6)	2.5083(3)	188.16(3)	5.096
$LaCuGa_3$ [b]	4.2825(4)	10.456(2)	2.4416(6)	191.76(7)	7.129
$PrCuGa_3$ [b]	4.2346(5)	10.4754(10)	2.4738(3)	187.84(6)	7.313
$NdCuGa_3$ [b]	4.2086(3)	10.5061(7)	2.4963(4)	186.09(4)	7.491
$GdAuGa_3$ [a]	4.1752(3)	11.0606(8)	2.6491(4)	192.81(4)	9.704

with Al 1 replaced by a transition element (T) and Al 2 replaced by a group B element (X). In LnT_2X_2 the T atoms in 4d positions form square layers, each T atom being surrounded by 4 X atoms at the apices of a squeezed tetrahedron. Thus slabs of X tetrahedra (formed by X atoms of one end of the X pairs) are stacked along the c axis and may be connected by covalent (fractional or single) X–X bonds (as in $CaCu_2P_2$) or by polar bonds to the large electropositive atoms between these layers (as in $KLiZnS_2$) [4].

A partially ordered 1:1:3 structure is met in the $CeCuAl_3$ type with a random distribution of $\frac{1}{2}$Cu + $\frac{1}{2}$Al in 4e positions [5]. This corresponds to a kind of *anti*-$ThCr_2Si_2$-type ordering if we count Cu and Au with the transition elements. To our knowledge the normal $ThCr_2Si_2$-derived ordering with $\frac{1}{2}$T + $\frac{1}{2}$X in 4d has not been observed so far and is definitely not realized in the compounds studied here. A completely ordered 1:1:3 structure is not possible without reducing the symmetry. In the $BaNiSn_3$ type met in $LnAuAl_3$ with Ln ≡ La, Ce,... the transition element replaces half of the Al 2 in 4e positions in such a manner that all TX "dipoles" have the same orientation. This structure type was meanwhile verified for $CeAuAl_3$ by Schank et al. [6] and for $CeCuGa_3$ by Mentink et al. [7]. Possibly a prolonged annealing at a relatively low temperature would convert the $CeCuAl_3$-type ordering into the complete $BaNiSn_3$-type order.

As one can see from Table 1, the a axis parallels the size of the rare earth elements in the $LnAuAl_3$ series, whereas the c axis (and therefore also c/a) shows a slight increase from Ln ≡ La to Tb, not strong enough to change also the slope of the characteristic length $d=(V/Z)^{1/3}$. According to Teatum et al. [8], the metallic radii of Al and Au are almost identical (Al 1.432 Å, Au 1.442 Å, Cu 1.278 Å for coordination number 12). Nevertheless, in the $r_{Ln^{3+}}$ dependence the $LnAl_4$ compounds differ distinctly from the $LnAuAl_3$ compounds. The approximated straight lines in Fig. 1 are fairly parallel for all the other related representatives. Surprisingly, the line for the $LnAu_2Al_2$ compounds (which crystallize in the $CaBe_2Ge_2$ structure) lies between the

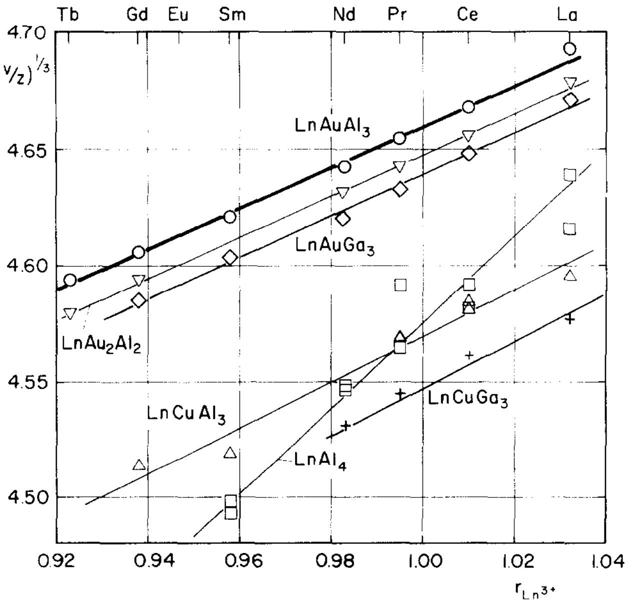

Fig. 1. Variation in $d=(V/Z)^{1/3}$ of the $LnAuAl_3$ compounds with the size of the rare earth element as compared with the corresponding data of the related $LnAuGa_3$ [9], $LnCuAl_3$ [3] and $LnAl_4$ [3] compounds as well as the $CaBe_2Ge_2$-type $LnAu_2Al_2$ compounds [1]. For the rare earth elements Shannon's radii [10] of the trivalent ions in six coordination are used. V/Z is the volume per formula unit.

lines of $LnAl_4$ and $LnAuAl_3$, which must be a consequence of the different ordering and bonding. The gallides nicely reflect the slightly smaller size of Ga with respect to Al (Ga 1.411 Å [8]). The difference is nearly the same between $LnAuAl_3$ and $LnAuGa_3$ and between $LnCuAl_3$ and $LnCuGa_3$.

One might expect that the different ordering should manifest itself also in the unit cell parameters. The $c/a(r_{Ln})$ curve (not shown) is curved upwards slightly towards smaller Ln elements, but if any discontinuity does exist, then it occurs between Nd and Sm (which could then mean that our $SmAuAl_3$ sample was incompletely ordered). The $(V/Z)^{1/3}$ vs. $r_{Ln^{3+}}$ representation of Fig. 1 is not sensitive enough to reveal any transition. Such a transition, however, is clearly visible in the case of the $LnCuAl_3$ compounds. The (disordered? *) orthorhombic $HoCuAl_3$-type compounds ($TbCuAl_3$–$TmCuAl_3$, space group *Imm*2 [11]) possess a distinctly smaller unit cell volume.

$EuAuAl_3$ is omitted from Fig. 1. Its crystal data as compared with $SrAuAl_3$ show a similar ratio to $EuAl_4$ vs. $SrAl_4$, which points to nearly divalent europium ($EuAl_4$: $\mu_{eff}=7.75$–7.79 μ_B, $T_N=13$ K [12]). The Curie–Weiss line of our $EuAuAl_3$ sample yielded 7.62 μ_B, somewhat less than the ideal 7.94 μ_B but rather similar to the values found in $EuAl_4$. From the reported lattice parameters [3] we deduce that Eu and Yb are also close to divalent in $EuCuGa_3$ (and probably $EuCuAl_3$, although our sample was not phase pure, $a=4.2707(4)$ Å, $c=11.148(2)$ Å), $YbCuAl_3$, $YbAuGa_3$ and $YbCuGa_3$ [3], verified in the last two cases by magnetic measurements [13]. However, it proved impossible to join isostructural compounds with divalent and trivalent “cations” in the same plot, obviously since the influence of the additional valence electron is then not taken into account.

In both the ordered and the disordered $BaAl_4$ structure the Ln atoms form square layers, each layer being shifted by ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$) relative to its neighbouring layers. The closest Ln–Ln distance is equal to the *a* parameter, i.e. larger than 4 Å. The interlayer Ln–Ln distance (greater than 6 Å) is even larger than the second-neighbour distance $\sqrt{2}a$ within the layers. Magnetic interactions are therefore anisotropic and indirect, and since they are mediated by conduction electrons, the magnetic properties will not vary strongly with the degree of ordering but with the stoichiometry.

Our $CeAuAl_3$ sample revealed no magnetic transition down to 1.6 K, quite in contrast with $CeAuGa_3$ which was reported to be ferromagnetic with a Curie temperature $T_C=3.5$ K [9]. In $CeAu_xGa_{4-x}$ the ordering temperature increases with increasing Ga concentration up to $T_C=6$ K in $Ce_{20}Au_{12}Ga_{68}$ [9]. In $CeCuAl_3$ Mentink et al. [7] detected antiferromagnetic order below $T_N=3.0$ K, whereas $CeCuGa_3$ remained paramagnetic down to 0.4 K. The susceptibility curve $\chi(T)$ of our $NdAuAl_3$ sample showed a sharp peak at $T_N=2.7$ K, again in contrast with $NdAuGa_3$ and $NdCuAl_3$. The gallide $NdAuGa_3$ was reported to be ferromagnetic below $T_C=4$ K [9], while our $NdCuAl_3$ sample showed a ferromagnetic behaviour below $T_C \approx 5$ K. Our $GdAuAl_3$ sample ordered at $T_N=11$ K and the transition to ferromagnetic order was not reached in 100 kOe at 2 K. With $T_N=22$ K $EuAuAl_3$ possesses the highest ordering temperature of all our samples.

It appears that off-stoichiometry is playing a more decisive role in the magnetic interactions than the small differences in lattice spacings between Au and Cu compounds as well as between Al and Ga compounds. Probably all these $BaAl_4$-type compounds exist in a more or less broad homogeneity range (see e.g. Ref. [14]) and the off-stoichiometry may manifest itself only in deviations from straight lines in Fig. 1.

Acknowledgements

I thank Stefan Siegrist for carefully preparing the samples and the Guinier patterns and Kurt Mattenberger for helping with the magnetic measurements. Moreover, I am grateful to Dr. Oscar Vogt for permission to use his moving-sample magnetometer. Last but not least, I am obliged to Professor H.C. Siegmann as well as to the Swiss National Science Foundation for years of support.

References

[1] F. Hulliger, H.U. Nissen and R. Wessicken, *J. Alloys Comp.*, *206* (1994) 263.

[2] K. Yvon, W. Jeitschko and E. Parthé, *J. Appl. Crystallogr.*, *10* (1977) 73.

[3] P. Villars and L.D. Calvert, *Pearson's Handbook of Crystallographic Data for Intermetallic Phases*, ASM, Materials Park, OH, 2nd edn., 1991.

[4] F. Hulliger, *Helv. Phys. Acta*, *58* (1985) 216.

[5] O.S. Zarechnyuk, P.I. Kripyakevich and E.I. Gladyshevskii, *Sov. Phys. – Crystallogr.*, *9* (1965) 706.

[6] C. Schank, F. Jährling, L. Luo, A. Grauel, C. Wassilew, R. Borth, G. Olesch, C.D. Bredl, C. Geibel and F. Steglich, *J. Alloys Comp.*, *207–208* (1994) 329.

[7] S.A. Mentink, N.M. Bos, B.J. van Rossum, G.J. Nieuwenhuys, J.A. Mydosh and K.H.J. Buschow, *J. Appl. Phys.*, *73* (1993) 6625.

[8] E. Teatum, K. Gschneidner and J. Waber, *LA-2345*, 1960 (Department of Commerce, Washington, DC), cited in W.B. Pearson, *The Crystal Chemistry and Physics of Metals and Alloys*, Wiley–Interscience, New York, 1972, p. 151.

---

* The structure was determined from a powder pattern [11]. The *R* value based on a completely disordered structure, $R=0.100$, and the one based on a partial preference of copper (2.6 Al + 1.4 Cu) in 4*i* (corresponding to 4*e* in the tetragonal form), $R=0.104$, probably differ by less than the total uncertainty.

[9] Y.N. Grin, P. Rogl, K. Hiebl, F.E. Wagner and H. Noël, *J. Solid State Chem., 70* (1987) 168.

[10] R.D. Shannon, *Acta Crystallogr. A, 32* (1976) 751.

[11] Yu.B. Kuz'ma and B.M. Stel'makhovich, *Dokl. Akad. Nauk USSR, Ser. B,* (11) (1988) 38.

[12] K.H.J. Buschow, *Rep. Prog. Phys., 42* (1979) 1373.

[13] Yu.N. Grin, M. Ellner, K. Hiebl and P. Rogl, *J. Alloys Comp., 196* (1993) 207.

[14] V.Ya. Markiv, I.P. Shevchenko, N.N. Belyavina and P.P. Kus'menko, *Dokl. Akad. Nauk USSR, Ser. A,* (7) (1985) 79.