ture yet to be given a detailed description. However, the CS mechanism would normally play a significant role in accounting for a variable oxygen loading, and the additional compositional flexibility which this mechanism allows could well account for the spread in both symmetry allocation and in superconducting properties reported for these compounds.

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$LaNi_2Al_3$, a Ternary Substitution Variant of the Orthorhombic $BaZn_5$ Type

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Abstract

Lanthanum dinickel trialuminide, $LaNi_2Al_3$, M_r = 337.28, orthorhombic, *oS*24, *Cmcm*–*gec*^{2} (No. 63), $a = 10.173\,(1)$, $b = 7.834\,(1)$, $c = 5.1374\,(7)$ Å, $V = 409.43\,(9)$ Å^3, $Z = 4$, $D_x = 5.471$ mg mm^{-3}, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 19.904$ mm^{-1}, $F(000) = 608$, $T = 293$ K, $R = 0.039$, $wR = 0.034$ for 318 contributing unique reflections. The structure is a ternary ordered variant of the $BaZn_5$ type. As in the two other structure types reported for RNi_2Al_3 compounds (R = rare-earth metal), *i.e.* the hexagonal YNi_2Al_3 and $PrNi_2Al_3$ types, Kagome nets are found. In $LaNi_2Al_3$ these nets are strongly distorted and are formed exclusively by Al atoms. The Ni atoms are located between the Kagome nets and the La atoms inside the nets. The $LaNi_2Al_3$ and $BaZn_5$ types can further be considered as vacancy variants of Pu_3Pd_5 which crystallizes in the same space group.

Introduction

Six compounds were reported for the La–Ni–Al system by Bodak & Gladyshevskii (1985). Structure types are known for two of these, *i.e.* $LaNi_{5\to4}Al_{8\to9}$ with $NaZn_{13}$ type and $LaNi_2Al_5$ (Yarmolyuk, Rykhal', Aksel'rud & Zarechnyuk, 1981) with

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Table 1. *Atomic positional and displacement parameters for* $LaNi_2Al_3$ *with space group Cmcm*

The equivalent isotropic atomic displacement parameters are expressed as $U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$. E.s.d.'s are given in parentheses.

	Wyckoff position	x	y	z	U_{eq} (Å^2 × 100)
Al(1)	8(*g*)	0.1968 (5)	0.2790 (5)	$\frac{1}{4}$	0.8 (1)
Ni	8(*e*)	0.2003 (2)	0	0	0.69 (5)
Al(2)	4(*c*)	0	0.0601 (8)	$\frac{1}{4}$	0.6 (2)
La	4(*c*)	0	0.6538 (2)	$\frac{1}{4}$	0.70 (4)

Table 2. *Interatomic distances up to* 4.0 Å *in* $LaNi_2Al_3$

E.s.d.'s are given in parentheses.

La—Al(2)	3.183 (7)	Al(1)—2Ni	2.397 (4)
2Al(1)	3.236 (5)	2Ni	2.535 (4)
4Al(1)	3.299 (3)	Al(2)	2.636 (7)
2Al(2)	3.409 (4)	2Al(1)	2.824 (3)
4Ni	3.521 (2)	La	3.236 (5)
2La	3.523 (1)	2La	3.299 (3)
2Al(1)	3.555 (5)	La	3.555 (5)
4Ni	3.627 (2)	Al(2)	3.790 (6)
Ni—2Al(1)	2.397 (4)	Al(2)—4Ni	2.454 (2)
2Al(2)	2.454 (2)	2Al(1)	2.636 (7)
2Al(1)	2.535 (4)	2Al(2)	2.736 (3)
2Ni	2.5687 (3)	La	3.183 (7)
2La	3.521 (2)	2La	3.409 (4)
2La	3.627 (2)	2Al(1)	3.790 (6)

$PrNi_2Al_5$ type. Al can further be dissolved in $LaNi_5$ with $CaCu_5$ type to the composition $LaNi_{3.5}Al_{1.5}$ (Dwight, 1977; Percheron-Guégan, Lartigue, Achard, Germi & Tasset, 1980). We report here the crystal structure determination of a new compound in this system, $LaNi_2Al_3$.

Experimental

Single crystals were taken from a sample of nominal composition $LaNiAl_2$, prepared by arc melting under an argon atmosphere (La, Ni and Al: 99.99%). The mass loss was 0.2%. A single crystal of irregular shape (mean radius 0.022 mm) was mounted on a Philips PW1100 automatic four-circle diffractometer, Mo $K\alpha$ radiation with graphite monochromator. The unit-cell parameters were refined from 2θ values of 17 reflections (Mo $K\alpha$, $\lambda = 0.71073$ Å, $15 < 2\theta < 31°$). 742 reflections were collected out to $(\sin\theta/\lambda) = 0.705$ Å^{-1} ($0 \leq h \leq 14$, $0 \leq k \leq 11$, $0 \leq l \leq 7$ and the anti-reflections) in ω–2θ scan mode, yielding 348 unique reflections ($R_{int} = 0.024$). Two standard reflections, $\bar{2}02$ and $02\bar{2}$, were measured with maximum intensity variations of 0.7 and 0.9%, respectively. Absorption correction was made using the program *LSABS* (Blanc, Schwarzenbach & Flack, 1991) with maximum and minimum transmission factors of 0.5444 and 0.5366. The anomalous-dispersion coefficients were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). Systematic absences led to the following possible space groups: $Cmc2_1$, $C2cm$ ($= Ama2$) and $Cmcm$ (*International Tables for Crystallography*, 1983, Vol. A). The structure was solved in space group $Cmcm$ by the *MULTAN*87 program (Debaerdemaeker, Germain, Main, Tate & Woolfson, 1987) and confirmed by structure refinement, based on $|F|$ values. 21 variables including anisotropic atomic displacement parameters refined to $R = 0.039$ and $wR = 0.034$ [$w = 1/\sigma^2(|F_{rel}|)$, $S = 3.578$] considering 318 contributing unique reflections with $|F_{rel}| > 3\sigma(|F_{rel}|)$. A secondary-extinction-correction parameter (Gaussian distribution of mosaic spread) was refined to $G = 0.013$ (2). The max. shift/e.s.d. in the last cycle was 0.0002.* The final residual electron density was $+2.4$ (-1.8) e Å^{-3}. The programs used to refine the structure were all from the *XTAL*3.0 system (Hall & Stewart, 1990). The atomic positional parameters were standardized by using the *STRUCTURE TIDY* program (Gelato & Parthé, 1987). The atomic positional and displacement parameters are given in Table 1 and the interatomic distances in Table 2.

Discussion

$LaNi_2Al_3$ is a ternary ordered substitution variant of the $BaZn_5$ structure type (Baenziger & Conant, 1956). Both structures are shown in projection along [001] in the upper row of Fig. 1. Ternary variants of $BaZn_5$ were reported in the compilation by Villars & Calvert (1985) for $BaFe_2S_3$ (Hong & Steinfink, 1972) and KFe_2S_3, rasvumite (Clark & Brown, 1980). These compounds, which are isopointal with $BaZn_5$, should not be considered as ordered substitution variants of this type, since the *b* parameter is greater than the *a* parameter and some atomic coordinates are considerably different, leading to tetrahedral coordination for the Fe atoms and trigonal prismatic coordination for the Ba or K atoms. Both sulfides crystallize, as mentioned by the authors of the original works, with the $CsCu_2Cl_3$ structure type (Brink, Binnendijk & van de Linde, 1954).

In $LaNi_2Al_3$ the Al atoms form distorted Kagome nets. The Ni atoms centre the strongly deformed trigonal prisms. The La atoms are situated inside the elongated hexagons of the Kagome nets and are strongly displaced away from the centre of the hexagons, neighbouring atoms along [001] being displaced in opposite directions. In the ordered ternary

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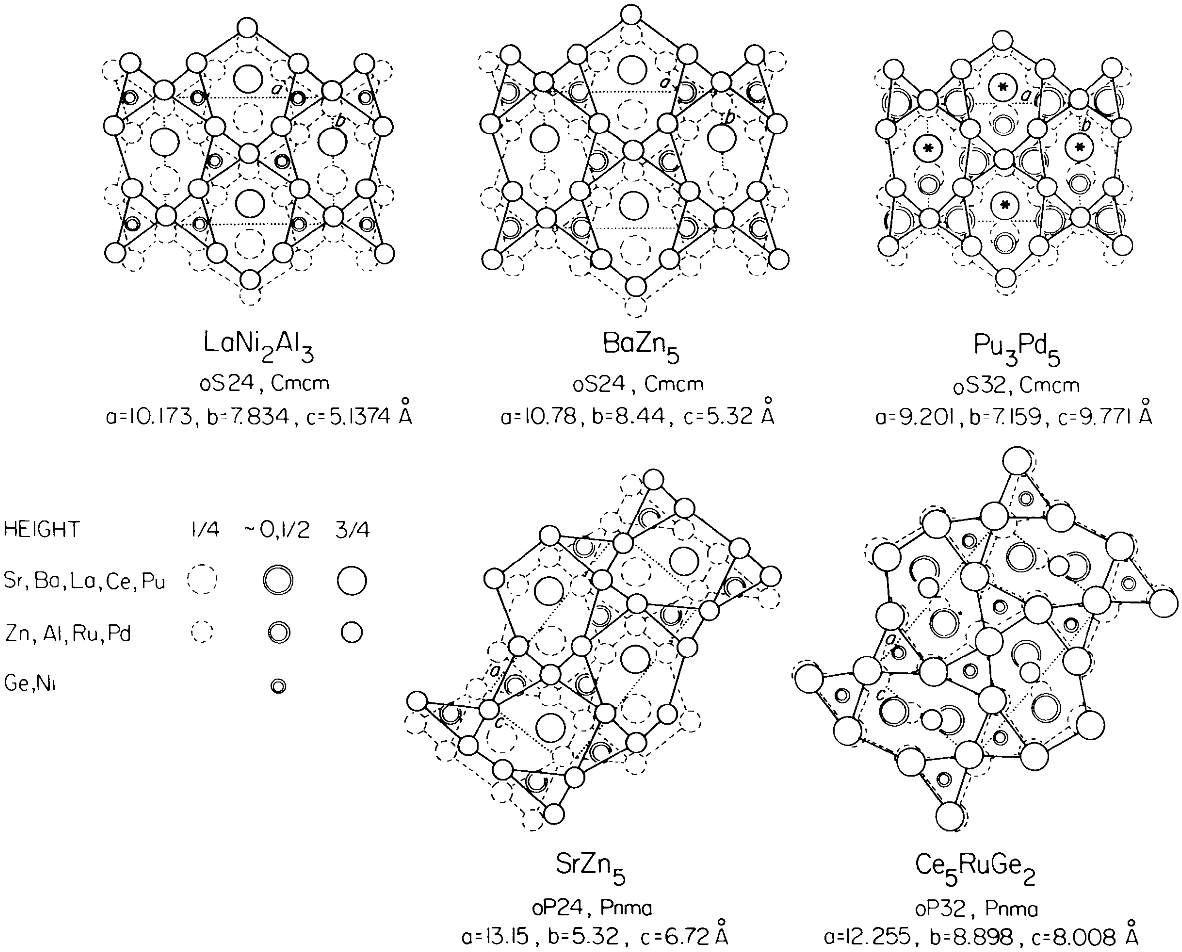
* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55001 (6 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: DU0308]

variant of $CaCu_5$ with the same stoichiometry, $PrNi_2Al_3$ (Rykhal', Zarechnyuk & Kuten, 1978), *hP*6, a site-exchange variant of $CeCo_3B_2$ (Kuz'ma, Kripyakevich & Bilonizhko, 1969), the Al atoms form regular Kagome nets. The Ni atoms centre the Al_6 trigonal prisms and the Pr atoms are situated between the Al layers, centring Al_{12} hexagonal prisms. The closely related structure of YNi_2Al_3 (Zarechnyuk & Rykhal', 1981), *hP*18, an ordered variant of $HoNi_{2.6}Ga_{2.4}$ (Yarmolyuk & Grin', 1979), contains Kagome nets of mixed composition Ni_2Al and in this case the trigonal prisms of composition Ni_4Al_2 are centred by Al atoms. In this structure $\frac{2}{3}$ of the *R* atoms are located between the Kagome nets, centring hexagonal prisms as in $PrNi_2Al_3$ (but here of composition Ni_6Al_6), the remaining $\frac{1}{3}$ of the *R* atoms being located inside the Kagome nets, centring hexagons as in $LaNi_2Al_3$ (here of composition Ni_6). The $PrNi_2Al_3$ type is also observed for $NdNi_2Al_3$ (Rykhal', Zarechnyuk & Yanson, 1979), the YNi_2Al_3 type for *R*–Ni–aluminides with smaller rare-earth metals: *R* = Y, Gd, Tb, Dy, Ho, Er (Zarechnyuk & Rykhal', 1981), Tm or Lu (Rykhal', Zarechnyuk, Protasov & Romaka, 1982).

In both the YNi_2Al_3 and the $PrNi_2Al_3$ types the coordination polyhedron around the *R*-atom sites is a hexagonal prism, the rectangular faces of which are capped by Ni or Al atoms and the hexagonal ones by rare-earth metal atoms at distances greater than 4 Å. The coordination polyhedron around La in $LaNi_2Al_3$ can be derived from this coordination; however, the rare-earth metal atoms are shifted away from the prism axis. Four Ni atoms of the strongly distorted hexagonal prism are significantly further away and only five of the Al atoms capping the rectangular faces are at contact distances. The La atoms capping the hexagonal faces are at a distance of 3.52 Å and infinite La zigzag chains are observed. Three addi-



$LaNi_2Al_3$
oS24, Cmcm
a=10.173, b=7.834, c=5.1374 Å

$BaZn_5$
oS24, Cmcm
a=10.78, b=8.44, c=5.32 Å

Pu_3Pd_5
oS32, Cmcm
a=9.201, b=7.159, c=9.771 Å

$SrZn_5$
oP24, Pnma
a=13.15, b=5.32, c=6.72 Å

Ce_5RuGe_2
oP32, Pnma
a=12.255, b=8.898, c=8.008 Å

Fig. 1. Projections of $LaNi_2Al_3$, $BaZn_5$ and Pu_3Pd_5 along [001], $SrZn_5$ and Ce_5RuGe_2 along [010]. The asterisks in the drawing for Pu_3Pd_5 indicate that Pd atoms at $z \simeq 0, \frac{1}{2}$ are hidden by the flagged Pu atoms. Cell indicated for $BaZn_5$ is shifted by $\frac{1}{2}$,0,0 and cell for Ce_5RuGe_2 by $\frac{1}{2},\frac{1}{2},\frac{1}{2}$ with respect to the standardized descriptions for these structures. The standardization procedure (Gelato & Parthé, 1987) applied the following cell vector transformations to the orginally published data: $SrZn_5$, $\mathbf{a}' = \mathbf{c}$, $\mathbf{b}' = \mathbf{a}$, $\mathbf{c}' = \mathbf{b}$ (from setting *Pmcn*), origin shift $\frac{1}{2}$,0,0; $BaZn_5$, $\mathbf{a}' = \mathbf{c}$, $\mathbf{b}' = -\mathbf{b}$, $\mathbf{c}' = \mathbf{a}$ (from setting *Amam*).

tional Al atoms situated above each hexagonal face are included in the coordination polyhedron. The slightly higher coordination number (21) for the La site in $LaNi_2Al_3$ as compared with the coordination number for the rare-earth atoms sites in the compounds crystallizing with YNi_2Al_3 or $PrNi_2Al_3$ type (18 + 2) is in agreement with the fact that the atomic radius of La is larger than the radii of Y and the trivalent lanthanides.

$BaZn_5$ and $LaNi_2Al_3$ can further be considered as vacancy variants of Pu_3Pd_5 (Cromer, 1976), which also crystallizes in space group *Cmcm* (see projection in Fig. 1). It can be seen that Pu_3Pd_5 contains eight additional atoms per unit cell, arranged in pairs of infinite straight chains inside the hexagonal channels. A stacking variant to $BaZn_5$ was reported for $SrZn_5$ (Baenziger & Conant, 1956), shown in the lower row of Fig. 1, for which no ternary derivative is known so far. Similar but less distorted Kagome nets with elongated hexagons are also found in the structures of β-Yb_5Sb_3 (Brunton & Steinfink, 1971) and its ternary ordered variant Ce_5RuGe_2 (Gladyshevskii, Cenzual, Zhao & Parthé, 1992), an anti-type of Y_2HfS_5 (Jeitschko & Donohue, 1975), drawn in the lower part of Fig. 1. These structures can be derived from the structure of $SrZn_5$ in a similar way to Pu_3Pd_5 from $BaZn_5$, by adding double strings of atoms inside the hexagonal channels, the space group remaining the same (*Pnma*).

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Note added in proof: The $LaNi_2Al_3$ structure is isotypic to $EuCo_2Ga_3$ and $CaNi_2Ga_3$ determined from powder diffraction data (Sichevich, Kim, Vasilechko, Grin' & Yarmolyuk, 1986).

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