angles in Table 2.* A stereographic packing plot is given in Fig. 1.

Discussion. $TlAuCl_4$ is isostructural with the corresponding rubidium salt (Strähle & Bärnighausen, 1970). The Au atom displays the expected square-planar coordination; the planarity is exact, since the Au lies on a symmetry centre at 0·25, 0·75, 0·5. The Au—Cl bond lengths [2·271, 2·277 (5) Å] agree well with other salts of the $AuCl_4^-$ anion (Jones, 1981).

The Tl ion lies on a twofold axis, 0, *y*, 0·25, and is coordinated by ten chlorines at distances from 3·35 to 3·58 Å. The coordination geometry corresponds to neither of the idealized forms (bicapped square antiprism or bicapped dodecahedron), since there are three approximately linear Cl···Tl···Cl units. The next longest Tl···Cl contact is 4·38 Å.

As discussed by Strähle & Bärnighausen (1970), the packing of the ions may be considered as a pseudo-hexagonal layer structure.

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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 43935 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structure (Neutron) of Er_3Al_2

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Abstract. $M_r = 555{\cdot}7$, tetragonal, $P4_2/mnm$, $a = 8{\cdot}1323$ (5), $c = 7{\cdot}5039$ (10) Å, $V = 496{\cdot}3$ (2) Å^3, $Z = 4$, $D_x = 7{\cdot}44$ Mg m^{-3}, $\lambda = 1{\cdot}237$ (1) Å neutrons, μ(calc.) = 0·28 mm^{-1}, $T = 294$ (1) K, final $wR = 0{\cdot}040$ for 953 reflections, 182 independent. At $T = 78$ (1) K. 324 reflections, 158 independent, final $wR = 0{\cdot}08$[illegible] same coordinates except z(Al) decreased by 0·003 (1), isotropic volume shrinkage approx. 0·9% and lower thermal parameters compared with 294 K values. High-resolution neutron powder diffraction at $T = 294$ K, $\lambda = 1{\cdot}893$ Å, $\mu R_s = 1{\cdot}54$, confirmed above results to $wR = 0{\cdot}064$ from 156 reflections.

Introduction. The only RE_3Al_2 (RE = rare earth) compounds whose structures have been determined are Gd_3Al_2 and Dy_3Al_2, reported (Baenziger & Hegenbarth, 1964) as belonging to space group $P4_2nm$. On the basis of X-ray powder diffraction results Buschow (1965) reported that RE_3Al_2 compounds with RE = Gd, Tb, Dy, Ho or Er are isostructural.

We present here the structure determination of Er_3Al_2 using neutron single-crystal and powder diffraction.

Experimental. (*a*) *Single crystal.* A prismatic crystal 1·50 × 2·75 × 2·61 mm was spark cut from a boule grown by the Czochralski method from 99·9% Er and 99·999% Al at the Laboratoire de Magnétisme, Grenoble, during the tenure by one of us (RKD) of a French Government Scholarship. An adjacent slice of boule was crushed to determine unit-cell parameters by least-squares fit to 17 reflections with $130 < 2\theta < 171°$ using a 114·6 mm diameter Debye–Scherrer camera and Cu $K\alpha$ X-radiation. $\theta/2\theta$ scans, four-circle neutron diffractometer 2TANA, HIFAR. Cryogenic Associates flow cryostat at 78 K [details given in square brackets below where different from 294 K]. One standard every 25 reflections within ±3σ of overall average; trends within this range detected and corresponding intensities corrected using cumulative intensity technique of Moore & Colyvas (1980). 935 [324] reflections with $2\theta < 75°$ [70] of which 182 [158] independent, $R_{\rm int}$ = 0·023 [0·022], *hkl* range 0/8 −8/8 −6/−3 and 0/6 [0/7 −7/0 0/7], max./min. absorption corrections 0·50/0·327 and Lorentz correction.

Starting atomic positions from Gd_3Al_2 (Baenziger & Hegenbarth, 1964) with one of the *z* coordinates arbitrarily fixed. Refinement of atomic positions in $P4_2nm$ diverged but indicated position parameters close to those of the higher-symmetry group $P4_2/mnm$. Final full-matrix least-squares refinement in space group $P4_2/mnm$ using all F^2 values, of scale factor, positional, anisotropic [isotropic] and thermal parameters with symmetry constraints [*International Tables for X-ray Crystallography* (1974), Peterse & Palm (1966), respectively], scattering lengths Er = 8·03, Al = 3·449 fm (Koester, Rauch, Herkens & Schröder, 1981).

Er(*d*) effectively isotropic and refined as such in final refinement where R = 0·020, wR = 0·040, [R = 0·077, wR = 0·089], $w = 1/\sigma^2(F_o^2)$, S = 2·28 [3·42], isotropic extinction g = 0·09 (1) (Coppens & Hamilton, 1970) with max. correction of 0·18 for 004. Max. ratio of LS shift/e.s.d. = 0·86 [0·64], ave. shift/e.s.d. = 0·17. No correction for $F^2(\lambda/2)$ [approx. 0·002 $F^2(\lambda)$] or multiple scattering. For 294 K, ten of 26 systematic absences $0kl$, $k + l$ = even, had $3\sigma(F^2) < F^2 < 6\sigma(F^2)$. Worst case $F^2_{100} = 9\sigma(F^2_{100})$.

Processing computer program system Elcombe, Cox, Pryor & Moore (1971); refinement program *LINUS* (Coppens & Hamilton, 1970); IBM 3033S computer.

(*b*) *Powder.* Powder was prepared by crushing buttons of Er_3Al_2 melted from 99·9% Er, 99·999% Al on a water-cooled copper hearth in a titanium-gettered argon arc furnace at the CSIRO Division of Applied Physics. Cell constants a = 8·1311 (5), c = 7·5030 (10) Å were determined as above for the single-crystal boule. The sample, 22·7 g, was lightly tamped into a 12 mm diameter standard thin-walled vanadium can. At 294 K this was rotated about the axis of the high-resolution neutron diffractometer, 6HB, HIFAR described by Howard, Ball, Davis & Elcombe (1983), but now with eight counters 6° apart. Data were collected at 0·05° steps between 10 and 138° (2θ) and averaged over the counters contributing at each angle after correction for small differences in detector efficiencies. The diffraction pattern was analysed using the Rietveld (1969) method and the Wiles & Young (1981) program including correction for peak asymmetry (Howard, 1982) and absorption [based on the algorithm of Rouse, Cooper, York & Chakera (1970) and the calculated absorption correction of Weber (1967)]. The background was refined with a three-parameter expression, $b_0 + b_1(2\theta) + b_{-1}(2\theta)^{-1}$.

Profile refinement in space group $P4_2/mnm$ using either the single-crystal anisotropic thermal parameters fixed, or refining isotropic individual thermal parameters, gave positional coordinates identical with those determined from the single-crystal data (Table 1) to within experimental error except for the Al(*j*) *x* coordinate value which refined to 0·383 (1) with a final R = 0·057, wR = 0·064, GOF = 1·45 for the 156 reflections. An alternative refinement in the lower-symmetry space group $P4_2nm$ converged towards the same fit as in $P4_2/mnm$ and the same positional values to within ±σ for *x* and ±3σ for *z* with one of the *z* coordinates arbitrarily fixed.

Discussion. The final positional and equivalent thermal parameters determined from the 294 K single-crystal work are shown in Table 1. Selected interatomic distances and angles are given in Table 2.*

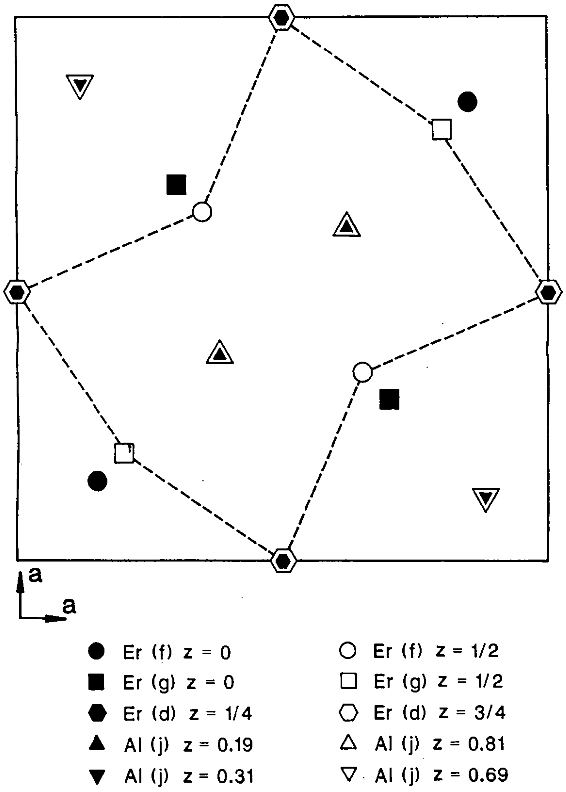

Fig. 1. Symbolic representation of the Er_3Al_2 unit cell.

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* Lists of structure factors, anisotropic thermal parameters and powder intensity data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44011 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional coordinates* ($\times 10^4$) *and equivalent isotropic temperature factors* ($Å^2$) *with e.s.d's in parentheses at* 294 K

$$B_{\rm eq} = \tfrac{4}{3}\textstyle\sum_i \sum_j \beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	$B_{\rm eq}$
Er(*f*)	1520 (2)	*x*	0	0·83 (3)
Er(*g*)	2018 (2)	*x*	5000	0·74 (3)
Er(*d*)	0	5000	2500	0·92 (1)
Al(*j*)	3807 (2)	*x*	1987 (2)	0·62 (3)

Table 2. *Selected interatomic distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses (including lattice-constant e.s.d.'s) at* 294 K

Al—Al	2·745 (4)	Al—Ef(*f*)—Al	51·3 (1); 91·0 (1); 59·1 (1)
Al—Al	2·983 (4)	Al—Er(*g*)—Al	52·9 (1); 57·9 (1); 95·4 (1)
Er(*f*)—Al	3·023 (2)	Er(*d*)—Er(*f*)—Er(*d*)	62·55 (3)
Er(*f*)—Al	3·170 (2)	Er(*d*)—Er(*g*)—Er(*d*)	65·30 (3)
Er(*g*)—Al	3·057 (2)		
Er(*g*)—Al	3·081 (1)	Er(*f*)—Er(*g*)—Er(*f*)	54·0 (4)
Er(*d*)—Al	3·267 (3)	Er(*g*)—Er(*f*)—Er(*g*)	60·21 (3)
Er(*g*)—Er(*d*)	3·478 (1)		
Er(*f*)—Er(*f*)	3·496 (3)		
Er(*f*)—Er(*d*)	3·613 (1)		
Er(*d*)—Er(*d*)	3·752 (1)		
Er(*f*)—Er(*g*)	3·795 (1)		
Er(*f*)—Er(*g*)	3·849 (1)		

The nearest interatomic distances of Er(*g*)—Er(*d*) = 3·478 and Er(*f*)—Er(*f*) = 3·496 Å are close to the nearest-neighbour distance in Er metal (3·470 Å) and Er(*f*)—Er(*d*) = 3·613 Å is comparable to the next-nearest-neighbour distance in Er metal of 3·559 Å.

The nearest Al—Al distances of 2·745 and 2·983 Å average 2·864 Å, which is close to that in Al metal (2·863 Å), and the Er(*f*)—Al distance of 3·170 Å is virtually that expected (3·167 Å) from the metallic radii, with other Er—Al distances within 0·15 Å of this value. In fact, the overall packing density of 0·73 is almost the same as that for the parent close-packed metals (0·74).

Important features may be appreciated by referring to Fig. 1 which includes the dotted outline of a distorted face-centred tetragonal (f.c.t.) sub-cell with Er(*d*) at the corners. Each pair of Al atoms around, but just outside, the *c*-face centres of this top sub-cell may be imagined to replace a single Er atom and distort the squares of Er(*f*) and Er(*g*) atoms on the other face centres at $z = \frac{1}{2}$. Beneath this sub-cell there is another with each Al pair now just inside the *c*-faces and a larger distorted square of Er(*f*) and Er(*g*) atoms at $z = 0$. The Al atom pairs form the rungs of a ladder with alternate unequal steps of $0{\cdot}4c$ and $0{\cdot}6c$ along the *c* axis. Each ladder is surrounded by four ladders going through identical sub-cell pairs but rotated 90° and $c/2$ out of step with the central ladder sub-cell pairs.

It is interesting to note that an approximation to this f.c.t. sub-cell can be found in the parent Er metal with $a_1 = c(\text{h.c.p.}) = 5{\cdot}587$ Å $\sim a_2 = \sqrt{3}a(\text{h.c.p.}) = 6{\cdot}164$ Å, $c = a(\text{h.c.p.}) = 3{\cdot}559$ Å which is comparable in size to the above sub-cells, each of which has $a(\text{sub-cell}) = 5{\cdot}570$, $c(\text{sub-cell}) = 3{\cdot}752$ Å.

In the alloy each Er(*f*) and Er(*g*) is surrounded by six Al atoms arranged on a distorted trigonal prism, as well as four Er(*d*) and four Er(*g* or *f* respectively), although the Er(*f*) also has another Er(*f*) in close proximity. The third Er(*d*) atom also has 14 neighbouring atoms, *viz.* four Al, four Er(*g*), four Er(*f*) and two Er(*d*).

The crystal packing described above and detailed in Table 1 is more regular than in the Gd_3Al_2 structure of Baenziger & Hegenbarth (1964), although the actual atomic positions are very similar.

The use of neutrons allows an accurate determination of the positions of the Al atoms which scatter X-radiation very weakly compared with rare-earth atoms. If, in fact, Gd_3Al_2 and Er_3Al_2 do *not* share the same space group, it will be interesting to observe to which space group the remaining RE_3Al_2 compounds belong.

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