

SHORT STRUCTURAL PAPERS

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New Investigation of the Structure of Mn_4Al_{11}

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Abstract. Mn_4Al_{11} , triclinic, $P\bar{1}$, $a = 5.095$ (4), $b = 8.879$ (8), $c = 5.051$ (4) Å, $\alpha = 89.35$ (7), $\beta = 100.47$ (5), $\gamma = 105.08$ (6)°, $Z = 1$, $V = 216.8$ Å³, $D_c = 3.96$ Mg m⁻³, calculated from the idealized composition, and 3.88 Mg m⁻³, if the population factors are taken into account, $R(F) = 0.067$ for 1180 reflections refined. This unit cell does not agree with the triclinic cell of Bland, but transforms properly to the monoclinic cell of the same author [Bland (1958). *Acta Cryst.* 11, 236–244]. The structure contains approximate layers consisting of Mn and Al atoms with a spacing of about 2.2 Å. The short Mn–Al and Al–Al bonds given by Bland have been reconfirmed in this three-dimensional study.

Introduction. The structure of the alloy Mn_4Al_{11} (δ -MnAl) was first determined by Bland (1958) using four zones of reflections. The structure shows strong regularities in the coordination of the two non-equivalent Mn atoms, with two Mn–Al bonds being much shorter than commonly occurring values (Bland, 1958). The structure can be approximately described as consisting of a series of layers parallel to (010), with an interplanar spacing of about 2.2 Å. As a preliminary to an electron density study of the metal–metal bonding in this alloy, its structure was redetermined from three-dimensional counter data.

Small single crystals were obtained from a lump of the material prepared at Argonne National Laboratory using a d.c. arc furnace. After cooling, the sample was sealed in an evacuated quartz tube and annealed for six days at 873 K. Unlike the preparation from a ternary melt described by Bland (1958), the method excludes

the possibility of Zn contamination. An irregular plate of approximate dimensions 0.2 × 0.15 × 0.06 mm was selected for data collection with Nb-filtered Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å). Cell dimensions were obtained by least-squares refinement of the setting angles of 28 reflections with $2\theta > 34^\circ$. A full sphere of reflections ($\sin \theta/\lambda < 0.7$ Å⁻¹) was measured at room temperature by an ω scan from $\omega - 3^\circ$ to $\omega + 1.6^\circ$, the ω scan being selected because of the relatively large mosaic spread of the crystal.

2607 reflections were averaged after correction for Lorentz–polarization and absorption effects ($\mu = 6.515$ mm⁻¹), to give 1254 unique reflections. The internal agreement factor between symmetry-related reflections was $R = 0.033$. Reflections with $F < 0$ were excluded yielding 1180 reflections for full-matrix least-squares refinement. Positional and anisotropic thermal parameters were refined starting from Bland's (1958) atomic coordinates. Refinement of the occupancy of the positions led to a slight lowering of the R factors which were $R(F) = 0.071$ and 0.067 and $R_w(F) = 0.074$ and 0.068 for the refinements without and with

Table 1. *Positional parameters in the triclinic unit cell*

| | <i>x</i> | <i>y</i> | <i>z</i> | Occupancy* |
|-------|--------------|--------------|--------------|------------|
| Mn(1) | 0.38915 (19) | 0.13307 (11) | 0.33365 (17) | 1.000 (6) |
| Mn(2) | 0.85543 (22) | 0.39943 (13) | 0.69743 (22) | 0.924 (6) |
| Al(0) | 0.0 | 0.0 | 0.0 | 0.489 (7) |
| Al(1) | 0.5327 (4) | 0.1255 (2) | 0.8439 (4) | 0.999 (10) |
| Al(2) | 0.8932 (4) | 0.1242 (2) | 0.4833 (4) | 0.991 (10) |
| Al(3) | 0.3316 (4) | 0.3717 (2) | 0.5738 (4) | 1.012 (12) |
| Al(4) | 0.7196 (5) | 0.3702 (3) | 0.1802 (5) | 0.997 (10) |
| Al(5) | 0.1705 (5) | 0.3214 (3) | 0.0547 (4) | 0.993 (11) |

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* Rescaled to make the occupancy of Mn(1) equal to one.

Table 2. Mn—Al bond lengths (Å)

| | Bland (1958) | Present Study | | Bland (1958) | Present study |
|-------------|---------------------------------|---------------------------------|-------------|---------------------------------|---------------------------------|
| | $\sigma \sim 0.012 \text{ \AA}$ | $\sigma \sim 0.003 \text{ \AA}$ | | $\sigma \sim 0.012 \text{ \AA}$ | $\sigma \sim 0.003 \text{ \AA}$ |
| Mn(1)—Al(0) | 2.42 | 2.404 | Mn(2)—Al(5) | 2.45 | 2.412 |
| Al(5) | 2.50 | 2.521 | Al(4) | 2.48 | 2.547 |
| Al(4) | 2.53 | 2.542 | Al(3) | 2.54 | 2.573 |
| Al(1) | 2.54 | 2.553 | Al(4) | 2.56 | 2.576 |
| Al(3) | 2.53 | 2.560 | Al(4) | 2.66 | 2.645 |
| Al(2) | 2.54 | 2.565 | Al(3) | 2.74 | 2.685 |
| Al(2) | 2.61 | 2.622 | Al(3) | 2.78 | 2.717 |
| Al(1) | 2.60 | 2.625 | Al(1) | 2.75 | 2.736 |
| Al(1) | 2.72 | 2.710 | Al(2) | 2.74 | 2.751 |
| Al(2) | 2.78 | 2.747 | Al(5) | 2.82 | 2.835 |
| Mn(2) | 3.20 | 3.194 | Mn(2) | 3.05 | 2.992 |
| Mn(1) | 3.19 | 3.210 | | | |

the occupancy parameters respectively $\{R(F) = \sum |F_o - |F_c|| / \sum |F_o|$; $R_w(F) = (\sum w|\Delta F|^2 / \sum wF_o^2)^{1/2}$, $w = 1/\sigma^2$, $\sigma(F) = [\sigma(F^2)^2 + (0.03F^2)^2]^{1/2}$. Extinction effects appeared to be insignificant. Final parameters are listed in Table 1,* while bond lengths are compared with earlier values in Table 2.

Discussion. The structural parameters of the earlier study are generally confirmed, though in some cases [such as Mn(2)—Al(4)] differences in bond lengths as large as 0.07 Å are observed. The separation between the anomalously short and the one but shortest Mn—Al bond for each of the coordination spheres is even more pronounced in the new results, the differences in length being 0.117 and 0.135 Å for Mn(1) and Mn(2) respectively, rather than 0.08 and 0.03 Å as observed previously (Table 2). Bond lengths of Bland (1958) in Table 2 are reproduced from Bland's triclinic parameters, and the triclinic cell obtained by transformation of his monoclinic cell. When the previously published triclinic cell is used, erroneous bond lengths are obtained, indicating a probable printing or copying error in the α value in the earlier publication.

The 'normal' value for the Mn—Al bond length suggested by Nicol (1953) is 2.68 Å. Thus the Mn(1)—Al(0) bond of 2.404 (3) Å, which is between layers, and the Mn(2)—Al(5) bond of 2.412 (3) Å within the layer are confirmed to be unusually short. Each of the Mn atoms is surrounded by ten Al atoms which form a bicapped distorted cubic arrangement.

The thermal motion of both Mn atoms is quite anisotropic, the largest principal component of the thermal-motion tensors being about ten times larger than the smallest eigenvalues. The maximum amplitudes for both atoms are close to being perpendicular to the

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34847 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

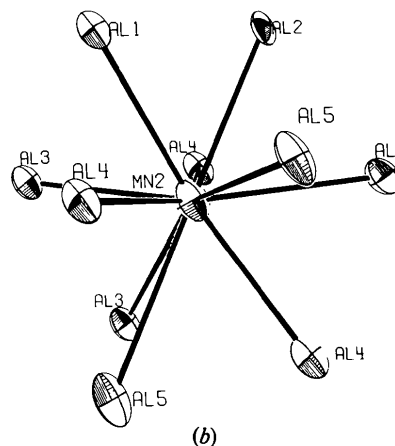
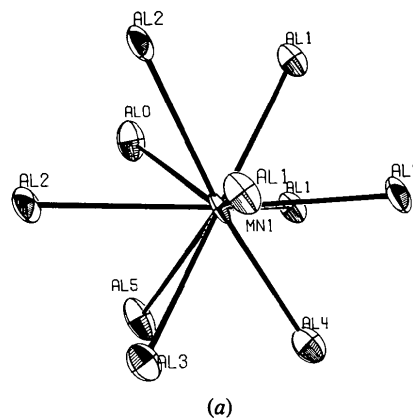


Fig. 1. The ten Al atoms surrounding (a) Mn(1) and (b) Mn(2). The b axis is approximately vertical. The ellipsoids correspond to 75% probability.

layers, rather than to the short Mn—Al bonds. The thermal motion is larger at the Mn(2) site, which also shows a deficiency in occupancy of about 8% according to the results of the least-squares refinement (Table 1). All other occupancies are not significantly different from the idealized values. Fig. 1 shows the vibration ellipsoids.

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