

It can be proved that this equation is equivalent to the one given by Kakinoki & Komura (1952), and that the formulae given by Wilson (1942), Jagodzinski (1949) and Gevers (1952, 1954) are special cases of (11).

With the aid of (4a) and (7) it can be proved that $C_0 = \frac{1}{3}$ and the C_r 's can be calculated by solving the system (2). The values of P_m ($m = 0, 1, \dots, 2s-1$) may indeed be calculated directly with the aid of (8), (9) and (4b), if we take into account that

$$p_0^{(i)} = W_i \quad \text{and} \quad p_1^{(i)} = 0 \quad (i = 1, \dots, s).$$

It has already been demonstrated (Gevers 1953, 1954) how the expression

$$\sum_r \frac{C_r(1-x_r^2)}{1-2x_r \cos A_3 + x_r^2}$$

of formula (1) can be calculated without solving the

characteristic equation (11) and the system (2), and how an equivalent numerical equation can be calculated from measurements of the diffuse X-ray intensity.

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References

- GEVERS, R. (1952). *Acta Cryst.* **5**, 518.
 GEVERS, R. (1953). *Natuurwet. Tijdschr.* **35**, 25.
 GEVERS, R. (1954). *Acta Cryst.* **7**, 337.
 JAGODZINSKI, H. (1949). *Acta Cryst.* **2**, 208.
 KAKINOKI, J. & KOMURA, Y. (1952). *J. Inst. Polyt. Osaka*, **B**, **2**, 35.
 WILSON, A. J. C. (1942). *Proc. Roy. Soc. A*, **180**, 277.

Acta Cryst. (1954). **7**, 494

The Determination of the Crystal Structure of $\text{Ni}_4\text{Mn}_{11}\text{Al}_{60}$

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The crystal structure of the intermetallic compound $\text{Ni}_4\text{Mn}_{11}\text{Al}_{60}$ has been determined using image-seeking functions on Patterson projections and sections. By choosing appropriate sections parallel to densely packed planes of atoms it has been possible to obtain in this way a trial structure which subsequent refinement has shown to be very accurate.

Introduction

The purpose of this paper is first to give a preliminary account of the structure of an intermetallic compound having the composition $\text{Ni}_4\text{Mn}_{11}\text{Al}_{60}$, and secondly to indicate a method of analysis which seems likely to be successful with *layered* structures, even though they may be very complicated. This method uses minimum image-seeking functions, as described by Buerger (1950, 1951), to analyse selected sections of the three-dimensional Patterson synthesis.

If a structure shows marked layering of atoms perpendicular to one particular direction, the Patterson synthesis, $P(U, V, W)$, must have a corresponding layered nature, so that it may be possible to include most of the important features of the full Patterson synthesis in a few sections lying parallel to the densely packed atomic planes. Analysis of such sections may be performed most conveniently by scanning with a plane, or nearly plane, image-seeking function. A suitable function might well be found by examination

of the origin region of the Patterson if one of the selected sections passes through the origin, or, if not, by exam-

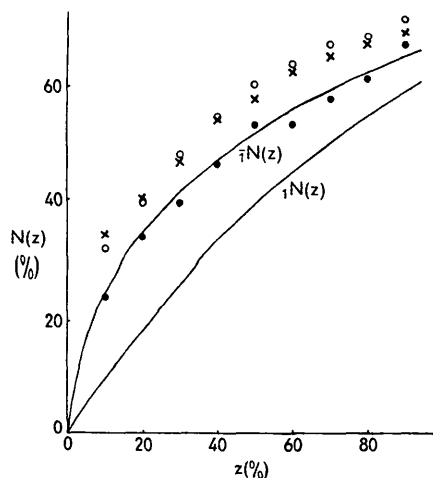


Fig. 1. Intensity distribution in the $(hk0)$, $(h0l)$ and $(hk4)$ sets, represented by crosses, open circles and full circles respectively; $N(z)$ is the fraction of intensities less than $z\%$ of the mean intensity.

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ination of the origin region of a Patterson projected on to a plane parallel to the densely packed atomic planes.

The X-ray photographs of intermetallic compounds having complicated structures frequently show a few reflexions whose intensities exceed all others by a large factor, suggesting marked layering of the atoms in the structures of these compounds. Clearly, such compounds should be amenable to examination by the method described above; this has been found to be the case with $\text{Ni}_4\text{Mn}_{11}\text{Al}_{60}$.

Unit cell and space group

Single crystals of the compound have been prepared by

Raynor (1944), who kindly supplied a sample to the author: their analysed composition is 14.5 atomic % Mn, 5.3 atomic % Ni, 80.15 atomic % Al, i.e. the aluminium content is slightly higher than that required for the formula $\text{Ni}_4\text{Mn}_{11}\text{Al}_{60}$. The orthorhombic cell dimensions are

$$a_0 = 23.8, b_0 = 12.5, c_0 = 7.55 \text{ \AA} \text{ (all } \pm \frac{1}{2} \%),$$

and the density determined by flotation is $3.62 \pm 0.05 \text{ g.cm.}^{-3}$ (Robinson, 1952). With the above composition there are 150 ± 5 atoms per unit cell.

Intensities of (hkl) X-ray reflexions with $l = 0, 1, \dots, 10$ or with $k = 0$ have been estimated by eye from equi-inclination Weissenberg photographs of a small crystal ($< 0.17 \text{ mm.}$) using $\text{Mo } K\alpha$ radiation

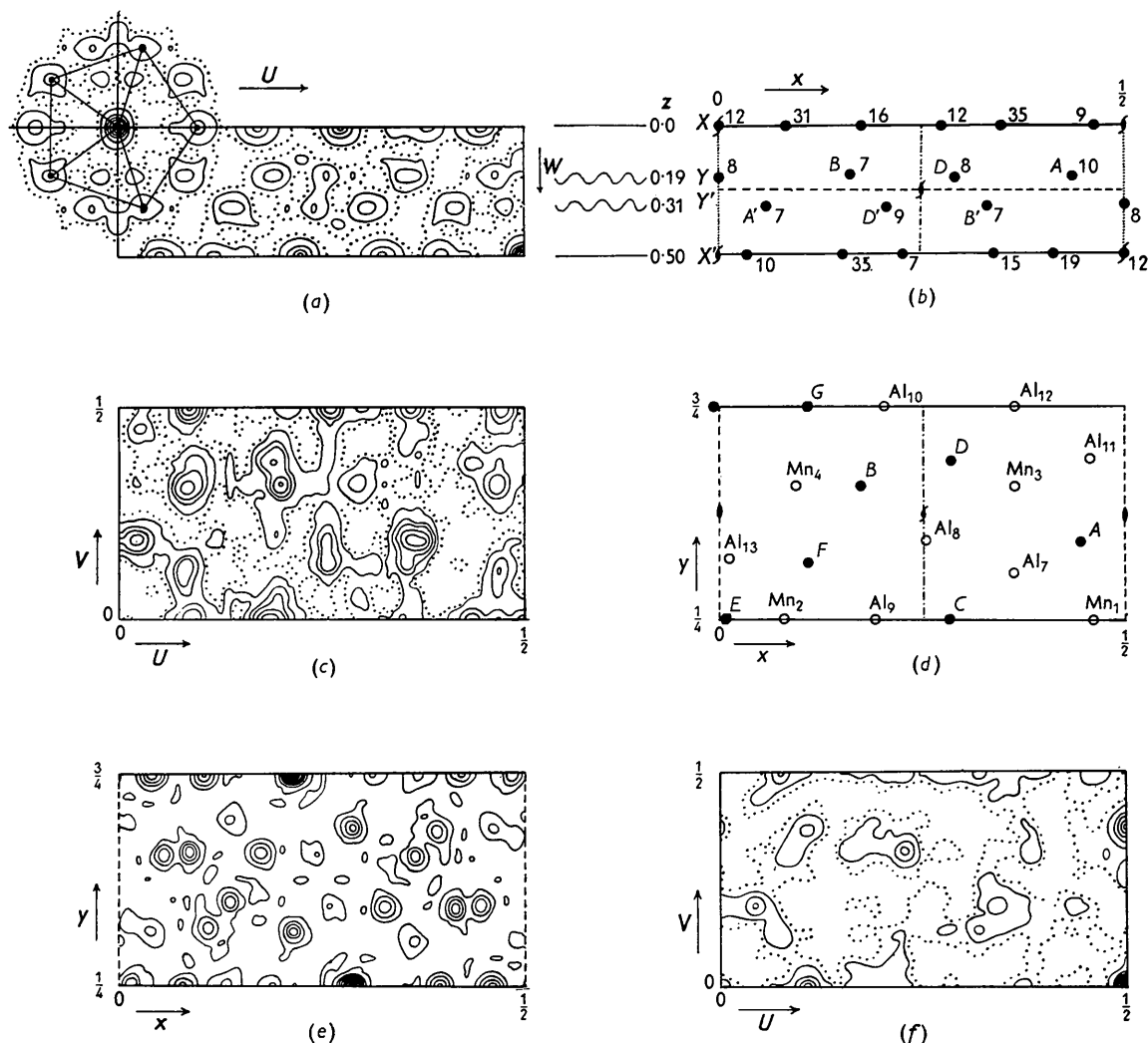


Fig. 2. Operation of plane image-seeking functions on Pattersons of $\text{Ni}_4\text{Mn}_{11}\text{Al}_{60}$. (a) Projection $P(U, W)$ and centred pentagon image-seeking function; arbitrary units at 5 (dotted), 10, 30, 50, 70, 90, 110. (b) The (x, z) projection of structure derived from (a). Figures represent the minimum value of $P(U, W)$ at each coincidence; units as in (a). (c) $P(U, V, 0.19)$; arbitrary units with contours at 25 (dotted), 50, 100, 200, 300, 400. (d) Full circles: image-seeking function representing atoms in the nearly flat Y layer, after increase in rank by operation on $P(U, V, 0.12)$, (f). Open circles: positions of atoms in the flat X layer derived by scanning (c) with the full circle image-seeking function. (e) The projection $g(x, y)$ computed with signs derived from the part-refined parameters shown in Table 1; arbitrary units with contours at 50, 150, 250, ..., 850. (f) $P(U, V, 0.12)$; units as in (c).

Table 1. Atomic parameters for Ni₄Mn₁₁Al₆₀

Atom	Number of equivalent positions	Co-ordinates from $P(U, V, 0.12)$		Partly refined co-ordinates		
		x	y	x	y	z
C Ni	8	0.716	0.750	0.715	0.750	0.181
A Al ₁	16	0.554	0.940	0.553	0.935	0.188
B Al ₂	16	0.830	0.065	0.828	0.065	0.190
D Al ₃	16	0.717	0.124	0.714	0.127	0.190
E Al ₄	8	0.007	0.250	0.014	0.250	0.206
F Al ₅	16	0.888	0.885	0.891	0.885	0.185
G Al ₆	8	0.890	0.250	0.894	0.250	0.185

Atom	Number of equivalent positions	Co-ordinates from $P(U, V, 0.19)$		$P(\text{min.})$ (arbitrary units)	Partly refined co-ordinates		
		x	y		x	y	z
Mn ₁	4	0.540	0.750	110	0.542	0.750	0
Mn ₂	4	0.920	0.750	60	0.920	0.750	0
Mn ₃	8	0.637	0.064	70	0.639	0.055	0
Mn ₄	8	0.908	0.067	90	0.913	0.068	0
Al ₇	8	0.637	0.858	35	0.637	0.853	0
Al ₈	8	0.746	0.935	50	0.738	0.938	0
Al ₉	4	0.809	0.750	40	0.813	0.750	0
Al ₁₀	4	0.798	0.250	50	0.797	0.250	0
Al ₁₁	8	0.543	0.127	35	0.538	0.122	0
Al ₁₂	4	0.637	0.250	25	0.637	0.250	0
Al ₁₃	8	0.990	0.897	25	0.988	0.897	0

and a multiple-film technique. They have been corrected for Lorentz and polarization factors and reduced to a common scale.

Systematic absences correspond to three possible space groups: $D_{2h}^{17}-Bbmm$ (centrosymmetric), $C_{2v}^{16}-Bbm2$ and $C_{2v}^{12}-Bb2m$; the last two have no centre of symmetry in the $(x, y, 0)$ and $(x, 0, z)$ projections, respectively. Intensity distributions in the $(hk0)$ and $(h0l)$ zones are shown in Fig. 1, and both resemble the hyper-symmetric distributions of Rogers & Wilson (1953) in that they lie well above the normal centric distribution. The occurrence of a few extremely strong reflexions coupled with a paucity of medium-strong reflexions from this compound has already been noted (Robinson, 1952), and may indeed arise from some unspecified type of 'hypersymmetry'. Such reflexions occur in both the $(hk0)$ and $(h0l)$ zones and have the effect of raising the 'observed' distribution. Since $D_{2h}^{17}-Bbmm$ is the only possible truly centrosymmetric space group the intensity distribution of the general (hkl) set should distinguish it from the other possible space groups. The distribution for the $(hk4)$ set—deliberately chosen to avoid any extremely large intensities—is also shown in Fig. 1 and lies very close to the normal centrosymmetric curve. All the evidence, therefore, seems to support $D_{2h}^{17}-Bbmm$ as the space group for this structure.

Determination of the atomic arrangement

A preliminary examination of the X-ray data immediately suggested pronounced layering of the structure at intervals of approximately $b_0/6$ perpendicular

to the b axis, and perpendicular to the c axis at heights $z = 0.0, 0.19, 0.31, 0.5, 0.69$ and 0.81 . This was confirmed by a superficial examination of the Patterson projections $P(\bar{U}, V)$ and $P(U, W)$.

The peaks in the Patterson projection $P(U, W)$ (Fig. 2(a)) can be associated to form numerous centred pentagons, all similarly orientated and having an edge equal in length to the normal Al-Al interatomic distance. This centred pentagon may therefore be used on Fig. 2(a) as an image-seeking function, and gives a number of maxima, plotted in Fig. 2(b), which may be taken as a rough representation of the structure projected down the b axis. With the aid of this roughly determined projection a more intensive analysis has been made of the possible atomic arrangements perpendicular to the short c axis.

The problem is simplified to a search for two types of sheet of atoms, one perfectly flat lying on a mirror plane at $z = 0$ (sheet X) and the other nearly flat at $z = 0.19$ (sheet Y), since the other parallel sheets, X', Y' , etc., are related to these two by the symmetry of the structure. It is therefore necessary to examine sections of the Patterson at $W = 0.19$ and $W = 0.12$ (Fig. 2(c) and (f)), since the former contains only vectors of the types $XY, X'Y'$ etc., and the latter contains only vectors of the types $YY', Y'Y''$ etc.

The point-atom image-seeking function used to examine these Patterson sections forms part of the Y layer, and is shown in Fig. 2(d). It has been developed in the following manner. First, possible y co-ordinates for the three groups of atoms A, B and D were estimated by direct examination of Fig. 2(f) in conjunction with packing considerations and the

known symmetry of the structure. These three points in the Y layer, together with four of their equivalents in the same layer, were then used as an image-seeking function on $P(U, V, 0.12)$ to increase the rank of the function. This confirmed the selected y co-ordinates of A , B and D and extended the function to include all the points $A-G$. Finally, all these points, together with some of their equivalents in the same layer, were used as the image-seeking function; this allowed slight modifications in the co-ordinates to be made, and gave the values shown in Table 1. No attempt had been made to attach different weights to these points, but comparison of Fig. 2(*f*) with a 'Patterson' calculated on the points $A-G$ indicated a double weight for the point C , i.e. it should represent one of the heavier atoms.

Scanning $P(U, V, 0.19)$, shown in Fig. 2(*c*), with the same image-seeking function (but with the point C given double weight) determines the form of the flat, X , layer and produces the (x, y) co-ordinates shown on the left-hand side of the lower half of Table 1. The magnitude of the minimum value of the Patterson function corresponding to each coincidence is also shown. One other coincidence of minimum magnitude 40 units and five others of minimum magnitude 25 units were found, but all were ruled out because of impossible packing with atoms in the Y layer.

Refinement of the structure is not yet complete. After four stages of refinement on the (x, y) projection, using electron density and $(F_o - F_c)$ syntheses, and after three stages on the (x, z) projection, the co-ordinates are those shown in the final columns of Table 1. Some estimate of the accuracy of the structure at this stage may be obtained from the arbitrary factor $R_1 = \Sigma|(F_o - F_c)| \div \Sigma|F_o|$, which takes values 0.18 and 0.21 for $(hk0)$ and $(h0l)$ planes respectively when all reflexions with $\sin \theta/\lambda$ less than 0.8 \AA^{-1} are included.

Clearly, the structure is essentially correct and is in an advanced stage of refinement, but two points are still not decided. First, in Table 1 the position C has been distinguished from the other heavy atoms and associated with Ni atoms. The evidence for this distinction, namely a reduction of slightly less than 0.01 in the R_1 factors for the $(hk0)$ and $(h0l)$ data,

is not sufficient. Judgment on this matter must await the results of a further examination of the compound, which is now in progress, using radiation capable of giving a greater effective distinction between Mn and Ni. Secondly, Table 1 shows 156 atomic sites per unit cell corresponding to two formula units of $\text{Ni}_4\text{Mn}_{12}\text{Al}_{62}$, i.e. more positions than had been expected from the density measurement. The electron densities associated with Mn_2 , Al_4 and Al_{13} have been found to be consistently low, but it remains to be confirmed that there are deficiencies of atoms on these sites.

Conclusion

It is not proposed to discuss the details of the atomic arrangement until the ambiguities mentioned in the previous section have been resolved.

The close agreement, shown in Table 1 and by comparison of Fig. 2(*d*) with Fig. 2(*e*), between the parameters derived directly from the Patterson sections at $W = 0.12$ and 0.19 and those obtained from the part-refined electron-density syntheses suggests that the use of image-seeking functions on appropriate sections of the three-dimensional Patterson is in some circumstances a highly sensitive method of structure analysis. It is to be noted that in the present examination *point atom* image-seeking functions, which are easier to manipulate, have been found to be quite adequate, and that it has not been found necessary to use sharpened Pattersons.

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References

- BUERGER, M. J. (1950). *Proc. Nat. Acad. Sci., Wash.* **36**, 738.
 BUERGER, M. J. (1951). *Acta Cryst.* **4**, 531.
 RAYNOR, G. V. (1944). *J. Inst. Met.* **70**, 507.
 ROBINSON, K. (1952). *Phil. Mag.* (7), **43**, 775.
 ROGERS, D. & WILSON, A. J. C. (1953). *Acta Cryst.* **6**, 439.