

that Σ_3 is of little or no importance. Since Σ_1 is at best useful for determining the signs of positive structure factors (except for extremely simple structures), they further conclude that the procedure used here is of limited usefulness, or will lead to only positive signs (Woolfson, 1954, p. 724). Nevertheless, as pointed out above, Σ_3 played an important role in extending the base of positive signs and the indispensable role of yielding the first negative signs.

It is of interest that, in this instance, using only the simple formulas (1), (2) and (3), the data contained within the copper sphere of reflection were sufficient to solve a complex structure involving 108 independent parameters. We plan to report further on the application of the phase-determining procedure and to describe the results of additional refinements of the structure in a future publication.

We are indebted to many people. Mr C. E. Miller of Bell Telephone Laboratories prepared the single crystals. Dr Seymour Geller of Bell Telephone Laboratories suggested that we apply the probability methods to this crystal and supplied us with some preliminary crystallographic data and diffraction photographs. Mr Peter O'Hara of the National Bureau of Standards computed

the K curve and the E map. Mr Alvin Hatch of the Service Bureau Corporation refined the approximate structure by means of the least-squares program developed by Dr David Sayre. We are grateful to all these people.

References

- CHRIST, C. L. & CLARK, J. R. (1956). *Acta Cryst.* **9**, 830.
 CHRIST, C. L., CLARK, J. R. & EVANS, H. T. (1954). *Acta Cryst.* **7**, 453.
 COCHRAN, W. & WOOLFSON, M. M. (1954). *Acta Cryst.* **7**, 450.
 COCHRAN, W. & WOOLFSON, M. M. (1955). *Acta Cryst.* **8**, 1.
 HAUPTMAN, H. & KARLE, J. (1953). *Solution of the Phase Problem. I. The Centrosymmetric Crystal*. A. C. A. Monograph No. 3. Brooklyn: Polycrystal Book Service.
 KARLE, I. L. (1956). A. C. A. Meeting at French Lick, Indiana.
 KARLE, J. & HAUPTMAN, H. (1953). *Acta Cryst.* **6**, 473.
 ROGERS, D. & WILSON, A. J. C. (1955). *Acta Cryst.* **8**, 365.
 VAND, V. & PEPINSKY, R. (1954). *Acta Cryst.* **7**, 451.
 WOOLFSON, M. M. (1954). *Acta Cryst.* **7**, 721.

Acta Cryst. (1957). **10**, 483

The crystal structure of the ordered alloy Au_4Mn . By DENJIRO WATANABE, *The Research Institute for Iron, Steel and Other Metals, Tôhoku University, Sendai, Japan*

(Received 18 March 1957)

It was found by Kussmann & Raub (1956) that the alloy Au_4Mn has an ordered face-centred tetragonal lattice ($c/a < 1$) below about 420°C ., but its atomic arrangement has as yet been unknown. According to the said authors, the ordered alloy is ferromagnetic below the Curie temperature at about 100°C . The structure determination of this ordered alloy therefore seemed to be desirable from the crystallographic as well as from the magnetic point of view. The present author studied the superstructure of Au_4Mn by electron diffraction, using

thin oriented films, and was able to determine its complex ordered structure*.

* Raub, Zwicker & Baur (1953) found the alloy Au_3Mn to possess an ordered structure with tetragonal symmetry below 625°C ., but did not report its atomic arrangement. This alloy was studied also by the present author and was found to possess a two-dimensional anti-phase domain structure of a new kind, whose fundamental cell, considered by referring to the original disordered structure, is rhombic. The details will, however, be reported elsewhere.

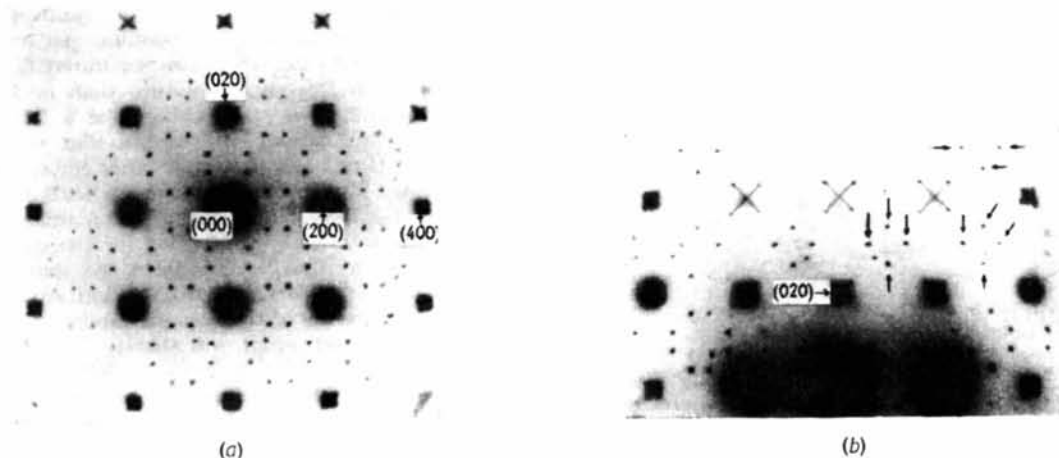


Fig. 1. (a) Electron-diffraction pattern of a thin alloy film containing about 20 atomic % Mn; normal incidence. Indices assigned to normal reflexions are referred to the original cubic system. (b) Electron-diffraction pattern of the same film as in (a); oblique incidence. Angle between the electron beam and the film normal was several degrees.

Fig. 1(a) and (b) show the electron-diffraction patterns of the alloy film containing about 20 atomic % Mn, which was rapidly cooled after annealing at 350° C. for 60 hr. The measured lattice spacings agreed well with those obtained from X-ray Debye photographs by Kussmann & Raub (1956). The fundamental unit cell of the alloy, considered by referring to the original disordered structure, is thought to be face-centred tetragonal, with the lattice constants

$$a = b = 4.08, c = 4.03 \text{ \AA}, c/a = 0.988.$$

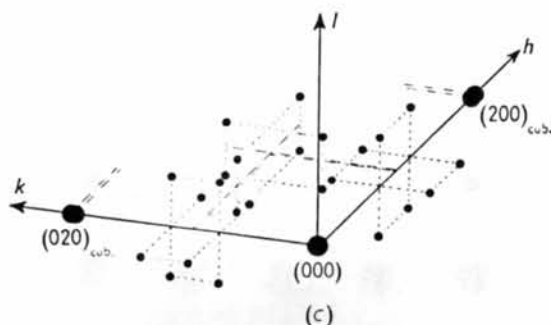
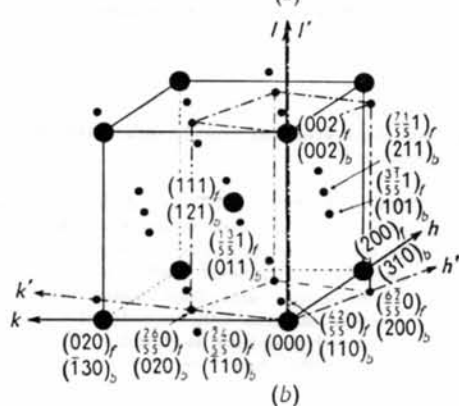
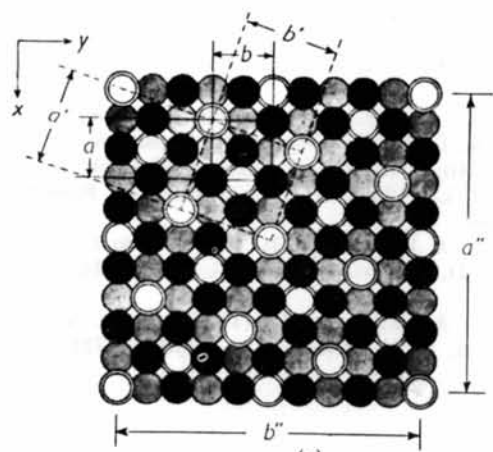


Fig. 2. (a) The Au_4Mn structure, viewed along [001]. The white and black circles represent Mn and Au atoms respectively. (b) Fundamental intensity distribution in reciprocal space corresponding to Fig. 2(a). Indices $(hkl)_f$ and $(hkl)_b$ refer to the fundamental f.c.t. cell and the large b.c.t. cell respectively. (c) Sixfold superposition of the intensity distribution in reciprocal space.

At first sight, the patterns resemble to some extent those of the ordered alloys CuAuII (Ogawa & Watanabe, 1954), Cu_3Pd (Watanabe & Ogawa, 1956) and Au_3Mn in the splitting of superlattice reflexions. The separations of the splittings in the present case suggested the periods of $5a$ and $5b$ to occur along the x and y directions, respectively, in the ordered lattice. After deliberate consideration, however, it was concluded that the ordered alloy has not the so-called 'long period', i.e. no out-of-steps occur in spite of the aspect of the superlattice reflexions. The true unit cell of the ordered lattice is indicated by the broken lines in Fig. 2(a). It is body-centred tetragonal and 2.5 times as large as the fundamental cell in volume, the lattice constants being

$$a' = b' = \sqrt{5/2}a = 6.45 \text{ \AA}, c' = c = 4.03 \text{ \AA}.$$

Atoms contained in the cell are ten, i.e. eight Au and two Mn atoms. The space group is $I4/m-C_{2h}$, and two Mn atoms are placed in $2(a)$ at $0, 0, 0$ and $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ and eight Au atoms in $8(h)$ with parameters $x' = 0.2, y' = 0.4, z' = 0$. The calculated intensities, using these parameters, agree satisfactorily with the observation. As shown in Fig. 2(a), the periods in this structure along the x and y directions are $a'' = 5a$ and $b'' = 5b$, respectively, in accordance with the observed separations of the split superlattice reflexions.

The intensity distribution in reciprocal space corresponding to the model in Fig. 2(a) is derived as shown in Fig. 2(b). In an actual ordered alloy there are six orientations, because, first, the tetragonal axis can lie along any of the three original cubic axes and, secondly, the a' axis in Fig. 2(a) can take either position making a positive or negative angle of 18.5° to one of the original cubic axes. In Fig. 2(c) the sixfold superposition of intensity distribution is given. The patterns in Fig. 1 coincide well with Fig. 2(c). Fig. 1(a) corresponds to the intensity distribution in the plane of coordinates of Fig. 2(c), while the arrows in Fig. 1(b) indicate the intensities not lying in the plane.

The type of superstructure revealed in Au_4Mn has been, however, already found by Harker (1944) in the alloy Ni_4Mo . He determined this structure, analyzing X-ray Debye patterns, and called the fifth superstructure of the face-centred cubic lattice. It seems noticeable that the Ni_4Mo -type superstructure was confirmed in the present case, using single-crystalline patterns of the evaporated films. Mn atoms are separated farther from one another in this superstructure than in Au_3Mn : all the twelve first nearest neighbors* of a Mn atom are Au atoms, and among the second and third nearest neighbors* there are only two and eight Mn atoms, respectively, Mn-Mn distances being 4.03 and 4.99 Å, which are far larger than in metallic manganese. These circumstances may be responsible for the occurrence of ferromagnetism. The mechanism of the structural transition between the ordered Au_4Mn and Au_3Mn can be considered in terms of the present model.

A more detailed report will shortly be published.

The author wishes to express his sincere thanks to Prof. S. Ogawa for his kind guidance and encouragement throughout the present work.

* In considering the nearest neighbors, the slight distortion of the lattice due to tetragonality is neglected.

References

- HARKER, D. (1944). *J. Chem. Phys.* **12**, 315.
 KUSSMANN, A. & RAUB, E. (1956). *Z. Metallk.* **47**, 9.
 OGAWA, S. & WATANABE, D. (1954). *J. Phys. Soc., Japan*,
9, 475.

- RAUB, E., ZWICKER, U. & BAUR, H. (1953). *Z. Metallk.*
44, 312.
 WATANABE, D. & OGAWA, S. (1956). *J. Phys. Soc., Japan*,
11, 226.

Acta Cryst. (1957). **10**, 485

Three-dimensional flexible molecular models. By FREDERICK S. LEE, *Metcalf Research Laboratory, Brown University, Providence 12, Rhode Island, U.S.A.*

(Received 3 May 1957)

The purpose of this communication is to point out another method of building three-dimensional experimental molecular models inexpensively and quickly.

In this method atoms are fashioned out of styrofoam and slid along stiff wires supported in an oil-based modeling clay. In Fig. 1 the clay base is shown covered with aluminum foil to make a clean working surface and to keep the clay in a pliable condition. The obvious ad-

vantage of using a clay base is that large holes which are formed by repeated positioning of wires in a small area can be easily removed, unlike rigid bases of cork, styrofoam, etc.

Styrofoam lends itself, however, very well for making atoms because of its lightness, strength, and easy working characteristics (Gibb & Bassow, 1957). Spheres of styrofoam may be purchased (Polymer Tempera Plastics, Inc., 166 Newbury St., Boston, Massachusetts, U.S.A.) or they may be very quickly made to any size by grinding a cube of styrofoam against the end of a glass tube which has a diameter slightly smaller than the desired finished diameter. Further, styrofoam may be tinted with colored inks or water-based tempera poster paints.

It is felt that this method offers a way of making accurate and attractive models. Because of its flexibility it also provides for easy visualization of trial structures.

If permanent close-packed or display models are to be constructed, a Polymer Tempera binding medium is available which will bond styrofoam together. Finely divided metals or pigments may be placed in this binding medium to form a vividly colored and waterproof coating material.

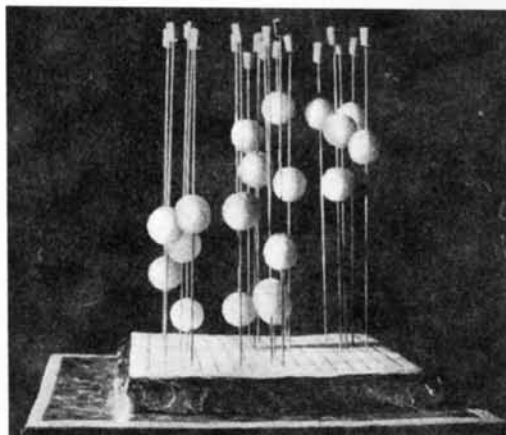


Fig. 1. Photograph of three-dimensional model.

Reference

- GIBB, T. R. P. & BASSOW, H. (1957). *J. Chem. Education*,
34, 99.

Notes and News

Announcements and other items of crystallographic interest will be published under this heading at the discretion of the Editorial Board. Copy should be sent direct to the British Co-editor (R. C. Evans, Crystallographic Laboratory, Cavendish Laboratory, Cambridge, England).

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