which now would appear to be only precariously tenable.

In connection with the importance of *B*-ion electronic configuration to magnetic interaction it should be noted that ferromagnetism has thus far been observed in compounds in the perovskite-structure system *only when the B ions are not all alike* (i.e., when all are not of the same valence or when all are not of the same atomic number).

More detailed data on the magnetic properties of $La(M_x, Mn_{1-x})O_3$ compounds will be published elsewhere later.

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Discussions and correspondence with others engaged in related work have enhanced my interest in this problem and influenced its course. These others are Prof. E. Banks and Drs E. W. Gorter, W. L. Roth, W. C. Koehler, and E. Prince.

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# The Crystal Structure of $U_2Mo$*

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The crystal structure of the $\gamma'$ phase in the U–Mo system has been determined to be the $C11b$ $MoSi_2$ type. The unit cell is tetragonal and the space group $D_{4h}^{17}$–$I4/mmm$. The lattice parameters are $a_0 = 3{\cdot}427$ Å, $c_0 = 9{\cdot}834$ Å, $c/a = 2{\cdot}871$. The $\gamma'$ phase is an ordered state of the body-centered cubic $\gamma$ phase.

## Introduction

The uranium–molybdenum system was first investigated by Pfeil (1950*a*). His results indicated that molybdenum was soluble in body-centered cubic $\gamma$-uranium to the extent of about 43 atomic % at 1280° C. The $\gamma$ phase was considered to be stable at room temperature as no effects were found in thermal analysis or dilatometric experiments. Further work by Pfeil (1950*b*) and by Tucker (1950) showed that equilibrium conditions had not been obtained and that the $\gamma$ phase transforms into a new tetragonal phase, $\gamma'$. Tucker found the unit cell to be body centered with the dimensions $a_0 = 3{\cdot}420$ Å, $c_0 = 3{\cdot}278$ Å. Pfeil found

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several additional weak lines which could not be attributed to any known uranium oxide, carbide, or nitride. Several additional weak lines were observed by Saller, Rough & Vaughan (1951), who indexed them on a larger tetragonal unit cell with dimensions $a_0 = 6{\cdot}84$ Å and $c_0 = 6{\cdot}55$ Å. The exact arrangement of the atoms within this cell was not determined. Electrical resistivity measurements suggested that the new phase might be an ordered form of the $\gamma$ phase.

## Experimental method

The alloy used for the structure determination was an ingot made by induction melting in a beryllia crucible. The molybdenum content was determined by chemical analysis to be 30·4 atomic%. The total impurity content, as determined by spectrographic analysis, was less than 600 p.p.m., with iron and copper the major impurities. The carbon content of the ingot was 270 p.p.m. The $\gamma'$ phase was formed from material which had been homogenized at 900° C., water quenched, and then vacuum annealed for a week at 590° C. To increase the degree of long-range order in the sample the temperature was lowered by 5° increments every third day until a temperature of 550° C. was obtained, then by 25° increments to a temperature of 400° C.

Attempts to obtain powder patterns from filings of the ordered $\gamma'$ phase were unsuccessful as the mechanical stresses produced during the filing process transformed the material back to the disordered $\gamma$ state. Filings of the $\gamma$ phase were then given a vacuum anneal to produce the ordered phase but were found to be badly contaminated with uranium monoxide and dioxide. Solid samples $\frac{1}{4}$ in. × $\frac{1}{2}$ in. × $\frac{3}{16}$ in. were then given the ordering treatment and after a light chemical etch to remove the oxide film were examined on the $\frac{1}{4}$ in. × $\frac{1}{2}$ in. face, using Cu $K\alpha$ radiation in a Norelco spectrometer with a sample spinner. These samples were obtained from $\frac{3}{16}$ in. disks cut from a cast cylindrical ingot. In the $\gamma$ state they exhibited a preferred orientation characteristic of a cubic cast structure, i.e. a cube face perpendicular to the cooling direction. From powder data obtained from these solid samples it was determined that a possible unit cell was a small distortion from a body-centered cubic cell. With this unit cell the lattice parameters would be

$$a_0 = 3{\cdot}427,\ c_0 = 3{\cdot}279\ \text{Å},\ c/a = 0{\cdot}9568\ .$$

Five additional weak lines were observed which could not all be indexed on this unit cell nor on a cell formed by doubling the above parameters. These five lines were all of greater breadth than the indexed reflections and were assumed to be due to an ordering of the atoms. However, these few superlattice reflections were not sufficient to determine uniquely the correct unit cell or the ordered arrangement. The structure factors calculated from the spectrometer tracings are tabulated in Table 1. Those enclosed within brackets were from reflections which were unresolved by the spectrometer; the structure factors were calculated after dividing the observed intensity into two components as predicted from intensities calculated from the final structure.

Table 1. *Comparison of observed and calculated line intensities for the $\gamma'$ phase*

| *hkl* | $(\sin^2\theta)_o$ | $F_c$ | $F_o$ | Film | *s* or *n** |
|---|---|---|---|---|---|
| 002 | 0·0246 | 111 | 84 | *w* | *s* |
| 101 | 0·0567 | 75 | 42 | *mw* | *s* |
| 004 | — | 34 | — | — | *s* |
| 110 | 0·1013 | 379 | 379 | *s* | *n* |
| 103 | 0·1056 | 375 | 368 | *vs* | *n* |
| 112 | 0·1257 | 100 | 80 | *mw* | *s* |
| 114 | — | 42 | — | — | *s* |
| 200 | 0·2022 | 339 | 433 | *m* | *n* |
| 105 | | 113 | 56 | *w* | *s* |
| 006 | 0·2206 | 326 | 377 | *m* | *n* |
| 202 | | 91 | 36 | *w* | *s* |
| 211 | 0·2585 | 63 | 45 | *vw* | *s* |
| 204 | — | 39 | — | — | *s* |
| 213 | 0·3078 | 308 | 230 | *m* | *n* |
| 116 | 0·3216 | 301 | 265 | *m* | *n* |
| 107 | — | 15 | — | — | *s* |
| 008 | 0·3930 | 115 | 67 | *vw* | *s* |
| 220 | 0·4046 | 286 | 222 | *m* | *n* |
| 215 | | 95 | 68 | *vw* | *s* |
| 206 | 0·4226 | 280 | 259 | *m* | *n* |
| 222 | | 79 | 71 | *vw* | *s* |
| 301 | — | 65 | — | *vw* | *s* |
| 118 | — | 107 | — | *vw* | *s* |
| 224 | — | 35 | — | — | *s* |
| 310 | 0·506– | 269 | 181 | *m* | *n* |
| 303 | 0·508– | 267 | 183 | *m* | *n* |
| 312 | — | 95 | — | *w* | *s* |
| 109 | 0·5463 | 253 | 246 | *m* | *n* |
| 217 | — | 13 | — | — | *s* |
| 208 | — | 102 | — | *w* | *s* |
| 314 | — | 32 | — | — | *s* |
| 305 | — | 86 | — | *vw* | *s* |
| 0,0,10 | — | 8 | — | — | *s* |
| 226 | — | 249 | — | *m* | *n* |
| 321 | — | 51 | — | *vw* | *s* |
| 323 | 0·7114 | 245 | 246 | *m* | *n* |
| 1,1,10 | — | 7 | — | — | *s* |
| 316 | 0·7247 | 241 | 244 | *m* | *n* |
| 219 | 0·7482 | 234 | 272 | *m* | *n* |
| 307 | — | 12 | — | — | *s* |
| 1,0,11 | — | 109 | — | *mw* | *s* |
| 228 | — | 96 | — | *w* | *s* |
| 400 | 0·8082 | 237 | 212 | *m* | *n* |
| 325 | — | 81 | — | *w* | *s* |
| 2,0,10 | — | 7 | — | — | *s* |
| 402 | — | 67 | — | *vw* | *s* |
| 411 | — | 49 | — | *vvw* | *s* |
| 0,0,12 | 0·8825 | 215 | 240 | *m* | *n* |
| 318 | — | 93 | — | *vw* | *s* |
| 404 | — | 30 | — | *vvw* | *s* |
| 330 | 0·909– | 229 | 180 | *m* | *n* |
| 413 | 0·913– | 227 | 178 | *m* | *n* |
| 332 | — | 65 | — | *vw* | *s* |
| 309 | — | 217 | — | *m* | *n* |
| 327 | — | 12 | — | — | *s* |

* *s*: superlattice; *n*: normal lattice.

In order to detect more of the weak reflections, which were attributed to an ordering of the uranium and molybdenum atoms, attempts were made to secure a single crystal. The sample used for the structure determination was obtained from a large grain of the $\gamma$ phase which was retained from the 900° C. quench. It was shaped into a rod about 10 mils in diameter and 100 mils long and then given the ordering treatment previously described. A rotation photograph taken with filtered Cu $K\alpha$ radiation about a cube axis revealed that each strong reflection was tripled. The sample thus consisted of a set of three twins which had been formed from a single $\gamma$ grain. A $c$ axis of the $\gamma'$ phase was directed along each of the three principal axes of the cubic $\gamma$ phase. Most of the additional weak reflections appeared along layer lines, while a few appeared along Debye–Scherrer rings corresponding to the strongest reflections. Metallography of bulk samples of the $\gamma'$ phase indicates that a thin laminar twinned structure is always present. Thus, it appeared that the probability of obtaining a single crystal free of twinning would be very small.

A series of 5° oscillation photographs were taken with filtered Cu $K\alpha$ radiation. The indexing was complicated by the presence of all three crystallites with their $c$ axes mutually perpendicular. Thus, for values of $h$, $k$, or $l$ equal to 1 or 2 it was difficult to distinguish an $a$ axis from a $c$ axis, using the small pseudo-cubic unit cell. One-hour exposures were taken with the sample held stationary and set at the correct azimuthal angle for each of the three possible superlattice reflections, as determined from the known orientations of the three normal lattices. The visually estimated intensities are tabulated in Table 1. By indexing the reflections with high values of $hkl$ first it was possible to determine to which of the three possible unit cells a given superlattice reflection should be assigned. The correct unit cell was then determined to be made up of three pseudo-cubes. From the measured density of 16·63 g.cm.$^{-3}$ the number of molecules of $U_2Mo$ per unit cell was found to be 2.

## The structure determination

The only reflections which occur are those for which $h+k+l$ is even. Those reflections for which $h+k+l$ is even and $l = 3n$ are all very strong and are due to the normal lattice. Those reflections for which $h+k+l$ is even and $l \neq 3n$ are all weak and are due to the superlattice.

As the only systematic absences observed are those of reflections for which $h+k+l$ is odd the lattice is established as body centered. Of the possible body-centered tetragonal space groups, the one with the highest symmetry, $D_{4h}^{17}$–$I_4/mmm$, gives an acceptable structure. The molybdenum atoms are at the positions $0, 0, 0$ and $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$. The uranium atoms are at the positions $0, 0, z$; $0, 0, \bar{z}$; $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}+z$; and $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}-z$. From known values of the atomic radii in the $\gamma$ phase and the dimensions of the $\gamma'$ unit cell the value of the parameter should be approximately $\frac{1}{3}$. As the structure factor is given by

$$F = 2f_{\text{Mo}}+4f_{\text{U}} \cos 2\pi lz$$

the value of $F$ should be independent of $l$ for $l \neq 3n$ and $z = \frac{1}{3}$.

The only reflections which appear for $l \neq 3n$ are those for which $l = 1, 2, 5, 8$ and 11, while those for $l = 4, 7$ or 10 are all extremely weak or absent. By plotting $F$ as a function of $z$ it was determined that the parameter should have a value of $z = 0{\cdot}328 \pm 0{\cdot}002$ so that $F$ for reflections with $l = 4, 7$ or 10 will be as small as possible. This value of $z$ allows reflections with $l = 1$ to have a value of $F$ sufficiently large so that they will be observed. This structure is the $C11b$ $MoSi_2$ type and has been found in the following intermetallic phases: $MoSi_2$, $WSi_2$, $ReSi_2$, $MgHg_2$, and $AlCr_2$.

The samples examined were not quite at the correct stoichiometric ratio, being deficient in molybdenum. By consideration of the unit cell and the measured density it was concluded that the structure did not consist of vacancies on the molybdenum sites but that these sites were randomly occupied by the excess uranium. The structure factors were calculated on this basis and are tabulated in Table 1. The temperature factor was determined from the spectrometer intensities of the normal lattice reflections, as the superlattice reflections are all uniformly low. The 49-day ordering treatment given these samples was not sufficient to produce perfect order. The failure of the spectrometer to detect several reflections with appreciable $F_c$ values can be attributed to the broadening of the superlattice reflections from the small domain size or to the preferred orientation of the cast structure in the case of the normal lattice reflections. Because of the high absorption of the uranium atoms, the fact that the morphological axes of the sample were not close to the crystal axes, breadth of the superlattice reflections, and the over-exposure of the normal lattice reflections, intensities on the oscillating or stationary films were visually estimated and ranked, rather than measured with a densitometer. The strongest evidence for the arrangement of the atoms in the ordered state is in the detection of 23 superlattice reflections and the fact that none with $l = 4, 7$ or 10 was observed.

## Discussion of the structure

The structure of $U_2Mo$ consists of layers of atoms with every third layer composed of molybdenum atoms. In the disordered $\gamma$ phase each atom is surrounded by eight atoms at a distance of 2·93 Å. In the ordered $\gamma'$ phase each molybdenum atom is surrounded by eight uranium atoms at a distance of 2·96 Å; each uranium atom is surrounded by four molybdenum atoms at 2·96 Å and four other uranium atoms at 2·87 Å. The interatomic distance for pure molybdenum is 2·72 Å. Thus, during the ordering process the larger uranium atoms become closer together and attain an arrangement of pairs of atoms similar to that of $\alpha$-uranium. The smaller molybdenum atoms after ordering are surrounded by atoms at a slightly greater distance than in the disordered state.

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# The Structure of $V_4Al_{23}$*

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The crystal structure of the intermetallic compound $V_4Al_{23}$ has been determined. The space-group symmetry was found to be $D_{6h}^4$–$P6_3/mmc$, and precision lattice parameters were measured as $a = 7{\cdot}692_8$ Å, $c = 17{\cdot}04_0$ Å. The compound is structurally related to $Co_2Al_5$, $Fe_3NiAl_{10}$, and $Mn_3SiAl_9$. The compound shows a pronounced, but imperfect, layering. Zone boundaries are prominent. Abnormally short Al–V bond distances were found.

## Introduction

A phase diagram of the aluminum–vanadium system has been published by Carlson, Kenney & Wilhelm (1955). This diagram indicates the existence of four compounds in the system, and the printed discussion of the article leaves open the possible existence of a fifth compound. In view of the interest in the compounds of aluminum with transition metals (Pratt & Raynor, 1951; Raynor & Waldron, 1948; Raynor, 1949), an examination of the structures of these aluminum–vanadium compounds has been undertaken. A determination of the structure of the compound designated as the $\beta$-phase, tentatively identified in the forementioned phase diagram as $VAl_6$, has been completed and is described in this paper.

## Sample preparation

An arc-melted aluminum–vanadium alloy containing 6·7 wt.% vanadium was heated to 710° C. and held at temperature for 175 hr. in a beryllia vessel under a helium atmosphere. At the end of the heating period the sample was quenched in an oil bath. Optical examination of the alloy indicated the presence of two phases, aluminum plus a compound. The aluminum matrix was dissolved with 1NNaOH. The residue consisted of deep metallic blue crystals in the form of long hexagonal prisms. A representative sample of this residue was selected and analyzed for vanadium (Freeland & Fritz, 1955). The analysis showed $24{\cdot}71 \pm 0{\cdot}18$ wt.% vanadium. This result compares with a theoretical value of 23·94 wt.% vanadium for $VAl_6$ and of 24·72 wt.% vanadium for $V_4Al_{23}$. Spectrographic analysis of the crystals showed the presence of Cu, Mn, Fe, Si, and Ti as trace impurities.

## Cell dimensions and crystal symmetry

A back-reflection Weissenberg camera, similar to the one described by Buerger (1942), was used to obtain precision lattice constants. A hexagonal unit cell was found with dimensions

$$a = 7{\cdot}692_8\ \text{Å},\quad c = 17{\cdot}04_0\ \text{Å}\,.$$

The measured density was found to be 3·089 g.cm.$^{-3}$ while the density calculated on the basis of 46 aluminum atoms and 8 vanadium atoms per unit cell is 3·134 g.cm.$^{-3}$.

Weissenberg patterns of the reciprocal space lattice taken about the unique axis showed $C_{6l}$ symmetry for all observed levels, $l = 0$ through $l = 10$. Thus Laue symmetry $D_{6h}$ was indicated. No systematic extinctions were observed in $(hkl)$ or $(h0l)$ reflections, but $(hhl)$ reflections occurred only with $l = 2n$. The Laue symmetry and extinction information limited the possible space groups to $D_{6h}^4$–$P6_3/mmc$, $C_{6v}^4$–$P6_3mc$, or $D_{3h}^4$–$P\bar{6}2c$. Three-dimensional intensity data were taken in order to select the proper space group. These data were obtained by a multiple-film technique, using Cu $K\alpha$ radiation and an equi-inclination Weissenberg camera. The intensities were estimated visually. The data were corrected for Lorentz and polarization factors in the manner of Lu (1943). A statistical examination of the intensity distribution was made, using the method of Howells, Phillips & Rogers (1950). The distribution curve is shown in Fig. 1 and indicates

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