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**Ordering of atoms in the sigma phase FeMo.** By C. G. WILSON and F. J. SPOONER, *Physics Branch, Royal Military College of Science, Shrivenham, Swindon, Wiltshire, England*

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The FeMo phase, first observed by Goldschmidt (1949), has a complex tetragonal structure in common with a number of binary and ternary alloys involving transition elements. The crystal structure of the sigma phase is now well known, but there is some doubt about the ordering of the atoms among the different sites. An attempt has been made in this work to obtain an ordering scheme for FeMo from powder photographs, assuming that the atomic coordinates in the unit cell are essentially the same as in the sigma phase FeCr.

The crystal structure of the FeCr system has been determined by Bergmann & Shoemaker (1954) using powder and single-crystal X-ray diffraction techniques, giving the space group  $D_{4h}^4-P4_2/mnm$ , with thirty atoms to the unit cell occupying the following atomic positions:

<i>A</i> 2 ( <i>a</i> )	0, 0, 0	
<i>B</i> 4 ( <i>f</i> )	<i>x</i> , <i>x</i> , 0	( <i>x</i> = 0.3981)
<i>C</i> 8 ( <i>i</i> )	<i>x</i> , <i>y</i> , 0	( <i>x</i> = 0.4632, <i>y</i> = 0.1316)
<i>D</i> 8 ( <i>i</i> )	<i>x</i> , <i>y</i> , 0	( <i>x</i> = 0.7376, <i>y</i> = 0.0653)
<i>E</i> 8 ( <i>j</i> )	<i>x</i> , <i>x</i> , <i>z</i>	( <i>x</i> = 0.1823, <i>z</i> = 0.2524).

The sample of  $\sigma$  FeMo used in our determination contained 50 at.% molybdenum and gave excellent powder diffraction photographs using a 19 cm. Debye-Scherrer camera and monochromatized Co  $K\alpha$  radiation. The photographs were readily indexed on the tetragonal system, and a Nelson-Riley extrapolation gave the following values for the lattice parameters:

$$a = 9.218 \pm 0.002, \quad c = 4.813 \pm 0.002 \text{ \AA}; \quad c/a = 0.522.$$

This result gave good agreement between observed and calculated  $\sin^2 \theta$  values as seen in Table 1.

Assuming that the FeMo atomic coordinates are the same as FeCr, the distribution of the atoms was determined as follows:

Position	No. of Fe atoms	No. of Mo atoms
<i>A</i>	2	0
<i>B</i>	1	3
<i>C</i>	2	6
<i>D</i>	8	0
<i>E</i>	2	6

This arrangement gave good agreement between the observed and calculated intensities of the diffraction lines (Table 1). For comparison the intensities were calculated assuming a random distribution, and are also listed in Table 1. All calculated intensities were corrected for absorption and dispersion. It should be noted that a few weak lines of a second phase, which we were not able to identify were present on all films.

### Discussion

The ordering scheme, which was obtained by trial and error, gave the best intensity agreement for both observed and unobserved reflections. The stronger lines on the powder photographs were not very sensitive to ordering and several schemes including the random distribution gave good agreement among these. The

Table 1. X-ray data

<i>(hkl)</i>	$\sin^2 \theta \times 10^4$		Intensities			
	obs.	calc.	<i>I</i> <sub>obs.</sub>	<i>I</i> <sub>calc.</sub>	<i>I</i> <sub>rand.</sub>	<i>I</i> <sub>ABE</sub>
(200)	—	381	—	0.2	0	1.3
(101)	443	445	<i>v</i> <sub>5</sub> <i>w</i>	2.7	1.0	0
(210)	—	477	—	2.1	0	4.7
(111)	—	539	—	0.9	0.2	0.3
(220)	—	763	—	0.9	0	3.8
(211)	—	825	—	1.5	0	0.8
(310)	953	955	<i>v</i> <sub>5</sub> <i>w</i>	3.0	0.2	0.5
(221)	—	1111	—	0.3	0.6	6.6
(301)	1208	1206	<i>v</i> <sub>4</sub> <i>w</i>	4.9	0.2	2.6
(320)	1233	1239	<i>v</i> <sub>4</sub> <i>w</i>	3.4	0.1	10
(311)	1299	1301	<i>v</i> <sub>2</sub> <i>w</i>	21	7.7	13
(002)	1393	1392	<i>v</i> <sub>2</sub> <i>w</i>	19	30	8.8
(400)	1517	1522	<i>v</i> <sub>4</sub> <i>w</i>	2.7	0	0.9
{(112)	—	1581	—	—	—	—
{(321)	1578	1585	<i>v</i> <sub>3</sub> <i>w</i>	11	4.7	1.4
(410)	1616	1618	<i>m</i>	130	125	134
(330)	1710	1713	<i>w</i>	70	59	72
(202)	1771	1771	<i>w</i>	74	57	85
(212)	1866	1866	<i>m</i>	128	117	156
(420)	1897	1903	<i>v</i> <sub>2</sub> <i>w</i>	1.2	0.4	1.5
(411)	1961	1963	<i>ms</i>	162	176	138
(331)	2055	2058	<i>w</i>	72	90	60
(222)	2147	2149	<i>v</i> <sub>3</sub> <i>w</i>	19	22	12
(421)	—	2248	—	0.8	0.8	0.8
(312)	2337	2340	<i>v</i> <sub>2</sub> <i>w</i>	23	27	35
(430)	—	2375	—	0.3	0.1	0.1
(510)	—	2470	—	0.6	0.7	1.6
(322)	—	2625	—	2.1	6.7	0.2
(501)	—	2723	—	0.3	0.6	4.5
(431)	—	2723	—	2.4	6.3	2.4
(520)	—	2755	—	0.5	0	1.6
(511)	—	2818	—	0.3	6.9	2.9
(402)	—	2910	—	1.3	0.3	0.8
(412)	—	3005	—	1.3	0.6	2.8
(440)	—	3034	—	0.3	0.1	1.7
(332)	—	3094	—	0.2	0.1	3.5
(521)	—	3096	—	0.7	3.1	9.2
{(530)	—	3223	—	1.2	0.4	2.9
{(103)	—	3218	—	0.9	0.4	0
(422)	3274	3280	<i>v</i> <sub>4</sub> <i>w</i>	5.8	0.2	0
(113)	—	3313	—	0.9	0	0.5
(441)	—	3381	—	0.3	0	0.1
(600)	—	3413	—	1.2	0	4.1
(610)	—	3508	—	0.3	0	5.4
(531)	—	3565	—	0	0	0
(213)	—	3593	—	0.5	0	0.3
(432)	3747	3753	<i>v</i> <sub>2</sub> <i>w</i>	22	8.8	19
(620)	—	3787	—	3.7	0.9	3.6
{(611)	—	3848	—	—	—	—
{(512)	3843	3848	<i>v</i> <sub>2</sub> <i>w</i>	17	9.8	24
(540)	—	3881	—	5.9	0.7	5.0
(223)	—	3877	—	0.2	0.4	3.7
(303)	—	3972	—	3.4	0.2	0.8
(313)	4061	4067	<i>v</i> <sub>4</sub> <i>w</i>	8.3	0.3	5.0
{(621)	—	4135	—	—	—	—
{(522)	4128	4132	<i>vw</i>	52	26	30
(541)	4221	4228	<i>v</i> <sub>3</sub> <i>w</i>	6.0	3.7	3.5
(630)	—	4260	—	4.0	7.3	4.4
(323)	—	4351	—	1.2	0.2	1.4
(442)	—	4410	—	0.6	0.1	2.7

*I*<sub>obs.</sub> = observed, *I*<sub>calc.</sub> = ordered calculated (Mo in 3*B*, 6*C* and 6*E*), *I*<sub>rand.</sub> = random calculated, *I*<sub>ABE</sub> = ordered calculated (Mo in *ABE* sites), *s* = strong, *m* = medium, *w* = weak, *v* = very.

weaker and absent reflections, however, were very sensitive to order and the determination was based on these, particularly on the planes of lower indices. While errors might be introduced by assuming the FeCr atomic coordinates for FeMo, these errors are minimized by giving far more weight to the low-angle reflections, and our final arrangement for these in particular, seemed conclusive.

The crude ordering scheme suggested by Bergmann & Shoemaker (1954) for FeMo, which was based on atomic-number parameters (again assuming the FeCr coordinates), allots the positions *A*, *B* and *E* to molybdenum. This scheme gives quite good agreement for the stronger

lines but shows many discrepancies among the weaker and missing reflections as indicated in the calculated intensities ( $I_{ABE}$ ) for the lower-angle reflections in Table 1.

It is significant that the 'hole' sizes of the *A* and *D* sites are the smallest, as indicated by the mean interatomic distances associated with these sites, and are occupied by the smaller Fe atoms, while the remaining sites are considerably larger and occupied mainly by the larger Mo atoms. If atomic size is a major factor in the distribution of atoms in this phase, it might be expected that the *B* site, which is the largest, would consist wholly of Mo atoms. The intensity agreement obtained by filling all the *B* site with Mo atoms, and dividing the rest of the Mo atoms equally among the *C* and *E* sites is almost but not quite as good as that suggested. Further refinements on the distribution were attempted, maintaining Mo atoms only in the *B* site, but it proved impossible to obtain any better agreement. However, it does appear from these results that the relative atom sizes of the  $\sigma$  components is important in deciding the ordering of this phase.

The ordering scheme adopted is also in general agreement with that suggested for  $\sigma$  phases by Kasper & Waterstrat (1956), where the *A* and *D* sites are occupied by elements to the right of Mn in the periodic table, the *B* site by elements to the left and the *C* and *E* sites by a mixture of the two.

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Table 2. *Interatomic distances for each kind of atom*

<i>A-B</i> 4	2.748 Å	<i>B-A</i> 2	2.748 Å
<i>A-D</i> 4	2.489	<i>B-B</i> 1	2.656
<i>A-E</i> 4	2.667	<i>B-C</i> 2	2.529
Mean value	2.635	<i>B-D</i> 4	2.847
		<i>B-E</i> 4	2.972
		<i>B-E</i> 2	3.064
		Mean value	2.841
<i>C-B</i> 1	2.529 Å	<i>D-A</i> 1	2.489 Å
<i>C-C</i> 1	2.519	<i>D-B</i> 2	2.847
<i>C-C</i> 4	2.994	<i>D-C</i> 1	2.579
<i>C-D</i> 1	2.606	<i>D-C</i> 1	2.606
<i>C-D</i> 1	2.579	<i>D-C</i> 2	2.608
<i>C-D</i> 2	2.608	<i>D-D</i> 1	2.597
<i>C-E</i> 2	2.905	<i>D-E</i> 2	2.672
<i>C-E</i> 2	2.898	<i>D-E</i> 2	2.681
Mean value	2.788	Mean value	2.657
		<i>E-A</i> 1	2.667 Å
		<i>E-B</i> 1	3.064
		<i>E-B</i> 2	2.972
		<i>E-C</i> 2	2.905
		<i>E-C</i> 2	2.898
		<i>E-D</i> 2	2.672
		<i>E-D</i> 2	2.681
		<i>E-E</i> 1	2.426
		<i>E-E</i> 1	2.387
Mean value	2.771		

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