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CRYSTALLOGRAPHY

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Abstract

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CRYSTALLOGRAPHY

E. I. GLADYSHEVSKII, P. I. KRIPYAKEVICH, R. V. SKOLOZDRA

CRYSTAL STRUCTURE OF THE COMPOUND Mo_3CoSi

(Presented by Academician N. V. Belov on 24 VIII 1966)

In an X-ray structural study of alloys of the Mo—Co—Si system (^{1}), a ternary compound was found that is in equilibrium with Mo, solid solutions based on Mo_6Co_7, Mo_3Si, and Mo_5Si_3, and with the ternary compound $Mo_5Co_3Si_2$ (R-phase); the homogeneity range of the compound (58-62 at.% Mo, 18-21 at.% Co, 17-21 at.% Si) includes the composition Mo_3CoSi. In the present work the results of determining its crystal structure are reported.

A single crystal of the compound was selected from an alloy prepared by melting molybdenum (99.9% Mo), cobalt (99.99% Co), and silicon (99.99% Si) in an arc furnace (Ar atmosphere). The symmetry of the Laue pattern indicated that the structure belongs to the Laue class $4/mmm$. By calculating rotation X-ray photographs (RKV-86a camera, Cu radiation), the periods $a = 12.7$ Å, $c = 4.93$ Å were obtained; the values of the periods refined from a powder pattern were: $a = 12.649$ Å, $c = 4.889$ Å, $c/a = 0.386$. The unit cell contains 11.2 formula units of Mo_3CoSi, i.e., 56 atoms ($\rho_{\text{exp}} = 8.82$ g/cm^3, $\rho_{\text{calc}} = 8.87$ g/cm^3).

The composition of the compound Mo_3CoSi lies between the compositions of compounds of the Mo—Co—Si system whose structures contain atoms with coordination number 12-16 (types W_6Fe_7, σ, R (^{2}), Cr_3Si) or 10-15 (type W_5Si_3 (^{3})). Proceeding from this, we assumed that the structure of Mo_3CoSi should also have similar coordination characteristics. It should be especially close to structures of the σ-phase, Cr_3Si, W_5Si_3, and also the P-phase $Mo_{21}Cr_9Ni_{20}$ (^{4}) and $CuAl_2$ (for example, Ta_2Si (^{5})), in which one of the lattice periods has approximately the same value as in Mo_3CoSi. The almost complete identity of the layer lines with $l = 0$ and $l = 4$ on the rotation X-ray photograph indicated that the z coordinates of the atoms in the structure must be equal or approximately equal to 0, 1/4, 1/2, and 3/4. By analogy with the structures mentioned, we considered it probable that the structure of Mo_3CoSi consists of alternating flat or slightly puckered densely and sparsely populated layers (“nets” and “intermediate layers,” respectively). There is a close relation between the construction of the nets and the number of atoms in the unit cell N of similar structures: N is equal to the number of all triangles in the net, i.e., the sum of actually existing figures of this type and the triangles formed as a result of centering and triangulating other polygons. For the structure of Mo_3CoSi, as having $N = 56$, we assumed a layer population similar to that of the P-phase structure (where N is also equal to 56, and the ratio of the number of larger atoms to smaller atoms is 4 to 3), i.e., alternation of nets of 20 atoms (56 triangles) and intermediate layers of 8 atoms.

To determine the space group, Weissenberg photographs taken in an RGIK camera with Cu radiation were used (developments of layer lines with $l = 0, 1,$ and 2). Analysis of the extinctions led to diffraction group No. 73 ([6]), i.e., the space groups $I4/mcm$, $I\bar{4}c2$, $I4cm$. In constructing the first model we proceeded from the most symmetric space group $I4/mcm$, in which only zna-

Table 1

Positions of atoms in the structure of Mo_3CoSi

First model *($I4/mcm$ – D_{4h}^{18})	First model *($I4/mcm$ – D_{4h}^{18})	First model *($I4/mcm$ – D_{4h}^{18})	First model *($I4/mcm$ – D_{4h}^{18})	Final model ($I\bar{4}c2$ – D_{2d}^{10})	Final model ($I\bar{4}c2$ – D_{2d}^{10})	Final model ($I\bar{4}c2$ – D_{2d}^{10})	Final model ($I\bar{4}c2$ – D_{2d}^{10})	C.n.
Mo	16	(k) $x, y, 0;$	$x = 0.150,\ y = 0.075$	Co	16	(i) $x, y, z;$	$x = 0.155,\ y = 0.085,\ z = 0.013$	15
Mo	16	(k) $x, y, 0;$	$x = 0.050,\ y = 0.275$	$Mo_{0.80}Co_{0.20}$	16	(i) $x, y, z;$	$x = 0.067,\ y = 0.294,\ z = 0.013$	14
Mo	4	(b) $0, \frac{1}{2}, \frac{1}{4}$		$Mo_{0.70}Co_{0.30}$	4	(c) $0, \frac{1}{2}, \frac{1}{4}$		14
Co, Si	8	(h) $x, \frac{1}{2}+x, 0$	$x = 0.150$	$Co_{0.60}Si_{0.40}$	8	(h) $x, \frac{1}{2}+x, 0$	$x = 0.138$	12
Co, Si	8	(e) $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$		$Si_{0.65}Co_{0.35}$	8	(e) $x, x, \frac{1}{4}$	$x = 0.250$	12
Co, Si	4	(a) $0, 0, \frac{1}{4}$		$Si_{0.72}Co_{0.28}$	4	(a) $0, 0, \frac{1}{4}$		10

* For the composition $Mo_{18}Co_5Si_5$.

values of z equal to 0, $\frac{1}{4}$, $\frac{1}{2}$, and $\frac{3}{4}$. We initially assumed the composition of the compound to correspond to the formula $Mo_8Co_3Si_3$ (32 Mo atoms in the unit cell). Since it was unlikely that 2 atoms could be located—

Table 2

Experimental and calculated values of the structure amplitudes of Mo_3CoSi

hkl	$\lvert F_{\text{exp}}\rvert$	$\lvert F_{\text{calc}}\rvert$	*hkl*	$\lvert F_{\text{exp}}\rvert$	$\lvert F_{\text{calc}}\rvert$	*hkl*	$\lvert F_{\text{exp}}\rvert$	$\lvert F_{\text{calc}}\rvert$	*hkl*	$\lvert F_{\text{exp}}\rvert$	$\lvert F_{\text{calc}}\rvert$
110	–	8.6	10,8,0 *	13.0	14.0	10,3,1	62.9	72.5	602	161.9	143.6
200	–	32.0	11,7,0	53.6	92.1	871	31.4	32.3	622	51.2	66.7
220	124.9	86.3	13,1,0	101.1	93.7	961	43.8	13.6	552	160.3	136.5
310	139.1	31.5	13,3,0	38.7	29.5	11,2,1	96.0	107.8	712	227.0	204.0
400 *	13.0	98.0	12,6,0	95.0	95.1	10,5,1	74.3	48.0	642	87.7	98.8
330 *	13.0	42.0	13,5,0	155.6	137.0	11,4,1	272.0	287.0	732	179.1	156.7
420	110.9	142.1	14,0,0	263.0	232.0	981	20.1	14.0	802	355.0	360.0
510	268.0	297.0	10,10,0	104.9	48.8	12,1,1	110.4	97.1	822	49.9	43.3
440	505.0	501.0	14,2,0	68.1	59.1	10,7,0	76.4	41.2	662	386.0	396.0
530	53.1	46.9	11,9,0	81.8	74.6	12,3,1	19.1	15.1	752 *	12.0	15.7
600	102.1	64.5	12,8,0	110.2	93.0	11,6,1	18.8	33.2	842	231.0	192.2
620	491.0	546.0	14,4,0 *	13.0	24.8	12,5,1	30.4	53.4	912	97.5	99.5
550	26.2	62.3	13,7,0	19.3	23.0	13,2,1	34.2	5.9	932	58.5	38.2
710	144.9	146.1	12,10,0	42.5	41.0	10,9,1	101.0	74.9	772	364.0	382.0
640	45.5	30.0	15,1,0	167.6	130.8	13,4,1	70.8	69.0	10,0,2	57.3	81.9
730	64.5	88.9	14,6,0	42.9	40.5	11,8,1	72.5	54.6	862	33.0	17.2
800	64.2	67.9	15,3,0	29.4	41.8	12,7,1	0	0.1	10,2,2	65.5	80.7
820	107.4	134.5	11,11,0	59.7	75.6	14,1,1	85.7	57.5	952	273.0	220.0
660	146.2	125.4	13,9,0	86.9	86.2	14,3,1	68.0	80.0	10,4,2	31.7	22.3
750	86.5	86.5	14,8,0 *	13.0	47.9	13,6,1	105.5	126.4	11,1,2	115.9	96.6
840	130.0	100.8	211	150.9	83.9	14,5,1	26.0	36.3	882	42.6	24.2
910	163.9	188.9	321	152.1	126.2	11,10,1	104.3	120.1	11,3,2	99.3	98.5
930	151.1	146.9	411	125.9	98.0	12,9,1	85.9	104.8	972	94.6	80.5
770	478.0	529.0	431	449.0	498.0	15,2,1	41.1	23.7	10,6,2	57.5	50.1
860	36.2	50.5	521	451.0	503.0	13,8,1	98.6	101.5	12,0,2	47.9	31.2
10,0,0 *	13.0	3.0	611	184.5	219.0	15,4,1	45.1	55.4	11,5,2	54.3	45.7
10,2,0	178.2	193.9	541	41.6	34.2	14,7,1	75.6	67.8	12,2,2	89.1	99.6
950	225.0	197.0	631	76.4	69.0	002	–**	768.0	12,4,2	128.9	132.5
10,4,0 *	13.0	45.7	721	100.6	86.1	112	–	150.1	13,1,2	127.5	129.1
11,1,0	24.0	49.9	651	105.5	46.3	222	–	92.3	11,7,2	86.7	121.5
880	304.0	277.0	741	23.6	23.5	222	521.0	551.0	13,3,2 *	12.0	14.2
970 *	13.0	33.1	811	105.6	86.5	312	89.0	78.3	12,6,2	30.4	54.1
11,3,0	185.4	178.2	831	66.6	76.5	402	515.0	509.0	992	86.8	69.3
10,6,0	210.0	178.5	761	103.9	79.5	332	170.1	79.1	13,5,2	57.0	85.0

Fig. 1. Structure of Mo3CoSi. On the left are shown nets with z 0 (thin lines) and z 1/2 (thick lines); on the right are coordination polyhedra of atoms: a –Mo in (i); b –Mo, Co in (i); c –Mo, Co in (c); d –Co, Si in (h); e –Si, Co in (e); f –Si, Co in (a)

Figure 1: Fig. 1. Structure of Mo3CoSi. On the left are shown nets with z 0 (thin lines) and z 1/2 (thick lines); on the right are coordination polyhedra of atoms: a –Mo in (i); b –Mo, Co in (i); c –Mo, Co in (c); d –Co, Si in (h); e –Si, Co in (e); f –Si, Co in (a)

hkl	$\|F_{\text{exp}}\|$	$\|F_{\text{calc}}\|$	*hkl*	$\|F_{\text{exp}}\|$	$\|F_{\text{calc}}\|$	*hkl*	$\|F_{\text{exp}}\|$	$\|F_{\text{calc}}\|$	*hkl*	$\|F_{\text{exp}}\|$	$\|F_{\text{calc}}\|$
11,0,0	162.6	191.1	921	328.0	401.0	422	37.0	24.4	14,0,2	118.2	167.1
11,5,0 *	13.0	2.2	851	146.1	122.6	512	168.6	138.0	14,2,2	66.7	82.7
12,2,0	45.6	64.0	941	22.6	10.9	442	36.0	6.0	10,10,2	132.9	182.6
12,4,0	30.3	48.0	10,1,1	55.4	53.9	532	61.9	54.9	11,9,2	17.5	30.5
990	63.6	46.2							12,8,2	49.2	47.6

* Reflections not observed; for them the accepted value of F is equal to $\frac{2}{3}F$ of the weakest reflection.
** Reflections that could not be recorded on the Weissenberg pattern.

–be placed in the unit cell with the same x, y (since $4r_{\text{Mo}} > c$), for all atoms of this element (or the principal part of them) the regular point systems (a)—(g), (i), (j) had to be excluded. The combination $16(k) + 2.8(h)$ was also impossible because of excessively small interatomic distances. Two point systems $16(k)$ remained, correspondingly–

positions, together with the positions $8(h)$, occupied by Co and Si atoms, form nets at $z = 0$ and $\frac{1}{2}$. For the placement of 16 Co and Si atoms in the intermediate layers there were positions $4(a)$, $4(b)$, and $8(e)$ with $z = \frac{1}{4}$ and $\frac{3}{4}$. Each net (per unit cell) had to contain, besides triangles, 2 squares (the coordinates of the projections of their centers x, y are $0, 0$ and $\frac{1}{2}, \frac{1}{2}$) and 6 polygons with a larger number of vertices (x, y equal to $0, \frac{1}{2}; \frac{1}{2}, 0; \frac{1}{4}, \frac{1}{4}; \frac{1}{4}, \frac{3}{4}; \frac{3}{4}, \frac{1}{4}; \frac{3}{4}, \frac{3}{4}$), of which the first two (with centers at the points of intersection of two planes m) necessarily had to be hexagons.

Fig. 1. Structure of Mo_3CoSi. On the left are shown nets with $z \approx 0$ (thin lines) and $z \approx \frac{1}{2}$ (thick lines); on the right, coordination polyhedra of atoms: *a* –Mo in (i); *b* –Mo, Co in (i); *c* –Mo, Co in (c); *d* –Co, Si in (h); *e* –Si, Co in (e); *f* –Si, Co in (a).

As geometrical analysis showed, the net can consist only of 2 squares, 2 hexa-, 4 penta- and 16 triangles (the total number of triangles after triangulation: $8 + 12 + 20 + 16 = 56$). The atomic positions initially adopted by us are indicated in Table 1; in order to reconcile the mode of distribution of atoms of the different components and the resulting coordination (normal 15- and 14-vertex polyhedra, icosahedron, tetragonal antiprism with two additional vertices), we assumed (temporarily) that all positions with c.n. 15 and 14 are occupied by Mo atoms, i.e., we adopted the composition $Mo_{18}Co_5Si_5$.

Refinement of the parameters x and y and determination of the mode of distribution were carried out by the two-dimensional Fourier method (projection onto XY; three cycles were performed) (^{7,8}); the intensities of 45 independent $hk0$ reflections of the Weissenberg pattern were used. Since discrepancies between the intensities calculated for the parameters found and those observed on the powder pattern occurred only for reflections with a large ratio $l^2/(h^2+k^2)$, it proved necessary to assume that the nets are slightly corrugated, i.e., to pass to the space group $I\bar{4}c2$ (Table 1). The parameters z were determined by trial and error, by comparing the experimental structure factors determined from the Weissenberg patterns with the calculated ones. The final atomic positions and their distribution for the composition Mo_3CoSi are given in Table 1, and a comparison of the structure factors in Table 2; with the indicated parameters the discrepancy factor R has the following values: for $hk0$, 19.7 (with allowance for unobserved reflections) or 16.6% (without taking them into account), for $hk1$, 20.1%, and for $hk2$, 14.7%.

The structure of Mo_3CoSi is shown in Fig. 1. Its closest analogue is the structure of the W_5Si_3 type. Both structures have the same set of coordination polyhedra, if one disregards a certain difference between the icosahedra (in W_5Si_3 the icosahedron is closer to the 10-vertex polyhedron of the $MnAl_6$ type (^{9})); when the components whose atoms have coordination numbers 15, 14, 12, 10 are denoted, respectively, by R′, R″, X′, X″, the structure W_5Si_3 is described by the formula $R_4'R''X_2'X''$, and the structure Mo_3CoSi by the formula $R_4'R_5''X_4'X''$. In the systematics based on the type of coordination polyhedron with the smallest number of vertices (^{10}), the Mo_3CoSi structure should belong to the class of structures with tetragonal-antiprismatic coordination. But because the content in Mo_3CoSi of atoms with this coordination is small (7.1%), the structure of the type mentioned approaches the class of "icosahedral" structures and, first of all, the types of σ-phases and Zr_4Al_3 (^{11}).

Table 3

Interatomic distances δ in the structure of Mo_3CoSi

Atoms	δ, Å	C.N.
Mo (i): 6 Mo (i)	3.26 (2); 3.19 (2); 2.63 (2)	15
Mo (i): 4 Mo, Co (i)	2.92 (2); 2.87 (1); 2.61 (1)	15
Mo (i): 1 Co, Si (h)	2.70 (1)	15
Mo (i): 2 Si, Co (e)	2.73 (1); 2.67 (1)	15
Mo (i): 2 Si, Co (a)	2.58 (1); 2.52 (1)	15
Mo, Co (i): 4 Mo (i)	2.92 (2); 2.87 (1); 2.61 (1)	14
Mo, Co (i): 3 Mo, Co (i)	2.98 (2); 2.47 (1)	14

Atoms	δ, Å	C.N.
Mo, Co (i): 2 Mo, Co (c)	3.03 (1); 2.98 (1)	14
Mo, Co (i): 3 Co, Si (h)	2.80 (1); 2.73 (1); 2.69 (1)	14
Mo, Co (i): 2 Si, Co (e)	2.71 (1); 2.65 (1)	14
Mo, Co (c): 8 Mo, Co (i)	3.03 (4); 2.98 (4)	14
Mo, Co (c): 2 Mo, Co (c)	2.44 (2)	14
Mo, Co (c): 4 Co, Si (h)	2.76 (4)	14
Co, Si (h): 2 Mo (i)	2.70 (2)	12
Co, Si (h): 6 Mo, Co (i)	2.80 (2); 2.73 (2); 2.69 (2)	12
Co, Si (h): 2 Mo, Co (c)	2.76 (2)	12
Co, Si (h): 2 Si, Co (e)	2.35 (2)	12
Si, Co (e): 4 Mo (i)	2.73 (2); 2.67 (2)	12
Si, Co (e): 4 Mo, Co (i)	2.71 (2); 2.65 (2)	12
Si, Co (e): 2 Co, Si (h)	2.35 (2)	12
Si, Co (e): 2 Si, Co (e)	2.44 (2)	12
Si, Co (a): 8 Mo (i)	2.58 (4); 2.52 (4)	10
Si, Co (a): 2 Si, Co (a)	2.44 (2)	10

The interatomic distances are given in Table 3. The range of values of the Mo—Mo and Mo, Co—Mo, Co distances in Mo_3CoSi is approximately the same as in the Mo_5Si_3 structure, and broader than in the structure of the σ-phase Mo_3Co_2 ([12]) (because of the higher content of atoms with C.N. 15). All three structures, as well as the Mo_3Si structure, are characterized by a strong (by ~12%) shortening of some of these distances in comparison with the sum of the atomic radii. The Mo—Co, Si and Co, Si—Co, Si distances lie in narrower ranges.

The Mo_3CoSi structure is characterized by a partial disorder in the distribution of atoms of all components—a phenomenon rather widely encountered in compounds of transition metals with one another (and with silicon) possessing structures with C.N. 12-16 ([13]); the deviation of the composition of the compound from the ideal $Mo_9(Co, Si)_5$, corresponding to an ordered distribution of atoms of different sizes, is evidently associated with a definite value of the electron concentration characteristic of this structural type.

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Lviv State University
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