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Disordered Modifications of Cobalt Molybdate

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The structures of recently discovered new high-temperature modifications of cobalt molybdate, a'-and a''-$CoMoO_4$, were determined. a'-and a''-$CoMoO_4$ appear after the phase a-$CoMoO_4$ is heated above the temperature range 700–1000°C. They seem to be the disordered modifications of a-$CoMoO_4$ with metal atoms distributed at random in an a-$CoMoO_4$ oxygen network.

The $F(hkl)$ values, calculated for variously disordered a-$CoMoO_4$ structure, were compared with the observed intensities of diffraction lines changing in the course of $a \to a'$ and $a \to a''$ transitions. It was concluded that a''-$CoMoO_4$ has a completely disordered structure with random distribution of both Co and Mo atoms in oxygen interatomic voids. The a'-$CoMoO_4$ is a partly disordered modification, with random distribution of some cations only.

The temperature and the kind of order–disorder transition depend on the method of preparation of a-$CoMoO_4$ samples.

The disordered modifications of cobalt molybdate may be supercooled—even to room temperature—before it transforms rapidly into low-temperature b-$CoMoO_4$ form.

Introduction

In our previous paper (*1*) the results of studies of cobalt molybdate polymorphic transformations were given. Two new high-temperature modifications of cobalt molybdate were discovered. They were called a'- and a''-$CoMoO_4$.

On heating the low-temperature b-$CoMoO_4$, a new phase a-$CoMoO_4$ is obtained at temperatures above 400°C. The structure of b-$CoMoO_4$ (space group $C2/m$) was determined by Smith and Ibers (2). The phase a-$CoMoO_4$ is isostructural with $MgMoO_4$ and $MnMoO_4$ (*3*, *4*). The structure of the last compound was described in detail by Abrahams and Reddy (*5*). The lattice constants of a-$CoMoO_4$ (space group $C2/m$ of monoclinic system) are $a = 10.21$, $b = 9.26$, $c = 7.02$ Å, $\beta = 106°56'$. The projection of a-$CoMoO_4$ structure on plane (010) is shown in Fig. 1.

On further heating of the phase a, the structural transition to a' takes place at 1000°C. On cooling, a'-$CoMoO_4$ transforms again into a-$CoMoO_4$. At temperatures between 100 and 25°C the $a \to b$-$CoMoO_4$ transformation takes place. Phase a heated below 1000°C and subsequently cooled is metastable at room temperature.

Phase a, obtained by thermal decomposition of solvated $CoMoO_4 \cdot aq$ or as the result of a solid-state reaction between the salts of cobalt and molybdenum, transforms to another a''-$CoMoO_4$ modification in the temperature range 700–930°C. The transition temperature depends on the method of phase a preparation. The transformation $a \to a''$ is not completely reversible; the sample obtained on cooling is a mixture of a and a'' modifications. The explosive transition to b-$CoMoO_4$ takes place between 100 and 25°C and it seems to be dependent on the presence of a'' modification. After cooling the samples heated below the temperature of transition $a \to a''$, phase a is metastable at room temperature and transforms to b-$CoMoO_4$ after prolonged grinding.

The purpose of the present work was to determine the structure of the newly discov-

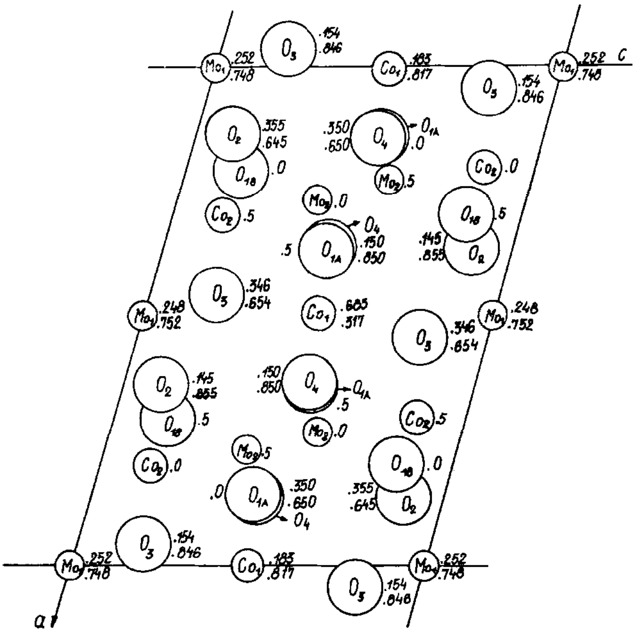

FIG. 1. Projection of *a*-$CoMoO_4$ structure on plane (010).

ered modifications *a*′- and *a*″-$CoMoO_4$, on the basis of observed changes of intensities of X-ray diffraction lines during the transformations *a* → *a*′ and *a* → *a*″.

Results

The changes of diffraction maxima intensities were recorded with a powder diffractometer on heating and cooling the sample in a high-temperature camera.

The X-ray pattern changes in the course of the *a* → *a*′ transformation were described in detail in our previous paper (*1*). Let us recall that a decrease of intensity and increasing splitting of the (220), (002) line of *a*-$CoMoO_4$ were observed. The observed splitting of the (220), (002) line, resulting in two separate reflections, is caused by a decrease in the intensity of the stronger line (220) while the intensity of the (002) line remains unchanged.

The transition *a* → *a*″ does not result in any new diffraction maxima on the X-ray pattern of phase *a*. In the course of this transition we observed the decrease of intensity of (220), (002) reflection followed by its separation into (220) and (002) lines. As opposed to *a*′-$CoMoO_4$ modification, the (220) reflection becomes weaker than the (002) reflection and frequently the (220) line can not be even detected on the X-ray pattern of *a*″-$CoMoO_4$. The intensities of the remaining maxima decrease too. The X-ray pattern of *a*″-$CoMoO_4$ has a small number of weak lines in the positions characteristic for phase *a*, as was illustrated in (*1*). Typical changes of the X-ray pattern of *a*-$CoMoO_4$ in the course of the *a* → *a*″ transition are shown in Fig. 2.

Determination of the Structure of *a*′, *a*″ Modifications

The changes in the structure of *a*-$CoMoO_4$ at heating affect only the intensities of reflections, whereas the line positions remain unchanged. It may be concluded, thus, that *a*′- and *a*″-$CoMoO_4$ are the disordered modifications of *a*-$CoMoO_4$. In the present work two possibilities were considered: first, a structure with a more or less random distribution of cations in the same oxygen network as in *a*-$CoMoO_4$; second, an *a*-$CoMoO_4$

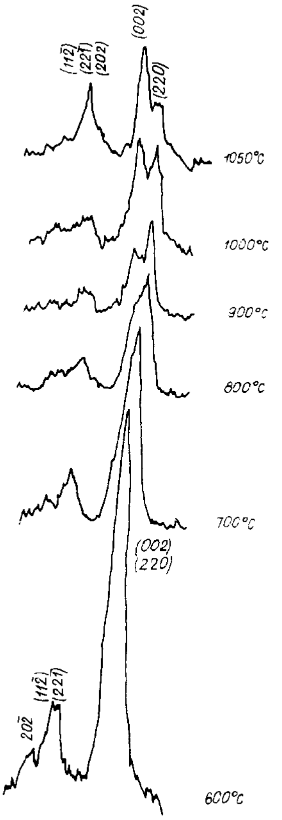

FIG. 2. Changes of X-ray pattern of *a*-$CoMoO_4$ in the course of $a \rightarrow a''$ transition in the temperature range 650–1050°C. At 900°, 1000°, 1050°C the double amplification of the registered patterns was used.

structure with distortions caused by vibration of atoms at higher temperatures.

The structure factors $F(hkl)$ calculated for various distortional models of the structure, indicate that distortions cannot cause the observed changes of intensities.

We thus attempted to calculate $F(hkl)$ for structures with a random distribution of Co and Mo in the oxygen network.

The structure of *a*-$CoMoO_4$ may be thought of as a distorted modification of the CoO structure. The cubic unit cell of CoO contains 4 atoms of oxygen in positions $00\tfrac{1}{2}\circlearrowright$, $\tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2}$ and 4 octahedral voids filled with cobalt atoms in positions 000, $0\tfrac{1}{2}\tfrac{1}{2}\circlearrowright$. Operating the matrix $\tfrac{3}{2}\bar{\tfrac{3}{2}}\bar{1}/\tfrac{3}{2}\tfrac{3}{2}0/002$ on unit cell vectors of CoO, we get the unit cell of *a*-$CoMoO_4$. The transformation matrix of atomic position coordinates corresponding to this change of the unit cell is $\tfrac{1}{3}\bar{\tfrac{1}{3}}0/\tfrac{1}{3}\tfrac{1}{3}0/\tfrac{1}{6}\bar{\tfrac{1}{6}}\tfrac{1}{2}$. The resulting unit cell is monoclinic and its volume is 9 times that of CoO cell. It contains 36 oxygen and 36 metal atoms sites. There are 8 molecules of $CoMoO_4$ per unit cell only, so 4 oxygen and 20 metal atom sites remain unfilled.

The positions of atoms in the real structure are displaced from calculated positions in the idealized CoO-like structure. The displacements of oxygen atoms are considerable, so that the coordination of Mo changes from octahedral to tetrahedral. A part of unfilled octahedral voids change their oxygen environment into tetrahedral one too. In Table I the metal atom positions in the *a*-$CoMoO_4$ structure are compared with calculated positions of cations in an idealized CoO-like structure. Finally, in Table I the coordinates of all filled and unfilled voids in the oxygen network of *a*-$CoMoO_4$ are given. These coordinates were used in calculations of $F(hkl)$ of disordered modifications of *a*-$CoMoO_4$. The sequence of voids down the *b* axis is shown in Fig. 3.

The structure factor for space group $C2/m$ is given by the expression

$$F_{hkl} = \sum_r f_r A_r,$$

where f = atomic scattering factor,

$$A_r = n_r \cos^2 2\pi \frac{h+k}{4} \cos 2\pi (hx_r + lz_r) \cos 2\pi k y_r$$

when $h+k = 2n+1$, $A_r = 0$; when $h+k = 2n$, $A_r = n_r \cos 2\pi(hx_r + lz_r)\cos 2\pi k y_r)$, x_r, y_r, z_r = coordinates of the r atom, hkl = indices of reflection, and n_r = number of positions occupied by the r atom. The contributions of cations to $F(hkl)$ of ordered and disordered structures will be denoted as $(f_r Ar)_{\mathrm{or}}$ and $(f_r A_r)_{\mathrm{dis}}$, respectively. Model I of the disordered structure assumes the random distribution of cations in rows of voids along the *b*-axis (see Fig. 3). The transformation to the structure of model I requires the shifts of cations from filled to unfilled voids, which differ only in y coordinate, having the same x, and z coordinates. In Table II $(fA)_{\mathrm{or}}$ and $(fA)_{\mathrm{dis}}$ (model I) are compared for reflections *h*0*l*, *h*1*l*, *h*2*l*, and *h*3*l*.

TABLE I

COORDINATES OF VOIDS IN OXYGEN NETWORK OF α-$CoMoO_4$ (SPACE GROUP $C2/m$)

Calculated coordinates of metal atom sites in the idealized CoO-like structure			Coordinates of metal sites in α-$CoMoO_4$ structure (according to Abrahams and Reddy (5))			Cation	Coordinates of voids in oxygen network of α-$CoMoO_4$			Oxygen environment of void
x	y	z	x	y	z		x	y	z	
0	$\frac{1}{6}$	$\frac{1}{2}$	0	0.183	$\frac{1}{2}$	Co(1)	0	$\frac{1}{6}$	$\frac{1}{2}$	Octahedral
0	$\frac{1}{2}$	$\frac{1}{2}$	Unfilled void				0	$\frac{1}{2}$	$\frac{1}{2}$	Octahedral
$\frac{5}{6}$	0	$\frac{1}{6}$	0.795	0	0.138	Co(2)	0.795	0	0.138	Octahedral
$\frac{5}{6}$	$\frac{1}{3}$	$\frac{1}{6}$	Unfilled void				0.795	$\frac{1}{3}$	0.138	Octahedral
0	$\frac{1}{6}$	0	0	0.252	0	Mo(1)	0	0	0	Tetrahedral
							0	0.250	0	Tetrahedral
0	$\frac{1}{2}$	0	Unfilled void				0	$\frac{1}{2}$	0	Tetrahedral
$\frac{1}{6}$	0	$\frac{1}{3}$	0.271	0	0.405	Mo(2)	0.271	0	0.405	Tetrahedral
$\frac{1}{6}$	$\frac{1}{3}$	$\frac{1}{3}$	Unfilled void				0.271	$\frac{1}{3}$	0.405	Tetrahedral

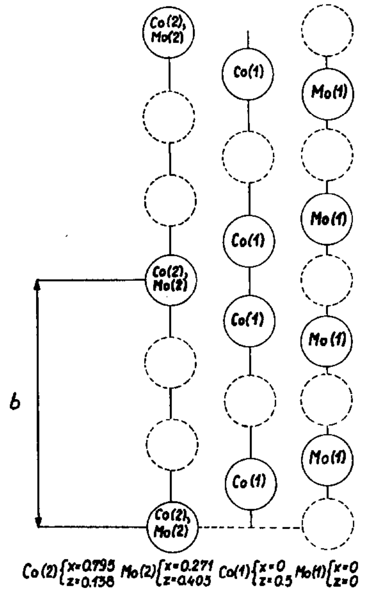

FIG. 3. Positions of voids in the oxygen network of α-$CoMoO_4$ (the solid line refers to the filled voids; the dotted line refers to the unfilled voids).

The oxygen atom positions do not change with order–disorder transformations. Thus, the contributions of oxygen atoms to $F(hkl)$ are the same for ordered and disordered structures. The results given in Table II indicate that $F(h0l)$ does not change in the course of the described order–disorder transition and $F(h3l)$ decreases slightly, whereas $F(h1l)$ and $F(h2l)$ decrease to very small values equal to the contribution of oxygen atoms only.

TABLE II

RELATIONSHIP BETWEEN THE $(fA)_{dis}/(fA)_{or}$ RATIO CALCULATED FOR PARTICULAR SETS OF INDICES, AND THE KIND OF CATION

	$(fA)_{dis}/(fA)_{or}$			
atom	$h0l$	$h1l$	$h2l$	$h3l$
Co(1)	1	0	0	1
Co(2)	1	0	0	1
Mo(1)	1	0	0	0
Mo(2)	1	0	0	1

As model II we considered a structure with random distribution of Co atoms in all octahedral voids and Mo atoms in all tetrahedral voids. In Table III the values of $F(220)$ and $F(002)$, calculated for α-$CoMoO_4$ and for models I and II of disordered structure, are given.

There could be suggested other models of disordered structures. However, they will lead

TABLE III

VALUES OF $F(220)$ AND $F(002)$ CALCULATED FOR ORDERED *a*-$CoMoO_4$ STRUCTURE AND FOR MODELS I AND II OF RANDOM STRUCTURE

	$(f_rA_r)_{or}$		$(f_rA_r)_{dis}$ (I)		$(f_rA_r)_{dis}$ (II)	
Atom	220	002	220	002	220	002
Co(1)	−61	91	0	91	0	61
Co(2)	−77	−16	0	−16	0	−21
Mo(1)	−144	144	0	144	0	115
Mo(2)	−139	53	0	53	0	64
0 (all atoms)	−39	35	−39	35	−39	35
$\sum_r f_rA_r$	−460	307	−39	307	−39	254

always to the same values of $F(h1l)$ and $F(h2l)$ and only slightly different values of $F(h0l)$ and $F(h3l)$ (see the results in Table III). It seems to be impossible to distinguish between all the possible models of disordered structures on the basis of the X-ray powder line intensities.

The observed intensities of reflections indicate that *a*″-$CoMoO_4$ has a completely disordered structure with random distribution of both Co and Mo in the oxygen network of *a*-$CoMoO_4$. The disordered state is probably labile resulting in the fluctuations of diffraction intensities.

The changes of intensity in the course of $a \rightarrow a'$ transitions indicate the order–disorder transition, too. However, it is most likely that the partly disordered structure is obtained. The observed intensity distribution indicates a decrease of the contributions of some cations only to $F(h1l)$ and $F(h2l)$.

Discussion

The transition temperature of *a*-$CoMoO_4$ into the disordered modifications and the kind of transition depend on the method of preparation of *a*-$CoMoO_4$ samples. There must be some differences between the various samples of *a*-$CoMoO_4$ in the degree of ordering and perfection of the structure. These differences, however, are not shown by the X-ray method.

Phase *a*, obtained by thermal decomposition of solvated $CoMoO_4$ or by solid-state reaction, on heating transforms into the completely disordered modification *a*″-$CoMoO_4$. The transition temperature is highest for stoichiometric compounds obtained by precipitation from solution and decreases for nonstoichiometric compounds ($CoMo_{1\cdot11}O_{4\cdot28}$) and for the sample obtained by sintering of cobalt nitrate and ammonium paramolybdate. The disordered *a*″-$CoMoO_4$ may be cooled down to room temperature before it transforms explosively into *b*-$CoMoO_4$.

Phase *a*, obtained by polymorphic transition from *b*-$CoMoO_4$ at 400°C, in the course of further heating transforms to the partly disordered modification *a*′-$CoMoO_4$. On cooling, *a*′-$CoMoO_4$ transforms nearly completely into *a*-$CoMoO_4$. In the absence of disordered modification in the cooled sample, the transition to *b*-$CoMoO_4$ is not as violent as the $a'' \rightarrow b$ transition, but it is only enhanced.

Phase *a* heated below the order–disorder transition temperatures is more or less metastable after cooling to room temperature.

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