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The Polymorphic Transformations of Cobalt Molybdate

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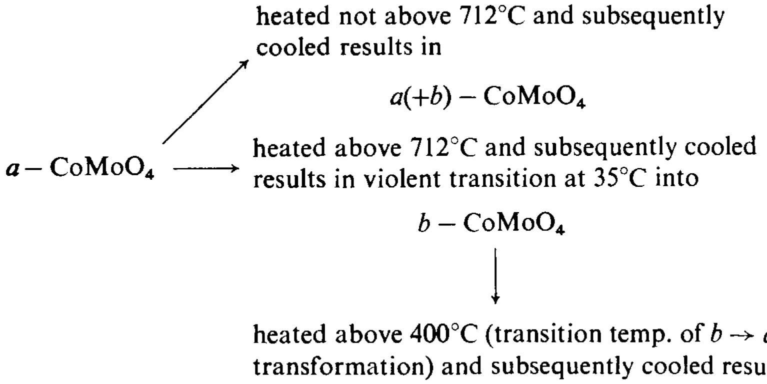
Polymorphic transformations of $CoMoO_4$ were studied by means of high temperature X-ray measurements within the temperature range 25–1200°C. On heating phase *a* obtained from low temperature modification *b* a new modification *a′* was discovered. Phase *a* obtained by thermal decomposition of solvated α-$CoMoO_4$ shows different behaviour. At 700–930°C depending on the conditions of preparation it transforms irreversibly into still another modification *a″*. On cooling, a mixture of phases $a + a''$ is obtained, the presence of *a″* being responsible for the explosionwise transition into *b*, observed around the room temperature.

Introduction

Cobalt molybdate is known to form 3 polymorphic modifications. The low temperature modification *b* was described in detail by Smith and Ibers (*1*), as consisting of blocks of edge-sharing CoO_6 and MoO_6 octahedra ($C2/m$ space group), whereas high temperature modification *a* was found by Courtine et al. (*2*) to be isostructural with $MgMoO_4$, which implied that cobalt ions occupy octahedral positions and molybdenum ions tetrahedral ones. The third modification appears under high pressures. The conditions of the formation of modifications *a* and *b* and their transformations have been investigated by several authors (*3*–*8*). It was found that on heating modification *b* transforms into *a* at about 400°C, whereas the reverse transformation is hindered and phase *a* may easily be supercooled to room temperature. The most detailed description was given by Lipsch and Schuit (*8*), who suggested the following scheme for $CoMoO_4$ phase transitions:



heated not above 712°C and subsequently cooled results in

$a(+b) - CoMoO_4$

$a - CoMoO_4$ ⟶ heated above 712°C and subsequently cooled results in violent transition at 35°C into

$b - CoMoO_4$

↓

heated above 400°C (transition temp. of $b \rightarrow a$ transformation) and subsequently cooled results in

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$CoMoO_4$ transformations were studied mainly by DTA and TG methods, accompanied by X-ray identification of materials obtained after cooling the samples to room temperature. These methods could not give the full information about the structural changes, which take place in higher temperatures.

It therefore seemed interesting to look more closely at the possible structural changes in the whole temperature range up to the melting point using the high temperature X-ray camera. As supplementary methods DTA and TG measurements were exploited.

Experimental

The solvated cobalt molybdate preparation was obtained by precipitation from the solution of cobalt nitrate and ammonium paramolybdate at pH = 5.5 adjusted by adding ammonia (μ9g). The precipitate, which will be called α-$CoMoO_4$ had the composition $CoMoO_4 \cdot xH_2O$. When such preparation is heated above 330°C the high-temperature modification *a*–$CoMoO_4$ is always formed. The low-temperature modification *b*–$CoMoO_4$ was prepared by annealing α-$CoMoO_4$ at 1000°C for 12 hr, cooling to room temperature and carefully grinding in an agate mortar.

The X-ray investigations were carried out with DRON-1 diffractometer in high temperature camera KW-1200, which enabled the measurements to be carried out in air within the temperature range up to 1200°C. The temperature was measured using Pt–Rh thermocouple. Cu*Kα* radiation with wavelength 1.5418 Å and Ni filter were used.

The DTA, DTG and TG curves were obtained with the Paulik–Paulik–Erdey apparatus at heating rate 5°/min. The precision measurements of thermal effects were made on KIPP high sensitivity DTA analyser (heating rate 10°/min).

Results

I. Structural Transitions of Low-Temperature b–*$CoMoO_4$ Modification*

The X-ray pattern of the initial sample at 20°C is shown in Fig. 1c. It agrees well with that quoted by Smith (*10*) for the low-temperature modification *b*–$CoMoO_4$. In the course of its heating, the well-known polymorphic transition takes place at the temperature of

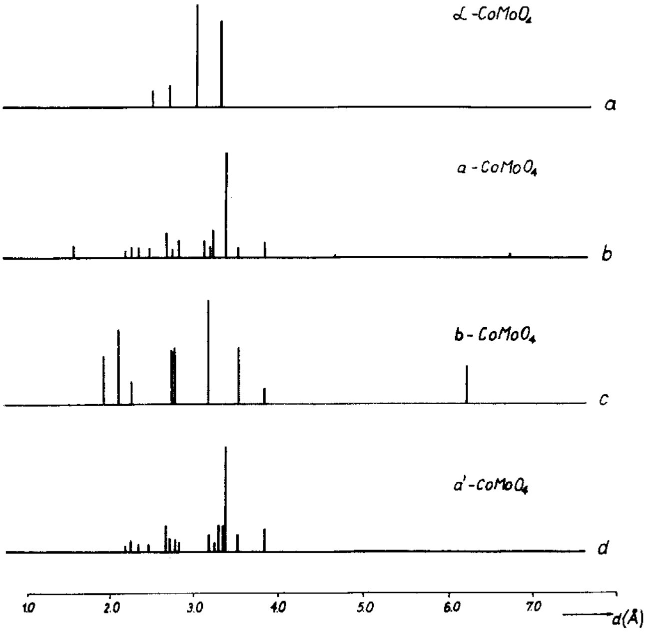

FIG. 1. X-ray patterns of various $CoMoO_4$ modifications.

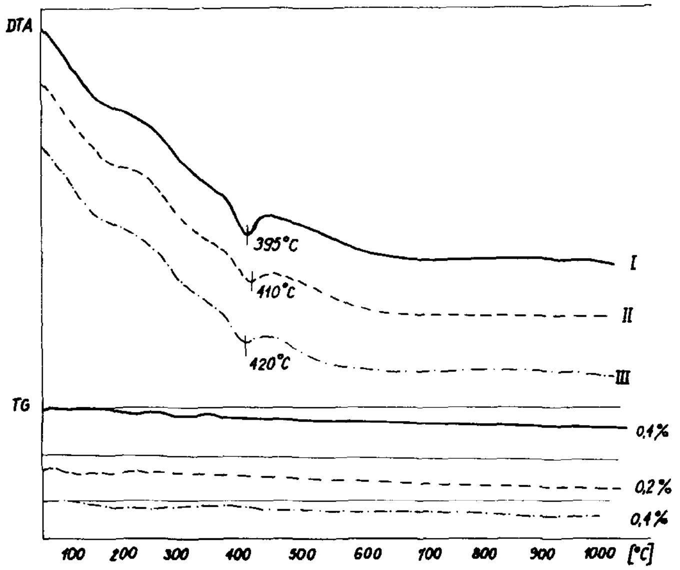

FIG. 2. DTA and TG curves of phase *b*: I. sample obtained by heating α-CoMoO$_4$ at 1000°C for 3 hr; II. repeated with sample I; III. sample obtained by the repeated transformations $b \rightarrow a \rightarrow b$.

about 400°C (Fig. 2), resulting in the formation of *a*–CoMoO$_4$. Its X-ray pattern is shown in Fig. 1b. and is in good agreement with literature data (*2*). On heating the *a*–CoMoO$_4$ further in the X-ray high temperature camera we discovered a new polymorphic transition at about 1000°C. The characteristic feature of the new modification which we shall denote as *a'* is the splitting of diffraction lines in the X-ray pattern of *a*–CoMoO$_4$. The main line of *a*–CoMoO$_4$ (3.360 Å) is replaced by two new maxima at 3.368 and 3.344 Å and 2.791 Å line of *a*–CoMoO$_4$ is split into lines 2.810 and 2.783 Å. The other lines of *a*–CoMoO$_4$ pattern remain unchanged. This is shown in Fig. 3, wherein the section of diffraction

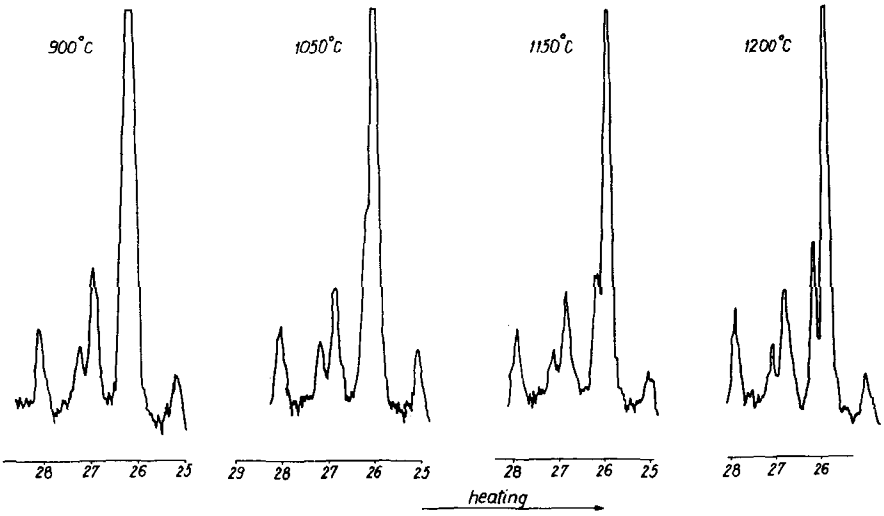

FIG. 3. The changes of X-ray pattern of *a*–CoMoO$_4$, obtained as the result of $b \rightarrow a$ transition, on heating between 900–1200°C (section of 2Θ 25–28° for CuK_α radiation).

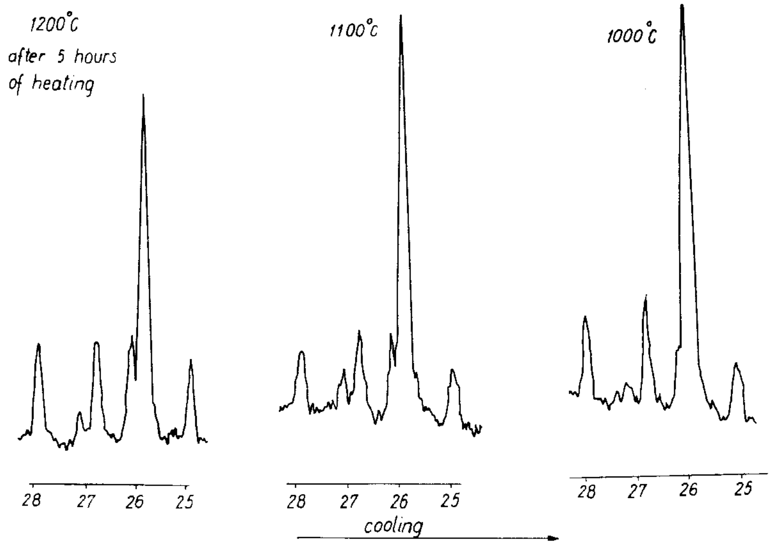

FIG. 4. The changes of X-ray pattern of a'-$CoMoO_4$ on cooling from 1200°C (the same section of 2Θ as in Fig. 3).

pattern is shown as recorded on heating the sample between 900–1200°C. The growing splitting of the main line is clearly visible. The X-ray pattern of a'-$CoMoO_4$ is shown in Fig. 1d.

Two lines, which split as the result of $a \rightarrow a'$ transition, are in fact composed of several overlapping reflections; the first one of reflections 002 (3.358 Å) and 220 (3.360 Å), the second one of 112 (2.789 Å), $13\bar{1}$ (2.787 Å) and 221 (2.790 Å). The splitting of a line on raising the temperature can be interpreted either as the result of the anisotropy of thermal expansion coefficients, or as the result of the changes of intensity of the overlapping lines, so that the separate reflections can be distinguished. The analysis of the temperature shifts of the positions of other maxima indicates rather that the second interpretation is valid.

The change of structural factor of the reflection must be connected with the change in the atomic positions. The fact that the splitting of lines increases with rising temperature seems to indicate that the transition is of the order disorder type. The detailed description of this transition would require further structural investigations.

On cooling of a' the reverse transition to a is observed. This is illustrated in Fig. 4, which shows the section of the diffraction pattern registered on cooling the sample from 1200°C. The phase a obtained in that way can be supercooled to the temperature of about 100°C, but between 100 and 25°C a rapid and complete transition into b takes place.

A different behaviour is observed, when phase a obtained from b above 400°C is not heated to higher temperatures. In such case no rapid transition to b is observed on cooling even to room temperature. Metastable modification a transforms, however, into b quite easily, under the influence of even weak mechanical shocks. With time, even in absence of any mechanical shocks the slow $a \rightarrow b$ transition takes place.

II. Structural Transitions of α-$CoMoO_4$

The X-ray diagram of the solvated cobalt molybdate α-$CoMoO_4$ is shown in Fig. 1a. On heating the sample within the temperature range 25–300°C we could not detect any changes of the crystalline structure. In this temperature range only a small decrease of mass (about 5 %) is observed, on the TG curve and is accompanied by a broad endothermic DTA peak (Fig. 5). These effects are related to the removal of adsorbed water.

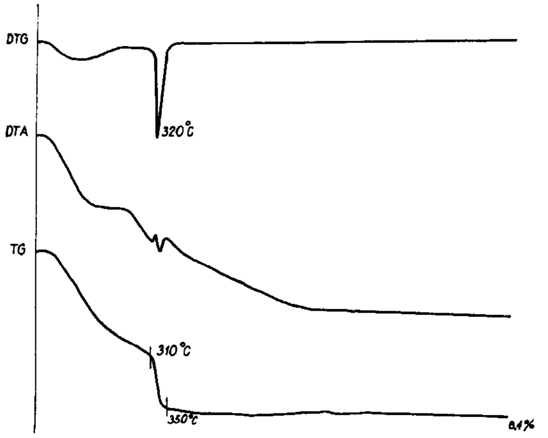

FIG. 5. DTA and TG curves of α-CoMoO$_4$.

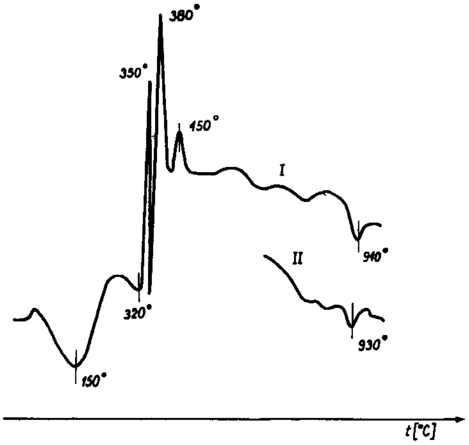

FIG. 6. Thermal microanalysis of α-CoMoO$_4$.

Transition of solvated CoMoO$_4$ to the anhydrous compound takes place at temperatures above 320°C. It is accompanied by an endothermic peak at 320° and rapid decrease of mass (about 3%). The resulting compound has the structure of *a*–CoMoO$_4$ and is present in partly amorphous and partly ill-defined crystalline form, as indicated by the very large broadening of its diffraction lines. In the course of further heating a recrystallization takes place as shown by the progressive sharpening of the diffraction pattern.

In order to obtain more informations on the mechanism of the dehydration of α-CoMoO$_4$ and crystallization of *a*–CoMoO$_4$ DTA measurements were repeated with a microanalyser. Results are shown in Fig. 6. The exothermic peaks at 350, 380, and 450°C may be connected with stepwise recrystallization of the initially amorphous anhydrous CoMoO$_4$. The diffraction measurements do not indicate any phase transitions in the above-mentioned temperature range.

Several samples of *a*–CoMoO$_4$ were prepared by decomposition of α–CoMoO$_4$ in the course of heating for 2 hr at temperatures 300, 400, 500, 600, 700, and 800°C and subsequent cooling to room temperature. The precise diffractographic measurements by inner standard method showed no change in the values of interplanar spacings *d*. In the temperature range 350–900°C neither mass changes, nor thermal effects were found. The diffraction sharpening indicates the complete recrystallization of the sample at about 700°C (grain size higher than 1000 Å).

We would like now to describe an experiment, in which a sample of α–CoMoO$_4$ was heated in the X-ray camera to higher temperatures. As already mentioned its diffraction pattern disappeared at about 320°C and the pattern of phase *a* began to develop. At about 700°C the recrystallization of this phase was completed. When, however, the sample was heated to still higher temperatures, a new polymorphic transformation was discovered, leading to the formation of a new phase which we shall denote as *a″*. This polymorphic transition is accompanied by the weak endothermal effect observed on the DTA curve (Fig. 6). The X-ray pattern of *a″* differs considerably from that of *a′*–CoMoO$_4$, although the majority of the lines of *a*–CoMoO$_4$ can still be found. The intensities however are changed. The splitting of lines 3.360 and 2.791 Å characteristic for *a′* appears only in some experiments.

In the course of heating within the temperature range 930–1200°C, as well as on heating at constant temperature over a longer period of time fluctuations of intensity are observed, although the line positions remain unchanged. The above-mentioned splitting appears and disappears quite randomly. The results of one of the experiments, in which a sample of *a″*

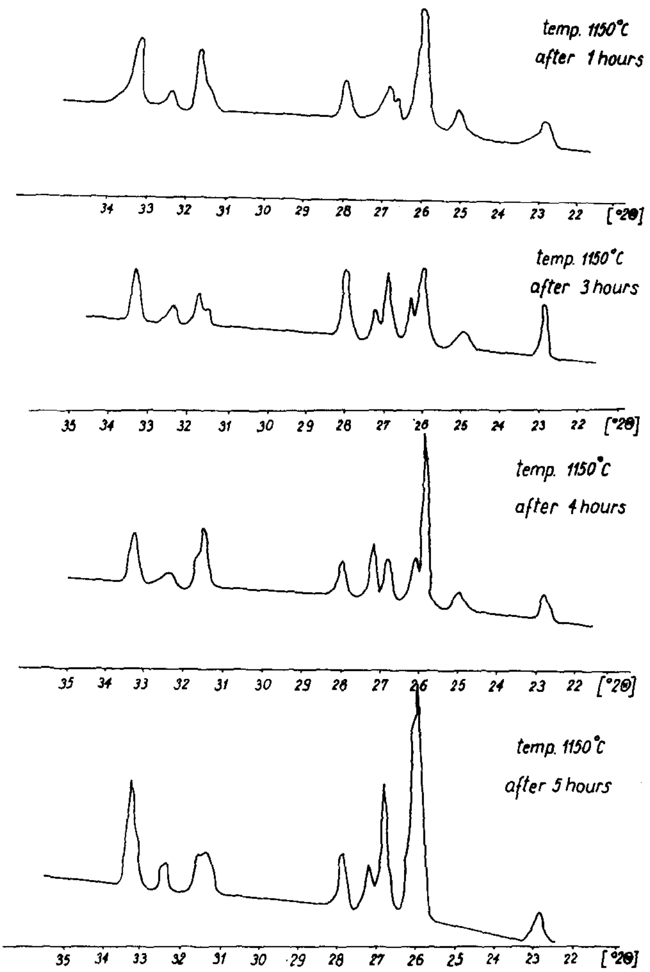

FIG. 7. The changes of X-ray pattern of a''–$CoMoO_4$ on heating at 1150°C (the section of 2Θ 22–34° for CuK_α radiation).

was heated at 1150°C over longer period of time, are presented in Fig. 7.

No new diffraction maxima appear after the phase transition from a–$CoMoO_4$ to a''–$CoMoO_4$. Apparently the differences in the structure of these modifications influence only the intensities, which additionally undergo variations with the time of measurement, as well as between the different experiments. Thus, we can assume that a'' modification has highly disordered a-type structure, varying randomly with time.

When the sample was cooled in the DTA apparatus to 600°C and heated again, the reappearance of the endothermic DTA peak at 930°C was observed. However, the X-ray pattern of the sample cooled below 930°C differs considerably from the standard pattern of a–$CoMoO_4$. It must be thus concluded that $a \rightarrow a''$ transition is only partially reversible and after cooling below 930°C the sample is composed of a mixture of both modifications a and a''.

On cooling such sample further an explosionwise transition into modification b takes place between 100 and 25°C, the crystallites disintegrating violently. This explosionwise transition is observed only if modification a'' appeared in the sample due to heating above 930°C. If the sample of modification a is

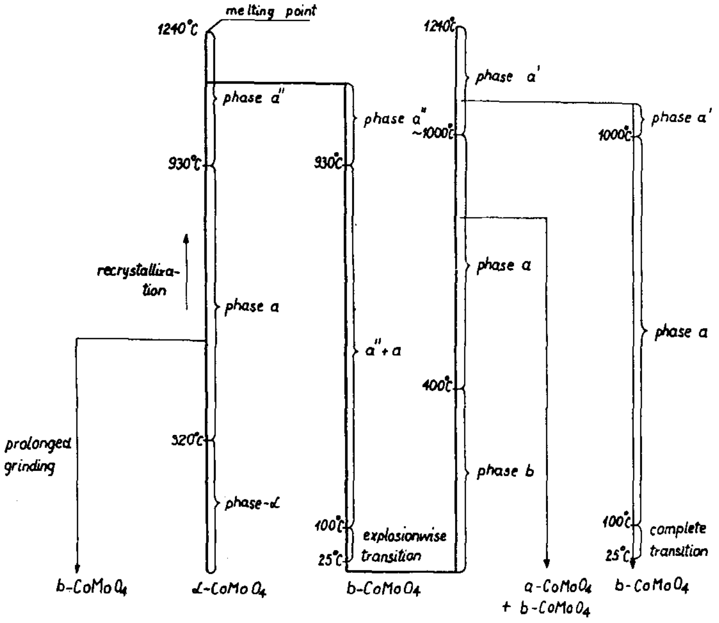

FIG. 8. Phase transitions of $CoMoO_4$.

heated only to temperatures below the $a \rightarrow a''$ transition point, it can be easily supercooled to room temperature and transforms into *b* only after grinding.

In view of the differences in the behaviour of phase *a* obtained by the transition of phase *b* and that prepared by decomposition of solvated α–$CoMoO_4$, it seemed interesting to collect more informations on the influence of the conditions of preparation on subsequent transformations of phase *a*. The preparation of phase *a* was thus obtained by melting of $Co/NO_3/_2 \cdot 6H_2O$ and $/NH_4/_6Mo_7O_{24} \cdot 4H_2O$ in molar ratio $Co/Mo = 1$. They were heated at 300°C to eliminate the ammonium nitrate, cooled and ground. Results obtained with this sample were similar to these for hydrate. As the result of the solid state reaction an ill-defined phase *a* was formed, which after crystallization underwent the transition to *a''* at 700°C. In the course of cooling of the sample heated above 700°C the explosionwise transition to *b* was observed.

Discussion

Phase transitions of $CoMoO_4$ can be diagrammatically represented in the way shown in Fig. 8.

Results presented in this paper clearly show that there is a distinct difference in the behaviour of high temperature modification *a* obtained as the result of the polymorphic transition of low-temperature modification *b*, and that prepared by decomposition of solvated cobalt molybdate, although their X-ray patterns are identical.

In the case of the first one a reversible transformation into *a'* is observed at 1000°C. The transformation $a \rightarrow b$ is hindered so that phase *a* can easily be supercooled even to room temperature, but it transforms then to *b* readily under the influence of even weak mechanical shocks. The rate of this transformation apparently depends on the degree of crystallization of phase *a* i.e., on the temperature of presintering.

In the case of phase *a* obtained by decomposition of solvated α–$CoMoO_4$ a transformation into phase *a''* is observed between 700–930°C depending on the conditions of preparation of the initial sample. This transition is irreversible, the cooled preparation being composed of a mixture of phase *a* and *a''*. The presence of phase *a''* seems to be responsible for the explosionwise transition observed on cooling to room temperature.

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