PHYSICS

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1963

SovietRxiv

Abstract

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PHYSICS

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ON A NEW MODIFICATION OF Ag_2O WITH A LAYERED STRUCTURE

Recently we established that at pressures $p > 80$ kbar and $t > 600$°C cuprous oxide decomposes according to the equation $Cu_2O \rightarrow CuO + Cu$ (in press). It was natural to assume that the structural analogue of Cu_2O—Ag_2O—would behave identically under the same conditions. However, the investigation unexpectedly led to a different result.

Table 1

Results of experiments at high pressures and temperatures *

No. No.	p, kbar	t, °C	Time	Results	No. No.	p, kbar	t, °C	Time	Results
1	125	200	2 h 40 min	Ag_2O I	6	125	1400	2 min	Ag_2O II
2	125	400	45 min	Ag_2O I	7	115	1000	2 min	Ag_2O I
3	125	600	2 min	Ag_2O I	8	115	1000	1 h 30 min	Ag_2O I
4	125	1100	1 h	mixture Ag_2O I and Ag_2O II	9	115	1200	2 min	Ag_2O I
5	125	1400	10 min	Ag_2O II	10	115	1400	30 min	Ag_2O II
					11	115	1400	50 min	Ag_2O II
					12	115	1400	1 h	Ag_2O II

Table 2

Interplanar spacings and structural amplitudes of Ag_2O II

hkl	d_{obs}, Å	d_{calc}, Å	F_{obs}	F_{calc}	hkl	d_{obs}, Å	d_{calc}, Å	F_{obs}	F_{calc}
100	2.64	2.66	5.9	9.5	203	1.04	1.03	16.5	12.3
002	2.46	2.47	10.3	11.8	121	0.986	0.986	18.1	18.5
101	2.33	2.34	25.1	17.3	114	0.961	0.963	15.9	20.9
102	1.81	1.81	17.6	11.0	105	0.928	0.926	13.8	13.9
003	1.64	1.65	10.5	0.6	204	0.905	0.905	11.7	6.2
110	1.53	1.54	18.4	19.4	300	0.887	0.887	9.7	14.0
103	1.40	1.40	22.5	16.2	123	0.857	0.858	14.4	15.3
200	1.33	1.33	6.7	7.7	302	0.834	0.835	8.8	12.3
112	1.30	1.30	22.0	22.9	006	0.817	0.822	6.5	7.0
201	1.28	1.28	17.4	15.5	205	0.794	0.792	16.0	11.2
004	1.24	1.24	10.3	10.0	106	0.788	0.787	5.1	6.6
202	1.17	1.17	13.0	8.7	303	0.781	0.781	4.6	0.5

Silver oxide was prepared by the action of caustic soda on a solution of silver nitrate. The product obtained, washed by decantation, after drying gave a Debye pattern of pure Ag_2O (cuprite structure ([1])). The substance under study was placed in a platinum ampoule in a high-pressure vessel; heating was carried out with the aid of a graphite heater introduced into the chamber. At $p = 115$–125 kbar** and $t = 1400 \pm 200$°C (Table 1) a new phase, Ag_2O II, was obtained. The Debye pattern of Ag_2O II contains 25 lines (Fig. 1), which were indexed in the CdJ_2 structure (see Table 2). The unit-cell parameters of the new phase were determined from the photograph

* In a number of experiments at high temperature, in addition to Ag_2O II, a small amount of greenish-yellow Ag_2CO_3 and a white powder were formed, giving on the X-ray pattern a system of unknown lines.

** The pressure values were taken according to the Kennedy scale ([2]).

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Fig. 1. *a* –X-ray diffraction pattern of Ag_2OI (cuprite structure); *b* –X-ray diffraction pattern of Ag_2OII (CdI_2 structure). Filtered copper radiation, RKU-114 camera

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Fig. 1. Microphotographs of cobalt precipitates obtained at different pH values (120×).
a –pH 1.7, *b* –pH 4.1

Fig. 2. Linear section of the three-dimensional Patterson synthesis along the direction $[\frac{1}{3}\ \frac{2}{3}\ z]$.

Figure 1: Fig. 2. Linear section of the three-dimensional Patterson synthesis along the direction $[\frac{1}{3}\ \frac{2}{3}\ z]$.

Ag_2O II in a mixture with NaCl. Their values in hexagonal axes are: $a = 3.072 \pm 0.003$ Å, $c = 4.941 \pm 0.004$ Å, $c/a = 1.608$. The space group is $D_{3d}^3 = C\bar{3}m$; $\rho_{\text{rentg}} = 9.53$ g/cm^3, $\rho_{\text{exp}} = 9.5 \pm 0.3$ g/cm^3, $\rho_{\text{starting phase}} = 7.3$ g/cm^3 (density measurements of Ag_2O II were carried out at the Institute of Mineral Raw Materials by means of a pycnometric method developed for application to small quantities of substance). The change in density in the transition $Ag_2OI \rightarrow Ag_2OII$ is $\sim 30\%$. The atoms in the crystal are arranged as follows: O occupies the position 000, and the two Ag atoms occupy $\frac{1}{3}\ \frac{2}{3}\ z$, $\frac{2}{3}\ \frac{1}{3}\ \bar{z}$. Thus, determination of the structure reduces to finding the parameter z for Ag. For this purpose, a linear section of the three-dimensional Patterson synthesis was constructed in the direction $[\frac{1}{3}\ \frac{2}{3}\ z]$. Summation of the series was carried out with the aid of 3° strips. The linear synthesis (Fig. 2) revealed two peaks with coordinates $z = 0.25$ and $z = 0.50$, of which the first corresponds to the interatomic vector Ag—O, and the second to Ag—Ag. The Ag parameter, calculated from both maxima, is $z = 0.25$.

Fig. 2. Linear section of the three-dimensional Patterson synthesis along the direction $[\frac{1}{3}\ \frac{2}{3}\ z]$.

In comparing the experimental and calculated structural amplitudes, the discrepancy factor R proved to be equal to -0.25 (for F_{calc} the temperature correction was not taken into account). Thus, it may be considered proven that the new phase has the CdI_2 structure and, consequently, is a close-packed hexagonal packing of silver atoms with filling by oxygen atoms of half the octahedral voids according to the motif: filled layer, empty layer. It may be added that Ag_2F (^{3}) also has a structure of the CdI_2 type. The distances between atoms in Ag_2O II (Ag—O 2.60 Å, Ag—Ag 2.86 Å) indicate the ionic character of the bond between the silver and oxygen atoms within a layer and the similarity of the interaction of neighboring silver atoms to the interaction in metallic silver (metallic radius Ag = 1.44 Å). The distances between atoms in the structure of Ag_2O I (cuprite) (Ag—Ag 3.34 Å and Ag—O 2.04 Å) characterize an obvious change in the bonds during the phase transformation. Thus, the transition $Ag_2OI \rightarrow Ag_2OII$ is accompanied by a change in the type of packing, the coordination number (2 and 4 to 3 and 6), and the character of the bond between individual atoms.

The appearance of a metallic luster and the Ag—Ag distance in the new phase permit the supposition that Ag_2O II is a layered semiconductor with a comparatively small band gap.

In conclusion, the authors consider it their duty to thank T. B. Zdorik for assistance rendered in determining the density of the substance studied.

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Received
14 VI 1963

CITED LITERATURE

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Note: Figure translations are in progress. See original paper for figures.