High-pressure x-ray study of Cu_2O and Ag_2O

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Pressure-induced phase transitions have been found in Cu_2O and Ag_2O by high-pressure x-ray diffraction technique at room temperature. Cu_2O transforms from the cuprite to a hexagonal structure at a pressure of 10 GPa. This hexagonal form changes in the pressure range from 13 to 18 GPa into another hexagonal form, with a $CdCl_2$-type structure. Up to 24 GPa, the highest pressure generated, no decomposition of Cu_2O into Cu and CuO was observed. Ag_2O transforms at 0.4 GPa from the cuprite structure to a hexagonal structure which is identical with that found above 10 GPa in Cu_2O. Extended p-T phase diagrams of Cu_2O and Ag_2O are presented using the results of the x-ray study and, in the case of Cu_2O, additional results of an optical investigation.

I. INTRODUCTION

Cu_2O and Ag_2O have a cubic structure with high symmetry (space group $O_h^4 \equiv Pn3m$).[1] This cuprite structure, displayed in Fig. 1, can be considered as two interpenetrating lattices: one is fcc occupied by the metal atoms and the other one is bcc occupied by the O atoms. This rather open structure suggests, at higher pressures, phase transitions to denser structures. Ultrasonic measurements[2] of Cu_2O at pressures up to 0.3 GPa give a negative pressure dependence of the elastic constant C_{44}. This indicates that the stability of the cuprite lattice decreases as the pressure increases.

The first x-ray measurements[3] of Cu_2O at pressures up to 16 GPa gave evidence of two phase transitions, one at 5 GPa (phase I → phase Ia) and a second one at 12 GPa (phase Ia → phase II). At pressures above 15 GPa a decomposition of Cu_2O into CuO and Cu was reported. The results of a room-temperature x-ray study of Cu_2O, presented in this paper, confirm the existence of phase II, but a transition pressure of 10 GPa instead of 12 GPa. In addition, our measurements show that there is no indication for a phase transition around 5 GPa, i.e.,

phase Ia does not exist. On the other hand, we find a continuous transition from phase II to a new phase which was not observed before. Furthermore, there is no evidence for a decomposition of Cu_2O up to 24 GPa, the highest pressure generated in this study.

In the case of Ag_2O volumetric measurements[4] show a drastic decrease of volume around 0.4 GPa. Our x-ray measurements confirm a phase transition at this pressure. The structure of the new phase is identical with that of phase II in Cu_2O. Up to 29 GPa no further phase transition was observed.

In this paper we present for the first time detailed descriptions of the high-pressure modifications of the cuprite structure and extended p-T phase diagrams of Cu_2O and Ag_2O.

II. EXPERIMENTAL

Fine powdered samples of Cu_2O were prepared from batches grown in our institute as well as from a larger batch from the group of Professor Carabatos, whereas Ag_2O was bought as a fine powder from "Ventron" with a purity of 99.999%. The Cu_2O crystals were grown in both cases by oxidation of crystalline copper by the grain-growth method.[5]

High pressure was generated in a gasketed diamond anvil cell,[6] using a 4:1 mixture of methanol and ethanol as well as silicon grease as pressure medium. The pressure was determined by the well-known ruby fluorescence technique.[7] X-ray diffraction patterns were taken at room temperature in the energy-dispersive mode.

The optical studies of the phase transition of Cu_2O were carried out with a microscope in connection with a cryostat for cooling down the diamond cell to liquid-nitrogen temperature. In this setup the pressure was determined again by the ruby fluorescence
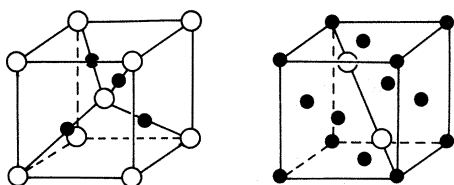

FIG. 1. Different plots of the cuprite structure show (a) the bcc lattice formed by the O atoms (open circles) and (b) the fcc lattice formed by the metal atoms Cu or Ag (closed circles).

technique and a color change of the Cu_2O crystal (30 μm thickness, 100 μm diameter) was observed by means of the microscope.

III. RESULTS AND DISCUSSION

A. Cu_2O

In Fig. 2 we have plotted the d values of the observed reflections of Cu_2O as a function of pressure. The different symbols indicate different runs. In the range 0–10 GPa we can follow the first five reflections of the cuprite structure. At 10 GPa a totally new x-ray pattern appears. If we increase the pressure we observe a continuous change of the pattern and above 18 GPa the x-ray pattern looks relatively simple. Decrease of the pressure to 0 GPa brings back the reflections of the original cubic structure of Cu_2O. As the positions as well as the intensities of the reflections are the same, we conclude that Cu_2O does not decompose into CuO and Cu up to 24 GPa.

To discuss in detail what happens in the three ranges, we begin with the range from 0–10 GPa. The lines connecting the data points of the cuprite structure in Fig. 2 were obtained by fitting the data of the (200) reflection with a polynomial of second order and calculating from that the pressure variation of the other reflections. But we want to mention here that the final values of the lattice constants (Table I) are calculated using all reflections.

The d values of the cuprite structure become smaller with increasing pressure, due to the hydrostatic compression of the sample. The intensities and the widths of the reflections do not change. This means there is no indication for a phase transition around 5 GPa reported in the earlier x-ray work.[3] The d values
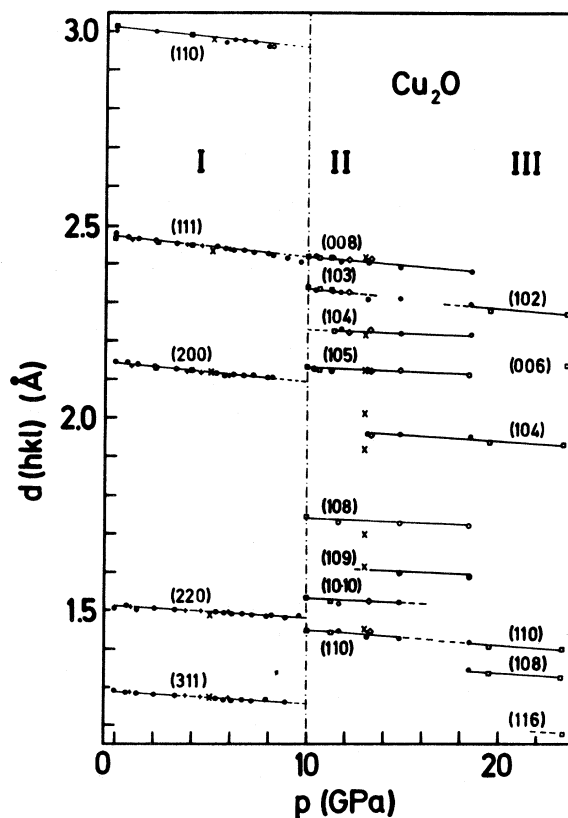

FIG. 2. Pressure dependence of the $d(hkl)$ values of the observed reflections in Cu_2O.

of the cubic pseudocell of the so-called new structure (phase Ia) of Cu_2O, published in Ref. 3, are plotted in Fig. 2 using the symbol "x." As we can see, these d values are in agreement with those expected for the original cubic form of Cu_2O.

TABLE I. Relevant data of phase transitions, structures, lattice parameters, and volume changes of Cu_2O and Ag_2O.

Substance	Pressure range (GPa)	Structure type	Lattice parameter (Å)	Volume change
Cu_2O	0	Cuprite	$a = 4.27$	
	10		$a = 4.18$	3.7%
	10	Hexagonal	$a = 2.90, \ c = 19.31$	
	18		$a = 2.82, \ c = 19.04$	11.1%
	13	$CdCl_2$	$a = 2.82, \ c = 12.70$	
	At least 24		(at 18 GPa)	
Ag_2O	0	Cuprite	$a = 4.736$	
	~0.4			6.5%
	~0.4	Hexagonal	$a = 3.24, \ c = 21.82$	
	At least 29			5.5–7%[a]

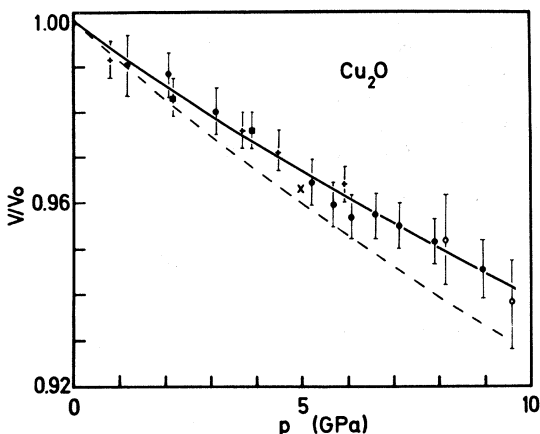[a] Value taken from Ref. 4.

FIG. 3. The volume change of Cu_2O as a function of pressure. The solid line represents a fit of our data with the Murnaghan equation of state and the dashed line is the Murnaghan equation of state calculated from the elastic data of Ref. 2.

In addition we have plotted in Fig. 3 the volume-pressure behavior of Cu_2O in the range 0–10 GPa, determined from the d values of Fig. 2. The solid line represents a fit of our data by the Murnaghan equation of state, with a zero-pressure bulk modulus $B_0 = 131$ GPa and its pressure derivative $B_0' = 5.7$. The deviation of the data points from this curve is the same above and below 5 GPa, which also indicates that no structural change occurs. Our data are also in good agreement with the Murnaghan equation of state, calculated by using the elastic data from the ultrasonic measurements[2] ($B_0 = 112$ GPa and $B_0' = 4.5$), represented by the dashed line.

In discussing the new phases II and III, we will start with the structure of phase III. At pressures above 18 GPa we observe six reflections shown in Fig. 2. The strong ones, i.e., starting from highest d value, the first, third, and fourth of them show some correspondence to the (111), (200), and (220) reflections of the cuprite lattice in phase I. Describing the reflections of the fcc lattice formed by the Cu atoms in phase I with hexagonal indices we get the relations

cubic: (111); (200); (220) ,

hexagonal: (003),(101); (102); (110),(104) ,

where the cubic cell contains four Cu atoms and the corresponding hexagonal one three Cu atoms. As we see from Fig. 2, the reflections of phase III are in agreement with a hexagonal cell in which the Cu atoms are still cubic close packed as in phase I. The indices in Fig. 2 are for a cell with a c axis twice as large. This doubling is due to the fact that the hexagonal cell of phase III must contain an integer number of Cu_2O units. Calculating the density of phase III we find a large increase compared to the density of phase I (see Table I and Fig. 5). That in-

dicates a drastic change of the packing efficiency which means the coordination number of the O atoms surrounding the Cu atoms must be much larger in the hexagonal structure of phase III than in the cuprite structure of phase I.

The assumption of a $CdCl_2$-type structure for phase III of Cu_2O describes well the facts presented above. In Fig. 4 the relations between the cubic form of Cu_2O and the $CdCl_2$-type high pressure form of it are shown. In this figure the Cu and O atoms are drawn in layers along the [111] direction of cubic Cu_2O. In the $CdCl_2$-type structure we have the same stacking of Cu atoms, but now along the direction of the c axis of the hexagonal cell. In the cubic form we have O atoms between each Cu-Cu layer and the O atoms are sitting in tetrahedral voids of the Cu lattice. In the $CdCl_2$-type structure we have Cu-Cu layers with O atoms and Cu-Cu layers without O atoms in between. Here the O atoms are in octahedral voids formed by the Cu atoms. Obviously the structure of phase III is denser than the cubic one of phase I. For comparison we have compiled in Table II our x-ray data and the data calculated assuming the $CdCl_2$-type structure for phase III of Cu_2O.

Now we turn our attention to phase II of Cu_2O. The phase transition we have observed at 10 GPa is identical with the phase transition Kalliomäki et al.[3] have found at 12 GPa. In agreement with their results we observe a sudden change of the red color of the Cu_2O crystals in phase I to black in phase II. As can be seen from Fig. 2 the large number of reflections in phase II are nearly the same ones published by Kalliomäki et al., indicated by an "×." As shown in Fig. 2 the (110) reflection of the hexagonal structure of phase III is still present in phase II and
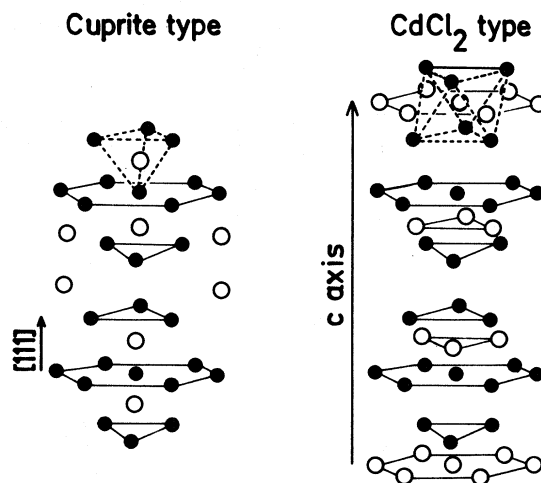

FIG. 4. Comparison of the cuprite structure and the $CdCl_2$-type high-pressure modification of Cu_2O. The closed circles are the Cu atoms. In the case of the cuprite structure only a few of the O atoms are drawn.

TABLE II. Compilation of d values and intensities of observed reflections in phase III of Cu_2O at 23.7 GPa ($\square$ in Fig. 2) and of calculated values, obtained by assuming a $CdCl_2$-type structure with $a = 2.818$ Å, $c = 12.67$ Å, $z = 0.25$. The observed intensities (I_{obs}) in the tables are corrected with respect to the absorption of the diamonds, the efficiency of the Ge detector, and the distribution of the x-ray intensity by taking a spectrum at an angle of zero degree. As the errors in the intensities may still be large we indicate the intensities by S = strong, M = medium, W = weak, and VW = very weak.

d (obs) Å	d (calc) Å	hkl	I (obs)	(I/I_0) (calc)
2.275	2.274	102	S	100
2.130	2.112	006	VW[a]	27
1.935	1.931	104	S	76
1.405	1.407	110	W	27
1.330	1.328	108	W	23
1.180	1.196	202	W	14
	1.171	116		28

[a] May be an effect of texture.

the (111) reflection of phase I is one of the reflections of phase II. An explanation for this observation may be the following: in phase II we have a hexagonal structure with the same value for the a axis as in the $CdCl_2$-type structure, but with a different c axis. Under the assumption that the (111) reflection of phase I changes into the (008) reflection of the hexagonal structure of phase II we can fit the observed reflections of that phase (see Table III). The large number of reflections which appear in phase II indicates that the stacking of the Cu layers is different from that in phase III. Instead of a cubic close packing found in phase III we have a mixing of a hexagonal and a cubic close packing of the Cu atoms in phase II. Such a stacking is well known for the I atoms in the polytypes of CdI_2.[1] Some information on the distribution of the O atoms in phase II

can be obtained from the small volume change of 4% by going from phase I to phase II (see Table I). This may indicate that nearly all O atoms are still in tetrahedral voids as in the case of the cuprite structure.

Figure 5 shows for all three phases of Cu_2O the volume change as a function of pressure. At 10 GPa the small decrease of volume by going from the cubic form of phase I to the hexagonal form of phase II is due to the above-mentioned fact that the O atoms are still surrounded by tetrahedra of Cu atoms. In phases II and III we have a hexagonal cell with the same a axis, but the distance between the Cu-Cu layers in phase III is shorter than in phase II. This is due to the fact that in the $CdCl_2$-type structure of phase III the O atoms are sitting in octahedral voids, causing the large decrease of volume of about 11% by

TABLE III. Compilation of d values and intensities of observed reflections in phase II of Cu_2O at 11.7 GPa (O in Fig. 2) and of calculated values obtained by assuming a hexagonal unit cell with $a = 2.897$ Å and $c = 19.228$ Å.

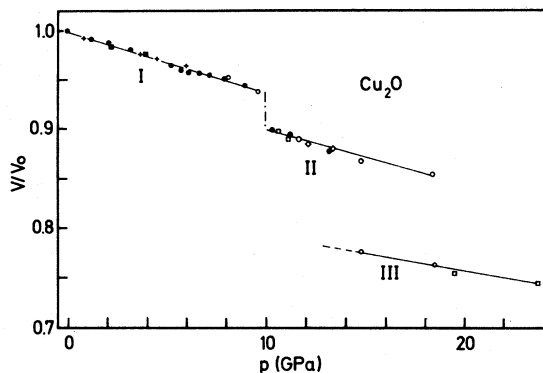| d (obs) Å	d (calc) Å	hkl	I (obs)
2.410	2.404	008	S
2.335	2.336	103	M
2.220	2.224	104	S
2.125	2.101	105	S
1.730	1.736	108	VW
(1.610)[a]	1.627	109	VW
1.520	1.526	1.0.10	W
1.445	1.449	110	W

[a] Estimated by interpolating the data in Fig. 2.

FIG. 5. Volume change of Cu$_2$O as a function of pressure.

going from phase II to phase III. The coexistence of phases II and III over a large pressure range (Fig. 2) can be understood keeping in mind that the change of the coordination number is rather drastic at the transition from phase II to phase III.

Figure 6 shows the p-T phase diagram of Cu$_2$O. To get information about the temperature dependence of the transition from phase I to phase II we have used the fact that the red color of Cu$_2$O in phase I changes suddenly to black in phase II. By transforming the crystal several times from phase I to phase II and vice versa and watching the color change we have determined a transition pressure of 106 ± 0.2 GPa at room temperature. Cooling down the diamond anvil to 100 K has resulted in an increase of the transition pressure of about 1.6 GPa. Thus we find only a small temperature dependence of the phase I–phase II transition pressure as indicated by the dashed line in Fig. 6. The solid lines represent the results of synthesis and decomposition measurements of a Russian group.[8] The dotted part of the
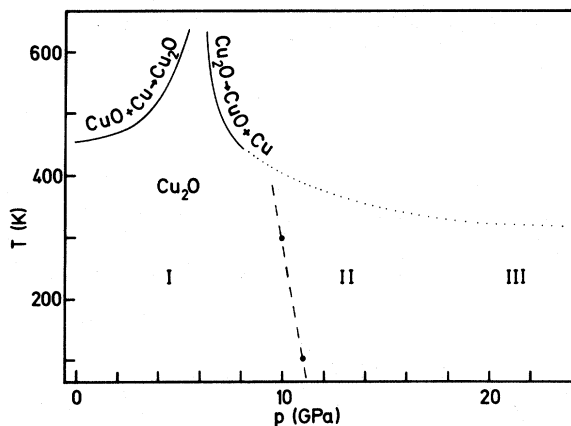
decomposition curve is based on the fact that at room temperature we have not observed a decomposition in the investigated pressure range up to 24 GPa.

At the end of this section we briefly discuss why the results of the earlier x-ray study[3] deviate from the one presented in this paper. As far as the authors know, Kalliomäki et al.[3] have used a diamond cell without gasket. It is well known that in such a squeezer large pressure gradients appear which can force a decomposition[9] of the sample in the cell. Beside that a pressure gradient will shift the transition pressures of phase transitions.

B. Ag$_2$O

In Fig. 7 we have plotted the d values of the observed reflections as a function of pressure. For $p > 0.4$ GPa new reflections appear, indicating a phase transition from the cuprite-type structure of Ag$_2$O in phase I to a new structure in phase II. The reflections of the new structure can also be described by a similar hexagonal cell as the one of phase II of Cu$_2$O, indicating a similarity between the two phase transitions. In Table IV the observed and the calculated d values for this hexagonal structure are compiled. The decrease of volume by going from phase I
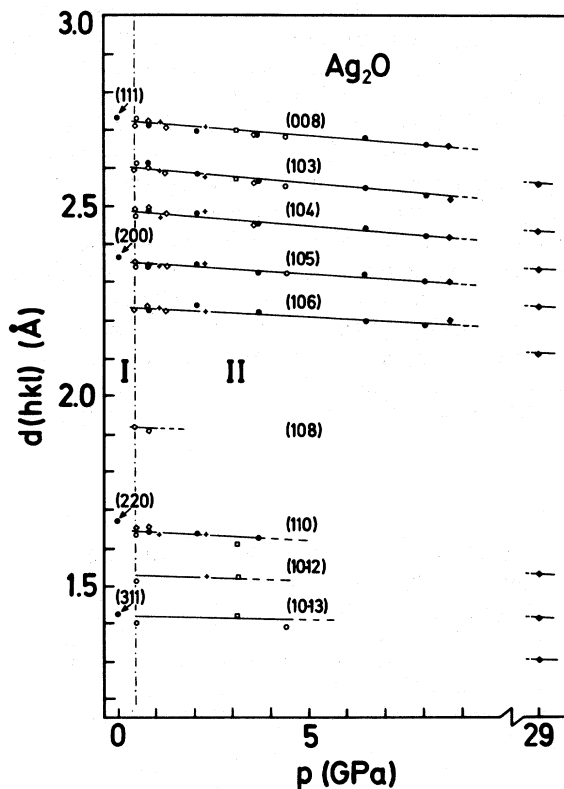

FIG. 6. p-T diagrams of Cu$_2$O. The solid curve represents the data of Ref. 7.

FIG. 7. Pressure dependence of the d(hkl) values of the observed reflections in Ag$_2$O.

TABLE IV. Compilation of d values and intensities of observed reflections in phase II of Ag_2O at 1.17 GPa (+ in Fig. 7) and of calculated values obtained by assuming a hexagonal unit cel with $a = 3.220$ Å and $c = 21.728$ Å.

d (obs) Å	d (calc) Å	hkl	I (obs)
2.712	2.716	008	S
2.592	2.602	103	M
2.477	2.481	104	S
2.345	2.347	105	S
2.225	2.209	106	W
(1.92)[a]	1.946	108	VW
1.63	1.610	110	W
1.54	1.519	1.0.12	VW
(1.42)[a]	1.434	1.0.13	VW

[a] Estimated by interpolation of the data in Fig. 7.

to phase II of 6% (see Table II) is larger than the value found for Cu_2O. But it is in good agreement with an early high-pressure study of Bridgman.[4] Bridgman has observed a volume change of 5.5–7% around 0.4 GPa by direct volumetric measurements. This fact supports our assumption about the structure of phase II in Ag_2O as well as in Cu_2O. In the case of Ag_2O this hexagonal structure is stable at least up to 29 GPa, the highest pressure we have generated.

Figure 8 shows the p-T diagram of Ag_2O. The solid line represents the results of differential thermal analysis measurements[10] of Ag_2O. These measurements give also a hint for a phase boundary as indicated by the dashed line, where the dot at 300 K indicates the phase transition mentioned by Bridgman and also found in our x-ray work. The dot-dashed line is a linear extrapolation of the black curve. Such an extrapolation will be in agreement with our measurements, which show the absence of further phase transitions in the range 0.4–29 GPa at room temperature. It would be of interest to do measurements
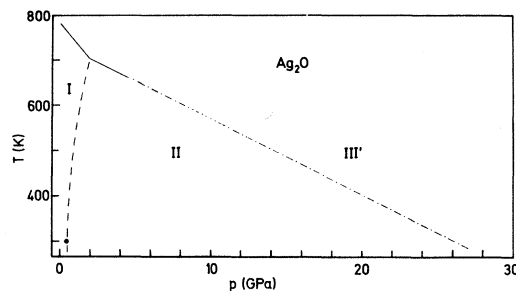

FIG. 8. p-T diagram of Ag_2O. The solid curve represents the data of Ref. 9.

at high temperatures to follow the phase boundaries. Unfortunately Ag_2O crystals are black and so optical investigations cannot easily be used to study phase transitions as a function of pressure and temperature.

IV. SUMMARY

Our room-temperature high-pressure x-ray study of Cu_2O has established the existence of two phase transitions in the pressure range 0–24 GPa. No decomposition occurred in this pressure range at temperatures ≤ 300 K. In the case of Ag_2O only one transition at 0.4 GPa was observed at room temperature in the pressure range 0–29 GPa. This transition leads to the same structure as the one found at 10 GPa in Cu_2O. Using additional results from other authors, extended p-T phase diagrams of Cu_2O and Ag_2O are presented.

ACKNOWLEDGMENTS

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