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The phase transitions of CoO under static pressure to 104 GPa

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Abstract

The phase transitions and equation of state of cobalt oxide (CoO) have been studied at ambient temperature under non-hydrostatic and hydrostatic high pressures, with the diamond-anvil cell technique. We discovered that under hydrostatic pressure conditions the CoO structure transformed from the low-density rhombohedral to a high-density rhombohedral phase at 90 ± 1 GPa with the molecular volume decreasing by about 2.7%. This phase transition with volume discontinuity may be related to magnetic collapse, which was predicted by theory. The pressure of the phase transition of CoO from face-centred cubic B1 to rhombohedral structure was 43 ± 2 GPa. The decompression spectrum data of CoO under non-hydrostatic pressure showed that these phase transitions are reversible.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

At room temperature, the crystal structure of CoO is of NaCl face-centred cubic (fcc) type (B1). At low temperature, a tetragonal distortion occurs with a smaller rhombohedral deformation in addition. Similar phenomena have been observed for other monoxides of transition metals such as MnO, FeO and NiO [1]. The behaviour of transition metal ions under high pressure plays an important role in explaining the deep interior of the Earth. The phase transition of magnetic collapse was predicted theoretically for transition metal oxides such as FeO, MnO, CoO and NiO [2]. Our non-hydrostatic pressure experiment results, partially published in the proceedings from *IUCr-HP98* and the *APS Meeting, 1999* [3, 4]. Some shock and static experiment data on CoO up to 131 GPa were published in 1999 [5, 6]. Our present study makes available further clear information on CoO rhombohedral structure phases under hydrostatic pressure, with helium as the pressure-transmitting medium, up to 104 GPa.

2. Experimental method

For the hydrostatic pressure experiment a pair of bevelled diamonds, with culet 190 μm, was used. The gasket was a steel disc with a 250 μm diameter piece of rhenium inserted in it and preindented to 40 GPa. The sample hole was about 70 μm in diameter. A polycrystalline CoO sample of size about 20 μm $\times$ 20 μm and 3–5 μm thick was put into the hole with a grain of gold and two chips of ruby around it for internal pressure standards. The helium gas was loaded as the high-pressure-transmitting medium; subsequently the sample was sealed at about 5 GPa pressure.

Stainless steel gaskets were used and polycrystalline CoO powders were compressed in Mao–Bell-type diamond-anvil cells (DACs) for the non-hydrostatic pressure experiments. Two samples were prepared. One of them was 25 μm in size and with a ruby chip in it while the other was 120 μm in size with two ruby chips and a 10 μm piece of gold foil added on top of sample as the internal pressure reference standards. No pressure media were used with these two samples.

All of the experiments were performed at the beamline of X17C, the National Synchrotron Light Source (NSLS) of Brookhaven National Laboratory, with energy-dispersive x-ray diffraction (EDXD) measurements [7]. The size of the white x-ray beam was 9 μm $\times$ 11 μm for the 25 μm sample, and 15 μm $\times$ 20 μm for the 120 μm sample. The decompression experiment was carried through to ambient pressure only for the 25 μm sample. For the hydrostatic pressure experiment, the x-ray beam size was chosen as 20 μm $\times$ 20 μm; with this the CoO sample can be covered while the signal of gold can be made not so strong as to interrupt the diffraction signal of the CoO sample.

The resolution of the energy dispersion was a serious concern in the hydrostatic pressure experiment. The resolution of the energy dispersion was checked with the cubic (200) spectrum line at ambient pressure. The ratio of the (200) linewidth to its energy was about 1% at ambient pressure when the 2θ angle was equal to 11° with a 300 μm slit in front of the detector and another 100 μm slit close to the sample. When the CoO sample was loaded in the DAC with hydrostatic pressure, the ratio of the width and energy of line 200 was about 1.5%. So if the 200 line split into two lines, this would be observed with the 1.5% spectrum resolution of our hydrostatic pressure experiment arrangement.

3. Results and discussion

We discovered that for CoO under hydrostatic pressures between 40 and 100 GPa, there are two phase transitions: one is at 43 GPa and the other is at 90 GPa. Figure 1 shows the relationships of pressure and d-spacing which were calculated from the EDXD spectrum of CoO powder under hydrostatic pressure conditions. When the pressure is less than 50 GPa the cubic symmetry structure can be fitted very well with the misfit of all indices for 111, 200 and 220 smaller than 0.1%. If the pressure is higher than 60 GPa the cubic index misfit for 200 becomes large and increases quickly with pressure increase. For pressure under 80 GPa the misfit of the 200 d-spacing is about 0.3%. For pressures between 50 and 80 GPa the structure of CoO can be described as of rhombohedral symmetry with misfits of all indices for 003, 101, 102, 104 and 110 d-spacings smaller than 0.2%. We refer to this phase as having low-density rhombohedral (LDR) symmetry. A more accurate pressure value for this phase transition from the cubic B1 phase to the LDR phase is 43 ± 2 GPa; this was extracted from the distortion of cubic unit cell (from the axis ratio c/a), from the hydrostatic pressure experiments. There is no steep volume change observed with this phase transition. The CoO decompression experiment with non-hydrostatic pressure conditions showed that, as in figure 2, this phase

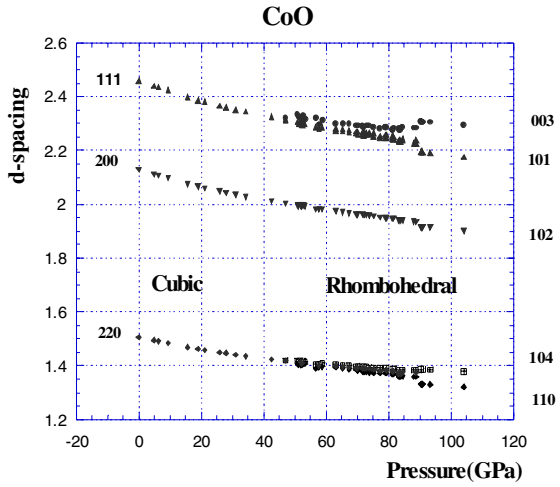

Figure 1. The d-spacing, calculated from EDXD spectra for CoO powder, versus pressure.

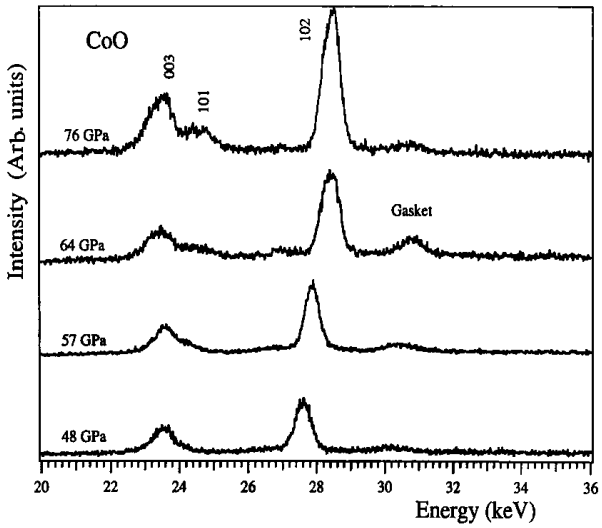

Figure 2. The EDXD spectrum of CoO at room temperature under non-hydrostatic pressure with decompression from 76 to 48 GPa.

transition is reversible, since the split 111 diffraction spectra line became a singlet again at low pressure.

The misfits of the observed d-spacing of CoO to the rhombohedral unit cell for several high pressures are listed in table 1. As is known, the effect of the non-hydrostatic pressure in the case of uniaxial stress will distort the symmetry of the unit cell due to the elastic anisotropy of the specimens [8]. The misfits in table 1 show that the helium, loaded as the high-pressure-transmitting medium, will show strong non-hydrostatic character with pressure over 80 GPa.

The uncertainties of the d-spacing calculation and pressure measurements in the hydrostatic pressure experiments are similar to the sizes of the symbols in the figure 1. CoO EDXD spectra at pressures of 69.7, 88.7, 90.7 and 102 GPa are displayed in figure 3. From

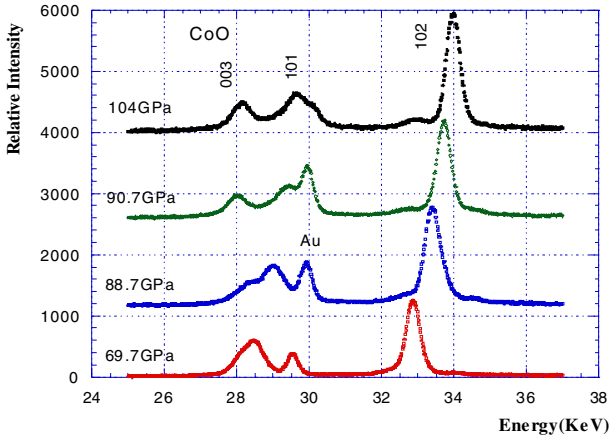

Figure 3. The EDXD spectra of CoO obtained at hydrostatic pressures of 69.7, 88.7, 90.7 and 104 GPa.

Table 1. The CoO refined d-spacing misfits to the rhombohedral symmetry with and without helium loaded as the high-pressure-transmitting medium. d(obs) and d(cal) are the observed and calculated d-spacings with rhombohedral symmetry respectively. The misfit (%) $= [d(\text{obs}) - d(\text{cal})]/d(\text{cal}) \times 100$.

With helium as pressure-transmitting medium (GPa)	*hkl*	d(obs) (Å)	d(cal) (Å)	Misfit (%)
104	003	2.2962	2.2939	+0.10
	101	2.1774	2.1714	+0.28
	102	1.9014	1.9054	−0.21
84.5	003	2.2883	2.2866	+0.07
	101	2.2367	2.2321	+0.21
	102	1.9415	1.9445	−0.15
77.3	003	2.2829	2.2825	+0.02
	101	2.2466	2.2456	+0.04
	102	1.9519	1.9526	−0.04
65.3	003	2.2999	2.2995	+0.02
	101	2.2715	2.2702	+0.06
	102	1.9715	1.9723	−0.04
Without any pressure-transmitting medium (GPa)				
76	003	2.3231	2.3217	+0.06
	101	2.2692	2.2652	+0.18
	102	1.9710	1.9736	−0.13

figures 1 and 3, it is obvious that there was a high-density rhombohedral (HDR) phase transition at a pressure of about 90 GPa because all of the d-spacings for 003, 101, 102 and 110 show a sudden change at this pressure.

The symmetry of the HDR phase, we believe, is a rhombohedral structure with some distortions, caused by the non-hydrostatic pressure effect at ultrahigh pressure even with helium as the high-pressure-transmitting medium, as mentioned above.

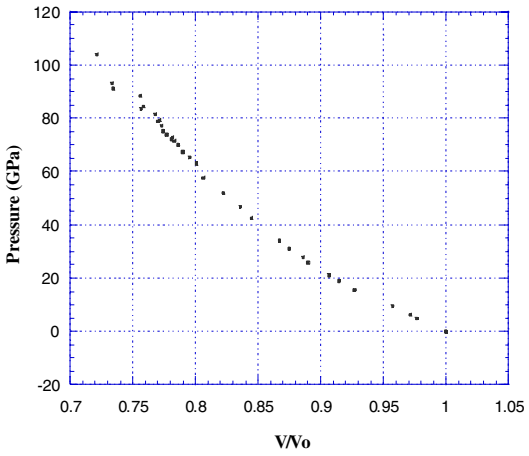

Figure 4. The relative volume–compression curve of CoO was calculated from the d-spacing with helium as the pressure-transmitting medium. The uncertainties in the volume and pressure are smaller than the symbols: for volume it is $\leqslant 0.2\%$ and for pressure about 0.5 GPa.

Table 2. A list of the values of the bulk modulus K_0 with its pressure derivative K' and the ambient pressure volume V_0 of CoO calculated using the Birch–Murnaghan equation of state and the Vinet equation of state ('BM' indicates the results calculated from the Birch–Murnaghan equation of state while 'Vinet' indicates the results calculated from the Vinet equation of state).

CoO	K_0 (GPa)	K'	V_0 (Å^3/atom)
Cubic B1			
BM	180	3.82	19.35
Vinet	178	3.99	19.35
Rhombohedral-LDR			
BM	171	4.58	19.29
Vinet	182	4.56	19.26

Figure 4 shows the volume–compression curve of CoO with helium used as the pressure-transmitting medium around it. The calculated uncertainties in the volume and pressure are smaller than the symbols in this figure. The estimated percentage volume decrease for the HDR phase at 90 GPa is about 2.7% with a calculated volume error of 0.2%. It should be emphasized that the behaviour of the rhombohedral structure of CoO under high pressure is more complex than that of FeO, since no data have shown there to be two rhombohedral phases at high pressure for FeO. We should also emphasize that splitting of the cubic 200 line was not observed in our hydrostatic or non-hydrostatic pressure experiments on CoO using the EDXD technique, although this has appeared in the published data (e.g. in [5, 6]).

At ambient temperature and pressure the crystal structure symmetry of CoO is cubic B1. The results for the calculated bulk modulus K_0 with its pressure derivative K' and the ambient pressure volume V_0, from our present hydrostatic pressure experiment, are listed in table 2. Table 2 just shows the cases of cubic B1 and the rhombohedral LDR phase, since compression data are lacking for the HDR phase. The calculated bulk modulus of CoO in a hydrostatic environment is consistent with the sock wave results [5].

Acknowledgments

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References

[1] Adler D 1968 *Solid State Physics, Transition Metal Oxides* vol 21, ed H Ehrenreich, F Seitz and D Turnbull (New York: Academic) p 75
[2] Cohen R E, Mazin I I and Isaak D G 1997 *Science* **275** 654
[3] Guo Q, Mao H K, Hu J, Shu J and Hemley R J 1998 *Report Present International Union of Crystallography at High Pressure (Argonne, IL, Nov. 1998)*
[4] Guo Q, Mao H K, Hu J, Shu J and Hemley R J 1999 *Centennial Mtg (Atlanta, GA, March 1999); Bull. Am. Phys. Soc.* 159
[5] Noguchi Y, Atou T, Kondo T, Tyagi T and Syono Y 1999 *Japan. J. Appl. Phys.* **38** L7
[6] Atou T, Noguchi Y, Kondo T, Tyagi T and Syono Y 2000 *Proc. AIRAPT-17* p 491
[7] Hu J, Mao H K and Hemley R J 1993 *Proc. High-Pressure Science and Technology—1993 (Colorado Springs, CO, 1993)* p 441
[8] Mao H K, Shu J, Fei Y, Hu J and Hemley R J 1996 *Phys. Earth Planet. Inter.* **96** 135–45