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Abstract
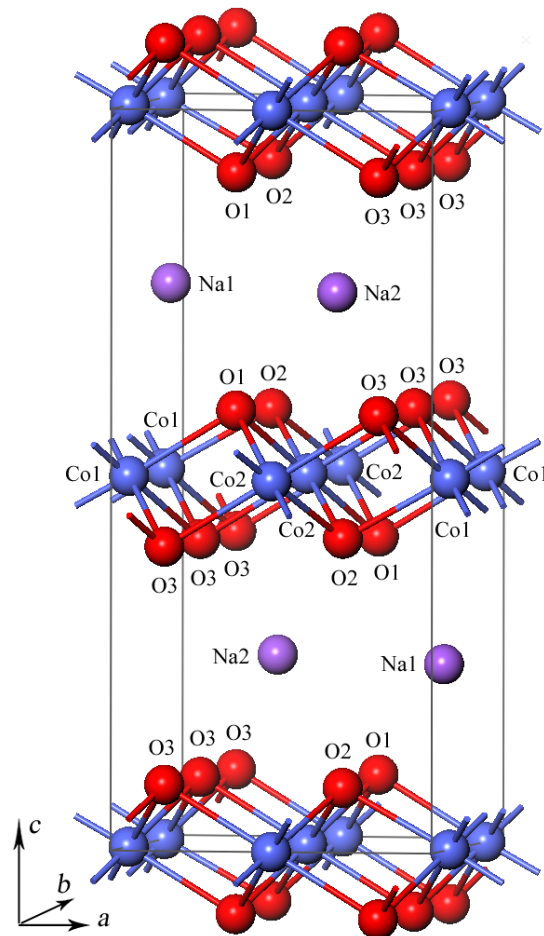
The crystal structure of layered polycrystalline $Na_{0.5}CoO_2$ has been studied
under high pressure to 47 GPa by *in situ* x-ray diffraction (XRD) measurements
with a synchrotron radiation source in a diamond anvil cell at room temperature.
The ambient pressure phase of $Na_{0.5}CoO_2$ was found to be stable at pressures
up to 47 GPa. The experimental data were well represented by the second-
order Birch equation of state, which gives values of $B_0 = 112 \pm 2.3$ GPa and
$B_0' = 2.3 \pm 0.1$. Simultaneously, the relative Co–O bond length and the Co–
O–Co bond angle versus pressure were derived from present experimental XRD
data and the data of Hung *et al* (2004 *J. Phys.: Condens. Matter.* **16** 5803). The
results revealed that the configuration of the CoO_2 plane distorted significantly
at high pressure, which may lead to different magnetic behavior in $Na_{0.5}CoO_2$.

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

1. Introduction

Na_xCoO_2 compounds continue to attract much experimental and theoretical attention, since
this layered cobaltate shows distinct magnetic properties with x varying from 0.3 to 0.75 [1–3].
Among the compounds with different Na concentrations, $Na_{0.5}CoO_2$ is of great interest,
because its insulating state at 53 K separates two distinct metallic domains with higher and
lower Na content. Structural studies revealed that the ground state of $Na_{0.5}CoO_2$ has an
orthorhombic symmetry, in which the Na layers are above and below the CoO_2 plane. The space

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Figure 1. The crystal structure of $Na_{0.5}CoO_2$ at ambient condition (space group *Pnmm*), displaying the layers of CoO_2 planes and Na ions within the intermediary layers.

group of its supercell is *Pnmm*, and its lattice parameters are $a = 4.8761$ (Å), $b = 5.63053$ (Å) and $c = 11.1298$ (Å) at ambient pressure [1, 4, 5]. Figure 1 shows the crystal structure of $Na_{0.5}CoO_2$, from which it is seen that two types of Na sites, Na1 and Na2, are trigonal prisms, one of which shares edges with adjacent CoO_6 octahedra (Na1), whereas the other prism shares faces with adjacent CoO_6 octahedra (Na2). Within the CoO_2 plane, there exist two distinct Co atoms (Co1 and Co2) and three types of O atom (O1, O2 and O3) which form a frustrated triangular lattice.

Pressure is an important thermodynamic variable in addition to temperature and composition. It alters the physical and chemical properties of materials via large changes of atom spacing, electronic structure and chemical bonding etc [6–9]. Pressure-induced phase transition can convert an insulator to a metal [10] or superconductor [11, 12]. How does $Na_{0.5}CoO_2$ behave under high pressure? Is there a phase transition at high pressure? What does the CoO_2 plane look like under compression? No experimental reports or theoretical predictions have been made to explain these questions to date. In this paper, we address the pressure effect on the structural properties of $Na_{0.5}CoO_2$ compounds.
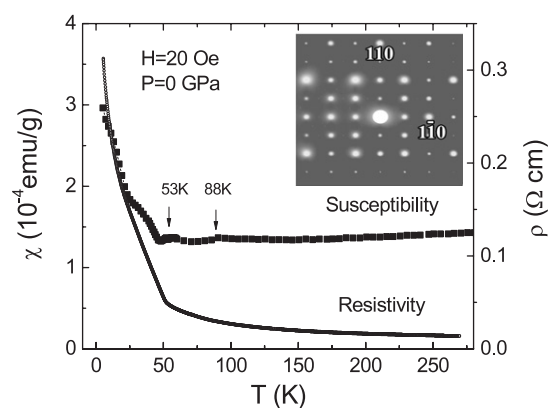
Figure 2. Magnetic and resistivity measurements in $Na_{0.5}CoO_2$, showing the characterization of the typical phase transitions at 53 and 88 K, respectively. The inset of the main figure is the electron diffraction pattern of $Na_{0.5}CoO_2$ at ambient pressure and room temperature.

2. Experimental details

$Na_{0.5}CoO_2$ compound was prepared through Na deintercalation from $Na_{0.75}CoO_2$. Polycrystalline parent samples of $Na_{0.75}CoO_2$ were synthesized by solid-state reactions, as reported in [13]. Stoichiometric amounts of Na_2CO_3 and Co_3O_4 were mixed homogeneously and sintered for 8–12 h in air in the temperature range 800–850 °C, then the products were pressed into pellets and sintered for another 8 h in the same temperature range. Chemical deintercalation of Na in solutions of I_2 dissolved in acetonitrile for about five days. To characterize our starting material, we carried out magnetic, resistivity and x-ray diffraction measurements and transmission electron microscope (TEM) observation. Figure 2 shows the magnetic and resistivity results, from which the typical phase transitions at 53 and 88 K in $Na_{0.5}CoO_2$ are seen. The inset of the main figure is an electron diffraction pattern taken from the starting sample. The superstructure reflections are very strong, which clearly indicates Na ordering in the $Na_{0.5}CoO_2$ sample [4].

High pressure was created using a diamond anvil cell (DAC). The tips of the diamond anvils used for this study were 400 μm in diameter. The polycrystalline sample was loaded in a hole of the metal gasket, which was put on the tip of the first diamond, and then the second diamond, whose face was parallel to the first one, clamped the sample. The initial size of the sample was 150 μm in diameter and 50 μm in thickness. The sample pressure was determined by the ruby technique [14]. To avoid the ruby chips being in contact with the diamonds, we chose the size of the ruby ($\sim$5 μm) to be much smaller than the sample thickness. A mixture of ethyl alcohol and water was used as a liquid pressure-transmitting medium. The energy-dispersive x-ray diffraction (XRD) experiments were performed at Beijing Synchrotron Radiation Facilities (BSRF). The incident x-ray beam from the synchrotron was collimated to 30×20 μm and focused on the center of the sample. The scattering angle was $2\theta = 18.0°$, which was calibrated with Au at ambient pressure.

The Co–O bond length and the Co–O–Co bond angle of the sample were computed using the software *Material Studio*. Inasmuch as the atom positions of Co(1), Co(2), Na(1), Na(2), O(1), O(2) and O(3) in $Na_{0.5}CoO_2$ have been determined by Huang *et al* [4] at ambient pressure, and the space group of $Na_{0.5}CoO_2$ is also known, we are able to perform calculations on the relative Co–O bond length and the Co–O–Co bond angle for the sample under high pressure on the basis of lattice parameter changes with pressure.
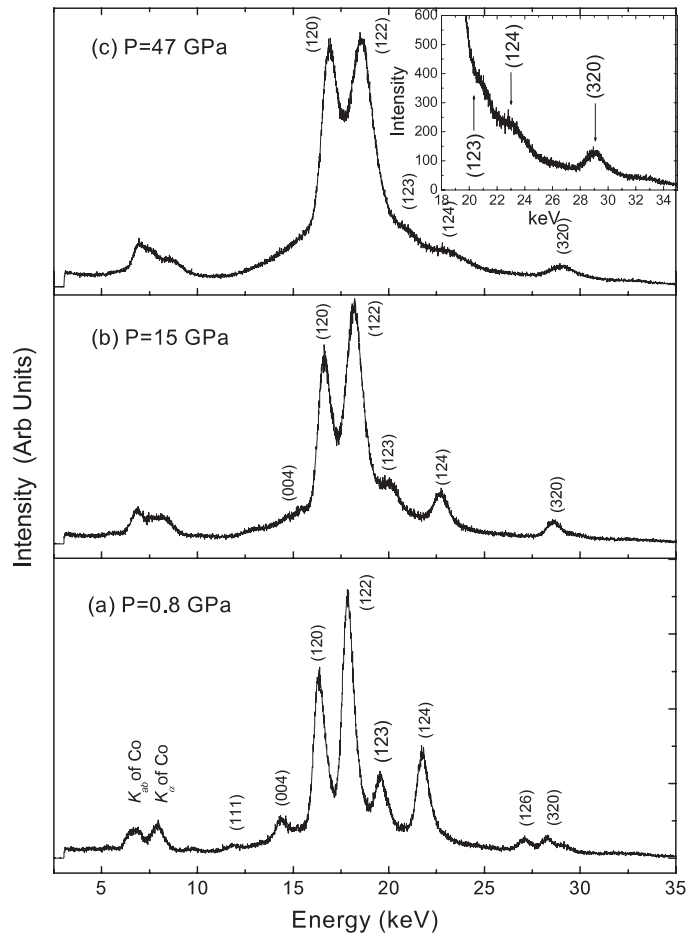
Figure 3. Energy-dispersive x-ray diffraction patterns of $Na_{0.5}CoO_2$ at three pressures taken with a synchrotron x-ray beam. The diffraction angle 2θ is $18.0°$ ($Ed = 39.854_9$ keV Å). The pressures were determined using the ruby fluorescence technique. The inset of the main figure (c) is a large view of the XRD pattern of the sample at 47 GPa.

3. Results and discussion

From the basic law of energy-dispersive XRD technique, the d-spacing (d) is determined by

$$d = hc/2E \sin\theta$$

where h is Planck's constant, c is the speed of light in vacuum, θ is the incidence angle of x-rays, and E is the photon energy. In this study, we adopted $2\theta = 18.0°$ for all high-pressure experiments, hence we have

$$Ed = 6.1933/\sin\theta = 39.854_9 \text{ (keV Å)}.$$

Based on the above equations, d can easily be determined given 2θ. Figure 3 shows representative XRD patterns for the $Na_{0.5}CoO_2$ sample at three pressures. At 0.8 GPa, all XRD peaks were well indexed as an orthorhombic structure, as is its ground state, except for two fluorescence peaks resulting from Co. With an increase in pressure, the peaks shifted to the high-energy side, indicating a decrease in the d-spacing. No new peaks were observed in

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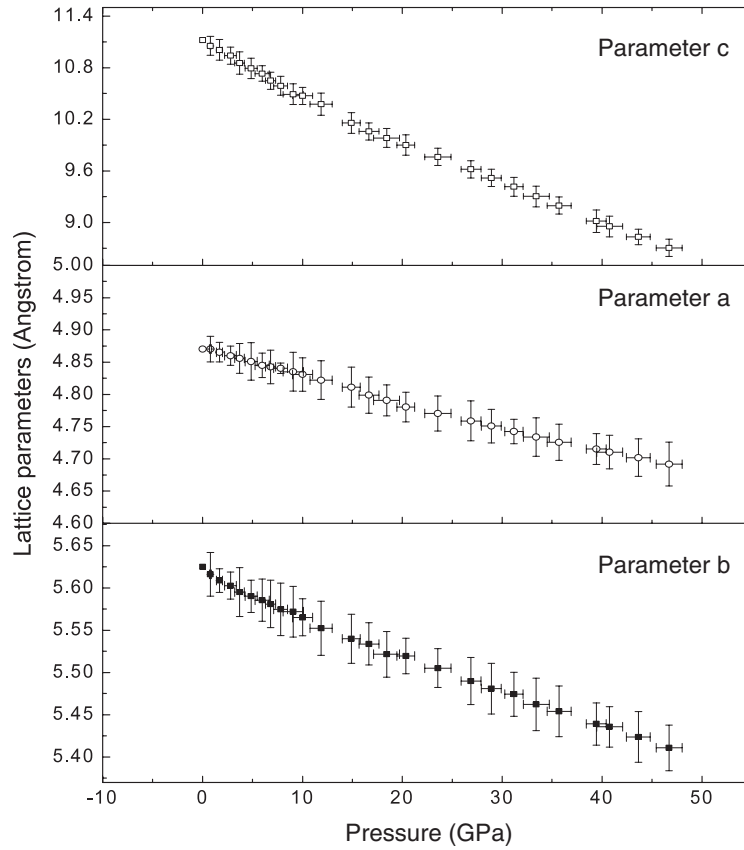
Figure 4. Pressure dependence of the lattice parameter *a*, *b* and *c* derived from synchrotron x-ray diffraction measurements. The error bars represent $\pm 2\sigma$.

the compressed sample at pressures of 0.8–47 GPa. It is found that the intensities of the 123 and 124 lines in the XRD pattern exhibit drastic dumping at 47 GPa compared to the intensity of the same line at 0.8 GPa, The decrease in the relative intensity may be attributed to sample deformation under high pressure in the DAC.

The lattice parameters determined from *d* values at each loading point are illustrated in figure 4. The compression under high pressure is rather anisotropic. The linear compressibility of the *c* axis is much larger than the *a* axis and the *b* axis. At 47 GPa, the supercell in the *c* direction was squeezed by ∼22% compared to the *c* value at zero pressure. The considerably strong anisotropy of the lattice compression is associated with the layered crystal structure of the $Na_{0.5}CoO_2$ sample.

From the lattice parameters, we calculated the unit cell volume (V) as a function of pressure, as shown in figure 5. No discontinuous change in volume was observed to 47 GPa. The data points were fitted to the second-order Birch equation of state [15],

$$P = \tfrac{3}{2}B_0\big[(V/V_0)^{-7/3} - (V/V_0)^{-5/3}\big]\big[1 + \tfrac{3}{4}(B_0' - 4)((V/V_0)^{-2/3} - 1)\big]$$

where P is the pressure, B_0 and B_0' are the bulk modulus at zero pressure and the derivative of the bulk modulus respectively, and V/V_0 is the ratio of high-pressure volume to zero-pressure volume. The resulting values of the parameters give $B_0 = 112 \pm 2.3$ GPa and
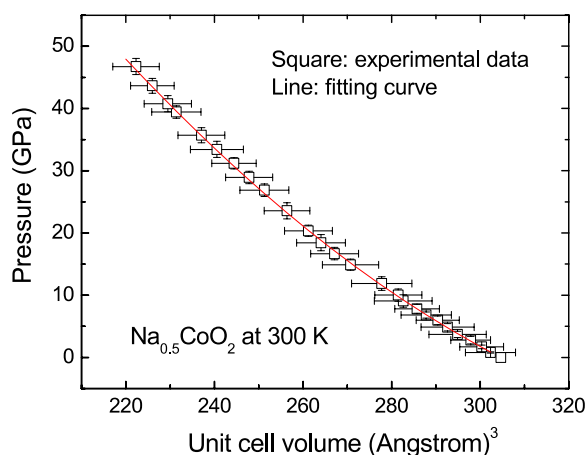
Figure 5. Pressure–volume equation of state for $Na_{0.5}CoO_2$. The curve is the fit of the Birch equation of state and the squares are the experimental data, which gives $B_0 = 112 \pm 2$ GPa and $B_0' = 2.3 \pm 0.1$.
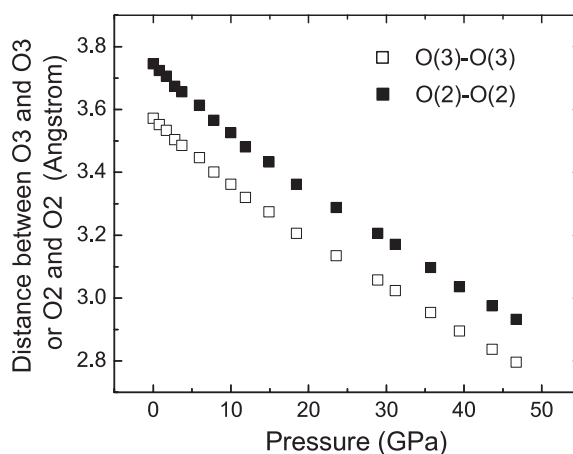
Figure 6. The changes in relative distance between O3 (or O2) and O3 (or O2) as a function of pressure, in which the two O3 and the two O2 are on different neighboring CoO_2 planes.

$B_0' = 2.3 \pm 0.1$. Here the ambient-pressure unit cell volume was fixed at the experimental value of $V_0 = 305.6$ (Å)^3.

Thompson and Downs [16] suggested that many structures become closest packed with pressure, and that this tendency drives the observed bond angle and bond length changes. In order to quantify the distortion within the CoO_2 plane and between the CoO_2 planes, we computed the changes in relative distance between neighboring CoO_2 planes, and the relative Co–O bond length as well as the Co–O–Co bond angle within the CoO_2 plane at pressures from 0.8 to 47 GPa (the atom positions of Co(1), Co(2), Na(1), Na(2), O(1), O(2) and O(3) for the $Na_{0.5}CoO_2$ sample at zero pressure are known from [4], and the lattice parameter a, b and c can be obtained from *in situ* XRD measurements, hence the changes in the relative bond length of the Co–O and in the relative bond angle of the Co–O–Co can be solved using *Material Studio*). Figure 6 shows the pressure dependence of the relative distance between O3
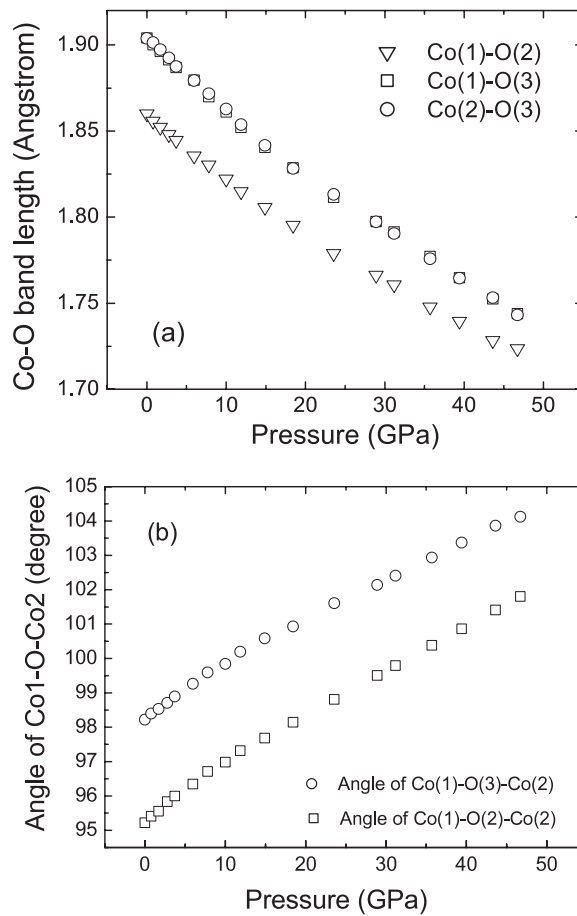
Figure 7. Pressure dependence of the relative Co–O bond length (figure (a)) and the relative Co–O–Co bond angle (figure (b)), revealing significant pressure-induced distortion in the CoO_2 plane.

(or O2) and O3 (or O2), in which the two O3 and the two O2 are on different neighboring CoO_2 planes. It is seen that the distances decreased as the pressure increased. At 47 GPa, the distance between O3–O3 was shortened by $\sim$21%. The pressure effect on the neighboring CoO_2 planes certainly enhanced the coupling between the planes. We also computed the variation in the relative bond length of the Co–O and the bond angle of the Co–O–Co as a function of pressure, as shown in figures 7(a) and (b). It is found that pressure decreased the Co–O bond length, whereas it increased the Co1–O–Co2 angle. The effects of pressure can be interpreted in terms of the closing up of voids in the structure, and this leads to a shortening of the Co–O bond length and of the distance between neighboring CoO_2 planes. Simultaneously, the significant compressibility in the *c* axis distorts the Co1–O–Co2 angle.

Recent theoretical calculations [17–19] revealed that the Co–O bond length within the plane coupled with the local spin moment on Co ions. The Co magnetic moment is increased with decreasing Co–O bond length. If that were the case, then our results suggest that pressure might induce an increase in the Co magnetic moment. As a result, we expect that there may exist different magnetic behaviors in $Na_{0.5}CoO_2$ material at high pressure. Further studies are underway.

4. Conclusion

The high-pressure behavior of polycrystalline $Na_{0.5}CoO_2$ has been studied by synchrotron x-ray diffraction in a diamond anvil cell at 300 K up to 47 GPa. The ambient pressure phase structure retains its form to 47 GPa. Pronounced anisotropy of the axis compressibility has been observed. The anisotropy can be associated with the rather compressible CoO_2 layer. The $P-V$ equation of state for the $Na_{0.5}CoO_2$ compound, fitted using the second-order Birch equation, gives $B_0 = 112 \pm 2$ GPa and $B_0' = 2.3 \pm 0.1$. Significant distortions are found, both in the CoO_2 plane and between the neighboring CoO_2 planes, which will motivate further study of the magnetic properties of $Na_{0.5}CoO_2$ in detail.

Acknowledgments

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