

Structural and electrical properties of infinite-layer CaCuO_2 under high pressure

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Abstract

The structural and electrical properties of infinite-layer CaCuO_2 (IL CaCuO_2) under high pressure at room temperature were studied using a diamond anvil cell by in situ high pressure energy-dispersive X-ray diffraction with synchrotron radiation and by simultaneous resistance and electrical capacitance measurements. The results indicate that the primary crystal structure of IL CaCuO_2 is stable under pressure up to 30 GPa with an anisotropic compressibility. The equation of state of IL CaCuO_2 was obtained from the $V/V_0 - P$ relationship based on the Birch–Murnaghan equation, which gives rise to a bulk modulus $B_0 = 96$ GPa in the low pressure range below 6 GPa, and $B_0 = 186$ GPa at pressures from 6 to 30 GPa for IL CaCuO_2 . The resistance and capacitance measurements of IL CaCuO_2 up to 20 GPa revealed several unusual changes. There is an abrupt resistance drop in the pressure range of 3–6 GPa followed by an abnormal hump occurring around 12 GPa with increasing pressure. Corresponding changes were also observed in the dependence of capacitance on pressure. The former drop is attributed to an isostructural phase transition as observed in the synchrotron radiation experiments. The latter is considered to be related to an electronic structure transition resulting from the anisotropic compression of the IL CaCuO_2 unit cell under high pressure.

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1. Introduction

High pressure synthesis is recognized to be quite effective to stabilize the high T_c superconductors with perovskite structures. Some novel superconductors that could not be synthesized at ambient pressure can be obtained under high pressure [1–9]. High pressure has an overall effect on the structure and physical properties of high- T_c superconductor (HTS) [10–15]. For example, the T_c of $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$ is 133 K at ambient pressure, yet it can be raised to 164 K under 30 GPa [15], which is the record T_c obtained so far. The infinite-layer structure is constituted by $[\text{CuO}_2]$ planes alternately stacked with alkaline earth cations [16] (Fig. 1). This is the simplest structure containing the conducting $[\text{CuO}_2]$ planes which are essential for HTS. Therefore, the infinite-layer structures

are the best candidate for the study of new physical mechanisms of high temperature superconductivity. Furthermore novel copper oxide superconductors can be obtained by electron and hole-doping in the infinite-layer structure [1]. So infinite-layer (Ca, Sr) CuO_2 has been drawing considerable attention since it was discovered in 1988 [16]. It must be noted that the IL CaCuO_2 compound, whose stoichiometric chemical composition completely matches those of the core structure of HTS, has not been synthesized at ambient pressure as yet. It has to be synthesized under high pressure as first reported by Kobayashi et al. [17]. The dependence of electrical properties on pressure could reveal either the crystallographical or the electronic phase transition. At the same time, the evolution of a structure under pressure may also affect its electronic configuration and consequently its transport properties. In situ high pressure X-ray diffraction is an effective means of investigating the structural properties of matter under high pressure. So the electrical measurement, if combined with the in situ high pressure energy dispersive XRD experiments, would provide more useful information for the physical property changes of

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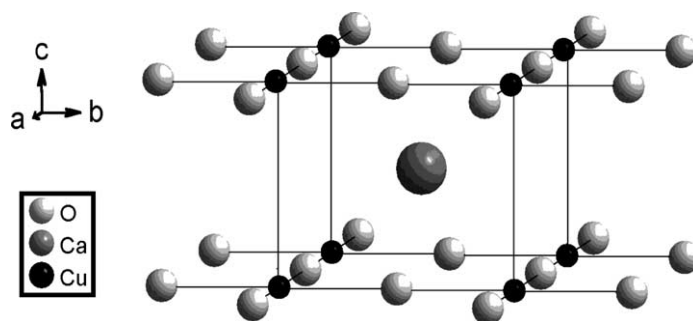


Fig. 1. A schematic representation of the crystal structure of infinite-layer CaCuO_2 .

materials under pressure, such as the positive effect of pressure on T_c in cuprate superconductors.

In present work, we report the studies of structural stability and electrical properties for IL CaCuO_2 under high pressures up to 30 GPa.

2. Experiment

The sample of ILCaCuO_2 was synthesized under high pressure conditions using a cubic anvil apparatus. Stoichiometric mixtures of CuO and CaO were completely ground and reacted under a pressure of 3 GPa, at a temperature of $\sim 1000^\circ\text{C}$ for 30 min. The sample was examined by X-ray powder diffraction (XRD) using $\text{Cu K}\alpha$ radiation at ambient pressure. The in situ high pressure energy-dispersive X-ray diffraction experiment on IL CaCuO_2 was carried out using a diamond anvil cell (DAC) with the synchrotron white-radiation source at the Beijing Synchrotron Radiation Facility (BSRF). The powder sample was loaded, together with a suitable amount of Pt powder for the inner pressure calibration, into a 300 μm diameter hole in a T301 stainless steel gasket, which was pre-indented before boring the hole. The internal pressure of the DAC was calculated according to the equation of state of Pt [18]. In our experiment, the relation between energy and channel was $E = 0.72453 + 0.00986 \times \text{chn}$, and θ was selected as 8.7° .

The relationships of resistance versus pressure (R–P) and capacitance versus pressure (C–P) for IL CaCuO_2 were

obtained on a DAC using resistance and capacitance measurements; in which two parallel molybdenum sheets were used as electrodes, as shown in Fig. 2(a). There was a 1 mm diameter hole at the center of the base, in which the powder sample was placed. The electrodes and lead-in wires were fixed on a Plexiglas insulating mount and connected by conductive glues, as shown in Fig. 2(b). The resistance and capacitance measurements were conducted using an Intelligent Model ZL5 LCR system, operated at 1 kHz. The sample studied was pre-compressed under a definite pressure to make a compact sample before the measurement. Then they were compressed to nearly 20 GPa. The pressure was calibrated using the ruby fluorescent line.

3. Results and discussion

The XRD measurement at ambient pressure shows that the sample is nearly single-phase and has a tetragonal structure with space group $P4/mmm$, the lattice parameters being $a = 3.855(8) \text{ \AA}$, $c = 3.180(7) \text{ \AA}$. The patterns of energy-dispersive X-ray diffraction of IL CaCuO_2 under different pressures at room temperature are shown in Fig. 3. The applied pressure was up to 30 GPa in our experiment. Four diffraction peaks of Pt and a few stronger diffraction peaks of the sample are shown in the ambient pressure spectra, respectively. All diffraction peaks except fluorescence ones shift to higher-energy with increasing pressure, as shown in Fig. 3. When pressure returns to

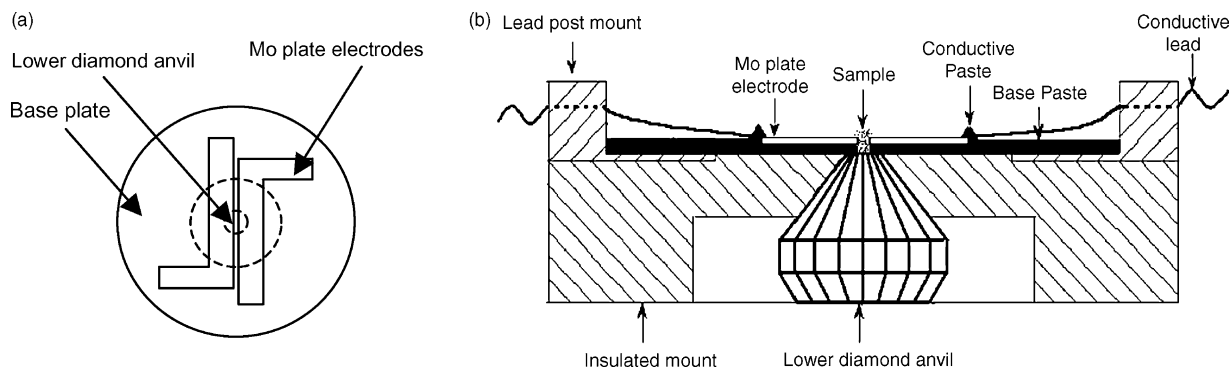


Fig. 2. A sketch map of the DAC assembly for the electrical measurements. (a) Top view of Mo electrodes placed on the lower diamond anvil. (b) Cross-section view of the Mo electrodes, electrode holder, and leads in place on the lower diamond anvil.

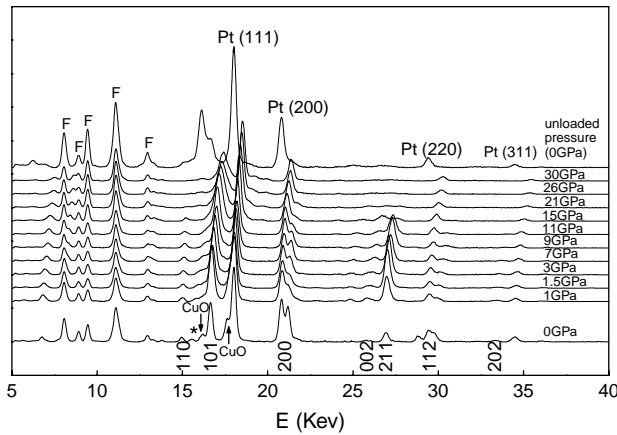


Fig. 3. The spectra of energy-dispersive X-ray diffraction of infinite-layer CaCuO_2 under various pressures (* is for Ca(OH)_2).

ambient, the peaks almost recover their original sites. In addition, there are more diffraction peaks and the intensity is stronger under lower pressure, while some weak peaks vanish under higher pressure. This is likely caused by reduction of sample amount due to the fact that part of the sample flows out of the chamber with increasing pressure. But no new diffraction peaks are found in the whole energy spectrum. So we infer that the primary crystal structure of IL CaCuO_2 keeps stable under pressure at least up to 30 GPa, which corresponds to the record pressure applied in any in situ high pressure experiment for HTS so far. The lattice parameters and the volumes of the IL CaCuO_2 unit cell under different pressures were calculated. The relationships of the change rate of lattice parameters and volume compressibility versus pressure for IL CaCuO_2 are shown in Fig. 4(a) and (b), respectively. It can be clearly seen in Fig. 4(a) that the crystal lattice is anisotropically compressed, especially above 10 GPa. The sudden disappearance of some diffraction peaks such as (211) above 11 GPa might originate from the lattice distortion caused by the anisotropic compression of the unit cell, and it is also caused from the possible structural transition in IL CaCuO_2 . The real reason need to be confirmed by further experiments

such as high pressure angular-dispersive XRD or neutron scattering experiments, by which we can make some refinement of crystal structure for IL CaCuO_2 . From Fig. 4(b), we can also see that the change of volume compressibility is different between below 6 GPa and above 6 GPa, which is possibly due to the isostructural phase transition in IL CaCuO_2 . Fitting the data to the Birch–Murnaghan equation,

$$P(\text{GPa}) = \frac{3}{2} B_0 \left[\left(\frac{V_0}{V} \right)^{7/3} - \left(\frac{V_0}{V} \right)^{5/3} \right] \times \left\{ 1 - \left(3 - \frac{3}{4} B'_0 \right) \left[\left(\frac{V_0}{V} \right)^{2/3} - 1 \right] \right\}$$

While the pressure derivative $B'_0 = 4$, the bulk modulus $B_0 = 96$ GPa at low pressure range below 6 GPa, and $B_0 = 186$ GPa at pressure from 6 to 30 GPa for IL CaCuO_2 are obtained. This value is comparable to those of other high T_c superconductors (see Table 1).

Fig. 5 shows the resistance–pressure and capacitance–pressure relationships for IL CaCuO_2 at room temperature. The pressure dependence of resistance can be divided into three regions: 0–3, 3–6, and 6–20 GPa. Resistance decreases very little in the first region. Because the examined sample was pre-compressed at 4–5 GPa, and it is an irreversible process. From 3 to 6 GPa, the resistance begins to drop dramatically with increasing pressure. This can be caused by three possible reasons, as follows: (1) the energy gap decreases with increasing pressure; (2) crystalline grains are joined more closely under high pressure, destroying most of the voids and defects, so that the resistance decreases drastically; (3) an isostructure phase transition occurs as observed in the synchrotron radiation experiments. Then the resistance begins to rise with increasing pressure from 6 GPa and shows a maximum around 12 GPa. This is possibly caused by an electronic structure transition caused by the anisotropic compression of the unit cell under high pressure in IL CaCuO_2 , which can be explained by the sudden disappearance of some diffraction peaks such as (211) above 11 GPa (see the Fig. 3). These abnormal

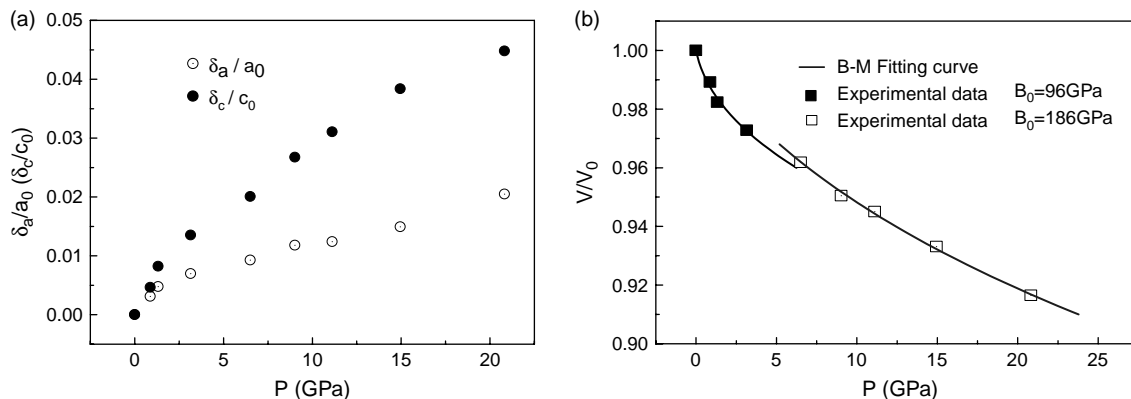


Fig. 4. The relationships of change rate of lattice parameters (a) and volume compressibility (b) versus pressure for infinite-layer CaCuO_2 .

Table 1
The comparison of bulk modulus for some HTS

System	B_0 (GPa)	Remarks
IL CaCuO ₂	181	X-ray diffraction
Cu-1234 polycrystalline	152	X-ray diffraction
Y-123 single crystal	115	X-ray diffraction
Y-124 polycrystalline	118	Neutron diffraction
Hg-1201 polycrystalline	65.4	X-ray diffraction
Hg-1223 polycrystalline	83.8	X-ray diffraction
Hg-1212 polycrystalline	91.6	X-ray diffraction
Tl-2201 polycrystalline	84.2	Neutron diffraction

changes were also correspondingly reflected in the simultaneous capacitance dependence on pressure as shown in Fig. 5.

As early as the discovery of HTS, it was found that pressure has a dramatic positive effect on the superconducting transition temperature [10]. The pressure dependence of the transition temperature of HTS has been given much attention [11–15] and is still an interesting subtopic of HTS. Generally the transition temperature of HTS is controlled by the carrier density n_H at the [CuO₂] plane and reaches its maximum at the average doping level $n_H=0.15$, showing a parabolic dependence on n_H . The enhancement of T_c by pressure was initially believed to be mainly due to the pressure's subtle tuning of the carrier density [11]. However, this vision was discredited by the research on Hg-12($n-1$) n , in which unusual positive increases were observed even in the optimally doped compounds. Therefore it has been argued that in addition to the pressure's effect on the doping itself, pressure also exerts a substantial influence on the coupling force of Cooper pair, i.e. the effective attraction becomes stronger under compression. Chen et al. predicted by theoretical calculation using a phenomenological model [14], two intrinsic variables, i.e. the effective attractive interaction V_{eff} that is intrinsic to the electronic structure at the Fermi surface, and the hole concentration n_H in the [CuO₂] plane, are responsible for the effect of pressure on T_c . Since the CaCuO₂ infinite layer structure is the pristine conducting unit for multi-layered HTS, its structural evolution with

varying pressure has direct impact on the overall understanding of HTS transport properties. Here we address the observation of IL CaCuO₂'s resistance evolution with pressure, especially the abnormal hump around 12 GPa, which may provide the experimental evidence for the unusual electronic structural change. The reasons for the electronic structural transition need to be further confirmed by more experiments, for example, electrical measurements under high pressure above the Néel temperature as well as some optical measurements. Whereas, understanding this behavior will be helpful to make the intrinsic mechanism causing high temperature superconductivity clear.

4. Conclusion

The results of this experiment show that the primary crystal structure of infinite-layer CaCuO₂ synthesized under high pressure is stable under pressures up to 30 GPa, but with an anisotropic compressibility within the a – b plane and along the c -axis. Assuming the pressure derivative $B'_0 = 4$, the bulk modulus $B_0=96$ GPa at low pressure range below 6 GPa, and $B_0=186$ GPa at pressure from 6 to 30 GPa for IL CaCuO₂ are obtained. Abnormal resistance and capacitance behavior was observed in the pressure range around 12 GPa, suggesting that an electronic structural transition may take place under pressure.

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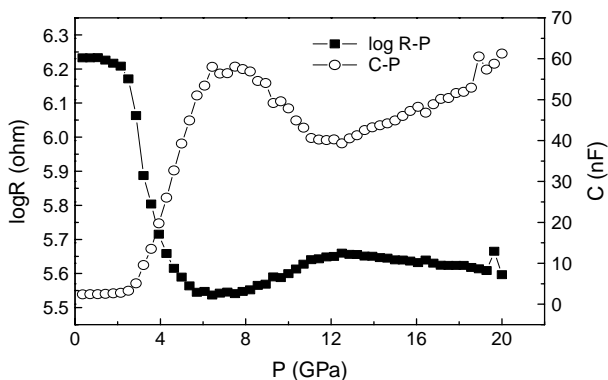


Fig. 5. The R–P and C–P relationships for infinite-layer CaCuO₂.

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