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### High-pressure structural behavior of the double perovskite $\text{Sr}_2\text{CrReO}_6$ : an experimental and theoretical study

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## High-pressure structural behavior of the double perovskite $\text{Sr}_2\text{CrReO}_6$ : an experimental and theoretical study

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The high-pressure structural behavior of  $\text{Sr}_2\text{CrReO}_6$  has been studied experimentally using synchrotron radiation and the diamond anvil cell and theoretically using density functional theory. The experimental zero-pressure bulk modulus is  $B_0 = 170 \pm 4$  GPa and the pressure derivative is  $B'_0 = 4.7 \pm 1.0$ . These results compare well with the calculated values 172.6 GPa and 5.7. A pseudo-cubic unit cell can describe the crystal structure at low pressure, but the tetragonal structure becomes evident at high pressure.

**Keywords:** bulk modulus; equation of state; phase transformation; X-ray diffraction; density functional theory; double perovskite  $\text{Sr}_2\text{CrReO}_6$

### 1. Introduction

Double perovskites have the general formula  $\text{A}_2\text{BB}'\text{O}_6$ , where A is an alkali metal or a lanthanide, and B and B' are transition metals. A high magnetoresistance at room temperature was discovered in  $\text{Sr}_2\text{FeMoO}_6$  [1]. Currently,  $\text{Sr}_2\text{CrReO}_6$  [2] and  $\text{Sr}_2\text{CrOsO}_6$  [3] have the highest Curie temperatures: 635 and 725 K. One can understand this behavior within a model of kinetic energy-driven ferrimagnetism [4], in which an increase in band filling contributes to a stabilization of the magnetism [5]. In  $\text{Sr}_2\text{CrOsO}_6$ , the ferromagnetic transition is accompanied by a cubic to trigonal transformation [3].

First band-structure calculations, including predictions of the magnetic moments for  $\text{Sr}_2\text{CrReO}_6$ , were published by Vaitheeswaran and Kanchana [6] and later experimentally confirmed by Majewski et al. [7]. The present work is a study of the high-pressure structural behavior of  $\text{Sr}_2\text{CrReO}_6$ . Experiments have been performed with synchrotron radiation and the diamond anvil cell, and the results are compared with *ab initio* calculations using density functional theory.

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## 2. Experimental procedure

Samples were prepared from a stoichiometric mixture of SrO<sub>2</sub>, Re, and CrO<sub>2</sub> powders in an evacuated silica tube. The parent structure of Sr<sub>2</sub>CrReO<sub>6</sub> is tetragonal with space group *I4/mmm*. The lattice parameters are  $a_{0,\text{tet}} = 5.52 \text{ \AA}$  and  $c_0 = 7.82 \text{ \AA}$  [2]. The  $c/a$  ratio is close to  $\sqrt{2}$ , indicating that a larger face-centered cubic (fcc) unit cell can describe the lattice at ambient conditions. The fcc cell has the lattice parameter  $a_0 = 7.82 \text{ \AA}$  [8] and twice the volume of the tetragonal cell.

Room temperature, high-pressure powder X-ray diffraction (XRD) spectra were recorded with synchrotron radiation. The diffractometer, working in energy-dispersive mode, has been described elsewhere [9]. High pressures were produced in a Syassen–Holzapfel-type diamond anvil cell [10]. A fine powder and a ruby chip were placed in a hole with diameter 200  $\mu\text{m}$  in an Inconel gasket, pre-indented to a thickness of 60  $\mu\text{m}$ . A 16:3:1 methanol:ethanol:water mixture was used as the pressure-transmitting medium. The pressure was determined by the ruby luminescence method, using the pressure scale of Mao et al. [11].

Lattice parameters and unit-cell volumes were derived and refined from the positions of the Bragg peaks using the PURUM code [12]. The compression curve was then described by the Birch–Murnaghan equation of state [13]:

$$P = \frac{3}{2}B_0(x^{-7/3} - x^{-5/3}) \left[ 1 - \frac{3}{4}(4 - B'_0)(x^{-2/3} - 1) \right], \quad (1)$$

where  $x = V/V_0$ ,  $V$  is the volume at pressure  $P$ ,  $V_0$  the volume at zero pressure,  $B_0$  the zero-pressure bulk modulus, and  $B'_0$  its pressure derivative. Values of  $B_0$  and  $B'_0$  were obtained from a least-squares fit of Equation (1) to the experimental  $P$ – $V$  data.

## 3. Theoretical calculations

Density-functional calculations were performed using an all-electron full-potential linear muffin-tin orbital method. In this method, space is divided into non-overlapping muffin-tin spheres, surrounding the atoms, and an interstitial region. Most importantly, this method assumes no shape approximation of the potential, the wave functions, or the charge density. Spin–orbit coupling was taken into account. For more details, please refer to [6].

## 4. Results and discussion

### 4.1. Experimental results

Figure 1 shows a diffraction spectrum at 20.4 GPa. Cubic indexing has been assumed at low pressure, but a tetragonal distortion becomes evident above 9 GPa (Figure 2). The distortion is only about 1.4%. Thus, any splitting of the Bragg peaks is too small to be seen within the 3% resolution of the energy dispersive method used in the present work. Further studies, using high-resolution angle-dispersive diffraction, would be desirable to elucidate the tetragonal structure in more detail. The inset graph in Figure 2 shows that the width of the Bragg peaks increases steadily with increasing pressure.

Figure 3 shows the volume compression. There is no observable volume change at the transition from pseudo-cubic to tetragonal structure, although the scatter of the data points becomes larger at high pressure. The experimental bulk modulus is  $B_0 = 170 \pm 4 \text{ GPa}$  and the pressure derivative is  $B'_0 = 4.7 \pm 1.0$ . To the best of our knowledge, there are no published data with which to compare the present results.

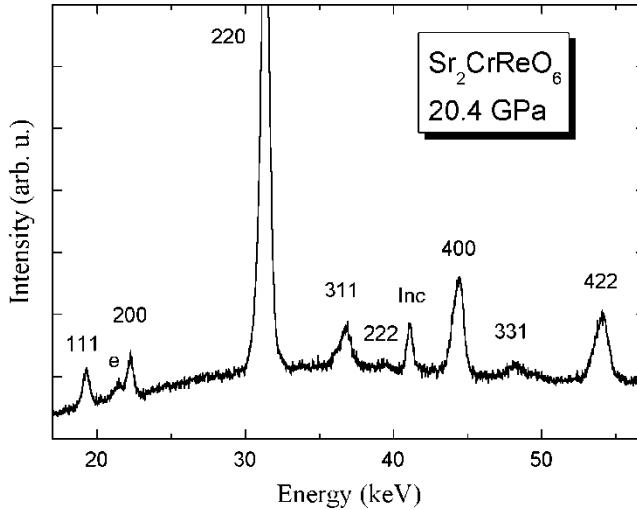


Figure 1. XRD spectrum of  $\text{Sr}_2\text{CrReO}_6$  at 20.4 GPa. The Bragg angle is  $\theta = 4.252^\circ$ ; e, escape peak; Inc, diffraction peak due to the Inconel gasket.

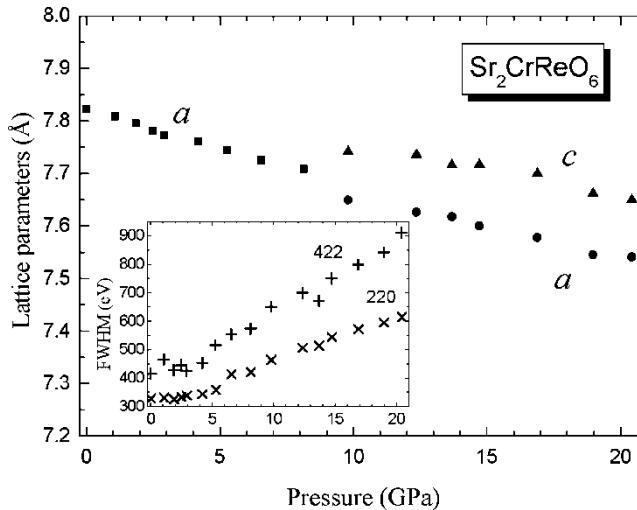


Figure 2. The lattice parameter,  $a$ , of the pseudo-cubic unit cell, and the parameters  $a$  and  $c$  of the tetragonally distorted cell of  $\text{Sr}_2\text{CrReO}_6$  as functions of pressure. The inset shows the full width at half maximum of the 220 and 422 peaks as functions of pressure.

#### 4.2. Theoretical results

Calculations of total energies using density functional theory indicate that the cubic phase is stable at zero pressure, whereas the tetragonal phase is favored under pressure. The calculated lattice parameter of the fcc unit cell at ambient conditions is  $a_0 = 7.872 \text{ \AA}$ , which agrees within  $<1\%$  with the experimental value. If instead a tetragonal unit cell is assumed, the calculated lattice parameters at ambient conditions are  $a_{0,\text{tet}} = 5.5478 \text{ \AA}$  and  $c_0 = 7.8477 \text{ \AA}$ . Thus, the  $c/a$  ratio is practically equal to  $\sqrt{2}$  at zero pressure.

The calculated equation of state is shown by the dashed curve in Figure 3. The bulk modulus is 172.6 GPa and the pressure derivative is 5.7. Thus, the calculated and the experimental bulk moduli agree within 1.5%. This close agreement must be considered very satisfactory.

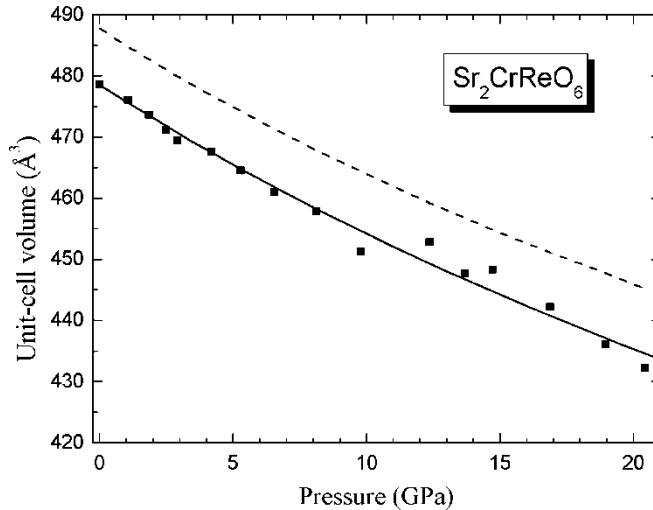


Figure 3. Unit-cell volume of  $\text{Sr}_2\text{CrReO}_6$  as a function of pressure. The full curve through the experimental data points has been calculated from the Birch–Murnaghan equation (1). The dashed curve is the result of the theoretical calculation.

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