High Pressure Raman Study of Cs2CuCl4

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Abstract. High-pressure Raman spectra of frustrated antiferromagnet Cs2CuCl4 is investigated in a diamond anvil cell. Four characteristic modes of Cs2CuCl4 are observed at ambient conditions. As the pressure increases, the sample undergoes a structure phase transition at 5 GPa. After decompressing, the low-pressure Raman spectra are recovered, which indicates a reversible phase transition. We discussed the results in terms of the change of structure with pressure.

1. Introduction

A2BX4(A = Cs,Rb, K B = Cu, Co, Zn and X = F, Cl, Br) -type compounds have received extensive attentions due to their rich physical properties, such as ferroelectricity [1 2], nonlinear optical response [3, 4], as well as quantum critical behavior [5-9]. Particularly, these properties depend strongly on the pressure, which usually attributes to the distortions of BX4 tetrahedra and the structure phase transition [3, 10, 11].

As one of the main members of frustrated spin system in A2BX4-type compounds, Cs2CuCl4 is an S = 1/2 quasi-two-dimensional quantum antiferromagnet material with distorted triangular lattice. In the past decades, Cs2CuCl4 has been considered as prototype system of quantum spin-liquid [12]. Cong et al. [13] show that the magnetic susceptibility of Cs2CuCl4,Brx exhibits discontinuous behavior in the dopant range of 1 ≤ x ≤ 4 due to the change of CuCl4 tetrahedral caused by a site-selective substitution of Br- for Cl-. The Cs2CuCl4 undergoes a structure phase transition around 40 kbar [11]. Kim et al. [14] reported that a new metastable magnetic phase was observed in Cs2CuCl4 due to the slight change between distance of Cu2+ ions induced by the application of hydrostatic pressure. It can be seen that the magnetic properties of Cs2CuCl4 are very sensitive to the atomics position and lattice constants. These interesting phenomena make it necessary to explore the structure of Cs2CuCl4 under high pressure. As one of the means of studying the change of structure, Raman spectroscopy can get more information about vibrations.

2. Experiments

2.1. Catalyst preparation:

Cs2CuCl4 single crystals were synthesized by the slow evaporation of aqueous solution. The CsCl (99.5%) and CuCl2·2H2O (99.99%) was dissolved in deionized water together with the mole ratio of 2:1 at room temperature and the solution was evaporated at 323 K. After 7 days, the yellow single crystals were obtained. Then the single crystals were ground into powders for further experiments.
2.2. Characterization:
The structure of the Cs₂CuCl₄ powder was measured by a Bruker D8 ADVANCE X-ray diffractometer with Cu-Kα radiation (λ = 0.15418 nm, Ni filter) at ambient conditions. The high-pressure experiments were carried out by using a diamond anvil cell with a pair of 300 μm culet size anvils. A hole of ~ 120 μm in diameter and ~ 30 μm in thickness drilled in a preindented a stainless-steel gasket was used as the sample chamber. Small amounts of ruby grains together with the Cs₂CuCl₄ powders were loaded in the gasket hole for calibrating pressure [15]. The in-situ high-pressure Raman scattering spectrum were measured using a micro-Raman spectrometer (Renishaw inVia, calibrated by single crystal silicon). Radiation of 532 nm from a solid-state laser (0.5 W CW) was used for the excitation source of the Raman spectra.

3. Results and Discussion
The structure of Cs₂CuCl₄ consists of CuCl₄²⁻ tetrahedra and Cs⁺ ions while the tetrahedra are connected along the b-axis as shown in Figure 1. Due to the existence of the Jahn-Teller effect in the CuCl₄ tetrahedron, Cu²⁺ ions arranged in the bc plane form a distorted triangular lattice. Figure 2 shows the XRD pattern of as-grown Cs₂CuCl₄. The Rietveld refinement shows that Cs₂CuCl₄ sample has an orthorhombic structure with a space group Pnma. The best fitting parameters for the lattice constants are a = 9.761(1) Å b = 7.612(1) Å c = 12.399(1) Å. The result is in consistent with the previous reports [16].

Figure 1. The structure of Cs₂CuCl₄ at ambient conditions.

![Figure 1](image1.png)

Fig. 3 shows the Raman spectrum of Cs₂CuCl₄ at ambient pressure. Four vibration peaks (118 cm⁻¹, 135 cm⁻¹, 252 cm⁻¹ and 296 cm⁻¹) can be observed at ambient pressure. Due to the existence of the Jahn-Teller effect in CuCl₄ tetrahedra, the distorted tetrahedra can be described in D₂d or C₂v point group instead of T₄ point group and the Raman spectrum at ambient pressure supporting C₂v symmetry [17].

Figure 2. XRD pattern of Cs₂CuCl₄ at ambient conditions.

![Figure 2](image2.png)
The Raman spectra of Cs$_2$CuCl$_4$ under different pressures are displayed in Figure 4 and 5. At low pressure, two new vibration modes at 200 cm$^{-1}$ and 302 cm$^{-1}$ appear (shown in Fig. 4), which can be assigned as the $v_4$(B2) Cu-Cl asymmetric deformation mode and $v_3$(B1) Cu-Cl asymmetric stretching mode, respectively. As the pressure increases, the Raman vibration modes shift to higher frequency except $v_4$(B2) mode under 4.5 GPa. Above 4.5 GPa, the Raman vibration modes of $v_4$(B2) shift to higher frequency, and two new vibration modes (Mode I and Mode II) appears at 250 cm$^{-1}$ and 305 cm$^{-1}$. The Raman vibration modes of $v_4$(B1), $v_4$(A1) and $v_3$(A1) are undetectable in our experiments above 4.5 GPa. The Raman vibration modes of $v_3$(B1) and $v_1$(A1) are disappeared above 6.2 GPa. After releasing the pressure, the low-pressure Raman spectrum is recovered (shown in Figure 5).

Figure 3. The Raman spectrum of Cs$_2$CuCl$_4$ under ambient pressure.

Figure 4. Raman spectra of Cs$_2$CuCl$_4$ under 4.5 GPa.

Figure 5. Raman spectra of Cs$_2$CuCl$_4$ above 4.5 GPa.
Fig. 6 shows the pressure dependence of the Raman shifts of the Cs$_2$CuCl$_4$ sample. Obviously two regions can be found clearly. The Raman shifts at the high-pressure region (> 5 GPa) and low-pressure region (< 5 GPa) have different slopes as the pressure increasing as shown in Table 1. It means that a structure phase transition occurs near 5 GPa consistent with Ref. 11.

![Figure 6](image_url)

**Figure 6.** Pressure dependence of the frequencies of Cs$_2$CuCl$_4$ for the modes in two regions.

**Table 1.** The pressure derivatives of frequencies $d\omega/dp$ for various Raman modes of Cs$_2$CuCl$_4$ in low pressure Pnma phase and high-pressure phase.

| Raman mode | Low pressure (Pnma) phase | High pressure phase | Mode | Mode
|---|---|---|---|---|
| $v_4(B1)$ | 8.6±0.5 | 3.6±0.1 | 4.9±0.2 | 4.6±0.2 |
| $v_4(A1)$ | 6.0±0.2 | 6.2±0.2 | 7.9±0.2 | 9±0.2 |
| $v_4(B2)$ | 0 | 7.9±0.2 | 9±0.2 |
| $v_3(A1)$ | 6.2±0.2 | 7.9±0.2 | 9±0.2 |
| $v_3(B1)$ | 7.9±0.2 | 9±0.2 |
| $v_1(A1)$ | 9±0.2 |

The Raman spectroscopy shows a very interesting phenomenon under 5 GPa. The peak intensity of the $v_4(B1)$ vibration mode is gradually weakened and merged with the $v_4(A1)$ vibration mode at 3.9 GPa and disappeared at 4.5 GPa. The $v_4(B2)$ vibration mode shows the zero pressure Raman shifts. Considering the CuCl$_4$ tetrahedron exists a significant structural distortion due to the Jahn-Teller effect. Simultaneously, the effect of pressure is to make the crystal structure more symmetrical. Xu et al. found that the flattening of the CuCl$_4$ tetrahedra decreases slightly with increasing pressure by high-pressure X-Ray diffraction methods in Ref. 11. Combined with the above phenomena, it can be suggested that the Jahn-Teller effect in Cs$_2$CuCl$_4$ is suppressed under 5 GPa.

**4. Conclusion**

In summary, high-pressure Raman scattering spectra of Cs$_2$CuCl$_4$ were measured by a micro-Raman spectrometer in a diamond anvil cell up to 14GPa. Pressure-induced lattice compression compensates for structural distortion caused by Jahn-Teller effect. The J-T effect is suppressed by pressure in low pressure $Pnma$ phase. The Raman spectra of Cs$_2$CuCl$_4$ above 5 GPa changes significantly, which indicates that a structure phase transition occurred around 5GPa.

**Acknowledgments**

This work was financially supported by the Key Technologies R&D Program of Guangzhou City (No. 201704020182 and 201803030008) and Water Resource Science and Technology Innovation Project of Guangdong Province (2017-23).
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