

ELECTRONIC AND MAGNETIC STRUCTURE OF THE HIGH PRESSURE PHASE OF Li_2CuO_2

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The magnetic and electronic structure of monoclinic phase Li_2CuO_2 under high pressure is studied by first principle with GGA+U calculations. It is shown that the C-type antiferromagnetic state of the ambient structure is maintained in the monoclinic high pressure phase. This is due to the preservation of the ferromagnetic CuO_2 chains in the structure. It is expected that the weak interchain antiferromagnetic interaction can easily disrupt by finite temperature, and the magnetocrystalline anisotropy in this insulator is extremely weak.

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1. Introduction

Li_2CuO_2 displays many interesting phenomena, such as spin order, spin-Peierls phase transition and low lying excitations.^{1–18} At ambient pressure, Li_2CuO_2 has an orthorhombic $Immm$ structure. Each Cu^{2+} ion is surrounded by four nearest neighboring (NN) O^{2-} ions in the b - c plane forming the 3D structure via edge-sharing CuO_4 . In view of the simple CuO_4 square planar coordination, Li_2CuO_2 has been a prototypical model for the study of electron–electron interactions in strongly correlated systems.^{19,20} At 9 K, a collinear magnetic structure in which the ferromagnetic CuO_2 chains are antiferromagnetically aligned and the magnetic moment perpendicular to the CuO_4 plane is observed.²¹ At even lower temperature of 2 K the magnetic structure changed to a canted spin state.^{22–24} The origin of this unusual spin state is still unknown. Another interesting phenomenon is that the magnetic moment of O^{2-} in Li_2CuO_2 of about $0.2 \mu\text{B}$ is quite large.²² Recently a high pressure phase of Li_2CuO_2 with the space group $C2/m$ (Fig. 1) was found.¹

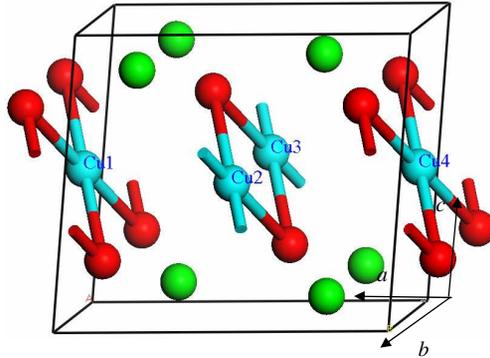


Fig. 1. (Color online.) Crystal structure of monoclinic structure of Li_2CuO_2 under high pressure. The cyan, red and green spheres represent Cu^{2+} , O^{2-} and Li^{1+} ions. The angle between lattice vectors a and c is β .

The monoclinic structure consists of Cu atomic layers stacked along the c -axis with the Li and O atoms interweaved between the layers. The Cu^{2+} ions are located in the center of distorted edge-sharing CuO_6 octahedral formed by its nearest neighbor and next nearest neighbor (NNN) O^{2-} ions. In contrast to orthorhombic Li_2CuO_2 where many studies have been reported,^{21–24} there is no detailed information on both the electronic and magnetic structure of the new monoclinic phase. In this paper, the evolution of magnetic structure of the orthorhombic to high pressure monoclinic phase is explored by first principles calculations. The layout of this paper is as follows. First, the equation of states (EOS) of monoclinic structure Li_2CuO_2 with E-type, C-type, ferromagnetic and nonmagnetic states were computed with the GGA+U method without spin-orbital coupling (SOC). Next, the effect of SOC to the magnetic structure was considered. The evolution of the electronic and magnetic structure under pressure will be analyzed and discussed.

2. Method of Calculation

Electronic structure calculations employing the gradient corrected density functional theory (GGA) augmented with the model Hubbard Hamiltonian GGA+U²⁵ as implemented in the Vienna *ab initio* simulations package (VASP)^{26,27} was used. The on-site Coulomb interaction of d electrons on the Cu^{2+} ion, U , was set to be 6.9 eV with the exchange parameter J set to be 0.9 eV. The GGA+U calculation was performed with the rotationally invariant approximation.²⁵ These parameters are the same as the effective ($U - J$) of 6.0 eV usually employed for copper oxide systems.⁴ Projector augmented-wave (PAW) pseudopotentials²⁸ with a 600 eV plane wave cutoff were used. A $8 \times 16 \times 10$ Monkhorst-Pack k -points mesh was used in the calculations of the electronic structure of the C-type and ferromagnetic magnetic structure; while a $8 \times 8 \times 10$ mesh was used in magnetic unit cell with E-type antiferromagnetism. The C-type and E-type magnetic structures are illustrated in

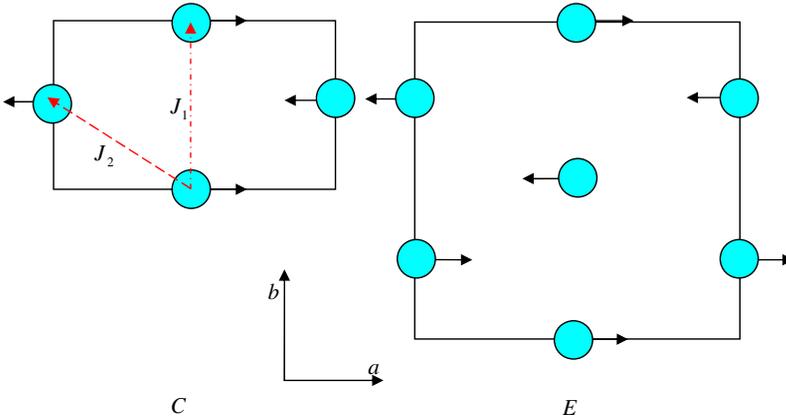


Fig. 2. The C-, E-type magnetic structure and spin coupling J_1 and J_2 .

Fig. 2. Since the longest Cu–Cu distance is along the c -axis, the spin–spin interaction along c -axis is assumed to be ferromagnetic and we will only focus on the intralayer spin–spin interaction.

3. Results and Discussion

The calculated phase transition pressure from the ambient orthorhombic to the monoclinic structure is about 7.2 GPa which is close to the observed 5.6 GPa.¹ Two types of spin–spin coupling between Cu^{2+} ions classified by their distances in the monoclinic structure were considered (Fig. 1). As shown in Fig. 2, J_1 is the spin–spin coupling between the nearest Cu^{2+} ions in the same CuO_2 chain. Both exchange and superexchange mediated by O^{2-} ion will contribute to it. J_2 is the spin–spin coupling between next nearest Cu^{2+} ions in different chains in the ab -plane of the same layer. To study the importance of the two spin–spin coupling schemes, EOS of FM, E-type and C-type magnetic structures calculated by GGA+U without SOC were first performed. The results are compared in Fig. 3. The nonmagnetic state is found to be not energetically competitive with the magnetic states and is not shown in Fig. 3. The GGA results showing the C-type structure will be the most stable. However, the energy difference between C-type antiferromagnetic and ferromagnetic state is less than 10 meV indicating that the interchain spin–spin coupling is very weak and may be destroyed at finite temperature. To verify this prediction by the GGA+U calculations, the effect of interchain coupling is examined by calculations including SOC correction. The magnetocrystalline anisotropy energy (MAE) of ferromagnetic and C-type structure is calculated at the experimental structure and lattice parameter at 28.8 GPa¹ and the results are reported in Table 1, The total energies with magnetization along the crystal a , b , c directions (i.e., [100], [010] and [001], respectively) as the spin quantization axes were calculated. It is found that the energetic sequence of the magnetic structures is not changed by the

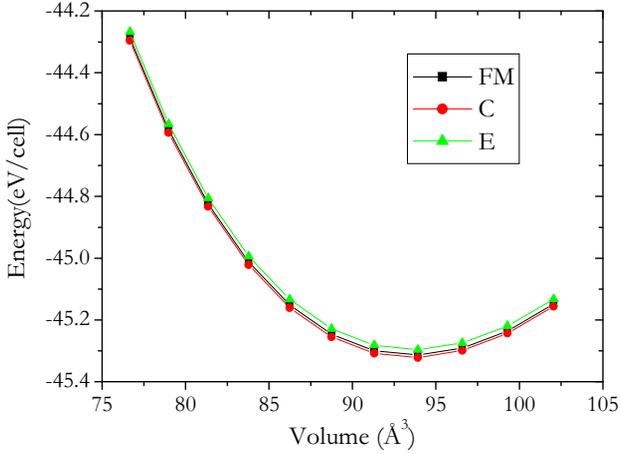


Fig. 3. EOS of the $C2/m$ structure Li_2CuO_2 with FM, C-type and E-type magnetic structures.

Table 1. Magnetocrystalline anisotropy energy (MAE) (in eV), relative to the energy of the nonmagnetic state.

| | E_C | E_{FM} |
|-----|-----------|-----------------|
| 100 | -1.342001 | -1.336250 |
| 010 | -1.341128 | -1.335365 |
| 001 | -1.341402 | -1.335651 |

inclusion of SOC. Moreover, the difference in the energies along different spin quantization axes at the same magnetic state is extremely small. The energy difference of less than 1 meV shows very weak magnetocrystalline anisotropy. Considering the very small energy difference between C-type and FM of less than 10 meV, the comparatively larger energy difference between the C-type and E-type antiferromagnetic states of 20 meV suggests the ferromagnetic intrachain coupling J_1 is stronger than the antiferromagnetic interchain coupling J_2 . Therefore, it can be concluded that the C-type antiferromagnetic state is the ground state for the high pressure monoclinic structure of Li_2CuO_2 . Incidentally, this magnetic structure is exactly the same as the magnetic structure of orthorhombic structure of Li_2CuO_2 at ambient pressure.^{29,30} In the latter, the magnetic state is the result of the antiferromagnetic arrangement of the ferromagnetic chains. At ambient pressure, the bond angle of Cu–O–Cu is $\sim 94^\circ$.¹⁹ In comparison, the Cu–O–Cu bond angle of the monoclinic phase is about 92° and is not very sensitive to increasing pressure (decreasing volume) from the calculations. The ferromagnetic spin–spin coupling constant J_1 from the calculations is in complete agreement with the Goodenough–Kanamori rules^{31–36} which predicted the spin coupling between Cu ions would be ferromagnetic if bond angle of Cu–O–Cu is close to 90° .

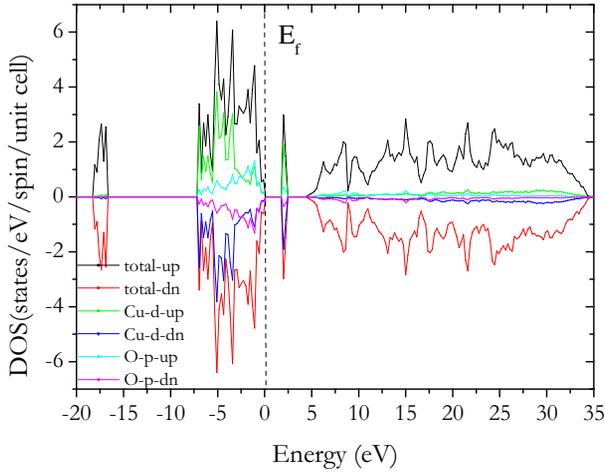


Fig. 4. Density of states (DOS) of monoclinic structure in the C-type magnetic state.

Another important aspect revealed from the calculations is that the remnant spin moment of O^{2-} ions is quite large. Nevertheless, there is a gradual increase of the transfer of p -electron from O^{2-} to the d -orbit of Cu^{2+} under high pressure. As a result, small amount of spin moment was transferred from O^{2-} to Cu^{2+} . Consequently, the spin moment on O^{2-} decreases from 0.155 to 0.145 μB with a concomitant increase in the spin moment on Cu^{2+} ion from 0.62 to 0.65 μB . The optimized lattice parameters of C-type antiferromagnetic state with unit cell volume $V = 76.67 \text{ \AA}^3$ are, $a = 5.6346 \text{ \AA}$, $b = 2.7853 \text{ \AA}$, $c = 4.9233 \text{ \AA}$, $\beta = 97.45^\circ$, Cu (2d) (0, 0.5, 0.5), O (4i) (0.1314, 0, 0.7492), Li (4i) (0.1662, 0, 0.1422) and the Cu–O bond in the CuO_4 square is 1.938 \AA . The density of state (DOS) [Fig. 4] was calculated within this optimized magnetic unit cell and the system is covalent insulator with bandgap about 1.5 eV and strong d - p hybridization. This result agrees with the large measured resistance.¹ Moreover, this gap is comparable with the bandgap calculated in the orthorhombic structure of Li_2CuO_2 at ambient pressure.⁷

4. Summary

The magnetic and electronic structures of the recently characterized monoclinic high pressure phase of Li_2CuO_2 under high pressure were studied with first principle GGA+U calculations. Same as the ambient structure, the high pressure phase is an insulator and has a C-type antiferromagnetic state.

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