

Supplementary material to “Opposite pressure effects in the orbitally-induced Peierls phase transition systems CuIr_2S_4 and MgTi_2O_4 ”

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PACS numbers: 71.30.+h, 71.45.Lr, 72.80.Ga

Keywords: orbitally-induced Peierls instability, pressure effect, metallic-insulating phase transition

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I. METHOD

In our numerical calculations, the full potential linearized augmented-plane-wave (FP-LAPW) scheme based on density functional theory (DFT) in the WIEN2K package [1] is adopted. Exchange and correlation effects are taken into account in the generalized gradient approximation (GGA) by Perdew, Burk, and Ernzerhof (PBE) [2]. To explore the evolutions of electronic structures with the increase of pressure, we first perform structural relaxation of the crystal structures of CuIr_2S_4 and MgTi_2O_4 under various pressures through optimizing the total energies of various structures within the framework of DFT. For more clearly revealing the effect of pressure, the electronic structure calculations are performed using 4 GPa.

II. CRYSTAL STRUCTURES AT PRESSURE

In order to compare our numerical results with the experimental data, we adopt the structural data of CuIr_2S_4 [3] and MgTi_2O_4 [4] as the initial crystal structures for the structural relaxation. For CuIr_2S_4 , the low-temperature phase has a triclinic space group $P\bar{1}$ (No. 2), the calculated structures at different pressures are listed in Table S I. For MgTi_2O_4 , the low-temperature phase has a tetragonal space group $P4_12_12$ (No. 92), the calculated structures at different pressures are listed in Table S II. The optimized lattice parameters are well consistent with the experimental ones at 0 GPa.

Table S I: The optimized lattice parameters of low-temperature triclinic phase of CuIr_2S_4 with $P\bar{1}$ space group at different pressures.

P(GPa)	0(<i>expt.</i> [3])	1.0	2.0	3.0	4.0
a(Å)	7.0273(6.988)	7.007	6.9873	6.9686	6.9507
b(Å)	12.1646(11.956)	12.1297	12.0959	12.0636	12.0329
c(Å)	12.1654(11.959)	12.1303	12.0962	12.0637	12.0333

Table S II: The optimized lattice parameters of low-temperature tetragonal phase of MgTi_2O_4 with $P4_12_12$ space group at different pressures.

P(GPa)	0(<i>expt.</i> [4])	1.0	2.0	3.0	4.0
a(Å)	6.0244(6.022)	6.0133	6.002	5.992	5.982
c(Å)	8.5123(8.4848)	8.4964	8.4812	8.466	8.4512

III. CALCULATED RESULTS

A. CuIr_2S_4

In CuIr_2S_4 compound, due to the monovalent Cu ion [5], the Ir ion has an average +3.5 valence. The $\text{Ir}^{3+/4+}$ ion with $5d^6/5d^5$ configuration is surrounded by six S^{2-} ions, which forms a IrS_6 octahedron. The octahedral crystal field splits the Ir-5d levels into lower energy triplet t_{2g} and higher energy doublet e_g orbitals [6]. With further elongated tetragonal distortion, the on-site energy of the xz/yz orbitals is lower than that of the xy orbital.

Figure S 1 shows the total density of states (tDOS) of low-temperature phase of CuIr_2S_4 at 0 (solid line) and 4 (dash line) GPa. It is clearly seen that with the increase of pressure, the tDOS around Fermi level decreases, and part of occupied states become unoccupied ones (see the inset of Fig. S 1). Noticed that the physical properties of material are dominantly determined by the electronic properties around Fermi level. Thus the decreased tDOS indicates that the system becomes insulating tendency under high pressure, which results in a decrease of resistivity observed experimentally.

Figure S 2 shows an atomically-resolved density of states of low-temperature phase of CuIr_2S_4 at 0 (solid line) and 4 (dash line) GPa. It can be found that the decreased tDOS is mainly contributed from Ir ions. Meanwhile, the contribution of S ions is due to the hybridization between S-3p and Ir-5d orbitals.

In order to understand the influence of pressure on the electronic properties, we plot the Ir-5d orbitally-resolved density of states of low-temperature phase of CuIr_2S_4 at 0 (solid line) and 4 (dash line) GPa, as shown in Fig. S 3. It should be noted that in CuIr_2S_4 , since the tetragonal distortion is elongated with $c > a$ (a (x) and c (z) axes are chosen along the Ir-S direction), the pressure effect on the z -component orbitals is relatively great. As it is

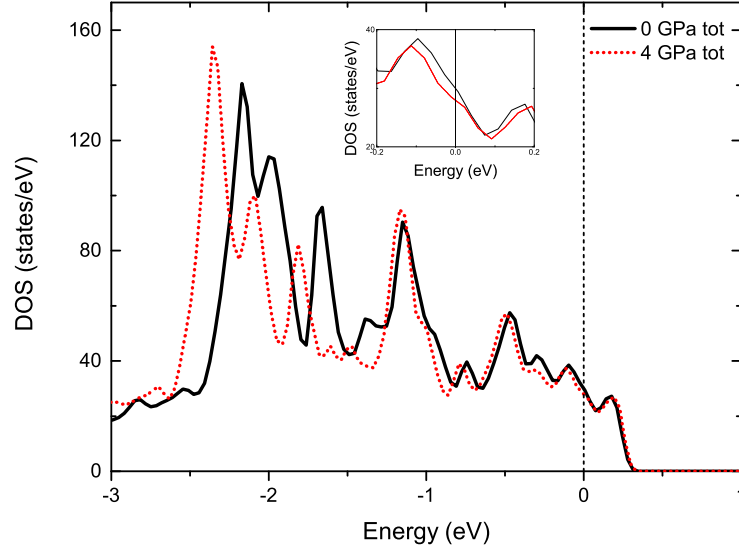


Fig. S 1: (Color online) Total density of states of low-temperature phase of CuIr_2S_4 under different pressures. The inset shows the magnification of the corresponding density of states.

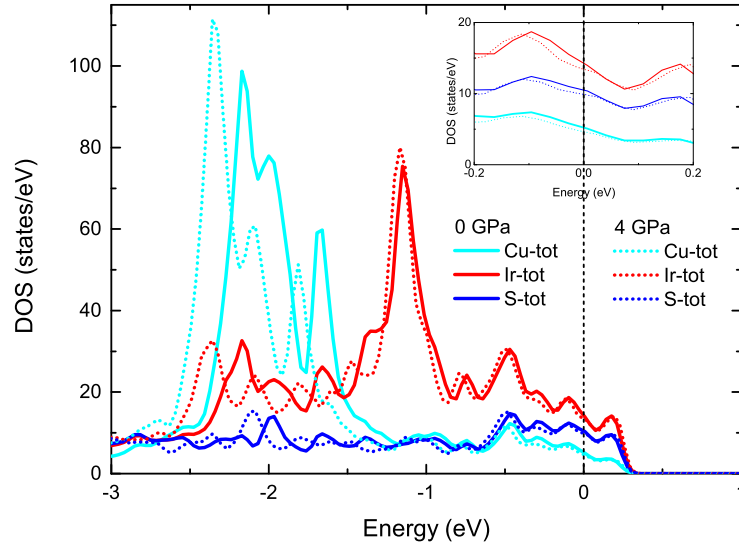


Fig. S 2: (Color online) Atomically-resolved density of states of low-temperature phase of CuIr_2S_4 under different pressures. The inset shows the magnification of the corresponding density of states.

expected, we find that the occupation of xz and yz orbitals decreases, which dominantly leads to the decrease of tDOS around Fermi level. In fact, the xy orbital order as suggested by previous study [6] is nearly not affected greatly. That is to say, this xy orbital order is not melted by the pressure. Thus, the system becomes more insulating tendency.

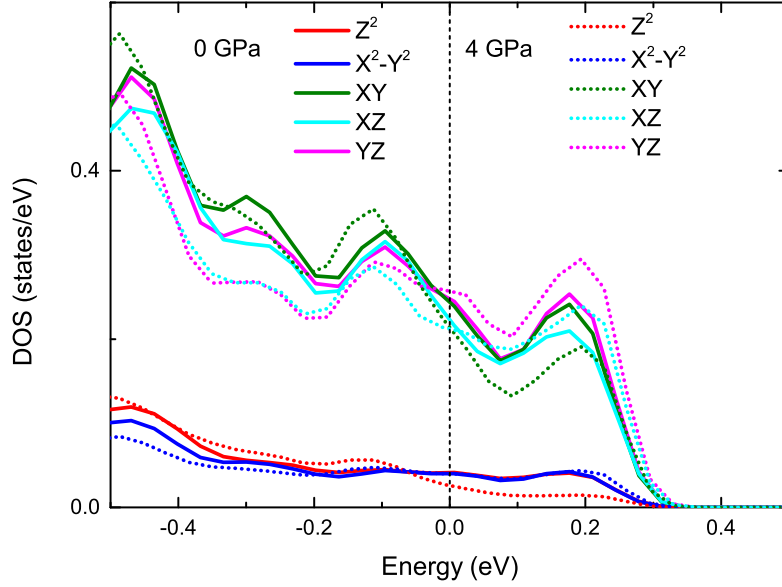


Fig. S 3: (Color online) Ir-5d orbitally-resolved density of states of low-temperature phase of CuIr_2S_4 under different pressures.

B. MgTi_2O_4

In MgTi_2O_4 compound, the Ti^{3+} ion with $3d^1$ configuration is surrounded by six O^{2-} ions, which forms a TiO_6 octahedron. The octahedral crystal field splits the Ti-3d levels into lower energy triplet t_{2g} and higher energy doublet e_g orbitals [6]. With further compressed tetragonal distortion, the on-site energy of the xy orbital is lower than that of the xz/yz orbitals, in contrast with the case in CuIr_2S_4 .

In MgTi_2O_4 compound, the pressure behavior is very different from that in CuIr_2S_4 . Fig. S 4 shows the tDOS of low-temperature phase of MgTi_2O_4 at 0 (solid line) and 4 (dash line) GPa. It is found that the unoccupied states around Fermi level decrease, while the occupied states around Fermi level increase with the increase of pressure. This result is consistent with the increasing tendency of resistivity observed experimentally.

From the atomically-resolved density of states of low-temperature phase of MgTi_2O_4 under pressure, as shown in Fig. S 5, we find that the increased tDOS is mainly contributed from the Ti ions. While the contribution from O or Mg is nearly neglected, indicating a rather weak $p-d$ hybridization between Ti-3d and O-2p orbitals.

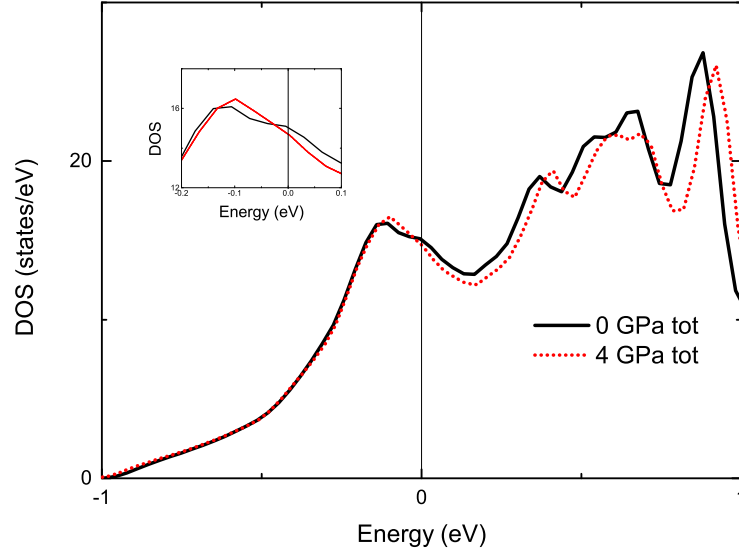


Fig. S 4: (Color online) Total density of states of low-temperature phase of MgTi_2O_4 under different pressures. The inset shows the magnification of the corresponding density of states.

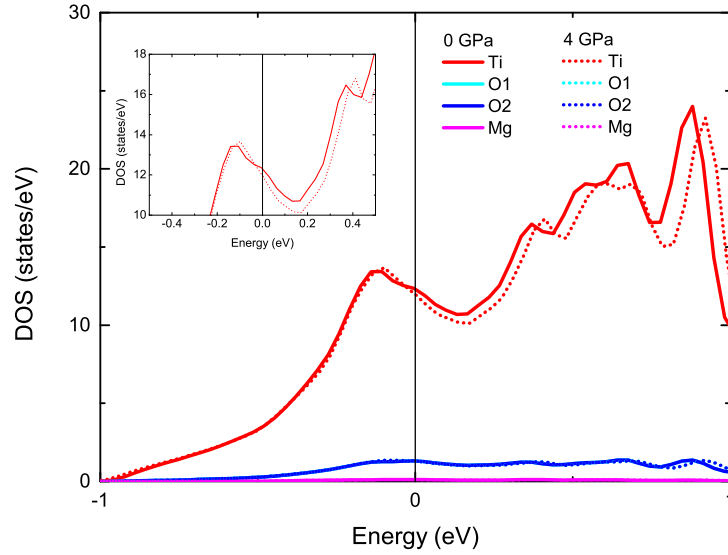


Fig. S 5: (Color online) Atomically-resolved density of states of low-temperature phase of MgTi_2O_4 under different pressures. The inset shows the magnification of the corresponding density of states.

Similarly, the Ti-3d orbitally-resolved density of states of low-temperature phase of MgTi_2O_4 under pressure are given in Fig. S 6. Noted that in MgTi_2O_4 , contrary to CuIr_2S_4 , the tetragonal distortion is compressed with $c < a$ (a (x) and c (z) axes are chosen along the Ti-O direction). The x - and y -component orbitals are affected relatively great by pressure. Although the change of xy orbital occupation is larger than that of xz and yz orbitals, all

these three orbitals are changed under pressure, which has a transfer from unoccupied states to occupied states. In fact, the xz/yz orbital order in MgTi_2O_4 is melted by the pressure [6]. Consequently, the melting orbital order results in the metallic tendency with the increase of pressure, as observed experimentally.

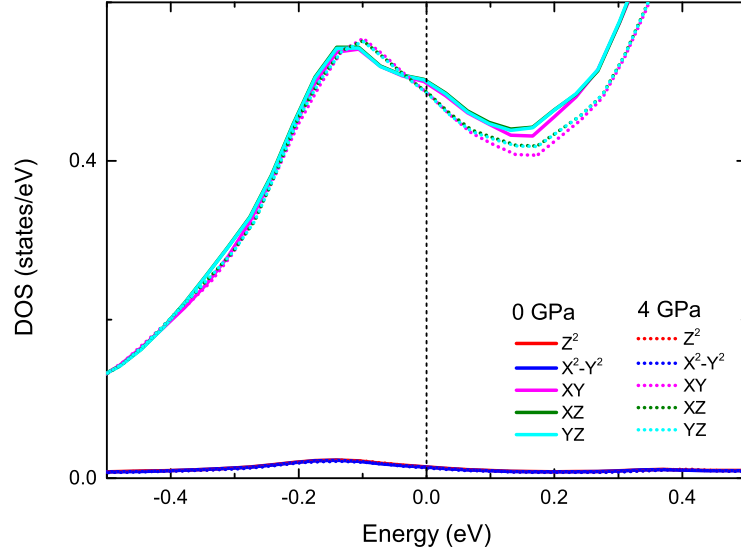


Fig. S 6: (Color online) Ti-3d orbitally-resolved density of states of low-temperature phase of MgTi_2O_4 under different pressures.

To summarize, the opposite pressure behaviors in CuIr_2S_4 and MgTi_2O_4 comes from the different orbital ordering configurations (xy orbital order, and xz/yz orbital order) due to the different tetragonal lattice distortions (elongation and compression of the c -axis) in these two compounds.

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