Opposite Pressure Effects in the Orbitally-Induced Peierls Phase Transition Systems CuIr2S4 and MgTi2O4

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Abstract

The iso-spinel structural systems CuIr2S4 and MgTi2O4 exhibit phase transitions of the similar nature at #24; 230 K and #24; 260 K respectively, which are explained as an orbitally-induced Peierls phase transition. However, in this work, we uncover that applied pressure has opposite pressure effects on the phase transitions in CuIr2S4 and MgTi2O4. As pressure increases, the phase transition temperature (TMI) for CuIr2S4 increases while that for MgTi2O4 decreases. In addition, the phase transition intensity becomes weaker for CuIr2S4 but gets stronger for MgTi2O4 under pressure. Our results indicate that the applied pressure suppresses the metallic phase in CuIr2S4, while enhances that in MgTi2O4. Combining the experimental observations with first-principle electronic structure calculations, we suggest that the opposite pressure effects in CuIr2S4 and MgTi2O4 originate from the different orbital ordering configurations (dxy, dyz/dxz) caused by different lattice distortions in these two systems. Our findings directly indicate that the interplay between the orbital and lattice degrees of freedom plays an important role in the orbitally-induced Peierls phase transition.

Full Text

Preamble

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The iso-spinel structural systems CuIr S and MgTi O exhibit similar phase transitions.

Introduction

The interplay between charge, orbital, spin, and lattice degrees of freedom gives rise to complex physical phenomena, among which orbitally-driven dimensionality transformation in a three-dimensional network is exceptionally rare [**?**, **?**, **?**, **?**, **?**]. A prominent example is the orbitally-induced Peierls phase transition discovered in the iso-spinel structural materials CuIr S and MgTi O [**?**]. At room temperature, both systems possess cubic unit cells belonging to space group Fd3m. Upon cooling, CuIr S undergoes a first-order metal-insulator transition at (cid:24) 230 K, accompanied by a sharp decline in magnetism caused by spin-dimerization and the emergence of octamer ordering in the low-temperature pseudo-tetragonal (strictly monoclinic) phase [**?**, **?**, **?**, **?**]. Similarly, MgTi O exhibits a metal-insulator transition at (cid:24) 260 K, characterized by a sharp reduction in magnetism and the appearance of helical ordering in the low-temperature tetragonal phase [**?**, **?**, **?**]. Both systems form a spin-singlet state in their low-temperature phases [**?**, **?**, **?**, **?**].

D. I. Khomskii and T. Mizokawa proposed that these phase transitions can be understood as orbitally-induced Peierls transitions, where anisotropic orbital coupling arising from a partially filled t g band along a specific direction generates orbitally-induced Peierls instability [**?**]. In CuIr S , the 5d level of the Ir ion is split by the crystal field of the IrS octahedron into a higher-energy doublet e_g level and a lower-energy triplet t g level. Due to the band-Jahn-Teller effect, coupling between 5d_xy orbitals of Ir ions along the xy direction leads to dimerization of Ir -Ir bonds along the [110] direction [**?**]. In MgTi O , the 3d level of the Ti ion is split by the crystal field of the TiO octahedron and the band-Jahn-Teller effect. However, with one electron per Ti^{3} ion, the degenerate 3d_xz and 3d_yz levels are alternately occupied. The coupling of alternating 3d_xz and 3d_yz orbitals of Ti^{3} results in helical dimers with compressed Ti-Ti distances alternating with long bonds along the [001] direction [**?**].

These orbitally-induced phase transitions are sensitive to hydrostatic pressure P [**?**, **?**]. The transition temperature in CuIr S increases with increasing pressure [**?**], though the pressure effect in MgTi O has not been previously reported. In this work, through hydrostatic pressure modulation of lattice structures, we find

that the orbitally-induced Peierls phase transitions in CuIr S and MgTi O exhibit opposite behaviors under pressure. The transition temperature of CuIr S shifts to higher values with increasing pressure, while that of MgTi O shifts to lower values. Moreover, the transport behavior becomes more insulating in CuIr S under pressure, whereas it shows a metallic tendency in MgTi O . Combining experimental observations with first-principles calculations, we propose that these opposite pressure effects originate from different one-dimensional band-Jahn-Teller effects in the two systems.

Experiment

A polycrystalline sample of CuIr S was prepared by solid-state reaction, and a polycrystalline sample of MgTi O was synthesized using spark plasma sintering (SPS). All sample preparation procedures were carried out in argon atmosphere; detailed preparation methods and physical properties have been reported elsewhere [**?**, **?**]. Resistivity measurements were performed using the conventional four-probe method with temperature variation achieved through a closed He-gas cycle refrigerator. For hydrostatic high-pressure resistivity measurements, we employed a clamp-type piston pressure cell with Daphne 7373 oil as the pressure-transmitting medium to ensure high homogeneity. Pressure calibration at room temperature was performed using Cu O powder as a manometer, whose nuclear quadrupole resonance frequency as a function of pressure has been accurately determined [**?**]. First-principles electronic structure calculations were performed using the full-potential linearized augmented-plane-wave (FP-LAPW) method based on density functional theory (DFT) as implemented in the WIEN2k package [**?**].

Results and Discussion

Figures 1(a) and 1(b) show the temperature dependence of resistivity [(cid:26)(T)] for CuIr S and MgTi O under various pressures. Under ambient pressure, CuIr S exhibits a typical metal-insulator transition upon cooling, as shown in Fig. 1 Figure 1: see original paper. The resistivity changes by approximately three orders of magnitude at (cid:24) 230 K from metallic to insulating state. Thermal hysteresis between cooling and heating cycles indicates a first-order phase transition. With increasing pressure, the phase transition shifts to higher temperatures and the hysteresis loop narrows. This pressure-induced trend is consistent with magnetization measurements [**?**] and previous reports [**?**]. Similarly, MgTi O under ambient pressure shows a transition from metallic to insulating state with a two-order-of-magnitude change in (cid:26)(T) at (cid:24) 260 K [Fig. 1(b)]. The transition is also first-order, as evidenced by thermal hysteresis in (cid:26)(T). The nature of the high-temperature phase in MgTi O remains controversial. Zhou et al. suggested that MgTi O is a semiconductor above the transition temperature, but this interpretation is inconsistent with Pauli paramagnetism in the high-temperature regime [**?**]. Isobe et al. proposed that the high-temperature

phase is metallic, with the gradual increase in (cid:26) upon cooling arising from grain boundary resistance [**?**]. In this paper, we treat the first-order phase transitions in both systems as metal-insulator transitions and define the transition temperature uniformly as T_MI.

In contrast to CuIr S , Fig. 1(b) shows that T_MI for MgTi O shifts to lower temperatures and the hysteresis loop expands with increasing pressure. To better understand these pressure effects, Figs. 1(c) and 1(d) present the temperature dependence of differential resistivity [d(cid:26)/dT(T)] under various pressures for CuIr S and MgTi O , respectively. Each d(cid:26)/dT(T) curve shows a peak corresponding to the resistivity change at T_MI, with the peak height quantifying the transition intensity [**?**]. For CuIr S [Fig. 1(c)], the peak moves to higher temperatures and its height decreases with increasing pressure, indicating pressure-induced weakening of the phase transition. For MgTi O [Fig. 1(d)], the peak shifts to lower temperatures and its height increases with pressure, implying pressure-induced enhancement of the phase transition.

The transition temperature T_MI can be precisely determined from the peak in the d(cid:26)/dT(T) curve. Figures 2(a) and 2(b) plot T_MI as a function of pressure for CuIr S and MgTi O , respectively. T_MI for CuIr S increases almost linearly with applied pressure. Linear fitting of T_MI versus pressure was performed using both heating and cooling curves, where values extracted from heating (cooling) curves are denoted as T_MI^H (T_MI^C). For CuIr S , T_MI^H increases at a rate of 21.32 K/GPa, while T_MI^C increases at 22.49 K/GPa, consistent with previously reported values [**?**, **?**]. For MgTi O , T_MI decreases linearly with applied pressure, with T_MI^H decreasing at 6.14 K/GPa and T_MI^C decreasing at 6.20 K/GPa. Meanwhile, the transition width (T), defined as the peak-to-peak width in the d(cid:26)/dT(T) curves as illustrated in the inset of Fig. 1(c), also characterizes pressure-induced changes in the phase transition. The pressure dependence of T for CuIr S and MgTi O is shown in Figs. 2(c) and 2(d), respectively (lines are guides to the eye). With increasing pressure, T decreases in CuIr S while increasing in MgTi O , corresponding to the shrinkage and expansion of thermal hysteresis, respectively. These changes indicate that the phase transition is weakened in CuIr S but enhanced in MgTi O under pressure.

The opposite pressure effects can also be understood by examining changes in the metallic phase as quantified by resistivity values—that is, suppression versus expansion of the metallic phase. Figure 3 [Figure 3: see original paper] shows the resistivity at 40 K ((cid:26)@40K) as a function of pressure for the insulating phases of CuIr S (left axis) and MgTi O (right axis). The 40 K resistivity values for CuIr S increase with pressure, indicating suppression of the metallic phase [**?**], whereas those for MgTi O decrease with pressure, suggesting enhancement of the metallic state. These results clearly demonstrate that hydrostatic pressure has opposite effects on the transport behaviors of CuIr S and MgTi O . In CuIr S , pressure suppresses the metallic phase, leading to increased T_MI, weakened transition intensity, and increased resistivity values. Conversely, in

MgTi O , pressure enhances the metallic phase, resulting in decreased T_MI, increased transition intensity, and decreased resistivity values.

Although the phase transitions in CuIr S and MgTi O are explained within a common framework of orbitally-induced Peierls transitions, our experimental results unambiguously demonstrate opposite pressure effects on transport behavior. Indeed, differences in lattice distortions between the two systems have been noted. Experiments show that lattice structures change differently during phase transitions: in the low-temperature insulating phase, the lattice constant ratio $c/a = 1.033 > 1$ for CuIr S [?], while $c/a = 0.997 < 1$ for MgTi O [?]. In other words, the c-axis elongates in CuIr S but compresses in MgTi O during the phase transition.

It is well known that Peierls transitions typically occur only in one-dimensional metallic chains due to their special band structure [?]. For a Peierls-like transition to occur in a three-dimensional material, a quasi-one-dimensional band structure must be present. In the spinel structure AB X , the crystal field _CF generated by the BX octahedron splits the d-band into a higher-energy doublet e_g sub-band and a lower-energy triplet t g sub-band, as shown in Fig. 4 [Figure 4: see original paper]. In CuIr S and MgTi O , the partially filled t g sub-bands (including degenerate xy, yz, and zx orbitals) play key roles in the phase transitions. However, crystal field splitting alone cannot produce the required quasi-one-dimensional band structure because the xy, yz, and zx levels of the t g sub-band remain degenerate. For partially filled t g sub-bands, the energy levels are further split through lattice elongation or compression—the Jahn-Teller effect—which broadens the t g sub-band to create the necessary quasi-one-dimensional band structure [?]. The resulting anisotropic orbital coupling, arising from this quasi-one-dimensional band, leads to orbitally-dependent electron hopping as described by the Kugel-Khomskii (KK) model [?, ?, ?].

In CuIr S , Jahn-Teller-induced elongation along the c-axis lowers the yz and xz levels of the Ir-t g sub-band. Given the 5d electronic configuration of Ir , the yz and xz levels become fully filled while the xy level is half-filled, as shown in the bottom panel of Fig. 4(a). Strong orbital anisotropy forms along the orbital lobe direction of the xy level—that is, the xy (or [110]) direction shown in the middle panel of Fig. 4(a)—resulting in orbitally-driven Peierls instability. In MgTi O , Jahn-Teller-induced compression along the c-axis lowers the xz and yz levels, as shown in the bottom panel of Fig. 4(b). However, with the $3d^1$ configuration of Ti^3 , the degenerate yz and xz levels are alternately occupied, leading to coupling along alternating xz and yz directions (i.e., chiral bonds along the [001] direction), as shown in the middle panel of Fig. 4(b). Although the coupling in MgTi O involves two directions (xz and yz) and is more complex than in CuIr S , a quasi-one-dimensional band structure still forms, as shown in the bottom panel of Fig. 4(b).

This quasi-one-dimensional band structure helps explain the opposite pressure effects. The Jahn-Teller distortion in the low-temperature phase implies that the phase transition is directly influenced by lattice compression or expansion. In

CuIr S , applied pressure suppresses the elongation tendency along the c-axis, thereby suppressing the metallic phase. This suppression leads to increased T_MI, weakened transition intensity, and increased resistivity values. Conversely, in MgTi O , pressure enhances the compressive tendency along the c-axis, causing expansion of the metallic phase. This enhancement results in decreased T_MI, increased transition intensity, and decreased resistivity values.

This scenario is confirmed by first-principles electronic structure calculations [**?**]. To more clearly reveal pressure effects, calculations were performed at P = 4 GPa. Figures 5(a) and 5(b) show the total density of states (tDOS) for the low-temperature phases under ambient and high pressure for CuIr S and MgTi O , respectively. For CuIr S , some occupied states become unoccupied under pressure, reducing the tDOS near the Fermi level [see inset of Fig. 5 Figure 5: see original paper]. Since physical properties are dominated by electronic states near the Fermi level, this reduction indicates that the system becomes more insulating under pressure, consistent with the experimental increase in resistivity. For MgTi O , some unoccupied states become occupied under pressure [see inset of Fig. 5(b)], opposite to the behavior in CuIr S . Consequently, the system shows enhanced metallic behavior under pressure, in agreement with experimental observations. To better understand pressure effects on electronic properties, we plot the atomically-resolved DOS in the low-temperature phase for CuIr S and MgTi O in Figs. 5(c) and 5(d), respectively. The decreased tDOS in CuIr S originates primarily from Ir ions, with some contribution from S ions due to hybridization between S-3p and Ir-5d orbitals [Fig. 5(c)]. The increased tDOS in MgTi O arises mainly from Ti ions, while contributions from O or Mg are negligible, indicating weak hybridization between Ti-3d and O-2p orbitals [Fig. 5(d)].

In summary, the opposite pressure-dependent behaviors in CuIr S and MgTi O arise from different orbital ordering configurations (xy versus xz/yz ordering) caused by elongated and compressed tetragonal distortions, respectively. The orbitally-induced Peierls phase transition occurs in a three-dimensional network when a quasi-one-dimensional band structure emerges from the interplay between charge, spin, orbital, and lattice degrees of freedom. Such dimensionality reduction phenomena are quite rare. In addition to the CuIr S and MgTi O studied here, layered ruthenate La Ru O and pyrochlore Tl Ru O exhibit similar transitions [**?**, **?**]. For La Ru O , the low-temperature phase shows b > a or c and spin-singlet formation by two S = 1 moments of Ru ions [**?**, **?**], suggesting it should exhibit pressure effects similar to CuIr S . The situation in Tl Ru O is more complex [**?**], having been modeled as a one-dimensional zig-zag Haldane antiferromagnetic chain rather than an orbitally-induced Peierls transition. The S = 1/2 moments of Ru ions do not form spin-singlets but exhibit antiferromagnetic order, and the zig-zag structure would lead to more complicated pressure effects.

Conclusion

In summary, we find that hydrostatic pressure has opposite effects on the orbitally-induced Peierls phase transitions in CuIr S and MgTi O . For CuIr S , the transition temperature T_MI increases and the transition intensity weakens under pressure. In contrast, for MgTi O , T_MI decreases and the transition intensity strengthens with increasing pressure. These observations demonstrate that applied pressure suppresses the metallic phase in CuIr S while enhancing it in MgTi O . Based on first-principles electronic structure calculations, we suggest these differences originate from distinct one-dimensional band-Jahn-Teller effects (xy versus yz/xz) caused by different tetragonal lattice distortions.

Acknowledgments

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FIG. 1: (Color online) Temperature dependence of resistivity [(cid:26)(T)] under different pressures for (a) CuIr S and (b) MgTi O [the inset of (b) shows a magnified view of the phase transition for MgTi O]; temperature dependence of

differential resistivity [d(cid:26)/dT(T)] under different pressures for (c) CuIr S and (d) MgTi O [the inset of (c) shows the definition of T].

FIG. 2 [Figure 2: see original paper]: (Color online) Transition temperature T_MI as a function of pressure for (a) CuIr S and (b) MgTi O (solid lines are fits); pressure dependence of the phase transition width (T) for (c) CuIr S and (d) MgTi O (lines are guides to the eye).

FIG. 3 [Figure 3: see original paper]: (Color online) Resistivity of CuIr S (right axis) and MgTi O (left axis) at 40 K ((cid:26)@40K) as a function of pressure.

FIG. 4 [Figure 4: see original paper]: (Color online) Schematic diagram of quasi-one-dimensional band formation for (a) CuIr S (left) and (b) MgTi O (right) [top panels illustrate distorted IrS and TiO octahedra, middle panels show orbital overlap directions, and bottom panels display one-dimensional band structures].

FIG. 5 [Figure 5: see original paper]: (Color online) (a) Total density of states (tDOS) in low-temperature phases for CuIr S and (b) MgTi O ; atomically-resolved DOS in low-temperature phase for (c) CuIr S and (d) MgTi O [insets show magnified views of the density of states near the Fermi level].

Note: Figure translations are in progress. See original paper for figures.