Optical study of MgTi$_2$O$_4$: Evidence for an orbital-Peierls state

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Dimension reduction due to the orbital ordering has recently been proposed to explain the exotic charge, magnetic and structural transitions in some three-dimensional (3D) transitional metal oxides. We present optical measurement on a spinel compound MgTi$_2$O$_4$ which undergoes a sharp metal-insulator transition at 240 K, and show that the spectral change across the transition can be well understood from the proposed picture of 1D Peierls transition driven by the ordering of $d_{xz}$ and $d_{yz}$ orbitals. We further elaborate that the orbital-driven instability picture applies also very well to the optical data of another spinel CuIr$_2$S$_4$ reported earlier.

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I. INTRODUCTION

In low-dimensional electronic system, Fermi surface instability often occurs at low temperature and drives the system into a symmetry-breaking insulating state. However, such instability is not expected to develop in a three-dimensional (3D) system. Recently, two types of highly exceptional orderings were discovered in two spinel compounds by Radaelli and co-workers: octamer ordering in CuIr$_2$S$_4$ and helical (or chiral) ordering in MgTi$_2$O$_4$. In both cases, sharp metal-insulator transitions (MIT) and spin-dimerizations associated with the structural distortions occur simultaneously. Those extraordinary magnetic, charge and structural transitions have generated a great deal of interest and discussion.

II. EXPERIMENTAL RESULTS

Fig. 1 displays the T-dependent dc resistivity and specific heat curves measured by a Quantum Design PPMS. The detailed description about sample preparation and other characterizations were presented elsewhere. The $\rho(T)$ increases sharply at $T_{MIT}$=240 K. A small hysteresis could be seen for the $\rho(T)$ curve. Accompanying the resistivity change, the specific heat curve displays a peak at the same temperature region. The hysteresis in $\rho(T)$ and the peak anomaly rather than a $\lambda$-shape in specific heat imply that the transition is of the first-order in nature. We note that the $T_{MIT}$ is lower than the reported values in literature, and the peak in specific heat is somewhat broad. This could be ascribed to the difference in the amount of Ti ions being substituted by Mg ions. Additionally, the $\rho(T)$ curve above $T_{MIT}$ also has a negative slope, suggesting non-metallic nature even in the high-T phase. This is similar to CuIr$_2$S$_4$ where a negative slope (though less value) is also seen even in single crystal samples. We think that this behavior may arise from two effects: one is the intrinsic “bad-metal” nature seen quite often in transitional metal oxides for which the mean free
FIG. 1: The dc resistivity and specific heat vs. temperature for MgTi$_2$O$_4$.

FIG. 2: Optical reflectance and conductivity spectra for MgTi$_2$O$_4$ at 320 K.

path of electrons might be close to the lattice constant. The other is the partial substitutions of Ti by Mg ions. The randomly distributed substitutions make the electrons further localized, and also broadens the transitions as seen in resistivity and specific heat curves. However, for consistency, we still use the term "MIT" in the rest part of the paper.

The frequency-dependent reflectance $R(\omega)$ was measured from 40 cm$^{-1}$ to 50,000 cm$^{-1}$ at different T on a Bruker 66v/s and a grating type spectrometer, respectively, using an in-situ gold (below 15,000 cm$^{-1}$) and aluminum (above 10,000 cm$^{-1}$) overcoating technique. Since the material has a 3D cubic structure at high T, we can determine its optical constants from the reflectance measurement on such high-dense polycrystalline sample. Fig. 2 shows the optical reflectance and conductivity spectra at 320 K over broad frequencies. The spectra show two apparent interband transitions. A weak interband transition, labelled as $\alpha$, starting from about 4,000 cm$^{-1}$ (0.5 eV) to 20,000 cm$^{-1}$ (2.5 eV) is due to the transition from $t_{2g}$ to $e_g$ bands, the strong one, $\beta$ peak, with onset near 36,000 cm$^{-1}$ (4.5 eV) is due to the transition from O$_{2p}$ bands to unoccupied states of $t_{2g}$ bands, as we shall explain in detail below. The low-$\omega$ reflectance increases towards unity, evidencing the conducting carrier response. However, the reflectance values are still very low, so that the low-$\omega$ conductivity extracted is almost flat, without showing Drude-like peak. The two sharp peaks below 700 cm$^{-1}$ are infrared phonons.

Fig. 3 shows the R($\omega$) and $\sigma_1(\omega)$ spectra at different temperatures below 8,000 cm$^{-1}$ (1 eV). As T decreases, the low-$\omega$ R($\omega$) decreases, meanwhile the R($\omega$) between 1,600 and 6,000 cm$^{-1}$ increases. As a result, the broad minimum centered near 3,000 cm$^{-1}$ at high T gradually disappears and the R($\omega$) displays a single broad peak above the phonon peaks. In $\sigma_1(\omega)$ spectra, the value below the onset of interband transition $\sim$4,000 cm$^{-1}$ is very low, without showing Drude-like peak. In fact, the conductivity tends to decrease with decreasing $\omega$. The higher values between 200 and 600 cm$^{-1}$ are due to phonons, which should be subtracted when trying to isolate the electronic contribution. Those results suggest that the electrons are rather localized even above $T_{MIT}$. In addition, we find that the low-$\omega$ conductivity decreases with decreasing T, furthering evidencing the non-metallic T-
Fig. 4, we show the &sigma;\(_1\) (ω) at high T (above MIT), the extrapolated values at zero frequency are in good agreement with the dc resistivity data. Another remarkable feature is that the optical spectra show very dramatic change as the temperature decreases across the MIT. It is noted that the R(ω) at our lowest measurement frequency decreases sharply from about 0.7 at 250 K to about 0.5 at 220 K, and the sharp increasing feature towards unity at zero frequency for T>250 K vanishes completely. Such low-ω R(ω) is a characteristic response behavior of an insulator. Correspondingly, we find a rather rapid removal of low-ω spectral weight in &sigma;\(_1\) (ω), leading to the formation of an energy gap. It is noteworthy that the removal of spectral weight shifts only to the region between 3,000 and 6,000 cm\(^{-1}\), as a result, the onset of interband transition occurs at a reduced energy. Above 6,000 cm\(^{-1}\), the optical spectra are almost T-independent. From &sigma;\(_1\) (ω) at the lowest measurement T=10 K, it is easy to identify the optical gap being about 2,000 cm\(^{-1}\) (0.25 eV). Additionally, there appears an abrupt change in phonon structure for temperature below and above T\(_{\text{MIT}}\). In Fig. 4, we show the &sigma;\(_1\) (ω) spectra in an expanded plot of the low frequency region. As seen clearly, a number of new phonon modes appears and the splitting of phonon mode occurs just below the transition. Those results are consistent with the first-order structural change with a lowering of lattice symmetry. Phonon modes in this material were analyzed in detail previously in this work we shall limit our discussion to the electronic behavior.

III. DISCUSSIONS

Let us now analyze the spectral change across the MIT. In the spinel structure, the Ti\(^{3+}\) ion locates at the center of TiO\(_6\) octahedron. As we mentioned above, those octahedra are arranged in 1D chains (along six different directions) through corner-sharing tetrahedra. At high T, the Ti 3d levels are split into triply degenerate \(t_{2g}\) level (orbitals \(d_{xy}, d_{xz}, \text{ and } d_{yz}\)) and a doubly degenerate \(e_g\) level (orbitals \(d_{z^2-r^2}\) and \(d_{x^2-y^2}\)) under local cubic environment. Since Ti\(^{3+}\) has a 3d\(^1\) electron configuration, this single electron occupies the \(t_{2g}\) level with equal distribution on the \(d_{xy}, d_{yz}, d_{xz}\) orbitals, leading to the partially filled \(t_{2g}\) band. The \(e_g\) orbitals are completely empty. The O 2p levels are fully occupied, and locate far away from the Fermi level, although some hybridizations with Ti 3d orbitals exist. This simple picture for the band structure is supported by the first-principle calculation\(^2\). The optical spectra can be easily understood from this simple picture, as illustrated in Fig 4. The lowest interband transition is from the occupied states of \(t_{2g}\) bands to empty \(e_g\) states. This corresponds to the \(\alpha\) peak. Because the direct \(d-d\) transition is forbidden, the observed weak transition is largely due to the hybridization with O 2p band which thus makes the transition allowed. The transition from occupied O 2p band to unoccupied part of \(t_{2g}\) band corresponds to the \(\beta\) peak. However, the observed interband transition energies are lower than the values obtained from the band structure calculation\(^3\). As the \(t_{2g}\) bands are partially filled, the intraband transition should result in metallic response at low frequency. Experimentally, the missing of Drude-like peak suggests that the carriers are rather localized. As discussed above, we think that this could be due to a combination of bad-metal nature of the material and the disorder effect caused by the substitution of Mg for Ti sites. We believe that a successful growth of single crystal with better chemical stoichiometry would reduce such non-metallic response. Nevertheless, the entire physical picture would not be affected.

Since an orbital has a specific shape, an important characteristic for spinels is that the spatial orientations of \(d_{xy}, d_{yz}, \text{ and } d_{xz}\) orbitals are along the 1D chain directions forms by the Ti site ions, respectively. As a result, the bands formed by those orbital levels have 1D characteristic and are susceptible to Peierls instability. This is believed to be the origin of the first order structural change and accompanied MIT. At low T phase, the lattice symmetry is lowered to tetragonal\(^2\). According to the band structure calculations\(^2\), this tetragonal distortion increases the bandwidths of the \(d_{xx}\) and \(d_{yz}\) bands, and decreases that of the \(d_{xy}\). With one electron per Ti ion, the electron occupies the lowest doubly degenerate \(d_{xx}\) and \(d_{yz}\) level. The \(d_{xy}\) level is pushed to higher energy and is unoccupied. In this case, the orbital in \(d_{xy}\) (or \(d_{zx}\)) chain is quarter occupied (i.e. the orbital is occupied in every two sites), which makes the \(d_{xx}\) (or \(d_{yz}\)) band quarter filled. This leads to the Peierls instability and to the formation of a tetramerization superstructure in the \(zx\) and \(yz\) directions: an ordered arrangement of short, intermediate and long bonds along \(d_{yz}\) and \(d_{xz}\) chains (four directions [0,1,1], [0,1,-1], [1,0,1], and [1,0,-1]), respectively, as illustrated in the upper panel of Fig. 4.\(^4\) Associated with the instability, the \(d_{xx}\) and \(d_{yz}\) bands are split, respectively; the lower parts of the split \(d_{xx}\) and \(d_{yz}\) bands are fully occupied, the upper part, to-
FIG. 5: (Color online) (a) Orbital ordering of MgTi₂O₄ at low T. The B-site ions (blue dots) are arranged in chains through corner-sharing tetrahedra. The short (pink), intermediate (black) and long (yellow) bonds together with $d_{yz}$ and $d_{xz}$ orbitals along the chains (four directions [0,1,1], [0,1,-1], [1,0,1], and [1,0,-1]) are displayed. (b) Schematic diagram of the electronic states above and below the MIT temperature. At high T, the 3$d^1$ electron of Ti$^{3+}$ ion occupies the $t_{2g}$ bands with equal distribution on the $d_{xy}$, $d_{yz}$, and $d_{xz}$ orbitals. The $e_g$ bands are at higher energy. The two arrows indicates the two interband transitions. Below $T_{MIT}$, the Ti 3$d^1$ electron occupies the $d_{yz}$ and $d_{xz}$ orbitals, leading to two quarterly filled 1D $d_{yz}$ and $d_{xz}$ bands, which were further split into lower and upper sub-bands due to Peierls instability. Then the lower sub-bands are fully occupied, the upper sub-bands, being mixed with $d_{xy}$ band, are empty, and a gap forms between them.

FIG. 6: (a) The optical conductivity of CuIr₂S₄ at 300 K and 20 K taken from ref. [8]. (b) Schematic diagram of the electronic states above and below the MIT temperature. At high temperature, the 5.5 d-electron of Ir$^{3+}$ ion occupies the $t_{2g}$ bands with equal probability on the $d_{xy}$, $d_{yz}$, and $d_{xz}$ orbitals. Arrow A indicates an interband transition from occupied $t_{2g}$ to empty $e_g$ states. Below $T_{MIT}$, the structure distortion splits the $t_{2g}$ bands. The doubly degenerate $d_{yz}$ and $d_{xz}$ orbitals are fully occupied, however, the 1D band along the $d_{xy}$ chain becomes quarterly filled, which was further split due to Peierls instability. As a result, new states above the Fermi level (i.e. upper sub-band of the split $d_{xy}$ band) were created. Arrow B indicates a new interband transition from occupied $t_{2g}$ to those new states.
tahedral distortion splits the $t_{2g}$ levels and lifts up the $d_{xy}$. Consequently, the doubly degenerate $d_{zx}$ and $d_{yz}$ orbitals are fully filled, only the $d_{xy}$ orbital of Ir$^{+4}$ ion is left to be partially occupied. Then, one can identify $3/4$-filled chains along $d_{xy}$ orbital directions, which also leads to a Peierls instability and formation of a tetramerization superstructure in $d_{xy}$ orbital directions with an ordered arrangement of short, intermediate and long bonds as that in MgTi$_2$O$_4$ (Fig. 2 of ref. [11]). This Peierls instability splits the $d_{xy}$ band into two subbands, which therefore creates new states above the Fermi level (upper sub-band of the split $d_{xy}$ band). The interband transition from occupied $t_{2g}$ to those states results in the new excitation peak B as observed in optical conductivity.

The above optical study leads to tentative identification of the novel orbital Peierls state in such 3D spinel compounds. It highlights the 1D physics driven by the ordering of the orbital degree of freedom in those compounds, despite of their 3D structure. Recently, the orbital ordering picture was also employed to other systems with similar phenomena, like NaTiSi$_2$O$_6$,$^{16,17,18}$ La$_x$Ru$_2$O$_y$,$^{19,20,21}$ VO$_2$,$^{22}$ and many other transition metal oxide compounds,$^{23,24}$ It would be very interesting to study or reexamine their optical and other physical properties in terms of orbital-ordering picture.

IV. CONCLUSIONS

The optical study on MgTi$_2$O$_4$ indicates that the orbital degree plays a crucial role in explaining the spectral evolution with T. Although the $t_{2g}$ spinel systems have a 3D structure, they behave more 1D-like. At high T, MgTi$_2$O$_4$ has a cubic structure, the low-lying excitations are dominated by the three degenerate 1D bands formed by the chains of Ti-site ions through corner-sharing tetrahedra. While at low T, the Ti 3d electrons tend to occupy the doubly degenerate $d_{yz}$ and $d_{zx}$ orbitals, leading to two quarter-filled 1D $d_{yz}$ and $d_{zx}$ bands. The optical transitions could be well explained by the Peierls splitting of the two 1D bands. We further elaborate that the orbital-ordering picture applies also extremely well to the optical data of CuIr$_2$S$_4$. The application of the 1D physics to 3D compounds with specific orbital occupations has important implication for understanding similar phenomena in other transitional metal oxides.

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