3 Orbitally Induced Peierls Mechanism for Charge-Orbital Orderings in Transition-Metal Compounds

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1 Introduction

1.1 Orbital degrees of freedom in transition-metal compounds

Transition-metal compounds exhibit rich physical properties which have been attracting overwhelming research activities in the field of condensed matter physics [1-4]. Their electrical and magnetic properties are governed by the transition-metal d electrons. The d orbitals have fivefold degeneracy in the atomic limit and are split into three-fold degenerate t_{2g} (xy, yz, and zx) and two-fold degenerate $e_q (3z^2 - r^2 \text{ and } x^2 - y^2)$ orbitals under the cubic ligand field. When the d electrons become itinerant in transition-metal compounds with octahedral or tetrahedral coordination, they are accommodated by the t_{2g} and/or e_g bands creating multiple Fermi surfaces. In quasi one-dimensional materials such as TaS₃, a charge-density wave or modulation of charge density is induced by a Peierls transition in which the Fermi-surface nesting and the electronlattice interaction play essential roles [5]. Also spin-density wave or modulation of spin density and direction in metallic transition-metal compounds such as LaFeAsO can be explained by nesting of the Fermi surfaces and the weak or moderate d-d Coulomb interaction [6]. On the other hand, the d electrons can be localized due to the strong d-d Coulomb interaction (Mott insulators and Wigner crystal states). In the localized case, the valence electrons are accommodated by the atomic like t_{2g} and e_g orbitals. The partially occupied t_{2g} or e_g orbitals exhibit orbital orderings due to Jahn-Teller effect [7], Kugel-Khomskii mechanism [8], and spin-orbit interaction [9]. For example, one of the e_q orbitals is occupied in multiferroic TbMnO₃ providing the $3x^2 - r^2/3y^2 - r^2$ orbital ordering which is stabilized by the strong Jahn-Teller effect, breaking the e_g orbital degeneracy through elongation of the MnO₆ octahedra [10]. As for the t_{2g} orbitals, the Jahn-Teller effect is relatively weak and the Kugel-Khomskii mechanism plays more important roles in determining the spin and orbital states via the superexchange interaction [4]. When one or two of the t_{2q} orbitals are occupied/unoccupied in 3d and 4d oxides, the Jahn-Teller effect, the Kugel-Khomskii mechanism, and the spin-orbit interaction may compete to determine the orbital ordering [11]. In YTiO₃, LaVO₃, and YVO₃ with one or two of the t_{2g} orbitals occupied, the orbital ordering is governed by the Kugel-Khomskii mechanism with possible interplay with the Jahn-Teller distortion and the tilting of the MO₆ octahedron (*M*=transition metal). In LaTiO₃ and Ca₂RuO₄, the spin-orbit interaction can play an important role with the Kugel-Khomskii effect and the Jahn-Teller distortion [12]. When one or two of the t_{2g} orbitals are occupied/unoccupied in insulating 5d oxides such as Sr₂IrO₄, the orbital degeneracy is lifted by the strong spin-orbit interaction [13].

Transition-metal compounds with MO_6 octahedra harbor various crystal structures such as perovskite, rocksalt, rutile, corundum, and spinel structures. In the perovskite (or layered perovskite) structure, the MO_6 octahedra share their corners and the transition-metal sites form a simple cubic lattice (or a square lattice). The transfer terms between t_{2g} orbitals at the neighboring sites are effectively given by the M-ligand-M hybridization governed by the transfer integral ($pd\pi$) and the ligand-to-d charge-transfer energy Δ [4]. In the spinel systems (or triangular lattice systems such as CdI₂-type and NaFeO₂-type structure), the MO_6 octahedra share



Fig. 1: (a) Spinel structure of $CuIr_2S_4$ and its pyrochlore lattice of Ir. (b) Ir 5d yz, zx, and xy orbitals form one-dimensional bands along (0, 1, 1) or (0, 1, -1) direction, (1, 0, 1) or (1, 0, -1) direction, and (1, 1, 0) or (1, -1, 0) direction, respectively. (c) 5.5 electrons (0.5 holes) per Ir are distributed to the three one-dimensional bands of yz, zx, and xy orbitals.

their edges and the transition-metal sites form a pyrochlore lattice (or a triangular lattice) as shown in Fig. 1. The transfer integrals between t_{2g} orbitals at the neighboring sites are given by the direct M-M transfer integral ($dd\sigma$) or the indirect M-ligand-M transfer governed by ($pd\pi$) and Δ .

1.2 Metal-insulator transitions in transition-metal compounds

Both in the corner-sharing and edge-sharing systems, once the *d* electrons are localized (Mott insulators and Wigner crystal states), their magnetic properties are primarily described by models made up from localized spins and orbitals. The inter-site charge excitation across the band gap provides the superexchange interaction between the localized spins and orbitals. In this situation, the interplay between spin ordering and orbital ordering is described by the Kugel-Khomskii model [8]. Several systems including V_2O_3 , Ca_2RuO_4 , $YNiO_3$, and NiS_2 exhibit metal-insulator transitions with cooling which can be viewed as Mott transitions [1–3]. The *d* electrons are localized below the transition temperature. Interestingly, the transitions of V_2O_3 , Ca_2RuO_4 , and $YNiO_3$ are accompanied by strong lattice distortions associated with orbital ordering (V_2O_3 and Ca_2RuO_4) or charge disproportionation (YNiO_3). In general, local-density approximation (LDA) band structure calculations fail to explain the magnitude of band gap (Mott gap).

When the *d* electrons are itinerant, the edge-sharing systems often exhibit more complicated behaviors than the corner-sharing ones due to the direct M-M transfer terms. Most of the metallic perovskites such as SrVO₃, SrCoO₃, SrRuO₃, Sr₂RuO₄, ReO₃, and SrIrO₃ are paramagnetic or ferromagnetic metals without any metal-insulator transitions. On the other hand, several spinel or triangular lattice systems such as MgTi₂O₄, LiRh₂O₄, CuIr₂S₄, and LiVS₂ are metallic at room temperature and undergo exotic metal-insulator transitions with cooling. Their metalinsulator transitions are accompanied by strong lattice distortion which will be discussed in the following chapters. The insulating phases are nonmagnetic and can be described by LDA band structure calculations if the lattice distortion are properly taken into account (There are some exceptions: It is still difficult to describe the nonmagnetic insulating states of MgTi₂O₄ and LiVO₂ by LDA). The lattice distortion is often characterized by the metal-metal dimerization or trimerization which is driven by the direct M-M transfer. It is expected that the geometry of Fermi surfaces plays an important role in the metal-insulator transitions of the relatively itinerant systems.

2 Orbitally induced Peierls mechanism

2.1 Case study on CuIr₂S₄

In the itinerant case, the moderate Coulomb interaction between the d electrons (d-d Coulomb interaction) remains and, therefore, a possible instability towards spin and/or charge ordering may occur due to Fermi-surface nesting. In addition, even without the d-d Coulomb interaction, the electron-lattice interaction can provide a lattice modulation and consequent charge modulation with a periodicity corresponding to the Fermi-surface nesting. Such charge and/or spin ordering (charge-density wave and/or spin-density wave) as well as the lattice modulation can open an energy gap at the Fermi level. Especially when the Fermi surfaces are purely onedimensional (planes in the k-space), Fermi-surface nesting is always realized and the system inevitably undergoes a Peierls transition in which an energy gap is formed at the Fermi level due to the charge and/or spin and/or lattice modulation. Even though the band structure near the Fermi level is changed by the modulation to open the energy gap, the d orbital occupation is not drastically changed by the charge/spin/lattice modulation. Usually, there is no interplay between spin/charge/lattice modulation and the d-orbital degrees of freedom in the itinerant transition-metal compounds. Yet there are several transition-metal compounds such as $CuIr_2S_4$ and LiRh₂O₄ which exhibit a charge/lattice modulation and band Jahn-Teller like distortion, suggesting an interaction between the charge ordering and the orbital ordering. Since the t_{2a} bands are degenerate near the Fermi level in the cubic systems, the tetragonal distortion can be stabilized by removing the band degeneracy due to band Jahn-Teller effect. Motivated by these peculiar phase transitions, the idea of an orbitally induced Peierls mechanism has been introduced [14, 15]. Historically, it has been applied to explain the complicated charge and orbital ordering in spinel-type t_{2q} transition-metal compounds in which the transition-metal sites form a pyrochlore lattice. Among them, $CuIr_2S_4$ with a pyrochlore lattice structure shows a metal-insulator transition around 230 K [16] with tetragonal distortion and octamer charge ordering [17]. In this subsection, we consider the orbitally induced Peierls description of CuIr₂S₄. Under octahedral coordination, the lobes of the e_g (t_{2g}) orbitals are directed towards (between)

the ligands. Therefore, in an edge-sharing octahedron, the t_{2q} orbitals have substantial transfer integrals between the neighboring transition-metal sites. Let us neglect the indirect transfer between the t_{2q} and e_q orbitals via the ligand orbitals and consider the direct ones between the t_{2g} orbitals on the pyrochlore lattice. Here, the transfer integrals between the t_{2g} orbitals are restricted by the cubic symmetry. As shown in Fig. 1(a), the Ir sites form a pyrochlore lattice in which Ir₄ tetrahedra share their corners. Along the $(1, \pm 1, 0)$ direction of the pyrochlore lattice, only the transfer integrals between the xy orbitals survive by symmetry. Also along the $(1, 0, \pm 1)$ and $(0, 1, \pm 1)$ directions, only the zx and yz orbitals have non-zero transfer integrals, respectively. Consequently, the xy, yz, and zx orbitals form one-dimensional bands along the $(1,\pm 1,0), (1,0,\pm 1), \text{ or } (0,1,\pm 1)$ directions, respectively. In CuIr₂S₄ there are 5.5 electrons (0.5 holes) in the t_{2g} bands. If the 0.5 holes are distributed in the three one-dimensional bands, each band accommodates 1/6 holes. The six pairs of one-dimensional Fermi surfaces (six pairs of parallel planes in the three-dimensional k-space) have a Peierls instability due to electronlattice or electron-electron interaction. Since the paired parallel planes are spanned by the wave vectors along $(1,\pm 1,0)$, $(1,0,\pm 1)$, $(0,1,\pm 1)$ with a magnitude of $\pi/6$ (the unit of the wave vectors is 1/a where a is the Ir-Ir distance.), the pyrochlore lattice undergoes a distortion with 12 times periodicity along the $(1,\pm 1,0)$, $(1,0,\pm 1)$, and $(0,1,\pm 1)$ directions. Such a Peierls instability of the pyrochlore lattice has two disadvantages from a theoretical point of view. First, the 12-times lattice modulation along the six directions is very complicated and the elasticenergy loss is expected to be large. Second, the indirect Ir-Ir transfers via the ligands, which are neglected in the above argument, are not negligibly small in CuIr₂S₄. There are finite transfer integrals between the different t_{2q} orbitals. Since the one-dimensional xy, yz, zx bands are degenerate in energy, the one-dimensional Fermi surfaces can be strongly deformed by the xyyz, yz-zx, and zx-xy indirect transfer terms. Indeed, the calculated Fermi surfaces for the cubic $CuIr_2S_4$ have no Fermi-surface nesting [18–20]. In addition, the predicted charge ordering is inconsistent with the octamer charge-ordering observed in CuIr₂S₄. Here, it should be noted that the calculated band structure (and the Fermi surfaces) for the high temperature metallic phase are roughly consistent with the yz, zx, and xy bands mixed with the xy-yz, yz-zx, and zx-xyindirect transfer terms [18]. For the low temperature insulating phase, the band gap opening by the lattice distortion is partially explained by band structure calculations [19, 20]. In addition, the unique electronic and lattice properties of CuIr₂S₄ harbor the metastable disordered state induced by light or x-ray illumination [21–24]. In the metastable state, the crystal symmetry is at least partially recovered indicating that the long-range charge-order is destructed [21]. However, the electrical conductivity is much smaller than that of the high temperature metallic phase, and the energy gap at the Fermi level remains [22]. In the weak coupling limit, the energy gap should be closed once the long-range order of the charge and lattice modulation is destroyed. The observation of the metastable disordered state with bad conductivity suggests that the Ir-Ir dimers can survive without long-range order and that the conductivity is derived from a kind of bi-polaron hopping in the valence-bond liquid state.

The multi-orbital Fermi surfaces of $CuIr_2S_4$ can be reorganized in a band Jahn-Teller manner to enhance their nesting character for spin- and/or charge-density wave formation. When the



Fig. 2: (a) Sketch of the yz, zx, and xy bands under a band Jahn-Teller distortion (elongated along the z-axis) for $CuIr_2S_4$. (b) Charge and orbital ordering with the octamer on the Ir pyrochlore lattice in $CuIr_2S_4$. The Ir 5d xy orbitals of the Ir^{4+} site form the strong Ir-Ir bonds along the (1, 1, 0) and (1, -1, 0) directions. (c) Charge and orbital ordering on the Rh pyrochlore lattice in $LiRh_2O_4$. (d) Ir^{4+} or Rh^{4+} tetramer model for $CuIr_2S_4$ or $LiRh_2O_4$.

cubic lattice is elongated along the z direction (c axis) while keeping its volume, the transfer integral between the xy orbitals becomes larger than that between the yz orbitals (and that between the zx orbitals) as illustrated in Fig. 2(a). Consequently, the width of xy band is much larger than that of the yz and zx bands. When the 0.5 holes are accommodated by the xy band, one-dimensional Fermi surfaces are formed along the $(1, \pm 1, 0)$ directions which are spanned by $Q = \pi/2$. Then the pyrochlore lattice shows modulation with four-times periodicity along $(1, \pm 1, 0)$ which can stabilize the $Ir^{3+}-Ir^{4+}-Ir^{4+}$ charge ordering. The $Ir^{4+}-Ir^{4+}$ bond length is shortened due to the molecular orbital formation of the xy orbitals. The four Ir⁴⁺-Ir⁴⁺ dimers created along the $(1, \pm 1, 0)$ directions form the Ir⁴⁺ octamer as shown in Fig. 2(b). The predicted charge ordering is consistent with the x-ray diffraction result reported by Radaelli et al. [17] Also the charge disproportionation between Ir^{3+} and Ir^{4+} is confirmed by core-level x-ray photoemission spectroscopy [22]. In this sense, the charge contrast along the $(1, \pm 1, 0)$ chains is much stronger than that of the weak coupling charge-density wave. The observed Ir 5dband width is comparable to that predicted by LDA [22], indicating weak electronic correlation. Therefore, the localized Ir⁴⁺-Ir⁴⁺ dimers are stabilized by the strong electron-lattice interaction rather than the electronic correlation. The fluctuations of the Ir-Ir dimers are observed even above T_c in CuIr₂S₄ by means of pair distribution function measurements [25].

2.2 Square lattice models for orbitally induced Peierls transition

In the present subsection, we extend the idea of the orbitally induced Peierls mechanism and apply it to simplified two- and three-band models of transition-metal compounds with a square lattice. In order to introduce the basic idea of the orbitally induced Peierls mechanism, we start from a yz/zx two-band model on a square lattice [see Fig. 3(a)]. The transfer term along the x (y) direction for the neighboring zx (yz) orbitals is given by t_{zx} (t_{yz}). Note that the transfer integrals between the neighboring zx (or yz) orbitals are positive. The zx and yzorbitals form one-dimensional bands with energy dispersions of $E = 2t_{zx}\cos(k_x)$ and E = $2t_{yz}\cos(k_y)$, respectively. Here, the unit for k_x and k_y is 1/a where a is the lattice constant of the square lattice. When the two one-dimensional bands accommodate some holes, onedimensional Fermi surfaces are created as displayed in the middle panel of Fig. 3(b). In a realistic system, however, the two bands are mixed by the transfer term between the yz and zx orbitals (t_{uz-zx}) and consequently the Fermi surfaces become two-dimensional as shown in the right panel of Fig. 3(b). Such two-dimensional Fermi surfaces have a hidden instability by the combination of band Jahn-Teller and Peierls effect. Let us assume that the square lattice is compressed along the x-axis and elongated along the y-axis. Then the magnitude of t_{zx} becomes larger than that of t_{yz} under the distortion. If the ratio of t_{zx}/t_{yz} is large enough, only the wider zx band can accommodate the holes (band Jahn-Teller effect). Without t_{uz-zx} , the zx band forms a one-dimensional band with nesting vector Q [see the middle panel of Fig. 3(c)]. The orbitally induced Peierls state is robust against the indirect transfer term t_{yz-zx} due to the energy splitting between the yz and zx orbitals. Under the effect of t_{yz-zx} , a quasi one-dimensional Fermi surface dominated by zx character is formed as shown in the right panel of Fig. 3(c) and gives nesting vector Q' rather than Q. In addition to the charge and/or spin modulation along the x-axis, the unit cell is doubled along the y-axis. In this scenario, by introducing the band Jahn-Teller distortion and ferro-type orbital ordering, charge- and/or spin-density waves are realized due to the Fermi-surface nesting. When the band Jahn-Teller distortion alone is enough to lower the energy, the orbital is restricted by it and then the Peierls instability follows (orbital restrictive case). On the other hand, the energy gain by the band Jahn-Teller distortion is not a necessary condition for the orbitally induced Peierls transition. Depending on the band width ratio t_{zx}/t_{yz} and the elastic-energy loss, the band Jahn-Teller distortion alone may not be enough to lower the energy since the system remains metallic. A Fermi-surface change by virtual Jahn-Teller distortion can be followed by a Peierls transition with wave vector Q or Q' to stabilize an insulating state with charge and lattice modulation. If the energy gain by the Peierls gap opening is large enough to compensate the elastic-energy loss by the band Jahn-Teller and Peierls distortion, one of the yz and zx orbitals is selected and the square lattice is distorted in a band Jahn-Teller manner (orbital selective case).

The orbitally induced Peierls state is robust against the interlayer transfer term t_z . With the t_z term illustrated in the right panel of Fig. 3(a), the zx and yz band dispersions are $E = 2t_{zx}\cos(k_x) + 2t_z\cos(k_z)$ and $E = 2t_{yz}\cos(k_y) + 2t_z\cos(k_z)$ providing the warped Fermi surfaces as shown in Fig. 4(a). Here, the unit for k_z is 1/c where c is the lattice constant along



Fig. 3: (a) Two-band model with yz/zx orbitals on a square lattice. t_{zx} (t_{yz}) is a transfer integral along the x (y) between zx (yz) orbitals. t_{yz-zx} is a transfer integral along the diagonal direction between zx and yz orbitals. (b) Left and middle: Band structure and Fermi surface without yz-zx mixing by t_{zx} and band Jahn-Teller effect. Right: Fermi surface with yz-zx mixing by t_{yz-zx} and without band Jahn-Teller effect. (c) Left and middle: Band structure and Fermi surface with yz-zx mixing by t_{yz-zx} mixing by t_{yz-zx} and with band Jahn-Teller effect. Right: Fermi surface. Right: Fermi surface with yz-zx mixing by t_{yz-zx} and with band Jahn-Teller effect. Right: Fermi surface with yz-zx mixing by t_{yz-zx} and band Jahn-Teller effect.

the z direction. With the band Jahn-Teller effect, the yz orbital is more stabilized and has smaller band width to be fully occupied. The holes are taken by the zx orbitals and their Fermi surfaces have the nesting vector Q'' as illustrated in Fig. 4(b). The yz band may reach the Fermi level around $k_z = \pi$ creating a small hole pocket as shown in the right panel of in Fig. 4(b). Under the Peierls distortion along the x and z directions due to the zx Fermi surface, the zxFermi surface disappears while the yz Fermi pocket can remain. Such a metallic state with charge-orbital modulation would be relevant for several layered materials including IrTe₂.

Fig. 4: (a) Fermi surfaces of a yz/zx two-band model with interlayer transfer integral t_z and without band Jahn-Teller effect. (b) Fermi surfaces of a yz/zx two-band model with interlayer transfer integral t_z and band Jahn-Teller effect. (c) Left and middle: Band dispersion and Fermi surface of a yz/zx/xy three-band model with yz and zx fully occupied. Right: Fermi surface of a yz/zx/xy three-band model with anisotropic xy-zx mixing.

In the next step, let us extend the idea of orbitally induced Peierls mechanism to a yz/zx/xy three-band model with a xy Fermi surface. Let us assume that the yz and zx bands are fully occupied by electrons and the remaining xy band with $E = 2t_{xy}\cos(k_x) + 2t_{xy}\cos(k_y) + 2t_{xy-xy}\cos(k_x+k_y)$ forms a closed Fermi surface. Note that t_{xy} and t_{xy-xy} are positive and negative, respectively. With such a circular Fermi surface without orbital degeneracy, an orbital instability or band Jahn-Teller effect is not expected. However, if a large energy gain by Peierls gap-opening is expected after a geometrical change of the Fermi surface (Lifshitz transition) by a sort of orbital anisotropy, the system may find its way to lower the symmetry for better Fermi-surface nesting. In the present model, a slight rhombic distortion lifts the degeneracy between the yz/zx bands and the xy-yz and xy-zx couplings become nonequivalent. Consequently, the Fermi surface of the xy band undergoes a Lifshitz transition and obtains good nesting character as schematically shown in Fig. 4(c).

2.3 Triangular lattice models for orbitally induced Peierls transition

Let us consider a yz/zx/xy three-band model on a triangular lattice. The transfer terms along the $(1, 0, 0), (1/2, \sqrt{3}/2, 0), \text{ and } (-1/2, \sqrt{3}/2, 0)$ directions (under the X-, Y-, and Z-coordinates with $X = 1/\sqrt{2}(x+y)$, $Y = 1/\sqrt{6}(-x+y+2z)$, $Z = 1/\sqrt{3}(x-y+z)$) are given by t_{xy} , t_{yz} , and t_{zx} for the neighboring xy, yz, zx orbitals. The xy, zx and yz orbitals form one-dimensional bands with energy dispersions with $E = 2t_{xy}\cos(k_x)$, $E = 2t_{zx}\cos(k_x/2+\sqrt{3}k_y/2)$, and $E = 2t_{yz}\cos(-k_x/2+\sqrt{3}k_y/2)$, respectively, as shown in the left panel of Fig. 5(a). Here, the unit for k_x and k_y is 1/a where a is the lattice constant of the triangular lattice. When the three one-dimensional bands accommodate one hole as shown in Fig. 5(a), one-dimensional Fermi surfaces with 5/6 filling are created as illustrated in the middle panel of Fig. 5(a). In a realistic system, the three bands are mixed by the transfer terms between them (t_{yz-zx}, t_{zx-xy}) , and t_{xy-yz}) and consequently, the Fermi surfaces become two-dimensional as shown in the right panel of Fig. 5(a). When the three one-dimensional bands accommodate one electron as shown in Fig. 5(b), one-dimensional Fermi surfaces with 1/6 filling are created as illustrated in the middle panel of Fig. 5(b). With the transfer terms t_{yz-zx} , t_{zx-xy} , and t_{xy-yz} , six electron pockets around the M point and one hole pocket at the zone center are created as shown in the right panel of Fig. 5(b). Similarly to the square lattice model, the triangular lattice can by deformed along one of the bond directions (The equilateral triangle is deformed into an isosceles one). Let us assume that the triangle is compressed along the horizontal axis (X-axis). Since $t_{xy} > t_{yz} = t_{zx}$ under the lattice distortion, only the wider xy band can accommodate the electron as illustrated in the left panel of Fig. 5(c). The xy band forms a one-dimensional band with nesting vector Q [see the middle panel of Fig. 5(c)]. The orbitally induced Peierls state is robust against the indirect transfer terms t_{xy-yz} and t_{xy-yz} due to the Jahn-Teller energy splitting between the xy and yz/zx orbitals. Under the effect of t_{xy-yz} and t_{xy-yz} , a quasi one-dimensional Fermi surface dominated by xy character still keeps the nesting condition. Since the xy band accommodates one electron and is half-filled, the periodicity along the X-axis is doubled with xy-xy dimers as shown in the right panel of Fig. 5(c).

Under the strong trigonal ligand field, the yz, zx, and xy orbitals are reconstructed to be the a_{1g} and e_g^{π} orbitals. This situation is relevant for the corundum system where the MO_6 octahedra share their faces along the *c*-axis. Yet, in several triangular lattice systems such as Na_xCoO₂, the a_{1g} and e_g^{π} orbitals are also more convenient to describe their Fermi surfaces. For example, when *x* is larger than 0.5 in Na_xCoO₂, the pudding-mold like a_{1g} bands form isotropic Fermi surfaces and the e_g^{π} orbitals are fully occupied [see the left and middle panels of Fig. 5(d)] [26, 27]. If the anisotropic hybridization between the a_{1g} and one of the e_g^{π} orbitals deforms the Fermi surface for better nesting with Q' as illustrated in the right panel of Fig. 5(d), then the orbitally induced Peierls mechanism is triggered to provide charge and orbital ordering. Such an anisotropic $a_{1g}-e_g^{\pi}$ coupling would be induced, for example, by the anisotropic Na ion arrangement in Na_xCoO₂ [28, 29].

Fig. 5: (a) Left: Band dispersion for a triangular lattice three-band model (yz/zx/xy orbitals)with one hole per site. k represents k_x or $k_x/2+\sqrt{3}k_y/2$ or $k_x/2-\sqrt{3}k_y/2$. t_{yz-zx} , t_{zx-xy} , and t_{xy-yz} are the inter-orbital transfer terms between the yz/zx/xy orbitals. Middle and right: Fermi surfaces without and with interorbital transfer terms. (b) Band dispersion, Fermi surfaces without and with inter-orbital transfer terms for the three-band model with one electron per site. (c) Left and middle: Band structure and Fermi surfaces with band Jahn-Teller effect. Right: Orbital ordering by the orbitally induced Peierls effect on the triangular lattice (half filled case). (d) Left and middle: Band dispersion and a_{1g} Fermi surface with fully occupied e_g^{π} . Right: Fermi surfaces deformed by anisotropic $a_{1g}-e_g^{\pi}$ mixing. Q' indicates a possible nesting vector.

Fig. 6: (*a*) Band gap opening and charge modulation for the weak coupling case. (b) Band gap opening and charge modulation for the strong coupling case.

2.4 Effect of strong coupling

In the previous arguments, it is implicitly assumed that the electron lattice interaction (or the d-d Coulomb interaction) responsible for the Peierls transition is assumed to be a weak perturbation to the metallic state. Therefore, perfect Fermi-surface nesting is a necessary condition for the Peierls transition. In such a weak-coupling case, the charge and lattice modulation is sinusoidal with relatively small amplitude as shown in Fig. 6(a). The mean field treatment works well to describe the transition, and the energy gap E_G and the transition temperature T_c should satisfy $E_G/k_BT_c \sim 3.5$. However, even in one of the most weakly correlated systems CuIr₂S₄, E_G/k_BT_c is about 10 (E_G is about 0.2 eV and T_c is 230 K). This indicates that the electron-lattice interaction is rather strong and that local charge- and lattice-fluctuations can survive even in the disordered phase. Under strong coupling, the charge is localized at the strongly distorted bond as shown in Fig. 6(a), and its fluctuation remains above T_c . Indeed, Ir-Ir dimers are observed in the cubic phase above T_c for CuIr₂S₄ [25]. Most of the transition-metal compounds discussed in the next chapter fall in the strong coupling regime.

3 Application of the orbitally induced Peierls mechanism to transition-metal compounds

3.1 Spinel systems

Apart from the metal-insulator transition in CuIr_2S_4 , the orbitally induced Peierls mechanism can be applied to that of LiRh_2O_4 around 170 K accompanied by the $\text{Rh}^{3+}/\text{Rh}^{4+}$ charge ordering [30, 31]. The charge ordering with four-times periodicity of $\text{Rh}^{3+}-\text{Rh}^{4+}-\text{Rh}^{4+}$ occurs along the (1, 1, 0) and (1, -1, 0) chains of the Rh pyrochlore lattice. This is similar to that of CuI_2S_4 and can be explained by the orbitally induced Peierls instability. However, the experimentally observed charge-ordering pattern of LiRh_2O_4 is different from the octamer structure of CuIr_2S_4 and satisfies the Anderson condition where each Rh₄ tetrahedron exactly accommodates two Rh⁴⁺ to minimize the Coulomb repulsion energy between them [31]. As a result, the Rh³⁺-Rh³⁺-Rh⁴⁺-Rh⁴⁺ arrangement along the (1, 1, 0) chain is shifted relative to that along the neighboring (1, -1, 0) chain as shown in Fig. 2(c). Shiomi *et al.* proposed that the electronic correlation, which is expected to be stronger in the 4*d* oxides than the 5*d* sulfides, is responsible for destabilization of the octamer structure which does not satisfy the Anderson condition [31]. If the electronic correlation is negligibly weak, the Rh₄ tetrahedron can be fully occupied by Rh⁴⁺ keeping the Rh³⁺-Rh³⁺-Rh⁴⁺-Rh⁴⁺ arrangement along the (1, ±1, 0) chains as illustrated in Fig. 2(d).

LiRh₂O₄ undergoes the cubic to tetragonal transition (c > a) at 220 K which is followed by a Rh³⁺/Rh⁴⁺ charge ordering and the Rh⁴⁺-Rh⁴⁺ dimerization. The Rh³⁺-Rh⁴⁺ charge fluctuations [32] and the local Rh⁴⁺-Rh⁴⁺ dimers [31] are observed between 220 K and 170 K, indicating that orbital symmetry-breaking plays a more important role in LiRh₂O₄. In the case of CuIr₂S₄, the local Ir-Ir dimers are observed even in the cubic phase [25], while the Rh-Rh dimers are observed only in the tetragonal phase. Most probably, the bond directions of the Rh-Rh dimers tend to be aligned through the stronger electronic correlation. While the electron-lattice interaction (or the dimerization) drives the distortion with the four-times periodicity of the chains in CuIr₂S₄, the inter-site electron-electron interaction plays a primary role in LiRh₂O₄.

MgTi₂O₄ exhibits a metal-insulator transition around 260 K which is accompanied by a structural transition from cubic to tetragonal (c < a) [33]. The metal-insulator transition is accompanied by the Ti³⁺-Ti³⁺ dimerization with suppression of magnetic susceptibility. The nearestneighbor Ti-Ti distances become nonequivalent and spirals of long and short Ti-Ti bonds are formed [34]. In the itinerant picture, the yz and zx bands get wider than the xy band under the tetragonal distortion and accommodate the Ti 3d electrons. Consequently, the one-dimensional yz and zx bands are formed along the $(0, 1, \pm 1)$ and $(1, 0, \pm 1)$ directions which respectively accommodate 0.5 electron per Ti site. The quarter filled yz and zx bands are stabilized by the orbital ordering with four-times periodicity of yz-yz and zx-zx dimers as shown in Fig. 7(a). The orbital ordering is consistent with the spirals of long and short Ti-Ti bonds. It is also possible to explain the orbital ordering based on the Kugel-Khomskii mechanism in the localized picture [35] although it is difficult to describe the metal-insulator transition. Starting from the itinerant picture, Heitler-London like correlation effects can be included to provide the Ti-Ti dimer with the spin-singlet bond character. The localized nature of the Ti-Ti dimer has experimentally been suggested from the survival of the local Ti-Ti dimers above the transition temperature [36] and the multiplet structure of the Ti 2p x-ray absorption spectrum [37]. Interestingly, both the itinerant model and the localized model provide the same conclusion on the orbital ordering of MgTi₂O₄. Also it should be noted that the LDA+U like approach cannot describe the spin-singlet ground state of MgTi₂O₄.

AlV₂O₄ harbors V²⁺/V³⁺ charge ordering along the (1, 1, 1) direction [38, 39] and exhibits peculiar V³⁺ trimerization and V²⁺ tetramerization [40]. (The combination of the trimer and the tetramer can be viewed as a heptamer [39].) Along the (1, 1, 0), (1, 0, 1), and (0, 1, 1) chains

Fig. 7: (a) yz-yz-zx-zx orbital ordering for $MgTi_2O_4$. (b) V^{2+}/V^{3+} charge ordering for AlV_2O_4 . The yellow circles indicate the orbitally disordered V^{3+} sites. In the left panel for the V^{3+} Kagome layer, the V^{3+} trimers are formed by the yz/zx, zx/xy, and yz/xy orbital ordering. In the right panel for the V^{2+} Kagome layer, the tetramers are formed with the V^{2+} sites (yz/zx/xy) in the neighboring triangular lattice layer.

which cross the (1, 1, 1) Kagome and triangular lattice layers, the xy, zx, and yz bands are quarter filled, respectively. Similarly to CuIr₂S₄ and MgTi₂O₄, each chain is expected to have a lattice distortion with four-times periodicity due to V²⁺(Kagome)-V²⁺(tri)-V³⁺(Kagome)-V³⁺(tri) charge ordering. Along the (1, -1, 0), (1, 0, -1), and (0, 1, -1) chains in the Kagome layers, the xy, zx, and yz bands are half filled respectively. The Peierls instability gives lattice distortion with two-times periodicity (alternating short and long bonds) to each chain, resulting in the trimer formation. As a result, while the V³⁺ sites harbor the trimers confined in the Kagome layer, the V²⁺ sites form the tetramers between the Kagome and triangular lattice layers. We speculate that the quarter-filled chains trigger this peculiar charge ordering and multimer formation.

The magnetite Fe₃O₄ harbors Fe³⁺-Fe²⁺-Fe³⁺ trimers below the Verwey transition temperature at 125 K [41–43]. In Fe₃O₄, since the minority spin t_{2g} electrons are tied to the majority spin t_{2g} and e_g electrons via Hund coupling at the Fe²⁺ site, it is not straightforward to apply the orbitally induced Peierls mechanism to describe the trimer. However, it is still possible to discuss the Fe³⁺-Fe²⁺-Fe³⁺ arrangement along the chains based on a half filled spin-polarized t_{2g} band. For example, when the yz band is selected by the minority spin electron, it provides site-centered charge modulation along the $(0, 1, \pm 1)$ chains forming an Fe³⁺-Fe²⁺-Fe³⁺ arrangement.

3.2 Pyrochlore systems

Several pyrochlore systems exhibit interesting metal-insulator transitions with possible charge or orbital ordering. However, none of them exhibit band Jahn-Teller like distortions. Since MO_6 octahedra share their conners in the pyrochlore structure, their t_{2g} band dispersions are strongly affected by the indirect t_{2g} -ligand- t_{2g} transfer terms and become more complicated than those of the spinel structure. Therefore, the energy gain by the band Jahn-Teller distortion, if it may exist, tends to be reduced.

Among the transition-metal oxides with pyrochlore structure, CsW₂O₆ exhibits a unique metalinsulator transition around 215 K which is accompanied by W trimers [44-46]. The crystal symmetry of the insulating phase just below the transition is still cubic although the tetrahedron of W sites in the pyrochlore lattice is strongly distorted by the trimerization [46]. While Ir^{3+}/Ir^{4+} (Rh³⁺/Rh⁴⁺) charge disproportionation is observed in CuIr₂S₄ (LiRh₂O₄), W⁵⁺/W⁶⁺ charge disproportionation is absent in CsW₂O₆ [47]. The absence of the band Jahn-Teller effect and the charge disproportionation is consistent with the complicated band structure. Streltsov et al. proposed that the Fermi surfaces calculated with the W 5d spin-orbit interaction satisfy nesting conditions with $(\pi, 0, 0)$, $(0, \pi, 0)$, and $(0, 0, \pi)$ and the metal-insulator transition can be explained by the simple Peierls mechanism [48]. However, it is still difficult to explain the trimer formation. Nakai and Hotta emphasized the electronic correlation effect due to a flat band created by the pyrochlore lattice geometry and the spin-orbit interaction [49]. Under the strong spin-orbit interaction, there are $\frac{1}{\sqrt{2}}(y'z'+iz'x')$ \uparrow , $\frac{1}{\sqrt{2}}(y'z'-iz'x') \downarrow$, $\frac{1}{\sqrt{6}}[2x'y' \uparrow -(y'z'+iz'x') \downarrow]$, and $\frac{1}{\sqrt{6}}[2x'y'\downarrow + (y'z'-iz'x')\uparrow]$ in the j = 3/2 branch. (Here, the x'-, y'-, and z'-axes are along the M-O bonds of the octahedron. In the spinel case, they are identical to the x-, y-, and z-axes in the figures.) The former two orbitals have substantial transfer integrals along the z'-axis which is roughly along the M-ligand-M bond or the chain direction. If such orbitals are selectively occupied, they can form a quasi one-dimensional band along one of the chains. The virtual one-dimensional bands are quarter filled and provide the lattice distortion with four-times periodicity along the chain. Once the short W-W bond is created, the two WO₆ octahedra with the shortened W-W bond are rotated and the other WO₆ octahedron connected to the two octahedra gets closer to the W-W bond. As a result, W trimers can be formed as shown in Fig. 8(a). In addition, such orbitals would be consistent with the zigzag chain order which was proposed by Hirai *et al.* for the low temperature phase [45]. If $z'x' \pm ix'y'$ and $(x'y' \pm iy'z')$ orbitals are occupied in the (0, 1, 1) and (1, 0, 1) chains (or (0, 1, -1) and (1, 0, -1) chains), the zigzag structure of the short W-W bonds can be formed through the distortion with the four-times periodicity along the chains.

There is no clear understanding for the difference between the multimer case and the zigzag chain case. Most probably, the rotation and Jahn-Teller distortion of the MO_6 octahedra should be analyzed more carefully. The zigzag chains are also formed in the nonmagnetic insulating phase of Tl₂Ru₂O₇ [50].

Fig. 8: (a) W trimers and possible orbital ordering for CsW_2O_6 . (b) Zigzag chains of short W-W bonds. The thick solid lines indicate the short bonds.

3.3 Triangular lattice systems

The MO_6 octahedra share their corners and form a triangular lattice of M sites as shown in Fig. 9(a). Among the triangular lattice systems, NaTiO₂ exhibits a transition to the nonmagnetic insulating state with lattice distortion from trigonal to monoclinic [51, 52]. The direct t_{2g} - t_{2g} transfer term would be important just like in the spinel systems. However, in band structure calculations for NaTiO₂ [53] as well as CoO₂, the t_{2g} band dispersion is upwardly convex around the Γ point indicating the indirect M-O-M transfer is dominant. In addition, the trigonal ligand field can break the three-fold degeneracy and the t_{2q} orbitals are split into the a_{1q} $\left[\frac{1}{\sqrt{3}}(xy+yz+zx)\right]$ and $e_g^{\pi}\left[\frac{1}{\sqrt{3}}(xy+e^{\pm 2\pi i/3}yz+e^{\pm 4\pi i/3}zx)\right]$ orbitals. As shown in the left panel of Fig. 5(b), the xy, yz, and zx orbitals may form one-dimensional bands along the (1, 0, 0), $(1/2, \sqrt{3}/2, 0)$, and $(-1/2, \sqrt{3}/2, 0)$ directions of the X-, Y-, and Z-coordinates. Inclusion of the mixing between the xy, yz, and zx orbitals provide the one hole pocket at the zone center (with a_{1g} character) and the six hole pockets around the M points (with e_q^{π} character) for the t_{2q}^1 system as shown in the right panel of Fig. 5(b). The Fermi surfaces calculated for the trigonal phase by Subedi [53] are roughly consistent with this simple picture except the hole pocket at the zone center. The absence of the hole pocket can be assigned to the trigonal ligand field which stabilizes the a_{1g} orbital. If the xy orbital has larger band width due to the contraction

Fig. 9: (a)Triangular lattice layers of edge-sharing MO_6 octahedra. (b) Electronic configurations for Ti^{3+} and Ir^{4+} . (c) Orbital ordering for the monoclinic phase.

along the X direction $[X = (x-y)/\sqrt{2}]$, the Ti 3d electron is accommodated by the quasi onedimensional xy band. Since the xy band is half-filled [Fig. 9(b)], the Ti-Ti dimerization with the two-times lattice modulation is realized by the Peierls transition [Fig. 9(c)]. However, the triangular lattice of NaTiO₂ is not clearly deformed from equilateral to isosceles. Instead, the TiO₆ octahedron is compressed to stabilize the xy orbital [52].

IrTe₂ with the Ir triangular lattice exhibits a structural phase transition at ~ 270 K from trigonal to monoclinic, accompanied by anomalies in electrical resistivity and magnetic susceptibility [54–57] An electron diffraction study by Yang *et al.* shows that the structural transition is accompanied by a superstructure with wave vector of Q = (1, 0, -1)/5 [57]. Such a superstructure can be explained by a charge-density wave driven by a perfect or partial nesting of multi-band Fermi surfaces [57]. However, the monoclinic distortion can be attributed to a band Jahn-Teller like instability, suggesting the orbitally induced Peierls mechanism. In addition, a charge modulation of Ir charge disproportionation is indicated by an Ir 4*f* x-ray photoemission study [58]. Although the formal valence of Ir is +4, partial charge transfer from Te to Ir induces a Ir³⁺/Ir⁴⁺ mixed valence and the Ir⁴⁺-Ir⁴⁺ dimers are arranged as illustrated in Fig. 10(b).

LiVO₂ is a classical system with V³⁺ (t_{2g}^2) which exhibits a magnetic-nonmagnetic transition around 500 K with V trimerization [1,59–61]. Pen *et al.* pointed out that the *xy*, *yz*, and *zx* orbitals are occupied at the V sites connected by the $(1,0,0), (1/2, \sqrt{3}/2, 0)$, and $(-1/2, \sqrt{3}/2, 0)$ bonds of the *X*-, *Y*-, and *Z*-coordinates (see Fig. 5) [62]. When *yz/zx*, *zx/xy*, and *xy/yz* orbitals are occupied, respectively, at the three V sites in the trimer, the three V³⁺ form three singlet bonds resulting in the nonmagnetic ground state with the trimer. Although the multiplet structure of V 2*p* x-ray absorption spectroscopy of LiVO₂ indicates localized V 3*d* electrons with Hund coupling, it is still possible to make a spin-singlet ground-state from three V³⁺ in the trimer [63]. Interestingly, such trimerization can be described by the orbitally induced Peierls mechanism or the orbital selective Peierls mechanism [64] in a manner similar to MgTi₂O₄. The triangular lattice can be decomposed into chains running along $(1,0,0), (1/2, \sqrt{3}/2, 0),$ and $(-1/2, \sqrt{3}/2, 0)$ directions. Therefore, the *xy*, *zx*, and *yz* orbitals can form quasi onedimensional bands along the three directions which are 2/3 filled and can induce orbital order-

Fig. 10: (a) Orbital ordering in $NaTiO_2$ (b) Charge and orbital ordering in $IrTe_2$. (c and d) Orbital ordering in $LiVO_2$ and $LiVS_2$. The thick solid lines indicate the short bonds.

ing and dimerization with three-times periodicity. The xy-xy, zx-zx, and yz-yz dimers are formed along the (1,0,0), $(1/2,\sqrt{3}/2,0)$, and $(-1/2,\sqrt{3}/2,0)$ chains, respectively. Here, the degenerate xy, yz, and zx bands are strongly modified by the inter-orbital transfer terms (t_{yz-zx} , t_{zx-xy} , and t_{xy-yz} ,) and lose the nesting condition as illustrated in Fig. 5(a) or (b). Therefore, the electron-lattice interaction should be strong enough to stabilize the dimer bonds even without perfect Fermi-surface nesting.

The dimer bonds are indicated by the thick lines in Fig. 10(c). The xy-xy and zx-zx dimers overlap at the intersection site of the (1,0,0) and $(1/2,\sqrt{3}/2,0)$ chains where both of the xy and zx orbitals are occupied. The $(-1/2,\sqrt{3}/2,0)$ chain goes through the other site of the xyxy (zx-zx) dimer, and the xy and yz (zx and yz) orbitals are occupied at the site. As a result, the three V³⁺ sites are connected by the xy-xy, zx-zx, and yz-yz singlet bonds as shown in Fig. 10(c). Here, it should be noted that the singlet bond picture is inconsistent with the Hund coupling of the t_{2g}^2 configuration which may weaken the V-V bond. It is still an open question whether the trimer is sustainable against the electronic correlation although its stability was suggested by cluster model calculations [63]. Li_{2-x}MoO₃ with Mo⁴⁺ (t_{2g}^2) on a triangular lattice also exhibits Mo trimers similar to LiVO₂ [65]. The Mo trimers can survive up to the highest temperature indicating the trimer due to the orbitally induced Peierls mechanism or the orbital selective Peierls mechanism is more stable in the more itinerant systems. Orbitally induced Peierls transitions can be classified into two categories: orbital restrictive or orbital selective. In case of CuIr₂S₄ and LiRh₂O₄, the t_{2g} orbital is restricted by band Jahn-Teller effect. As for AIV_2O_4 and $LiVO_2$, one of the t_{2q} orbitals is selected depending on the bond direction.

Katayama *et al.* found that LiVS₂ undergoes a metal-insulator transition at 314 K which is accompanied by V trimerization similar to LiVO₂ [66]. Since the V 3*d* electrons are more itinerant in LiVS₂ than LiVO₂, the orbitally induced Peierls description is more suitable. Also in LiVS₂, the *xy*-*xy*, *zx*-*zx*, and *yz*-*yz* singlet bonds are stabilized by the strong lattice distortion. E_G/k_BT_c (E_G is the magnitude of the band gap, and T_c is the transition temperature.) is about 6 indicating strong coupling [67]. Indeed, short range order of the zigzag chain structure and lattice fluctuations are observed above the transition temperature [68]. Interestingly, the zigzag chain structure can be stabilized by the ferro-type orbital order as shown in Fig. 10(d). In the figure, the *xy* and *zx* orbitals are occupied at every V site and the *xy*-*xy* and *zx*-*zx* dimers form the zigzag chains. There are two other domains where the *zx* and *yz* orbitals or *yz* and *xy* orbitals are occupied at every site. Since the *d* electrons in LiVS₂ are rather itinerant, the band Jahn-Teller effect and the Fermi-surface nesting can collaborate to provide the ferro-type orbital order and the lattice modulation with three-times periodicity.

BaV₁₀O₁₅ with V²⁺/V³⁺ mixed valence exhibits a structural transition at 123 K driven by V trimerization [69] and V 3*d* orbital order similar to LiVO₂ [70]. At the three V³⁺ sites in the trimer, the *xy*, *yz*, and *zx* orbitals are unoccupied respectively. It is possible to create molecular orbitals from them and to put an extra electron in the bonding molecular orbital. Therefore, the trimer is expected to be stable against electron doping (up to the doping level of 1/3 per V site). Indeed, the V trimer in BaV₁₀O₁₅ is likely to accommodate one extra electron. The extra electron is shared by the three V sites. In addition, V²⁺/V³⁺ charge fluctuation is observed by x-ray photoemission spectroscopy [71] indicating that the ground state is a superposition of V²⁺-V³⁺, V³⁺-V²⁺-V³⁺, and V³⁺-V²⁺ configurations.

3.4 Honeycomb lattice systems

Since the honeycomb lattice cannot be decomposed into chains, it is not straightforward to apply the orbitally induced Peierls description to its charge-orbital ordering. The dimerization on the honeycomb lattice can be more exactly described by the theory of Jackeli and Khomskii [72] in which the orbital degeneracy is broken by the bond selection. However, in this subsection, following the idea of orbitally induced Peierls mechanisms, we would like to discuss dimerization induced by possible orbital order.

Assuming ferro-type orbital order of xy, local xy-xy bonds can be created for t_{2g}^1 or t_{2g}^5 systems as shown in Fig. 11(a). Since the number of xy-xy bonds is limited, the energy gain by the singlet bond formation may not be enough for a metal-insulator transition by orbitally induced Peierls mechanism. However, several insulating systems undergo magnetic-nonmagnetic transitions by dimerization. TiCl₃ and TiBr₃ with Ti³⁺ (t_{2g}^1) become nonmagnetic with Ti-Ti dimerization below 217 K [73] and below 178 K [74], respectively . The dimerization can be described by ab-initio band structure calculations [75, 76]. Ilmenite MgVO₃ with V⁴⁺ (t_{2g}^1) also exhibits V-V dimers on the honeycomb lattice below 500 K [77]. Similar to TiCl₃ and TiBr₃, ferro-type orbital order is expected as shown in Fig. 11(a).

Fig. 11: (a) Orbital ordering for t_{2g}^1 on a honeycomb lattice. (b and c) Orbital ordering for t_{2g}^2 on a Kagome lattice in Li_2RuO_3 . (d) Orbital ordering for t_{2g}^3 on a Kagome lattice in $MoCl_3$. The thick solid lines indicate the short bonds.

4d and 5d honeycomb systems with t_{2g}^1 and t_{2g}^5 configurations (such as Na₂IrO₃ and RuCl₃) do not show dimerization at ambient pressure due to the strong spin-orbit interaction [78, 79]. In this context, it is striking that Li₂RuO₃ exhibits a metal-insulator transition about 540 K due to Ru-Ru dimerization on the honeycomb lattice [80]. In Li₂RuO₃, the Ru⁴⁺ (t_{2g}^4) ion has two holes in the t_{2g} orbitals. Assuming ferro-type orbital order of xy and yz holes, xy-xy and yzyz singlet bonds can be created as illustrated in Fig. 11(b). Although the arrangement of the short Ru-Ru bonds (indicated by the thick lines in the figure) is consistent with the experimental result [80], the number of these bonds is limited, and the energy gain by the singlet bonds may not be enough. Kimber *et al.* pointed out that the $\frac{1}{\sqrt{2}}(yz+zx)$ orbitals form π -bonds in addition to the $xy-xy\sigma$ -bonds [81]. Under the orbital order with yz, $\frac{1}{\sqrt{2}}(zx+xy)$ and xy, $\frac{1}{\sqrt{2}}(yz+zx)$, the short Ru-Ru bonds are stabilized by the double bonding in the nonmagnetic phase of Li₂RuO₃. Interestingly, a recent experimental work reports that the xy-xy σ -bonding is more robust than the π -bonding by the yz and zx orbitals and that the partially disordered phase can be created by optical breaking of the π bonding [82]. TcCl₃ with Tc³⁺ (t_{2q}^4) has the Tc-Tc dimers on the honeycomb lattice [83]. The arrangement of the dimers is the type of Fig. 11(a) rather than that of Fig. 11(c).

Another striking system is MoCl₃ which undergoes a magnetic-nonmagnetic transition around 585 K with the strong Mo-Mo dimerization below 585 K [84–86]. The Mo-Mo dimerization in the honeycomb lattice is illustrated in Fig. 11(d). The Mo³⁺ ion has three holes in the t_{2g} orbitals in MoCl₃. Therefore, in addition to the xy-xy σ -bonds and the $\frac{1}{\sqrt{2}}(yz+zx)$ π -bonds, the $\frac{1}{\sqrt{2}}(yz-zx)$ orbitals may form δ -bonds although δ -bonding is usually weak.

Fig. 12: (a) Orbital ordering for t_{2g}^1 on a Kagome lattice. (b) Orbital ordering for $Na_2Ti_3Cl_8$. The thick solid lines indicate the short bonds.

3.5 Kagome lattice systems

 $Na_2Ti_3Cl_8$ consists of a Ti²⁺ (t_{2a}^2) Kagome lattice and undergoes a two step structural phase transitions around 210 K (partial trimerization) and 190 K (full trimerization) on cooling [87-89]. It is possible to describe the spin singlet trimer based on localized spins [90]. On the other hand, the substantial lattice distortion of the trimerization by itself suggests that a strong Ti-Ti interaction plays a vital role beyond the localized picture. Therefore, it is also useful to describe the trimerization based on the itinerant picture: an orbitally induced Peierls mechanism [91]. In contrast to the honeycomb lattice, the Kagome lattice can be decomposed into chains running along the (1,0,0), $(1/2,\sqrt{3}/2,0)$, and $(-1/2,\sqrt{3}/2,0)$ directions. Therefore, the yz, zx, and xy orbitals can form quasi one-dimensional bands along the three directions. As illustrated in Fig. 12(a), each one-dimensional band is half filled and induces a lattice modulation with twotimes periodicity (The short Ti-Ti bonds are indicated by the thick lines). The short Ti-Ti bonds along the three directions form the trimers in agreement with the experimental observation. The Mo⁴⁺ (t_{2a}^2) Kagome lattice in Zn₂Mo₃O₈ hosts Mo trimers similar to Na₂Ti₃Cl₈ [92, 93]. The Mo trimers with six t_{2q} electrons are stable up to the highest temperature available indicating that the trimer is more stable in the more itinerant system. At the three Mo sites in the trimer, one can construct a molecular orbital with bonding character from the unoccupied t_{2q} orbitals to accommodate an extra electron. Indeed, the Mo trimers can survive in $LiZn_2Mo_3O_8$ with seven Mo 4d electrons in the Mo trimer [92, 93]. The Mo trimers have localized spin-1/2 due to the extra electron and form a geometrically frustrated spin-1/2 triangular lattice. This can be viewed as a cluster Mott insulating state [94, 95] providing exotic spin-liquid behaviors [92,93]. Very recently, Mo³⁺/Mo⁴⁺ charge fluctuation were observed by x-ray photoemission spectroscopy [96]. This situation is similar to the V trimer in $BaV_{10}O_{15}$ and is different from the W trimer in CsW₂O₆. A possible relationship between the charge-fluctuation and the spin-liquid behavior should be examined by further studies. Nb₃Cl₈ has a Kagome lattice with Nb trimers. Since Nb²⁺: Nb³⁺ = 1:2 in Nb₃Cl₈, the Nb trimer accommodates seven t_{2q} electrons and hosts localized spin-1/2 [97-99]. The spin-1/2 triangular lattice of the cluster Mott insulating state is a new playground to study spin liquids and exotic superconductivity [100]. Interestingly, Nb₃Cl₈ exhibits a further magnetic-nonmagnetic transition around 90 K although orbital degeneracy is already lifted. Haraguchi *et al.* proposed charge disproportionation between the trimers [99]. Apart from the fabrication of atomic layer systems, the origin of this exotic phase transition will be a target of future work.

4 Conclusion

By combining band Jahn-Teller effect (or local orbital polarization) and Peierls instability (or local singlet bond formation), the orbitally induced Peierls mechanism can explain charge-orbital ordering in a wide range of nonmagnetic (spin singlet) transition-metal compounds with edgesharing octahedra and t_{2q} orbital degrees of freedom. With the ferro-type t_{2q} orbital ordering mostly due to the band Jahn-Teller effect, quasi one-dimensional bands are created by one of the t_{2q} orbitals. Consequently, charge ordering and/or dimerization are induced by Fermi-surface nesting. In some cases, intervening quasi one-dimensional bands provide trimers or tetramers. Without ferro-type orbital ordering, collaboration between local orbital polarization and singlet bond formation can stabilize nonmagnetic ground states with multimers. In most of the cases, both the itinerant model and the localized model predict the same charge-orbital order, probably due to the approximate one-to-one correspondence between the Fermi surface geometry and the bond direction. However, there are still several unsolved questions even in the most studied CuIr₂S₄. The energy landscape for various lattice distortion should be elucidated in order to fully understand the space and time fluctuation and evolution of the Ir-Ir dimers and the orbital polarization. Since the electronic correlation is stronger in the Ti oxides (NaTiO $_2$ and MgTi₂O₄) than the Ir chalcogenides, the Heitler-London like wave function should be taken into accounts to describe their electronic properties. Such a theoretical approach on the multiband lattice model is highly challenging. As for the t_{2g}^2 and t_{2g}^4 systems such as LiVO₂ and Li₂RuO₃, the effect of Hund coupling should be clarified theoretically and experimentally.

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