

## V.1

# ELECTRONIC STATE IN Co-OXIDE -SIMILAR TO CUPRATES?-

S. Maekawa, W. Koshibae  
*Institute for Materials Research Tohoku University, Sendai 980-8577, Japan*

**Abstract:** It is shown that the electronic structure in layered cobalt oxides with hexagonal crystal structure is described as a Kagomé lattice hidden in the  $\text{CoO}_2$  layer which consists of stacked triangular lattices of oxygen ions and of cobalt ones. The Kagomé lattice is derived because of the degeneracy of  $t_{2g}$  orbitals. We discuss that the electronic structure causes a variety of unique properties in the cobalt oxides such as superconductivity and ferromagnetism, which are in contrast to the high- $T_c$  cuprates.

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## 1. INTRODUCTION

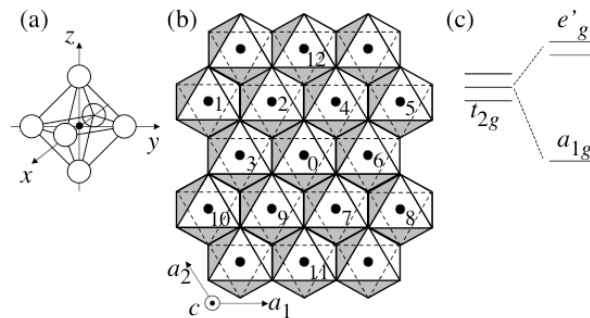
There is a growing interest in cobalt oxides (cobaltates) with layered hexagonal crystal structure. They show giant thermopower [1-4], giant Hall effect [5], ferromagnetism [6,7] depending on the material details. In particular, the superconductivity [8] has received special attention [9-21] in connection to the high- $T_c$  superconductivity in cuprates. This is because of the following reasons: (i) The superconductivity occurs on the triangular lattice in cobaltates whereas it does on the square lattice in cuprates, (ii) ferromagnetism appears in cobaltates and antiferromagnetism does near the superconducting states in cuprates, and (iii) the active electronic states are  $t_{2g}$

with orbital degeneracy and the  $e_g$  without degeneracy in cobaltates and cuprates, respectively.

It has been pointed out that the giant thermopower in cobaltates is caused by the degeneracy of the  $t_{2g}$  orbitals of Co ions [22, 23]. Here, we show that the orbital degeneracy brings about a Kagomé lattice electronic structure hidden in the  $\text{CoO}_2$  triangular crystal lattice [15]. This is because the electron hopping occurs between Co ions via neighboring oxygens by exchanging the orbitals in the triangular lattice. In Sec. 2, the electronic structure is examined. The unique physical properties of cobaltates are discussed in Sec.3 based on the electronic structure.

## KAGOMÉ IN TRIANGULAR LATTICE

The  $\text{CoO}_2$  layer is formed by the edge-shared  $\text{CoO}_6$  octahedra which are compressed along  $c$ -axis (Fig. 1). The rhombohedral distortion of the  $\text{CoO}_6$  octahedra is measured by the deviation of the O-Co-O bond angle from  $90^\circ$ ,  $95^\circ \sim 99^\circ$  [2, 24-27]. The distortion leads to the crystal-field splitting in  $t_{2g}$  states of  $3d$  electrons as shown in Fig. 1(c).



*Figure V:1:1.* (a)  $\text{CoO}_6$  octahedron. Solid and open circles indicate cobalt and oxygen ions, respectively. (b)  $\text{CoO}_2$  layer.  $c$  and  $a_1$  axes are along  $(1,1,1)$  and  $(-1,1,0)$  directions in  $xyz$  coordinate system shown in (a). The numbers (0 ~12) on solid circles are the labels of Co sites. (c) The crystal-field splitting of the distorted  $\text{CoO}_6$  octahedron.  $e'_g$  is used to distinguish from the  $e_g$  ( $x^2-y^2$  and  $3z^2-r^2$ ) states.

The wave functions are expressed as

$$(|xy\rangle + |yz\rangle + |zx\rangle)/\sqrt{3} \quad (1)$$

for the  $a_{1g}$  state and

$$(|xy\rangle + e^{\pm i\frac{2\pi}{3}}|yz\rangle + e^{\pm i\frac{4\pi}{3}}|zx\rangle)/\sqrt{3}$$

for the doubly degenerate states where  $|xy\rangle$ ,  $|yz\rangle$  and  $|zx\rangle$  denote the wave functions of the  $t_{2g}$  states. The  $a_{1g}$  state extends to the  $c$ -axis whereas the  $e'_{1g}$  states spread over the plane perpendicular to the  $c$ -axis. Since the apex oxygens approach the plane in the distorted  $\text{CoO}_6$  octahedra, the  $a_{1g}$  state is stabilized [28] for an electron.

The band calculation [24] in  $\text{Na}_{0.5}\text{CoO}_2$  has shown that the energy splitting between  $a_{1g}$  and  $e'_{1g}$  states at the  $\Gamma$  point is  $\sim 1.6\text{eV}$  which is the total band width of the  $t_{2g}$  manifold and the  $a_{1g}$  state is higher than the  $e'_{1g}$  states.

This fact shows that the energy splitting does not originate in the crystal field due to the distortion but is determined by the kinetic energy of electrons.

Let us consider the hopping-matrix-elements between neighboring  $3d$  orbitals of cobalt ions neglecting the rhombohedral distortion. There are two mechanisms for the hopping of an electron: one is the hopping integral between adjacent  $3d$  orbitals, and another is owing to the hopping between a  $3d$  orbital of a cobalt ion and a  $2p$  one of an oxygen ion. First, let us consider the latter mechanism, i.e., the hopping of a  $3d$  electron through the  $2p$  orbital on the neighboring oxygen. The  $\text{CoO}_2$  layer in the hexagonal structure is expressed as a triangular lattice of cobalt ions sandwiched by those of oxygen ions, i.e., both the upper and lower layers of oxygens form triangular lattices. The lower layer is drawn by broken lines in Fig. 1(b). In the following, the  $t_{2g}$  orbitals on the  $i$ -th cobalt ion are expressed as  $|xy, i\rangle$ ,  $|yz, i\rangle$  and  $|zx, i\rangle$ , respectively. The  $\text{CoO}_6$  octahedra share edges each other, so that Co-O-Co bond angle is  $\pi/2$ . The state  $|xy, 0\rangle$  has a hopping matrix element with  $|zx, 7\rangle$  through the  $2p_x$  orbital of the oxygen ion which exists in the upper layer and shares  $\text{CoO}_6$  octahedra involving cobalt ions 0 and 7, respectively (Fig. 2).

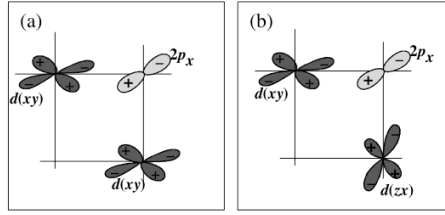


Figure V:1:2. Hopping-matrix between neighboring Co ions. (a) There is no hopping matrix between  $|xy,0\rangle$  and  $|xy,7\rangle$ . (b) There is the hopping matrix between  $|xy,0\rangle$  and  $|zx,7\rangle$ .

The hopping matrix element ( $t$ ) is expressed as  $t \sim t_{pd}^2/\Delta(>0)$ , where  $\Delta$  is the energy level of the  $2p_x$  orbital measured from that of  $t_{2g}$  states and  $t_{pd}$  is the hopping integral between the  $2p_x$  and  $|xy,0\rangle$  (or  $|zx,7\rangle$ ) orbitals. There also exists a hopping matrix element between  $|zx,0\rangle$  and  $|xy,7\rangle$  which is due to the  $2p_x$  orbital of an oxygen ion on the lower layer. On the other hand, there is no hopping matrix element between  $|xy,0\rangle$  and  $|xy,7\rangle$  because of the symmetry. In the same way, we find the hopping matrix elements between the following pairs of orbitals: ( $|xy, 0\rangle, |zx, 2\rangle$ ), ( $|zx, 0\rangle, |xy, 2\rangle$ ), ( $|xy, 0\rangle, |yz, 4\rangle$ ), and ( $|yz, 0\rangle, |xy, 4\rangle$ ). As a result, the hopping matrices of a  $3d$  electron in  $\vec{a}_1$ ,  $\vec{a}_2$  and  $\vec{a}_1 + \vec{a}_2$  directions where  $\vec{a}_1$  and  $\vec{a}_2$  are the elementary translation vectors along  $a_1$  and  $a_2$  axes, are expressed as

$$\begin{array}{c} xy \quad yz \quad zx \\ xy \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & t \\ 0 & t & 0 \end{pmatrix}, \quad \begin{array}{c} xy \quad yz \quad zx \\ \begin{pmatrix} 0 & 0 & t \\ 0 & 0 & 0 \\ t & 0 & 0 \end{pmatrix} \end{array} \quad \text{and} \quad \begin{array}{c} xy \quad yz \quad zx \\ \begin{pmatrix} 0 & t & 0 \\ t & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \end{array}, \quad (3)$$

respectively. In the Fourier-transformed representation, we have the tight binding Hamiltonian

$$H_t = \sum_{\vec{k}, \sigma, \gamma, \gamma'} \epsilon_{\vec{k}, \gamma, \gamma'} c_{\vec{k}, \sigma, \gamma}^\dagger c_{\vec{k}, \sigma, \gamma'}, \quad (4)$$

with

$$\epsilon_{\vec{k}} = 2t \begin{bmatrix} 0 & \cos(k_1 + k_2) & \cos k_2 \\ \cos(k_1 + k_2) & 0 & \cos k_1 \\ \cos k_2 & \cos k_1 & 0 \end{bmatrix}, \quad (5)$$

where  $k_1$  and  $k_2$  are the component of the wave vector  $\vec{k}$  of the triangular lattice spanned by  $\vec{a}_1$  and  $\vec{a}_2$ , respectively. The indices  $\gamma, \gamma (= xy, yz, zx)$  and  $\sigma (= \uparrow, \downarrow)$  denote the  $t_{2g}$  orbitals and electron spin, respectively, and  $c_{\vec{k}\sigma\gamma}^\dagger$  ( $c_{\vec{k}\sigma\gamma}$ ) is the creation (annihilation) operator of an electron with  $k$ ,  $\sigma$  and  $\gamma(\gamma')$ . Eq. (2) shows the well-known dispersion relation of the Kagomé lattice (see Fig. 3). This means that the Kagomé lattice structure stays in hiding in the triangular lattice of cobalt ions.

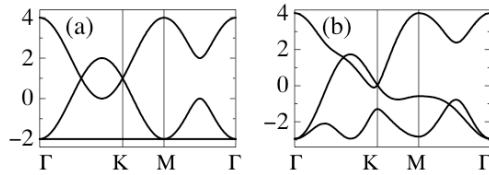


Figure V:1:3. (a) Dispersion relation of Eq. (5) for  $t = 1$ . (b) Dispersion relation of  $\epsilon_{\vec{k},\gamma,\gamma'}$  for  $t = 1, t_{dd} = -0.63, t_1 = -0.08$  and  $t_2/t_1 = -1.5$ .

Let us discuss how to realize the Kagomé lattice in the motion of an electron given by Eq. (5). An electron in the state  $|zx, 1\rangle$  can go to  $|yz, 2\rangle$  and  $|xy, 3\rangle$ . An electron in  $|yz, 2\rangle$  can go to  $|xy, 12\rangle$  and  $|xy, 3\rangle$  but cannot go to any orbitals on cobalt 0 due to the symmetry. In this way, an electron starting from  $|zx, 1\rangle$  propagates through the  $t_{2g}$  orbitals on cobalt ions, 1 ~ 12, and thus the trace of the motion forms a Kagomé lattice (see Fig. 4(a)). The triangle made of the states  $|zx, 1\rangle, |yz, 2\rangle$  and  $|xy, 3\rangle$  is an elementary unit of the Kagomé lattice. Therefore, the energy scheme of the triangle determines that at  $(0,0)$  in the  $k$  space. The eigenstates of the triangle are

$$(|xy, 3\rangle + |yz, 2\rangle + |zx, 1\rangle) / \sqrt{3} \quad (6)$$

with the eigenvalue  $2t$  and

$$(|xy, 3\rangle + e^{\pm i\frac{2\pi}{3}} |yz, 2\rangle + e^{\pm i\frac{4\pi}{3}} |zx, 1\rangle) / \sqrt{3} \quad (7)$$

with  $-t$ . The eigenstates correspond to the  $a_{1g}$  and  $e'_g$  symmetries, respectively. Note that they are completely different from the states Eqs. (1) and (2). The eigenstates in Eqs. (6) and (7) lie on the top and bottom of the band, respectively. This is a character of the Kagomé lattice structure.

When an electron propagates starting from  $|yz, 1\rangle$ , the trace can form another Kagomé lattice which is drawn by black triangles in Fig. 4(b). Following the procedure, we obtain four Kagomé lattices as shown in Fig. 4(b). Because the unit cell of the Kagomé lattice is four times as large as that of the triangular one, the four Kagomé lattices complete the Hilbert space.

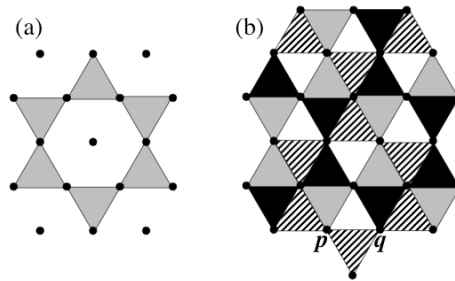


Figure V:1:4. Kagomé lattice in the triangular lattice of cobalt ions. (a) Solid circles indicate the cobalt ions in Fig. 1(b). Gray triangles form a Kagomé lattice which is made by a trace of the travel of an electron starting from  $|zx, 1\rangle$  (see text). (b) Layout of the four (gray, black, hatched and white) Kagomé lattices.

In the  $\text{CoO}_2$  layer where the  $\text{CoO}_6$  octahedra share the edges as shown in Fig 1, the hopping integral between adjacent  $3d$  orbitals should also be taken into account to analyze the band structure. Between the cobalt ions 1 and 2, the leading term of the hopping matrix element ( $t_{dd}$ ) occurs between  $|xy, 1\rangle$  and  $|xy, 2\rangle$ . The sign of the hopping matrix element  $t_{dd}$  is negative due to the configuration of the orbitals on the hexagonal  $\text{CoO}_2$  layer. Although there exist the other hopping matrix elements between the ions 1 and 2, e.g., between  $|zx, 1\rangle$  and  $|yz, 2\rangle$ , their magnitude may be much smaller than the leading term. The hopping between  $xy$  orbitals forms a one-dimensional chain along  $a_1$ -axis. In the same way, the hopping between  $yz$  ( $zx$ ) orbitals

forms another chain along  $a_2$ -axis (the direction of  $\vec{a}_1 + \vec{a}_2$ ). Consequently, the hopping matrix in the Fourier-transformed expression is diagonal, i.e.,  $(xy, xy)$ ,  $(yz, yz)$  and  $(zx, zx)$  components are written as  $2t_{dd} \cos(k_1)$ ,  $2t_{dd} \cos(k_2)$ ,  $2t_{dd} \cos(k_1+k_2)$ , respectively. Note that the hopping matrix does not give the energy-level splitting at  $(0,0)$  in the  $k$  space.

For more detailed analysis, we introduce the effect of the hopping integral of  $2p$  orbitals between neighboring oxygen ions. Let us consider the configuration of  $2p$  orbitals on the oxygen ions labeled  $i \sim vi$  in Fig. 5 where the relation between  $xyz$  and  $a_1a_2c$  coordinate systems are the same as that in Fig. 1.

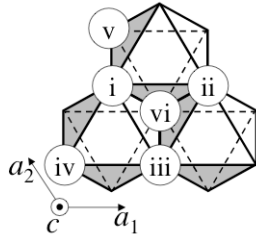


Figure V:1:5. Triangular lattices of oxygen ions in  $\text{CoO}_2$  layer. Cobalt ions are not drawn.  $i \sim iv$  ( $v$  and  $vi$ ) are on the upper (lower) triangular lattice of oxygen ions.

The  $2p_z$  orbitals on  $i$ ,  $ii$  and  $v$  are on an  $xy$ -plane, but those on  $i$  and  $iii$  are not. Using the table by Slater and Koster [29], we find two kinds of hopping integrals as follows:  $t_{pp,1} = V_{pp\pi}$  for the neighboring pair of oxygen ions,  $(i,ii)$  and  $(i,v)$ , and  $t_{pp,2} = (1/2)(V_{pp\sigma} + V_{pp\pi})$  for  $(i,iii)$ ,  $(i,iv)$  and  $(i,vi)$ , where  $V_{pp\sigma}/V_{pp\pi} = 4$ ,  $t_{pp,2}/t_{pp,1} = -1.5$  and  $t_{pp,1} < 0$ . Following the procedure, all of the hopping integrals of  $2p$  orbitals between neighboring oxygen ions are expressed as  $t_{pp,1}$  and  $t_{pp,2}$ , which lead to the hopping matrix elements,  $t_1$  and  $t_2$ , of the  $3d$  electron to the second nearest neighbors:  $t_n \sim (t_{pd})^2 t_{pp,n} / (\Delta)^2$  where  $n = 1$  or  $2$ . As a result, we obtain the hopping matrix  $E_{\vec{k},\gamma,\gamma'}$  of the  $\text{CoO}_2$  layer:

$$\begin{aligned}
E_{\bar{k}, \gamma, \gamma}^- &= 2(t_{dd} + 2t_2) \cos k_a^{\gamma, \gamma} \\
&\quad + 2(t_1 + 2\bar{t}_2) [\cos k_b^{\gamma, \gamma} + \cos(k_a^{\gamma, \gamma} + k_b^{\gamma, \gamma})] \\
&\quad - 2t_2 [2 \cos(2k_a^{\gamma, \gamma} + k_b^{\gamma, \gamma}) + \cos(k_a^{\gamma, \gamma} - k_b^{\gamma, \gamma})] \\
E_{\bar{k}, \gamma, \gamma'}^- &= 2t \cos k_b^{\gamma, \gamma'} + 2t_1 \cos 2k_b^{\gamma, \gamma'} \\
&\quad + 2t_2 [\cos(k_a^{\gamma, \gamma'} + 2k_b^{\gamma, \gamma'}) + \cos(k_a^{\gamma, \gamma'} - k_b^{\gamma, \gamma'})],
\end{aligned}$$

where  $k_a^{xy, xy} = k_a^{xy, zx} = k_1$ ,  $k_b^{xy, xy} = k_b^{xy, zx} = k_2$ ,  $k_a^{yz, yz} = k_a^{xy, yz} = k_2$ ,

$k_b^{yz, yz} = k_b^{xy, yz} = -(k_1 + k_2)$ ,  $k_a^{zx, zx} = k_a^{yz, zx} = -(k_1 + k_2)$  and  $k_b^{zx, zx} = k_b^{yz, zx} = k_1$ ,

respectively. The dispersion relation captures the band structure calculated by Singh [24]. Although the more parameters may result in the more quantitative agreement with the band structure, it is not the purpose of this paper.

The dispersion relation Fig. 3(b) clearly shows that the upper lying band takes over the nature of the Kagomé lattice structure hidden in the triangular lattice of cobalt ions (see Fig. 4) despite of the presence of  $t_{dd}$ ,  $t_1$  and  $t_2$ . Therefore, it is of crucial importance to study the effect of the Kagomé lattice structure to clarify the electronic state in the CoO<sub>2</sub> layer.

## Mutual Interactions

Let us discuss the effect of the strong Coulomb interaction in the Kagomé lattice structure shown in Fig 3. The cobalt ions  $p$  and  $q$  are shared by white and hatched Kagomé lattices. The  $3d$  orbitals  $|yz, p\rangle$  and  $|zx, q\rangle$  belong to the white Kagomé lattice, whereas  $|zx, p\rangle$  and  $|yz, q\rangle$  do in the hatched one. The on-site Coulomb interaction brings about the following interaction between  $p$  and  $q$  when an electron is in the white Kagomé lattice and another is in the hatched one:

$$\left( \vec{T}_p \cdot \vec{T}_q - \frac{1}{4} \right) \left[ J \left( \vec{S}_p \cdot \vec{S}_q + \frac{3}{4} \right) + J' \left( \vec{S}_p \cdot \vec{S}_q - \frac{1}{4} \right) \right],$$

where  $\vec{S}_p$  ( $\vec{S}_q$ ) is the electron spin on  $p$  ( $q$ ). The orbital state on  $p$  ( $q$ ) is described by the pseudo-spin operator  $\vec{T}_p$  ( $\vec{T}_q$ ) with 1/2 in magnitude, i.e.,  $|yz, p\rangle$  ( $|zx, p\rangle$ ) is the eigenstate of  $T_p^z$  with the eigenvalue 1/2 (−1/2) and



$|zx, q\rangle$  ( $|yz, q\rangle$ ) is the eigenstate of  $T_{\vec{q}}$  with the eigenvalue  $1/2$  ( $-1/2$ ). The interactions  $J$  and  $J'$  are expressed as  $J = 4t^2/(U' - K)$  and  $J' = 4t^2/(U' + K)$  with the Coulomb interaction  $U'$  of the inter-orbitals and Hund's rule coupling  $K$ . Due to the Hund's rule coupling,  $J > J'$ , i.e., there exists a ferromagnetic spin coupling with a singlet state of orbitals on the edge shared by the Kagomé lattices.

We propose a fundamental model to study the electronic structure of the  $\text{CoO}_2$  layer under the local constraint;  $\sum_{\sigma\gamma} c_{i\sigma\gamma}^\dagger c_{i\sigma\gamma} \geq 5$ . The Hamiltonian  $H = -H_t + H_J$  with

$$H_J = \sum_{im} \left( H_{2n\vec{a}_1+m\vec{a}_2}^{(1)} + H_{m\vec{a}_1+2n\vec{a}_2}^{(2)} + H_{2n(\vec{a}_1+\vec{a}_2)+m\vec{a}_2}^{(3)} \right),$$

Table V:1:1. Relation between  $t_{2g}$  ( $xy$ ,  $yz$  and  $zx$ ) orbitals and eigenstates of  $T_i^{(I),z}$  with  $i = n\vec{a}_1 + m\vec{a}_2$ . The letters with (without) the bracket denote the orbitals corresponding to the eigenstates in the case that  $n + m$  is odd (even).

eigenvalue	1/2	-1/2
$I = 1$	$yz$ ( $zx$ )	$zx$ ( $xy$ )
$I = 2$	$zx$ ( $xy$ )	$xy$ ( $zx$ )
$I = 3$	$xy$ ( $yz$ )	$yz$ ( $xy$ )

where  $n$  and  $m$  are integer numbers and

$$H_i^{(I)} = J \sum_{\vec{\delta}(I)} \left( \vec{T}_i^{(I)} \cdot \vec{T}_{i+\vec{\delta}(I)}^{(I)} - \frac{1}{4} n_i^{(I)} n_{i+\vec{\delta}(I)}^{(I)} \right) \times \left( \vec{S}_i \cdot \vec{S}_{i+\vec{\delta}(I)} + \frac{3}{4} n_i^{(I)} n_{i+\vec{\delta}(I)}^{(I)} \right),$$

where  $I$  is an index and  $\vec{\delta}(1) = \pm\vec{a}_1$ ,  $\vec{\delta}(2) = \pm\vec{a}_2$ , and  $\vec{\delta}(3) = \pm(\vec{a}_1 + \vec{a}_2)$ , in the summation. The orbitals corresponding to the eigenstates of  $T_i^{(I),z}$  are summarized in the Table I, and  $n_i^{(I)} = n_{i+}^{(I)} + n_{i-}^{(I)}$  where  $n_{i\pm}^{(I)}$  is the electron number in the eigenstates of  $T_i^{(I),z}$ .

This model involves the ingredients for the unique transport and magnetic properties of the  $\text{CoO}_2$  layer: A spin-triplet with orbital-singlet is stabilized on a nearest-neighbor cobalt bond. The pairing mechanism acts in

a different way from the so-called resonating-valence-bond picture discussed by several authors [18-21], where the key is the singlet state of orbitals. Khaliullin and Maekawa [30] discussed a liquid state of  $t_{2g}$  orbitals in a perovskite titanate. In the  $\text{CoO}_2$  layer, the resonance and dynamics of the singlet states are developed in the Kagomé lattice but not in the triangular lattice. Note that the orbitals are characterized by four flavors, i.e., the four Kagomé lattices as shown in Fig 4(b), rather than three  $t_{2g}$  states. This system has ferromagnetic interaction  $H_J$ . Thus, the carrier doping may cause a spin-triplet superconductivity [11-14]. This is based on the Kagomé lattice structure and is different from that on a single band model in a triangular lattice.

The Kagomé lattice involves a triangle as a basic unit. On the triangle, the mechanism by Kumar and Shastry [18, 31] for the anomalous Hall effect will be available and explain the experiments by Wang *et al.*

The triangle gives the  $a_{1g}$  state Eq. (6) as the upper lying band in the reciprocal space. In the real space, however, a cobalt ion in the triangle is shared by three Kagomé lattices (see Fig 4), so that the  $t_{2g}$  orbitals are identical. The orbital degree of freedom causes the large thermopower [22, 23] at high temperatures.

The Kagomé lattice structure clearly explains the non-symmetric nature of the band structure of the  $\text{CoO}_2$  layer. When the effect of the Kagomé lattice becomes dominant, the bottom band, i.e., the flat band as shown in Fig. 3(a) will play a crucial role on the electronic state. Mielke [32] has shown that the flat band with the Coulomb interaction has the ferromagnetic ground state at around half filling. A prospective system for the ferromagnet will be  $d^1$  transition metal oxides, i.e., the layered titanates with iso-structure of the cobalt oxides.

In conclusion, since the cobaltates are in sharp contrast to the high- $T_c$  cuprates in many respects, the study of cobaltates will provide an opportunity to understand the cuprates as well.

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28. When we adopt a point charge model for the distorted  $\text{CoO}_6$  octahedron with the parameters, i.e., the O-Co-O bond angle ( $98.5^\circ$ ), the ratio of the Co-O bond length and Bohr radius ( $\sim 4$ )  $10Dq=2.5\text{eV}$ , and the Racah parameter ( $B = 1065\text{ cm}^{-1}$ ) for a cobalt ion (See Y. Tanabe and S. Sugano *J. Phys. Soc. Jpn.* 9, 766 (1954).), the stabilization energy of the  $a_{1g}$  state against the  $e'_g$  states is estimated to be  $\sim 0.025\text{ eV}$ .
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