Kagomé in triangular lattice:
electronic state of CoO\textsubscript{2} layer with hexagonal structure

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The electronic state in layered cobalt oxides with hexagonal structure is examined. We find that the electronic structure reflects the nature of the Kagomé lattice hidden in the CoO\textsubscript{2} layer which consists of stacked triangular lattices of oxygen ions and of cobalt ions. A fundamental model for the electron system is proposed and the mechanism of the unique transport and magnetic properties of the cobalt oxides are discussed in the light of the model.

Cobalt oxides with layered hexagonal structure have attracted much attention. The oxides Na\textsubscript{2}CoO\textsubscript{2}, [Bi\textsubscript{2−x}Pb\textsubscript{x}Sr\textsubscript{2}]\textsubscript{y}CoO\textsubscript{2} and [CaCo\textsubscript{3}]\textsubscript{2}CoO\textsubscript{2} exhibit large thermapower and have potentials for thermoelectric materials \cite{1, 2, 3}. In addition, the anomalous high-temperature Hall effect has been observed in Na\textsubscript{0.68}CoO\textsubscript{2} \cite{4}. It is known that Na\textsubscript{0.75}CoO\textsubscript{2} shows a magnetic transition at 22 K \cite{5}, and [Bi\textsubscript{2−x}Pb\textsubscript{x}Sr\textsubscript{2}]\textsubscript{y}CoO\textsubscript{2} is ferromagnetic below $T_c = 3.2$K \cite{6}. Recently, superconductivity \cite{7} has been discovered in water-intercalated Na\textsubscript{0.35}CoO\textsubscript{2−1.3H\textsubscript{2}O}. Since then, experimental and theoretical studies have been done extensively \cite{8, 9, 10, 11, 12, 13, 14, 15}. Several authors \cite{14, 16, 17, 18} have examined the electronic state based on a single band model in triangular lattice of Co ions of the CoO\textsubscript{2} layer.

In this paper we show that a Kagomé lattice structure is hidden in the CoO\textsubscript{2} layer, and the electronic state is based on the Kagomé lattice but not the single band model in the triangular lattice. We propose a fundamental model for the electron system and discuss the mechanism of the unique transport and magnetic properties in the cobalt oxides.

The crystal structure is presented in Fig. 1. The CoO\textsubscript{2} layer is formed by the edge-shared CoO\textsubscript{6} octahedra which are compressed along $c$-axis. The rhombohedral distortion of the CoO\textsubscript{6} octahedra are estimated by the deviation of the O-Co-O bond angle from 90°, 95° $\sim$ 99° \cite{10, 19, 20, 21, 22}. The distortion leads to the crystal-field splitting in $t\textsubscript{2g}$ states of 3$d$ electrons as shown in Fig. 1(c). The wave functions are expressed as

\begin{equation}
(xy > +|yz > +|zx >)/\sqrt{3}
\end{equation}

for the $a\textsubscript{1g}$ state and

\begin{equation}
(xy > +e^{±i2\pi}|yz > +e^{±i2\pi}|zx >)/\sqrt{3},
\end{equation}

for the doubly degenerate $e\textsubscript{g}'$ states where $|xy >, |yz >$ and $|zx >$ denote the wave functions of the $t\textsubscript{2g}$ states. The $a\textsubscript{1g}$ state extends to the $c$-axis whereas the $e\textsubscript{g}'$ states spread over the plane perpendicular to the $c$-axis. Since the apex oxygens approach the plane in the distorted CoO\textsubscript{6} octahedra, the $a\textsubscript{1g}$ state is stabilized \cite{22} for an electron.

The band calculation \cite{13} in Na\textsubscript{0.5}CoO\textsubscript{2} has shown that the energy splitting between $a\textsubscript{1g}$ and $e\textsubscript{g}'$ states at the $\Gamma$ point is $\sim 1.6$eV which is the total band width of the $t\textsubscript{2g}$ manifold and the $a\textsubscript{1g}$ state is higher than the $e\textsubscript{g}'$ 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 3$d$ 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 3$d$ orbitals, and another is owing to the hopping between a 3$d$ orbital of a cobalt ion and a 2$p$ orbital of an oxygen ion. First, let us consider the latter mechanism, i.e., the hopping of a 3$d$ electron through the 2$p$ orbital on the neighboring oxygen. The CoO\textsubscript{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 $t\textsubscript{2g}$ orbitals on the $i$-th cobalt ions are expressed as $|xy, i >, |yz, i >$ and $|zx, i >$, respectively. The state $|zx, 0 >$ has a hopping matrix element with $|yz, 6 >$ through the 2$p$\_ orbital of the oxygen ion which exists in the lower layer and shares CoO\textsubscript{6} octahedra involving cobalt ions 0 and 6, respectively. The hopping matrix element ($t$) is expressed as $t \sim (t\textsubscript{pd})^2/\Delta$ ($\Delta > 0$), where $\Delta$ is the energy level of the
The tight binding Hamiltonian is written as

\begin{pmatrix}
xy \\
yz \\
zx
\end{pmatrix}
\begin{pmatrix}
0 & 0 & t \\
0 & 0 & t \\
t & 0 & 0
\end{pmatrix}
\begin{pmatrix}
xy \\
yz \\
zx
\end{pmatrix},
(3)

respectively. In the Fourier-transformed representation, the tight binding Hamiltonian is written as

\[ H_t = \sum_{\mathbf{k},\sigma,\gamma,\gamma'} \epsilon_{\mathbf{k}\gamma} c_{\mathbf{k}\sigma\gamma}^\dagger c_{\mathbf{k}\sigma\gamma'}, \]

with

\[ \epsilon_{\mathbf{k}} = 2t \begin{bmatrix}
0 & \cos(k_1 + k_2) & \cos k_2 \\
\cos(k_1 + k_2) & 0 & \cos k_1 \\
\cos k_2 & \cos k_1 & 0
\end{bmatrix}, \]

where \( k_1 \) and \( k_2 \) are the component of the wave vector \( \mathbf{k} \) in the representation of the reciprocal lattice of the triangular lattice spanned by \( \mathbf{u} \) and \( \mathbf{v} \). \( \gamma, \gamma' = (x, y, z, \text{zx}) \) and \( \sigma = (\uparrow, \downarrow) \) are the indices for the \( t_{2g} \) orbitals and electron spin, respectively, and \( c_{\mathbf{k}\gamma}^\dagger (c_{\mathbf{k}\gamma}) \) denotes creation (annihilation) operator of an electron with \( \mathbf{k}, \sigma \) and \( \gamma (\gamma') \). Eq. (5) shows the well-known dispersion relation of the Kagomé lattice (see Fig. 2). This means that the Kagomé lattice structure stays in hiding in the triangular lattice of cobalt ions. Let us discuss how to realize the Kagomé lattice in the motion of an electron given by Eq. (4). 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 \( |xy, 1\rangle \) and \( |zx, 3\rangle \) 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, \( 1 \sim 2 \), using Eq. (3), and thus the trace of the motion forms a Kagomé lattice (see Fig. 3(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

\[ (|xy, 3\rangle > + |yz, 2\rangle > + |zx, 1\rangle >) / \sqrt{3} \]

with the eigenvalue \( 2t \) and

\[ (|xy, 3\rangle > + e^{\pm i\pi/3} |yz, 2\rangle > + e^{\pm i\pi/3} |zx, 1\rangle >) / \sqrt{3}, \]

with \(-t\). The eigenstates have the \( a_{1g} \) and \( e'_{g} \) symmetries, respectively. Note that they are completely different from the states Eqs. (4) and (5). 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 \( |zx, 1\rangle \), the trace forms another Kagomé lattice which is drawn by black triangles in Fig. 3(b). Following the procedure, we obtain four Kagomé lattices in the triangular lattice of cobalt ions as shown in Fig. 3(b). Because the unit cell of the Kagomé lattice is four times as large as that of the triangular lattice of cobalt ions, the four Kagomé lattices complete the Hilbert space.

In the CoO\(_2\) layer where the CoO\(_6\) octahedra share the edges as shown in Fig. 1, the hopping integral between adjacent 3d orbitals should be taken into account to analyze the band structure as well. 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 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 \( \mathbf{u} \) and \( \mathbf{v} \)). Consequently, the hopping matrix in the Fourier-transformed expression is diagonal and is written as \( 2t_{dd} \cos(k_1) \) for \( |xy, xy\rangle \), \( 2t_{dd} \cos(k_2) \) for \( |yz, yz\rangle \) and \( 2t_{dd} \cos(k_1 - k_2) \) for \( |zx, zx\rangle \) component, 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, which depends on the configuration of adjacent \( 2p \) orbitals. Let us consider the configuration of \( 2p_z \) orbitals on the oxygen ions labeled \( i \sim vi \) in Fig. 4 where the relation between \( xgy \) and \( a_1a_2a_3 \) coordinate systems are the same as that in Fig. 1. The \( 2p_z \) orbitals on \( i, ii \) and \( v \) are parallel to each other but those on \( i \) and \( iii \) are not. Using the table by Slater and Koster [24], we find and \( v \) are parallel to each other but those on \( i \) and \( iii \) are not. Following the procedure, all of the hopping integrals of \( 2p \) orbitals between neighboring oxygen ions are expressed as \( t_{pp,1} = V_{pp\pi} \) for the neighboring pair of oxygen ions, \((i, ii)\) and \((i, v)\), and \( v \) are parallel to each other but those on \( i \) and \( iii \) are not. Following the procedure, all of the hopping integrals of \( 2p \) orbitals between neighboring oxygen ions are expressed as \( t_{pp,1} = V_{pp\pi} \) for the neighboring pair of oxygen ions, \((i, ii)\) and \((i, v)\), which lead to the hopping matrix elements, \( t_1 \) and \( t_2 \), of the 3d electron to the second nearest neighbors. The hopping matrix element is derived in the form \( t_{nn} \sim (tpd)^2 / V_{pp\pi}n/(\Delta)^2 \) where \( n = 1 \) or \( 2 \). As a result, we obtain the hopping matrix \( E_{k,\gamma,\gamma'} \) of the CoO\(_2\) layer:

\[
E_{k,\gamma,\gamma'} = 2 \left( t_{dd} + 2t_2 \right) \cos k_{a,\gamma} + 2 \left( t_1 + 2t_2 \right) \cos k_{a,\gamma} + \cos (k_{a,\gamma} + k_{b,\gamma}) - 2 / 2 \cos (k_{a,\gamma} + k_{b,\gamma}) + \cos (k_{a,\gamma} - k_{b,\gamma})
\]

where \( k_{a,\gamma} = k_{a,\gamma}^{x,y} = k_1, k_{b,\gamma} = k_{b,\gamma}^{y,z} = k_2, k_{a,\gamma}^{x,y} = k_{a,\gamma}^{x,y} = k_1, k_{b,\gamma}^{y,z} = k_{b,\gamma}^{y,z} = - (k_1 + k_2), k_{a,\gamma}^{x,y} = k_{a,\gamma}^{x,y} = -(k_1 + k_2), k_{a,\gamma}^{x,y} = k_{a,\gamma}^{x,y} = k_1, \) respectively. The dispersion relation reproduces the band structure calculated by Singh [10]. 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. 2(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. 3) despite of the presence of \( t_{dd} \) and the correction of the higher order terms \( t_1 \) 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\(_2\) layer.

So far, we have not discussed the effect of Coulomb interaction. In reality, the effective on-site Hubbard \( U \) of 5-8 eV is the largest scale of energy in the electron system. Let us discuss the effect of the strong Coulomb interaction in the Kagomé lattice structure shown in Fig. 3. The four Kagomé lattices share the edges each other. Each edge consists of two cobalt ions on both ends, e.g., the cobalt ions \( p \) and \( q \) form the edge shared by white and hatched Kagomé lattices. The 3d orbitals \( |yz, p \rangle \) and \( |xz, q \rangle \) belong to the white Kagomé lattice. On the other hand, \( |yz, p \rangle \) and \( |xz, q \rangle \) are in the hatched Kagomé lattice. The orbitals on a cobalt ion belonging to the different Kagomé lattices are orthogonal to each other. 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:

\[
\left( T_p \cdot T_q - \frac{1}{4} \right) \left( J \left( \vec{S}_p \cdot \vec{S}_q + \frac{3}{4} \right) + J' \left( \vec{S}_p \cdot \vec{S}_q - \frac{1}{4} \right) \right),
\]

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 \( T_p \) (\( T_q \)) with \( 1/2 \) in magnitude, i.e., \( |yz, p \rangle \sim (|xz, p \rangle \) is the eigenstate of \( T_p \) with the eigenvalue \( 1/2 \) (\( 1/-2 \)) and \( |xz, q \rangle \sim (|yz, q \rangle \) is the eigenstate of \( T_q \) with the eigenvalue \( 1/2 \) (\( 1/-2 \)). \( J \) 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 \( K \) of the \( t_{2g} \) orbital on the cobalt ions. 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 CoO\(_2\) layer under the local constraint; \( \sum_{\sigma, \gamma} \epsilon_{\sigma, \gamma} c_{\sigma, \gamma} c_{\sigma, \gamma} \geq 5 \). The Hamiltonian is expressed as:

\[
H = H_t + H_J,
\]

with

\[
H_J = \sum_{nm} \left( H_{1,2n\bar{u}+m\bar{v}}^{(1)} + H_{m\bar{u}+2n\bar{v}}^{(2)} + H_{2n(\bar{u}+\bar{v})+m\bar{v}}^{(3)} \right),
\]

where \( n \) and \( m \) are integer numbers and

\[
H_{i}^{(1)} = J \sum_{\delta(I)} \left( T_i^{(I)} \cdot \delta(I) - \frac{1}{4} n_i^{(I)} n_i^{(I)} \right) \times \left( \vec{S}_i \cdot \vec{S}_i^{(I)} + \frac{3}{4} n_i^{(I)} n_i^{(I)} \right),
\]

where \( I \) is an index and \( \delta(I) = \pm \bar{u}, \delta(2) = \pm \bar{v}, \) and \( \delta(3) = \pm (\bar{u} + \bar{v}) \) in the summation. The orbitals corresponding to the eigenstates of \( T_i^{(I)} \) are summarized.

FIG. 4: Triangular lattices of oxygen ions in CoO\(_2\) layer. Cobalt ions are not drawn. \( i \sim iv \) (\( v \sim vi \)) are on the upper (lower) triangular lattice of oxygen ions.
TABLE I: Relation between $t_{2g}$ ($xy$, $yz$, and $zx$) orbitals and eigenstates of $T_i^{(L)}$ with $i = n\bar{u} + m\bar{v}$. 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 |
|------------|-----|------|
| $I = 1$    | $yz$ ($zx$) | $xx$ ($xy$) |
| $I = 2$    | $zx$ ($xy$) | $xy$ ($yx$) |
| $I = 3$    | $yx$ ($xy$) | $yz$ ($xy$) |

The Kagomé lattice structure involves a triangle as the basic unit, and the Kagomé lattice structure clearly explains the non-symmetric nature of the band structure of the CoO$_2$ layer. When the effect of the Kagomé lattice becomes dominant, the bottom band, i.e., the flat band as shown in Fig. 4(b), will play a crucial role on the electronic state. Mielke [28] have 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 $d^t$ transition metal oxides, i.e., the layered titanates with iso-strucuture of the cobalt oxides. Although there exist many effects which disturb the flat band structure in reality, exploring of the ferromagnet based on the mechanism will be a challenging problem.

In summary, we have shown that the Kagomé lattice structure is hidden in the CoO$_2$ layer. The electronic structure strongly reflects the nature of the Kagomé lattice but not the single band model with a triangular lattice. We have proposed a fundamental model for the electron system and discussed the mechanism of the unique transport and magnetic properties of the cobalt oxides.

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