New Type Phase Transition of Li$_2$RuO$_3$ with Honeycomb Structure

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Abstract

A new-type structural transition has been found in Li$_2$RuO$_3$ with honeycomb lattice of edge-sharing RuO$_6$-octahedra. With decreasing temperature $T$, the electrical resistivity exhibits an anomalous increase at $T = T_c \sim 540$ K, suggesting the (metal to insulator)-like transition and the magnetic susceptibility also shows a sharp decrease. Detailed structure analyses have revealed that the high temperature space group $C2/m$ changes to $P2_1/m$ at $T_c$. The most striking fact is that a significant reduction of the bond lengths is found between two of six Ru-Ru pairs of the hexagon in the low temperature phase, indicating a new type phase transition by the mechanism of the formation of molecular orbits of these Ru-Ru pairs.

KEYWORDS: Li$_2$RuO$_3$, honeycomb structure, structural transition

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Compounds with the honeycomb lattice often present interesting behavior originating from their characteristic structures. For example, in the course of the studies on the physical properties of localized spin systems of A$_3$T$_2$SbO$_6$ (A=Na, Li; T=Cu, Ni, Co) and Na$_2$T$_2$TeO$_6$ on the (distorted) honeycomb lattice, spin gap behaviors have been found for T=Cu, while the magnetic transitions to the spin-ordered state have been observed for T=Co and Ni.

As one of possible examples of conductive electrons on honeycomb lattice, we have investigated physical properties of Li$_2$RuO$_3$. It has the layers of the honeycomb lattice of edge-sharing RuO$_6$ octahedra with a LiO$_6$ octahedron at the center of each hexagon of RuO$_6$ (Fig. 1). The Ru valence is +4 and the four electrons exist in the 4$d^{5}$-5 orbit. For this system, we have found a phase transition at temperature $T = T_c \sim 540$ K, where the crystal symmetry changes from monoclinic (space group $C2/m$) to another monoclinic (space group $P2_1/m$) one with decreasing $T$. As described in detail later, the transition is associated with the molecular orbit formation of Ru$^{4+}$-Ru$^{4+}$ ions of the edge-sharing RuO$_6$ pair, presenting a new mechanism of structural transitions.

Fig. 1 Schematic figures of Li$_2$RuO$_3$ viewed from the direction perpendicular to the $ab$-plane (left) and from the $b$-direction (right). At the corners of the octahedra, O atoms exist, and a Ru or Li atom is within each octahedron. Li atom layers are between the Ru$_2$LiO$_6$ layers.

Polycrystalline samples of Li$_2$RuO$_3$ were prepared by sintering pellets of mixtures of RuO$_2$ and Li$_2$CO$_3$ with proper molar ratio at 1000 °C for 24 h in air. The powder neutron diffraction patterns of these samples indicate that a small amount of RuO$_2$ (molar fraction of ~1.20 %) exists. There also exists an impurity peak of the unidentified phase, which has the integrated intensity of ~4.5 % of the maximum integrated intensity of the main phase as shown later. The magnetic susceptibilities $\chi$ were measured using a Quantum Design SQUID magnetometer under a magnetic field $H=1$ T in the temperature range of 2-700 K. The electrical resistivities $\rho$ were measured by the standard four-terminal method using an ac-resistance bridge from 4.6 K to 695 K. The specific heats $C$ were measured by a thermal relaxation method in the temperature range of 5-60 K using a Physical Property Measurement System (PPMS, Quantum Design). Powder X-ray diffraction measurements were carried out with Cu Kα$_1$ radiation. Powder neutron diffraction measurements were carried out at room temperature (RT) and 600 K using the high-resolution powder diffractometer (HRPD) installed at JRR-3 of JAEA in Tokai. The 331 reflection of Ge monochromator was used. The horizontal collimations were open...
The resistivity cannot explain the superlattice peaks indicated by the open and gray arrows, respectively. (From the experimental data, it is not easy to definitely distinguish if it is the second order transition or the first order one.)

In the fitting, we have obtained satisfactory results (Figs. 4 and 5). As stated above, the superlattice peaks observed at RT(<Tc) are indicated by the black arrows. (The peaks from RuO2 and the unidentified phase are indicated by the open and gray arrows, respectively.) The obtained R factors are as follows. At RT, Rwp=4.17, R=3.07 and S=1.36 for P21/m. At 600 K, Rwp=4.32, R=3.07 and S=1.41 for C2/m. The lattice constants and atomic coordinates at 600 K for C2/m are as follows. a=5.0466(3) Å; b=8.7649(2) Å; c=5.9417(3) Å; β=124.495(4); Ru (4g) y=0.3308(3); Li1 (2a); Li2 (4h) y=0.3425(9); Li3 (2c); O1 (8j) x=0.0162(7), y=0.1701(2), z=0.2324(2); O2 (4i) x=0.4991(8), z=0.2325(4). Those at RT for P21/m are a=4.9210(2) Å; b=8.7829(2) Å; c=5.8941(2) Å; β=124.342(2); Ru (4f) x=0.2737(6), y=0.0766(2), z=-0.0063(6); Li1 (2e) x=0.706(3), z=-0.068(2); Li2 (4f) x=0.253(3), y=0.0991(7), z=0.493(3); Li3 (2e) x=0.772(4), z=0.513(5); O1 (4f) x=0.7525(7), y=0.0805(6), z=0.2489(6); O2 (4f) x=0.7757(6), y=0.0819(6), z=0.7685(6); O3 (2e) x=0.255(1), z=0.2144(9); O4 (2e) x=0.267(1), z=0.761(1). We think that the space group is C2/m above Tc and the second order transition takes place at Tc. If the transition is the first order one, the space group at 600 K might be C2/c. (The Rietveld

![Fig. 2](image2.png)

**Fig. 2** Magnetic susceptibility χ measured under the magnetic field H=1 T and the electrical resistivity ρ of Li2RuO3 are shown against T.

![Fig. 3](image3.png)

**Fig. 3** Lattice parameters obtained by powder X-ray diffraction are shown against T, where the dotted lines are guides for the eyes.

(35°)-20'-6' and the neutron wavelength λ was ~1.824 Å. The diffraction intensities were measured in the 20-range from 2.5 to 165° at a step of 0.05°. Rietveld analyses were carried out for these data using RIETAN-2000.7)

The results of the measurements of χ and ρ of the polycrystalline samples of Li2RuO3 are shown in Fig. 2 against T. A steep decrease of χ has been found at Tc~540 K with decreasing T. The increase of χ found with decreasing T in the low T region is possibly due to the existence of impurities or other kinds of lattice imperfections. The resistivity ρ exhibits a steep increase at Tc with decreasing T. We could not check if the system exhibits the metallic T dependence in the T region far above Tc, where no critical fluctuation of the transition exists, because the system is not stable above the highest temperature studied here.

Measuring the specific heat of Li2RuO3 (the data not shown), we have estimated the electronic specific heat coefficient γ to be ~1.40 (mJ/mol·K²). Because the value is much smaller than the value of 22 mJ/mol·K² obtained by assuming that the χ value observed at low temperatures is due to the Pauli spin susceptibility, almost whole part of the low T value of χ is considered to be the contribution from the Van Vleck paramagnetism. We do not know if the nonzero value of γ is due to the existence of the small and intrinsic Fermi surface or it is just due to the small amount of metallic parts existing in the samples.

The powder X-ray measurements were carried out and the obtained lattice parameters are shown in Fig. 3 against T. The lattice parameter a (b) decreases (increases) rapidly at Tc with decreasing T. The value of b/a is ~√3 above Tc, indicating that the honeycomb structure changes from a nearly ideal form to a distorted one as the result of the transition.

Neutron Rietveld analyses have been carried out at 600 K and RT (see Figs 4 and 5). Although the space group at RT was reported previously to be C2/c,5,6 it cannot explain the superlattice peaks indicated by the black arrows in Fig. 5. To reproduce these reflections, we have to adopt the space group P21/m, for which the conventional unit cell with a half volume of that for C2/c can be used. (The cell for P21/m has the single Ru-honeycomb layer, while that for C2/c has two Ru-honeycomb layers.) The result of the Rietveld fitting by P21/m is rather well. As the possible space group at 600 K, we have adopted C2/m, the minimal non-isomorphic supergroup of P21/m, because for this space group, we can take the unit cell with the single RuO6-honeycomb layer and because it allows the second order transition at Tc. (From the experimental data, it is not easy to definitely distinguish if it is the second order one or the first order one.)
fitting is equally well for C2/c at 600 K. The obtained R factors are $R_{wp}=4.27$, $R_e=3.07$ and $S=1.39$ for C2/c.

Figure 6 shows Ru-honeycomb skeletons at 600 K and RT. At 600 K, Ru atoms form almost ideal honeycomb structure with the Ru-Ru distances $a_1=2.966$ Å and $a_2=2.894$ Å, where the difference between $a_1$ and $a_2$ is just ~2.5% of these distances. At RT, the hexagons are distorted very significantly: $a_1=3.045$ Å, $a_2=3.049$ Å and $a_3=2.568$ Å, where $(a_2-a_3)/a_3 \sim 19\%$. The value of $a_3$ is reduced by an amount as large as 0.326 Å.

Why do such drastic changes take place? To answer the question, we consider the coupling of the lattice distortion with the formation of the molecular orbitals of the $t_{2g}$ electrons of Ru$^{IV}$-Ru$^{IV}$ of edge-sharing RuO$_6$ octahedra. The $\sigma$, $\pi$, and $\delta$-molecular orbitals (bonding orbits) schematically shown in the lower part of Fig. 7, are, we think, formed by the three pairs of the $t_{2g}$ orbitals.
The corresponding antibonding states are $\sigma^\ast$, $\pi^\ast$ and $\delta^\ast$-orbits, respectively. The energy levels of these orbits are shown in the upper part of the figure and we find that the nonmagnetic electron configuration is realized above 540 K is $\sim 13\%$. However, these systems do not exhibit a phase transition. The $T$ dependent susceptibility due to the similar electronic configuration has also been reported for various complexes with metal ion pairs.\textsuperscript{12,15} Of course, these complexes do not exhibit phase transitions. $\text{Li}_2\text{RuO}_3$ is considered to be present, as far as we know, a new type of phase transitions associated with the structural distortion induced by the molecular orbit formation of the $d$ electrons. In this sense, it is interesting to study the band structure of this system at both temperatures above and below $T_c$.

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