

Dimer solid-liquid transition
in the honeycomb-lattice
ruthenate $\text{Li}_{2-x}\text{RuO}_3$

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I would like to dedicate this thesis to
my loving parents and my sister:

Juana Segura Amezcua,
Leopoldo Jimenez Arce, and
Valeria Haide Jimenez Segura.

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Abstract

Since the discovery of the Ru-Ru dimer transition at $T_d \sim 540$ K in Li_2RuO_3 , a number of theoretical and experimental groups have been focusing on understanding the precise nature of this dimer transition. Unlike the common Peirls transition proposed initially, a recent experiment using high-energy X rays suggests that the transition occurs because of the freezing of Ru-Ru dimers from a dimer liquid into a dimer solid. Accordingly, a band-structure calculation suggests that at high temperatures the ruthenium spins behave like spin $1/2$ ions. Thus, the predictions of phases that exhibit topological superconductivity in honeycomb lattice with spin $S = 1/2$ have stimulated the search for superconductivity at low temperatures.

In the present work, we improve the coherence of dimer configuration in stoichiometric Li_2RuO_3 . We show how the unconventional Ru-dimer liquid-solid transition at $T_d \sim 540$ K depends on the dimer coherence configuration that exhibits a strong dependence on the crystallinity and on the cell parameters which vary with the preparation methods of the pristine Li_2RuO_3 .

Furthermore, in this study, the honeycomb-lattice ruthenate Li_2RuO_3 is made heavily Li-deficient by chemical oxidation by iodine. The delithiation triggers a different phase $\text{Li}_{2-x}\text{RuO}_3$, the “D-phase”, with superlattice. For the first time we disclose the magnetic and structural properties of the D-phase in the dimer-solid state. The low temperature magnetic susceptibility and the bond lengths indicate a bonding configuration consisting of both $\text{Ru}^{4+}\text{-Ru}^{4+}$ and $\text{Ru}^{5+}\text{-Ru}^{5+}$ dimers.

List of publications

1. Effect of disorder on the dimer transition of the honeycomb-lattice compound Li_2RuO_3 ,
M.-P. Jimenez-Segura, A. Ikeda, S. Yonezawa, and Y. Maeno, Phys. Rev. B 93, 075133 (2016).
2. Effect of delithiation on the dimer transition in the honeycomb-lattice compound $\text{Li}_{2-x}\text{RuO}_3$,
M.-P. Jimenez-Segura, A. Ikeda, S. A. J. Kimber, C. Giacobbe, S. Yonezawa, and Y. Maeno, Phys. Rev. B submitted (2016).

List of reference papers

1. Glassy magnetic behavior in the metamagnetic DyAlO_3 doped with Cr,
R. Escudero, B.L. Ruiz-Herrera, M.P. Jimenez S., and F. Morales, J Mater Sci 48, 7238 (2013).
2. Superconducting properties of noncentrosymmetric superconductor CaIrSi_3 investigated by muon spin relaxation and rotation,
B. A. Frandsen, S. C. Cheung, T. Goko, L. Liu, T. Medina, T. S. J. Munsie, G. M. Luke, P. J. Baker, M. P. Jimenez S., G. Eguchi, S. Yonezawa, Y. Maeno, and Y. J. Uemura, Phys. Rev. B 91, 014511 (2015).

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Chapter 1

Introduction

1.1 Magnetic honeycomb-lattice compounds

A honeycomb lattice consists in a repeatable unit conformed by six atoms that are in the same plane forming a hexagon. A very well known example is the graphene. One of the peculiarities of the graphene is the presence of Dirac cones in its band structure.

In the Dirac cones there are quasiparticles with an effective speed of light $\mu_F \approx 10^6 m^{-1} s^{-1}$. Their energies can be described by the Dirac equation rather than the Schrödinger equation. This massless Dirac fermions can be regarded as electrons without mass m_o or as neutrinos with charge [1].

There is also another type of honeycomb lattice. This type of honeycomb lattice is chemically formed by A_2BO_3 where A are non magnetic ions $A = \text{Li, Na}$ and B are magnetic ions $B = \text{Ti, Ru, Ir, Rh}$ etc. In the A_2BO_3 honeycomb lattices the non magnetic ions A have orbitals $2s$ or $3s$. Meanwhile, the magnetic ions B have orbitals $3d$, $4d$ or $5d$. Fig. 1.1 shows a cell of A_2BO_3 honeycomb lattices.

The study of honeycomb lattices has gained importance recently due to experimental results that show that honeycomb lattices have uncommon properties [2, 3]. Namely, honeycomb-lattice iridates of the type $A_2\text{IrO}_3$ ($A=\text{Li, Na}$) exhibit strong spin-orbit coupling [4–6].

One of the most powerful models for describing the honeycomb lattices with $S = 1/2$ is the Kitaev model [7]. For this reason when the ion B in A_2BO_3 has total spin $S = 1/2$, this kind of lattices are also called Kitaev-type lattice. This model can be solved exactly introducing Majorana particles leading to a new state denominated Kitaev-liquid.

The Kitaev model [7] considers a system with spin $S = 1/2$ in which spins are at the vertices of every hexagon, see (Fig. 1.2). This lattice is formed by two equivalent

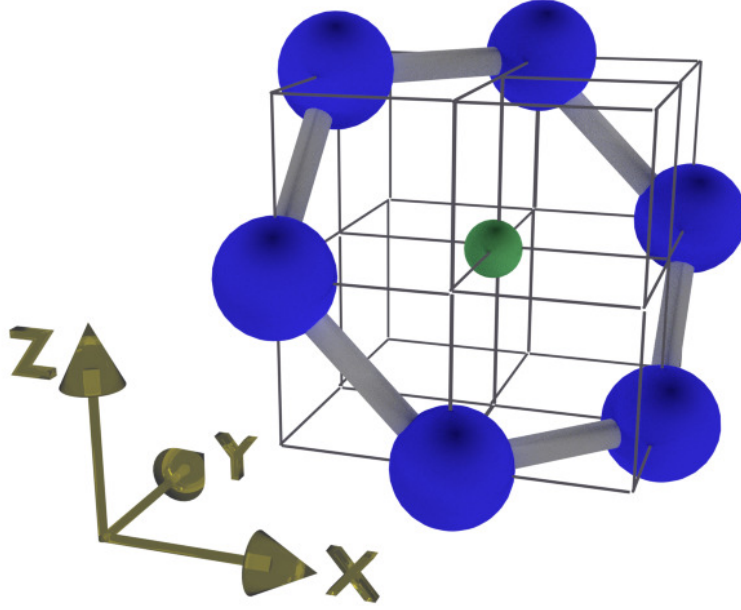


Fig. 1.1 Honeycomb unit cell type A_2BO_3 where $A = \text{Li, Na}$ and $B = \text{Ti, Ru, Ir, Rh}$ etc. Green spheres represent the ions A $2s$ or $3s$. Blues spheres represent magnetic ions B $3d$, $4d$ or $5d$, while intersections of thin bars represent oxygen ions.

sublattices, (shown by empty and full circles). A unit cell of the lattice contains one vertex of each kind. The interactions among the ion spins are divided into three parts of Ising ferromagnetic type, depending on their direction; “ x -links”, “ y -links”, and “ z -links” (illustrated in Fig. 1.2). The Hamiltonian is as follows:

$$\mathcal{H}_K = -J_x \sum_{x\text{-links}} \sigma_j^x \sigma_k^x - J_y \sum_{y\text{-links}} \sigma_j^y \sigma_k^y - J_z \sum_{z\text{-links}} \sigma_j^z \sigma_k^z \quad (1.1)$$

where J_x , J_y , J_z are positive exchange constants, σ refers to the spins, and j , k denotes the nearest neighbors.

In order to include antiferromagnetic interactions in the Kitaev model, it has been combined with the Heisenberg model. This is called the Kitaev-Heisenber model. It is conformed by a term of kinetic energy $\mathcal{H}_{\text{kin}}$, a term for the Kitaev interactions $\mathcal{H}_K$, and a term for the Heisenberg interactions $\mathcal{H}_H$:

$$\mathcal{H} = \mathcal{H}_{\text{kin}} + \mathcal{H}_K + \mathcal{H}_H, \quad (1.2)$$

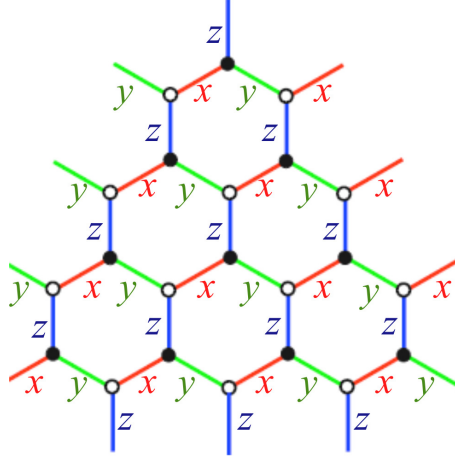


Fig. 1.2 Kitaev type lattice. The interaction between the ions is represented by three different type of links “x-link”, “y-links” and “z-links”

where the Heisenberg hamiltonian is:

$$\mathcal{H}_H = J_H \left(\sum_{\langle ij \rangle} \vec{S}_j \cdot \vec{S}_i - \frac{n_i n_j}{4} \right) \quad (1.3)$$

The Kitaev-Heisenber model has also allowed other predictions about honeycomb lattices. For example topologically non-trivial states [8], including topological superconductivity predicted to emerge with hole doping in the Kitaev-Heisenberg model with spin $S = 1/2$ [9–14]. The resulting figure 1.3 shows the phase diagram for the condensation in the spin-singlet and spin-triplet states as a function of Heisenberg interaction J_H and doping δ , for Kitaev interaction strength $J_K = t_0$ where $J_K = J_x = J_y = J_z$ assumes an isotropic case of Eq. 1.3. It shows superconductivity in several doping levels and topologically nontrivial superconductivity is suggested for $\delta > 0.25$.

Some examples that can be modeled with the Kitaev-Heisenberg Hamiltonian are $A_2\text{IrO}_3$ ($A = \text{Li}, \text{Na}$). However, experimental evidence of superconductivity has not been reported yet [4–6, 15, 16].

Iridates $A_2\text{IrO}_3$ ($A = \text{Li}, \text{Na}$) are characterized by the space group $C2/c$ (No. 15) and have an angle $\beta \sim 99.8^\circ$. They exhibit antiferromagnetic behavior $T_N = 15$ K. Although, Na_2IrO_3 and Li_2IrO_3 have similar structure and magnetic properties, they exhibit different Weiss temperature: $\Theta \sim -116$ K for Na_2IrO_3 , and $\Theta \sim -40$ K for Li_2IrO_3 . Thus, the antiferromagnetic interaction in Na_2IrO_3 is stronger [4, 5]. Recently, it was found that the bond-directional interactions between Ir ions are dominant in Na_2IrO_3 [17].

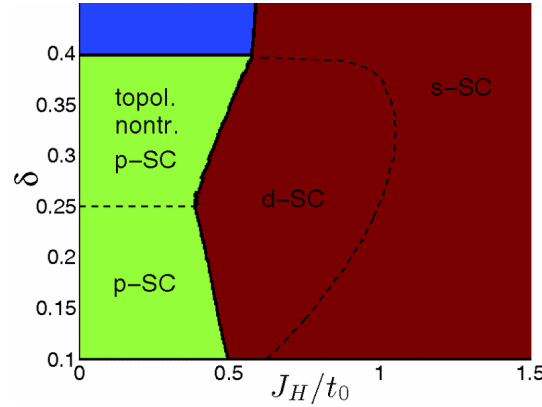


Fig. 1.3 Phase diagram for the condensation in the spin-singlet and spin-triplet states as a function of Heisenberg interaction J_H and doping δ , for Kitaev interaction strength $J_K = t_0$. Within the p -wave triplet phase, there is a topological phase transition (indicated by a dashed line) between topologically trivial $\delta < 0.25$ and topologically nontrivial $\delta > 0.25$ time-reversal invariant superconducting states. Taken from Ref. [10] (republish license by the American Physical Society: 3830041285170).

Another important iridate is β - Li_2IrO_3 . This compound exhibits a hyperhoneycomb lattice (3D), instead of the 2D honeycomb lattice of the Li_2IrO_3 (also called α - Li_2RuO_3). In β - Li_2IrO_3 it has been confirmed by magnetic susceptibility that the dominant interactions are ferromagnetic with a positive Weiss temperature $\Theta \sim 40$ K. At $T_c = 38$ K the β - Li_2IrO_3 exhibits a transition that has been associated with a noncollinear ordering below T_c [6]. This order occurs close to the boundary of the Kitaev liquid in the theoretical phase diagram of Kitaev-Heisenberg for 2D and 3D [18, 19]. Thus, the β - Li_2IrO_3 has become a stronger candidate for exhibiting Kitaev-like interactions.

The substitution of Ir^{4+} ($5d^5$) by Ru^{4+} ($4d^4$) in Li_2IrO_3 has been studied [20]. In the compound $\text{Li}_2\text{Ir}_{1-x}\text{Ru}_x\text{O}_3$ it was found that the antiferromagnetic phase characteristic of Li_2IrO_3 disappears for $x > 2$ and bond dimers appear in the averaged structure for $x > 0.5$. Contrary to the expectations based on the Kitaev-Heisenberg model, this system remains non-metallic [20]. This insulating behavior of $\text{Li}_2\text{Ir}_{1-x}\text{Ru}_x\text{O}_3$ has been attributed to a quasimolecular-orbital Jahn-Teller instability, that leads to the large effects of electron-phonon coupling which cooperates with the electron-electron interaction to account for the persistent insulating character and bond dimerization [20].

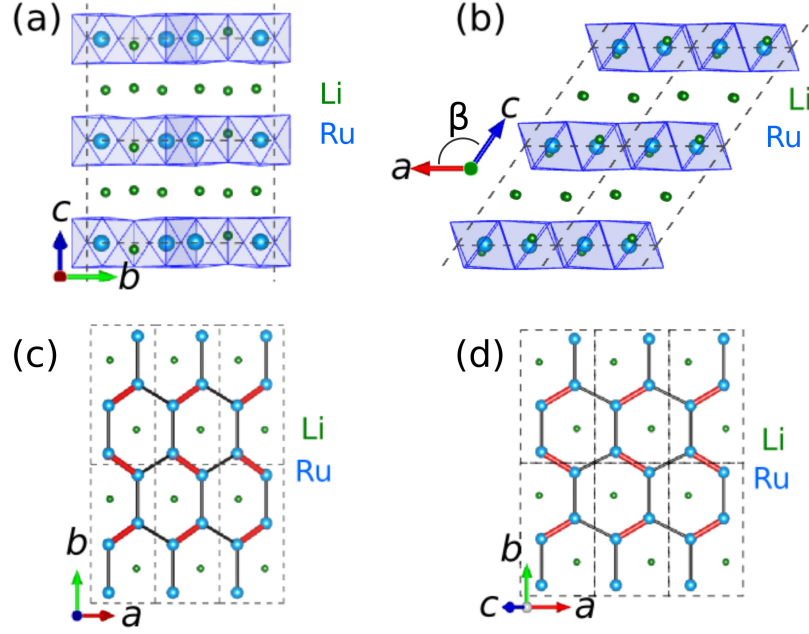


Fig. 1.4 Room-temperature structure of Li_2RuO_3 with the space group $P2_1/m$ viewed from several directions. Blue and green spheres represent Ru and Li ions, while vertices of the octahedra represent O ions. Black and red lines represent the long and short bonds within the Ru honeycomb lattice. Panels (a), (b), and (c) show the structure as viewed along the a , b and c directions, while (d) is along c^* , the direction perpendicular to the ab plane. The figures are prepared with the program VESTA [26].

1.2 Dimer transition in Li_2RuO_3

Other examples of honeycomb-lattice compounds are $A_2\text{RuO}_3$ ($A = \text{Li}, \text{Na}$) [16, 21–23] with nominally $S=1$ originating from Ru^{4+} in the low-spin state. In contrast to $A_2\text{IrO}_3$ ($A = \text{Li}, \text{Na}$), it has been discovered that Li_2RuO_3 exhibits an unusual phase transition at $T_d \sim 540$ K [24]. Below T_d , two of the six Ru-Ru bonds in the honeycomb hexagon become substantially shorter than the others, forming static Ru-Ru dimers, as schematically shown with thick red lines in Fig. 1.4. Because of this static dimerization, the high-temperature structure with a nearly ideal honeycomb lattice, in average belonging to the space group $C2/m$, is reduced to a less symmetric structure with distorted honeycomb lattice belonging to the space group $P2_1/m$ below T_d (Fig. 1.5) [20, 24, 25]. Interestingly, this dimer transition is accompanied by a strong decrease of the magnetic susceptibility.

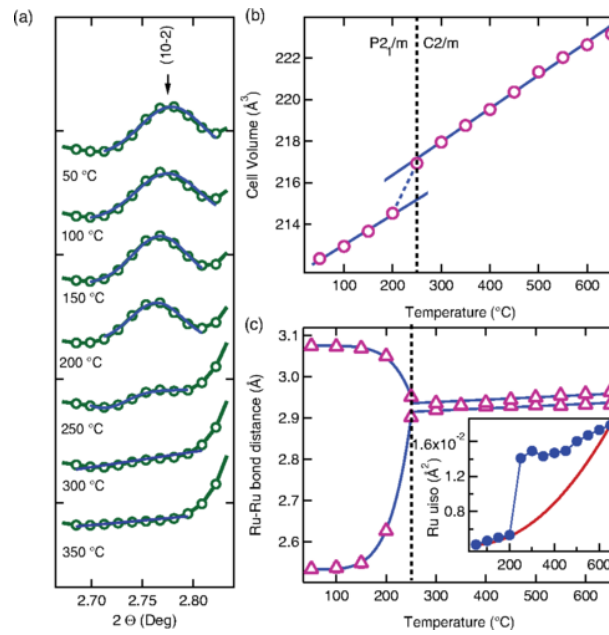


Fig. 1.5 (a) Selected region of the x-ray diffraction profile of Li_2RuO_3 as a function of temperature, showing the disappearance of the (10-2) reflection at the structural phase transition. The tail to higher angles originates from the intense (11-2) reflection. (b) Temperature dependence of the refined unit cell volume of Li_2RuO_3 . (c) Temperature dependence of the Ru-Ru bond distance extracted from Rietveld refinement against the powder x-ray diffraction data; the inset shows the refined Ru atomic displacement parameter with an extrapolated Debye dependence (red line). Taken from Ref. [25](republish license by the American Physical Society: 3830070010348).

The actual mechanism of this phase transition in Li_2RuO_3 has provoked debate due to the different schemes that have been proposed, such as the transition from a highly correlated metal to a molecular orbital insulator accompanied by bond-dimer formation [24, 27] by a magneto-elastic mechanism [28].

The ground state of the spin-orbital model of Li_2RuO_3 has been discussed. The used model considers that the ions are spin-one with partially filled t_{2g} levels [28]. It considers also that the low temperature phase of Li_2RuO_3 is Mott-Hubbard type and is applicable for the low energy physics of the Kugel-Khomskii type spin-orbital Hamiltonian [29]

$$\mathcal{H} = \sum_{\langle ij \rangle} \{ J [\vec{S}_i \cdot \vec{S}_j - 1] \vec{O}_{ij} - [J_0 \vec{S}_i \cdot \vec{S}_j + J_1] O_{ij}, \} \quad (1.4)$$

where the sum is taken over pairs of nearest-neighbor NN sites. $\vec{S}_i$ are spin operators and O_{ij} and $\vec{O}_{ij}$ are orbital operators. This model considers only the σ -type overlap formed by orbitals d_{xy} , d_{yz} , and d_{xz} (x , y , and z are in cubic notation 1.9).

Starting from the undistorted honeycomb lattice, it was found that the dimerization can be induced by the the orbital degrees of freedom, driving the spin $S = 1$ to a nonmagnetic state $S = 0$ [28]. In this study, it was found that configurations of dimers are energetically more favorable than long short chains. It has been proposed that once one of the dimers is formed, the contraction induces a distortion in the proximate Li ion, inducing a dimerization in next Ru ion. This mechanism is provoked by magnetoelastic coupling. It has been called cooperative “dimer Jahn-Teller” effect.

As shown in Fig. 1.9 a hexagon of a honeycomb lattice enclosed in a cubic cell. The x , y , and z axis are indicated in yellow. The thicker white bars indicate the σ -interactions among the Ru ions, described by [28, 30]. When the dimers are formed, two out of six σ -interactions become shorter in Li_2RuO_3 as depicted in Fig. 1.4(c,d). It has been proposed that the decrease of magnetic susceptibility below the transition temperature is due to formation of more molecular orbitals (MO) leading to $S = 0$. This MO's can form σ , π , and δ bonding MO's and σ^* , π^* and δ^* anti-bonding MO's. The MO's forming π and δ bonds cannot be formed directly through the pure orbitals shown in Fig.1.9, instead new hybrid orbitals of Ru $4d t_{2g}$ $[(y'z' - z'x'), (y'z' + z'x')]$ are required [24, 27].

More recently, a pair distribution function (PDF, Fig. 1.6) analysis based on high-energy X-ray diffraction (XRD) and calculations of density functional theory (DFT) revealed that the dimers exist even above T_d (Fig. 1.7). However, if the average of the structure is measured by XRD, the lengths of all Ru-Ru bonds is equivalent 1.5. Since

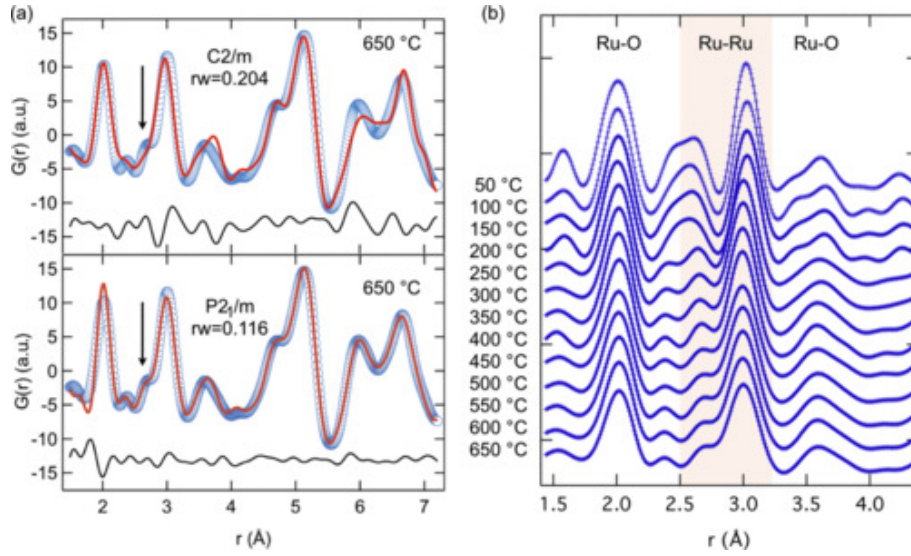


Fig. 1.6 (a) Results of fitting the $C2/m$ (top) and $P2_1/m$ (bottom) structures via $G(r)$ to the PDF data at 650 °C (open blue circles: experiment; solid red lines: model calculations). The measured profile versus the calculated profile is the offset black line. (b) Temperature evolution of the PDF. The region containing the Ru-Ru bonds is highlighted and other important distances are also indicated. Taken from Ref. [25] (republish license by the American Physical Society: 3830070010348).

the PDF analysis shows the local structure, these experimental results show that the positions of the dimers change dynamically [25]. Thus, the transition at T_d is not an ordinary Peierls transition as was thought initially, instead it can be regarded as the “melting” transition between a static “dimer solid” at low temperature and a dynamic “dimer liquid” above the T_d [25].

In these recent finding, it has been proposed that the MO’s leading to the σ -bonds are maintained in all below and above the dimer-transition temperature T_d . However, the π - and δ -bonds are broken at temperatures above the T_d . Due to this partial rupture, the total spin at temperature above T_d has been considered to behave as $S = 1/2$ [25]. The molecular orbitals of both states, dimer solid and dimer liquid, are depicted in Fig. 1.8.

The potential utility of Li_2RuO_3 as a material for batteries has motivated investigation on its electrochemical properties as well [31]. The delithiated series $\text{Li}_{2-x}\text{RuO}_3$ has been synthesized from Li_2RuO_3 by electrochemical deintercalation of lithium [32–34] and by chemical oxidation by I_2 [35]. Moreover, it has been revealed that a part of Ru^{4+} changes to Ru^{5+} by delithiation based on a sequence of experiments [36–38].

However, concerning the physical properties of $\text{Li}_{2-x}\text{RuO}_3$, only magnetic susceptibility has been reported in the limited temperature range between 83 and 293 K [35].

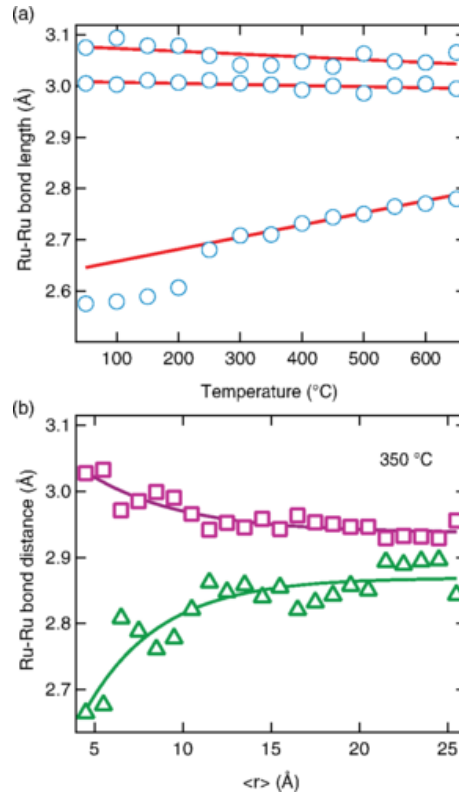


Fig. 1.7 (a) Temperature dependence of the fitted Ru-Ru distances from the PDF analysis of Li_2RuO_3 in the range $1.5 < r < 7.25$ Å. Error bars are smaller than the markers. (b) r dependence of the Ru-Ru distances extracted from model fits to the PDF at 350°C . The two inequivalent longer distances have been averaged for plotting. Taken from Ref. [25] (republish license by the American Physical Society: 3830070010348).

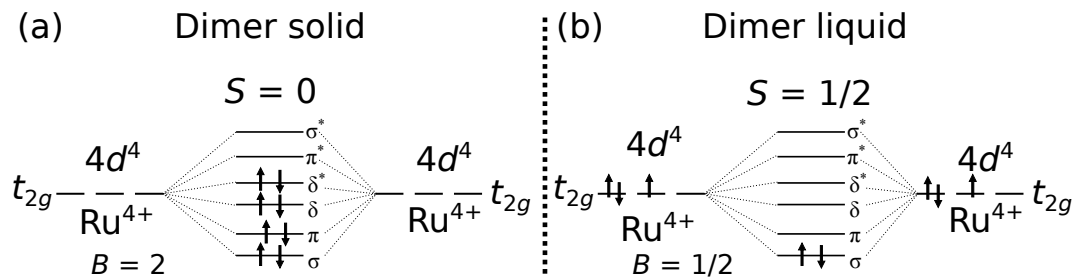


Fig. 1.8 Molecular orbital diagram of Ru-Ru in the (a) dimer solid phase (low temperature) and (b) dimer liquid phase (high temperature). B is the bond order described in the section 4.3. These diagrams are based on Refs. [25].

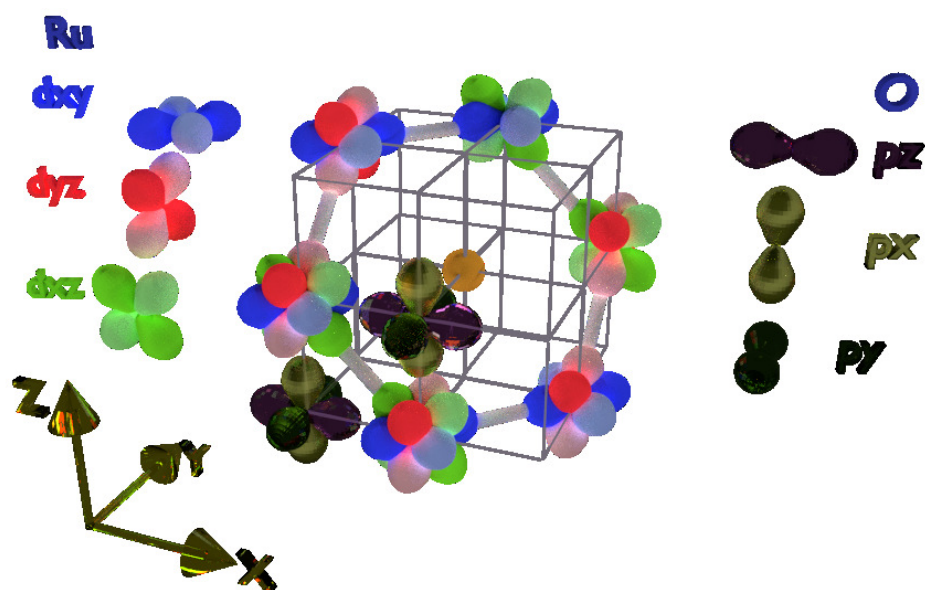


Fig. 1.9 Structure of Li_2RuO_3 including pure atomic orbitals. Labels in the right and left side indicate the orbitals of Ru and O. The yellow sphere in the center indicate the s orbital of Li. Orbitals of Ru not contributing to the σ -bond are not depicted except for the two Ru ions in front. The orbitals of only two oxygen atoms are shown. Other oxygen ions are located in the intersections of the thin gray bars. This figure does not consider hybrid orbitals. It is based on Refs. [28, 30]

In particular, the relation between the dimer transition and delithiation has not been reported.

1.3 Motivation and purpose

In this work we are motivated by the presence of the unconventional Ru-Ru dimerization in Li_2RuO_3 . Our goal is to obtain novel information about the origin and mechanisms that lead to the dimerization.

Although, Li_2RuO_3 has nominally $S = 1$, under some circumstances, it seems possible to induce different S . Thus, we look for the experimental realization of the predicted properties of the honeycomb lattices with $S = 1/2$: Kitaev liquid [7]; topological phases [14]; and if the system is hole doped, topological superconductivity [9–11]

As a collateral result, the study of Li_2RuO_3 provides useful information for understanding the behavior of the isostructural iridates $A_2\text{IrO}_3$ ($A = \text{Li}, \text{Na}$) [39]. Furthermore, the results of the properties of Li_2RuO_3 might provide information to the electrochemical properties of Li_2RuO_3 as potential material for batteries [15, 32, 35].

In order to achieve the previous goals we divide the work in two main parts. In the first part we study the correlation between the cell parameters of Li_2RuO_3 and the magnetic behavior of the dimer transition, focusing on the importance of the crystallinity for the observation of intrinsic properties of Li_2RuO_3 . In the second part, we introduce hole doping to Li_2RuO_3 via heavy delithiation, and found $\text{Li}_{2-x}\text{RuO}_3$ with a different crystal structure as well as a different electronic structure.

1.4 Overview of this thesis

The contents of this thesis are as follows:

- Chapter 2 describes the experimental methods used: sample preparation, crystal structure characterization, magnetic susceptibility and transport measurements.
- Chapter 3 is focused on the importance of the dimer coherence configuration in the stoichiometric Li_2RuO_3 . We emphasize the correspondence of the crystal structure and the magnetic properties. We propose a model to explain the observed results. As an outcome, a proper method of synthesis for the study of the dimer transition is shown.
- Chapter 4 is dedicated to the study of the physical properties of the delithiated ruthenate $\text{Li}_{2-x}\text{RuO}_3$. First, the results of the crystal structure determination

are shown. Next, the results of the magnetic properties of $\text{Li}_{2-x}\text{RuO}_3$ and a comparison with those of Li_2RuO_3 are shown. Then, aiming to understand the local structure of $\text{Li}_{2-x}\text{RuO}_3$, the correlation of magnetic properties and structure is presented.

- In the conclusions, the interpretation of results and proposed explanations are summarized. Finally, we propose future work that is important for the understanding of the origin of the dimer states in Li_2RuO_3 and $\text{Li}_{2-x}\text{RuO}_3$.
- Appendix A shows the calibration of thermometers at high temperatures and the importance of the thermometer calibration in this particular work.
- Appendix B shows the results of pair distribution function (PDF) analysis of Li_2RuO_3 that we performed in the European synchrotron radiation facility (ESRF).

Chapter 2

Experimental methods

2.1 Sample preparation

2.1.1 Synthesis of polycrystalline Li_2RuO_3

Polycrystalline Li_2RuO_3 samples were prepared from Li_2CO_3 (Aldrich, 99.997%) and RuO_2 (Rare Metallic, 99.9%). Li_2CO_3 was dried at 300° C for 2 hours. Their masses were measured, and then they were mixed and ground for 1 hour in a conventional mortar. This starting powder was pelletized and heated for 24 hours as the first heating process. The process of grinding, pelletizing and heating was repeated several times for some samples. Details of the synthesis are summarized in Table 3.1.

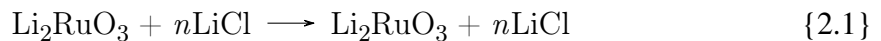
2.1.2 Single crystal growth of Li_2RuO_3

Flux method

Single crystals of Li_2RuO_3 were prepared from Li_2CO_3 (Aldrich, 99.997%), RuO_2 (Rare Metallic, 99.9%) and LiCl (Furuuchi Chemical, 99.9%). Li_2CO_3 was dried at 300° C for 2 hours and LiCl was dried at 110° C under vacuum for 12 hours.

Their masses were measured, and then they were mixed and ground for 1 hour in a conventional mortar in argon atmosphere. This starting powder was pelletized and heated.

The following method was tried with different profiles of heating/cooling.



The Reac.2.2 was tried at temperatures lower than 1000° C. However, the experimental result was the following.



According to previous studies done by thermogravimetric analysis (TGA) [40] Li_2RuO_3 is stable up to $\sim 1200^\circ \text{C}$ without any detectable loss in the mass. The Reac.2.2 shows that the slow cooling required to grow single crystals decomposes Li_2RuO_3 while losing lithium. Thus, the following reaction was used in order to add an initial excess of Li_2CO_3 :



In order to obtain large single crystals several conditions were modified. The parameters that were modified in ~ 60 samples were the following:

- Initial quantity of Li_2CO_3 .
- n of LiCl .
- Maximum temperature.
- Heating rate.
- Cooling rate.
- Controlled atmosphere: air/Ar

The different combinations are shown together with the resulting size of the crystals in Table 3.2.

Using an image furnace

General details of the floating zone technique and the image furnace (IF) and can be found in Ref. [41]. Li_2CO_3 was dried at 300°C for 2 hours. 10% (mol/mol) excess of Li_2CO_3 (Aldrich, 99.997%) and RuO_2 (Rare Metallic, 99.9%) were measured, and then they were mixed and ground for 1 hour in a conventional mortar. This starting powder was compacted by hydrostatic pressure (400 kgf/cm^2) forming a rod of approximately 7 cm and 10 mm of diameter. The rod was sintered at 750°C 1 h with a heating rate of 25°C/min . The rod was introduced in the chamber of an image furnace (NEC-SCK15HD K). The growth was done under a mixture of 90% Ar and 10 % O_2 .

Temperature was enhanced gradually up to the feeding rod was melt (90 V), after some seconds the melt zone of the rod solidified and temperature was decreased at a rate of 3 min/V.

2.1.3 Delithiation to obtain $\text{Li}_{2-x}\text{RuO}_3$

Pristine Li_2RuO_3 samples were prepared from Li_2CO_3 (Aldrich 99.997%) and RuO_2 (Rare metallic, CO. LTD. 99.9%). After the starting powders were dried, stoichiometric quantities were mixed and ground for 1 hour, and then in a conventional mortar. We added acetone to improve the homogeneity of the powder. The powder was pelletized and heated at 1000°C for 24 hours in the first step. Next, the pellet was re-ground in acetone for 1 hour pelletized and heated at 900°C for 48 hours followed by natural cooling. The choice of the synthesis method is based on results of chapter 3 [42]. Purity, as well as the dimer coherence of the obtained sample was verified by X-ray diffraction (XRD) and magnetic susceptibility measurements, whose details are described below.

For delithiation, a solution of I_2 (Wako 99.9%) in acetonitrile (CH_3CN) of concentration 0.3384 mol/L was prepared. Powder of Li_2RuO_3 , whose mass was measured before, was soaked in the solution for 3 days at room temperature. Then Li_2RuO_3 was washed with clean acetonitrile and soaked in a new solution of I_2 0.3683 mol/L for 18 hours under stirring at 560 rpm. The containers were covered with aluminum foil in order to avoid decomposition of I_2 into I^- triggered by light. The $\text{Li}_{2-x}\text{RuO}_3$ samples were taken out, and rinsed with clean acetonitrile until the color of the acetonitrile become completely transparent. A less delithiated sample of $\text{Li}_{2-x}\text{RuO}_3$ was prepared in a solution of I_2 0.18457 M soaked 3 days. Since this sample was found to be mainly combination of Li_2RuO_3 and $\text{Li}_{2-x}\text{RuO}_3$ we don't show further analysis of it.

There is not noticeable decomposition at room temperature in any of the samples. However, they have been maintained in vacuum in order to prevent changes.

The steps to prepare the solution for delithiation of Li_2RuO_3 by chemical oxidation with I_2 is described below. They correspond to Fig. 2.1.

1. Weight the mass of I_2 in a beaker using a scale. I_2 sublimates at room temperature. Since the initial mass of I_2 is important to later determine the Lithium content in Li_2RuO_3 , once the desired mass of I_2 is achieved, it must be dissolved in acetonitrile as soon as possible.
2. Stir to dissolve completely. A magnetic stirrer was used.

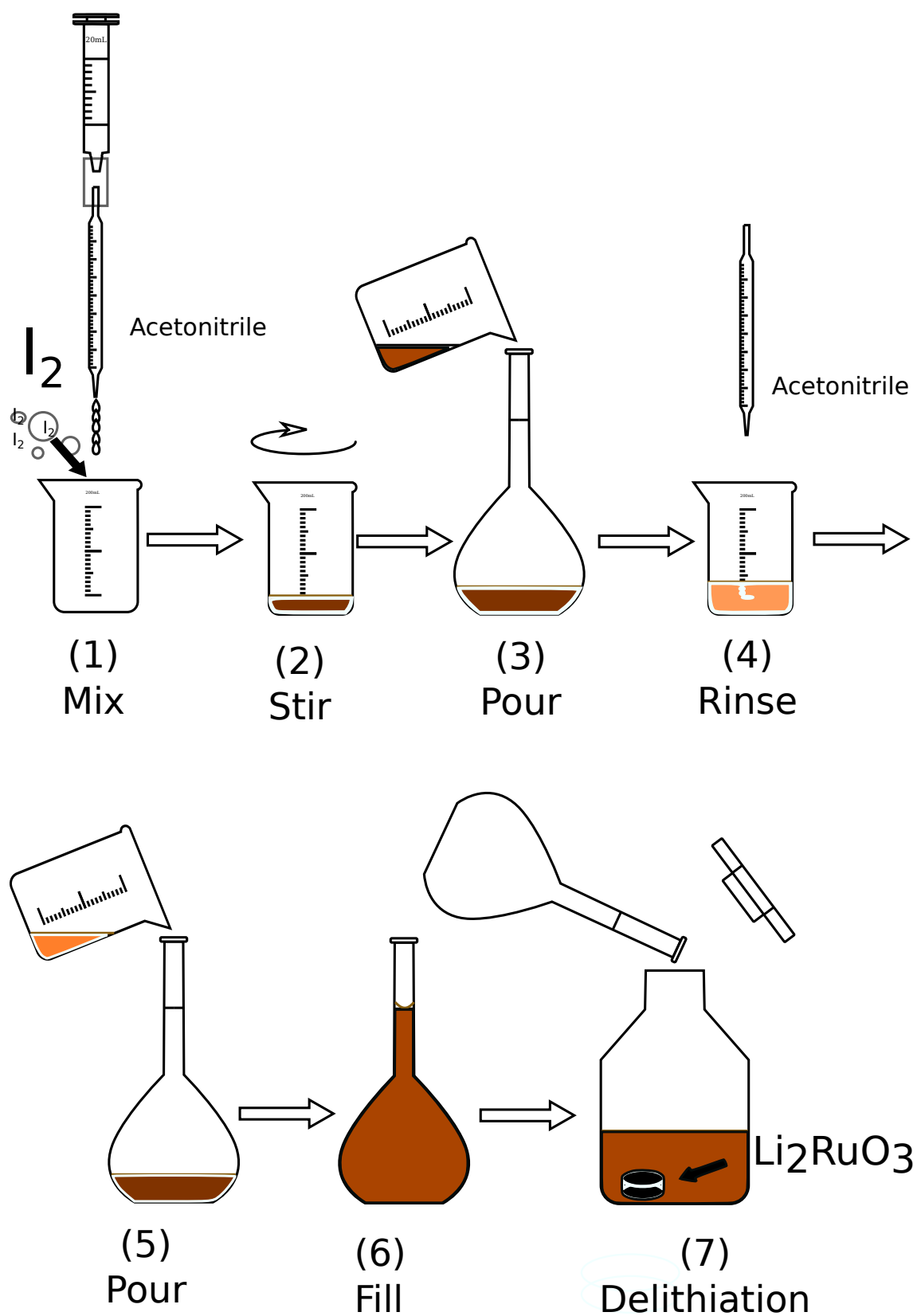


Fig. 2.1 Procedure delithiation by chemical oxidation with I_2 .

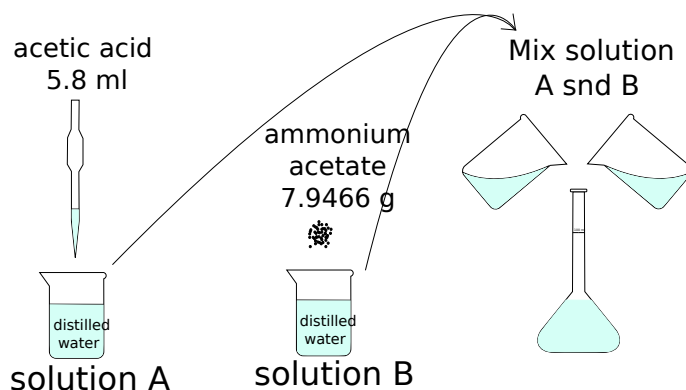
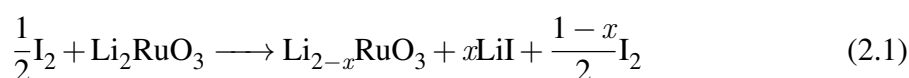


Fig. 2.2 Procedure for the elaboration of solution buffer. *Figure prepared by Ikeda Atsutoshi.*

3. Pour the solution into a volumetric flask of 1 L.
4. In the beaker there will be remaining I_2 rinse the beaker with acetonitrile.
5. Pour the solution used for rinsing into the volumetric flask. Repeat the previous and this step till the acetonitrile is clean. Consider that you should not exceed the volume of the volumetric flask (1 L).
6. Fill the volumetric flask till the mark of 1 L, close it and shake it for approximately 1 minute.
7. Pour the solution into a glass container of 1 L and introduce the Li_2RuO_3 . The mass of Li_2RuO_3 must be weighted before.

The chemical reaction involved in the delithiation is the following:



2.1.4 Quantification of lithium in $Li_{2-x}RuO_3$

Chemical titration

In order to evaluate x , the remaining quantity of I_2 in the solution of acetonitrile was measured through titration with a standard

Na_2SO_3 (Wako, 0.1 mol/L and 0.01 mol/L *for volumetric analysis*) at 20° C. The glassware used for the titration was calibrated at 20° C: for acetonitrile. Details are described below.

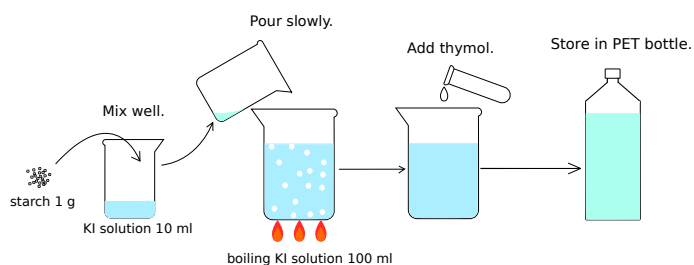


Fig. 2.3 Procedure for the elaboration of indicator redox based on starch. *Figure prepared by Ikeda Atsutoshi*

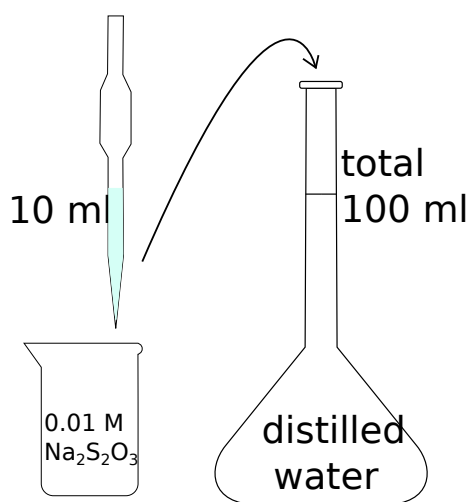


Fig. 2.4 Procedure for the preparation of $\text{Na}_2\text{S}_2\text{O}_3$ of appropriate concentration. *Figure prepared by Ikeda Atsutoshi*

1. Preparation of aliquot

We have I_2 solution used for delithiation from Li_2RuO_3 and LiI , which is insoluble, is at the bottom of the solution container. We take supernatant of the solution with a pipette and titrate remnant I_2 .

2. Preparation of solutions

Indicator: Suspend 1 g of soluble starch in 10 mL of saturated KI solution, and stir slowly into 100 mL of boiling saturated KI solution. Add 0.2 g of thymol to prevent degradation of starch [1] (see Fig. 2.3). Store the solution in a pet bottle. Since the solution degrades fast, it should be used within a week, and store the bottle in a refrigerator. Before using it, it should be in a dropper bottle.

3. Solution of $Na_2S_2O_3$ 0.001 M

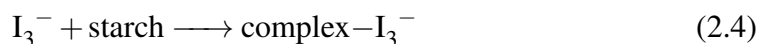
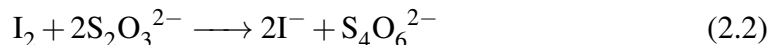
Take 10 ml with a volumetric pipette of the standard solution of 0.01M $Na_2S_2O_3$ and dissolve them in distilled water using a volumetric flask to make the total volume 100 ml (see Fig. 2.4).

4. Buffer solution

Take 5.8 ml of acetic acid 99% and mix it slowly with approximately 15 ml of distilled water (solution A). Weigh 7.9466 g of ammonium acetate 97% and dissolve it in distilled water (solution B). Mix solution A and B, pour them in a 100 ml volumetric flask and add distilled water up to the limit (see Fig. 2.2).

5. Titration

The reaction between I_2 and Li_2RuO_3 happens according the Reac. 2.1. We quantify the remnant I_2 through the following reactions:



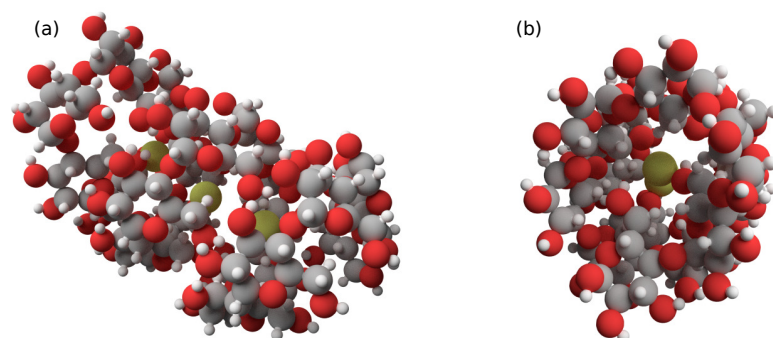


Fig. 2.5 Complex of starch and Iodine that has a purple color in solution. (a) Side view. (b) Front view. Red spheres represent oxygen, gray ones carbon, white ones hydrogen and yellow ones iodine.

The starch works as a detector of I_2 , the complex (Reac. 2.4) formed by I_3^- and starch (see Fig. 2.5) has a deep purple color.

The setup for the titration is shown in Fig. 2.6. The burette is cleaned with the solution of $Na_2S_2O_3$. We fill the burette with the $Na_2S_2O_3$ solution. Then we take 1 or 0.5 mL of an aliquot (with a volumetric pipette) and pour it in an Erlenmeyer flask. The Erlenmeyer flask should be cold. For this sake it was kept in a refrigerator. It is important not to touch the walls of the flask with the pipette or the I_2 sample. Add 10 mL of distilled water and 20 mL of the buffer solution. Pour $Na_2S_2O_3$ with the burette till the brown color of sample disappears. Add the indicator and the color changes into blue. Pour $Na_2S_2O_3$ again till the blue color vanishes.

Inductively coupled plasma mass spectrometry (ICP-MS) analysis

As a cross-check of the accuracy of the obtained value of x , we dissolved $Li_{2-x}RuO_3$ in hot HCl (37%), and performed the inductively coupled plasma mass spectrometry (ICP-MS) analysis using a commercial apparatus (Seiko Instruments, SPS 6100). Quantification by ICP-MS was not successful due to a non homogeneous digestion; we find out that putting $Li_{2-x}RuO_3$ in hot HCl produces a small amount of RuO_2 , which is not soluble in HCl and makes the quantification by ICP-MS inaccurate.

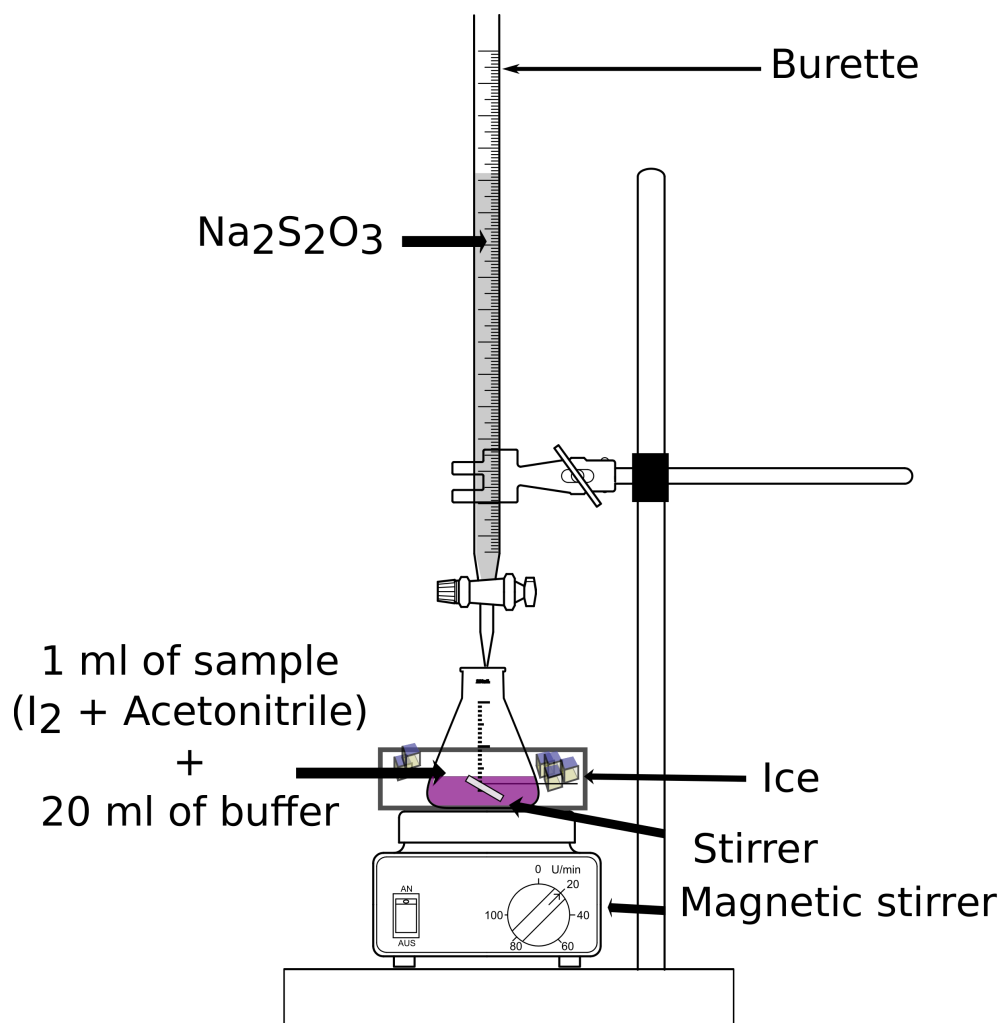


Fig. 2.6 Apparatus used for titration. The container of the ice must be white in order to allow detecting changes of coloration of the solution.

2.2 Structural characterization

2.2.1 Powder X-ray diffraction (XRD)

Powder X-ray diffraction (XRD) measurements were performed at room temperature with a commercial diffractometer (Bruker AXS, D8 Advance) using the $\text{CuK}\alpha$ radiation equipped with a one-dimensional array of detectors and a nickel monochromator. The sample stage was spun at 30 rpm. Peak indexing was carried out using the program Topas 4.2. The tube tails as well as other instrument parameters were calibrated using a standard reference plate of alumina provided by the National Institute of Standards and Technology.

2.2.2 High-energy XRD at different temperatures

High-energy XRD measurements at room temperature were performed at the beam line ID22 of the European Synchrotron Radiation Facility (ESRF). X-ray beam of the energy 30.993 keV ($\lambda = 0.40003 \text{ \AA}$) was used. High-energy XRD measurements at various elevated temperatures were performed at the beam line ID11 at ESRF. A double Laue monochromator was used to select X-ray of the energy of 87.5 keV ($\lambda = 0.14169 \text{ \AA}$). The beam was focused to ca. 100 μm using refractive lenses. The scattered X-ray was detected using a CCD camera (FReLoN). Temperature control was achieved using a hot-air blower. Data were continuously collected upon heating to 723 K at 2.5 K/min, and upon cooling to room temperature at the same rate. Typical temperature resolution was 0.2 K/pattern. We find a noticeable difference between the actual sample temperature and the thermometer temperature. Thus, a lineal correction to the thermometer temperature was made, so that T_d of Li_2RuO_3 recorded in the XRD measurement matches with the T_d of the magnetization measurements.

2.2.3 Pair distribution function (PDF) analysis

Refinements against Bragg intensities are sensitive only to the average crystallographic structure. We therefore performed pair distribution function (PDF) analysis, which is sensitive to local order as it includes the diffuse scattering signal.

High energy X-ray scattering measurements for PDF were performed at the beam line ID11 and at the ESRF. The experimental configuration is similar to the configuration for XRD described in the Sec. 2.2.2 but the detector was located very close to the sample (ca. 100 mm) to obtain high angle data suitable for the PDF analysis.

The XRD data was transformed using Igor Pro based software (iPDF) developed by Simon Kimber at the European Synchrotron Resource (ESRF), we corrected the raw diffraction data for background, incoherent inelastic scattering, and the atomic form factors.

For the transformation we used the magnitude of the scattering vector $\mathbf{Q}$ Eq. 2.5

$$Q = |\mathbf{Q}| = \frac{4\pi \sin \theta}{\lambda} \quad (2.5)$$

where θ is the angle between the incident X-ray beam and the detector measuring the scattered intensity, and λ is the wavelength of the X-rays.

We Fourier-transformed the structure factors $S(Q)$ defined in the reciprocal space Q into real space using Eq. 2.6

$$G(r) = \frac{2}{\pi} \int_{Q_{\min}}^{Q_{\max}} Q [S(Q) - 1] \sin(Qr) dQ \quad (2.6)$$

where $G(r)$ is the distribution of pairs of atoms separated by a distance r .

Samples were mounted in a capillary of quartz.

2.3 Magnetization measurements

The magnetization measurements were performed using a commercial superconducting quantum interference device magnetometer (Quantum Design, MPMS). The magnetization at high temperatures (300 to 700 K) were measured using the oven option for MPMS. We used quartz tubes as sample holders for the high temperature measurements. The sample tubes were sealed with ceramic bond (Resbond, 907GF) in order to prevent any gas released from the sample to damage the inside of the oven sample space. We checked the thermometer calibration of the oven by measuring the ferromagnetic transition ($T_C = 627.2$ K) of Ni (Rare metallic, 99.99%) at several fields [43]. The calibration error in T_C of Ni is less than 0.2%. Measurements from 1.8 to 300 K were performed with the ordinary setup of MPMS in zero-field-cooled (ZFC) and field-cooled (FC) sequences.

AC magnetization measurements were performed from 0.1 to 5 K using an adiabatic demagnetization refrigerator and a set of coils developed by S. Yonezawa *et al.* [44] that were installed in a commercial physical properties measurement system (Quantum Design, MPMS).

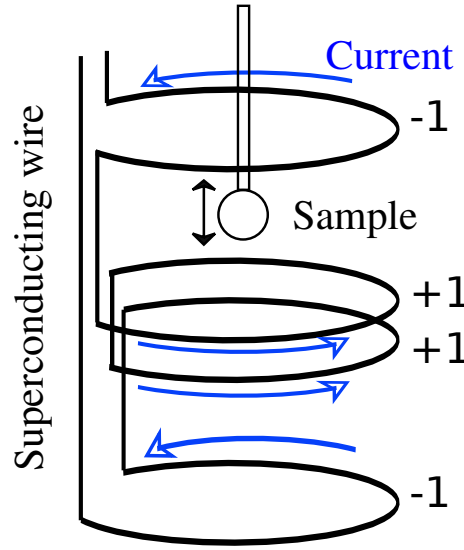


Fig. 2.7 System of coils in MPMS.

2.3.1 SQUID magnetometry

The MPMS is mainly consist of a magnet, a detection coil, a super quantum interference device (SQUID), and magnetic shield.

The the sample is moved through the detection coils. The movement of the magnetic moment of the sample induces an electric current in the detection coils. The coils and the SQUID are connected by superconducting wires in a closed loop that has a persistent current. Thus, any change in the magnetic flux produces a proportional change in the persistent current.

The SQUID is a loop based on Josephson junctions. It is superconducting ring with two “weak links”, each half of the ring is connected to the different terminals of the collection coil. The weak links refer to a tunnel barrier, or a thin normal metallic spacer (Ref. [45, 46]).

Since the SQUID is very sensitive, it requires a superconducting shield that maintains the field constant and prevents external fields to disturb the signal produced by the sample.

The detection system (Fig. 2.7) is conformed by a set of three coils: On the top, one with a turn in clockwise; in the middle, one with two turns in counter-clockwise; and in the bottom one with turns in clockwise [47].

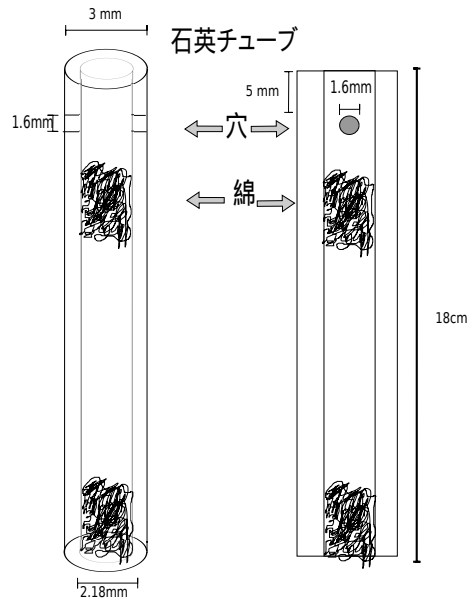


Fig. 2.8 Design of quartz sample holder for high-temperature measurements in oven of MPMS. First 18 cm length quartz tube is cut. A hole of more or less 1.6 mm diameter is done. Cotton is inserted before the hole is done to prevent impurities to enter while the hole is done. Finally, the cotton is removed.

2.3.2 Sample mounting

Low-temperature measurements

The sample holders for low-temperature measurements were quartz tubes sealed with ceramic cement for high temperatures (Resbond, 907GF) in order to prevent any gas release from the samples to damage the inside of the oven sample space.

High-temperature measurements

The sample holders for high temperature measurements were quartz tubes sealed with ceramic cement for high temperatures (Resbond, 907GF) in order to prevent any gas release from the samples to damage the inside of the oven sample space. The sample holder are hanged by a cooper wire from the sample rod of MPMS. In the Fig. 2.8 is shown a design to fabricate the sample holders.

In Fig 2.8 is shown a model for production of sample holders for high-temperature magnetization measurements.

2.3.3 Calibration of thermometer at high temperatures of magnetometer oven

We checked the calibration of the thermometer of the oven by measuring the ferromagnetic transition ($T_C = 627.2$ K) of Ni (Rare metallic CO. LTD., 99.99%) at several fields [43]. The calibration error of T_C of Ni was found to be less than 0.2%. Measurements from 1.8 to 300 K were done with the ordinary setup of MPMS in zero-field-cooled (ZFC) and field-cooled (FC) sequences.

2.4 Transport measurements

Transport measurements were performed based on the 4 points method. Gold wires were attached with silver paste (Dupont RT4929N) diluted with diethyl succinate (Wako). Measurements were done using a PPMS and an adiabatic demagnetization refrigerator.

Chapter 3

Coherence of dimer configuration in stoichiometric Li_2RuO_3

In this chapter, we study the correlation between the cell parameters of Li_2RuO_3 and the magnetic behavior of the dimer transition, focusing on the importance of the crystallinity for the observation of intrinsic properties of Li_2RuO_3 .

We discuss the dependence of magnetic properties on the crystalline disorder in Li_2RuO_3 with Ru honeycomb lattice. We demonstrate that the cell parameters, related to the coherence of the dimer formation, are strongly dependent on the synthesis procedure. We show that the magnetic behavior at the dimer transition is closely related to the lattice parameters. In particular, we revealed that samples with dimer coherence exhibit a first-order magnetic transition with the onset exceeding 550 K, higher than that reported previously. We discuss possible dimer configurations leading to this magneto-lattice coupling.

3.1 Crystal structure

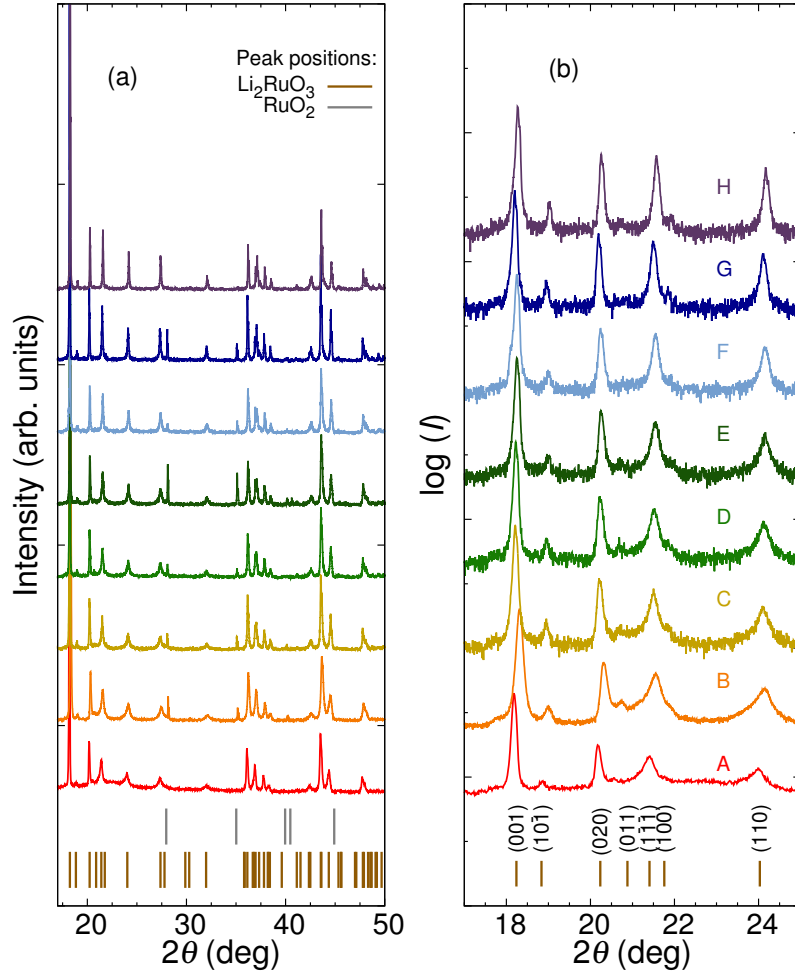


Fig. 3.1 Comparison of XRD spectra of several samples of Li_2RuO_3 . The labels A–H identify samples listed in Table 3.1. Small horizontal shifts of the spectra mainly arisen from small variation in the position of the sample surface are observed. This shift was corrected when the cell parameters were obtained. The panel (a) shows the intensity I vs 2θ and (b) the semi-logarithmic intensity I vs 2θ in a narrower angle range. Expected peak positions for Li_2RuO_3 ($P2_1/m$) and RuO_2 are indicated with brown and gray vertical lines.

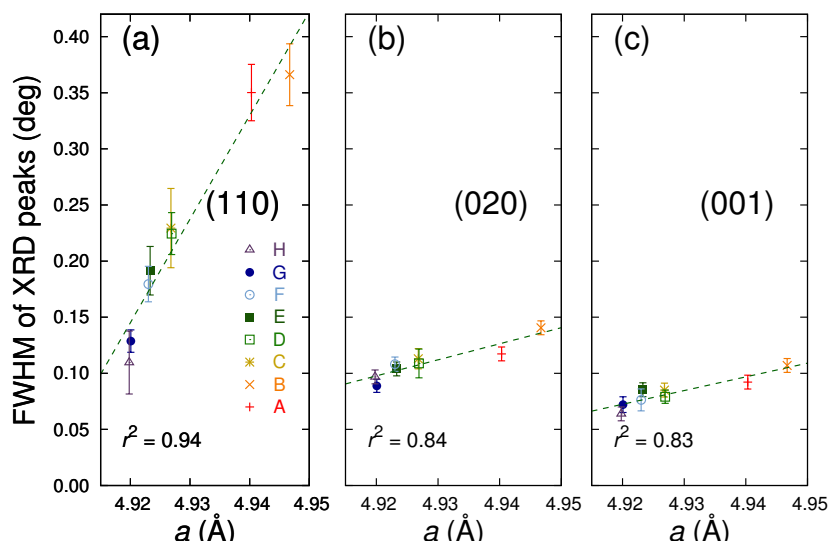


Fig. 3.2 Full width half maximum (FWHM) of the peaks (110), (020) and (001) of the XRD peaks as a function of the cell parameter a , shown in the panels (a), (b), and (c) respectively.

Table 3.1 Summary of lattice parameters of $\text{Li}_{2-x}\text{RuO}_3$ and synthesis conditions.

sample label	starting composition Li : Ru (mol : mol)	Max. temp. of the 1st heating step ^{a, b} (°C)	Max. temp. of the 2nd heating step ^{b, c} (°C)	Max. temp. of the 3rd heating step ^{b, c} (°C)	a (Å)	b (Å)	c (Å)	β (°)
A	2.08 : 1	1000	-	-	4.9403(13)	8.7655(23)	5.8893(17)	124.4395(40)
B	2 : 1	1000	-	-	4.9470(05)	8.7622(09)	5.8916(06)	124.4615(29)
C	2 : 1	1000	900	-	4.9268(10)	8.7755(18)	5.8958(13)	124.3760(31)
D	2 : 1	1000	900	900	4.9269(13)	8.7773(23)	5.8974(16)	124.3757(30)
E	2 : 1	1000	900	900	4.9233(09)	8.7741(15)	5.8941(11)	124.3726(31)
F	2 : 1	1000	900	1000	4.9230(08)	8.7806(14)	5.8959(10)	124.3610(23)
G	2 : 1	1000	1000	-	4.9200(04)	8.7809(08)	5.8940(06)	124.3501(14)
H ^d	2 : 1	1000	1000	-	4.9198(04)	8.7822(07)	5.8932(05)	124.3485(13)

^a For 24 hours.^b We spent 2.5 hours from room temperature to T_{max} .^c For 48 hours.^d Acetone was added while grinding in order to enhance the homogeneity.

In this study, we compare results of 8 samples. The characters of the samples can be divided by their synthesis procedures (Table 3.1): samples A and B were heated only once at 1000° C [24]; samples C, D, and E were heated two or more times with final heating at 900° C [21]; samples F to H were heated two or more times with final heating at 1000° C. All samples were furnace-cooled after the heater was switched off. In addition, in order to improve the homogeneity of the starting powder for sample H, acetone was added to the powder during the grinding.

In Fig. 3.1, powder XRD spectra of samples A to H are presented. All the spectra are well fitted with the reported space group $P2_1/m$ with the static Ru-Ru dimers [24]. Samples A and H do not show any secondary phase by XRD, while the other samples contain a small amount (at most 4%) of RuO_2 .

Surprisingly, we found that the cell parameters and crystallinity of the samples are strongly affected by the synthesis process. In Fig. 3.1(b), spectra between 17° and 25° are presented with a logarithmic vertical scale. It is clear that peaks become sharper for samples with labels in the order of the alphabet (A to H). In particular, peaks related to the a parameter, i.e. (hkl) peaks with $h \neq 0$, exhibit stronger sample dependence. For instance, the $(10\bar{1})$ and (110) peaks have evidently different sharpness depending on the samples and these peaks are significantly broader for samples A and B, which were heated only once. In contrast, the peaks belonging to directions that only include the c direction (i.e. $(00l)$ peaks) exhibit a weaker change.

For a more quantitative analysis, Fig. 3.2 compares the full width half maximum (FWHM) of the (110) , (020) and (001) XRD peaks as a function of the a -axis length. It is clear that the change in the FWHM of the (110) peak amounts 300%, much stronger than those of the other peaks (40% for (020) and 16% for (001)). This contrast indicates that the broadening is intimately related to the degree of dimer formation since the dimer-bond direction is predominantly along the a axis, but not to the degree of mosaicity which would broaden all peaks equally.

The cross section of the X-ray scattering is sensitive to the atomic number (Z). Since both lithium ($Z = 3$) and oxygen ($Z=8$) are light elements, conventional XRD used in this study does not contain much of their information. To confirm this, we performed simulations of XRD patterns (not shown) changing the structure factor of the O ($Z = 8$) using the space group $P2_1/m$. The relative intensity of the peaks (110) , (020) and (001) are found to remain invariant despite structure factor is changed. This fact confirms that these peaks in Li_2RuO_3 are sensitive only to Ru atoms. Thus the broadening of those peaks is related to the Ru positions.

The difference in sharpness of the peaks is attributed to the spatial coherence of the short bond (dimer), which is mainly aligned along the a -axis with a smaller component along the b -axis (see Fig. 1.4(d)); non-dimerized Ru ions result in incoherence of the Ru dimers, leading to broader peaks. Thus, the present results indicate that the degree of formation of the Ru dimers is crucially dependent on the sample preparation process.

This scenario is supported by the variation in the obtained lattice parameters, which are summarized in Table 3.1. It is clear that the variations of the cell parameters have a definite tendency. The strongest sample dependence among the four lattice parameters is seen in the a parameter (nearly 0.41%). Shorter a for well treated samples indicates well-ordered Ru-Ru dimers. In contrast, the changes in b , c and β are only 0.19, 0.06% and 0.07%, respectively. It is a bit surprising that samples with well-ordered dimers (such as G and H) have longer b , in contrast to shorter a in such samples. Possible scenarios for this systematic enlargement of b when a is shorter are proposed in Sec. 3.2.

We note that broadening of peaks due to stacking faults has been previously discussed in Li_2MnO_3 , which has a similar honeycomb structure [48]. According to that study, the variation of the layer stacking results in a different space group, and a random stacking makes all the peaks broader. In case of Li_2RuO_3 in contrast, all samples studied here are well fitted with the same space group $P2_1/m$, and the broadening of the $h \neq 0$ peaks is more significant than those of the other peaks. Because of such essential differences, we conclude that the stacking faults do not play a main role of the broadening of peaks in the present study.

3.2 Magnetic behavior and its correlation with the crystal structure

In Fig. 3.3(a), we present the temperature dependence of the magnetization at 10 kOe normalized by the maximum magnetization $m \equiv M/M_{\text{max}}$ ($M_{\text{max}} \sim M_{610 \text{ K}}$ depending on samples) of representative samples. In this plot, diamagnetic contributions of ion cores [49] have been subtracted. Similar to the lattice parameters, the magnetic behavior is strongly sample dependent. In particular, the magnetic transition is very broad for samples A and B, prepared with only one heating process. In contrast, for samples G and H, which have been prepared by more elaborate processes, a jump-like behavior in $m(T)$ at T_d is observed. As shown in the inset of Fig. 3.3(a), sample G exhibits a sharp onset at 553 K, noticeably higher than the previously reported T_d of

540 K [24]. The difference in the sharpness of the magnetic transitions is more evident in the temperature derivative of $m(T)$ plotted in Fig. 3.3(b). For samples G and H, dm/dT has a much sharper peak with large height and smaller width compared to other samples. The jump in $m(T)$ and the sharp behavior in dm/dT for samples G and H indicate that the dimer transition is intrinsically the first-order transition, with a finite jump in the magnetization for an ideal case. This is compatible with a recent study where the dimer transition is found to be the first-order transition by means of differential thermal analysis (DTA) [50].

One comment should be made on the high-temperature crystal structure above T_d . Initially, the space group at high temperature was proposed to be $C2/m$ [24]. However, it was mentioned in that paper that the Rietveld refinement of neutron diffraction is equally good for the space groups $C2/m$ and $C2/c$. The space group $C2/m$ was chosen under the premise that the dimer transition is a second-order one. Since the transition is now found to be first order, the possibilities of the space group $C2/c$ as well as $C2/m$ for the high temperature phase need to be reconsidered on equal footing [24]. We should note that this assignment is for the averaged “thermodynamic” structure which consists of dynamical changes of dimer configurations.

Sharp changes of physical quantities at a first-order transition can be rounded by the effect of inhomogeneities (disorder) and the discontinuity can be completely vanished when the amount of disorder reaches a certain limit, as explained in Ref. [51]. Based on the rounded curves of samples A and B (Fig. 3.3(a)) and the heating treatment of those samples (Table 3.1), it is suggestive that the rounding of the transitions is caused by disorder. We confirmed that measuring several times from 300 K to 700 K and vice versa does not affect the sharpness of the transition or the value of the magnetization at 300 K (not shown). This indicates that the disorder is retained even in the high temperature phase (at least up to 700 K). The possible distortions will be discussed in the final part of this section.

Given these data, it is important to investigate relations between the crystal structure and magnetic behavior. We plot in Fig. 3.4 the inverse of the FWHM of the peak in dm/dT , as functions of several lattice parameters. The former characterizes the sharpness of the magnetic transition. According to the values of the square of the Pearson correlation coefficients (r^2) shown in Fig. 3.4, the main correlation between the structural parameters and sharpness of the magnetic transition is present in the cell parameters a , b and β , but not in c (see the definitions of the cell parameters in Fig. 1.4).

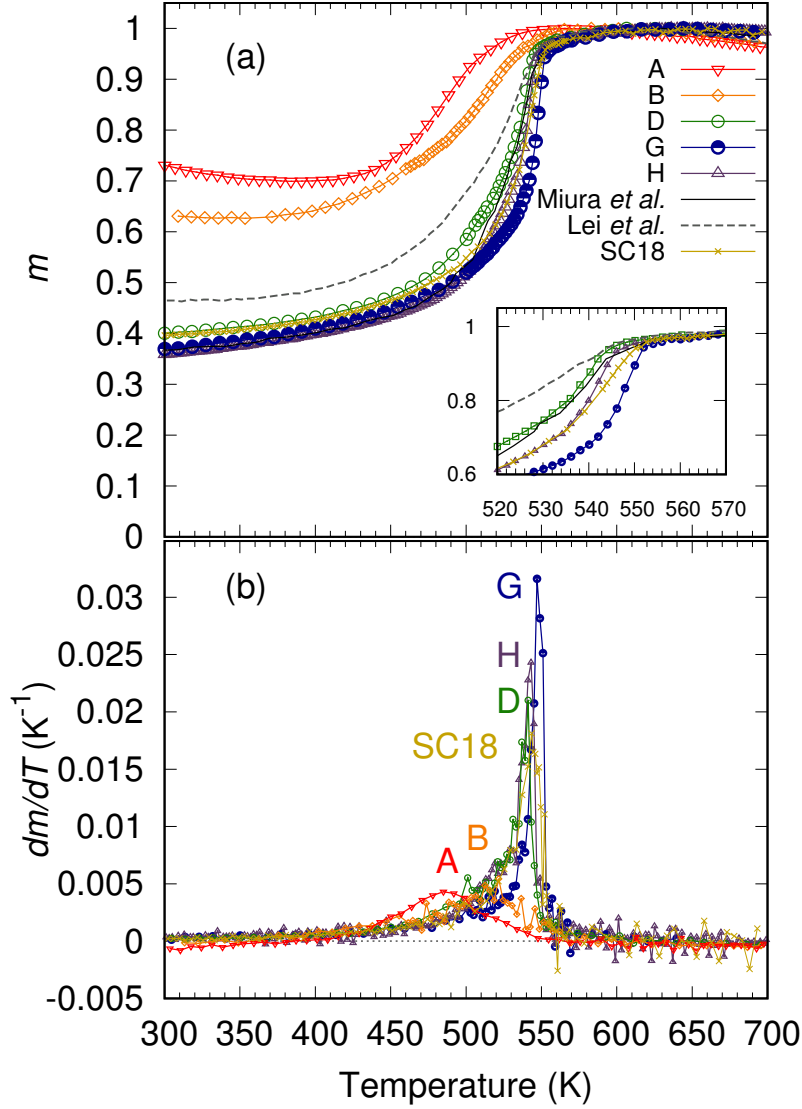


Fig. 3.3 (a) Temperature dependence of the magnetization ratio $m \equiv M/M_{\text{max}}$ at 10 kOe of representative samples. Results taken from Miura *et al.* [24] and Lei *et al.* [20] are included for comparison. Further analysis cannot be performed since the method and devices for the measurement may differ from ours. Data of single crystals randomly oriented is also included (SC18 Table 3.2). Inset shows the behavior near the transition. The diamagnetism due to the core electrons has been subtracted [49]. (b) Temperature derivative of m .

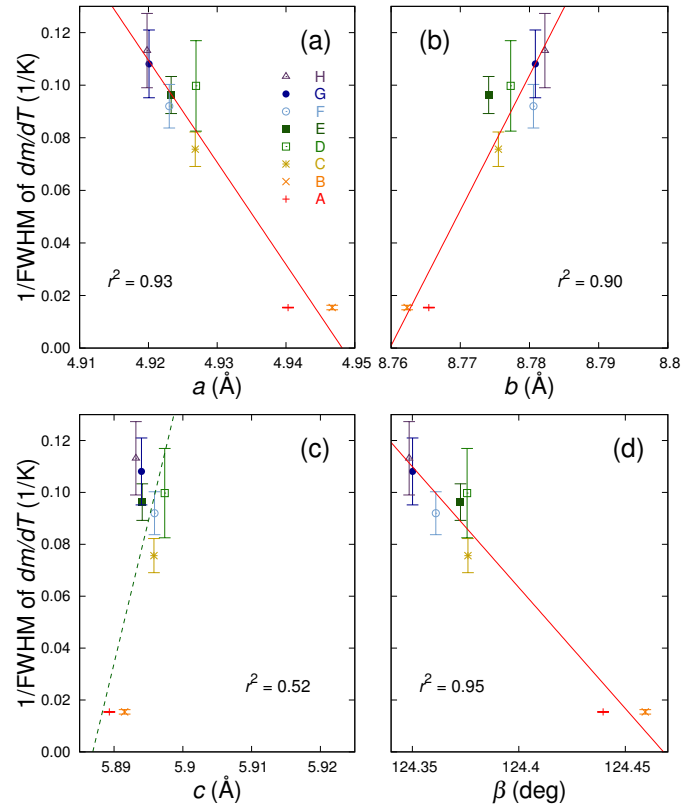


Fig. 3.4 Comparison between the sharpness of the magnetic transition and various structural parameters. The former is characterized by the inverse of the full width at half maximum (FWHM) of $dm/dT(T)$. We plot this quantity as functions of the cell parameters a , b , c and β in (a–d). In (a–c) the same horizontal scales (0.04 Å) for the full scale are used to highlight the differences in the change of the lattice parameters. The red and green lines are linear fittings whose square of the Pearson correlation coefficients (r^2) are shown in these panels. Alphabets A, B, C, etc. correspond to the sample labels in Table 3.1.

We have chosen the parameter a for quantifying the in-plane distortion for hexagonal lattices and examine relations to behavior at the magnetic transition. As seen in Fig. 3.4(a), samples whose a value is larger have a broader magnetic transition, whereas samples whose a is shorter have a sharper transition (i.e. samples F, G and H). The temperature of the magnetic transition, T_d , is also related to the lattice parameters. Here, T_d is determined by the maximum point in dm/dT . In Fig. 3.5(a), we present T_d plotted against a . Samples exhibiting shorter a tend to have higher T_d .

In addition to the sharpness of the magnetic transitions, values of the normalized magnetization at 300 K $m_{300\text{ K}} = M_{300\text{ K}}/M_{\text{max}}$ also exhibit correlation with some other properties. In Fig. 3.5(b), we show the relation between the FWHM of dm/dT and $m_{300\text{ K}}$. From the linear fitting, we can extrapolate to the ideal case of FWHM $\rightarrow 0$ to yield $m_{300\text{ K}} = 0.33 \pm 0.02$. Since magnetization measurements with the commercial SQUID magnetometer we use require the movement of the sample, it is important to consider that due to temperature and field inhomogeneities extrinsic broadening in dm/dT might occur besides noise. Assuming a broadening of 1 K in the FWHM due to instrumental reasons, the extrapolated ratio $m_{300\text{ K}}$ remains essentially the same. The measured value of the maximum susceptibility of sample H after the diamagnetic corrections is $\chi_{\text{max}} = 5.04 \times 10^{-4}$ emu/mol at 610 K. By using this ideal ratio $m_{300\text{ K}}$ and χ_{max} for sample H, we deduce for an ideal dimer structure the magnetization at room temperature to be $\chi_{300\text{ K}} \sim 1.68 \times 10^{-4}$ emu/mol. So far this large residual magnetization at room temperature has been attributed to the Van Vleck paramagnetism [24, 28, 52], but not confirmed yet.

Here, we discuss the origin of the observed coupling between the lattice and magnetic features. As already described, the sample dependence of lattice properties can be explained by the coherence of the dimer formation. The variation in the magnetic transition is also related to the coherence of the dimer ordering. Since the spins are expected to form non-magnetic spin-singlet within a dimer [24, 25], the reduction of magnetization represents the amount of Ru ions participating in the dimer formation. Overall, these results indicate that the coherent formation of the Ru dimers is the origin of the magneto-lattice coupling.

We further discuss possible magnetic and crystalline defects responsible for the broadening of the ($h00$) peaks, elongation of the parameter a , shortening of the parameter b , and the broadening of the magnetic transition. Naively, an unpaired Ru ion, represented by a red sphere in Fig. 3.6(b), is accompanied by an active magnetic moment. Such non-dimerized ions should contribute to elongate the cell parameter a as well as the broadening of the peaks with $h \neq 0$ compared with the ideal dimer

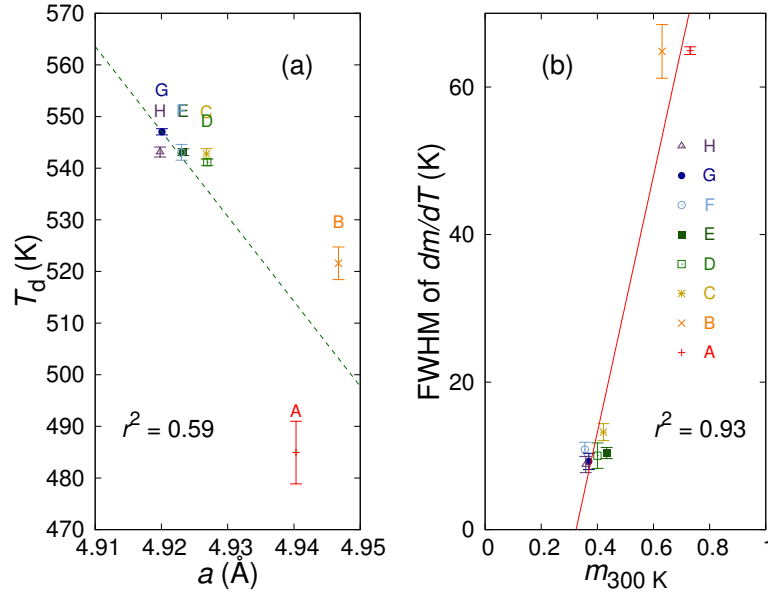


Fig. 3.5 (a) Relation between T_d determined by the peak of $dm/dT(T)$ and the lattice parameter a . (b) Correlation between the sharpness of the magnetic transition and $m_{300\text{ K}}$. The diamagnetic contributions of the ionic cores have been subtracted [49]. The red line indicates linear correlation while the green dashed line indicate weak linear correlation.

phase. Since unpaired ions have higher energy as pointed out in Ref. [25], formation of dimers along the b direction (Fig. 3.6(c)) should also be considered. Indeed, the energy required to form the b -axis dimer is expected to be similar to the energy of the other dimers [25], which we shall call the “ a -axis dimer”. Such dimers should be accompanied by unpaired ions with active spins, increasing the magnetization at room temperature ($m_{300\text{ K}}$). Formation of the b -axis dimer may also explain shrinkage of the b -axis length for samples A and B. In addition, misplaced “ a -axis dimers” (Fig. 3.6(d)) also result in the broadening of the $h \neq 0$ peaks of XRD, accompanying unpaired Ru ions that contribute to the enhancement of magnetization. Another possible defect is domain walls between regions with opposite dimer patterns, as shown in Fig. 3.6(e). Note that, in each hexagon, the four Ru bonds having the a -axis component are equivalent in the high-temperature phase [24]. Thus, formation of two different domains is plausible. Along the domain wall, either b -axis dimers or unpaired Ru ions exist. So far it is an open and interesting question which defects is most dominant in actual samples.

As we already mentioned, these defects in the Ru dimer formation are triggered by another kind of defects already imprinted in the high-temperature structure. According to the previous thermogravimetric analysis (TGA) of Li_2RuO_3 [40], this compound

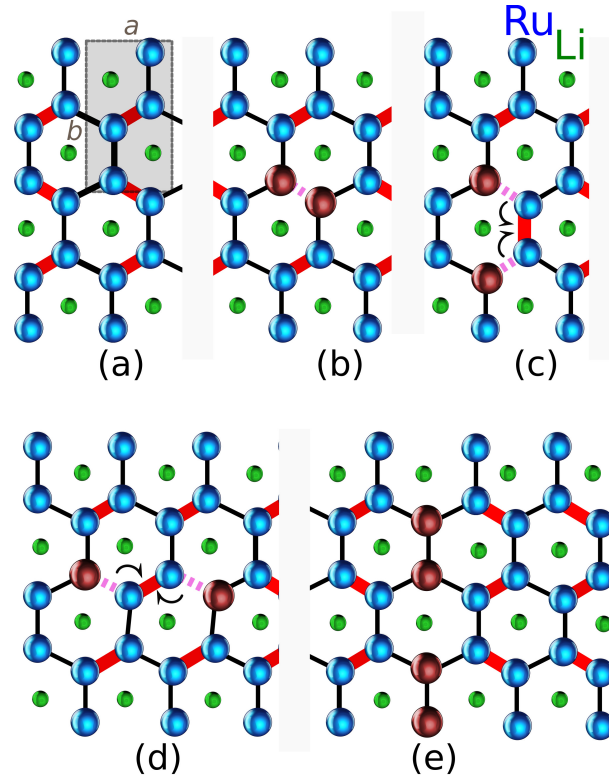


Fig. 3.6 Schematic of the Ru honeycomb layer of Li_2RuO_3 with Ru-Ru dimers. Red and black lines indicate the short (dimer) and long bonds. Dashed pink lines indicate the positions where dimer bonds are located in a perfect dimerized structure. Blue and red spheres represent dimerized and non-dimerized Ru ions. A unit cell [24] in the ab plane, as well as the cell parameters a and b , is also shown. (a) Ideal dimer pattern with “ a -axis dimer”. (b) With a pair of non-dimerized Ru-ions. (c) With a dimer in the b direction. (d) With a misplaced “ a -axis dimer”. (e) With a boundary of dimer domains.

is stable up to $\sim 1200^\circ\text{C}$ without any detectable loss in the mass. On the other hand, we observe increment of the amount of impurity RuO_2 phase while improving the dimer coherence by repeating the grinding and heating process. This segregation of RuO_2 implies that Li is deficient in samples with less coherent dimers, probably due to the evaporation of Li_2CO_3 in the initial heating. Then, samples with coherent dimers are formed after heating again to 1000°C by rearranging Li and releasing RuO_2 . In Li_2RuO_3 , there are two Li sites in the crystal structure: the inter-plane site and the in-plane site at the center of the Ru hexagon. Since Li at the inter-plane site is expected to be more movable and defects in this site should be relaxed at lower temperatures, we infer that defects in the in-plane site are more likely to be responsible for the incoherence of the Ru dimer formation. To verify this scenario, studies of the intentional introduction of Li defects may be valuable.

Before closing this section, we compare our results with those in previous studies. The broad magnetic transition of samples with less coherent dimers such as samples A and B (Fig. 3.3) resembles those reported for samples partially substituted with Ir or Ti [20, 50]. This fact raises a possibility that the effects on the dimer transition are mainly caused through the randomness introduced by isovalent substitution, rather than changes in the electronic structure. Similarly, the randomness effect on the absence of the dimer transition in single crystals reported in Ref. [53] should be re-examined.

3.3 First-order transition of the S-phase Li_2RuO_3

Initially the dimer transition of the pristine Li_2RuO_3 was considered to be second order [24]. However, recent studies indicate that the dimer transition is a first-order transition [42, 50]. Figure 3.7 shows the high-energy XRD spectra of pristine Li_2RuO_3 at three different temperatures. At the temperature close to the dimer transition, the spectrum shows the combination of the structures of the dimer-solid and dimer-liquid states. This coexistence provides additional evidence for the first-order transition.

3.4 Comparison between powder and single-crystalline samples of Li_2RuO_3

The parameters that were modified and the resulting size of the crystals grown by the flux zone method (Sec. 2.1.2) are shown in Table 3.2.

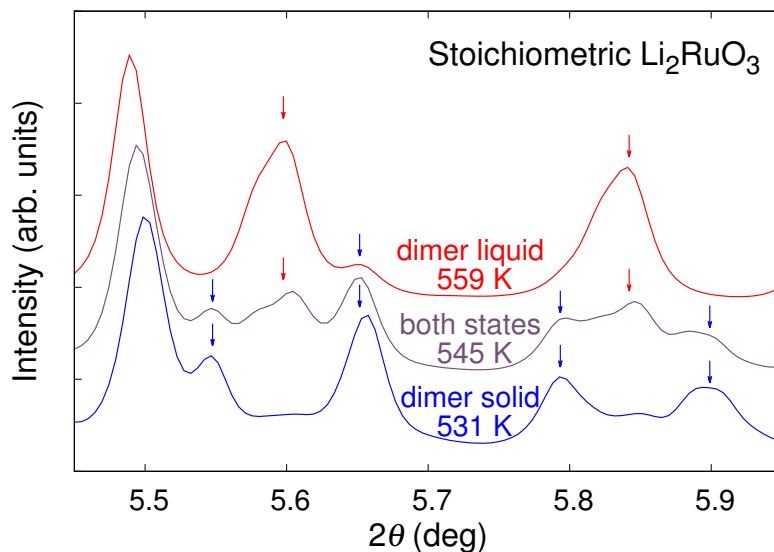


Fig. 3.7 (color online) High-energy XRD spectra of pristine Li_2RuO_3 sample at three different temperatures: Below $T_d \sim 550$ K, close to T_d , and above T_d . It shows the coexistence of the dimer-solid and dimer-liquid states, which is typical of a first-order transition. The blue arrows indicate peaks characteristic of the dimer-solid state and red arrows peaks of the dimer-liquid state. The measurements with $E = 87.5$ keV ($\lambda = 0.14169$ Å) were performed at the beam line ID11 of ESRF.

Fig. 3.8(a) shows pictures of crystals grown by the flux method and (b) with a IF. Although, the crystals by IF furnace are bigger than the crystals grown by IF, based on the magnetization measurements we determined that the dimers are decoherent in single crystals grown by IF. On the contrary, the crystals grown by the flux method have coherent dimers (Fig. 3.3) but the maximum size achieved is smaller (Table 3.2).

Table 3.2 Parameters modified for crystal growth by flux and results. The table is done according Eq.2.3

Sample num.	Sample name	n LiCl mol	Initial T °C	Time to Max. T hr	Max. T °C	Ann. time hrs	Cool. rate °C/hr	Final ctrl. T °C	S.c. size μm	Result	Comments
1	MPLR7	1	25	3	1000	10	5	500	50	Li_2RuO_3	
2	MPLR8	3	25	3	1000	10	5	500	50	Li_2RuO_3	
3	MPLR9	5	25	3	1000	10	5	500	50	Li_2RuO_3	
4	MPLR11	5	80	3	1000	10	5	500	50	Li_2RuO_3	half pot surrounding
5	MPLR12	3	80	3	1000	10	5	500	50	Li_2RuO_3	half pot surrounding
6	MPLR13	1	80	3	1000	10	5	500	50	Li_2RuO_3	half pot surrounding
7	MPLR14	10	50	12	1000	12	2	400	—	Ru_2O	—
8	MPLR15	15	50	12	1000	12	2	400	—	Ru_2O	—
9	MPLR16	20	50	12	1000	12	2	400	—	Ru_2O	—
10	MPLR17	10	25	0.3	1000	12	2	400	50	Li_2RuO_3	—
11	MPLR18	15	25	0.3	1000	12	2	400	150	Li_2RuO_3	—
12	MPLR19	12	25	0.3	1000	12	2	400	50	Li_2RuO_3	—
13	MPLR20	12	25	1	1000	2	2	400	100	Li_2RuO_3	—
14	MPLR21	13	25	1	1000	2	2	400	200	Li_2RuO_3	—
15	MPLR22	15	25	1	100	2	2	400	200	Li_2RuO_3	—
16	MPLR23	16	25	1	1000	2	2	400	200	Li_2RuO_3	—
17	MPLR24	17	25	1	1000	2	2	400	50	Li_2RuO_3	—
18	MPLR25	15	25	1	900	2	1	600	50	Li_2RuO_3	—
19	MPLR26	17	25	1	900	2	1	600	200	Li_2RuO_3	—
20	MPLR27	20	25	1	900	2	1	600	210	Li_2RuO_3	—
21	MPLR28	8	25	1	800	2	2	400	50	Li_2RuO_3	LiCl present
22	MPLR29	10	25	1	800	2	2	400	50	Li_2RuO_3	LiCl present
23	MPLR30	15	25	1	800	2	2	400	50	Li_2RuO_3	LiCl present
24	MPLR31	10	25	1	800	2	1	500	50	Li_2RuO_3	LiCl present
25	MPLR32	15	25	1	800	2	1	500	50	Li_2RuO_3	LiCl present
26	MPLR33	20	25	1	800	2	1	500	50	Li_2RuO_3	LiCl present
27	MPLR34	15.5	25	1	1000	2	2	400	200	—	—
28	MPLR35	16.5	25	1	1000	2	2	400	200	—	—
29	MPLR36	16	25	1	900	2	1	600	—	Ru_2O	—
30	MPLR37	18	25	1	900	2	1	600	—	Ru_2O	—
31	MPLR38	16	25	1	900	2	0.5	750	30	Li_2RuO_3	—
32	MPLR39	17	25	1	900	2	0.5	750	30	Li_2RuO_3	—
33	MPLR40	18	25	1	900	2	0.5	750	—	Mainly RuO_2	—
34	MPLR41	19	25	1	900	2	0.5	750	—	Mainly RuO_2	—
35	MPLR42	20	25	1	900	2	0.5	750	—	Mainly RuO_2	—
36	MPLR43	17	25	1	900	2	0.5	600	50	Li_2RuO_3	—
37	MPLR44	18	25	1	900	2	0.5	600	50	Li_2RuO_3	—
38	MPLR45	19	25	1	900	2	0.5	600	50	Li_2RuO_3	—
39	MPLR46	20	25	1	900	2	0.5	600	50	Li_2RuO_3	—
40	MPLR48	10	25	1	950	2	1	850	10	Li_2RuO_3	—
41	MPLR49	15	25	1	950	2	1	850	10	Li_2RuO_3	—
42	MPLR50	20	25	1	950	2	1	850	10	Li_2RuO_3	—
43	MPLR51	10	25	1	900	2	1	600	—	RuO_2	Initial Pure Li_2RuO_3
44	MPLR52	15	25	1	900	2	1	600	—	RuO_2	Initial Pure Li_2RuO_3
45	MPLR53	20	25	1	900	2	1	600	—	RuO_2	Initial Pure Li_2RuO_3
46	MPLR51b	1	25	1	790	2	1	590	10	Li_2RuO_3	—
47	MPLR52b	3	25	1	790	2	1	590	10	Li_2RuO_3	—
48	MPLR53b	5	25	1	790	2	1	590	10	Li_2RuO_3	—
49	MPLR54	7	25	1	790	2	1	590	10	Li_2RuO_3	—
50	MPLR55	10	25	1	790	2	1	590	10	Li_2RuO_3	—
51	MPLR56	13	25	1	790	2	1	590	10	Li_2RuO_3	—
52	MPLR57	15	25	1	790	2	1	590	10	Li_2RuO_3	—
53	MPLR58	17	25	1	790	2	1	590	10	Li_2RuO_3	—
54	MPLR59	20	25	1	790	2	1	590	10	Li_2RuO_3	—
55	MPLR60	23	25	1	790	2	1	590	10	Li_2RuO_3	—
56	MPLR61	26	25	1	790	2	1	590	10	Li_2RuO_3	—
57	MPLR62	17	25	1	900	2	1	600	—	Ru	SUS tube
58	MPLR63	17	25	1	900	2	1	600	—	Ru	SUS tube

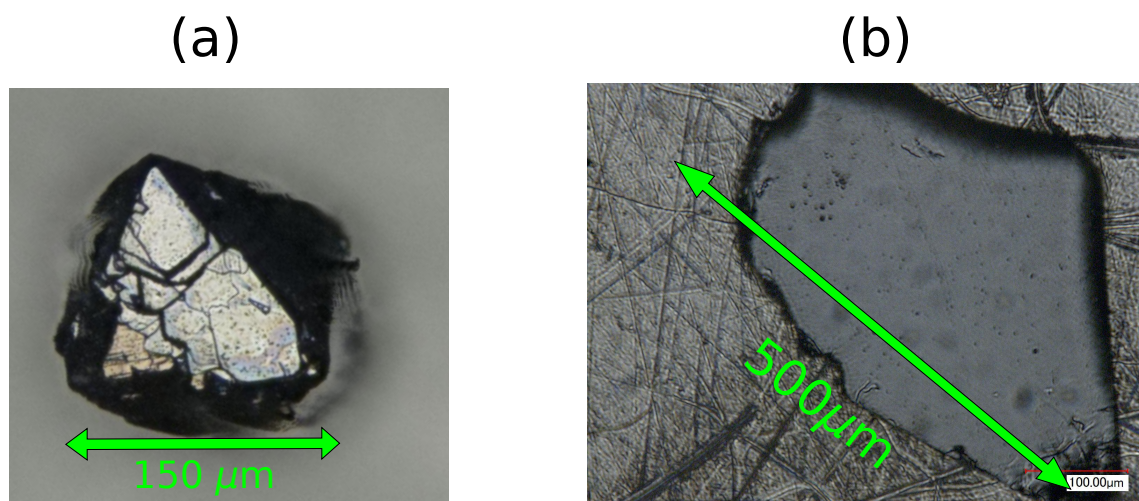


Fig. 3.8 Single crystals of Li_2RuO_3 . (a) Grown by the flux method. Shape of octahedron (b) Grown using a floating zone furnace. Shape of flakes. The face visible in the picture is the direction (001).

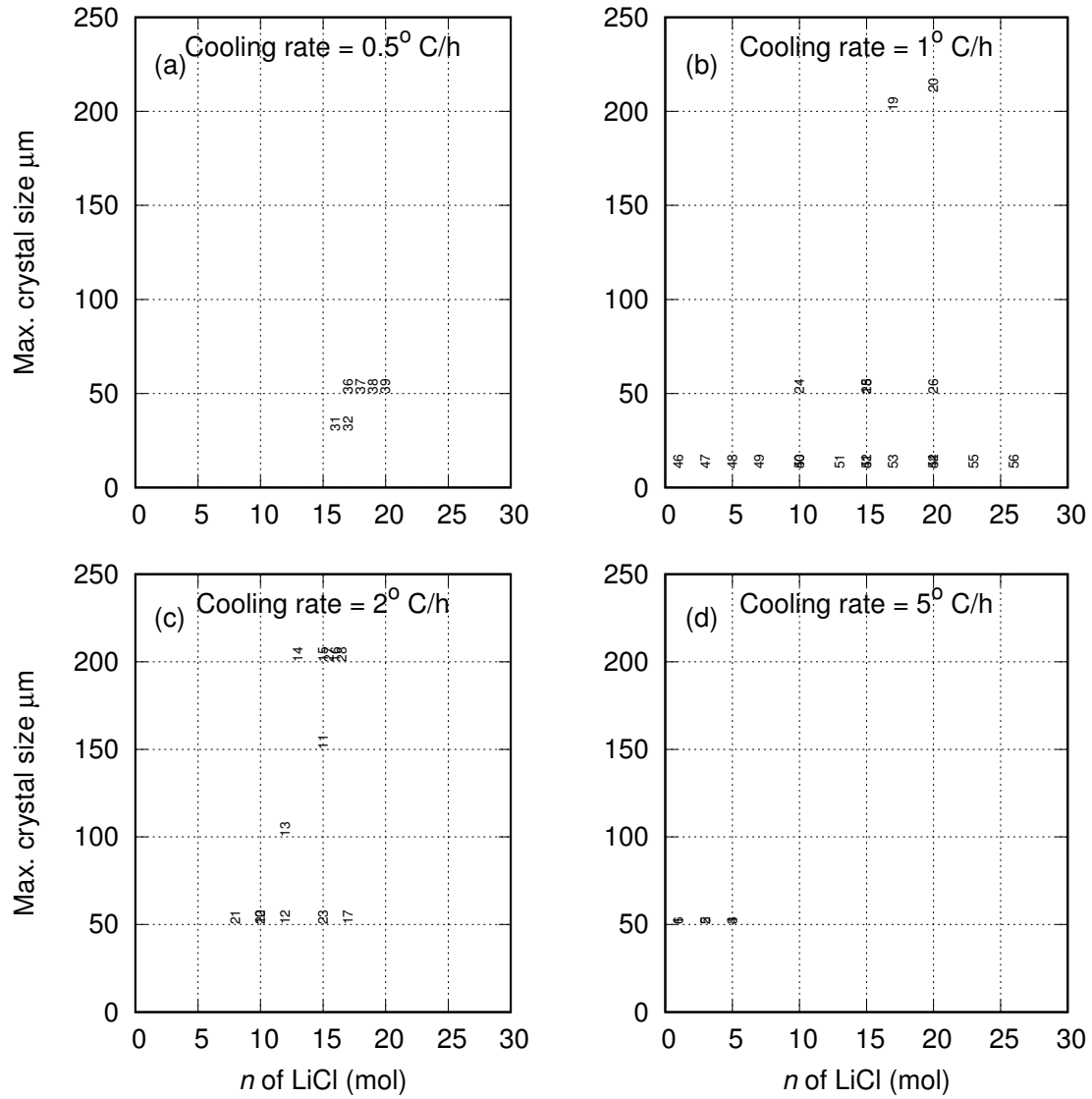


Fig. 3.9 Correlation of crystal size of Li_2RuO_3 , initial quantity of LiCl and cooling rate. In (a-d) are plotted the different cooling rates. The numbers in the plot correspond to the sample number in Table 3.2.

Chapter 4

Dimer transition in the delithiated system $\text{Li}_{2-x}\text{RuO}_3$

4.1 Crystal Structure

Figure 4.1 shows the high-energy powder XRD spectra for $\text{Li}_{2-x}\text{RuO}_3$ samples with various values of x measured at room temperature. This provides high-resolution spectra containing clear superlattice peaks at low angles. Figure 4.2 shows $\text{CuK}\alpha$ XRD with Rietveld fitting. The pristine ($x = 0$) sample exhibits the patterns expected for the pure Li_2RuO_3 . The spectrum can be well fitted with the space group (SG) $P2_1/m$ [No. 11, Fig 4.2(a)] as reported previously [20, 24, 25, 42, 50].

The delithiated samples exhibit patterns with substantial differences compared with the $x = 0$ sample as described below. The $x \approx 0.73$ sample, exhibiting almost single-phase behavior, has the $(h00)$ and $(00l)$ peaks shifted to lower angles and the $(0k0)$ peaks shifted to higher angles (Fig.4.1(c)), indicating increase in the values of a and c and decrease in the value of b [Fig.4.6(c)]. Nevertheless, the spectrum of this delithiated sample can be well fitted also with the SG $P2_1/m$ [Fig 4.2(b)]. We designate the crystallographic phase observed in the $x \approx 0.73$ sample as the D-phase. In addition to the main peaks associated with the D-phase, we can identify minor phases such as the S-phase Li_2RuO_3 , RuO_2 , and yet another delithiated phase $\text{Li}_{2-x}\text{RuO}_3$ with $x \approx 1.1$ (SG $R\bar{3}$, No. 148) [32].

For the sample with $x \approx 0.34$, we find that the XRD peaks such as (001) and (020) are clearly split into two peaks [Fig.4.1(c)]: one group similar to those of the $x = 0$ sample and the other similar to those of the $x \approx 0.73$ sample. This fact indicates that the crystal-structure change due to delithiation is not continuous: there are two

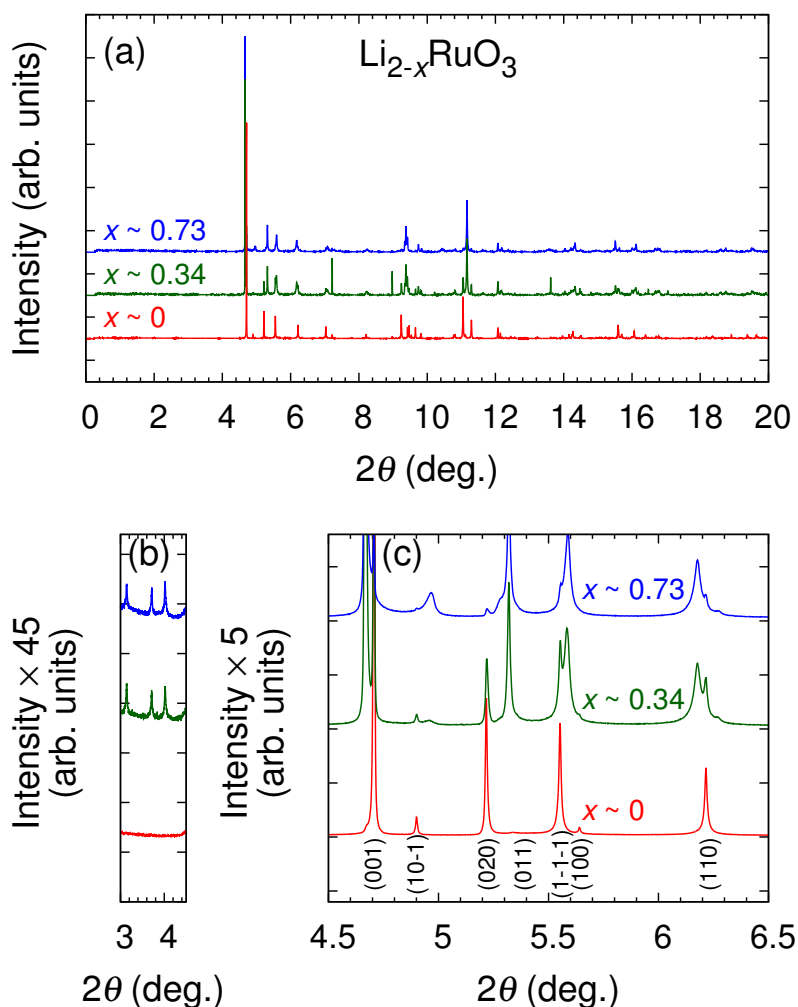


Fig. 4.1 Temperature variations of high-energy powder XRD spectra at room temperature of $\text{Li}_{2-x}\text{RuO}_3$ samples with $x = 0, 0.34, \text{ and } 0.73$, taken with X-ray of 30.993 keV ($\lambda = 0.40003739(180) \text{ \AA}$) at the beam line ID22 of the ESRF. Panels (a), (b), and (c) present data in the ranges $0^\circ < 2\theta < 20^\circ$, $3^\circ < 2\theta < 4.5^\circ$, and $4.5^\circ < 2\theta < 6.5^\circ$, respectively. The peak indices of the stoichiometric Li_2RuO_3 are shown in (c) based on the room-temperature crystal structure reported by Miura *et al.* [24]. The $(10\bar{1})$ peak is characteristic of the dimer-solid state [24, 25]

Table 4.1 Cell parameters of Li_2RuO_3 (S-phase) and $\text{Li}_{2-x}\text{RuO}_3$ ($x \approx 0.73$, D-phase) at room temperature obtained from laboratory XRD spectra. The space group used for both phases is $P2_1/m$.

x	a (Å)	b (Å)	c (Å)	β (°)	$\sqrt{3}a/b$	R_{wp}	R_e	GOF
0	4.922	8.787	5.896	124.36	0.970	10.96	7.31	1.50
0.73	4.937	8.630	5.898	123.54	0.991	11.35	4.37	2.60

crystallographically distinct phases with $x = 0$ and $x > 0$ and they coexist in similar ratio in the $x \approx 0.34$ sample.

In addition to the shifts in the main peaks, three small peaks but sharp peaks are observed in the delithiated samples at $2\theta = 3.140^\circ$, 3.714° , and 4.017° [$d = 7.30$, 6.18 , and 5.71 Å, Fig.4.1(b)], indicating the presence of a superlattice structure. Although these small peaks have not been reported in pristine or delithiated Li_2RuO_3 , a superlattice in $\text{Li}_{2-x}\text{Ru}_{1-y}\text{M}_y\text{O}_3$ ($M = \text{Mn}, \text{Sn}$) has been recently found as additional spots in electron diffraction [36, 37]. In these studies, the structure has approximately been described with the SG $C2/m$ (neglecting the presence of the superlattice and Ru-Ru dimers even for small values of y). It has been suggested that the origin of the superlattice is the distortion in the oxygen positions [36, 38]. Another possibility is an ordering of Ru valency (charge order) as we discuss latter. Since the SG in $\text{Li}_{2-x}\text{RuO}_3$ with the superlattice taken into account is not trivial, we hereafter consider the SG $P2_1/m$ to evaluate the cell parameters and the Ru ion positions.

The cell parameters of the S and D-phases, obtained from the laboratory XRD data, are compared in Table 4.1. The parameters a and b of $\text{Li}_{2-x}\text{RuO}_3$ are longer and shorter than those of Li_2RuO_3 , respectively. Studies on $\text{Li}_2\text{Ru}_{1-y}\text{Mn}_y\text{O}_3$ revealed the same trend of change in a and b when lithium is deintercalated, although the structure of $\text{Li}_2\text{Ru}_{1-y}\text{Mn}_y\text{O}_3$ is described with the SG $C2/m$ [37]. Furthermore, the relation $\sqrt{3}a/b$ of $\text{Li}_{2-x}\text{RuO}_3$ is closer to the unity than that of Li_2RuO_3 (Table 4.1). Thus, on average, the structure of $\text{Li}_{2-x}\text{RuO}_3$ seems to be more symmetric. Figure 4.3 compares the difference in the bond lengths between the S and D-phases. Reflecting the dimer-solid state in the S-phase, the dimer bond L_2 is $\approx 16\%$ shorter than the long bonds L_1 and L_3 . In contrast, for the D-phase, the difference is only about 6%. In Sec. 4.3, we will discuss local structures in more detail.

Figure 4.4 shows high-energy XRD patterns ($E = 87.5$ keV, $\lambda = 0.14169$ Å) of the $x \approx 0.73$ sample (dominated by the D-phase) at selected temperatures on heating (302 K to 694 K) and after subsequent cooling (333 K). While heating, the three superlattice peaks between $2\theta = 1.1^\circ$ and 1.5° disappear at ≈ 609 K. At the same

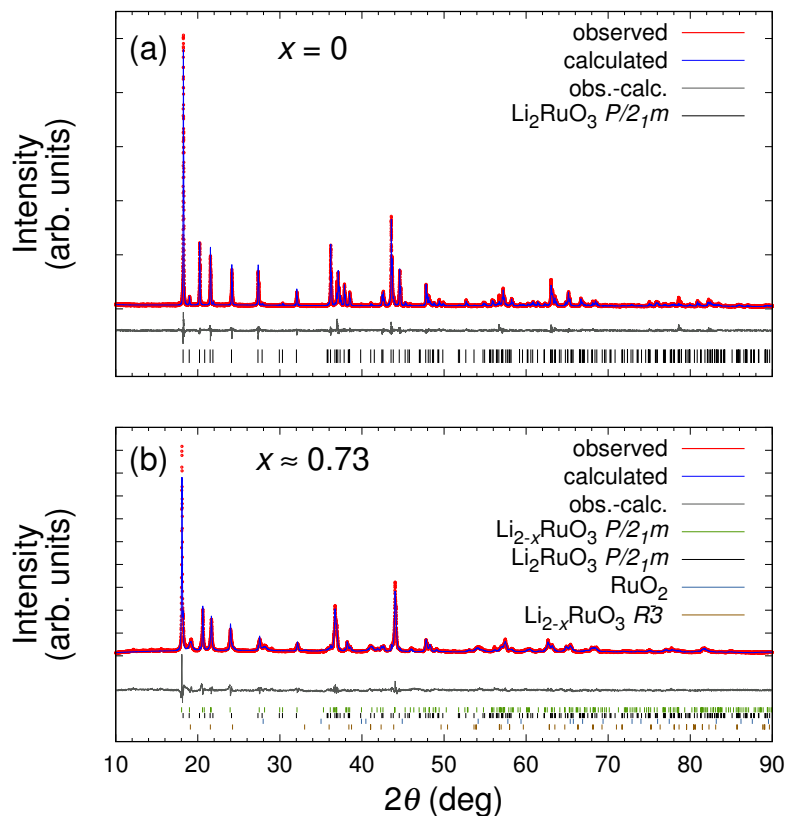


Fig. 4.2 (color online) Rietveld refinement of the Cu XRD ($\lambda = 1.54184 \text{ \AA}$, $E = 8.041 \text{ keV}$) of the samples (a) Li_2RuO_3 with $x = 0$ and (b) $\text{Li}_{2-x}\text{RuO}_3$ with $x = 0.73$. In both cases SG $P2_1/m$ was used. Parameters of the fitting are shown in Table 4.1. The structure factor used in both cases is the one of Ru^{4+} because the structure factors of Ru^{5+} are not available in our software. The measurement time for $x = 0.73$ was approximately twice longer than that for $x = 0$.

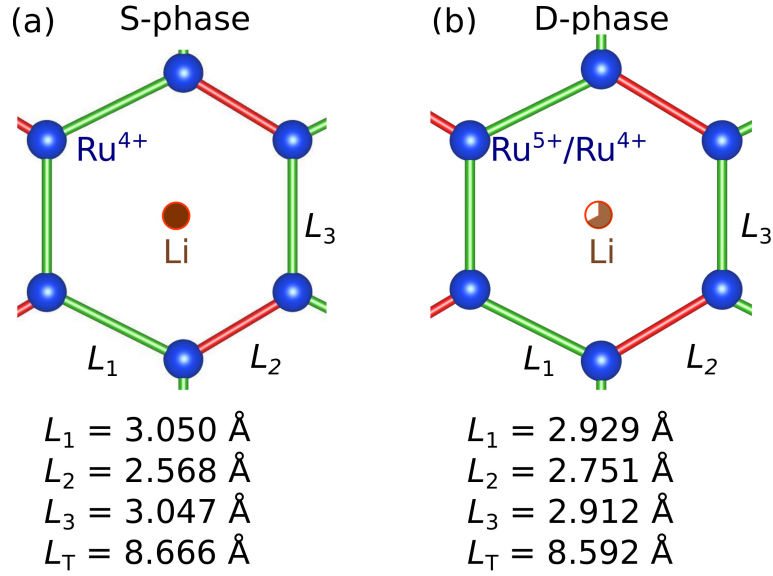


Fig. 4.3 (color online) Bond lengths L_1 , L_2 and L_3 of the S-phase and D-phase. The sum of the bond lengths L_T is given by $L_1 + L_2 + L_3$. Blue and brown spheres represent the Ru and Li ions. Red and green bars are the short and long bonds, respectively. The figures are prepared with the program VESTA [26].

temperature, a sudden increase in the RuO_2 peak intensity, for example the one at $2\theta = 3.2^\circ$, is observed. These facts indicate the decomposition of $\text{Li}_{2-x}\text{RuO}_3$ ($x \approx 0.73$) into Li_2RuO_3 and RuO_2 starting from this temperature (see Appendix 4.4 for details).

4.2 Magnetic properties

Figure 4.5 shows the temperature dependence of the magnetic susceptibility of the $x = 0$ and $x \approx 0.73$ samples. Diamagnetic contributions of ion cores have been subtracted [49]. The overall shapes of curves for these samples differ in several aspects. At low temperatures, both samples exhibit Curie-like behavior; the difference will be discussed later. Both samples exhibit a minimum of magnetic susceptibility but at different temperatures: $\sim 150 \text{ K}$ for the sample with $x = 0$ and $\sim 200 \text{ K}$ for the sample with $x \approx 0.73$. With increasing temperature, the magnetic susceptibility of both samples increases toward the transition from dimer solid to dimer liquid. The change of the magnetic susceptibility in the pristine sample Li_2RuO_3 is relatively gradual below $\sim 500 \text{ K}$, followed by a sharp jump characteristic of the first-order transition (Appendix 3.3). In contrast, the sample with $x \approx 0.73$ does not exhibit a gradual change below the transition but exhibits a clearer change in the slope of the $M(T)/H$ curve at $T \approx 539 \text{ K}$. Between this temperature and 609 K , no clear

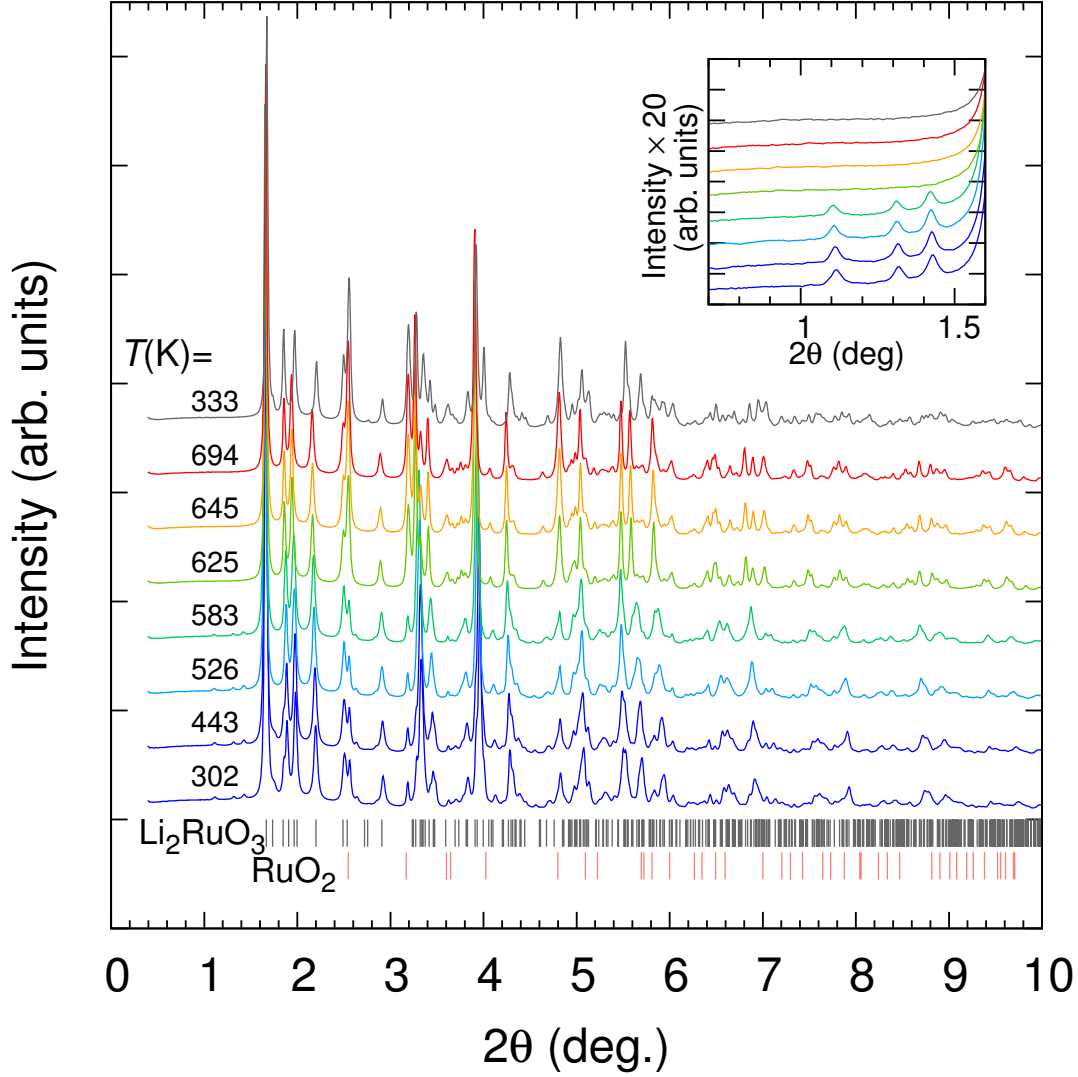


Fig. 4.4 (color online) Temperature variations of the high-energy XRD spectra for the $x \approx 0.73$ sample with $E = 87.5$ keV ($\lambda = 0.14169$ Å) measured at the beam line ID11 of ESRF. Colors of the spectral curves correspond to the temperature region in the magnetization curve of the $x \approx 0.73$ sample in Fig. 4.5. The inset shows spectra in the range $0.7^\circ < 2\theta < 1.5^\circ$. Spectra for 302 K to 664 K are obtained during the heating process, while the spectrum at 333 K was measured after cooling. The vertical lines at the bottom indicate the expected peak positions for Li_2RuO_3 and RuO_2 .

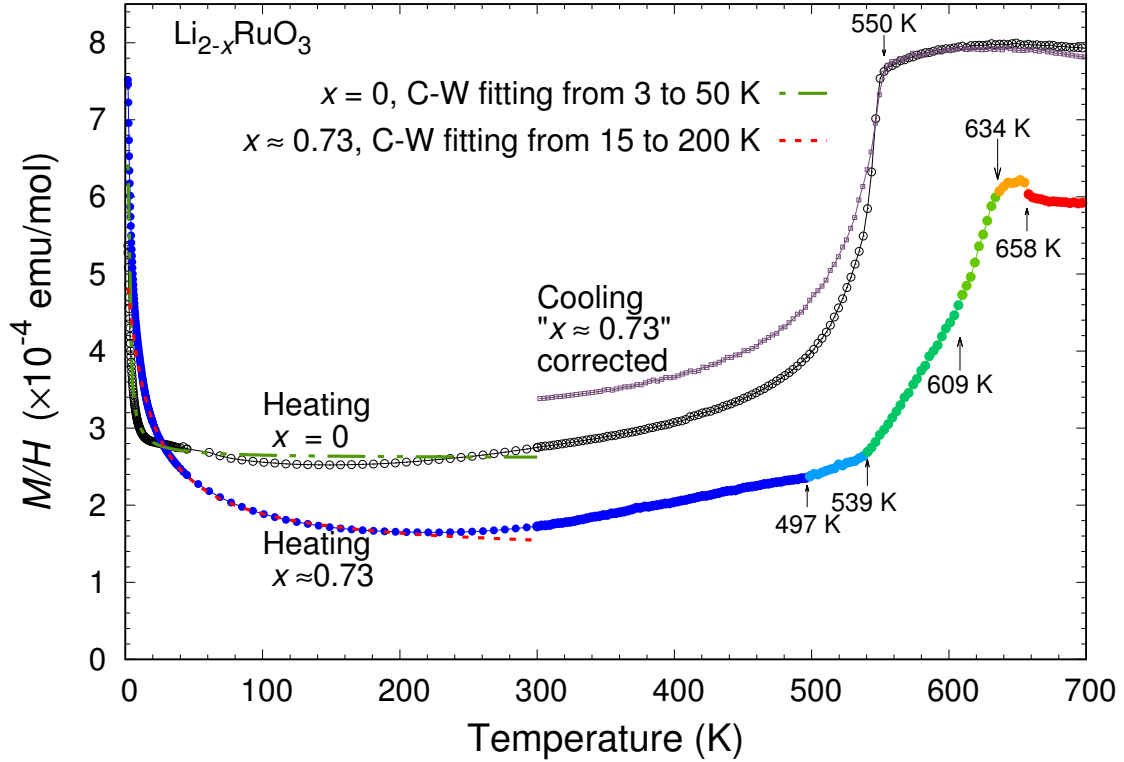


Fig. 4.5 (color online) Magnetic susceptibility vs temperature of the $x = 0$ sample (S-phase) and the $x \approx 0.73$ sample (mostly D-phase) from 1.8 to 700 K at $H = 10$ kOe. Corrections of diamagnetic contributions of ion cores have been made [49]. From 1.8 to 300 K, the magnetization was measured while warming up after ZFC. From 300 to 700 K the magnetization was measured in temperature up sweep, except for the purple curve which is for the molar susceptibility of Li_2RuO_3 contained in the $x \approx 0.73$ sample on cooling from 700 K to 300 K (see text). Results of the Curie-Weiss fitting ($\chi = C/(T - \Theta) + \chi_0$) are also shown with broken curves. Colors of the curve for $x \approx 0.73$ correspond to those in Fig. 4.4.

Table 4.2 Curie-Weiss fitting parameters, expected Curie constant and localized spins.

x	Curie const. (emu K/mol)	Θ (K)	χ_0 (emu/mol)	μ_{eff} μ_B	Fitting range (K)	Expec. spin	Loc. spins (%)
0	0.00039	0.96	0.0002610	0.056	3–50	1	0.039
0.73	0.00625	-16.0	0.0001349	0.22	15–200	3/2	0.333

change in the averaged crystalline structure was observed and the superlattice peaks are maintained (inset of Fig. 4.4). Thus, the change in the susceptibility seems to be mainly linked to changes in the electronic state, but not to chemical decomposition.

At 609 K, there is another change of slope in the $M(T)/H$ curve (Fig. 4.5). As already explained, the decomposition of $\text{Li}_{2-x}\text{RuO}_3$ into Li_2RuO_3 begins at this temperature (see also Appendix 4.4). Therefore, the slope change at 609 K is mainly due to the decomposition. Thus, in the warming run the susceptibility of the $x \approx 0.73$ sample above 609 K represents the sum of those of evolving multiple phases. While warming above 658 K, there is a slight but sharp drop in the susceptibility of the $x \approx 0.73$ sample (dominated by the S-phase at this temperature). Across this temperature, there is no noticeable anomaly in the XRD spectra. Thus, the sharp drop probably reflects a reorganization of lithium or oxygen induced by the vacancies of lithium in the initial $\text{Li}_{2-x}\text{RuO}_3$.

The purple curve in Fig. 4.5 is obtained from the susceptibility in the cooling process of the $x \approx 0.73$ sample after decomposition. Under this condition, the sample is dominated by Li_2RuO_3 and RuO_2 (see Appendix 4.4). The raw data matches with the susceptibility shown by the red curve of the $x \approx 0.73$ sample above $T = 658$ K. The molar susceptibility of Li_2RuO_3 contained in the decomposed ≈ 0.73 sample was estimated by using Eq. 4.3 and the susceptibility of RuO_2 [54]. The result is shown by the purple curve in Fig. 4.5, which indeed matches with that of the for the pristine Li_2RuO_3 above ~ 550 K. However, the molar susceptibility shown by the purple curve at room temperature is $\sim 18\%$ larger than that of the pristine $x = 0$ sample. This is attributable to less coherent dimer configuration in Li_2RuO_3 after decomposition of $\text{Li}_{2-x}\text{RuO}_3$ [42].

We performed a Curie-Weiss fitting to the susceptibility at low temperatures. The fitting temperature ranges (shown in Table 4.2) are chosen so that the positive slope in $M(T)/H$ associated with the dimer transition at T_d does not affect the fittings. Results of the fitting with the Curie-Weiss law $\chi(T) = \chi_0 + C/(T - \Theta)$ are shown with the broken curves in Fig. 4.5. From the fittings, we obtain the Curie constant (C) and

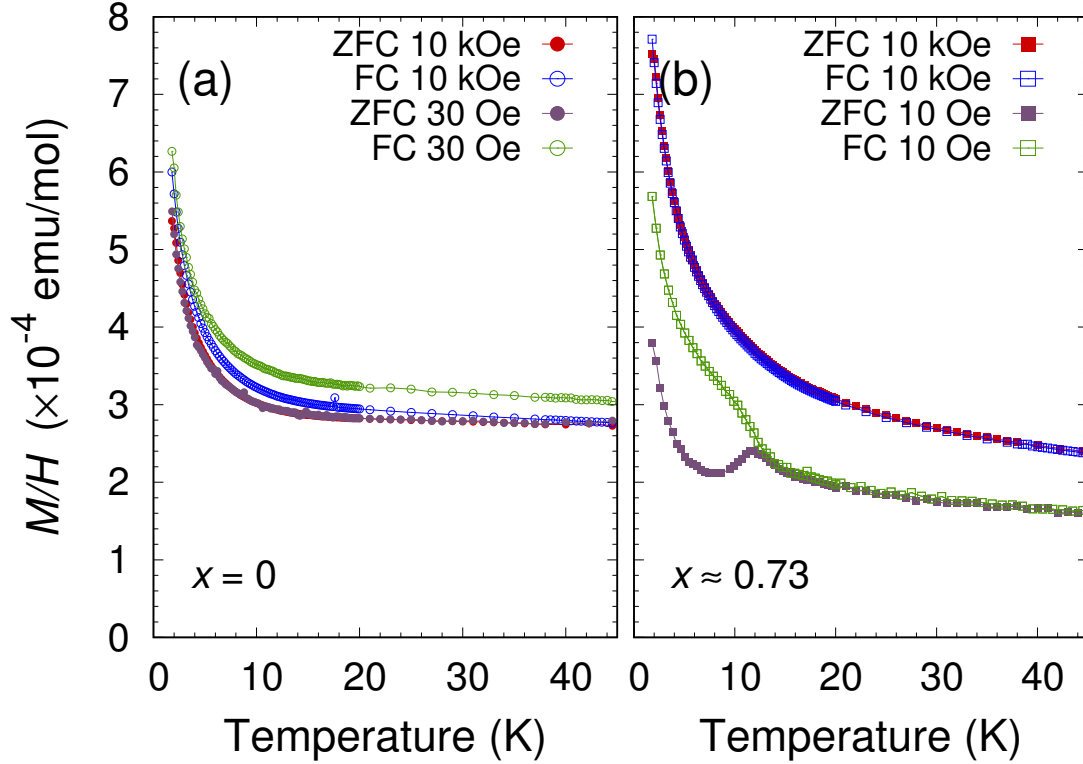


Fig. 4.6 Magnetic susceptibility vs temperature of (a) Li₂RuO₃ and (b) Li_{2-x}RuO₃ ($x \approx 0.73$) from 1.8 to 45 K at different magnetic fields measured in ZFC (closed symbols) and FC (open symbols) processes.

the Weiss temperature (Θ) as $C = 0.00039$ emu K/mol and $\Theta = 0.96$ K for the $x = 0$ sample, and $C = 0.00625$ emu K/mol and $\Theta = -16$ K for the $x \approx 0.73$ sample. These results imply that the number of localized spins is rather small even for the $x \approx 0.73$ sample.

In an earlier study, it is proposed that samples with broad magnetic transitions at T_d are accompanied by a dimer decoherent configuration, namely dimer patterns breaking the long-range ordered configuration [42]. Such dimer decoherent configuration results in nondimerized Ru ions with finite spin. To examine the number of such nondimerized ions, we assume that they exhibit $S = 1$ and $S = 3/2$ for the S-phase and D-phase, respectively, and that they can be treated as nearly free spins. From the Curie-Weiss fitting described above, the quantity of nondimerized ions is 0.039% for the $x = 0$ sample and 0.33% for the $x \approx 0.73$ sample. It is important to note that the obtained number of nondimerized ions in the $x \approx 0.73$ sample is much smaller than the number of vacancies of lithium, or equivalently the number of Ru⁵⁺ ions. This fact indicates that most of the Ru ions form dimers even in the D-phase.

Figures 4.6(a) and (b) compare the low-temperature susceptibilities for the $x = 0$ and $x \approx 0.73$ samples. It is noticeable in Fig. 4.6(b) that the sample with $x \approx 0.73$ at low fields exhibits magnetic hysteresis below 12 K. Since the Weiss temperature Θ is negative, this hysteresis is probably due to magnetic ordering with antiferromagnetic interactions. No trace of superconductivity was found by AC susceptibility measurements using an adiabatic demagnetization refrigerator [44] or transport measurements down to 0.1 K.

4.3 Electronic configuration of dimers

According to the outcome of the last section, the D-phase is dominated by Ru-Ru dimers. In this section, we discuss the electronic configuration of these dimers and their correlation with the crystalline structure.

We first discuss the probable valency of Ru ions in the D-phase. It has been demonstrated by X-ray photoemission spectroscopy, Mössbauer spectroscopy, electronic paramagnetic resonance measurements, and DFT calculations, that the deintercalation of lithium from Li_2RuO_3 leads to the valence change from Ru^{4+} to Ru^{5+} . In higher x range than $x = 1$, where Ru ions are fully oxidized to pentavalent, it is revealed that further delithiation induces loss of oxygen, presence of peroxides (O_2^{2-}), and oxidation of Ru^{5+} into Ru^{6+} ions [36–38]. Thus, in the sample of the present study with $x \approx 0.73$, the ratio of the amount of Ru^{5+} among the total Ru ions would be similar to this x value and the others remain Ru^{4+} . In other words the valency of the sample can be approximately expressed as $\text{Li}_{2-x}\text{Ru}_{1-x}^{4+}\text{Ru}_x^{5+}\text{O}_3$.

For the S-phase, it is expected that the magnetization is governed by the Ru^{4+} ($4d^4$) ion. The origin of the decrease of the magnetization below T_d has been attributed to the formation of dimers with molecular orbitals (MOs) with $S \approx 0$ [27]. In contrast, the greater magnetization above T_d has been explained by the partial breakdown of MOs. In the dimer-liquid state above T_d , the Ru $4d$ orbitals keep the MO formed only by the σ bonds, leading to dynamic dimers [25].

Since the Curie-Weiss analysis indicates that most of the Ru ions form dimers with $S = 0$ even in $\text{Li}_{2-x}\text{RuO}_3$, there are three possible electronic configurations of the dimers in the dimer-solid state as depicted in Fig. 4.7. The configuration in panel (a) is what already proposed for the S-phase (Refs. [24, 25, 27]).

We propose that in the D-phase the most probable configuration for Ru^{5+} is the dimer formed between Ru^{5+} and Ru^{5+} [Fig. 4.7(b)], since such a dimer has electrons only in the lower-energy bonding states. In contrast, the dimers formed between Ru^{4+}

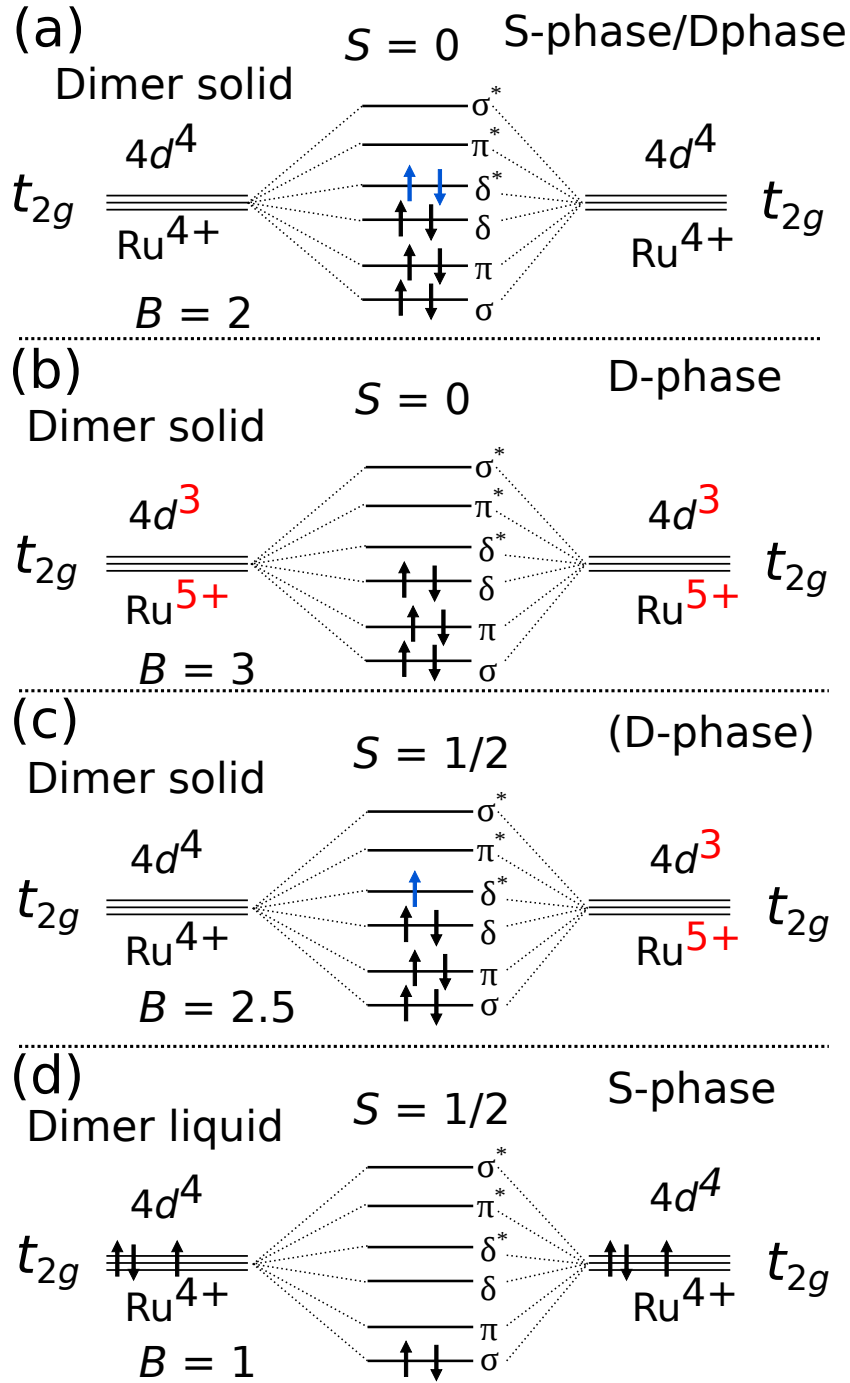


Fig. 4.7 Molecular orbital diagrams of possible configurations of the dimers of Li_2RuO_3 (S-phase) and $Li_{2-x}RuO_3$ (D-phase). Panels (a), (b), and (c) depict the molecular orbitals in the dimer-solid state consisting of $Ru^{4+}-Ru^{4+}$, $Ru^{5+}-Ru^{5+}$, and $Ru^{4+}-Ru^{5+}$ dimers, respectively. Configuration in the panel (c) is less likely to occur based on the observed magnetic susceptibility. Panel (d) depicts the molecular orbitals in the dimer-liquid state formed by $Ru^{4+}-Ru^{4+}$ ions proposed in Ref. [25]. B is the bond order defined by Eq. (4.1).

and Ru^{4+} ions or Ru^{4+} and Ru^{5+} ions [Fig. 4.7(a, c)] contain electrons also in higher-energy antibonding states. Actually, the amount of dimers with the configuration $\text{Ru}^{5+}\text{-Ru}^{4+}$ accompanied by spin $S = 1/2$ must be quite small based on the observed small Curie constant.

The situation that most of the Ru ions form isovalent-spinless dimers is actually difficult to be realized if Ru^{5+} and Ru^{4+} ions distribute randomly. Thus, the Ru ions in the D-phase may exhibit charge ordering between Ru^{4+} and Ru^{5+} ions. Such charge ordering may be the origin of the observed superlattice.

Since $\text{Ru}^{4+}\text{-Ru}^{4+}$ dimers contain a MO with higher energy than those of $\text{Ru}^{5+}\text{-Ru}^{5+}$ dimers i.e. δ^* , it is more likely that the δ^* of the $\text{Ru}^{4+}\text{-Ru}^{4+}$ dimers breaks at lower temperature than MOs of $\text{Ru}^{5+}\text{-Ru}^{5+}$ [Fig. 4.7(b)]. The T_d where MOs of Li_2RuO_3 break has been demonstrated to depend on the dimer coherence configuration [42]. Thus, similar to the S-phase, the enhancement of magnetization in the D-phase at ~ 539 K (Fig. 4.2) is probably related to the breaking of MOs of the $\text{Ru}^{4+}\text{-Ru}^{4+}$ dimers.

In the context of the linear combination of atomic orbitals, the bond lengths L of different dimer configurations can be estimated in terms of the quantity called the bond order B , which is evaluated as

$$B = \frac{1}{2}(n_b - n_a), \quad (4.1)$$

where n_b and n_a are the numbers of electrons in the bonding and antibonding states, respectively. In Fig. 4.7 the values of B of the possible electronic configurations are shown. Pauling found an empirical relation between B and the bond length L [55, 56]:

$$L = L_0 - f \log_{10}(B), \quad (4.2)$$

where the value of f depends on the atoms and L_0 is the bond length for $B = 1$. Later this relation was derived from the Friedel model [57]. In order to evaluate the constant f , we use the value of the bond length of the dimer-liquid state of the S-phase ($L_0 = 2.68$ Å) [25], where only the σ -MO is occupied i.e. $B = 1$ [Fig. 4.7(d)]. We also use the bond lengths of the short bond in the dimer-solid state of the S-phase ($L = 2.58$ Å) where the σ , π , δ , and δ^* MOs are occupied i.e. $B = 2$ [Fig. 4.7(a)]. From these values, we obtain $f = 0.332$ Å. By using these values we estimate the length of the $\text{Ru}^{5+}\text{-Ru}^{5+}$ bond in the dimer-solid state to be $L = 2.52$ Å.

Since in the dimer-solid state of the $x \approx 0.73$ sample, around 73% of the dimers are formed by $\text{Ru}^{5+}\text{-Ru}^{5+}$ ions and the rest by $\text{Ru}^{4+}\text{-Ru}^{4+}$ ions, the average length of

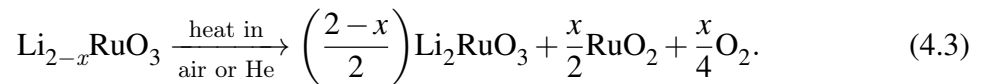
the short bonds is expected to be 2.56 Å if we assume that the dimers are all located in the L_2 bonds. This is 0.04 Å shorter than the dimer entirely formed between Ru^{4+} and Ru^{4+} ions in the S-phase. On the other hand, the observations for the sum of the bond lengths ($L_T = L_1 + L_2 + L_3$) of the D-phase ($L_T = 8.592$ Å) is 0.074 Å shorter than that of the S-phase ($L_T = 8.666$ Å). The excess of shrinkage of L_T maybe due to the difference in ionic size between Ru^{4+} ($r = 0.62$ Å) and Ru^{5+} ($r = 0.565$ Å) [58] in the nondimer bonds, although covalency needs to be considered. The reduced difference between short and long bonds in the D-phase suggests that some dimers are distributed in L_1 and L_3 as well.

4.4 Reaction of $\text{Li}_{2-x}\text{RuO}_3$ at high temperatures

In the XRD spectra shown in Fig. 4.4, the peak intensities of the RuO_2 ($P4_2/mnm$) peaks at 625 K are markedly higher than those at 583 K. See for example the peak at $2\theta = 2.57$. We find that this enhancement starts at ≈ 609 K (not shown in the figure). The structure of the main phase after heating above $T \approx 609$ K is equivalent to that of the S-phase Li_2RuO_3 .

Besides, as shown in Fig. 4.5 the temperature dependence of the susceptibility of $\text{Li}_{2-x}\text{RuO}_3$ $x \approx 0.73$ changes substantially before and after heating to 700 K. The behavior after heating to 700 K becomes similar to that of pristine Li_2RuO_3 (compare purple and black lines in Fig. 4.5). While repeating magnetization measurements, the obtained curves remain almost equivalent to the purple curve in Fig. 4.5.

These results indicate that, when $\text{Li}_{2-x}\text{RuO}_3$ is heated above $T \approx 609$ K, it decomposes into Li_2RuO_3 and RuO_2 according to the following reaction:



This decomposition reaction seems to be triggered by the loss of oxygen.

The minor phase $\text{Li}_{2-x}\text{RuO}_3$ with $x \approx 1.1$ (SG $R\bar{3}$), decomposes at lower temperatures. The peak at $2\theta = 1.75^\circ$ seen as a shoulder in Fig. 4.4, characteristic of this phase, disappears at 497 K. The magnetization exhibits a small change of slope at this temperature (Fig. 4.5).

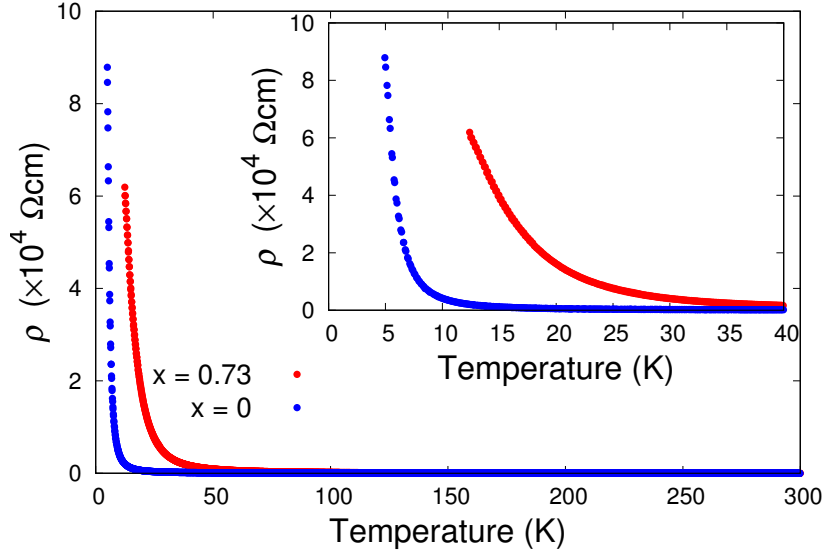


Fig. 4.8 Resistivity vs Temperature of Li_2RuO_3 and $\text{Li}_{2-x}\text{RuO}_3$. Inset shows different scale of temperature. It is observable that sample $x = 0$ is more insulating than $x \approx 0.73$

4.5 Electric transport measurements

The Fig. 4.8 shows the temperature dependence of resistivity of the samples of $x = 0$ and $x \approx 0.73$. The plot suggests that both samples are semiconductors. The $x \approx 0.73$ sample is more insulating than the $x \approx 0$ sample. However, strong conclusions cannot be taken from these measurements for two reasons: in the $x \approx 0.73$ sample RuO_2 is present as secondary phase, since RuO_2 is metallic it would mask the behavior of $\text{Li}_{2-x}\text{RuO}_3$; we find that while measuring the current provokes an irreversible process in the sample, probably migration of lithium ions.

Chapter 5

Conclusions

5.1 Summary of the present study

We have examined crystalline and magnetic properties of various Li_2RuO_3 samples. In order to obtain high-quality polycrystalline samples exhibiting intrinsic coherent dimer formation in Li_2RuO_3 , the following elements are important: more than one grinding/heating process, final heating at 1000°C , and thorough homogenization before heating to reduce RuO_2 impurities. In fact, by improving the sample dimer coherence, we show that the intrinsic magnetic transition is of first order and has a sharp onset at as high as 553 K, noticeably higher than 540 K reported previously. It has been demonstrated that disorder sensitively affects the coherence of dimerization, which is reflected systematically in the lattice parameters as well as the magnetic transition. We expect these results provide important bases for elucidating the intrinsic properties of Li_2RuO_3 .

Moreover, we successfully synthesized the delithiated phase $\text{Li}_{2-x}\text{RuO}_3$, the D-phase, with structures distinct from the stoichiometric Li_2RuO_3 , the S-phase. For the first time, we identify the magnetic properties of the D-phase. We found that the Ru ions also form dimers as in the S-phase. The absence of local moments indicates that there should be two kinds of dimers in the D-phase: $\text{Ru}^{4+}\text{--Ru}^{4+}$ dimers as in the S-phase and additional $\text{Ru}^{5+}\text{--Ru}^{5+}$ dimers. The latter should have a new molecular orbital configuration, in which no electrons occupy antibonding states. We find that above $T \approx 539\text{ K}$ the D-phase exhibits a strong linear increase in the susceptibility. In analogy to the S-phase, this magnetic feature is most likely associated with the change from the dimer-solid to dimer-liquid states. Structural and magnetic properties indicate that the dimers in the dimer-solid state are located not only in the L_2 bonds

but also in the L_1 and L_3 bonds. Such dimer distribution may lead to the observed superlattice structure.

5.2 Future prospects

The origin of the superlattice observed in XRD (described in Sec. 4.1) is not clear so far. The structure factors of Ru^{4+} and Ru^{5+} ions are different and this makes the Rietveld refinement of XRD patterns complicated. Besides, O and Li ions cannot be accurately detected by XRD. For these reasons, it becomes important the study of the crystalline structure by neutron diffraction.

It has been revealed (Sec. 4.3) that the electronic configuration of the dimer-solid state of the D-phase is different from that in the S-phase. In order to characterize the dimers state, it is very relevant to measure the local configuration of the dimers below and above 539 K. The local configuration can be determined with PDF analysis. In combination with such a method, the nature of the dimer state close to this temperature would be better understood in the future.

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Appendix A

Calibration of thermometers at high temperatures

This section is focused on the temperature calibration of the oven of the commercial SQUID magnetometer (Quantum Design, MPMS XL). The confirmation of the temperature calibration became important because we found that the temperature of the dimer transition of pristine Li_2RuO_3 can be up to 15 degrees higher than the reported T_d 540 K [24]. Furthermore since the temperature in the high-energy XRD is less accurate due to the nature of the experimental setup, we corrected this temperature scale based on that of the oven of MPMS.

The calibration of the thermometer of the oven of the MPMS was performed based on the antiferromagnetic transition temperature T_N of the NiO (Rare Metallic 3N). Since the antiferromagnetic transition of NiO is not too sharp as can be seen in Fig. A.1, we revised the calibration as well with metallic Ni (Rare Metallic 4N) Fig. A.2. We compare the observed value with the literature [43, 59]. The calibration error of the thermometer at the Curie temperature T_C of Ni was found to be less than 0.2%.

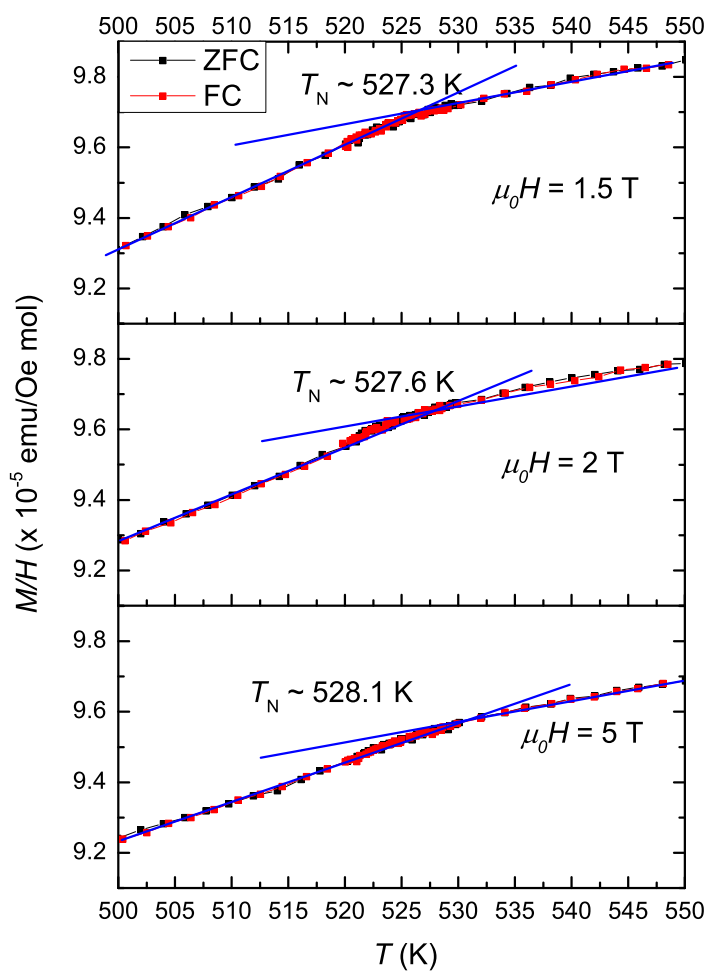


Fig. A.1 $M/H(T)$ of NiO for calibration of thermometer of MPMS at different magnetic fields. Antiferromagnetic transition is observed.

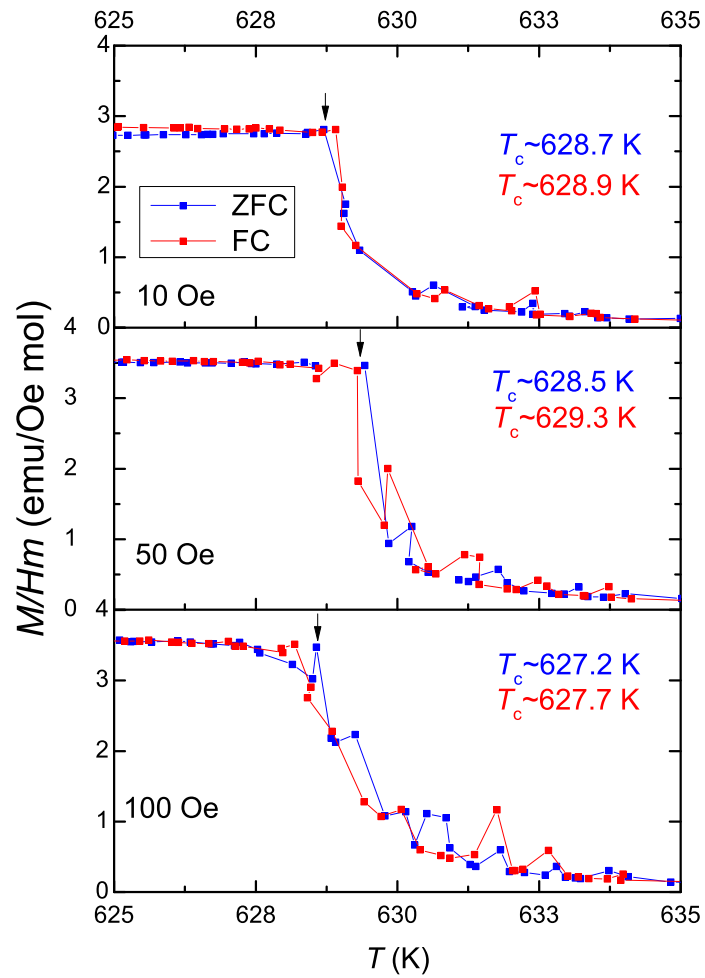


Fig. A.2 $M/H(T)$ of Ni for calibration of thermometer of MPMS at different magnetic fields. Ferromagnetic transition is observed.

Appendix B

Pair distribution function analysis of Li_2RuO_3

The PDF, symbolized by $G(r)$, describes the distribution of distances between pairs of particles. Figure B.1(a) shows the results of PDF of Li_2RuO_3 at different temperatures. The peaks at ≈ 2.6 and ≈ 3.1 Å correspond to the Ru-Ru bonds L_3 and L_1/L_2 . As can be observed, $G(r)$ indicates the presence of short Ru-Ru bonds in Li_2RuO_3 even above T_d . (b) Shows the Ru-Ru bond length vs temperature. The Ru-Ru distance of $\text{Li}_{2-x}\text{RuO}_3$ is extracted from the center of the peaks of the PDF (a). Previous results [25] of persistence of short dimer bonds above T_d are reproduced on the present pristine sample exhibiting a sharp magnetic transition.

In the present samples we find a behavior not observed previously [25]. In Fig. B.1(a) at T 642 K peaks of short bonds are split into two different peaks ($r = 2.55$ and $r = 2.7$) suggesting that the Ru-Ru have two different types of bonds in the dimer-liquid phase. This splitting seems to be merged in only one peak aleatory in some temperatures. Because of that we cannot assure the splitting is an intrinsic property of Li_2RuO_3 indicating dynamism of the dimer-liquid state or it just is result of some noise in the apparatus.

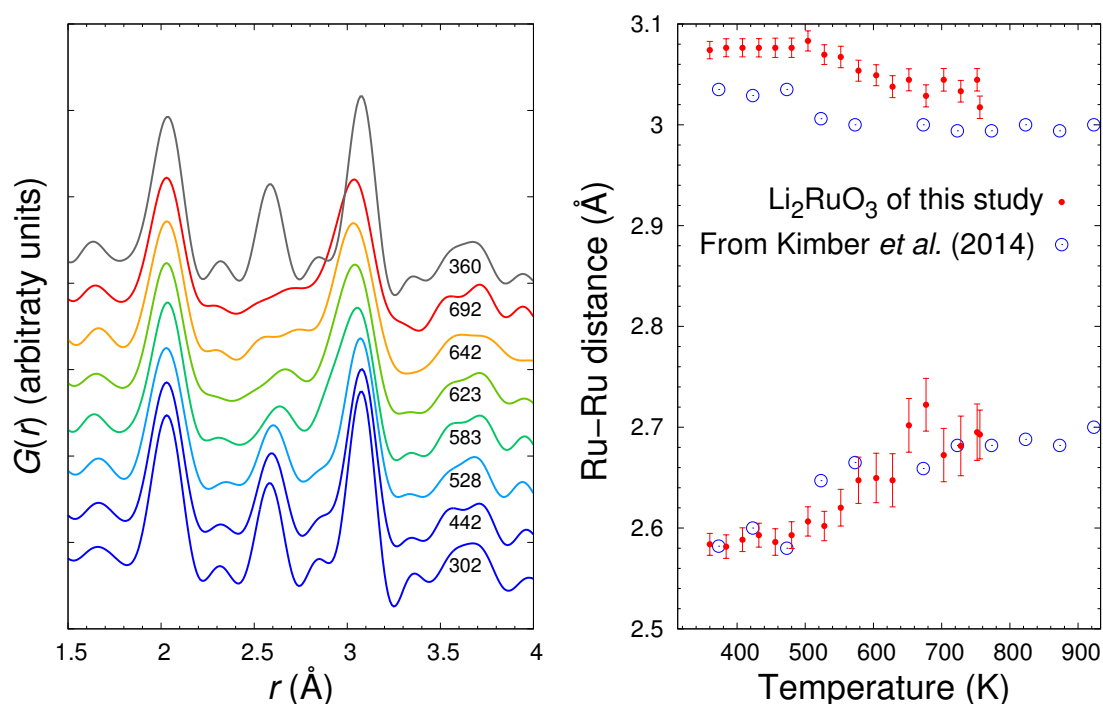


Fig. B.1 (color online) (a) Temperature evolution of the PDF of Li_2RuO_3 . Peaks close to ≈ 2.6 and ≈ 3.1 Å are related to Ru-Ru bonds. (b) Temperature dependence of Ru-Ru bonding distances of Li_2RuO_3 taken from the central point of the peaks of $G(r)$. Error bars based on the intensity of the data shown in (b). Blue circles are obtained from the PDF of Ref. [25] also from the central peak of $G(r)$