A valence bond liquid on the honeycomb lattice

Simon A. J. Kimber,1 I. I. Mazin,2 Juan Shen,3 Harald O. Jeschke,3 Sergey V. Streltsov,4,5 Dimitri N. Argyriou,6,7 Roser Valenti,3 and Daniel I. Khomskii8

1European Synchrotron Radiation Facility (ESRF), 6 rue Jules Horowitz, BP 220, 38043 Grenoble Cedex 9, France
2Code 6393, Naval Research Laboratory, Washington, DC 20375, USA
3Institut für Theoretische Physik, Goethe-Universität Frankfurt, 60438 Frankfurt am Main, Germany
4Institute of Metal Physics, S. Kovalevskaya Street 18, 620041 Ekaterinburg, Russia
5Ural Federal University, Mira Street 19, 620002 Ekaterinburg, Russia
6European Synchrotron Source ESS AB, Box 176, 22100, Lund, Sweden
7Department of Synchrotron Research, Lund University, Box 118, Lund, Sweden.
8II. Physikalisches Institut, Universität zu Köln, Zülpicher Strasse 77, 50937 Köln, Germany

(Dated: May 19, 2014)

The honeycomb lattice material Li$_2$RuO$_3$ undergoes a dimerization of Ru$^{4+}$ cations on cooling below 270°C, where the magnetic susceptibility vanishes. We use density functional theory calculations to show that this reflects the formation of a 'valence bond crystal', with a strong bond disproportionation. On warming, x-ray diffraction shows that discrete three-fold symmetry is regained on average, and the dimerization apparently disappears. In contrast, local structural measurements using high-energy x-rays, show that disordered dimers survive at the nanoscale up to at least 650°C. The high temperature phase of Li$_2$RuO$_3$ is thus an example of a valence bond liquid, where thermal fluctuations drive resonance between different dimer coverages, a classic analogue of the resonating valence bond state often discussed in connection with high Tc cuprates.

PACS numbers: 61.05.cp,61.05.fm,61.50.-f,71.15.Mb

Introduction.—Honeycomb layered systems are of particular interest in solid state physics, due to their fascinating electronic, magnetic and superconducting properties. Recently, honeycomb iridates A$_2$IrO$_3$ (A=Li,Na) have attracted a lot of attention due to the presence of large spin-orbit coupling that was suggested to lead to interesting topological properties [1] and possibly to unconventional Kitaev magnetic interactions [2]. The latter proposition, however, is presently under discussion [3]. Analogues containing 4d metals, where the spin-orbit coupling is much weaker, might thus offer further insights into the iridates [4].

A well known member of the 4d family is Li$_2$RuO$_3$, which is similar to Li$_2$RhO$_3$ and Na$_2$IrO$_3$, but with one more hole in the transition metal t$_{2g}$ bands. In Li$_2$RuO$_3$ an intriguing ground state is found below $\sim$ 270°C, where the Ru atoms form structural dimers with a very strong disproportionation of the short and long bonds ($t_1/t_s \sim 1.2$) [5]. The origin of this dimerization is controversial, and it has been unclear to what extent this behavior is present in the corresponding d$^5$ compounds; existing experimental evidence suggests that Na$_2$IrO$_3$ remains highly symmetric, with less than a 3% variation in Ir-Ir distances [3], and the same is probably true for Li$_2$RhO$_3$ and Li$_2$IrO$_3$ [6, 7]. On the other hand, the relatively low quality of the samples does not allow excluding a possible local structural dimerization without long range order, in which case the average crystal structure remains symmetric, but the electronic physics would be highly influenced by a local-scale dimerization. To assess this possibility, first of all one needs a clear microscopic understanding of the well established dimerization in Li$_2$RuO$_3$. The authors of the original work reporting dimerization [5] later interpreted it as formation of covalent bonds between a particular pair of Ru orbitals [7], and supported this conjecture by looking at the character of the wave functions at two high-symmetry points in the Brillouin zone.

In this Letter, we show that the tendency to dimerization is local and, as previously conjectured [5], driven by covalency. Moreover, we find experimentally that the dimerization locally survives well above the transition temperature, forming a valence bond liquid (VBL). Approximately 1/3 of all Ru-Ru bonds are dimerized at all temperatures and the dimer ordering is short ranged with a correlation length of the order of a few nanometers at high temperatures. The VBL we propose is not to be confused with the so-called resonating valence bond (RVB) liquid [8] that has received much attention in connection with high Tc cuprates; in the latter the many-body electron wave function is a linear combination of the electronic states with all possible spin singlets (called “valence bonds”). In particular one can define a RVB state with dimer singlets (short-range RVB) [9] where the resonating nature is a result of the quantum fluctuations. In the present case the valence bond liquid originates from existing dimer patterns that resonate due to thermal fluctuations and could be described as the classical analog of short-range RVB.

Our density functional theory (DFT) calculations strongly favor the formation of local dimers with the experimentally observed long range order providing the...
lowest energy. However, other mutual arrangements of Ru-Ru dimers have similar energies, varying by \( \approx 40 \) meV, while all dimerized patterns have the energy much lower (by \( \approx 150 \) meV) than the energy of the uniform state without structural dimers. This explains the fact that the long range ordering of dimers is destroyed at \( T_c \approx 270^\circ C \) (\( \approx 47 \) meV), whereas dimers survive up to much higher temperatures. This result supports the concept of a valence bond liquid, and is consistent with our experimental observation that upon quenching the high-temperature phase to 50\(^\circ\) C the dimerization is recovered. Finally, by analyzing the total density of states (DOS), we conclude that not only the orbital identified in Ref. 7 contributes to the covalency of the dimerized bond via direct overlap, but also another orbital provides an additional contribution via an O-assisted hopping. These findings play a very important role in understanding the microscopic physics of other 4d and 5d honeycomb oxides.

**Experiment.** We synthesized a ceramic sample of \( \text{Li}_2\text{RuO}_3 \), which was characterized by both neutron [10] and synchrotron x-ray powder diffraction. Both methods gave results consistent with the dimerized \( P2_1/m \) structure reported in Ref. 5 at room temperature. Diffraction experiments were performed using the ID15B beam-line at the ESRF, Grenoble. A wavelength of 0.1422 Å was used and the scattered x-rays were detected by a Mar345 image plate. Two detector distances were used at each temperature, such that data suitable for both Rietveld [11] and pair distribution function analysis were collected (see Supplementary Information (SI)). At room temperature, the dimerized structure is evidenced by the presence of \((h+k=odd)\) reflections which break C-centering (Fig. 1(a)). The corresponding difference in Ru-Ru distances is pronounced, with 1/3 short bonds [12] (2.55 Å) and 2/3 long (~3.1 Å) (see Fig. 1(a)). Upon warming toward the transition, the \((h+k=odd)\) reflections lose intensity, merging into the background above 250\(^\circ\)C. The refined Ru-Ru distances converge to a single value of \( \approx 2.95 \) Å, and at 350\(^\circ\)C, excellent fits to the data were obtained using the undistorted \( C2/m \) structure (see SI). The honeycomb layers are as symmetric as those seen [3, 10] in the metallic honeycomb ruthenate \( \text{Ag}_3\text{LiRu}_2\text{O}_6 \) or \( \text{Na}_2\text{IrO}_3 \). Although the bond lengths converge in a manner indicative of a displacive phase transition (Fig. 1(c)), a small volume anomaly is also observed (Fig. 1(b)), with a slight expansion upon entering the high temperature phase. Furthermore, a sharp increase in the Ru atomic displacement parameter is observed, which implies an increase in disorder beyond that expected in a simple Debye model (inset Fig. 1(c)).

Reframements 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. Using Igor Pro based software (iPDF) developed by one of the authors (SAJK), we corrected the raw diffraction data for background, incoherent inelastic scattering, and the atomic form factors (see SI). To visualize any short-range disorder, we Fourier transformed the structure factors into real space using:

\[
G(r) = \frac{2}{\pi} \int_0^\infty Q[S(Q) - 1]\sin(Qr)dQ,
\]

where \( S(Q) \) is the structure factor. Models were fitted to the PDF data using the PDFgui package [13].

Deep within the dimerized phase of \( \text{Li}_2\text{RuO}_3 \), we obtained good fits to the pair distribution functions using the \( P2_1/m \) crystal structure described above. How-
ever, upon examining the data at our highest temperature (650°C), we found that the fit of the average $C/2/m$ model was poor ($rw=0.204$), when refined against the PDF in the range $1.5 < r < 7.25$ Å (Fig. 2(a)). In particular, the model does not reproduce a prominent peak (arrowed) at 2.68 Å. However, when we used the dimerized model which describes the low-temperature phase, this peak, and indeed the whole $r$-range was well-fitted. The quality of the fit was nearly twice as good ($rw = 0.116$), and the 2.68 Å peak was due to Ru-Ru dimerization surviving at high temperatures. Furthermore, the excellent agreement of the $P2_1/m$ structure shows that $h/l_u$ is approximately conserved. The PDFs are shown in Fig. 2(b). The peak corresponding to the short Ru-Ru distance is highlighted for the whole temperature region. Although there is a small shift of this peak to larger $r$-values upon heating, the converging bond distances observed by Rietveld analysis (Fig. 2(c)) are clearly not observed on the local length scale. When we repeated refinements of the $P2_1/m$ structure on the local length scale for the whole temperature range, we obtained the results shown in Fig. 3(a) for the Ru-Ru distances. The temperature variation is almost linear with only a small anomaly at the $P2_1/m \rightarrow C/2/m$ transition. Extrapolating our data suggests that the short-range dimerization would persist up to at least 1400°C, i.e. well beyond chemical decomposition. This energy scale ($\theta \sim 140$ meV), which in a mean-field picture corresponds to the dimerization energy, is rather large for magnetic exchange interactions, although consistent with metal-metal covalent bonding [7, 14]. The energy scale of the ordering transition, $\sim 47$ meV, on the same level of approximation, should correspond to the inter-dimer interaction.

Having shown that the low temperature $P2_1/m$ structure provides a reasonable model for the short-range dimer correlations at high temperatures, we then proceeded to investigate the length scale of this order. We performed so-called box-car refinement of this structure against the PDF at 350°C. We used an 8.5 Å box and stepped $r$-min from 1.5 to 32.5 Å in 2.5 Å steps. The so refined Ru-Ru distances are shown in Fig. 3(b). We find that the difference between the short and long bonds is progressively lost as the length scale increases demonstrating that the dimer order at $T = 350$°C has a length scale of $\sim 1.5$ nm (about two unit cells). At even higher temperatures we found that the ordering of dimers vanishes beyond the first coordination sphere. Thus, at $T \gg T_c = 270$°C there is little correlation between individual dimers, but $\sim 1/3$ of all Ru-Ru bonds remain dimerized.

**Theory.**- The origin of the room-temperature dimerization has been discussed differently, depending on the starting point, i.e. localized versus itinerant description. Jackeli and Khomskii [15] considered a localized picture and argued that dimerization is controlled by spin physics, essentially, promoting singlet formation on the short bonds. A drastic reduction of the paramagnetic spin susceptibility below the structural transition is consistent with this concept. On the other hand, an itinerant scenario was put forward in Ref. [7]. These authors suggested that the driving force of dimerization is covalent bonding. Both electrons of Ru$^{4+}$ can contribute to dimer formation. Indeed, we observe in our electronic structure calculations that for each bond there is one pair of Ru 4$d$ orbitals that can overlap directly (in an appropriately chosen local coordinate system, these could be selected as $xy$ orbitals), with the amplitude $t_{dd\sigma}/(E_d - E_p)$. Details and visual illustrations can be found, for instance, in Ref. [16]. One can also construct linear combinations, $u_+ = (xz + yz)/\sqrt{2}$ and $u_- = (xz - yz)/\sqrt{2}$. Both of them provide the same hoppings via bridging oxygens, but only the former describes the direct hopping ($t_{dd\sigma}$). For really short dimers (the low-T phase) the direct hopping dominates, although it is largely offset by the indirect hopping, and as a result the bonding-antibonding splitting between the $u\pm$ orbitals is

![Fig. 3: (color online) (a) Temperature dependence of the fitted Ru-Ru distances from the PDF analysis of Li$_2$RuO$_3$ in the range $1.5 < r < 7.25$ Å. Error bars obtained by directly fitting Gaussians to the data shown in Fig. 2(b) are smaller than the markers; (b) $r$-dependence of the Ru-Ru distances extracted from model fits to the PDF at 350°C as described in the text. The two inequivalent longer distances have been averaged for plotting.](image-url)
splitting due to the $xy$ orbital. For longer dimers (the high-$T$ phase) $t_{ddπ}$ becomes smaller, which results in smaller and less differentiated splitting between the $u_±$ bands, “unbounding” the second hole and freeing it to respond to external fields.

To analyze this picture, we have performed full structural relaxations of Li$_2$RuO$_3$ within DFT as implemented in the VASP code [17]. The final energies were computed using an all-electron method [18]. We considered a large sampling of initial structures, including the experimentally reported structures and found several energetically favorable structures; the simplest two are shown in Figs. 4 (a) and (b). The main results of our calculations are that (1) the calculated ground state corresponds to a strong bond disproportionation ($h_1/h_s \sim 1.2$), in quantitative agreement with the experiment; (2) The disproportionation was only slightly stronger when magnetization of Ru is included; (3) Examination of the DOS (Figs. 4 (c) and (d)) confirms that the directly overlapping $xy$ orbitals form a very strong covalent bond (bonding-antibonding splitting of more than 2 eV). One of the two holes of Ru residing in the $t_{2g}$ band is occupying this antibonding state, with a substantial energy gain; (4) The $u_-$ orbital also contributes to the total covalency, albeit considerably less. The corresponding bonding-antibonding splitting is about 0.7 eV and the second hole takes advantage of this fact. Moreover, this contribution is only weakly dependent on the bond length, and therefore its contribution to dimerization is much smaller than to covalency in general; (5) Examination of the Ru effective moment in spin-polarized calculation shows that it is at most spin 1/2 and never 1; this indicates that at least one electron spin is quenched. The second, $u_±$, spin may or may not be quenched depending on temperature. Our calculations find rather small energy differences between ferro- and antiferromagnetic arrangement of the $u_±$ spins, so when they are unbound and their covalent bond is broken at high temperature, they behave magnetically as nearly free spin 1/2 electrons. Indeed the difference between the experimental susceptibility at low temperatures (spin gap) and at high temperatures [7] is consistent with this scenario. Finally, (6) all investigated long range orders of the structural dimers are energetically strongly favorable when compared with the undimerized structure. The differences among the dimerized structures are of the order of 40 meV (≈ 450 K), comparable with the ordering transition temperature. On the other hand, the (optimized) uniform structure is 155 meV (≈ 1800K) above the ground state structure, which explains why dimers themselves survive well above $T_c$.

Discussion.- Our experimental results combined with theoretical calculations render the following picture: Ru-Ru bonds in Li$_2$RuO$_3$ have a very strong tendency to form local dimers with covalent bonds via direct overlap of Ru 4$d$ orbitals. The structural transition at $\sim 270^\circ$C is of the order-disorder type: the dimers at $T \leq 270^\circ$C do not disappear at higher temperatures, nor does their concentration (1/3 of all bonds) change. Dimer-dimer interaction, presumably of elastic origin (as evidenced by the fact that the disordered phase has a larger $a$ lattice parameter (see SI), due to a lack of proper dimer packing), is much weaker and responsible for mutual ordering of the dimers in the observed “armchair” structure. [13] In the high temperature phase there is no ordering of dimers at a length scale $\gtrsim 1.5$ nm, or 2-3 lattice parameters. The ordering temperature is consistent with the calculated energy differences between dimerized phases with different dimer long range ordering. Upon quick cooling to 50$^\circ$, the long-range dimer ordering was restored suggesting that the high-temperature phase is a valence bond liquid (not a glass), where dimerization occurs dynamically on a time scale long compared to the characteristic time scale of our X-ray measurements. While the concept of quantum spin liquid of dynamically disordered spin-singlets is well known, its classical analog, a liquid of valence bonds dynamically disordered due to thermal fluctuations, as it is our case, has been less investigated [19]. Statistical physics of such an object should be nontrivial, bearing resemblance to Maier-Saupe transitions in liquid crystals and solid hydrogen [20]. We hope that our results will stimulate further experimental and theoretical studies in
this direction.

We thank M. Di Michiel and G. Khaliullin for useful
discussions and the ESRF for support. I.I.M. acknowl-
edges support from the Funding from the Office of Naval
Research (ONR) through the Naval Research Labora-
tory’s Basic Research Program. M.A., H.O.J. and R.V.
thank the German Science Foundation (DFG) for funding
through SFB/TRR 49 and FOR 1346. S.S.V. thanks the
Russian Foundation for Basic Research and the Ministry
of education and science of Russia for research programs
RFFI-13-02-00374 and MK-3443.2013.2. The work of
D.Kh. was supported by the DFG via FOR 1346 and
Research grant 1484/2-1, and by Cologne university via
the German excellence initiative.

* Email of corresponding author: kimber@esrf.fr
† Email of corresponding author: valenti@itp.uni-
frankfurt.de

[1] A. Shitade, H. Katsura, J. Kuneš, X.-L. Qi, S.-C. Zhang,
N. Nagaosa, Phys. Rev. Lett. 102, 256403 (2009).
[2] G. Jackeli, G. Khaliullin, Phys. Rev. Lett. 102, 017205
(2009).
[3] S.K. Choi, R. Coldea, A.N. Kolmogorov, T. Lancaster,
I.I. Mazin, S.J. Blundell, P.G. Radaelli, Y. Singh, P.
Gegenwart, K.R. Choi, S.W. Cheong, P.J. Baker, C.
Stock, J. Taylor, Phys. Rev. Lett. 108, 127204 (2012).
[4] I.I. Mazin, S. Manni, K. Foyevtsova, H.O. Jeschke, P.
Gegenwart, R. Valentí, Phys. Rev. B 88, 035115 (2013).
[5] Y. Miura, Y. Yasui, M. Sato, N. Igawa, K. Kakurai, J.
Phys. Soc. J. 76, 033705 (2007).
[6] H. Gretarsson, J.P. Clancy, Y. Singh, P. Gegenwart, J.P.
Hill, J. Kim, M.H. Upton, A.H. Said, D. Casa, T. Gog,
Y.-J. Kim, Phys. Rev. B 87, 220407 (2013).
[7] Y. Miura, M. Sato, Y. Yamakawa, T. Habaguchi, Y. Ono,
Journal of the Physical Society of Japan 78, 094706
(2009).
[8] P.W. Anderson, Science 235, 1196-1198 (1987).
[9] D.S. Rokhsar, S.A. Kivelson, Phys. Rev. Lett. 61, 2376
(1988).
[10] S.A.J. Kimber, C.D. Ling, D.J.P. Morris, A. Chemes-
dine, P.F. Henry, D.N. Argyriou, J. Mat. Chem. 20,
8021-8025 (2010).
[11] A. Larson and R. V. Dreele, General Structure Analysis
System (GSAS), Los Alamos National Laboratory Re-
port LAUR 86-748 (1994).
[12] Note that the measured short bond is shorter than the
Ru-Ru metallic bond distance of 2.65 Å.
[13] C.L. Farrow, P. Juhas, J.W. Liu, D. Bryndin, E.S. Bozin,
J. Bloch, T. Proffen and S.J.L. Billinge, J. Phys. Con-
dens. Matter 19, 335219 (2007).
[14] S.A.J. Kimber, M.S. Senn, S. Fratini, H. Wu, A.H. Hill,
P. Manuel, J.P. Attfield, D.N. Argyriou, P.F. Henry,
Phys. Rev. Lett. 108, 217205 (2012).
[15] G. Jackeli, D.I. Khomskii, Phys. Rev. Lett. 100, 147203
(2008).
[16] I.I. Mazin, H.O. Jeschke, K. Foyevtsova, R. Valentí, D.I.
Khomskii, Phys. Rev. Lett. 109, 197201 (2012).
[17] G. Kresse, J. Hafner, Ab initio molecular dynamics for
liquid metals, Phys. Rev. B 47, 558 (1993).
[18] K. Koepernik, H. Eschrig, Full-potential nonorthogo-
nal local-orbital minimum-basis band-structure scheme.
Phys. Rev. B 59, 1743 (1999; http://www.FPLO.de).
[19] S. Lakkis, C. Schlenker, B.K. Chakraverty, R. Buder, M.
Marezio, Phys. Rev. B 14, 1429 (1976).
[20] A.F. Goncharov, I.I. Mazin, J.H. Eggert, R.J. Hemley,
H.k. Mao, Phys. Rev. Lett. 75, 2514 (1995).