A valence bond liquid on the honeycomb lattice. Supplementary Information

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SUPPLEMENTARY INFORMATION

Theoretical

We performed structure relaxations using the Vienna ab initio simulation package (VASP). We considered as initial configurations (i) the experimental Li_2RuO_3 structures as reported by Miura *et al.*, J. Phys. Soc. Jpn. **78**, 094706 (2009) as well the experimental structure of Na_2IrO_3 (Choi *et al.*, Phys. Rev. Lett. **108**, 127204 (2012). In the conventional unit cell of the latter, we replaced Na by Li and Ir by Ru and adjusted the Ru positions to obtain the initial geometry of configurations with armchair or parallel dimers. We performed full structure relaxations including cell shape, cell volume and internal coordinates, until the forces on all atoms was less than 0.005 eVÅ^{-1}. Structure relaxations were done using the Born-Oppenheimer procedure as implemented in VASP. The wave functions were represented using the projector augmented wave (PAW) method. Exchange and correlation effects were treated in the generalized gradient approximation (GGA) in the formulation of Perdew, Burke and Ernzerhof. A plane wave cutoff of 500 eV was used. The Brillouin zone was sampled with a Γ centered $9\times7\times9$ k mesh.

While the structure candidates were obtained using full relaxation in VASP without symmetry ($P\,1$), we determined the resulting symmetry after relaxing and performed an additional local structural optimization within this symmetry using FPLO; this calculation was done with $10 \times 10 \times 10$ k points. The results are given in Tables SI and SII. The Ru-Ru bond distances in these two structures form the two patterns shown in Fig. 4(a,b) of the main text. We list the complete structural information in Table SIII. Finally, the energy differences we found are given in Table SIV.

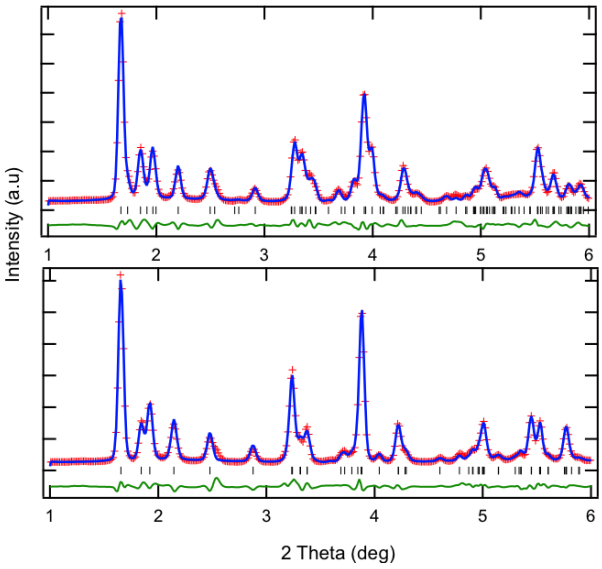

FIG. S1: (color online) Observed, calculated and difference profiles shown for the Rietveld fits at 50 and 650°C. Fits were performed using the average symmetry as determined by Miura *et al.* as described in the main text.

TABLE SI: Theoretical $P\,2_1/m$ structure of Li_2RuO_3; lattice constants are $a = 4.95658$ Å, $b = 8.86492$ Å, $c = 5.20619$ Å, $\beta = 71.23964°$.

Li(1)	−0.2327	0.09047	0.4893
Li(2)	−0.2247	0.25	0.0025
Li(3)	0.2482	0.25	−0.4830
Ru	0.2856	0.0775	−0.003
O(1)	0.4994	0.084	0.2631
O(2)	0.004	0.078	−0.2203
O(3)	0.043	0.25	0.2234
O(4)	−0.4890	0.25	−0.2389

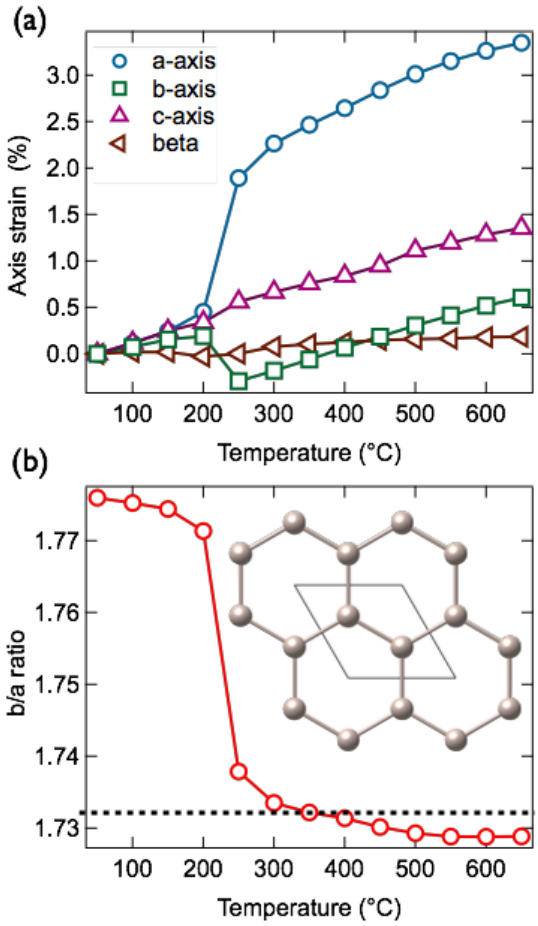

FIG. S2: (color online) (a) Structure factors for Li_2RuO_3 at 50 and 650°C plotted in the form $Q.[S(Q) - 1]$. (b) Fit of the dimerized structure to the pair distribution function of Li_2RuO_3 at 50°C calculated from the data in panel (a).

TABLE SII: Theoretical $C\,2/m$ structure of Li_2RuO_3; lattice constants are $a = 5.25698$ Å, $b = 8.46179$ Å, $c = 5.25278$ Å, $\beta = 69.76231°$.

Li(1)	0	0	0
Li(2)	0	−0.1680	−0.5
Li(3)	0	0.5	0.5
Ru	0	0.3507	0
O(1)	−0.2463	0.17530	0.2195
O(2)	0.2494	0	0.2702

Experimental

All x-ray scattering data were collected using the ID15B high energy beam line at the European Synchrotron Radiation Facility, Grenoble, France. The incident energy of 87 KeV was selected using a bent Si (311) crystal in Laue geometry. The beam size on the sample was 0.4 x 0.4 mm. The sample was contained in

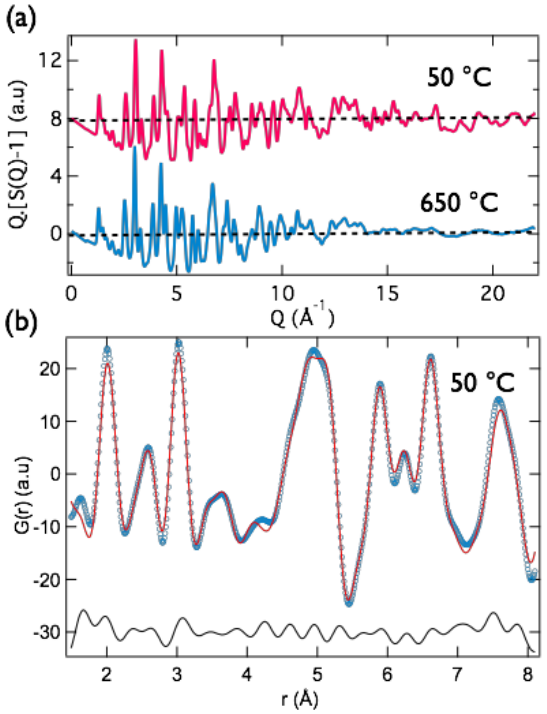

FIG. S3: (color online) (a) Temperature dependence of the refined lattice parameters from Rietveld refinement against the synchrotron x-ray diffraction profiles of Li_2RuO_3. Error bars are smaller than the point size. (b) Temperature dependence of the b/a ratio from the data in panel (a). This is an indication of how distorted the honeycomb layers are from three fold symmetry.

TABLE SIII: Uniform $C\,2/m$ structure of Li_2RuO_3 considered in this work; relaxed lattice constants are $a = 5.01842$ Å, $b = 8.67707$ Å, $c = 5.24354$ Å, $\beta = 71.56134°$.

Li(1)	0	0	0
Li(2)	0	−0.1586	0.5
Li(3)	0	0.5	0.5
Ru	0	0.3331	0
O(1)	−0.2493	0.1699	0.2392
O(2)	0.2595	0	0.2396

a 1 mm diameter quartz capillary and was heated using a Cyberstar gas blower. For the pair distribution data

TABLE SIV: Energy differences per formula unit between theoretical Li_2RuO_3 structures. The energy E_0 for the $P\,2_1/m$ structure given in Table SI is used as reference energy.

Structure	$E - E_0$ (meV)
Armchair (Table SI)	0
Parallel (Table SII)	42
Uniform (Table SIII)	155

sets, an empty capillary was measured and the resulting pattern scaled by monitor counts then subtracted. The raw 2D data sets were radially integrated using Fit2D. PDF model fitting was performed using PDFGui (Farrow *et al*) and the model calculations were convoluted with a sinc function to reflect the experimental Q-range used ($1 < Q < 21.5$,Å^{-1}).

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