Supporting Information

Nonmetallic Metal toward Pressure-Induced Bad-Metal State in Two-Dimensional Cu₃LiRu₂O₆

Bin Huang,^a Ziyi Liu,^b Yifeng Han,^a Shuang Zhao,^a Meixia Wu,^a Corey Frank,^c Martha Greenblatt,^c Mark Croft,^d Nicholas F. Quackenbush,^e Sizhan Liu,^f Trevor A. Tyson,^f Lei Zhang,^g Junliang Sun,^g Peifei Shan,^{b,h} Jianhong Dai,^b Xiaohui Yu,^{b,h,i} Jinguang Cheng,^{b,h,i,*} Man-Rong Li^{a,*}

^{a.} Key Laboratory of Bioinorganic and Synthetic Chemistry of Ministry of Education, School of Chemistry, Sun Yat-Sen University, Guangzhou 510275, P. R. China.

^{b.} Beijing National Laboratory for Condensed Matter Physics and Institute of Physics, Chinese Academy of Sciences, Beijing 100190, P. R. China

^{c.} Department of Chemistry and Chemical Biology, Rutgers, The State University of New Jersey, 610 Taylor Road, Piscataway, New Jersey 08854, United States.

^{d.} Department of Physics and Astronomy, Rutgers, the State University of New Jersey, 136 Frelinghuysen Road, Piscataway, New Jersey 08854, United States.

^{e.} Materials Measurement Science Division, Material Measurement Laboratory, National Institute of Standards and Technology, Gaithersburg, Maryland 20899, United States.

^{f.} Department of Physics, New Jersey Institute of Technology, Newark, New Jersey 07102, United States.

^{g.} College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, P. R. China

 ^{h.} School of Physical Sciences, University of Chinese Academy of Sciences, Beijing 100190, P. R. China

ⁱ Songshan Lake Materials Laboratory, Dongguan 523808, P. R. China

Email: limanrong@mail.sysu.edu.cn; jgcheng@iphy.ac.cn

SUPPLEMENTARY TEXT

1. Method

Synthesis. The preparation of $Cu_3LiRu_2O_6$ is based on the following topotactic metathesis reaction (**Fig. S1**):

$$2 \text{Li}_2 \text{RuO}_3 + 3 \text{CuCl} \rightarrow \text{Cu}_3 \text{LiRu}_2 \text{O}_6 + 3 \text{LiCl},$$

where the Li₂RuO₃ precursor was prepared from a mixture of Li₂CO₃ (Macklin, 99.99%) and RuO₂ (Macklin, 99.95%) with molar ratio of 1.05 : 1 (excess Li₂CO₃ was added to compensate for Li volatilization at high temperature). The mixture was pressed into a pellet and first heated to 923 K at a rate of 3.5 K/min, held for 48 h, and then to 1173 K at a rate of 4.2 K/min and kept for another 48 h in air without intermediate grinding. Finally, the furnace was cooled to 923 K at the rate of 0.8 K/min before naturally cooling to room temperature (RT). A mixture of CuCl (Alfa Aesar, 99.9%) and as-prepared Li₂RuO₃ with molar ratio between of 1 : 2.03 to 1 : 3.0 was heated at 673 K (heating rate of 1-5 K/min) for 16 h in a quartz tube under vacuum and then cooled to RT at 1-5 K/min. The product was washed five times with ammonium hydroxide (NH₄OH, Aladdin, 28%) to remove excess CuCl and then washed twice with deionized water before being dried in an oven at 323 K. Part of the obtained powder was pressed into a dense tablet under 3 GPa of pressure at RT for physical properties measurements.

Chemical and Crystal Structure Characterizations. For phase and purity identification, powder X-ray diffraction (PXD) data were measured with a Rigaku (D-MAX 2200 VPC) instrument with a Cu-K α radiation source ($\lambda = 1.5418$ Å).

Synchrotron powder X-ray di \Box raction (SPXD) data were collected at ambient conditions on beamline BL14B ($\lambda = 0.69004$ Å) at the Shanghai Synchrotron Radiation Facility (SSRF). The sample was loaded into a 0.5 mm glass capillary and the diffraction data were collected in spinning-mode. The Mythen1K detector system was used for high quality data acquisition, and the wavelength was obtained using an Al₂O₃ (NIST 676a) standard. Detailed information about beamline BL14B1 has been referenced below.^{1,2} Diffraction data analysis and Rietveld refinement were performed with the Topas-Academic software package.³ An SDT Q600 (V20.9 Build 20) analyzer was used to perform thermogravimetric analysis (TGA).

Scanning electron microscope and energy disperse spectroscopy (SEM-EDS) were carried out on a Dual beam FIB (Helios nanolab G4 CX,FEI,USA) equipped with a SDD-EDS detector (AZtec X-Max 150, Oxford, UK). Selected area electron diffraction (SAED) was measured on a transmission electron microscope (TEM, JEM-2100) with an accelerating voltage of 200 kV. The X-ray absorption near edge spectroscopy (XANES) was performed at the Brookhaven National Synchrotron Light Source (NSLS-II) using double crystal monochromators with the Ru-L₂, L₃ edges being measured at the 8-BM, TES beamline (with Si-111 crystals) and the Cu-K edges being measured at 6-BM, BMM (with higher resolution, Si-311 crystals). The Cu-K edge data were collected in both the transmission and fluorescence mode with simultaneous standards. Cu-standards run at NSLS-I on beamline X19-A have also been included. Due to the low energy of the Ru-L edges the data was collected in the fluorescence mode with adjacently run standards.

Physical Properties Measurements. The temperature dependent resistivity for a sample of $Cu_3LiRu_2O_6$ under different pressures was measured with the palm cubic anvil cell (CAC) apparatus up to 11 GPa and diamond anvil cell (DAC) up to 35 GPa. A standard four-probe method was used for the resistivity measurements. Glycerol was employed as the pressure transmitting medium and the pressure values were estimated from the pressure-load calibration curve at RT. Details about the experimental setup for CAC can be found elsewhere.^{4, 5} Magnetic measurements were performed with a Quantum Design Magnetic Property Measurement System in the temperature range from T = 2 to 300 K. The susceptibility was measured in both field-cooled (FC) and zero-field-cooled (ZFC) modes at magnetic fields between 0.1 and 5 T. The specific heat of $Cu_3LiRu_2O_6$ was measured with two-tau relaxation method in a PPMS-9T. The sample mass is 2.35 mg and the sample coupling close to 100% has been maintained during the measurements.

2.Composition

The topotactic ion exchange reaction depends largely on experimental conditions such as the mass scale and the cooling rate. Cava et al. prepared Cu₃NaIr₂O₆ via a mixture of Na₂IrO₃ and CuCl (molar ratio of 1 : 3.1 with mass scale of 0.4 to 2 g) at 400 °C for 24 h in fused silica jacket, followed by oven cooling to RT,⁶ while Tafti et al. performed the similar synthesis at 350 °C for 16 h (heating and cooling rate of 1 °C/min and mass scale of 0.15 to 0.3 g), but obtained the fully substituted product Cu₂IrO₃.^{7,8} In our case, the title compound can be prepared with a CuCl : Li₂RuO₃ ratio between 2.03 : 1 and 3 : 1 and a mass scale between 0.36 and 1 g at varied heating and cooling rates (1 °C/min - naturally furnace cooling). Attempts to increase the Cu⁺ substitution degree at higher temperatures were unsuccessful and resulted in decomposition (**Fig. S4**). SEM-EDS measurements were carried out on the as-made sample (hereafter the Li₂RuO₃/CuCl = 1/2.03 batch sample was used for the characterization unless specified) after phase examination by PXD, giving Cu : Ru ratio of 1.4(1):1 (**Fig. S5**), suggesting a compositional formula of Cu₃LiRu₂O₆ under charge balance. To further confirm the composition and oxygen content, TGA was conducted with a heating rate of 10 K/min from 300 to 873 K in a reducing atmosphere of 1% H₂/Ar gas mixture (**Fig. S6**). PXD pattern after TGA (**Fig. S7**) indicates that Cu₃LiRu₂O₆ was reduced to a mixture of Cu and Ru (Li is too light to be observed by PXD), corresponding to a weight (oxygen) loss percentage Δ m/m about 19.19(1)%, which coincides well with the expected value (19.36%) of the nominal formula, Cu₃LiRu₂O₆. Had Li been fully replaced by Cu to form Cu₂RuO₃, the weight loss would be expected to be 17.4(1)%.

3. Crystal Structure

The atomic occupancies of Cu1 at 4h sites, Cu2 at 2d sites, O1 at 4i sites, and O2 at 8j sites were close to fully occupied within the standard deviation (no more than 1%) during the refinements, and thus fixed to be unit. The mixed (Li/Ru)1 and (Li/Ru)2 at 4g (0, y, 0) and 2a (0, 0, 0) sites were constrained to be fully occupied to ensure the overall Cu/Li/Ru ratio of 3/1/2 according to the SEM-EDS and TGA analyses. The final atomic occupancy was converged to Ru1/Li1 = 0.718/0.282(6) and Ru2/Li2 =

0.436/0.564(1), respectively. The crystal structure of Cu₃LiRu₂O₆ is shown in **Inset of Fig. 1**, where the Cu atoms are sandwiched between the edge-sharing (Li/Ru)₁O₆ and (Li/Ru)₂O₆ octahedral layers along [001] direction. The metal-metal distances between the centroid of octahedra vary from 2.994 to 3.034 Å. Each metal site is surrounded by six nearest metal neighbors in the octahedral layer, forming distorted 2D hexagonal network (**Fig. S8a**, where (Li/Ru)1 and (Li/Ru)2 were denoted as Ru1 and Ru2, respectively). The Ru1-centered hexagon (packed by three-neighboring Ru1 (3.034 Å, 2.994 Å × 2) and three-neighboring Ru2 (3.014 Å × 2, 2.995 Å)) is less regular than the Ru2-centered one (six Ru1 with Ru2-Ru1 of 3.014 Å × 4 and 2.995 Å × 2). The hexagonal network in the alternative Cu-layers displays similar (**Fig. S8b**) connections, where the Cu-Cu distance varies between 2.910 and 3.203 Å. Geometrically, the anisotropic Cu-Cu distance is correlated to the O-Cu-O bond angles, in which O1-Cu2-O1 is in linear dumbbell-arrangement (180.0(4)°), while that of O1-Cu2-O1 is bent to be 177.9(5)°.

4. XANES

XANES is a useful tool for locally probing the valence states at atomic sites in solids. The $L_{2,3}$ edges of 4d transition metals (TM) are dominated by intense "white line" (WL) features due to dipole transitions into final 4d states (see in **Fig. S9a**). One signature of increasing TM-valence states (decreasing d-count) is the chemical shift of the centrum of the WL-feature to higher energy. In **Fig. S9a** the chemical shift in $Cu_3LiRu_2O_6$ is very clearly lower than that of the Ru⁵⁺ standard Sr₂YRuO₆ and is quite

comparable to that of the Ru^{4+} standard $Y_2CoRuO_{6,9}$ supporting a Ru^{4+} state in $Cu_3LiRu_2O_6$.

A second, more prominent, signature of TM-valence/d-configuration lies in the systematic evolution of the prominent bimodal A/B - the structure of the L2.3 WLfeatures for octahedrally coordinated TM-O compounds as illustrated for 4dº-4d4 materials in Fig. S10a and b. This bimodal A (t_{2g}-hole related)/B (e_g-hole related) structure reflects the octahedral O-coordination ligand field (LF), splitting of the dstates, into a lower energy, 6-fold, t_{2g} and higher energy, 4-fold, eg multiplets. This LF splitting is most clearly illustrated in the d⁰ standard compound spectra shown in Fig. **S10**. The systematic filling of the t_{2g} orbitals with increasing 4d-orbital-count (decreasing final state hole-count) clearly leads to a systematic decrease of the Afeature (t_{2g}-hole coupled) intensity (see Fig. S10) for a series of compounds spanning d⁰-d⁴. Referring to Fig. S9a the relative A-feature Ru-L_{3,2} intensities of Cu₃LiRu₂O₆ are very substantially reduced below those of the $Sr_2YRuO_6,\,d^3\text{-}Ru^{5\text{+}}$ standard and are comparable to the Y2CoRuO6 d4-Ru4+ standard. Thus, the Ru-L32 spectral feature structure the Cu₃LiRu₂O₆ spectrum further supports the $d^{4}-Ru^{4+}$ of configuration/valence in this compound.

The near edge features at the K-edges of 3d row transition-metal (TM(3d)) compounds are due to transitions from the 1s to 4p states, combined with a step feature for the continuum onset, multiple 4p features associated with different local ligand coordination, mixed 3d configurations, differing orbital orientations, and complicate near edge structure. Nevertheless, the systematic energy shifts in the TM(3d) K edges

and doping/chemical changes can serve as indicators of charge transfer.^{10, 11} The Cu-K near edge of Cu₃LiRu₂O₆ was compared to various standard compound spectra in **Fig. S9b**. Both the structure and the chemical shifts of the near edge structure are sensitive to the valence and local atomic environment. Specifically, **Fig. S9b** displays Cu-K edge of a series of standard Cu compounds with varying formal valences and Cu-O coordination: Cu⁺, Cu₂O with linear 2-fold coordination;¹² the ~Cu²⁺ square planar coordinated CuO and the perovskite based La₂CuO₄.¹³ Before proceeding, it should be reiterated that the layered crystal structure of Cu₃LiRu₂O₆ involves: honeycomb hexagonal planes of edge sharing RuO₆ octahedra with a 6-coordinate Li in the center of the hexagon (**Fig. S8a**); a plane of linear O-Cu-O moieties is located between the honeycomb layers (seen in **Fig. 1**). The linear O-Cu-O sites are closely resembled the geometry in the Cu⁺ standard Cu₂O (seen in **Fig. S9b**) is a solid confirmation of both the Cu⁺ state and the linear O-Cu-O structure in this material.

SUPPLEMENTARY FIGURES



Fig. S1 Topotactic reaction of precursor Li_2RuO_3 and CuCl to form ruthium containing honeycomb delafossites $Cu_3LiRu_2O_6$



Fig. S2 Rietveld refinement of the SPXD data for Cu₃LiRu₂O₆ in C2/c structure at RT.



Fig. S3 SAED patterns in the $[\overline{1}10]$ reciprocal lattice plane for Cu₃LiRu₂O₆.



Fig. S4 PXD patterns for Cu₃LiRu₂O₆ at different temperature.



Fig. S5 SEM-EDS image of Cu₃LiRu₂O_{6.}



Fig. S6 TGA result in 1% H₂/Ar from 300 to 873 K.



Fig. S7 PXD patterns for $Cu_3LiRu_2O_6$ after TGA in 1% H₂/Ar.



Fig. S8 The crystal structure of $Cu_3LiRu_2O_6$ from the refinements of SPXD (a) Hexagonal network of the (Ru/Li)1 (denoted as Ru1) and (Ru/Li)2 (denoted as Ru2) layer. (b) Hexagonal network of the Cu-layer alternatively stacked with the Li/Ru later along [001] direction.



Fig. S9 (a) comparison of the Ru-L₃ edge spectra for Cu₃LiRu₂O₆ to the Sr₂YRuO₆ and Y₂CoRuO₆ standards (lower left) along with the Ru-L₂ edge spectra for the same compounds (inset upper right). Note the A- and B-features related respectively to transitions into empty t_{2g} and e_g final states. (b) Cu-K edge of Cu₃LiRu₂O₆ compared to those of standard compounds: Cu¹⁺, Cu₂O; and ~Cu²⁺, La₂CuO₄.



Fig. S10 The systematic TM-L₃ (a) and L₂ (b) edge WL-feature variation with 4delectron (hole) count from d⁰ to d⁴ (10 to 6).¹⁴⁻²² Note: the bimodal A/B structure corresponding to transitions into t_{2g}/e_g final states respectively; and the systematic

decrease in A-feature spectral intensity (relative to the B-feature) with increasing t_{2g} electron count (decreasing hole count). These spectra were mostly collected on NSLS beamline X19A in the total electron yield mode where the short sampling depth minimized self-absorption effects that are sizable in fluorescence mode measurements in this energy range.

SUPPLEMENTARY TABLES

Table S1. Structural parameters of Cu₃LiRu₂O₆. Refined from the SPXD data collected at RT.

Atom	Position	Х	у	Z	Occ.	B(Å ²)
Ru1	4g	0	0.332(1)	0	0.718(3)	0.84(13)
Li1	4g	0	0.332(1)	0	0.282(3)	0.84(13)
Ru2	2a	0	0	0	0.436(6)	0.80(27)
Li2	2a	0	0	0	0.564(6)	0.80(27)
Cu1	4h	1/2	0.322(1)	1/2	1	3.59(4)
Cu2	2d	1/2	0	1/2	1	3.59(4)
01	4i	0.427(4)	0	0.163(3)	1	2.23(6)
O2	8j	0.416(3)	0.319(2)	0.168(2)	1	2.23(6)

*Monoclinic, space group C2/m (No. 12), a = 5.2085(2) Å, b = 9.0236(2) Å, c = 6.0267(2) Å, $\beta = 106.59(1)^{\circ}$, V = 271.42(2) Å³, Z = 2, R_{wp}%= 5.65, R_p% = 6.92.

Table S2. Selected interatomic distances(Å), bond angles(°), and BVS of $Cu_3LiRu_2O_6$ at RT.

MO ₆ /MO ₂ Cu ₃ LiRu ₂ O ₆	-01	-02	<m-o></m-o>	BVS		
(Li/Ru)1	1.904(1) × 2	$2.116(1) \times 2$ $1.818(1) \times 2$	1.946(1)	3.846(1)		
(Li/Ru)2	2.159(1) × 2	$2.036(1) \times 4$	2.077(1)	2.029(1)		
Cu1		1.925(1) × 2	1.925(1)	0.854(1)		
Cu2	1.957(1) × 2		1.957(1)	0.783(1)		
$\Delta_{(\text{Li/Ru})1} = 4.14 \times 10^{-3}; \ \Delta_{(\text{Li/Ru})2} = 0.779 \times 10^{-3}$						
<o-(li ru)1-o=""> <o-(li ru)2-o=""> <o-cu-o> <li ru="" ru-o-cu=""></o-cu-o></o-(li></o-(li>						

01-		01-		01-		(Li/Ru)1	02 1(2)
(Li/Ru)1	74.4(4)	(Li/Ru)2	180.0(1)	Cu2-	180.0(4)	-02-	95.1(5) 101.8(2)
-01		-01		01		(Li/Ru)2	101.8(3)
O2- (Li/Ru)1 -O2	83.4(4) 81.1(3) 93.9(3) 173.4(4)	O2- (Li/Ru)2 -O2	72.9(3) 180.0(3) 107.1(3)	O2- Cu1- O2	177.9(5)	(Li/Ru)1 -O1- (Li/Ru)2	95.6(3)
O1- (Li/Ru)1 -O2	87.9(4) 101.1(3) 175.3(4) 97.3(4)	O1- (Li/Ru)2 -O2	83.5(3) 96.5(3)				

References

- M. Gao, Y.- L. Gu, L. Li, Z.- L. Gong, X.- Y. Gao, W. Wen, J. Appl. Crystallogr., 2016, 49, 1182-1189.
- T.-Y. Yang, W. Wen, G.-Z. Yin, X.-L. Li, M. Gao, Y.-L. Gu, L. Li, Y. Liu, H. Lin, X.-M. Zhang, B. Zhao, T.-K. Liu, Y.-G. Yang, Z. Li, X.-T. Zhou, X.-Y. Gao, Nucl. Sci. Tech., 2015, 26, 020101.
- 3. A. Coelho, J. Appl. Crystallogr., 2003, **36**, 86-95.
- 4. J.-G. Cheng, Rev. Sci. Instrum. , 2014, **85**, 093907
- 5. J.-G. Cheng, Chin. Phys. B 2018, **27**, 077403.
- 6. J. H. Roudebush, K. A. Ross and R. J. Cava, Dalton Trans., 2016, **45**, 8783-8789.
- M. Abramchuk, C. Ozsoy-Keskinbora, J. W. Krizan, K. R. Metz, D. C. Bell and F. Tafti, J. Am. Chem. Soc., 2017, **139**, 15371-15376.
- Y. S. Choi, C. H. Lee, S. Lee, S. Yoon, W. J. Lee, J. Park, A. Ali, Y. Singh, J.-C. Orain, G. Kim, J.-S. Rhyee, W.-T. Chen, F. Chou and K.-Y. Choi, Phys. Rev. Lett., 2019, 122, 167202.
- Z. Deng, M. Retuerto, S. Liu, M. Croft, P. W. Stephens, S. Calder, W. Li, B. Chen,
 C. Jin, Z. Hu, M.-R. Li, H.-J. Lin, T.-S. Chan, C.-T. Chen, S. W. Kim and M.
 Greenblatt, Chem. Mater., 2018, **30**, 7047-7054.

- M. Croft, D. Sills, M. Greenblatt, C. Lee, S. W. Cheong, K. V. Ramanujachary and D. Tran, Phys. Rev. B, 1997, 55, 8726-8732.
- 11. J. M. Tranquada, S. M. Heald, A. R. Moodenbaugh, G. Liang,; M. Croft, Nature, 1989, **337**, 720.
- 12. J. M. Zuo, M. Kim, O'Keeffe, M. Amp and J. C. H. Spence, Nature, 1999, **401**, 49-52.
- 13. S. Asbrink and A. Waskowska, J. Phys. Condens. Matter, 1991, **3**, 8173.
- R. O. Bune, M. V. Lobanov, G. Popov, M. Greenblatt, C. E. Botez, P. W. Stephens, M. Croft, J. Hadermann and G. Van Tendeloo, Chem. Mater., 2006, 18, 2611-2617.
- 15. Z. Zeng, I. D. Fawcett, M. Greenblatt and M. Croft, Mater. Res. Bull., 2001, **36**, 705-715.
- 16. G. M. Veith, M. Greenblatt, M. Croft and J. B. Goodenough, Mater. Res. Bull., 2001, **36**, 1521-1530.
- 17. K. V. Ramanujachary, S. E. Lofland, W. H. McCarroll, T. J. Emge, M. Greenblatt and M. Croft, J. Solid State Chem., 2002, **164**, 60-70.
- G. M. Veith, M. Greenblatt, M. Croft, K. V. Ramanujachary, J. Hattrick-Simpers, S. E. Lofland and I. Nowik, Chem. Mater., 2005, 17, 2562-2567.
- L. W. Whaley, M. V. Lobanov, D. Sheptyakov, M. Croft, K. V. Ramanujachary, S. Lofland, P. W. Stephens, J.-H. Her, G. Van Tendeloo, M. Rossell and M. Greenblatt, Chem. Mater., 2006, 18, 3448-3457.
- M. Retuerto, M. R. Li, Y. B. Go, A. Ignatov, M. Croft, K. V. Ramanujachary, J. Hadermann, J. P. Hodges, R. H. Herber, I. Nowik and M. Greenblatt, Inorg. Chem., 2012, 51, 12273-12280.
- M.-R. Li, D. Walker, M. Retuerto, T. Sarkar, J. Hadermann, P. W. Stephens, M. Croft, A. Ignatov, C. P. Grams, J. Hemberger, I. Nowik, P. S. Halasyamani, T. T. Tran, S. Mukherjee, T. S. Dasgupta and M. Greenblatt, Angew. Chem. Int. Ed., 2013, 52, 8406-8410.
- 22. T. Yang, T. Perkisas, J. Hadermann, M. Croft, A. Ignatov and M. Greenblatt, J. Solid State Chem., 2010, **183**, 2689-2694.