Local Structural Evidence for Strong Electronic Correlations in LiRh$_2$O$_4$ Spinel

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The local structure of the spinel LiRh$_2$O$_4$ has been studied using atomic pair distribution function (PDF) analysis of powder x-ray diffraction data. This measurement is sensitive to the presence of short Rh-Rh bonds that form due to dimerization of Rh$^{4+}$ ions on the pyrochlore sublattice, independent of the existence of long range order. We show that structural dimers exist in the low-temperature phase, as previously supposed, with a bond shortening of $\Delta r \sim 0.15$ Å. The dimers persist up to 350 K, well above the insulator-metal transition, with $\Delta r$ decreasing in magnitude on warming. Such behavior is inconsistent with the Fermi surface nesting-driven Peierls transition model. Instead, we argue that LiRh$_2$O$_4$ should properly be described as a strongly correlated system.

The interplay of charge, spin, orbital and lattice degrees of freedom driven by electron correlation is a unifying principle across a wide range of transition metal systems [1–3]. Such a picture provides the framework of understanding needed when one-electron physics is inadequate. In this paper we argue, based on structural principles, that the spinel LiRh$_2$O$_4$, whose coupled spin, charge, and lattice behaviors have been understood in terms of single particle physics (band Jahn-Teller transition and charge density wave (CDW) formation [4]), is better described as a strongly correlated system.

LiRh$_2$O$_4$, discovered in 2008 [4], belongs to a class of spinels described by the common formula AB$_2$X$_4$. Like LiRh$_2$O$_4$ these systems often exhibit interesting phenomena such as spin frustration, charge, spin and orbital ordering and metal insulator transitions (MIT) [5–14]. For example, spinels with Ti or Ir on the B site undergo a symmetry lowering phase transition from a high-temperature metallic phase into a low temperature insulating symmetry lowering phase transition from a high temperature (HTC) phase to an intermediate temperature tetragonal (ITT) phase [16]. The electron filling of the orbitals oriented along different crystallographic directions. At $T_{c1} = 170$ K a second transition occurs into a low temperature orthorhombic (LTO) phase. This state is insulating with, presumably, a CDW along the chains. In related materials the CDW is seen in average [8] and local [17] structural measurements as a very strong metallic B-B bond, although it has not been experimentally established in LiRh$_2$O$_4$ before this work.

The nominal charge of Rh in LiRh$_2$O$_4$ is 3.5+, implying that, on average, there are 5.5 electrons in the $t_{2g}$ manifold since the $e_g$ levels are at higher energy and unpopulated. If the charge were distributed evenly there would be 0.5 holes per Rh atom shared among the $t_{2g}$ levels (Fig. 1 (b)(i)). Charge can disproportionate between the available orbitals in two distinct ways. First, it can separate between the three $t_{2g}$ orbitals, $d_{xy}$, $d_{yz}$ and $d_{xz}$, on a single atomic site (sub-band disproportionation -
cation, Fig. 1 (b)(ii)). Second, the charge may distribute itself unevenly between atoms along the chain directions, forming a CDW, regardless of the partitioning of charge between orbitals on an individual atom (Fig. 1 (b)(iii)). In this paper we will use CDW, dimerization and short-bond interchangeably to describe this since they highlight different aspects of the same phenomenon. In the extreme case this would result in 3+ and 4+ Rh ions along the chain [4]. The LTO structure in LiRh$_2$O$_4$ has not been solved, but in a similar system, CuIr$_2$S$_4$, the pattern of charge is nominally -(3+)-(3+)-(4+)-(4+)- [18] with the 4+ ions dimerizing.

The main result of this work is the observation of short Rh-Rh distances over a wide temperature range, which includes all three structural phases. This means that in LiRh$_2$O$_4$ the dimers are confirmed to exist at low temperature, but also well above the LTO insulating state. Thus, the ITT to LTO transition may be thought of as a crystallization of dimers from a liquid formed at higher temperatures in the metallic phase. We argue that, taken together, all the experimental data are at odds with the existing understanding [15] where the phase transitions in AB$_2$X$_4$ systems are explained by the Peierls mechanism driven by Fermi surface effects.

LiRh$_2$O$_4$ was synthesized using a solid state reaction under high pressure oxygen. High purity Rh$_2$O$_3$ was mixed with a 10 weight-percent excess of Li$_2$O$_2$. The mixed powders were fired at 900 °C for 20 hours under an oxygen pressure of 0.6 MPa. The resulting powder was found to be single phase by laboratory x-ray diffraction. DC susceptibility data were measured on cooling in a 1 T field using a Quantum Design PPMS. Resistivity was measured using a standard four-terminal technique.

X-ray total scattering data were collected at the X17A beam line (beam energy 67.42 keV) of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory (BNL) in the 80-500 K temperature range using standard protocols [17, 19, 20]. Experimental PDFs of LiRh$_2$O$_4$ were obtained by Fourier transforming the reduced total scattering structure function, $F(Q)$, over a broad range of momentum transfer, $Q$ ($Q_{max} = 28$ Å$^{-1}$).

Lattice parameters were obtained using a Le Bail fit to the diffraction data using GSAS [21], utilizing Fd3m (HTC), $\Gamma 41 amd$ (ITT), and Fmmm (LTO) models from the literature [4]. Structural refinement of PDF data was carried out using PDFgui [22].

Our sample exhibits resistivity, magnetic susceptibility and average structural changes (shown in Fig. 2) consistent with earlier reports [4]. The structural phase transitions are clearly observed, with corresponding changes in resistivity and magnetization.

Despite the lack of a low temperature crystallographic model, evidence of a dimerized state can be immediately seen by comparing high and low temperature experimental LiRh$_2$O$_4$ PDFs in the low-$r$ regime. Figure 3 (a) shows the low-$r$ region of the LiRh$_2$O$_4$ PDF in the LTO and HTC phases along with a difference curve. Since the atomic number of Rh is significantly larger than those of Li and O, the PDF intensity in this region is dominated by Rh-O (2.0 Å peak) and Rh-Rh (3.0 Å peak) atomic pair correlations. In the average HTC model there is only one near-neighbor Rh-Rh distance, corresponding to the sharp PDF peak at 3.0 Å, whereas in the LTO phase the orthorhombic distortion splits the near-neighbor Rh-Rh distance into three average distances, the shortest of which is $\sim$ 2.95 Å. However, an additional contribution to the PDF clearly appears at $\sim$ 2.7 Å in the LTO phase. A similar observation has been made in CuIr$_2$S$_4$ (Fig. 3 (b)) where the presence of dimers in the low-temperature phase is well established [8, 17]. The formation of dimers along 1D chains is characterized by the redistribution of PDF intensity into short (dimerized) and long (non-dimerized) bonds.

![FIG. 2. (Color online) (a) Temperature dependence of LiRh$_2$O$_4$ resistivity (red) and magnetic susceptibility (blue). (b) Lattice parameters determined from Le Bail fit of the x-ray data. Vertical dashed lines denote structural phase transitions at 170 K (blue) and 225 K (red).](image1)

![FIG. 3. (Color online) Comparison of experimental PDFs at 240 K (red) and 160 K (blue) for (a) LiRh$_2$O$_4$ and (b) CuIr$_2$S$_4$. Difference curves (green) are offset for clarity. Dotted lines indicate $r$-position of short (dimerized) and long (undimerized) peaks. $\Delta r$, defined as half the distance between the long and short bonds, is used as a measure of the distortion associated with dimerization.](image2)
bond peaks. This redistribution of intensity emerges in Fig. 3 as a signature M-shape in the difference curve. In CuIr$_2$S$_4$ dimerization occurs along the shorter of two inequivalent Ir chains, which contains the active electronic orbitals that are available for dimerization [8]. Similarly, in LiRh$_2$O$_4$ dimerization is expected to occur along the shortest of three Rh chains [4]. Thus, in both systems the loss of PDF intensity occurs at the leading edge of the Rh-Rh (Ir-Ir) peak at ~3.0 Å (~3.5 Å). The associated structural distortion, $\Delta r$, is ~0.15 Å in LiRh$_2$O$_4$ and ~0.45 Å in CuIr$_2$S$_4$. This unambiguously establishes the presence of dimers in the LTO phase of LiRh$_2$O$_4$, experimentally confirming prior speculation based on anomalies in transport and susceptibility and by analogy with CuIr$_2$S$_4$ [23, 24].

We now turn our attention to the temperature evolution of the Rh-dimers, which is observable in the raw data. Figure 4 (a) shows the temperature evolution of the radial distribution function (RDF), $R(r)$, a related form of $G(r)$ [20]; $R(r)dr$ represents the number of bonds with lengths between $r$ and $r+dr$. While the region surrounding the peak at 2 Å is largely unchanged, a significant redistribution of PDF intensity occurs in the 2.5 - 3.25 Å range with increasing temperature. It is clear from a careful examination of the inset to Fig. 4(a) that this redistribution does not occur abruptly at $T_d$. Rather, the short bond lengthens slightly on warming from 160 K to 170 K. Then, as the sample is heated through the ITT phase and into the HTC phase intensity is gradually transferred from the 2.7 Å region to the leading edge of the large peak at 3 Å. This implies that the dimer does not disappear at the LTO to ITT phase transition. Rather, it survives into the ITT and HTC phases with gradually diminishing intensity.

The temperature evolution of the dimers is further quantified by tracking the peak position and integrated intensity of the relevant $R(r)$ features. The size of the distortion associated with the dimer formation, $\Delta r$ (see Fig. 3), is determined by subtracting a reference RDF at 500 K from all measured RDFs and analyzing the resulting difference curves. As evident from Fig. 4 (b) $\Delta r$ is nearly constant as the sample is heated through the LTO phase. Then, it changes rapidly in the 160 - 170 K range, decreasing from ~ 0.146 to 0.14 Å as the LTO/ITT phase transition is approached. As temperature is further increased through the ITT phase $\Delta r$ changes smoothly, gradually decreasing until it stabilizes at 0.133 Å at the ITT/HTC phase boundary.

An estimate of the number of dimers present in the sample is obtained by following the integrated intensity of the short-bond peak in the RDF difference curve. As shown in Fig. 4(c) the dimer fraction is relatively stable through the LTO phase. A rapid drop is observed between 160 and 170 K. Notably, the dimer fraction does not drop to zero at $T_d$, but decreases gradually through the ITT phase. It survives even into the HTC phase, disappearing at ~350 K.

Further confirmation of our results is obtained by model dependent analysis of the LiRh$_2$O$_4$ PDFs. Fig. 5 (a) shows a best-fit of the ITT model to the LiRh$_2$O$_4$ PDF at 200 K in the 1.5 Å to 20 Å range. The fit is poor throughout the entire refinement range, but significantly poorer in the shaded region below 5 Å, as evident from the difference curve. However, this should not come as a surprise if dimers exist in the ITT phase; the $i41am$ model does not allow for the presence of a nearest neighbor Rh-Rh bond that is significantly shorter than the average bond. The average tetragonal distortion obtained by Le Bail fitting results in a small splitting (less than 0.02 Å) of the nearest-neighbor Rh-Rh distance, but cannot account for the significantly shorter Rh-Rh bond that is associated with dimer formation, which corresponds to a distortion that is nearly an order of magnitude larger.

Fits of the $i41am$ structural model to experimental PDFs were carried out throughout the temperature range studied. Since the dimers cannot be accounted for by this model, their presence will result in an increase in the refinement residual, $R_w$. Assuming that the short-bond distortion is the major contributor to the poor fit,
evolution of the local dimers with temperature. The observation of the dimer signal in the PDF gives direct evidence for the presence of the CDW along the chains in all the phases, distinct from the sub-band disproportionation that leads to an overall lowering of the cubic symmetry. This is illustrated in Fig. 5(d) and contrasted with the previous view in Fig. 5(c). This behavior is different from that observed in CuIr2S4 where the dimers disappear in both the average and local structure at the MIT [17]. This view is also supported by a comparison of the specific heat and entropy of CuIr2S4 and LiRh2O4. The electronic contribution to the entropy is found to be ~2.2 Rhn2 in LiRh2O4, which is significantly larger than 0.03 Rhn2 in CuIr2S4, but comparable to Rhn2 in Fe3O4 [25] (see Supplementary Material). This difference may be explained by electron correlation effects in LiRh2O4, which are not present in CuIr2S4.

Additionally, an explanation for the different behavior of the magnetic susceptibility, $\chi$, in LiRh2O4 as compared to CuIr2S4 may reside in our PDF data. In the HTC phase of LiRh2O4 the sample contains few dimers and a balance of itinerant spins; thus it is weakly metallic and $\chi$ is roughly constant with decreasing $T$. At the HTC to ITT phase transition, the spins localize, but many are initially unpaired, resulting in a slight upturn in $\chi$. Then, on cooling through the ITT phase, dimers gradually freeze out. However, significant undimerized Rh$^{4+}$ ions remain (as evidenced by the dimer fraction plotted in Fig. 4(c)), which contribute to the paramagnetic response and overcome the decrease in $\chi$ due to dimer formation from the other Rh$^{4+}$ ions, thus leading to the observed increase in $\chi$. This coexistence of dimerized and undimerized Rh$^{4+}$ ions in LiRh2O4 is consistent with the presence of significant electron correlations leading to frustration in this system.

Our results point to an interesting aspect of the pyrochlore sublattice, namely the corner shared $B_4$ tetrahedra consisting of intersecting quasi-1D chains of B-ions (Fig. 1(a)). This sublattice plays host to a competition between one-dimensional (1D) and three-dimensional (3D) physics. In a more metallic spinel, such as CuIr2S4 the system can lower its dimensionality through orbital ordering along the chains of B-ions resulting in a 1D chain that is unstable to the formation of a CDW. On the other hand, in a less metallic spinel, such as Fe3O4, the physics is driven by the geometric frustration of ordering different partial charges ($\pm \delta$) on the vertices of the 3D network of tetrahedra [26–29]. LiRh2O4 lies between these extremes, where the effects of inter-site coulomb interaction and kinetic energy are more comparable, resulting in a competition that leads to the unusual behavior observed in this material.

$R_w$, which is a sensitive measure of the goodness-of-fit, can be used to track this distortion. Figure 5(b) shows $R_w(T)$ over the entire temperature range. As expected from the inadequacy of the $\text{I41amd}$ model to describe the low temperature state, its value is high in the LTO phase. After an abrupt drop upon crossing into the ITT phase, $R_w$ remains unusually large and decreasing with $T$ throughout the ITT phase, consistent with the observations that the local structure is not explained by the average crystallographic model. While reaching reasonably small values in the HTC phase, $R_w(T)$ exhibits a sudden change in slope at $\sim$350 K (Fig. 5(b)), reminiscent of the dimer fraction shown in Fig. 4(c). Notably, both $R_w(T)$ and the dimer fraction (Fig. 4(c)) resemble $\rho(T)$ (Fig. 2(a)), suggesting that the transport behavior is marked by the evolution of the dimers. The presence of a dimer bond and its temperature evolution is also seen in the atomic displacement parameter of Rh, and further confirmed through a model independent Gaussian fitting of the PDF data (see Supplementary Material).

These results indicate a complicated and unexpected
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Local Structural Evidence for Strong Electronic Correlations in LiRh$_2$O$_4$ Spinel - Supplementary Material

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100 200 300 400
T (K)
0.004
0.005
0.006
0.007

FIG. 1. (Color online) (a) Temperature dependence of the isotropic atomic displacement parameter (ADP), $U_{iso}$, of Rh obtained from the ı41amd model. The black dashed line represents a fit of the Debye model to the high temperature end of the ADP T-dependence. (b) Differential ADP, $\Delta U_{iso}$, obtained from data shown in (a) by subtracting the Debye curve values from the refined ADPs at all temperatures. Vertical dashed lines mark the phase transitions discussed in the Main Article.

ı41amd modeling

As described in the Main Article, fits of the ı41amd structural model to LiRh$_2$O$_4$ PDFs were carried out throughout the temperature range studied. Since this model does not allow for short Rh-dimer distances, the presence of dimers is indirectly evidenced through anomalously high values of the refinement residual, $R_w$. Another sensitive measure of the presence of dimers is the isotropic atomic displacement parameter associated with the Rh crystallographic site. This is shown in Fig. 1(a). The canonical temperature dependence of ADPs in materials on cooling is their gradual decrease with decreasing temperature, reflecting the decrease in thermal-motion. However, this trend is not observed in the Rh-ADP obtained from our structural refinement; instead, the Rh-ADP is seen to increase with decreasing temperature in the ITT and LTO phases, indicating that the ı41amd model is inadequate to describe these phases. Additionally, although the refined Rh-ADP decreases on cooling through the HTC phase, it deviates from canonical Debye behavior (see Eqn. 1) between 300 and 350 K. This behavior reflects the inability of the ı41amd model to properly account for the structural features in the data, and the values of Rh-ADP become anomalously high in the model’s effort to provide the best fit.

The temperature dependence of ADPs is often described by a Debye-type model as:

$$U^2(T) = \frac{3h^2}{4\pi^2mk_B\Theta_D} \left( \frac{\Phi(\Theta_D/T)}{\Theta_D/T} + \frac{1}{4} \right) + U_0^2,$$

where

$$\Phi(x) = \frac{1}{x} \int_0^x \frac{x'dx'}{e^{x'} - 1}.$$ 

Any deviation from this behavior is typically ascribed either to overall inadequacy of the structural model or to the presence of nanoscale features that deviate from the average structure. Thus, the presence of dimers that are not long range ordered and, hence, unaccounted for by the average structural model, would result in anomalous behavior of the associated ADP. The dashed black line in Fig. 1(a) represents a fit of the Debye-model to the high temperature tail of the Rh $U_{iso}(T)$ curve. As can be seen in the figure, the fit is reasonable at high temperature. However, the data deviate from the canonical behavior described by the model while the sample is still in the HTC phase. In Fig. 1(b) we show the difference between the ADP data and the high temperature Debye fit. Again, the characteristic curve shows up, reminiscent of $\rho(T)$, $R_w(T)$, and the dimer fraction temperature dependence shown in the Main Article.
To confirm the temperature evolution of the short Rh-dimer bond, a structural model independent assessment of the experimental PDFs was performed; the low-r portion of the LiRh$_2$O$_4$ PDFs were fit with Gaussians convolved with Sinc functions to account for termination effects [1]. The Gaussians were used to fit the range from 1.5 Å to 3.5 Å to account for the peaks at 2.0 Å and 3.0 Å (inset to Fig. 2(a)). The short bond peak associated with dimerization was intentionally left out of this model, and any unaccounted PDF intensity (such as from the Rh-dimer peak) shows up in the difference curve. In this way, the evolution of the dimer peak may be followed directly by plotting the difference curve obtained by subtracting the best fit of the 2-Gaussian model from the data. A representative fit to the 80 K PDF profile is shown in Fig. 2(a), with the unaccounted dimer peak in the difference curve marked with arrow. The temperature evolution of this difference curve is shown in panel (b). As the sample is warmed through the LTO phase, it is clear that the short bond peak is roughly constant in both position and intensity until 160 K at which point it rapidly moves towards higher r in advance of the phase transition at 170 K. The peak then persists through the ITT phase and well into the HTC phase with gradually diminishing intensity.

Gaussian modeling

Fig. 3(a) compares the specific heat, $C$, of LiRh$_2$O$_4$ (obtained from Ref. [2]) with that of CuIr$_2$S$_4$ (obtained from Ref. [3]). Both are expressed as functions of the renormalized temperature, $T/\Theta_D$, where $\Theta_D$ was obtained by fitting the data over the whole temperature range from 0 to 300 K with the Debye specific heat expression

$$C = 9N\rho \left( \frac{T}{\Theta_D} \right)^3 \int_0^{\Theta_D/T} \frac{x^4e^x}{(e^x - 1)^2} dx \quad (3)$$

The fitted Debye temperatures are $\Theta_D = 420$ K for CuIr$_2$S$_4$ and 672 K for LiRh$_2$O$_4$. The larger value of $\Theta_D$ for LiRh$_2$O$_4$ can be ascribed to the smaller atomic masses of Li, Rh, and O as compared to Cu, Ir, and S, respectively.

It is clear that, after scaling, the $C$ curves of LiRh$_2$O$_4$ and CuIr$_2$S$_4$ differ only at the peaks around the transition temperatures. This indicates that the phonon contributions to the specific heat of these materials are rather similar. Additionally, their values at 300 K are close to $3N\rho = 174.6$ J mol$^{-1}$ K$^{-1}$ where $N = 7$ (the number of atoms in the chemical formula) and $\rho = 8.314$ J mol$^{-1}$ K$^{-1}$ (the universal gas constant), which indicates that phonon contributions dominate $C$ in this temperature regime. Indeed, it is clear that both curves closely follow the Debye model away from the transition temperatures.

Since $C$ only deviates substantially from the Debye curve near the transition temperatures, it is straightforward to confirm the temperature evolution of the short Rh-dimer bond, a structural model independent assessment of the experimental PDFs was performed; the low-r portion of the LiRh$_2$O$_4$ PDFs were fit with Gaussians convolved with Sinc functions to account for termination effects [1]. The Gaussians were used to fit the range from 1.5 Å to 3.5 Å to account for the peaks at 2.0 Å and 3.0 Å (inset to Fig. 2(a)). The short bond peak associated with dimerization was intentionally left out of this model, and any unaccounted PDF intensity (such as from the Rh-dimer peak) shows up in the difference curve. In this way, the evolution of the dimer peak may be followed directly by plotting the difference curve obtained by subtracting the best fit of the 2-Gaussian model from the data. A representative fit to the 80 K PDF profile is shown in Fig. 2(a), with the unaccounted dimer peak in the difference curve marked with arrow. The temperature evolution of this difference curve is shown in panel (b). As the sample is warmed through the LTO phase, it is clear that the short bond peak is roughly constant in both position and intensity until 160 K at which point it rapidly moves towards higher r in advance of the phase transition at 170 K. The peak then persists through the ITT phase and well into the HTC phase with gradually diminishing intensity.

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Specific Heat Analysis

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$$C = 9N\rho \left( \frac{T}{\Theta_D} \right)^3 \int_0^{\Theta_D/T} \frac{x^4e^x}{(e^x - 1)^2} dx \quad (3)$$

The fitted Debye temperatures are $\Theta_D = 420$ K for CuIr$_2$S$_4$ and 672 K for LiRh$_2$O$_4$. The larger value of $\Theta_D$ for LiRh$_2$O$_4$ can be ascribed to the smaller atomic masses of Li, Rh, and O as compared to Cu, Ir, and S, respectively.

It is clear that, after scaling, the $C$ curves of LiRh$_2$O$_4$ and CuIr$_2$S$_4$ differ only at the peaks around the transition temperatures. This indicates that the phonon contributions to the specific heat of these materials are rather similar. Additionally, their values at 300 K are close to $3N\rho = 174.6$ J mol$^{-1}$ K$^{-1}$ where $N = 7$ (the number of atoms in the chemical formula) and $\rho = 8.314$ J mol$^{-1}$ K$^{-1}$ (the universal gas constant), which indicates that phonon contributions dominate $C$ in this temperature regime. Indeed, it is clear that both curves closely follow the Debye model away from the transition temperatures.

Since $C$ only deviates substantially from the Debye curve near the transition temperatures, it is straightfor-
ward to extract the electronic contributions. This was done by subtracting a linear background from the peaks near the transition temperatures as shown in Fig. 3(b). Figs. 3(c) and (d) compare $\Delta C/T$ and the electronic contribution to the entropy, $\Delta S(T) = \int_0^T \Delta C/TdT$, respectively. Integrating $C/T$ for these peaks shows a significantly larger entropy increase for LiRh$_2$O$_4$ than for CuIr$_2$S$_4$. Since the phonon contributions have already been accounted for, this difference can only arise from contributions to the entropy from the electronic system, including the charge, spin, and orbital degrees of freedom.

It is useful to express the entropy change in the familiar units of $R \ln 2$, which would be appropriate for a system of localized objects with spin $\frac{1}{2}$ (note that we do not wish to imply by this that LiRh$_2$O$_4$ contains localized spins) and is also the value of the entropy change of the Verwey transition in Fe$_3$O$_4$. The entropy associated with the transition in CuIr$_2$S$_4$ is 0.03 $R \ln 2$, confirming its weakly correlated nature. However, the corresponding entropy change in LiRh$_2$O$_4$ is about $R \ln 2$ for the low-T transition and an additional $R \ln 2$ for the high-T transition. This large electronic entropy indicates the existence of many degenerate states above the transition, a hallmark of strong electron correlation. Although the origin of this large entropy is unclear at this moment (and calls for further theoretical and experimental investigation), it is reasonable to conclude that LiRh$_2$O$_4$ and CuIr$_2$S$_4$ belong to two different regimes in terms of electron correlation.

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