Band Jahn-Teller Instability and Formation of Valence Bond Solid in a Mixed-Valent Spinel Oxide LiRh$_2$O$_4$

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We have synthesized a new spinel oxide LiRh$_2$O$_4$ with a mixed-valent configuration of Rh$^{3+}$ and Rh$^{4+}$. At room temperature it is a paramagnetic metal, but on cooling, a metal-insulator transition occurs and a valence bond solid state is formed below 170 K. We argue that the formation of valence bond solid is promoted by a band Jahn-Teller transition at 230 K and the resultant confinement of $t_{2g}$ holes within the $xy$ band. The band Jahn-Teller instability is also responsible for the observed enhanced thermoelectric power in the orbital disordered phase above 230 K.

Among the wide variety of structural categories of complex transition metal oxides, spinel, with chemical formula AB$_2$O$_4$, is one of the most common structures and provides a unique playground for the physics of geometrical frustration. The B-sublattice of the spinel structure consists of a three-dimensional network of tetrahedra, known as the pyrochlore lattice and can underpin strong geometrical frustration effects. When antiferromagnetically coupled spins are placed on the pyrochlore lattice, long range magnetic ordering is suppressed substantially leading to, amongst other things, quantum spin liquid behavior. In many cases, however, a nontrivial self-organized state of spins marginally emerges by means of coupling with lattice distortion and/or orbital ordering. In analogy with spins, when a spinel B-sublattice is occupied by ions with a formally half-integer valence, suppression of charge ordering and the eventual formation of a nontrivial state of charges results. Such charge frustration has attracted much interest since the discovery of Verwey ordering in the spinel Fe$_3$O$_4$ (Fe$_2$FeO$_4$) with $1 : 1$ ratio of Fe$^{2+}$ and Fe$^{3+}$ on spinel B-sublattice several decades ago, the spatial pattern of the ordering of which has been the subject of much debate.

Novel mixed-valent spinels have emerged recently, notably CuIr$_2$S$_4$, AlV$_2$O$_4$, LiV$_2$O$_4$, LiRh$_2$O$_4$ and AlV$_2$O$_4$, with nominally $1 : 1$ ratio of Ir$^{3+}$ and Ir$^{4+}$ and V$^{2+}$ and V$^{3+}$, respectively, were found commonly to show nontrivial charge ordering on cooling. In the charge ordered state, an array of spin-singlet "molecules", Ir octamer and V heptamer, were discovered, which might be viewed as a kind of valence bond solid (VBS). In LiV$_2$O$_4$ with $1 : 1$ ratio of V$^{3+}$ and V$^{4+}$, no charge or spin ordering takes place down to below 1 K resulting in a novel heavy Fermon ground state being stabilised. This may represent a charge analogue of quantum spin liquid. LiV$_2$O$_4$ was recently discovered to show a charge ordering under pressure, where a VBS state analogous to CuIr$_2$S$_4$ and AlV$_2$O$_4$ is very likely formed. The question arises whether such VBS state is common to this class of mixed-valent spinel oxides and what is the mechanism behind it.

In order to address these questions, we report the discovery and the study of a mixed-valent spinel oxide LiRh$_2$O$_4$. LiRh$_2$O$_4$ consists of $1 : 1$ ratio of low spin Rh$^{3+}$ ($S = 0$, $4d^6$) and Rh$^{4+}$ ($S = 1/2$, $4d^5$). Rh$^{4+}$ has

\[\text{FIG. 1: (color online) Powder XRD pattern of LiRh}_2\text{O}_4 \text{ at 300 K (a) and the temperature evolution of cubic 311 reflection at 250 K, 190 K and 150 K (b). The asterisks show reflections of Rh}_2\text{O}_3 \text{ impurities. (a) Reflections except for those asterisked could be indexed on the basis of the cubic spinel structure with } a = 8.458 \text{ Å. The inset shows the crystal structure of LiRh}_2\text{O}_4 \text{ in the cubic phase, spinel structure (left), and a [011] electron diffraction pattern at 100 K (right).}\]
enhancement of thermoelectric power, providing us with a useful, new strategy to develop novel thermoelectric materials.

Ceramic samples of LiRh$_2$O$_4$ were synthesized by solid-state reaction. Stoichiometric amounts of Li$_2$O$_2$ and Rh$_2$O$_3$ were mixed, and the mixture was calcined at 900°C for 24 h under 5 atm. of oxygen pressure. Sample characterization and structural analysis were performed by powder X-ray diffraction (XRD) using Cu-Kα radiation and electron diffraction. Hard X-ray photoemission spectroscopy (HAXPES) measurements with an incident photon energy of 8175 eV were performed at the beamline BL19LXU in SPring-8. $^6$Li-NMR spectra were obtained by Fast Fourier Transformation of the spin-echo signals.

The powder XRD pattern of LiRh$_2$O$_4$ at room temperature in Fig. 1 (a) was consistent with the formation of a cubic spinel structure, where all the Rh sites are equivalent. Figure 2 demonstrates the temperature dependence of various physical properties of LiRh$_2$O$_4$. The resistivity at 300 K is slightly less than 10 mΩcm and almost temperature independent down to 230 K (Fig. 2 (a)). Since the sample is sintered polycrystal, empirically, the intrinsic resistivity can be more than one order of magnitude smaller than 10 mΩcm, consistent with the metallic nature. In agreement with this, a well-defined Fermi cut-off was observed in the HAXPES spectrum at 250 K, as shown in the inset of Fig. 2 (a). The weakly temperature dependent paramagnetic susceptibility around 300 K can then be interpreted as Pauli paramagnetism (Fig. 2 (b)).

With decreasing temperature, we observed a kink-like anomaly both in the resistivity and in the magnetic susceptibility at 230 K, suggestive of the second order phase transition. The resistivity shows a very weak increase on cooling down to 170 K. As shown in the inset of Fig. 2 (a), the HAXPES spectrum at 210 K indicates the presence of a well-defined Fermi cut-off analogous to those at 250 K. It implies that in the temperature range between 170 K and 230 K the system remains poorly metallic and incoherent transport due to, for example, polaronic and/or disorder effects are likely responsible for the weakly semiconducting behavior of resistivity.

At 170 K, the resistivity shows a discontinuous jump of several orders of magnitude, suggestive of a metal-insulator transition, possibly associated with an ordering of charges (Fig. 2 (a)). Simultaneously, a clear shift in the Fermi edge by $\sim$ 0.2 eV to a higher binding energy side is observed in the HAXPES spectrum (inset of Fig. 2 (a)), indicating the opening of a charge gap with an energy scale of around a fraction of eV. The presence of a tiny but clear hysteresis between warming and cooling indicates that the transition at 170 K is first order in contrast to the transition at 230 K (inset of Fig 2 (a)). Associated with the transition, the magnetic susceptibility shows discontinuous drop to a very small and almost temperature independent susceptibility, implying the formation of a spin singlet. The nonmagnetic nature

only one hole for six-fold orbital and spin degenerate $t_{2g}$ orbitals and the coupling with these multiple degrees of freedom may give rise to a channel to lift the degeneracy of charge distribution. We found that the ground state of this compound is a charge-ordered VBS triggered by a band Jahn-Teller transition. This strongly suggests that orbital physics drives the VBS formation. In the non-Jahn-Teller phase at high temperatures, the proximity to the Jahn-Teller instability manifests itself as a drastic
that very robust singlet bonds are formed in the insulating phase below $T_{MI} = 170$ K. Electron diffraction and the synchrotron XRD pattern indicate that the new spots emerge at $(2l + 1, 2m, 2n)$ and $(2l, 2m + 1, 2n + 1)$, implying that the propagation vector of modulation $k = (1, 0, 0)$. $k$ of LiRh$_2$O$_4$ is distinct from those of CuIr$_2$S$_4$ ($k = (0, 0, 1), (1/2, 1/2, 1/2)$) and AlV$_2$O$_4$ ($k = (1/2, 1/2, 1/2)$).

The results of specific heat measurement shown in Fig. 2 (d) suggest that the transition at 230 K is in fact a drastic electronic transition in addition to the 170 K transition. The change of entropy $\Delta S_{entropy}$ associated with the transitions, estimated from specific heat and DSC measurements, was found to be 1.0 J/KmolRh at 230 K and 2.9 J/KmolRh at 170 K, which corresponds to 0.24R/mole Rh$^{4+}$ and 0.70R/mole Rh$^{4+}$, respectively. It may not be surprising to see a large entropy change of the order of $R$ at 170 K transition associated with a charge ordering. It is surprising, however, to observe a large entropy change for the cubic to tetragonal transition. A structural phase transition alone, as would have been expected from the weak anomaly at 230 K in the resistivity and the magnetic susceptibility, is unlikely to be able to account for such a large entropy change. A drastic reconstruction of electronic states should be invoked to account for the hidden and large entropy change.

The 230 K transition can be naturally understood now in terms of a band Jahn-Teller transition. The large tetragonal distortion ($c/a_c \sim 1.04$) should split the triply degenerate $t_{2g}$ band manifold into bands with stabilized $yz$ and $zx$ character and a band with destabilized $xy$ character (Fig. 3). Then, while the $yz$ and $zx$ bands are fully occupied with 4 electrons, the $xy$ band accommodates 0.5 holes (1.5 electrons). Stabilization of the fully occupied $yz$, $zx$ bands and destabilization of the partially filled $xy$ band enables the system to gain a Jahn-Teller energy. By inspecting the band structure of transition metal oxides with a spinel structure including LiTi$_2$O$_4$, LiV$_2$O$_4$ and ZnRh$_2$O$_4$, we note that the transition metal $t_{2g}$ band commonly has relatively high density of states (DOS) near the top of the band manifold into bands with stabilized $xy$, $yz$ and $zx$ character (Fig. 3). Then, while the $yz$ and $zx$ bands are fully occupied with 4 electrons, the $xy$ band accommodates 0.5 holes (1.5 electrons). Stabilization of the fully occupied $yz$, $zx$ bands and destabilization of the partially filled $xy$ band enables the system to gain a Jahn-Teller energy. By inspecting the band structure of transition metal oxides with a spinel structure including LiTi$_2$O$_4$, LiV$_2$O$_4$ and ZnRh$_2$O$_4$, we note that the transition metal $t_{2g}$ band commonly has relatively high density of states (DOS) near the top of the band manifold, which arises from bands with flat dispersion produced by geometrical frustration [15-18]. Recent band calculation indicated that the same is true for LiRh$_2$O$_4$ F. Since the Fermi level $E_F$ should be located near the top of $t_{2g}$ manifold in LiRh$_2$O$_4$, a relatively high DOS at $E_F$ can be anticipated. Such high DOS can couple with the degenerate orbital degrees of freedom, leading to a band Jahn-Teller instability. The large entropy change observed at 230 K then should be ascribed to the lifting of the band degeneracy through orbital ordering.

The high entropic state with band Jahn-Teller instability realized in the cubic phase can merit enhancing the thermoelectric power $S$. The presence of a flat band near $E_F$ can drastically enhance $S$, as pointed out for the
well known thermoelectric Na$_2$CoO$_2$ [20] [21]. LiRh$_2$O$_4$ indeed indicates a large and positive $S$ above 230 K, as large as 80 $\mu$V/K at 800 K, where the system remains orbitally degenerate (Fig. 2 (c)). Below the band Jahn-Teller transition at 230 K where the orbital degeneracy is lifted, $S$ rapidly decreases by $\sim$ 20 $\mu$V/K. Assuming that $S$ is simply entropy per charge carrier $S_{\text{entropy}}/ne$, the large entropy change $\Delta S_{\text{entropy}} \sim 1.0$ J/KmolRh at the 230 K transition, estimated from the specific heat anomaly, gives an enhancement of thermoelectric power $\Delta S = 21$ $\mu$V/K in the cubic (orbital disordered) phase, as compared with the tetragonal (orbital ordered) phase. This agrees well with the observed change of thermoelectric power $\Delta S \sim 20$ $\mu$V/K, implying that the large entropy change at the cubic to tetragonal transition indeed represents an “electronic” reconstruction of degenerate bands and manifests itself as an enhanced $S$ in the cubic orbital-disordered phase.

Below 230 K, the conduction should be dominated by the carriers (0.5 holes) in the band primary with $xy$ character. Since the $xy$ orbitals overlap strongly along the edge of Rh-tetrahedron perpendicular to the $c$-axis, [110] and [110], the $xy$ band should be more dispersive along these directions and quasi-one-dimensional in nature (Fig. 3). The confinement of Rh$^{4+}$ holes within the quasi-one-dimensional $xy$-band, associated with the band Jahn-Teller transition, very likely promotes the formation of VBS despite the presence of charge frustration. This picture is essentially nothing but the “orbital induced Peierls” transition proposed by Khomskii and Mizokawa as a model for the VBS formation in CuIr$_2$S$_4$ [22]. CuIr$_2$S$_4$ is isoelectronic to LiRh$_2$O$_4$ but shows only one transition from a paramagnetic metal to a spin-singlet insulator [5]. The lattice distortion in the insulating phase was decomposed by Khomskii and Mizokawa into Jahn-Teller like elongation of $c$-axis ($c/a \sim 1.03$) and tetramer formation within the [110] or [110] chain and they argued that the transition is essentially a Peierls transition within the one-dimensional $xy$ band [22]. The occurrence of a band Jahn-Teller transition in LiRh$_2$O$_4$ at higher temperature than the charge ordering transition clearly indicates that there is an intrinsic band instability in the 0.5 hole doped $t_{2g}$ system on a frustrated pyrochlore lattice, and sets up the possibility of formation of VBS. This implies that the band Jahn-Teller instability, rather than the instability for spin-singlet bond formation, is the driving force for the suppression of charge frustration in this system. In accord with this, although the Jahn-Teller distortion presents as a common ingredient of lattice distortion in the insulating state of LiRh$_2$O$_4$ and CuIr$_2$S$_4$, the overall lattice distortion pattern representing the charge ordering is clearly different between the two, implying the ordering pattern is determined reflecting materials-dependent details.

In conclusion, a new mixed-valent spinel oxide LiRh$_2$O$_4$ was synthesized, which provides us with an intriguing playground for the physics of charge-orbital-spin composites on geometrically frustrated lattices. A novel interplay of the orbital degeneracy of $t_{2g}$ manifold and the high electronic density of states, linked to the unique geometry of the pyrochlore lattice, gives rise to a band Jahn-Teller instability in this 0.5 hole-doped system. This drives the system to a transition from an orbital-disordered metal to an orbital-ordered metal at 230 K. The large electronic entropy in the orbital disordered phase manifests itself as a remarkable enhancement of thermoelectric power, compared with the orbital-ordered metal. Materials displaying a band Jahn-Teller instability could be a good strategy to develop high performance thermoelectric materials. A charge-ordered VBS state is formed below 170 K. The formation of VBS is apparently driven by the band Jahn-Teller transition, which confines the holes within the quasi-one-dimensional $xy$ band. Such a charge ordering induced by an orbital ordering appears to be quite ubiquitous to this class of charge frustrated mixed-valent systems.

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Supplementary information.

Comment on the crystal structure of the charge-ordered insulating phase. Below 170 K, LiRh$_2$O$_4$ shows complicated lattice distortion due to the dimerization of Rh$^{4+}$. We are able to index the X-ray diffraction pattern at 100 K with an orthorhombic unit cell. Since some peaks originating from the orthorhombic phase, however, show a noticeable broadening, there might be a further lowering of symmetry. The superlattice spots including 100 and 011 in fact appear in a [011] electron diffraction pattern. We determined a reciprocal lattice of the orthorhombic phase as shown in the supplementary figure (a), by combining it with the electron diffraction patterns along some other directions and the synchrotron X-ray diffraction pattern. This reciprocal lattice indicates that the propagation vector of modulation is $\mathbf{k} = (1, 0, 0)$. On the other hand, Rh$^{4+}$-Rh$^{4+}$ dimers are likely formed in the $xy$ plane, because the $xy$ band is preferentially occupied by 0.5 holes in the tetragonal phase, which is also supported by the lattice distortion and Ir$^{4+}$-Ir$^{4+}$ dimerization pattern in spinel sulfide CuIr$_2$S$_4$ isoelectronic to LiRh$_2$O$_4$. Considering that the charge ordering modulated by $\mathbf{k} = (1, 0, 0)$ and the Rh$^{4+}$-Rh$^{4+}$ dimerization in the $xy$ plane, the only two charge-ordering configuration models, shown in the supplementary figure (b), are allowed.
FIG. 4: Supplementary figure. (a) A schematic reciprocal lattice of the orthorhombic phase of \( \text{LiRh}_2\text{O}_4 \) determined by electron diffraction measurements (crystal axis was determined by the synchrotron X-ray powder diffr action). Blue and green spheres represent fundamental spots of the cubic spinel structure and the forbidden spots, which were observed at both 300 K of the cubic phase and at 100 K of the orthorhombic phase due to multiple reflections, respectively. Small red spheres represent new spots at \( (2l + 1, 2m, 2n) \) and \( (2l, 2m - 1, 2n - 1) \), where \( l, m \) and \( n \) are integer numbers, only observed at 100 K of the orthorhombic phase.

(b) Pictures of two charge ordering configuration models suggested by the reciprocal lattice (a) under condition that all \( \text{Rh}^{4+} \) ions form singlet bonds within the chains, represented by thick blue lines. Both models consist of Rh tetramers with an alternation of \( \text{Rh}^{4+}-\text{Rh}^{3+}-\text{Rh}^{3+}-\text{Rh}^{2+} \) along [110] or [110] Rh chain.