Almost pure \( J_{\text{eff}} = 1/2 \) Mott state of In\(_2\)Ir\(_2\)O\(_7\) in the limit of reduced inter-site hopping

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The pyrochlore iridate In\(_2\)Ir\(_2\)O\(_7\) is a strong \( J_{\text{eff}} = 1/2 \) Mott insulator with frustrated magnetism. Despite the large trigonal crystal field, a small admixture of \( J_{\text{eff}} = 3/2 \) component in the \( J_{\text{eff}} = 1/2 \) bands and a small splitting of \( J_{\text{eff}} = 3/2 \) bands are observed as compared with other pyrochlore iridates \( A_2\)Ir\(_2\)O\(_7\) (\( A: \) trivalent cation). We argue that the reduced inter-site hopping between the \( J_{\text{eff}} = 1/2 \) and the \( J_{\text{eff}} = 3/2 \) manifold plays a predominant role in the distinct behavior of In\(_2\)Ir\(_2\)O\(_7\) compared with other \( A_2\)Ir\(_2\)O\(_7\). The effect of the intersite hopping should not be dismissed in the local physics of spin-orbital-entangled \( J_{\text{eff}} = 1/2 \) Mott insulators.

Recently, transition-metal oxides containing 5\( d\) elements have been receiving attention in the search for novel electronic states generated by the interplay between moderate on-site Coulomb repulsion, \( U \sim 2 \) eV, and strong spin-orbit coupling, \( \lambda_{\text{SOC}} \sim 0.5 \) eV\(^2\) [1]. Complex iridium oxides have been studied both experimentally and theoretically as a platform in this pursuit due to the simple and prototypical spin-orbital-entangled ground state of Ir\(^{4+}\) cations [2]. The common building block in many of those iridium oxides is an IrO\(_6\) octahedron, where five \( d\)-electrons occupy the \( t_{2g} \) manifold. Strong spin-orbit coupling splits the \( t_{2g} \) manifold into the completely-filled lower quartet \( J_{\text{eff}} = 3/2 \) states and the half-occupied upper doublet \( J_{\text{eff}} = 1/2 \) states. \( J_{\text{eff}} = 1/2 \) states, consisting of the superposition of \( d_{xy}, d_{xz} \) and \( d_{yz} \) orbitals including complex components [3], dominate the transport and magnetic properties. A rich variety of exotic phases formed by \( J_{\text{eff}} = 1/2 \) electrons is anticipated, such as Kitaev spin liquid in honeycomb-based \( \text{A}_2\)IrO\(_3\) (\( A = \) Li, Na) [4], Dirac semimetal in the perovskite SrIrO\(_3\) [5] and Weyl semimetal in pyrochlore iridates [6].

Among the family of complex iridium oxides, the pyrochlore iridates, \( \text{A}_2\)Ir\(_2\)O\(_7\) (\( A: \) trivalent ion), have drawn attention not only because of the interplay of spin-orbit coupling with the other relevant parameters but also the frustrated Ir\(^{4+}\) sub-lattice, which is predicted to render non-trivial topological phases [6–8]. \( \text{A}_2\)Ir\(_2\)O\(_7\) crystallize in a cubic structure with space group \( \text{Fd}\overline{3}m \) and consisting of two interpenetrating pyrochlore networks of \( A \) and Ir cations. Their electronic ground state has been shown to evolve with the ionic radius of the \( A \) cation [9, 10]. The ionic size of \( A \) cations in \( \text{A}_2\)Ir\(_2\)O\(_7\) is too small to maintain the regular IrO\(_6\) octahedron and therefore the lattice distorts. The IrO\(_6\) octahedron is compressed, with a compression axis perpendicular to two opposite triangular oxygen planes (trigonal distortion), which decreases the Ir-O-Ir angle in the neighboring two IrO\(_6\) octahedra (Fig. 1(b)). The bond-bending reduces the inter-site hopping between the neighboring two Ir sites and thus controls the width of the \( t_{2g} \) bands. The smaller the ionic radius is, the smaller the bandwidth is. With the largest \( A \) cation reported so far, Pr\(_2\)Ir\(_2\)O\(_7\) is a semimetal with a quadratic band-dispersion and remains paramagnetic down to the lowest temperature [11, 12]. With decreasing \( A \) size, namely reducing the bandwidth, the system undergoes a metal-insulator transition [10] accompanied by a magnetic transition. There has been accumulating evidence that an all-in all-out (AIOO) structure of the \( J_{\text{eff}} = 1/2 \) moments is realized in the magnetically ordered phase [13, 14]. The AIOO ordered phase around the metal-insulator transition is discussed to be a Weyl-semimetal [15, 16]. With decreasing the size of \( A \) cations further to Y\(^{3+}\), the system becomes a strong insulator with Mott character. While the resistivity shows an insulating behavior up to room temperature, the magnetic transition occurs only at low temperatures.

The trigonal distortion of IrO\(_6\) octahedra has a pronounced impact not only on the bandwidth but also on the local orbital states. The trigonal distortion for an isolated regular IrO\(_6\) octahedron is known to split the \( J_{\text{eff}} = 3/2 \) quartet into two Kramers doublets and mixes up the \( J_{\text{eff}} = 1/2 \) and \( J_{\text{eff}} = 3/2 \) states [17, 18]. The \( J_{\text{eff}} = 1/2 \)-derived state in the trigonally-distorted IrO\(_6\) octahedron should have an admixture of \( J_{\text{eff}} = 3/2 \) component and cannot be described by the pure \( J_{\text{eff}} = 1/2 \) wave function. In \( \text{A}_2\)Ir\(_2\)O\(_7\) with the lattice of connected IrO\(_6\) octahedra, the inter-site hopping between the orbitals comes into play and may further modify the \( J_{\text{eff}} = 1/2 \)-derived states.

To identify how the trigonal distortion influences the \( J_{\text{eff}} = 1/2 \) state of \( \text{A}_2\)Ir\(_2\)O\(_7\) through the crystal field effect, the inter-site hopping, and the interplay between the two, we attempted to synthesize new pyrochlore iridates with a very small \( A \) cation and therefore an even larger trigonal distortion. In the process of our exploration, we discovered a new pyrochlore iridate In\(_2\)Ir\(_2\)O\(_7\) with non-magnetic In\(^{3+}\) occupying the \( A \) site. In\(^{3+}\) has the smallest \( A \)-site ionic radius (0.92 Å) among the reported \( \text{A}_2\)Ir\(_2\)O\(_7\) pyrochlores and renders the most distorted IrO\(_6\) octahedra. In\(_2\)Ir\(_2\)O\(_7\) is an insulator as expected from the strong distortion and shows antiferromagnetic ordering at \( T_m = 55 \) K. In the
resonant inelastic x-ray scattering (RIXS) spectrum, the presence of a sizable splitting of J_{eff} = 3/2 states was identified. However, despite the expected enhancement of trigonal crystal field, the magnitude of splitting of J_{eff} = 3/2 states was found to be smaller than those of other A_{2}Ir_{2}O_{7} with much more reduced trigonal distortion. The electronic structure calculations demonstrate that the J_{eff} = 1/2-derived band of In_{2}Ir_{2}O_{7} consists of the predominant J_{eff} = 1/2 wave function in contrast to the less distorted Y_{2}Ir_{2}O_{7}, again contrary to the expected enhancement of the admixture of J_{eff} = 3/2 component in the J_{eff} = 1/2-derived states. We argue that the enhanced inter-site hopping in the less trigonally-distorted A_{2}Ir_{2}O_{7} pyrochlores brings more J_{eff} = 3/2 character in the J_{eff} = 1/2-derived band and may give rise to the large splitting of J_{eff} = 3/2 band, which makes In_{2}Ir_{2}O_{7} distinct in the A_{2}Ir_{2}O_{7} family.

The polycrystalline sample of In_{2}Ir_{2}O_{7} was synthesized by a high-pressure synthesis technique [19]. The x-ray powder diffraction (XRPD) pattern of the product, shown in Fig. 1(a), indicates a high purity phase of pyrochlore In_{2}Ir_{2}O_{7}. The result of Rietveld analysis is consistent with a cubic pyrochlore structure with space group Fd3m. The refined structural parameters are listed in Table I. As expected, In_{2}Ir_{2}O_{7} has the smallest cubic lattice parameter a = 9.9884(4) Å among the pyrochlore iridates known so far. The degree of trigonal distortion in cubic pyrochlores can be parameterized by the x fractional coordinate of the O1 atom, which determines the shape of the oxygen cage surrounding iridium. x_{c} = 0.3125 corresponds to the case of a completely regular IrO_{6} octahedron. x_{c} \neq x_{c} indicates that IrO_{6} octahedron is trigonally distorted, where x > x_{c} gives trigonal compression, commonly found in pyrochlore iridates. The position of O1 also defines the Ir-O-Ir angle, which decreases (bends more) with increasing trigonal compression. x = 0.3405(5) for In_{2}Ir_{2}O_{7} (Table I) yields the largest trigonal compression and the smallest Ir-O-Ir angle of 125.8°. This implies that In_{2}Ir_{2}O_{7} has small 5d bandwidth and represents the insulating limit of the family of pyrochlore iridates.

The resistivity measurement (Fig. 2(a)) shows that In_{2}Ir_{2}O_{7} is an insulator, which is consistent with the expected small bandwidth. From the Arrhenius fit displayed in the inset of Fig. 2(a), the activation energy around 100 meV, which is comparable to those of strongly insulating Ir oxides such as Ba_{2}IrO_{4} and Li_{2}IrO_{3} [20, 21] and suggestive of a charge gap of a few 100 meV. Magnetic susceptibility M/H(T) in Fig. 2(b) shows a Curie-Weiss behavior on cooling from room temperature [22]. Since In^{3+} is non-magnetic, the magnetic response of insulating In_{2}Ir_{2}O_{7} originates from the 5d electrons of Ir^{4+}. The Curie-Weiss fit between 350 K and 600 K yields a predominant antiferromagnetic interaction of θ_{CW} = -443 K and an effective magnetic moment μ_{eff} of 1.72 μ_{B}. The effective moment is close to that of J_{eff} = 1/2 or S = 1/2 state with g = 2, which means that the admixture of J_{eff} = 3/2 and other states is not appreciably large. At a temperature T_{m} = 55 K, an anomaly accompanying a hysteresis between the field-cooling and the zero-field-cooling measurement is observed. The history-dependent contribution originates from an extremely weak ferromagnetic moment of 10^{-4} μ_{B}. In the specific heat C(T) shown in Fig. 2(c), we observe a clear jump at the onset temperature of the weak ferromagnetic moment, evidencing that the magnetic anomaly does not originate from a minor ferromagnetic phase but represents a bulk magnetic transition. Analogous behavior was observed in other pyrochlore iridates such as Y_{2}Ir_{2}O_{7}, where an AIAO-type magnetic ordering

### Table I. Refined structural parameters of In_{2}Ir_{2}O_{7} at room temperature. The space group is Fd3m : 2 (No. 227) and Z = 8. The lattice constant a is 9.9884(4) Å. g corresponds to occupancy. The isotropic displacement parameter U_{iso} converged to 0.0(1) for all atoms. The R indices are R_{wp} = 0.0562 and R_{p} = 0.0414.

| Atom | Site | x | y | z | g |
|------|------|---|---|---|---|
| In   | 16d  | 1/2 | 1/2 | 1/2 | 1 |
| Ir   | 16c  | 0  | 0  | 0  | 1 |
| O1   | 48f  | 0.3405(5) | 1/8 | 1/8 | 1 |
| O2   | 8b   | 3/8 | 3/8 | 3/8 | 1 |

![FIG. 1. (a) Powder x-ray diffraction pattern and Rietveld analysis of In_{2}Ir_{2}O_{7} polycrystalline sample at collected with Ag-Kα room temperature. The black crosses, red line and grey line represent the observed pattern, the Rietveld fit profiles and the difference curve between the observed and calculated profiles, respectively. The blue, red and black bars correspond to reflection positions of In_{2}Ir_{2}O_{7} (97.81 wt. %), IrO_{2} (1.26 wt. %) and Ir (0.93 wt. %), respectively. The inset shows the crystal structure of In_{2}Ir_{2}O_{7}, where the grey octahedra depict IrO_{6} octahedra and the purple spheres are In atoms. (b) Local structure of two corner-sharing IrO_{6} with increasing O1 x fractional coordinate, the trigonal distortion of IrO_{6} increases and the Ir-O-Ir angle decreases.](image)
L has previously played a crucial role in unveiling the local inelastic x-ray scattering (RIXS) measurement, which large trigonal lattice distortion, we performed resonant coupling than those of other insulating pyrochlore iridates such as represents the strength of exchange coupling, which is lower as expected from the frustrated pyrochlore lattice. It is reasonable to ascribe the magnetic transition at $T_m$ of iridium moments takes place at $T_m$ [23]. The extremely small magnetic moment below $T_m$ is discussed to originate from the AIAO domain boundaries [24]. It is reasonable to ascribe the magnetic transition at $T_m$ = 55 K in In$_2$Ir$_2$O$_7$ to AIAO ordering. The large ratio $f = |\theta_{\text{CW}}|/T_m \sim 8$, together with the small magnetic entropy change at $T_m$ ($\sim 5\%$ Rhn2), implies the presence of strong frustration, as expected from the frustrated pyrochlore lattice.

The Curie-Weiss temperature of $|\theta_{\text{CW}}| \sim 450$ K may represent the strength of exchange coupling, which is lower than those of other insulating pyrochlore iridates such as Y$_2$Ir$_2$O$_7$ and Lu$_2$Ir$_2$O$_7$ [19]. We argue that this reflects the smaller inter-site hopping $t$ and thus bandwidth, expected in the strongly distorted Ir-O network, since the exchange coupling $J_{xx}$ is scaled by $t^2$ as $J_{xx} \sim t^2/U$.

In order to study the orbital states in the presence of the large trigonal lattice distortion, we performed resonant inelastic x-ray scattering (RIXS) measurement, which has previously played a crucial role in unveiling the local structure of the 5d manifold in iridates [25–27]. The RIXS spectrum at the Ir $E_g$-edge of In$_2$Ir$_2$O$_7$ is presented in Fig. 3(a). In addition to the elastic peak, we observe three clear features at 0.48 eV, 0.86 eV and 4.14 eV. The two sharp peaks located at 0.48 eV and 0.86 eV correspond to excitations within the $t_{2g}$ manifold, while the broader peak at 4.14 eV corresponds to excitations from the $t_{2g}$ to the $e_g$ manifold. The split between the $t_{2g}$ and $e_g$ manifold (10Dq) is larger than those of other pyrochlore iridates reflecting the smaller Ir-O bond-length (see Table II). In the absence of distortion in an isolated IrO$_6$ octahedron, only one excitation peak from $J_{\text{eff}} = 3/2$ to $J_{\text{eff}} = 1/2$ would be observed as the excitation within $t_{2g}$ manifold. The presence of two sharp excitations in the relevant energy region implies the splitting of $J_{\text{eff}} = 3/2$ quartet into two Kramers doublets ($\phi_0$ and $\phi_2$ in Fig. 3(c)), which was observed in other pyrochlore iridates as well [18, 28, 29]. The two low-energy peaks in RIXS spectrum of In$_2$Ir$_2$O$_7$ are significantly sharper than those in other reported pyrochlore iridates, which is a signature of its narrower bandwidth as a result of the smaller Ir-O-Ir angle.

In Table II, the ionic radius of A cations $r_A$, the deviation ($\Delta x$) of the $x$ coordinate of the O1 atom from the ideal value, the energies of the two low-lying peaks $E_1$ and $E_2$ in RIXS spectrum, and $\Delta E = E_1 - E_2$ are compared for In$_2$Ir$_2$O$_7$ with Y$_2$Ir$_2$O$_7$ and Pr$_2$Ir$_2$O$_7$. The energy difference $\Delta E$ represents the splitting of $J_{\text{eff}} = 3/2$. One may naively expect that the splitting of $J_{\text{eff}} = 3/2$ states
TABLE II. Comparison of structural and electronic parameters of the pyrochlore iridates. From the second column the ionic radius of A$^{3+}$ cation, deviation of O1 $x$ fractional coordinate from the ideal value, $\Delta x = x - x_c$ ($x_c = 0.3125$), $t_{2g}$ $- e_g$ split (10Dq), lower energy and higher energy intra-$t_{2g}$ excitations $E_1$ and $E_2$, and their difference $\Delta E = E_2 - E_1$ representing the split of $J_{eff} = 3/2$ states are shown. Values for compounds marked by $\dagger$ were taken from Ref. [29] and $\ddagger$ were taken from Ref. [28].

| Compound         | $r_A$ (Å) | $\Delta x$ | 10Dq (eV) | $E_1$ (eV) | $E_2$ (eV) | $\Delta E$ (eV) |
|------------------|-----------|------------|-----------|------------|------------|----------------|
| Pr$_2$Ir$_2$O$_7$|$\uparrow$ | 1.126      | 0.0165    | 3.40       | 0.52       | 0.98          | 0.46           |
| Y$_2$Ir$_2$O$_7$ | $\ddagger$| 1.019      | 0.0228    | 3.90       | 0.53       | 0.98          | 0.45           |
| In$_2$Ir$_2$O$_7$|           | 0.92       | 0.0280    | 4.14       | 0.48       | 0.86          | 0.38           |

FIG. 4. Density of states for Ir $t_{2g}$ bands in In$_2$Ir$_2$O$_7$ (top) and Y$_2$Ir$_2$O$_7$ (bottom) resolved for $J_{3/2}$ and $J_{5/2}$ characters. We note the difference in the contribution of $J_{3/2}$ and $J_{5/2}$ states between A = In and Y at the Fermi level (black vertical line). Coulomb $U$ is not included in the calculation.

The band structure calculations for In$_2$Ir$_2$O$_7$ and Y$_2$Ir$_2$O$_7$ with different degrees of trigonal lattice distortion were conducted to estimate the degree of $J_{eff} = 1/2$-ness of the states at the Fermi level $E_F$. The density of states (DOS) of $t_{2g}$ bands of Ir 5d orbitals around $E_F$ resolved with $J = 5/2$ ($J_{5/2}$) and $J = 3/2$ ($J_{3/2}$) characters are shown in Fig. 4. Since the on-site Coulomb repulsion, $U$, is not incorporated, the calculations produce a metallic ground state for both In$_2$Ir$_2$O$_7$ and Y$_2$Ir$_2$O$_7$. The $t_{2g}$ bands are appreciably narrower for In$_2$Ir$_2$O$_7$, consistent with the reduced Ir-O-Ir hopping caused by the strong trigonal distortion.

The states near $E_F$ within $\pm 0.5$ eV is the $J_{eff} = 1/2$-derived band, while those below $-0.5$ eV is the $J_{eff} = 3/2$-derived band. The pure $J_{eff} = 1/2$ wave function comprises only the $J_{5/2}$ wave function for the full 5d orbital states while the pure $J_{eff} = 3/2$ wave function consists of mixture of $J_{5/2}$ and $J_{3/2}$ wave functions. By considering only the trigonal crystal field effect, one would expect more admixture of the $J_{eff} = 3/2$ state, namely more $J_{3/2}$, in the $J_{eff} = 1/2$ state of In$_2$Ir$_2$O$_7$ than Y$_2$Ir$_2$O$_7$ due to the enhanced trigonal distortion. However, in Fig. 4 we observed a completely opposite behavior from the naïve expectation. The state near $E_F$ of In$_2$Ir$_2$O$_7$ predominantly consists of the $J_{3/2}$ character, indicating almost pure $J_{eff} = 1/2$ character. In sharp contrast, $J_{3/2}$ contributes appreciably to the $J_{eff} = 1/2$-derived band of Y$_2$Ir$_2$O$_7$, indicative of strong admixture of the $J_{eff} = 3/2$ states with the $J_{eff} = 1/2$ in agreement with Ref. [30].

Clearly, the effect of trigonal crystal field on an isolated IrO$_6$ octahedron does not describe the contrast of orbital characters between In$_2$Ir$_2$O$_7$ and Y$_2$Ir$_2$O$_7$. Strong mixing of $J_{eff} = 1/2$ and $J_{eff} = 3/2$ states induced by the reduced trigonal lattice distortion indicates that the inter-site hopping between the $J_{eff} = 1/2$ and $J_{eff} = 3/2$ states plays a predominant role here as discussed for other iridates [31, 32] and masks the effect of the trigonal crystal field. The enhanced trigonal lattice distortion in In$_2$Ir$_2$O$_7$ on the other hand limits such inter-site mixing of $J_{eff} = 1/2$ and 3/2 states, giving rise to the unexpected realization of almost pure $J_{eff} = 1/2$ and 3/2 states.

Besides the trigonal crystal field, we find that the quantum chemistry of In$^{3+}$ ions plays a role in Ir-O-Ir hopping and reduces the bandwidth [19]. The calculation for virtual In$_2$Ir$_2$O$_7$, which was obtained by replacing the Y atoms of Y$_2$Ir$_2$O$_7$ with In atoms whilst retaining the same crystal structure, yields a small $t_{2g}$ bandwidth and enhanced $J_{eff} = 1/2$ character at $E_F$, indicating a similar electronic structure with the original In$_2$Ir$_2$O$_7$. We argue that the more covalent character of In-O bonds reduces the Ir-O hybridization and thus the $t_{2g}$ bandwidth, amplifying the effect of Ir-O-Ir bond bending.

The picture of orbital states based on the crystal field splitting for an isolated IrO$_6$ octahedron holds far better for In$_2$Ir$_2$O$_7$ than for the other pyrochlore iridates. The splitting of $J_{eff} = 3/2$-derived states in In$_2$Ir$_2$O$_7$, $\Delta E \sim 0.4$ eV observed by RXIS, is likely dominated by the trigonal crystal field. The $\Delta E \sim 0.5$ eV, which is ex-

would be dominated primarily by the trigonal crystal field splitting and would be scaled by the magnitude of the trigonal distortion parameterized by $\Delta x$. In sharp contrast to such a naïve expectation, however, we find in Fig. 3(b) that $\Delta E$ does not appreciably depend on $\Delta x$ and even decreases with increasing $\Delta x$. Clearly, factors other than the trigonal distortion of the IrO$_6$ octahedron should play a dominant role in determining the splitting of $J_{eff} = 3/2$ band in the family of pyrochlore iridates.

Hozoi et al. recently pointed out that crystal fields other than that from the O$_6^{2-}$ octahedron, in particular those produced by the nearest-neighbour Ir$^{4+}$ ions and the A cations, should not be dismissed as a factor determining the crystal field splitting [28]. This crystal field produced by A cations should contribute appreciably to the crystal field splitting of In$_2$Ir$_2$O$_7$ as in the other A$_2$Ir$_2$O$_7$, but cannot be dominant over the crystal field from O$_6$ octahedron. It is highly unlikely that the crystal field splitting from A cations can account for the inverse correlation between $\Delta x$ and $\Delta E$. 
perimentally observed in Y$_2$Ir$_2$O$_7$ and Pr$_2$Ir$_2$O$_7$ and even larger than in In$_2$Ir$_2$O$_7$, should involve mechanisms of splitting other than the trigonal crystal field. We suggest that the large inter-site orbital mixing (hopping) together with moderately strong electron correlations may split the degenerate $J_{\text{eff}} = 3/2$ bands into distinct sub-bands, which may reflect the much broader excitations within the $t_{2g}$ manifold in the RIXS spectrum as compared with In$_2$Ir$_2$O$_7$. The incorporation of such hopping processes in the cluster calculation is a theoretical challenge and what we have observed here would provide a useful test ground for such on-going attempts.

Assuming the dominant trigonal crystal field effect in In$_2$Ir$_2$O$_7$, one can estimate the values of spin-orbit coupling, $\lambda_{\text{SOC}}$, and the trigonal crystal field splitting, $\Delta_{\text{trg}}$, from the energy of the two doublets detected by RIXS (0.48 eV and 0.86 eV) much more reliably than in other pyrochlore iridates. Following the procedure described in [27], we estimate $\lambda_{\text{SOC}} = 0.38$ eV and $\Delta_{\text{trg}} = 0.48$ eV for the newly discovered In$_2$Ir$_2$O$_7$, which unambiguously evidences the expected non-negligible trigonal crystal field effect as compared with the spin-orbit coupling.

In summary, In$_2$Ir$_2$O$_7$ is the strongest Mott insulator among the family of Ir$^{4+}$ pyrochlore oxide A$_2$Ir$_2$O$_7$ (A: trivalent ions) due to small inter-site hopping suppressed by Ir-O-Ir bond-bending. A magnetic order, likely all-in trivalent ions) due to small inter-site hopping suppressed by Ir-O-Ir bond-bending. A magnetic order, likely all-in

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The magnetization data included a very small ferromagnetic signal in all measured temperature range in addition to the one below 55 K, most likely originating from tiny amount of unknown ferromagnetic impurity. The ferromagnetic moment was estimated to be $\sim 0.18$ emu/mol from the magnetization curve at 100 K. We subtracted this ferromagnetic component from the raw data by assuming that its temperature dependence is negligibly small.