Evidence for strong 5d electron correlations and electron-magnon coupling in a pyrochlore, Y2Ir2O7

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We report the observation of an unusual behavior of highly extended 5d electrons in Y2Ir2O7 belonging to pyrochlore family of great current interest using high resolution photoemission spectroscopy. The experimental bulk spectra reveal an intense lower Hubbard band in addition to weak intensities in the vicinity of the Fermi level, \( \epsilon_F \). This provides a direct evidence for strong electron correlation among the 5d electrons, despite their highly extended nature. The high resolution spectrum at room temperature exhibits a pseudogap at \( \epsilon_F \) and \( |\epsilon - \epsilon_F|^2 \) dependence demonstrating the importance of electron correlation in this system. Remarkably, in the magnetically ordered phase (\( T < 150 \) K), the spectral lineshape evolves to a \( |\epsilon - \epsilon_F|^{1.5} \) dependence emphasizing the dominant role of electron-magnon coupling.

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It is generally believed that electron-electron Coulomb repulsion strength, \( U \), among the d electrons decreases as one traverses from 3d to 5d ions, due to the increase in radial extension of the these orbitals. For example, while the effective electron correlation strength, \( U/W \) (\( W = \) bandwidth) in 3d transition metal oxides (TMOs) is significantly strong [1], \( U/W \) in 4d TMOs is weak enabling first principle approaches to capture the experimentally determined electronic structure [2, 3]. Signature of electron correlation in 5d transition metal compounds has not been observed [1]. In this letter, we offer a clear evidence for strong correlation among 5d electrons in a compound, Y2Ir2O7, which has not been paid enough attention in the literature.

This compound belongs to pyrochlore structure, which have drawn significant attention in recent times due to the possibility of geometrical frustration leading to a varieties of novel phenomena e.g., spin ice behavior [6], superconductivity [8], correlation induced metal insulator transitions [9] etc. In particular, a Ir based pyrochlore, Pr2Ir2O7 has been recently identified to show spin-liquid behavior [7], anomalous Hall effect [10] etc. It is believed that the interaction between the Pr 4f moments mediated by Ir 5d conduction electrons plays a key role here. While Pr2Ir2O7 is a metal, the Y-analogue, Y2Ir2O7 is an insulator. Y2Ir2O7 is described to be a Mott insulator, where large \( U/W \) leads to insulating phase in a metal [12, 13, 14]. In addition, Y2Ir2O7 has been proposed to exhibit a weak ferromagnetic transition at around 150 K [13, 14]. Therefore, this system appears to be an ideal system to probe 5d electron correlation.

In this letter, we report the results of our investigation on the origin of unusual properties in Y2Ir2O7 using state-of-the-art high resolution photoemission spectroscopy. We find that the bulk Ir 5d band exhibits a signature of intense lower Hubbard band as observed in strongly correlated 3d TMOs [1, 15]. It is remarkable that no hard gap is observed in the bulk spectra although it is an insulator. The spectral lineshape in the vicinity of the Fermi level, \( \epsilon_F \), changes from \( |\epsilon - \epsilon_F|^2 \) behavior at 300 K corresponding to a correlated Fermi liquid system to \( |\epsilon - \epsilon_F|^{1.5} \) behavior in the ferromagnetic phase suggesting importance of electron-magnon coupling.

High quality Y2Ir2O7 was prepared by solid state reaction route using high-purity (> 99.9%) ingredients (Y2O3 and IrO2 powders). To achieve large grain size and good intergrain binding, the sample was sintered in pellet form at 900 °C for a day and subsequently, at 1000 °C for more than two days with an intermittent grinding. The sample quality was characterized by x-ray diffraction and scanning electron microscopy. There was no evidence for any impurity feature. Rietveld refinement reveals a single cubic phase (\( a = 10.20 \) Å; space group \( Fd\bar{3}m \)). The sample was further characterized [16] by magnetization measurements and found to show a magnetic transition at about 150 K in agreement with the literature [13, 14]. Photoemission measurements in the temperature range 10 K - 300 K were performed using monochromatic photon sources and SES2002 Gammadata Scienta analyzer. The energy resolutions were set to 300 meV, 4 meV and 1.4 meV for the measurements with Al Kα (1486.6 eV), He ι (40.8 eV) and He ν (21.2 eV) photons, respectively. The sample surface was cleaned by in situ scraping (base pressure = 3×10^{-11} torr) and cleanliness of the sample surface was ensured by negligible (< 2%) impurity contributions in the O 1s spectral region and the absence of C 1s peak. The electronic band structure calculations were carried out using full potential linearized augmented plane wave method (WIEN2k software) [17] within the local density approximations, LDA. The convergence was achieved considering 512 k points within the first Brillouin zone and the error bar for the energy convergence was set to \( \sim 0.25 \) meV.

In Fig. 1, we show the density of states (DOS) cal-
The experimental valence band photoemission spectra at room temperature are shown in Fig. 2(a). The spectra corresponding to ultraviolet (UV) photons (21.2 eV and 40.8 eV) exhibit two distinctly separated features. A dominant intensity appears between 3 - 9 eV binding energies (\(= \epsilon_F - E \), \(E\) = energy) and a weak feature, \(A\), near \(\epsilon_F\). The intensity pattern becomes drastically opposite in the 1486.6 eV spectrum; the feature \(A\) becomes the most intense one compared to the intensity of the other feature. The ratio of the photoemission cross section of Ir 5d states to the O 2p states increases significantly for 1486.6 eV incident photon energy compared to UV energies; the feature \(A\) in the figure can therefore be attributed to the photoemission signal from the bands having essentially Ir 5d character. The O 2p features appear above 3 eV binding energy. A rigid shift of the calculated O 2p band by about 1.5 eV towards higher binding energies provides a remarkable representation of the experimental spectra as shown in Fig. 2(b). Such a rigid shift of the completely filled O 2p bands is often observed due to the underestimation of the correlation effects in the band structure calculations [18].

It is clear from Figs. 1 and 2 that O 2p and Ir 5d related features are distinctly separated. Thus, Ir 5d contributions appearing near \(\epsilon_F\) can be delineated by subtracting the tail of the O 2p band. We have simulated the O 2p contributions using a combination of Lorentzians convoluted by a Gaussian representing resolution broadening as shown by solid line in the case of 1486.6 eV spectrum in Fig. 2(a). The extracted Ir 5d bands are shown in Fig. 3(a) after normalizing to the integrated intensity. The 1486.6 eV spectrum clearly shows different lineshape and energy position compared to the UV spectra. This is demonstrated by overlapping the resolution broadened 21.2 eV spectrum (dashed line) over the 1486.6 eV spectrum. The x-ray photoelectrons have larger escape depth than the ultraviolet photoelectrons. Thus, the difference in the 1486.6 eV and UV spectra is attributed to the different bulk and surface electronic structures.

The intensity in the photoemission spectra can be expressed as \(I(\epsilon) = (1 - e^{-d/\lambda})I^s(\epsilon) + e^{-d/\lambda}I^b(\epsilon)\), where \(I^s(\epsilon)\) and \(I^b(\epsilon)\) are the surface and bulk spectra, respectively. \(d\) is the effective surface layer depth and \(\lambda\) is escape depth of the photoelectrons. To calculate \(I^s(\epsilon)\) and \(I^b(\epsilon)\).
and $I^b(\epsilon)$, we use $d/\lambda = 1.8$ and 0.5 for UV and x-ray photoemission spectra, respectively as used for several other systems [2, 19]. The extracted surface and bulk spectral functions are plotted in Fig. 3(b). The surface spectrum exhibits a peak around 1.8 eV with no intensity at $\epsilon_F$ suggesting insulating character of the surface electronic structure. The bulk spectrum, on the other hand, exhibits a substantial intensity at $\epsilon_F$ suggesting metallic phase in addition to an intense peak at around 1 eV.

In order to address the issue of electron correlation among 5d electrons, we compare the surface and bulk spectra with the \textit{ab initio} results. The dashed line in Fig. 3(b) represents the Gaussian-convoluted (full width at half maximum = 0.3 eV) occupied TDOS at 300 K. The calculated spectrum exhibits a peak around 0.5 eV, spreading down to about 1 eV binding energy, and it is significantly narrower than the width of the bulk spectra. Since, the electron correlation is significantly underestimated in the band structure calculations within LDA, the difference between the calculated spectrum and the experimental one is often attributed to the electron correlation effects [1]. Thus, the intensities appearing at higher binding energies in the bulk spectrum represent photoemission signal from the correlation induced localized electronic states (lower Hubbard band), and is termed as ‘incoherent feature’. The intensities in the vicinity of $\epsilon_F$ represent the signature of delocalized electronic states and is termed as ‘coherent feature’. The large intensity of the incoherent feature compared to the coherent feature intensity indicates strong electron correlation effects, in sharp contrast to the observations in other Ir compounds [6]. Such a strong correlation in the highly extended 5d bands is unusual. The deviation from LDA results is most evident in the surface spectrum. Only the incoherent feature is observed along with a large gap at $\epsilon_F$ suggesting a Mott insulating phase corresponding to the two dimensional electronic structure at the surface.

We now focus on the influence of the magnetic phase transition on the electronic structure.

For this purpose, we first discuss the surface and bulk spectra at 20 K shown by solid lines in Fig. 3(b). The surface spectra remain unaffected with the change in temperature. No hard gap is observed in the bulk spectra down to the lowest temperature studied, which evidently rules out the possibility of Mott insulating phase in the bulk even at low temperatures. The lineshape of the 20 K bulk spectrum is very similar to that at 300 K indicating that the magnetic phase transition has insignificant influence if viewed in the energy scale of the figure. However, a closer look near $\epsilon_F$ region reveals subtle changes with temperature as described below.

Although the electron correlation effects are manifested in the large energy scale as described above, various thermodynamic properties are essentially determined by the electronic states near $\epsilon_F$ ($|\epsilon - \epsilon_F| \approx k_B T$). High energy resolution employed in the present investigation enables to address this issue. We investigate the evolution of the He I spectra near $\epsilon_F$ as a function of temperature in Fig. 4(a), which represent the bulk features as the surface spectra exhibit a large gap (see Fig. 3(b)). Normalization of all the spectra at around 200 meV binding energy shows similar line shape down to about 50 meV binding energy at all the temperatures. The spectra in the energy range closer to $\epsilon_F$ reveal interesting evolution along with the appearance of a sharp Fermi cut off at low temperatures.

Since the energy resolution is very high and various lifetime broadenings are insignificant in the vicinity of $\epsilon_F$, one can extract the spectral density of states (SDOS) directly from the raw data by symmetrizing the spectra; $SDOS = I(\epsilon) + I(-\epsilon)$. Thus obtained SDOS shown in Fig. 4(b), provide a good representation of the density of states in this small energy window. There is a dip in SDOS at $\epsilon_F$, which gradually increases with the decrease in temperature down to 100 K. Further reduction in temperature does not show any significant change in the intensity at $\epsilon_F$. It is often observed that the intensity at $\epsilon_F$ decreases with the decrease in temperature due to the disorder induced localization of the electronic states at $\epsilon_F$ [20, 21]. In such a case, the DOS at $\epsilon_F$ follows $(a + b\sqrt{T}; T$ is temperature) behavior [21, 22], which is qualitatively different from the behavior in the present case.

In order to investigate the energy dependence of the spectral lineshape, we analyzed SDOS as a function of $|\epsilon - \epsilon_F|^\alpha$ for different values of $\alpha$. All the spectra could not be simulated for one value of $\alpha$. We show the two extreme cases in Fig. 4(c) and 4(d). The SDOS at 300 K is better represented by $\alpha = 2$ indicating strong influence...
of the theoretical prediction of correlation induced effects. This finding may serve as an experimental demonstration of electron correlation effect in the electronic structure.

In summary, we have addressed the issue of electron correlation within 5d band by choosing Y2Ir2O7, a compound belonging to a family of great current interest. A comparison of the electronic structure calculations and the high-resolution photoemission data offers distinct evidence for strong Coulomb correlation among Ir 5d electrons. No hard gap is observed in the bulk spectra down to the lowest temperature studied. The surface spectra exhibit an insulating phase at all the temperatures presumably due to the enhancement of $U/W$ at the surface compared to bulk. Analysis of the spectral lineshape in the vicinity of $\varepsilon_F$ as a function of temperature emphasizes the need to consider electron-magnon coupling in addition to electron correlation while trying to understand the solid state behavior of the 5d electrons.

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