Heavy-Fermion-like State in a Transition Metal Oxide LiV_2O_4 Single Crystal: Indication of Kondo Resonance in the Photoemission Spectrum

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We have performed a vacuum ultraviolet laser excited photoemission spectroscopy on a *d*-electron heavy-fermion-like material LiV_2O_4 single crystal. We observed a sharp peak structure in the density of states at ~4 meV above the Fermi level (E_F). The evolution of the peak height corresponds well with the crossover behavior to the heavy-fermion-like state as observed in the thermal and transport properties. The position, shape, and temperature (T) dependence of the peak structure is quite similar to the Kondo resonance observed in conventional *f*-electron heavy Fermion compounds.

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Heavy fermion (HF) materials have attracted many researchers as an exotic system where the strong electron correlation manifests itself in a wide range of variety [1,2]. The important key in understanding the HF phenomenon is the well-known Kondo effect, which mixes the localized magnetic moment (practically *f* electrons) and the itinerantly conducting electrons by spin-singlet formation. In such a HF phase as realized in many $4f$ and $5f$ (e.g., Ce, Yb, and U) compounds, a great enhancement of an electron effective mass ($m^* = 100$–$1000m_e$) below the Kondo temperature (T_K) is indicated by the measurements of specific heat and magnetic susceptibility. The electronic state is characterized by a sharp peak structure in the density of states (DOS) located at $\sim k_B T_K$ apart from E_F, known by the name of Kondo resonance (KR) peak [2], which has been actually observed by photoemission spectroscopy (PES) in several Ce-based materials [3].

The discovery of the heavy-fermion-like behavior in LiV_2O_4 newly shed light on the possibility of HF state solely composed of V3*d* electrons. The magnetic susceptibility and the electronic specific heat coefficient (γ) show anomalously large values below $T^* \sim 20$ K [4]. γ (~ 420 mJ/mol K^2) is about 25 times larger than that estimated from the bare mass obtained by a local-density-approximation (LDA) band calculation [5]. This value is comparable to that of the typical *f*-electron HF compounds [1]. The electrical resistivity ρ of LiV_2O_4 single crystals, on the other hand, exhibits a T^2 dependence $\rho = \rho_0 + AT^2$ with an enhanced A at $T \ll T^*$, which is another character of the HF state [6]. LDA calculation in LiV_2O_4 indicates that three bands derived from the V3*d* orbitals cross E_F, doubly degenerate E_g, and a nondegenerate A_{1g}, whose bandwidths are 2 eV and 1 eV respectively [5]. By considering A_{1g} as the ''localized band'' and E_g as the ''itinerant bands'' in analogy with the case of *f*-electron compounds, the possibility of heavy Fermion state by Kondo effect was suggested for the first time in *d*-electron system [7]. However, since there is no significant difference in their band widths like those in the *f*-electron system, it has been long discussed whether the heavy-fermion-like state in LiV_2O_4 could be explained within a simple Kondo scenario.

Another characteristic feature of LiV_2O_4 is the cubic spinel structure which gives rise to the geometrical spin frustration [8]. LiV_2O_4 shows Curie-Weiss-like behavior in the magnetic susceptibility for $T \gg T^*$ region, indicating the existence of local magnetic moments [4]. However, there is no evidence of the long-range magnetic order (nor spin glass) down to 0.02 K [4], possibly being suppressed by the geometrical magnetic frustration. In addition, recent neutron scattering [9,10] and muon spin relaxation [11,12] experiments indicate that the local magnetic moments with short-range correlation remain down to $T \ll T^*$ region. Based on these results, the possible role of dynamical spin fluctuation has also been often discussed to account for the anomalous thermal, magnetic, and transport properties in LiV_2O_4 [13–15].

To clarify the origin of the heavy-fermion-like state in LiV_2O_4, more detailed experimental findings are essential. Especially, the peculiarity of the heavy-fermion-like state should be reflected onto the low-energy electronic structure around E_F. For example, the observation of Kondo resonance peak near E_F in $CeCu_2Si_2$ revealed the validity of high-resolution PES for this purpose [3]. Fortunately, recent instrumental development of the laser PES spectrometer allows us to perform the bulk sensitive and high-resolution measurements [16]. Taking advantage of these capabilities, we can investigate the intrinsic electronic structure in more detail.

In this Letter, we report the result of high-resolution PES study on the *d*-electron heavy-fermion-like compound LiV_2O_4 using vacuum ultraviolet (VUV) laser excited

PES system. A sharp peak structure located above E_F is observed in the PES spectrum divided by the Fermi-Dirac function (FDF), which approximates the DOS. The T dependence of the peak structure is similar to that of the KR in conventional f-electron HF materials. The result indicates that the origin of the heavy-fermion-like state realized in LiV_2O_4 may be ascribed to Kondo effect.

PES experiments were performed using a Scienta R4000 analyzer with a VUV laser (6.994 eV) [16]. The advantage of using the VUV laser is the long escape depth of the low-energy photoelectrons [17], which allows us to probe the bulk electronic states. While the highest energy resolution of this instrument is 360 μeV, we fixed the energy resolution 4.0 meV in our measurement to obtain a high signal-to-noise ratio. The single crystals of LiV_2O_4 were grown by a flux method [18]. The sample was fractured *in situ* at 11 K just before the measurement to obtain a clean surface. The base pressure of the measurement chamber was lower than 2×10^{-11} Torr. The E_F of the sample was determined by that of a gold film evaporated onto the sample substrate within error of $\delta E_F < \pm 0.25$ meV. The reliability of the T-dependent spectra was carefully checked by the temperature-cycled measurements.

Figure 1 shows the T dependence of PES spectra. The spectra are normalized to the spectral intensities at 35–50 meV in binding energy (E_B), where the intensities are T dependent and coincide very well with each other. The inset shows the spectra of Au in the same energy region as a reference. The spectral edge of Au PES has the midpoint just at E_F with its shape nearly symmetric for above and below E_F, just like the FDF. In contrast, the Fermi edge of LiV_2O_4 takes its midpoint slightly above E_F for all T, with an apparent tail toward the unoccupied ($E_B < 0$) state. This result is strongly indicative of a significant amount of DOS located above E_F. These spectral features in LiV_2O_4 are very similar to that in $CeCu_2Si_2$ [3].

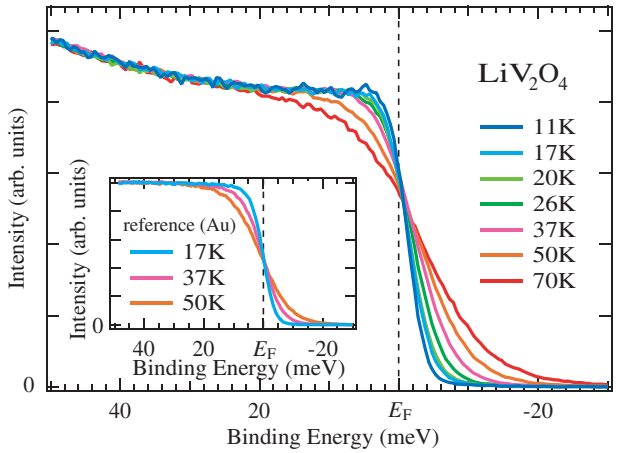

FIG. 1 (color). Temperature dependence of photoemission spectra in LiV_2O_4. The spectra are normalized to the spectral intensity at 35–50 meV in binding energy. The inset shows the PES spectra of Au as a reference.

To discuss the electronic structure more into the detail following the $CeCu_2Si_2$ case [3], the experimental PES spectra are divided by FDF convoluted by a Gauss function with a FWHM of $\Delta E = 4.0$ meV. Thus we can estimate the DOS weighted by ion cross section. The result is shown in Fig. 2. We adopted the spectra up to $3k_BT$ above E_F, where high enough signal-to-noise ratio is available. The T-dependent spectra of Au, shown as the reference in the inset, are flat for whole E_B region. By contrast, a clear peak structure is observed in LiV_2O_4 at $\sim$4 meV above E_F for high T region ($T > 26$ K) owing to the occupation of DOS by the thermally excited electrons, while merely the left-side tail of the peak is observed at lower T. As T decreases, the peak width becomes narrower simultaneously as the peak height evolves. The T dependence of the peak structure above T^* is qualitatively similar to that of the KR peak observed in $CeCu_2Si_2$ or $CeRu_2Si_2$ [19]. At 26 K, the lowest T where the peak shape is available, we can estimate that the peak is located at 4.0 meV above E_F and its width is 10.4 meV. Here we have defined the peak width by twice the half width at half maximum (HWHM) of the peak. The background underneath the peak is determined by the upturning point of the spectral intensity. The inset of Fig. 3 shows how we have estimated the background and

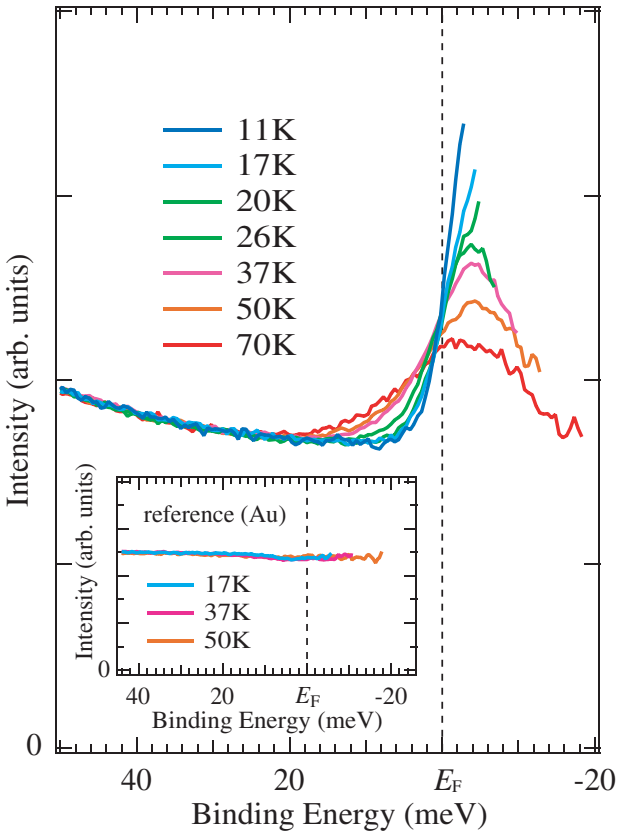

FIG. 2 (color). PES spectra of LiV_2O_4 divided by the broadened FDF at respective temperatures (see text), which approximate the DOS. The inset shows the T-dependent spectra of Au as a reference.

the HWHM of the peak, which are represented by the horizontal broken line and an arrow, respectively. Considering the instrumental resolution of 4.0 meV, the intrinsic peak width should be approximately $\sqrt{\{(10.4\ \mathrm{meV})^2\text{-}(4.0\ \mathrm{meV})^2\}} = 9.6$ meV. It is expected theoretically in HF systems that the KR peak at the ground state has the width of $\sim k_B T_K$ and lies at the order of $k_B T_K$ apart from E_F [2]. The KR peak actually observed for the case of $CeCu_2Si_2$ also had a narrow peak width with the order of $k_B T_K$ [3,19]. In our case for LiV_2O_4, the energy scale of the peak position ($E_B \sim -4$ meV) and the width (9.6 meV at 26 K) seems to be comparable with the order of coherent temperature $T^* \sim 20$ K reported by the preceding thermal, magnetic, and transport property measurements [4,6]. These results indicate that the peak feature observed in our PES measurement also corresponds to some electronic structure akin to the Kondo resonance as often observed in HF systems.

To estimate the T evolution of the KR-like peak structure, we defined the peak height by the subtraction of the background intensity from the peak intensity. Since we cannot reach the top of the peak below T^*, we take the maximum intensity at the lowest E_B instead, which gives a lower limit of the intrinsic peak height. Figure 3 shows the T dependence of the peak height. Filled circles indicate the obtained peak height while the open circles represent the lower limit of the height for $T < 26$ K. The error bar is estimated by considering the experimental accuracy of the E_F. As T decreases from 70 K, the peak height gradually increases reflecting the evolution of the peak. Below T^*, the increasing rate of the peak height with respect to T becomes obviously higher than that above T^*, even though the peak height below T^* is merely the lower limit of the intrinsic peak height. The abrupt enhancement of peak height across T^* reflects the rapid evolution of KR-like peak below T^*, which is in a good accordance with the mass renormalization behavior as indicated in the T dependence of electronic heat capacity, magnetic susceptibility, and electrical resistivity [4,6].

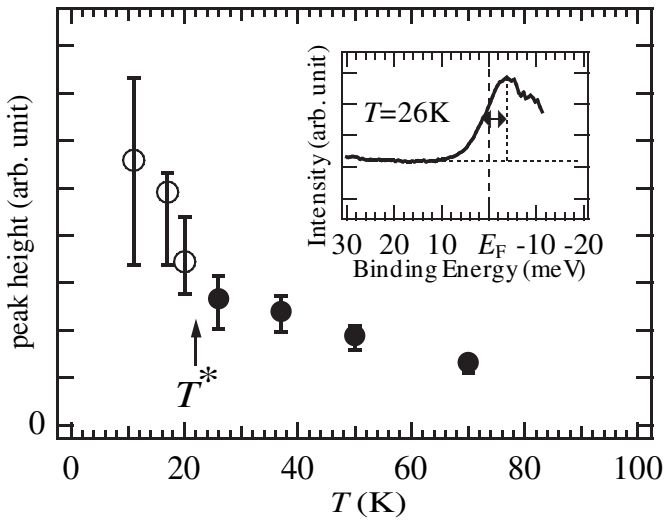

FIG. 3. Temperature dependence of the peak height (see text). The filled circles show the peak height while the open circles indicate the lower limit of the peak height below 26 K. T^* corresponds to the crossover temperature of LiV_2O_4. The error bar is estimated by the experimental accuracy of E_F. The inset shows an example of how we determined the peak width, the peak height, and the background.

In a Kondo scenario, the evolution of the KR peak reflects that the mass renormalization rapidly becomes enhanced below T_K due to the strong hybridization between localized and itinerant electrons. It has been proposed by a calculation based on the two-band Hubbard model [20] that the quasiparticle state with a sharp KR peak can be similarly formed in LiV_2O_4 case, even though the widths of the bands are not in an extreme contrast (1 eV and 2 eV for A_{1g} and E_g, respectively). In the calculation, the interband Coulomb repulsion plays an important role, which strongly emphasizes the small difference between the two bands, making one of the d electrons localized in the lower A_{1g} band. As a result, a strong renormalization due to the Kondo effect takes place, which creates a sharp peak structure just above E_F in the calculated density of states at $T = 0$ K. The peak we observed in our spectrum shows the similarity with the KR peak obtained in this model. Thus, such a particular Kondo scenario might be an appropriate candidate in explaining the heavy-fermion-like state realized in LiV_2O_4.

One of the other possible origins for the anomalous behavior in LiV_2O_4 is the spin (and/or orbital) fluctuation, which may remain at low T. It is reported theoretically that such spin and orbital fluctuation could contribute to the large γ [13]. It is also expected in some model [14] that although the Kondo renormalization does not occur, the ground state with spin fluctuation shows the behavior like a nearly normal Fermi liquid with an enhanced effective mass. These models may explain the mass enhancement behavior in the thermal physical properties [4,6] together with the magnetic response characteristic of frustrated spin system [9,10]. However, it is not straightforward whether the electronic state dominated by such spin (and/or orbital) fluctuation will correspond to a sharp (<10 meV) peak structure in the observed DOS. Further theoretical investigation will be necessary to discuss the origin of the heavy-fermion-like state in the light of these residual degrees of freedom.

In summary, we performed PES on the heavy-fermion-like LiV_2O_4 single crystal and observed a sharp peak structure at $\sim$4 meV above E_F in the electronic density of states. The peak position, as well as its width, has the energy scale comparable to $k_B T^* \sim 20$ K, suggesting that it corresponds to the Kondo resonance peak frequently observed in heavy fermion compounds. The peak structure gradually evolves as T decreases toward T^*. When cooled below $T^* \sim 20$ K, the peak height starts to increase rap-

idly, indicating the abrupt evolution of a KR peak. The features of the peak structure observed in the electronic density of states are analogous to the case of Ce-based heavy fermion systems, which may attribute the origin of the heavy-fermion-like behavior in LiV_2O_4 to the Kondo scenario.

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