

Correlation-Driven Heavy-Fermion Formation in LiV_2O_4

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(Received 26 February 2007; published 19 October 2007)

Optical reflectivity measurements were performed on a single crystal of the d -electron heavy-fermion (HF) metal LiV_2O_4 . Our results evidence the highly incoherent charge dynamics above $T^* \approx 20$ K and the redistribution of the spectral weight of the optical conductivity over broad energy scales (~ 5 eV) as the quantum coherence of the charge carriers is recovered. This reveals that LiV_2O_4 is close to a correlation-driven insulating state and indicates that, in sharp contrast to f -electron HF Kondo-lattice systems, strong electronic correlation effects dominate the heavy quasiparticle formation in LiV_2O_4 .

DOI: [10.1103/PhysRevLett.99.167402](https://doi.org/10.1103/PhysRevLett.99.167402)

PACS numbers: 78.30.Er, 71.27.+a, 75.20.Hr

Electrons in solids, by coupling with spins and lattices, form dressed particles called *quasiparticles* (QP). The mass of such QPs can in some cases be extremely heavy, 100–1000 times the bare electron mass. The systems with extremely heavy QPs are called *heavy fermions* (HF) and have been attracting considerable interest since they display a variety of novel phenomena including exotic superconductivity [1]. Recently, a few d -electron systems have been found to exhibit physical properties characteristic of HF systems, e.g., $\text{Y}(\text{Sc})\text{Mn}_2$ [2], $\text{Na}_{0.75}\text{CoO}_2$ [3], and LiV_2O_4 [4–7]. Conventional HF metals are f -electron systems containing rare-earth or actinide ions, in which the low-temperature heavy QP formation can be understood based on the Kondo coupling between localized f -electron moments and itinerant electrons. In the case of d -electron metals, it is not obvious to identify the same Kondo coupled itinerant and localized electrons. A common point for the d -electron HF metals is instead that the magnetic ions occupy sites on geometrically frustrated lattices. It has been discussed that the HF behavior of d -electron systems might imply a new route to the formation of heavy quasiparticles.

Among the d -electron HF metals the spinel LiV_2O_4 has the largest quasiparticle specific heat coefficient $\gamma = 420$ mJ/mol \cdot K² [4]. It exhibits a short-range antiferromagnetic order below 80 K [8] and no other kind of long-range magnetic order at any measured temperature. At a characteristic temperature, $T^* \approx 20$ K, the heat capacity over temperature C/T shows a steep increase and the electrical resistivity ρ a sharp drop, suggesting that coherence is formed [6]. This, in addition to a Fermi liquid ground state [6] and a peak in the density-of-states (DOS) located ~ 4 meV above the Fermi level (E_F) [7], confirms the low- T HF properties. Band structure calculations on LiV_2O_4 indicate that mainly vanadium $3d$ t_{2g} bands cross the Fermi level [9,10]. These $V(3d)$ t_{2g} bands are well separated from the filled $O(2p)$ bands and the empty $V(3d)$ e_g bands. The triply degenerate t_{2g} orbitals

are split into doubly degenerate E_g and nondegenerate A_{1g} orbitals due to the trigonal crystal field. As a result of this trigonal splitting and d - d Coulomb interaction, it has been proposed that the A_{1g} orbitals can be considered as localized and the E_g orbitals as itinerant permitting to map the electronic structure of LiV_2O_4 into a Kondo-lattice picture [10]. It requires, however, a subtle cancellation of ferromagnetic coupling through double exchange with antiferromagnetic coupling through Kondo-like exchange. Other scenarios have been proposed in which the geometrical frustration is an important ingredient for the HF formation [11,12]. Still, the origin of the HF formation in LiV_2O_4 is a matter of controversy, which can only be resolved by new detailed experiments. In particular, a method probing the electronic structure over wide energy scales, such as optical spectroscopy, may reveal valuable information about the mechanisms responsible for the low-energy HF formation.

In this Letter, we report the first detailed investigation of the optical properties of single crystals of LiV_2O_4 . The incoherent charge dynamics at $T > T^*$ and the transfer of spectral weight over broad energy scales (~ 5 eV) reveal that LiV_2O_4 , in contrast to conventional f -electron HF metals, is a correlated metal in proximity to a correlation-driven insulating state. We outline a scenario in which strong correlation effects are controlling the formation of heavy QP states, while the key role of the geometrical frustration is to limit the extension of charge and spin orderings.

Single crystals of LiV_2O_4 were grown by the flux method described in Ref. [13]. Near-normal incident reflectivity spectra were measured on the as-grown shiny surface of crystals with octahedral shape and $\{111\}$ faces with edges of at most 1 mm. We confirmed that the reflectivity at room temperature was the same as that of a small cleaved surface. The reflectivity was measured using a Fourier-type interferometer for the photon energy range of $\hbar\omega = 0.01$ –1.0 eV and grating spectrometers for the

energy range 0.5–6 eV. The crystal size was sufficient for optical measurements using microscopes designed for the infrared (IR) and visible-ultraviolet spectrometers. As a reference mirror we used an evaporated Au film on a glass plate with the same shape and size as the sample for the far-to-near IR regions, in order to cancel out diffraction effects. The experimental error of the reflectivity, determined by the reproducibility, was less than 1%. The optical conductivity $\sigma(\omega)$ was determined from the reflectivity data by Kramers-Kronig transformation. To do this, we assumed the Hagen-Rubens formula in the low-energy region and used a constant reflectivity above 6 eV followed by a well-known function of ω^{-4} in the vacuum-ultraviolet region. The dc resistivity ρ was measured using a four-probe technique.

The reflectivity spectra measured on the as-grown surface at different temperatures are shown in Fig. 1. A reflectivity edge, observed around 1.5 eV, reflects the metallic character of this system, which produces the far-infrared (FIR) spectral weight in the optical conductivity due to charge carriers. In ordinary metals, the edge is steep and the reflectivity below the edge is already close to 1. However, in LiV_2O_4 the reflectivity shows a gradual increase below the edge, and the reflectivity in the mid-infrared (MIR) and near-infrared (NIR) regions are rather suppressed, suggesting the incoherent nature of the charge carriers. With decreasing temperature the reflectivity edge becomes sharper, and the reflectivity in the FIR to MIR region higher, indicating that coherence is gained at lower temperatures. No significant change was observed in the reflectivity spectra from 50 K down to the lowest measured temperature of 6 K in the considered frequency range.

The room temperature reflectivity for a polished surface is also shown in Fig. 1. The reflectivity of the polished

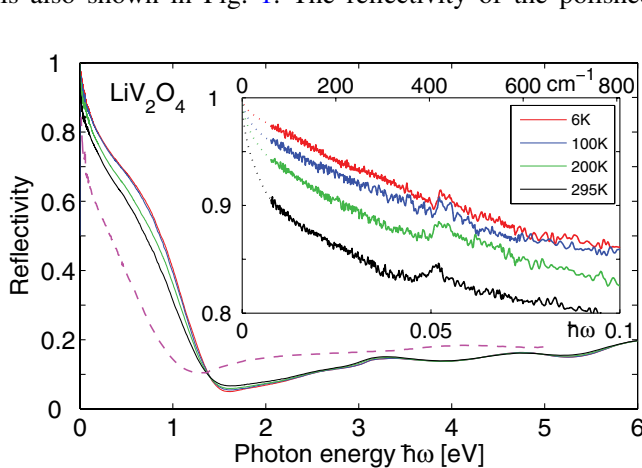


FIG. 1 (color online). Optical reflectivity spectra measured on the as-grown surface of LiV_2O_4 crystals at temperatures of 6, 100, 200, and 295 K (solid lines, from top to bottom) and on the polished surface (using lapping films with diamond powder of diameter 1 μm) at 295 K (dashed line). The inset shows the low-energy part of the as-grown surface spectra with an optical phonon peak at $\sim 420 \text{ cm}^{-1}$ (0.05 eV). The dotted lines are the extrapolations using the Hagen-Rubens formula.

surface is significantly reduced in the mid-to-near IR region and rather enhanced in the visible-to-ultraviolet region. If the scattering of the incident light is increased simply due to residual surface roughness, the reflectivity measured on the polished surface would be suppressed over *all* energy regions. We therefore consider that the observed variation of the reflectivity reflects changes in the electronic states. The charge excitations are sensitive to static imperfections and/or structural strain. The suppressed IR reflectivity indicates the tendency of the charge carriers to localize while the enhanced visible-to-ultraviolet reflectivity suggests an intimate relation between the charge carrier dynamics and the higher-lying interband transitions. This sensitivity of the reflectivity to surface treatment, similar to that of some manganites in a metallic phase [14], suggests the importance of electronic correlations in LiV_2O_4 [15].

Group theory predicts that four F_{1u} phonons are IR active in a cubic spinel. For insulating cubic spinels, the two lower-energy modes have much smaller spectral weight compared with the two higher-energy modes [16,17]. In MgTi_2O_4 , only the two higher-energy phonons are observed at 420 cm^{-1} and 600 cm^{-1} [18], the 420 cm^{-1} mode having the largest spectral weight in the metallic (semiconducting) phase. Only one phonon is observed at 420 cm^{-1} in metallic LiV_2O_4 (inset of Fig. 1). Taking into account the screening by free carriers, the other phonon modes are likely buried in the noise level of the reflectivity spectrum.

The optical conductivity in the low-energy region is shown in Fig. 2, and the connection with the dc conductivity $\sigma_{\text{dc}} (= \rho^{-1})$ in the right inset. The evolution of $\sigma(\omega)$

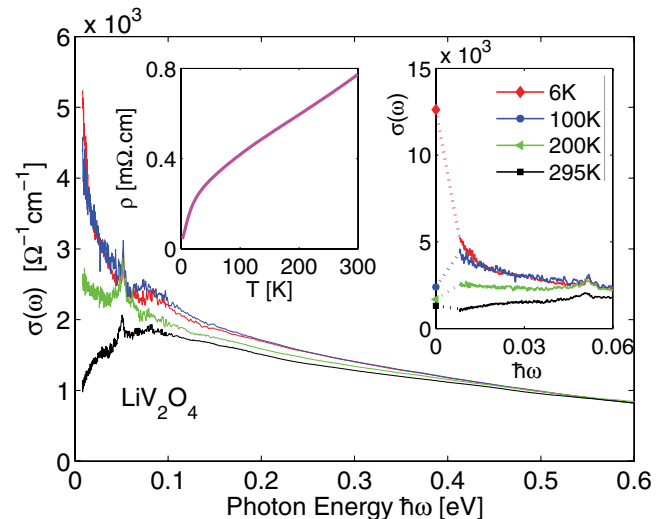


FIG. 2 (color online). Real part of $\sigma(\omega)$ of LiV_2O_4 at $T = 6, 100, 200,$ and 295 K (from top to bottom). The peaks near 0.05 eV are due to optical phonons. The left inset shows the temperature dependence of the resistivity ($\rho = \sigma_{\text{dc}}^{-1}$). The right inset shows the connection between $\sigma(\omega)$ (solid lines) and σ_{dc} (markers); the dotted lines are only guides for the eye.

as a function of temperature clearly demonstrates a cross-over from coherent to incoherent charge dynamics. At $T = 6$ K (below $T^* \approx 20$ K), by extrapolating the measured $\sigma(\omega)$ to σ_{dc} , a clear Drude contribution is identified at low energies, consistent with the formation of coherent quasiparticles. The optical conductivity shows a very slow decay with ω , which is typical for strongly correlated transition-metal oxides. A sharp coherence peak in the DOS, located ~ 4 meV above E_F , was observed recently by high-resolution photoemission spectroscopy at temperatures below T^* [7]. The DOS of f -electron HF systems exhibits a similar low- T DOS peak, known as the Kondo resonance, yielding an narrow Drude peak in $\sigma(\omega)$ [1]. In addition, a pseudogap and a broad MIR peak, originating from optical interband transitions between renormalized hybridization bands, appears for many f -electron HF systems [19,20]. While the low-temperature narrow Drude peak is observed in $\sigma(\omega)$ of LiV_2O_4 , the broad MIR peak and pseudogap cannot clearly be identified.

Above $T^* \approx 20$ K, the Drude contribution is not well defined anymore; instead, a finite-energy peak shows up in $\sigma(\omega)$. This is most clearly seen in the spectrum at 295 K, where a broad peak centered around 0.1 eV is observed. The presence of such finite-energy peak is less clear at lower temperatures. However, the fact that σ_{dc} above $T^* \approx 20$ K is much lower than naively anticipated from low-energy $\sigma(\omega)$ indicates the presence of a low-energy peak. The resistivity, shown in the left inset of Fig. 2 exhibits almost T -linear dependence above T^* , followed by a rapid decrease below T^* with decreasing temperature. Although the temperature dependence of ρ is seemingly metallic above T^* , the large magnitude of the resistivity in this temperature range yields $k_F l \lesssim 1$ [6]. Combining this violation of the Ioffe-Regel limit and the absence of a Drude peak, it is clear that the system is incoherent above T^* .

With increasing temperature to above T^* , the FIR conductivity does not only become incoherent but also loses its spectral weight. The missing spectral weight is transferred over an extremely broad energy region as shown in Fig. 3. The effective carrier density defined as

$$N_{\text{eff}} = \frac{2m_0V}{\pi e^2} \int_0^\omega \sigma(\omega') d\omega' \quad (1)$$

(m_0 is set to the bare electron mass and V to the volume per formula unit in order to define the unit of N_{eff} as number per formula unit) indicates that the f -sum rule is finally fulfilled above ~ 5 eV. Hence, the recovery of quantum coherence is accompanied by a spectral weight transfer over energies larger than the bandwidth W of the conduction band. This is a feature characteristic of correlated metallic systems close to a Mott insulating or charge-ordered state [21], but in sharp contrast to f -electron HF systems in the Kondo-lattice regime [1,22]. In HF metals, spectral weight redistribution is confined to energies $\hbar\omega < W$ [23]. Typically this energy scale is very low, of the order of 10–100 meV [1,22]. The possibility of Kondo-lattice

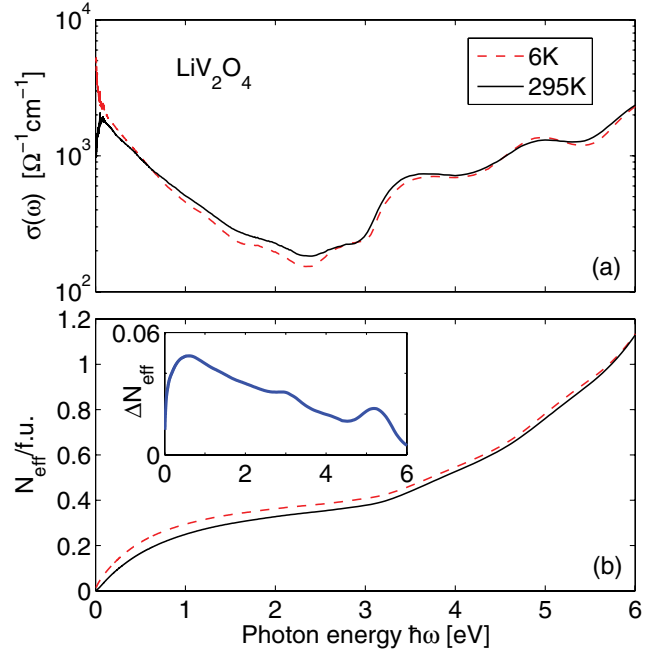


FIG. 3 (color online). (a) Real part of $\sigma(\omega)$ on a semilogarithmic scale. (b) Integrated spectral weight N_{eff} per formula unit. Inset: $\Delta N_{\text{eff}}(\omega) = \frac{2m_0V}{\pi e^2} \int_0^\omega [\sigma_{6\text{K}}(\omega') - \sigma_{295\text{K}}(\omega')] d\omega'$.

formation resulting from the band structure and d - d Coulomb correlations has been proposed for LiV_2O_4 [10]. In that model, the mechanism for the heavy QP formation is similar as for f -electron systems, i.e., hybridization between the “localized” A_{1g} band and the “itinerant” E_g band. While such a model may explain the resonance peak in the DOS, it is not obvious that it can account for the redistribution of spectral weight over the energy range of 5 eV in Fig. 3.

The incoherent transport in LiV_2O_4 is similar to that of a wide range of correlated bad metals, including vanadates [24], manganites [25], cobaltates [26], cuprates [27], ruthenates [28], and organic conductors [29]. In correlated metals, the coherence temperature is suppressed down to room temperature or lower and the charge dynamics is incoherent at higher temperatures. In the incoherent regime, $\sigma(\omega)$ is characterized by a finite-energy peak instead of a conventional zero-energy (Drude) peak. The metallic T dependence of the dc resistivity does not reflect the broadening of a Drude peak as in ordinary metals, but the collapse of the Drude peak into a finite-energy peak and the reduction of the FIR spectral weight with increasing temperature. These features typical of correlated bad metals, as well as the transfer of spectral weight over a large energy scale (shown in Fig. 3) demonstrate that strong electronic correlations dominate the charge dynamics and the recovery of the quantum coherence at low temperatures in LiV_2O_4 .

LiV_2O_4 is a mixed valent spinel with equal ratio of V^{3+} and V^{4+} , and it is very likely located in the close vicinity of

a charge-ordered state. In general, the QP mass is enhanced when approaching a correlation-driven metal-insulator transition from the metallic side [30]. In most cases, however, spin and/or charge ordering occurs before any gigantic enhancement of the mass is realized, giving rise to only a moderately enhanced mass. In LiV_2O_4 , however, the long-range spin-orbital-charge order is prevented by the geometrical frustration and hence the mass enhancement may proceed further. Accordingly, theoretical studies of simple models for strongly correlated electron systems suggest a considerable suppression of the temperature scale of electronic coherence by magnetic frustration [31] and a Kondo-like resonance in the metallic phase close to a Mott or charge-ordered transition [32].

In summary, we have investigated the temperature dependent optical properties of LiV_2O_4 using well-characterized single crystals. A strongly incoherent charge dynamics is found for all temperatures above $T^* \approx 20$ K, in agreement with the “bad-metal” behavior observed in resistivity measurements. The transfer of spectral weight occurs over an extremely wide energy range when the quantum coherence of the electrons is recovered, as observed in correlated metals close to a correlation-driven insulating state. This clearly indicates that strong correlation effects are controlling the formation of quasiparticle states at low energies in LiV_2O_4 . We propose the geometrical frustration, which limits the extension of charge and spin ordering, as an additional key ingredient of the low-temperature HF formation. This general scenario might be extended to other geometrical frustrated d -electron metals with heavy quasiparticles.

We are grateful to K. Okazaki for his help with the IR measurements and to J. Matsuno for valuable discussions. This work was supported by Grant in Aids for Creative Scientific Research from the Ministry of Education, Culture, Sports, Science, and Technology of Japan.

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