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Dramatic Change of the Magnetic Response in LiV_2O_4: Possible Heavy Fermion to Itinerant d-Metal Transition

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The magnetic relaxation of the d-metal oxide LiV_2O_4 has been measured by means of quasielastic neutron scattering. At low temperatures, the observed residual linewidth of 0.5 meV and a square-root temperature dependence of the magnetic relaxation rate are canonical features of heavy-fermion systems. For $T > 40$ K the magnetic response changes dramatically and can be characterized as a metal close to ferromagnetic order. [S0031-9007(99)08823-7]

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LiV_2O_4 is a transition-metal oxide that crystallizes in the cubic spinel-type structure [1]. In this compound the vanadium ions have the formal charge $V^{+3.5}$ and it was shown two decades ago that LiV_2O_4 is metallic [2]. No sign of magnetic order or superconductivity could be observed for $T \geq 0.02$ K [3] as opposed to the isostructural compounds $LiTi_2O_4$ [4] and ZnV_2O_4 [5] which become superconducting ($T_c = 13.7$ K) and magnetically ordered ($T_N = 40$ K), respectively. In the fcc spinel structure the transition-metal ions occupy corner-sharing tetrahedral sites and, due to this inherent geometrical frustration, magnetic order can easily be suppressed. Indeed, the antiferromagnetic (AFM) order in ZnV_2O_4 becomes possible only due to a cubic-to-tetragonal structural phase transition at 50 K [5]. Based on the results of specific heat, susceptibility and NMR measurements, Kondo *et al.* [3] proposed that LiV_2O_4 be the first example of a d-metal compound exhibiting heavy-fermion (HF) behavior [6] with a characteristic temperature of $T^* \approx 30$ K [3]. Subsequently, Chmaissem *et al.* [7] reported an anomalous temperature dependence of the lattice constants below $T = 20$ K and interpreted it in terms of a strongly enhanced Grüneisen parameter, which again is a characteristic fingerprint of HF systems. ^{7}Li NMR results, similar to those presented by Kondo *et al.* [3], were published by Fujiwara *et al.* [8] but were interpreted in terms of a spin-fluctuation theory.

Quasielastic neutron scattering experiments provide a unique characterization of the dynamic properties of a magnetic system. The most fundamental property is the dynamical susceptibility $\chi''(Q, \omega, T)$ that can be measured via the dynamic structure factor $S(Q, \omega, T)$,

$$S(Q, \omega, T) = (1 - e^{-\hbar\omega/k_B T})^{-1} \chi''(Q, \omega, T). \quad (1)$$

In the absence of interactions, a local magnetic moment will give a sharp delta-function peak in $S(Q, \omega, T)$. Exchange interactions with conduction electrons will yield Lorentzian line shapes and the corresponding width $\Gamma(Q, T)$ at low temperatures gives a rough estimate of the hybridization strength and determines a characteristic temperature T^*. In strongly correlated f-electron compounds, two different classes have been observed: (i) Kondo systems with a residual linewidth for $T \to 0$ and a monotonous increase with increasing temperature, which are characteristics for pure HF systems, and (ii) linewidth of mixed-valence compounds, which are large and roughly temperature independent. Bickers *et al.* [9] calculated the temperature dependence of the magnetic relaxation rate and showed that at low temperatures $\Gamma(Q, T)$ displays a minimum around T^* followed by a high-temperature behavior that can be well described by a square-root dependence. Hence, the magnetic relaxation rate is a fundamental property of strongly correlated electron systems and allows for a definite characterization. For the first time, in this Letter, we report on detailed neutron scattering experiments on the Q and T dependence of the magnetic relaxation rate in LiV_2O_4.

Polycrystalline samples of LiV_2O_4 were prepared by sintering a mixture of powders of $LiVO_3$ and VO with a slight excess of $LiVO_3$ in order to compensate for Li evaporation. Platinum crucibles were used for reaction of the powders at 750 °C for 10 days. In x-ray diffraction experiments we found the nominally pure fcc normal spinel structure with a lattice constant $a = 8.240(1)$ Å. From EPR and magnetic susceptibility measurements, we estimated a number of 0.1% V defects.

Quasielastic neutron scattering experiments have been performed on the time-of-flight spectrometer IN6 at the Institut Laue Langevin (ILL), Grenoble. The incoming neutron wave length was 5.1 Å. Carefully powdered polycrystalline samples were filled in a flat-plate sample holder and mounted in a cryostat, allowing for temperatures $1.5 \leq T \leq 300$ K. Since natural LiV_2O_4 contains the highly absorbing ^{6}Li isotope, a sample holder of 2 mm thickness was chosen to ensure a transmission of 85%. Additionally, a vanadium plate and an empty

sample holder were measured to account for detector efficiency and background signal, respectively. The raw data were corrected in a standard way employing standard routines of the ILL. The detectors of the spectrometer covered a scattering angle of $11° \leq 2\Theta \leq 113°$, and to analyze the Q dependence of the quasielastic signal they were binned into six groups with a mean angular step width of 17°. Good agreement of measured and calculated intensities was achieved assuming a single quasielastic Lorentzian multiplied by the detailed balance factor and convoluted with the instrumental resolution.

Figure 1 shows the dynamic structure factor $S(Q, \omega)$ at two different temperatures at low Q (Figs. 1a and 1b) and for $Q = 1.95$ Å^{-1} at $T = 80$ K (Fig. 1c). There is a large elastic ($\omega = 0$) contribution due to elastic scattering contributions. Additionally, substantial quasielastic intensities can easily be identified which decrease with increasing momentum transfer Q, thus indicating that these intensities are of magnetic origin. To parametrize our data we used a simple relaxational ansatz for the dynamic susceptibility:

$$\chi''(Q, \omega, T) = \omega \Gamma(Q, T) \frac{\chi_0(Q, T)}{\omega^2 + \Gamma^2(Q, T)}. \quad (2)$$

$\Gamma(Q)$ is the Q-dependent half width at half maximum and $\chi_0(Q, T)$ is related to the bulk susceptibility $\chi_0(T)$ via the magnetic form factor $f^2(Q)\ \chi_0(T)$. The solid lines in Fig. 1 have been calculated using Eqs. (1) and (2).

Figure 2 shows the Q dependence of the energy-integrated intensities for temperatures between 4 and 80 K. We recall that the magnetic scattering is modulated by the square of the neutron magnetic form factor $f(Q)$. The Q dependence of $f^2(Q)$ for the two possible electronic configurations of V in LiV_2O_4 is shown in the inset of Fig. 2. At $T = 80$ K, on increasing Q, the intensity decreases strongly, as can be explained by the form factor alone, indicating the importance of FM fluctuations at elevated temperatures. At low temperatures, a strong modulation of the integrated intensities appears with a maximum of the Lorentzian intensities close to a Q value equivalent to the reciprocal lattice spacing. We conclude that AFM spin fluctuations significantly contribute to the spectra at low temperatures. The existence of AFM fluctuations which vanish at elevated temperatures while FM correlations still exist have been reported for the HF system UPt_3 [10]. Of course, in LiV_2O_4 this is only a rough estimate since we cannot account for the different crystallographic directions using polycrystalline samples.

The most important result of this communication is shown in Fig. 3. A residual quasielastic linewidth $\Gamma = 0.5$ meV for $T \rightarrow 0$ followed by a square-root temperature dependence up to $T = 40$ K (solid line in Fig. 3). This behavior of the magnetic relaxation rate is the hallmark for the formation of a canonical heavy-fermion state at low temperatures in LiV_2O_4. The absence of any significant Q dependence of the linewidth within this temperature range indicates that HF behavior in LiV_2O_4 originates predominantly from local on-site Kondo interactions. As is evident from Fig. 3, a dramatic change of the magnetic response is observed for higher temperatures. At $T = 80$ K and $T = 150$ K, the quasielastic linewidth for large Q values follows the square-root behavior (solid line in Fig. 3), indicating that the single-ion (large-Q values) properties are still dominated by on-site

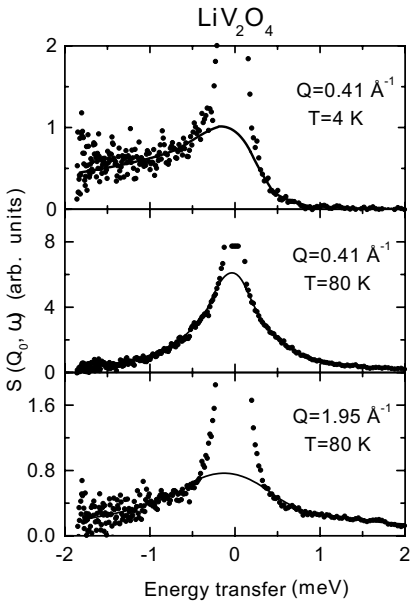

FIG. 1. Quasielastic scattering signal of LiV_2O_4 at $T = 4$ and 80 K for $Q = 0.41$ Å^{-1} and $Q = 1.95$ Å^{-1}, respectively. The data are fitted by a single quasielastic Lorentzian multiplied by the detailed balance factor and convoluted with the instrumental resolution (solid line).

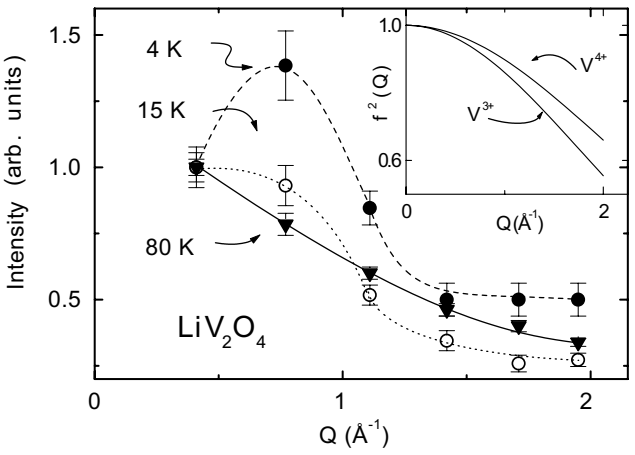

FIG. 2. Q dependence of the energy-integrated intensity of the quasielastic scattering of LiV_2O_4 at 4, 15, and 80 K, respectively. For comparison, the inset shows the Q dependence according to the square of the neutron magnetic form factor of the two vanadium configurations possible in LiV_2O_4. The maximum around $Q = 0.76$ Å^{-1} at 4 K corresponds to the reciprocal lattice spacing a^*. Dashed or dotted lines are guides to the eye.

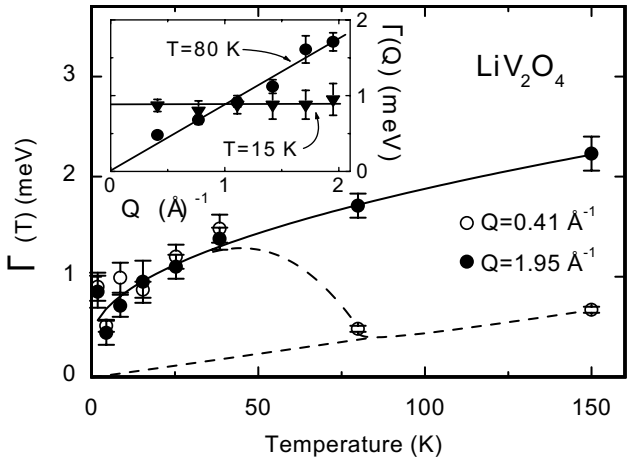

FIG. 3. Temperature dependence of the quasielastic linewidth of LiV_2O_4 for $Q = 0.41$ Å^{-1} and $Q = 1.95$ Å^{-1}, respectively. The solid line is a fit according to $\Gamma(T) = \Gamma_0 + b\sqrt{T}$ with the residual linewidth $\Gamma_0 = \Gamma(T \to 0) = 0.48$ meV, while the dashed line is a guide to the eye. The inset shows the completely different Q dependence of the width of the quasielastic scattering for $T = 80$ K and $T = 15$ K, respectively.

Kondo interactions. However, the linewidth for low-Q values reveals an abrupt decrease and an almost linear increase for further increasing temperatures (dashed line in Fig. 3). This Korringa-type behavior roughly extrapolates towards zero linewidth at zero temperature and is the characteristic feature of a local moment weakly hybridized with the band states.

Based on these experimental results, one may conclude that LiV_2O_4 is characterized by a sudden increase of the hybridization strength between local moments and band states at temperatures above 40 K. However, a closer inspection of the width of $S(Q, \omega, T)$ points towards an even more fundamental change of the magnetic properties. The dramatic change of $\Gamma(Q, T)$ is demonstrated in the inset of Fig. 3. At $T = 15$ K, the linewidth is of the order of 1 meV, independent of Q. At $T = 80$ K, a linear Q dependence has developed which extrapolates to zero linewidth for zero momentum transfer within experimental uncertainties. A linear Q dependence of the magnetic relaxation rate is expected in Fermi-liquid theory and also has been predicted in the framework of phenomenological spin fluctuation theories of weakly FM metals [11]. An almost linear Q dependence of Γ has been reported for $Pd_{0.99}Ni_{0.01}$ [12], a system which is close to a FM ground state. Following this line of evidence, LiV_2O_4 might be characterized as a metal with itinerant d electrons close to weak ferromagnetism [11]. The Q dependence of the magnetic relaxation has also been studied in HF systems. A Q dependence of Γ at low temperatures has been observed in single crystalline $CeCu_6$ by Aeppli *et al.* [13] and has been explained by intersite couplings of Kondo singlet-triplet excitations. However, in $CeCu_6$, Γ decreases upon increasing the wave vector.

The fundamental difference in the magnetic behavior for $T \leq 40$ K, on the one hand, and $T > 40$ K, on the other hand, is also reflected in the temperature dependence of the dynamic structure factor $S(Q_0, \omega_0, T)$ for fixed energy $\hbar\omega_0$ and momentum transfer Q_0, as shown in Fig. 4 in a double logarithmic plot. In a first crude approximation, $S(Q_0, \omega_0, T)$ corresponds to the spin-lattice relaxation rate $1/T_1$ in NMR experiments [14]. This is valid in the high-temperature approximation and when assuming a Q-independent hyperfine coupling. For $T > 40$ K, $S(Q_0, \omega_0, T)$ follows roughly a linear increase indicating a Korringa-type of behavior consistent with the observations of Fig. 3. This behavior is in accord neither with the ^{7}Li nor with the ^{51}V NMR results (Refs. [3], [8], and references therein) which show a decreasing spin-lattice relaxation rate on increasing temperature in this temperature range. But, of course, our results were measured at high frequencies ($\hbar\omega_0 = 0.25$ meV = 70 GHz), at low-Q values ($Q_0 = 0.41$ Å^{-1}) and in zero external field. At 40 K, precipitously strong deviations from this high-temperature Korringa behavior appear, which can be explained by a sudden onset of strong AFM intersite correlations attempting to compensate the local moments. For $T < 10$ K, $S(Q_0, \omega_0, T)$ turns into Korringa behavior again, but now with a strongly enhanced Korringa rate revealing fully compensated moments and a highly enhanced density of states characteristic of a Fermi liquid with heavy quasiparticles. Also from NMR experiments, a magnetic relaxation rate has been determined which follows a square-root temperature dependence [3,8] and is in rough agreement with our present results at high-Q values, as shown in Fig. 3.

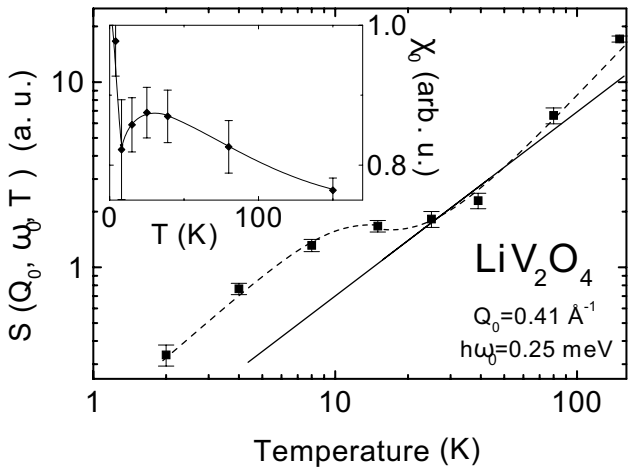

FIG. 4. Temperature dependence of $S(Q, \omega)$ of LiV_2O_4 for fixed energy transfer $\hbar\omega_0 = 0.25$ meV and fixed scattering angle (momentum transfer) $Q_0 = 0.41$ Å^{-1}. The inset shows the temperature dependence of the susceptibility as determined by integrating the quasielastic scattering intensities. For comparison, the solid line indicates linear, Korringa-type behavior, whereas the dashed line is a guide to the eye.

From $S(Q_0, \omega_0, T)$, we can directly calculate the bulk susceptibility $\chi_0(T)$ without any free parameter. The result is shown in the inset of Fig. 4. On decreasing temperatures, $\chi_0(T)$ reveals a Curie-Weiss-like increase, passes through a smooth maximum close to $T = 30$ K, and decreases towards low temperatures, closely resembling the results of Knight-shift measurements [3,8]. The strong increase at the lowest temperatures remains unexplained.

Let us summarize the experimental findings so far: The neutron scattering data provide clear experimental evidence for heavy-fermion behavior for $T \leq 40$ K with a characteristic (Kondo-lattice) temperature $T^* \approx 5 - 10$ K. The magnetic relaxation stays finite for $T \rightarrow 0$ and follows a square-root dependence with increasing temperatures. $S(Q, \omega, T)$ reveals a constant width as a function of Q. Antiferromagnetic spin fluctuations characteristic of HF systems dominate at low temperatures. The situation is less clear for $T \geq 40$ K where a dramatic change of the magnetic relaxation behavior appears. With decreasing Q, $S(Q, \omega, T)$ narrows linearly and provides some evidence that the d electrons behave almost itinerantly. $\Gamma(Q, T)$ then has to be explained assuming spin fluctuations in a weakly FM metal, i.e., such as in Pd:Ni [12]. Itinerancy of the d-electron system could possibly also resolve the problem with the paramagnetic moment which is considerably enhanced as compared to a localized $S = 1/2$ system. Fits to the high-temperature Curie-Weiss behavior result in unphysical g values of $g \approx 2.2$ [3]. However, we cannot exclude that a stable d^1 configuration exists but that long-wavelength FM spin fluctuations dominate the system. Indications of a single ion Kondo effect become evident at high-Q values only (Fig. 3).

Band-structure calculations [15] reveal that the t_{2g} states are close to the Fermi level and, due to a slight distortion of the octahedral environment, are split into a low-lying singlet and two excited doublets. For $T \leq 40$ K the d^1 electrons occupy the singlet and are strongly hybridized with the band states (0.5 electron per V site) which are formed by the excited t_{2g} levels. This, of course, is the archetypical situation for heavy-fermion formation. The dramatic change of the magnetic response could result from a change of this electronic configuration. The possible origin of this transition may be explained by an interplay of Hubbard interactions, Hund's-rule coupling, and orbital degrees of freedom.

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