Orbital state and magnetic properties of LiV$_2$O$_4$


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LiV$_2$O$_4$ is one of the most puzzling compounds among transition metal oxides because of its heavy-fermion-like behavior at low temperatures. In this paper we present results for the orbital state and magnetic properties of LiV$_2$O$_4$ obtained from a combination of density functional theory within the local density approximation and dynamical mean-field theory (DMFT). The DMFT equations are solved by quantum Monte Carlo simulations. The trigonal crystal field splits the V $3d$ orbitals such that the $a_{1g}$ and $e_{g}$ orbitals cross the Fermi level, with the former being slightly lower in energy and narrower in bandwidth. In this situation, the $d$-$d$ Coulomb interaction leads to an almost localization of one electron per V ion in the $a_{1g}$ orbital, while the $e_{g}$ orbitals form relatively broad bands with 1/8 filling. The theoretical high-temperature paramagnetic susceptibility $\chi(T)$ follows a Curie-Weiss law with an effective paramagnetic moment $p_{eff}=1.65$ in agreement with the experimental results.

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I. INTRODUCTION

Heavy-fermion (HF) materials are typically intermetallic compounds containing Ce, U, or Yb atoms. They are characterized by extraordinarily strongly renormalized effective masses $m^* \approx 100-1000 m_e$, as inferred from the electronic specific heat coefficient $\gamma(T) = C_s(T)/T$ at low temperature. They also show an apparent local moment paramagnetic behavior with a strongly enhanced spin susceptibility $\chi$ at low temperatures. The discovery by Kondo et al. of the HF behavior in LiV$_2$O$_4$ with a Kondo or spin fluctuation temperature $T_k \approx 28$ K has significant importance, because this is the first d-electron system that shows HF characteristics. Kondo et al. reported a large electronic specific heat coefficient $\gamma \approx 0.42 J/(mol K^2)$ at 1 K, which is much larger than those of other metallic transition metal compounds such as, e.g., Y$_{1-x}$Sc$_x$Mn$_2$ [$\gamma \approx 0.2 J/(mol K^2)$] and V$_{2-x}$O$_3$ [$\gamma \approx 0.07 J/(mol K^2)$]. Also a crossover from the local moment to a renormalized Fermi-liquid behavior was observed with decreasing temperature. Recently Urano et al. reported that the electrical resistivity $\rho$ of single crystals exhibits a $T^2$ temperature dependence $\rho = \rho_0 + AT^2$ with an enormous $A$, which as in conventional HF systems scales with $\gamma^2$. In the temperature range 50–1000 K the experimental magnetic susceptibility follows a Curie-Weiss law with a negative Curie-Weiss temperature, which indicates a weak antiferromagnetic (AF) V-V spin interaction (see later in the text). No magnetic ordering was observed down to 0.02 K.

These unexpected phenomena entailed numerous experiments, which confirmed the HF behavior of LiV$_2$O$_4$ in a variety of physical quantities: Johnston et al. carried out specific heat and thermal expansion measurements. Hayakawa et al. investigated Metal-Insulator transition in LiTi$_{1-x}$V$_x$O$_4$ at $x = 1$. Kondo et al. described the synthesis, characterization and magnetic susceptibility versus temperature. Onoda et al. explored spin fluctuations and transport in the spinel systems Li$_{1-x}$Mg$_x$V$_2$O$_4$ and Li$_{1-x}$Zn$_x$V$_2$O$_4$ through measurements of x-ray diffraction, electrical resistivity, thermoelectric power, magnetization, and nuclear magnetic resonance (NMR). The electron-spin resonance (ESR) and the magnetic susceptibility in pure and doped LiV$_2$O$_4$ were measured by Lohmann et al. Photo-emission studies of the hole doped Mott insulator Li$_{1-x}$Zn$_x$V$_2$O$_4$ were done by Fujimori et al. A series of Li$_{1-x}$NMR experiments were carried out by Fujiwara et al. for LiV$_2$O$_4$ and also for Li$_{1-x}$Zn$_x$V$_2$O$_4$. The Knight shift, spin susceptibility and relaxation times were determined from Li$_{1-x}$NMR experiments by Mahajan et al. Krimmel et al. presented results for the magnetic relaxation of LiV$_2$O$_4$ obtained by means of quasistatic neutron scattering. Trinkl et al. investigated spin-glass behavior in Li$_{1-x}$Zn$_x$V$_2$O$_4$. Urano et al. experimentally observed results for $C(T)$, $\chi(T)$, resistivity $\rho(T)$ and Hall coefficient $R_H(T)$ for single crystal samples. Recently, Lee et al. performed inelastic neutron scattering measurements and Fujiwara et al. studied the spin dynamics under high pressure. A review of various experiments and theoretical research is collected in the work of Johnston.

Let us summarize the experimental efforts concerning the measurements of the spin susceptibility $\chi(T)$. As mentioned before, a temperature dependent spin susceptibility $\chi(T)$ is observed in the temperature range from 50 to 1000 K, which fits well to the Curie-Weiss law $\chi(T) = \chi_0 + C/(T - \theta)$. However, depending on the quality of samples and experimental techniques, the values of the Curie constant $C$ obtained from fitting the experimental data are in the range from 0.329–0.468 cm$^3$/K/mol. More important and of direct physical importance is the value of the effective

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paramagnetic moment $p_{\text{eff}}$, which is defined via the Curie constant as $p_{\text{eff}}^2 = 3Ck_B/(N_A\mu_B^2)$. The extracted value $p_{\text{eff}}$ lies in the range between 1.62 and 2.1. The Curie-Weiss temperature obtained in those experiments is also slightly different and encompasses the interval $\theta = -20 \ldots -60$ K, which indicates a weak antiferromagnetic (AF) V-V spin interaction. If one further assumes that the effective spin value is $S=1/2$, an experimental estimation of the Landé factor $g^2 = p_{\text{eff}}/[S(S+1)]$ leads to values between 1.87 and 2.25.

From a theoretical point of view, LiV$_2$O$_4$ has been intensively studied by standard band structure calculations by various groups using different implementations of density functional theory (DFT) within the local density approximation (LDA). Anisimov et al. investigated the possibility of localization of the $d$-states in LiV$_2$O$_4$ within the linearized muffin-tin orbitals (LMTO) basis supplemented by the LDA+U method. The electronic structure was furthermore studied by Eyert et al. with the scalar-relativistic augmented spherical wave (ASW) basis, while Matsuno et al. used a full-potential, scalar-relativistic implementation of the linear augmented plane wave (LAPW) approach for the band structure calculation and furthermore applied a simple tight-binding (TB) model. Singh et al. also used the full potential LAPW (Ref. 43–45) for calculating the band structure and a TB-LMTO method to analyze the band symmetry.

A relative comparison of LiV$_2$O$_4$ and lithium titanate (LiTi$_2$O$_4$) with original HF systems was done by Varma to provide some qualitative understanding of these compounds. The two-band Hubbard model in the slave-boson mean-field approximation was applied to LiV$_2$O$_4$ by Kusunose et al. to investigate the evolution of bands due to the Coulomb interactions. Hopkinson et al. presented a simple two-band model and a $t$-$J$ model with a strong Hund’s coupling for the $d$ electrons to find evidence for a two-stage screening in LiV$_2$O$_4$. Fujimoto investigated the Hubbard chains network model on corner-sharing tetrahedra as a possible microscopic model for the HF behavior in LiV$_2$O$_4$. The competition between the Kondo effect and frustrating exchange interactions in a Kondo-lattice model within a large-$N$ approach for the spin liquid together with dynamical mean-field theory were studied by Burdin et al.

Despite all this theoretical effort, there does not yet exist an undisputed microscopic explanation of the HF behavior of LiV$_2$O$_4$ at low temperatures. It has been attempted to explain the low-temperature properties of LiV$_2$O$_4$ by a mechanism analogous to one for systems with local moments on a pyrochlore lattice, which are frustrated with respect to the antiferromagnetic interactions. An attempt to provide a microscopic model based on material properties of LiV$_2$O$_4$, which does not evoke the idea of frustration was suggested by Anisimov et al. Their basic idea is a separation of the electrons on partially filled $t_{2g}$ orbitals into localized ones, forming local moments, and delocalized ones, producing a partially filled metallic band. The hybridization between those two subsets of electrons, as in $f$-electron materials, can give rise to heavy-fermion effects. However, in this work the conclusions were based on an LDA+U calculation, which is essentially a static mean-field approximation and surely too crude to give a proper description of LiV$_2$O$_4$.

The present work reports on the investigation of the orbital state and the magnetic properties of LiV$_2$O$_4$ using the LDA+DMFT(QMC) approach. This material specific theory extracts informations about the noninteracting band structure from a DFT/LDA calculation, while treating the local Coulomb interactions via the dynamical mean-field theory (DMFT), which is a well-established nonperturbative approach to study localization effects in strongly correlated materials. The resulting DMFT equations are then solved by quantum Monte Carlo simulations. The main goal of this study is to further explore the idea of a separation of the $d$ electrons in LiV$_2$O$_4$ into two subsets, localized and itinerant as proposed in Ref. 33. The rest of the paper is divided into two parts: In the first we discuss standard DFT/LDA results (Sec. II) and then present our LDA+DMFT(QMC) results in the second (Sec. III). A short summary concludes the paper.

II. LiV$_2$O$_4$: DFT/LDA RESULTS

A. Crystal structure and $d$ orbital splitting

LiV$_2$O$_4$ has the fcc normal-spinel structure with nonsymorphic space group $Fd3m$ and was first synthesized by Reuter and Jaskowsky in 1960. The Li ions are tetrahedrally coordinated by oxygens, while the V sites are surrounded by a slightly distorted edge-shared octahedral array of oxygens (Fig. 1). The corresponding unit cell of the face-centered cubic lattice contains two LiV$_2$O$_4$ formula units (14 atoms) with four V atoms, which form a tetrahedron (Fig. 2). The LiV$_2$ substructure is the same as the C15 structure $AB_2$, where the local moments at the $B$ sites are highly frustrated. The observed lattice constant of LiV$_2$O$_4$ is 8.22672 Å at 4 K. The eight oxygen atoms in the primitive cell are situated at the 32e-type sites, at positions which are determined by the internal-position parameter $x = 0.2611$ in units of the lattice constant.

The total space group of the crystal is cubic but the local point group symmetry of the V ion crystallographic position...
is trigonal $D_{3d}$. The different trigonal axes of every V atom in the unit cell are directed toward the center of the tetrahedron (Fig. 2). Since the formal oxidation state of V is non-integer V$^{3.5+}$ (configuration $d^{11.5}$) and the V ions are crystallographically equivalent, LiV$_2$O$_4$ must be metallic as it is observed.$^{52}$

The octahedral crystal field at the V sites in the spinel structure splits the V $3d$ bands into three degenerate and partially filled $t_{2g}$ bands and two empty $e^\sigma_g$ bands. The Fermi level lies within the $t_{2g}$ complex, thus the transport properties of LiV$_2$O$_4$ are solely associated with the $t_{2g}$ bands. The trigonal symmetry of the V ions splits the cubic $t_{2g}$ levels into one $a_{1g}$ and two degenerate $e^\pi_g$ levels (Fig. 3). However, this splitting is not large enough to separate the $t_{2g}$ band into two subbands.$^{38}$

B. DFT/LDA band structure

Based on DFT/LDA (Refs. 31,32) within the LMTO method,$^{34}$ we performed first-principle calculations of the electronic structure of LiV$_2$O$_4$. The radii of the muffin-tin spheres were $R_V=2.00$ a.u., $R_O=2.05$ a.u., and $R_O = 1.67$ a.u. The resulting densities of states (DOS) are shown in Figs. 4 and 5. In Fig. 4, there are three well-separated sets of bands: completely filled O-2$p$ bands, partially filled $t_{2g}$ bands, and empty $e^\pi_g$ bands. The bands in the energy range from $-8$ eV to $-3$ eV originate mainly from O-2$p$ states and have only small admixtures from V-3$d$ states. The upper two groups of bands, which extend from $-1.0$ to 0.8 eV and from 2.3 to 3.2 eV, are predominantly derived from the V-3$d$ states. Although additional small O-2$p$ contributions are apparent in this energy range, the $p-d$ hybridization is much reduced compared to other early transition metal oxides.$^{55}$ Due to the crystal field of the slightly distorted octahedral coordination of the V atoms by the oxygen atoms, a clear separation of the $3d$ $t_{2g}$ and $e^\pi_g$ groups of bands is visible in Fig. 4. Whereas the former states appear exclusively around the Fermi energy, the $e^\pi_g$ states prevail at higher energies. Contributions of the V $3d$ states to the oxygen-derived bands originate almost exclusively from the $e^\pi_g$ states, which form $\sigma$ bonds and experience a strong overlap with the O-2$p$
states. In contrast, the \( t_{2g} \) orbitals, which give rise to \( \pi \) bonds, yield only a negligible contribution in this energy range. In addition to \( p-d \) bonds, the \( t_{2g} \) states experience strong \( \sigma \)-type overlap with the \( t_{2g} \) orbitals at neighboring vanadium sites of the fcc sublattice. Hence, these \( d \) states take part in two different types of bonding, namely, \( \sigma \)-type V-V and \( \pi \)-type V-O bonding, which leads to two different bandwidths for \( t_{2g} \) and \( e^g \) states. Since both the metal-metal and metal-oxygen bonds are mediated through the same orbital, a simple analysis of the partial DOS would not allow to distinguish the different roles played by the \( t_{2g} \) orbitals. Eyert et al.\textsuperscript{36} used a local coordinate system with the \( Z \) axis along the trigonal direction (111) pointing towards the center of the tetrahedron formed by V ions (see Fig. 2) and plotted the \( V d_{3z^2-r^2}, d_{xy}, d_{xz}, \) and \( d_{x^2-y^2} \) partial DOS. While \( d_{3z^2-r^2} \) orbitals are of pure \( t_{2g} \) character, the other four orbitals comprise a mixture of \( t_{2g} \) and \( e^g \) states. We have calculated the partial DOS for \( a_{1g} \) and \( e^g \) orbitals, using the irreducible representations of the \( D_{3d} \) group according to Terakura et al.\textsuperscript{36} with the following linear combinations of the \( t_{2g} \) cubic harmonics: the \( a_{1g} \) orbital is given by \((xy + xz + yz)/\sqrt{3}\) and the two \( e^g \) orbitals by \((zx - yz)/\sqrt{2}\) and \((yz + 2zx - 2xy)/\sqrt{6}\). These three particular linear combinations are valid if the coordinate axes \( X, Y, \) and \( Z \) are directed along V-O bonds. If the \( Z \) direction is chosen along one of the trigonal axes described above, then the \( a_{1g} \) orbital is the \( 3z^2-r^2 \) orbital in the local coordinate system.

The projected partial LDA DOS of the \( a_{1g} \) and the \( e^g \) orbitals are shown in Fig. 5. The bandwidth of the \( a_{1g} \) orbital \( W_{a_{1g}} = 1.35 \) eV is almost a factor of 2 smaller than the \( e^g \) bandwidth \( W_{e^g} = 2.05 \) eV. Nonetheless, we found within LDA for all three \( t_{2g} \) derived orbitals nearly the same occupancies: \( n_{a_{1g}} = 0.60 \) and \( n_{e^g} = 0.45 \). Almost all spectral weight of the \( a_{1g} \) orbital is concentrated around the Fermi level in the region from \(-0.2\) to \(0.3\) eV. In contrast to the \( a_{1g} \) orbital the \( e^g \) DOS is flat at the Fermi level. The largest part of the spectral weight of the \( e^g \) orbitals is situated in the interval from \(0.3\) to \(0.85\) eV. Despite such a different spectral weight the \( a_{1g} \) and \( e^g \) bands are not completely separated in energy. However, there is a significant difference in the centers of gravity calculated from the corresponding partial DOS, which can be interpreted as a measure for the trigonal splitting of the \( t_{2g} \) states.

The trigonal splitting is much smaller than the bandwidth but has a great importance for the understanding of the physics of the \( \text{LiV}_2\text{O}_4 \) system in the presence of strong Coulomb interaction. The value and the sign of the trigonal splitting will determine the orbital in which the \( V 3d \) electrons should be localized when a strong Coulomb interaction, which is larger than the bandwidth, is taken into account.\textsuperscript{33} We found that this trigonal splitting value is very sensitive to the accuracy of the band structure calculations. In order to increase the accuracy, the overlap between atomic spheres in our LMTO calculation was set to zero and more empty spheres were introduced. For the following we define the trigonal splitting of the \( t_{2g} \) states as the difference of the centers of gravity of the \( a_{1g} \) and the \( e^g \) projected DOS. We find that the \( a_{1g} \) center of gravity is \(0.26\) eV lower than that of the \( e^g \) band (\( e_{a_{1g}} = 0.14\) eV, \( e_{e^g} = 0.40\) eV; see Fig. 5). One can thus conclude from our LDA calculations that the \( a_{1g} \) orbital is more favorable for the localization of electrons.

The effective mass \( m^* \) is known to be a measure for the Coulomb correlations and can be obtained from the electronic specific heat coefficient \( \gamma \) at low temperatures. From the LDA-calculated electronic specific heat coefficient \( \gamma_{\text{LDA}} \), one can infer the ratio of the effective mass to the band mass \( m^*/m_b = \gamma/\gamma_{\text{LDA}} \). Here, the former is related to the LDA DOS at the Fermi level via \( \gamma_{\text{LDA}} = \pi^2 k_b^2 n(A)(E_F)/3 \), and \( \gamma \) is the experimental value of the electronic specific heat coefficient taken from.\textsuperscript{3} For \( \text{LiV}_2\text{O}_4 \) we found \( m^*/m_b = 25.8 \), which is in good agreement with previous results.\textsuperscript{38} Such a huge enhancement of the quasiparticle mass \( m^* \) is a strong evidence that Coulomb correlations are important in \( \text{LiV}_2\text{O}_4 \) and have to be taken into account in order to describe the physics of this system.

III. A MICROSCOPIC THEORY FOR LiV\(_2\)O\(_4\)

A. LDA+DMFT(QMC) scheme

Based on the \( d = \infty \) limit,\textsuperscript{57} the dynamical mean-field theory (DMFT) (Refs. 58–60) was developed as a nonperturbative approach to describe strongly correlated electron systems. It permits the calculation of electronic spectra for systems with local electronic Coulomb correlations. The LDA+DMFT approach is a merger of the DFT/LDA and the DMFT techniques.\textsuperscript{61,62} It combines the strength of the DFT/LDA, viz describing the weakly correlated part of the \textit{ab initio} Hamiltonian, i.e., electrons in \( s \) and \( p \) orbitals and the long-range part of the Coulomb interaction, with the ability of the DMFT to treat electronic correlations induced by the local Coulomb interaction. In this paper we will only briefly discuss the relevant parts of the LDA+DMFT approach and refer the reader to a recent report by Held et al.\textsuperscript{63} for more details.

For a given material, one can extract a LDA Hamiltonian \( \hat{H}_{\text{LDA}}^0 \) and supplement the local Coulomb interactions

\[
\hat{H} = \hat{H}_{\text{LDA}}^0 + \sum_m \sum_i \langle n_m \r_i \rangle \hat{n}_m \r_i + \sum_i \sum_{\sigma \sigma'} \langle U' \delta_{\sigma \sigma'} \hat{n}_{\sigma \r_i} \hat{n}_{\sigma' \r_i} \rangle .
\]

Here, the index \( i \) enumerates the \( V \) sites, \( m \) denotes the individual \( t_{2g} \) orbitals, and \( \sigma \) the spin. \( \hat{H}_{\text{LDA}}^0 \) is a one-particle Hamiltonian generated from the LDA band structure with an averaged Coulomb interaction subtracted to avoid a double counting of the Coulomb interaction.\textsuperscript{61} \( U \) is the local intraorbital Coulomb repulsion and \( J \) the exchange interaction. The local interorbital Coulomb repulsion \( U' \) is then fixed by rotational invariance: \( U' = U - 2J \). The actual values for \( U \) and \( U' \) can be obtained from an averaged Coulomb parameter \( \bar{U} \) and Hund’s exchange \( J \), which can be calculated with LDA. The quantity \( \bar{U} \) is related to the Coulomb parameters \( U \) and \( U' \) via

\[
\bar{U} = U - \frac{3}{2} J.
\]
\[
\bar{U} = \frac{U + (N_{\text{orb}} - 1)U' + (N_{\text{orb}} - 1)(U' - J)}{2N_{\text{orb}} - 1},
\]

where \(N_{\text{orb}}\) is the number of interacting orbitals (\(N_{\text{orb}} = 3\) in our case). Since \(U\) and \(U'\) are not independent, the two values \(\bar{U}\) and \(J\) are sufficient to determine \(U\) from this relation.\(^{65,69}\)

The DMFT maps the lattice problem (1) onto an effective, self-consistent impurity problem. A reliable method to solve this (multiband) quantum impurity problem is provided by quantum Monte Carlo (QMC) simulations,\(^64\) which are combined with the maximum entropy method\(^{65}\) for the calculation of spectral functions from the imaginary time QMC data. This technique has been applied to calculate properties of several transition metal oxides.\(^{66,68,70}\)

A computationally important simplification is due to the fact that in cubic spinel the \(t_{2g}\) states do not mix with the \(e_{g}^{\pi}\) states. In this particular case the self-energy matrix \(\Sigma_{m\sigma}(z)\) is diagonal with respect to the orbital and spin indices. Under this condition the Green functions \(G_{m\sigma}(z)\) of the lattice problem can be expressed in the DMFT as Hilbert transform of the noninteracting DOS \(N_{m}^{0}(\epsilon)\),

\[
G_{m\sigma}(z) = \int d\epsilon N_{m}^{0}(\epsilon) \frac{e^{\mu_{B}z\sigma - \Sigma_{m\sigma}(\epsilon)} - e^{-\epsilon}}{\epsilon}.
\]

This procedure avoids the rather cumbersome and problematic \(k\) integration over the Brillouin zone by the analytical tetrahedron method.\(^{71}\) The LDA DOS \(N_{m}^{0}(\epsilon)\) for different orbitals (different \(m\)) of the \(3d\) \(t_{2g}\) states in LiV\(_2\)O\(_4\) is displayed in Fig. 5.

A particularly interesting quantity for LiV\(_2\)O\(_4\) is the magnetic susceptibility \(\chi(T)\). In order to calculate \(\chi(T)\) we use the definition \(\chi(T) = \lim_{B \rightarrow 0} M(T)/B\), where \(M(T)\) is the magnetization due to the applied magnetic field \(B\). Obviously, \(M(T)\) can be obtained directly from the QMC data via

\[
M(T) = \mu_{B} \sum_{m=1}^{N_{\text{orb}}} \langle n_{m} \rangle - \langle n_{m} \rangle
\]

and

\[
\langle n_{m\sigma} \rangle = G_{m\sigma}(\tau = 0^+) .
\]

Since QMC results are subject to both statistical and systematic errors, a direct evaluation of \(M(T)/B\) for small \(B\) will inevitably lead to unpredictable scattering of the results for \(\chi(T)\). To avoid these problems, we perform calculations for \(M(T,B)\) for a series of small fields \(B\) and extract \(\chi(T)\) from a least-squares fit as the slope of \(M(T,B)\) as \(B \rightarrow 0\).

### B. Single-particle properties

The DMFT calculations are based on the DFT/LDA-DOS \(N_{m}^{0}(\epsilon)\) for the \(a_{1g}\) and \(e_{g}^{\pi}\) orbitals presented in Fig. 5. The total number of electrons in these three orbitals was fixed to \(n = 1.5\), in accordance with the +3.5 valency of V ions in LiV\(_2\)O\(_4\). The \(d-d\) Coulomb interaction parameter \(\bar{U} = 3.0\) eV and exchange Coulomb interaction parameter \(J = 0.8\) eV were calculated\(^{33}\) by the constrained LDA method.\(^{72}\) The temperature used in our QMC simulations was approximately 750 K. While the scheme in principle poses no restrictions on the temperature values, the QMC code used presently limits our calculations to these rather high temperatures because of computing power limitations.\(^{66}\)

The partial DOS of \(a_{1g}\) and \(e_{g}^{\pi}\) orbitals obtained from the analytical continuation of the QMC results are shown in Fig. 6. In comparison with the non-interacting case (see Fig. 7), a considerable transfer of spectral weight has taken place, especially the \(a_{1g}\) orbital appears to be strongly renormalized by Coulomb interactions. Furthermore, in contrast to the LDA results, where the occupation of the \(a_{1g}\) and \(e_{g}^{\pi}\) orbitals is roughly the same, the DMFT yields \(n_{a_{1g}} \approx 0.9\) and \(n_{e_{g}^{\pi}}\) roughly the same, the DMFT yields \(n_{a_{1g}} \approx 0.9\) and \(n_{e_{g}^{\pi}}\) roughly the same.
The main result of this calculation was the localization of one electron per V ion in the \( a_{1g} \) orbital and \( e_g^\pi \) orbitals. The possible single-particle excitations of the \( a_{1g} \) orbital with \( \omega_0 < 0 \) have two distinct contributions, namely one of the usual type “singly occupied \( \rightarrow \) unoccupied,” and a second that actually involves a doubly occupied state build of a mixture of \( a_{1g} \) and \( e_g^\pi \) states, i.e., a mixed-valent state. The energy of this latter excitation is given directly by the trigonal splitting, i.e., this feature can also serve as a means to extract this number from photoemission experiments.

That the excitations listed in Table II directly map to the peaks in the DOS Fig. 6 can be shown by using another technique to solve the DMFT equations, namely resolvent perturbation theory and NCA (see, e.g., Ref. 69). This approach allows for a direct identification of different excitation channels (i.e., different initial particle numbers) and a distinction between \( a_{1g} \) and \( e_g^\pi \) states. The result is shown in Fig. 9, where the black lines denote \( a_{1g} \) and the gray ones \( e_g^\pi \) single-particle excitations. Full lines stand for a singly occu-

### Table I. Eigenstates and eigenenergies of the atomic Hamiltonian for total occupations less or equal to 2. \( \epsilon_{a_{1g}} \) denotes the one particle energy of the \( a_{1g} \) orbital and \( \Delta \epsilon = 0.26 \text{ eV} \) the trigonal splitting between \( a_{1g} \) and \( e_g^\pi \) orbitals.

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<tr>
<th>( a_{1g} )</th>
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### Table II. Single-particle excitations for the atomic model filled with 1.5 electrons. For spin-degenerate processes only one representative is listed.

<table>
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C. Paramagnetic susceptibility: Competition of two exchange processes

The LDA+DMFT(QMC) result that roughly one electron is localized in the $a_{1g}$ orbital has several immediate consequences, which can be tested with experimental findings. A rather direct consequence is that the electron localized on the $a_{1g}$ orbital leads to a local moment corresponding to $S = 1/2$ per vanadium atom and thus a Curie-like susceptibility, consistent with experiment. The remaining 0.5 electrons per V ion in the metallic $e_g$ band will lead to a small and temperature independent Pauli contribution to the susceptibility.

From an experimental point of view, the magnetic properties of LiV$_2$O$_4$ pose several puzzles. LiV$_2$O$_4$ exhibits a paramagnetic Curie-Weiss susceptibility $\chi(T) = C/(T-\theta) + \chi_0$, in the temperature range 50–1000 K. The best fit to the experimental data is obtained under the assumption that the magnetic susceptibility $\chi(T)$ is the sum of a Curie-Weiss and a $T$-independent part $\chi_0$, which contains Pauli paramagnetic, core diamagnetic and orbital Van Vleck contributions to the total susceptibility. If all V-3$d$ electrons (1.5 per V ion) would equally contribute to the formation of a local moment, one would expect a mixture of $S=1$ and $S'=1/2$ vanadium ions and consequently an effective paramagnetic moment 2.34. If only one localized electron in the $a_{1g}$ orbital contributes to the Curie constant the effective paramagnetic moment is 1.73. However, the experimentally observed values of the Curie constants, as discussed above, in general are close to the latter value of the effective paramagnetic moment or slightly larger. Under the assumption that the local spin $S$ is exactly 1/2 one gets a slightly enhanced $g$ factor from experiment. Whereas the negative Curie-Weiss temperature in the range $\theta = -20 \cdots -60$ K indicates antiferromagnetic interactions between local $S=1/2$ moments, the large $g$ value points towards ferromagnetic interactions between local moments and conduction electrons.

A similar ambiguity is revealed by the results of $^7$Li NMR measurements. The spin-lattice relaxation rate $1/T_1(T)$ shows a broad maximum around 30–50 K and becomes almost temperature independent above 400 K. The high-temperature data ($T \geq 50$ K) have been interpreted either as an indication of localized magnetic moments or, on the contrary, as characteristics of an itinerant electron system close to a ferromagnetic instability.

The debate on the relevant magnetic interactions was continued after the spin fluctuation spectrum of LiV$_2$O$_4$ was determined by means of quasielastic neutron scattering. These neutron data showed a transition from ferromagnetic correlations at elevated temperatures ($T \geq 40$ K) to antiferromagnetic spin fluctuations with a wave vector $q = 0.7 \, \text{Å}^{-1}$ at low temperatures ($T \leq 40$ K), as shown in Fig. 10. However, a subsequent inelastic neutron scattering study on LiV$_2$O$_4$ reported the continuous evolution of antiferromagnetic fluctuations out of a high-temperature paramagnetic state without indications of ferromagnetic interactions at elevated temperatures.

In order to clarify these inconsistencies, most recently, a polarized neutron scattering study on a set of LiV$_2$O$_4$
peratures (Tmagnetic) next nearest neighbor spin correlations at high temperatures show a temperature induced cross-over from purely ferromagnetic to predominantly antiferromagnetic correlations at low temperatures. The measured magnetic cross-section has been fitted within our LDA/DMFT calculation, thus giving further experimental confirmation of our proposed picture of a separation of the vanadium d states into a strongly correlated a1g orbital with one localized electron and weakly localized e2g orbitals which form a metallic band filled with ~0.5 electrons.

The evolution of antiferromagnetic spin correlations with q~0.7 Å⁻¹ at low temperatures is now experimentally well established. However, the temperature-induced cross-over from ferromagnetic to RKKY-like spin correlations is still unclear at present.

We performed LDA+DMFT(QMC) calculations of the high-temperature magnetic susceptibility for a set of different inverse temperatures β=5, 7, 9, 10, 11, 12, 13 eV⁻¹ and magnetic fields B=0.005, 0.01, 0.02 eV. The results are shown as triangles and diamonds for a Hund’s exchange coupling J=0.8 eV and J=0, correspondingly, in Fig. 11 together with a fit to a Curie-Weiss law

\[
\chi(T) = N_e k_B \frac{\mu^2_B \rho_{eff}^2}{3k_B(T-\theta)}.
\]

The resulting value of the Curie-Weiss temperature is θ~640 K for J=0.8 eV, the fitted Curie-Weiss constant C gives an effective magnetic moment \( \rho_{eff} = 8^2 S(S+1) = 2.71 \) which corresponds to an effective paramagnetic moment \( p_{eff} = 1.65 \). The deviation from \( p_{eff} = 1.73 \) for a spin \( S = 1/2 \) can be accounted for if one recalls that the occupancy of the \( a_{1g} \) orbital is not exactly 1 but 0.88. Such a reduced
occupancy should ideally lead to a decrease of $p_{\text{eff}}$ from 1.73 to 1.52. The slightly larger (calculated) value $p_{\text{eff}}=1.65$ is due to contributions from the $e_g$ states. For the calculation with $J=0$, where $a_{1g}$ and $e_g$ orbitals do not couple via a local exchange interaction the value of the effective paramagnetic moment is 1.3, which agrees with the expectations if one takes into account that for $J=0$ the occupancy of the $a_{1g}$ orbital is 0.75, and hence $p_{\text{eff}}=1.73\times0.75=1.3$.

While our value of $p_{\text{eff}}$ is in good agreement with known experimental data, the large ferromagnetic Curie-Weiss temperature of about 640 K is in contrast with experiment. A similar result was obtained by Anisimov et al.,33 where a rather strong effective ferromagnetic intersite exchange parameter $J_{\text{dir}}=530$ K (which is the sum of direct and double exchanges) was obtained. A ferromagnetic exchange coupling between local moments in LiV$_2$O$_4$ can be readily understood in the double exchange picture. The presence of two types of $d$ electrons, localized ones forming local moments and delocalized ones producing a partially filled, relatively broad band, is a necessary ingredient for the double exchange mechanism, resulting in a strong ferromagnetic coupling between local moments. This requirement is fulfilled in the case of LiV$_2$O$_4$ with one electron localized in the $a_{1g}$ orbital and a 1/8 filled broad $e_g^\pi$ band.

A second important condition for the double exchange mechanism is Hund’s intra-atomic exchange, i.e., the ferromagnetic exchange interaction between electrons within the $t_{2g}$ states. If one switches off this intra-atomic exchange interaction, the double exchange mechanism will be switched off, too. This becomes apparent from the result of our calculations for $\chi^{-1}(T)$ with Hund’s exchange $J$ equal to zero (see Fig. 11, diamonds). Again, we obtain a Curie-Weiss-like behavior with $p_{\text{eff}}=1.3$. This time, however, the Curie-Weiss temperature $\theta_{\text{dir}}\approx-450$ K is negative, i.e., pointing to an effective antiferromagnetic exchange. In the absence of intra-atomic exchange and $a_{1g}\cdot e_g^\pi$ hybridization, the only contribution to an exchange coupling can arise from the direct hybridization between the $a_{1g}$ electrons. Obviously, this will result in the observed antiferromagnetic exchange coupling.

These results clearly show that, neglecting the $a_{1g}\cdot e_g^\pi$ hybridization, one has to expect a subtle competition in LiV$_2$O$_4$ between antiferromagnetic direct exchange and ferromagnetic double exchange from the $e_g^\pi\cdot e_g^\pi$ hybridization. Obviously, for the present set of Coulomb parameters the ferromagnetic contribution wins in our DMFT calculations. Note, that this result is a direct consequence of the value of J used in our calculations. There are also available experimental results from high-energy spectroscopy, which lead one to expect a value of $J=0.65\cdots0.7$ eV (Ref. 75) instead of $J=0.8$ eV used in our calculation. We found that such a smaller value of $J$ does not change our results significantly.

There is, however, an important part missing in our present calculation. Since we use the LDA DOS and not the full Hamiltonian in the DMFT calculations, the $a_{1g}\cdot e_g^\pi$ hybridization is neglected completely. As has been pointed out by Anisimov et al.,33 this hybridization can give rise to an antiferromagnetic Kondo coupling between $a_{1g}$ and $e_g^\pi$ orbitals and its value was estimated to be $J_K=-630$ K.33

Thus, in LiV$_2$O$_4$ there are possibly three important exchange interactions present between the $a_{1g}$ and $e_g^\pi$ electrons of the V 3$d$ shell: ferromagnetic double exchange ($J_{\text{dir}}=1090$ K), antiferromagnetic direct exchange ($J_{\text{dir}}=\approx-450$ K) and antiferromagnetic Kondo exchange ($J_{\text{dir}}=\approx-630$ K (Ref. 33) not taken into account in our calculation). All these interactions effectively cancel, eventually leading to a small Curie-Weiss temperature of the order of 0 K in accordance with experiment. Finally, one puzzle remains, namely, that the data from neutron scattering experiments show ferromagnetic spin fluctuations at high temperatures.18,76

The competing exchange terms described above may also explain the change from antiferromagnetic to ferromagnetic spin fluctuations at $T=40$ K found in neutron scattering experiments. This is about the same energy scale as the coherence temperature of the Kondo lattice.33 Thus, one might argue that, while below $T_{\text{coh}}$ the combined antiferromagnetic direct and Kondo exchanges are stronger than the ferromagnetic double exchange, this changes above $T_{\text{coh}}$, where the Kondo effect becomes ineffective, such that the ferromagnetic exchange prevails.

IV. CONCLUSION

We investigated the effect of Coulomb correlations on the electronic structure, orbital state and magnetic properties of LiV$_2$O$_4$. The analysis of the noninteracting partial densities of state obtained by standard LDA calculations shows that, while the trigonal splitting of the $t_{2g}$ states into $a_{1g}$ and $e_g^\pi$ orbitals is not strong enough to produce separate bands, it leads to a significant difference in the effective bandwidths and average energy of the trigonal orbitals. The LDA + DMFT(QMC) calculations gave orbital occupancies and spectra which indicate a nearly complete localization of one electron out of 1.5 $3d$ electrons per V ion in the $a_{1g}$ orbital, while the $e_g^\pi$ orbitals form a relatively broad partially filled metallic band. The calculated temperature dependence of the paramagnetic susceptibility corresponds to the experimentally observed Curie-Weiss law and gives an effective paramagnetic moment $p_{\text{eff}}=1.65$ in agreement with experimental data. The experimentally observed small value of the Curie-Weiss temperature, formerly a puzzle, is supposed to be the result of a competition between three different contributions to the effective exchange interaction between $a_{1g}$ and $e_g^\pi$ electrons in the V 3$d$ shell: ferromagnetic double exchange, antiferromagnetic direct exchange and antiferromagnetic Kondo exchange described in Ref. 33. The present calculations show a dominance of the first two exchanges. We suppose that including the hybridization between $a_{1g}$ and $e_g^\pi$ (next step of our research), can lead to an almost cancellation of all three exchanges and the experimentally observed small residual antiferromagnetic Curie-Weiss temperature might become possible.
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Recently the Curie-Weiss law was derived analytically in dynamical mean-field theory for the Hubbard model [K. Byczuk and D. Vollhardt, Phys. Rev. B 65, 134433 (2002)].

Experimental data were interpreted as a sum of Pauli and Curie-Weiss paramagnetic contributions to the susceptibility (Ref. 17). However, for high temperatures the dominant contribution is of Curie-Weiss type. As DMFT calculations were done for very high temperatures (1000 K and more), we neglected Pauli contribution in our analysis of calculated data.
