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Electronic structure and magnetic interactions in $\mathrm{LiV_2O_4}$

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Abstract. – We present results of all-electron electronic structure calculations for the recently discovered d electron heavy fermion compound $\mathrm{LiV_2O_4}$. The augmented spherical wave calculations are based on density functional theory within the local density approximation. The electronic properties near the Fermi energy originate almost exclusively from V $3d$ t_{2g} states, which fall into two equally occupied subbands: While σ-type metal-metal bonding leads to rather broad bands, a small π-type p-d overlap causes a narrow peak at E_F. Without the geometric frustration inherent in the crystal structure, spin-polarized calculations reveal an antiferromagnetic ground state and ferromagnetic order at slightly higher energy. Since direct d-d exchange interaction plays only a minor role, ordering of the localized vanadium moments can be attributed exclusively to a rather weak superexchange interaction. With the magnetic order suppressed by the geometric frustration, the remaining spin fluctuations suggest an explanation of the low-temperature behaviour of the specific heat.

The magnetic porperties of the metallic spinel structure transition metal oxide $\mathrm{LiV_2O_4}$ have remained an unresolved issue for some time [1-4]. Apart from a temperature-independent contribution, the susceptibility was found to follow a Curie-Weiss law due to local V magnetic moments [3,4]. The negative Weiss temperature of -63 K indicates antiferromagnetic exchange interactions between the vanadium spins [3]. However, a transition to long-range magnetic order above 1.8 K could be excluded from both susceptibility and ^{7}Li NMR measurements [4,5]. This apparent contradiction was attributed to possible geometric frustration inherent in the vanadium sublattice of the normal spinel structure with only nearest-neighbour interaction, which might prohibit long-range antiferromagnetic order [4, 6].

Recently, Kondo *et al.* reported a crossover from localized moment to heavy Fermi-liquid behaviour with a Kondo temperature of $T_\mathrm{K} \approx 28$ K and an electronic specific heat coefficient of $\gamma \approx 0.42$ J/mol K^2 at 1 K [5, 7]. Thus for the first time heavy-fermion (HF) behaviour, characteristic of f electron systems, has been observed in a d electron material. Below 30 K, the resistivity exhibited a pronounced smooth downturn consistent with Kondo lattice behaviour [5]. The nearly temperature-independent susceptibility and the ^{7}Li Knight shift in the low-temperature range [4, 5, 8] were interpreted as due to the disappearance of the V local moments. Neither static magnetic order nor superconductivity was observed above 0.02 K [5]. Yet, low-temperature μSR data displayed anomalies indicative of static spin freezing below 0.8 K [5, 9]. The specific heat shows an upturn between 0.8 and 0.5 K, which might point to a $T^3 \ln T$ dependence characteristic of large spin fluctuations [10]. Low-temperature ^{7}Li and ^{51}V NMR data likewise showed deviations from uniform heavy Fermi-liquid behaviour [11-13]. From neutron diffraction experiments, structural transitions between 4 and 295 K could be excluded [14]. In addition, these measurements revealed a large electronic Grüneisen parameter comparable to that of f electron HF compounds, which indicates strong coupling of the electronic and lattice degrees of freedom [14, 7]. In contrast to the f electron systems, however, where HF behaviour as well as long-range antiferromagnetic order result from the hybridization of localized and bandlike orbitals, the origin of the electron-lattice coupling and the mechanisms leading to HF formation in the d band metal LiV_2O_4 are as yet unclear [14].

In this letter, we present for the first time results of all-electron first-principles calculations for LiV_2O_4. Our extensive study is based on density functional theory (DFT) within the local density approximation (LDA) [15]. As a calculational scheme we used the scalar-relativistic augmented spherical wave (ASW) method [16]. As a result, we find i) a superposition of narrow and broad bands at the Fermi energy. Allowing for magnetic ordering of the vanadium moments, we obtain ii) an antiferromagnetic ground state resulting from weak superexchange coupling, which is accompanied by ferromagnetic order at a slightly elevated energy. Due to the geometric frustration only large spin fluctuations remain, while the reduced overlap of the magnetic orbitals points to a possible localization transition.

LiV_2O_4 crystallizes in the normal spinel structure, which is based on an fcc lattice with space group $Fd\bar{3}m$ (O_h^7) [6, 17]. We used the values of $a = 8.22672$ Å for the lattice constant and $x_{\rm O} = 0.26111$ for the oxygen parameter as resulting from the 4 K neutron diffraction data [14]. In the normal spinel structure, the oxygen atoms form an almost perfect cubic close-packed sublattice with tetrahedral and octahedral interstices. The lithium atoms occupy 1/8 of the tetrahedral sites whereas the vanadium atoms occupy half of the octahedral sites and form two interpenetrating fcc sublattices of corner-sharing tetrahedra with a V-V bond length of 2.9 Å [6]. Due to cation ordering, the crystal field at the transition metal sites is trigonal rather than cubic. The deviation of the oxygen $x_{\rm O}$ parameter from the ideal value 0.25 causes a shift of 0.158 Å in $\langle 111 \rangle$ direction, which enlarges/compresses the available volume at the tetrahedral/octahedral sites; the V-O distance is decreased by 4.6%. At the same time, the V-O-V bond angle changes to 95.2°.

Figure 1 displays the dominant partial densities of states (DOS). States not included play only a negligible role in the energy interval shown. Three groups of bands are identified: While bands in the energy range from -8 to -3.3 eV originate mainly from O $2p$ states and have only a small admixture from V $3d$ states, the upper two groups of bands, which extend from -1.3 to 0.8 eV and 2.4 to 3.4 eV, are predominantly derived from the V $3d$ states. Although additional O $2p$ contributions are apparent in this energy range, p-d hybridization is much reduced as compared to other early transition metal oxides [18]. As concerns the occupied states our findings are in good agreement with the photoemission data [19]. Octahedral crystal field splitting, as expected from the nearly cubic coordination of the V atoms by the oxygen atoms, leads to clear energetical separation of the $3d$ t_{2g} and e_g groups of bands as is visible in fig. 1. Whereas the former states appear exclusively around $E_{\rm F}$, the e_g states dominate at higher energies. Contributions of the V $3d$ states to the oxygen-derived bands originate

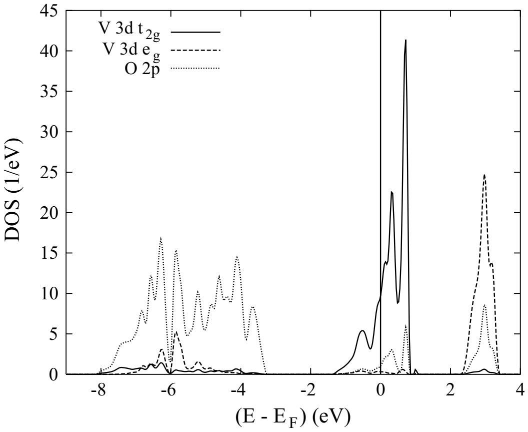

Fig. 1. – Partial densities of states (DOS) of LiV_2O_4 per unit cell.

almost exclusively from the e_g states, which, forming σ bonds, experience a larger overlap with the O $2p$ states. In contrast, the t_{2g} orbitals, which give rise to π bonds, yield only a negligible contribution in this energy range. In addition to these rather weak *p*-*d* bonds, the t_{2g} states experience, however, strong σ-type overlap with the t_{2g} orbitals at neighbouring vanadium sites of the fcc sublattice. Hence, these *d* states take part in two different types of bonding, namely σ-type V-V- and π-type V-O-bonding, which leads to two different band widths. Nevertheless, since both the metal-metal and the metal-oxygen bonding are mediated by the *same* orbitals, a simple analysis of the partial DOS would not allow to distinguish the different roles played by the t_{2g} orbitals.

We solved this problem by complementing the calculations for the observed crystal structure ($x_{\rm O} = 0.26111$) with another set, where the oxygen positional parameter was hypothetically adjusted to its ideal value of $x_{\rm O} = 0.25$. Since this leaves the vanadium-vanadium bonding unaffected, the changes of the electronic structure due to the oxygen shift allow to make the afore-mentioned distinction. The results are shown in fig. 2, where we display the partial DOS for the V $3d$ dominated bands. We used the trigonal representation of the fcc lattice and plotted the V $d_{3z^2-r^2}$, $d_{xz} + d_{yz}$ and $d_{x^2-y^2} + d_{xy}$ partial DOS. While the $d_{3z^2-r^2}$ orbitals, which correspond to the a_{1g} orbitals in a trigonal crystal field, point along the $\langle 111 \rangle$ direction and are of pure t_{2g} character, the other four orbitals comprise a mixture of t_{2g} and e_g states. However, the latter states are dominated by the d_{xz} and d_{yz} orbitals, which are almost empty.

For $x_{\rm O} = 0.26111$ we observe a clear separation of the t_{2g} states into an ≈ 2.1 eV wide group formed by the $d_{x^2-y^2}/d_{xy}$ states and another group due to the much narrower $d_{3z^2-r^2}$ bands, which, apart from the peak at 0.7 eV, extend over an energy range of only 0.6 eV. On the other hand, for the idealized structure this difference of the band widths is removed due to the striking change of the $d_{3z^2-r^2}$ partial DOS: The peak at ≈ 0.35 eV is replaced by a nearly rectangular shaped DOS of ≈ 1.2 eV width. While the O $2p$ DOS closely follows these changes, the partial DOS due to the other *d* orbitals are almost unaffected by the oxygen atom shift. From inspection of the band structures the drastic changes of the $d_{3z^2-r^2}$ states can be attributed almost exclusively to the striking downshift of a single band by up to 0.45 eV. A similar situation has been found for $LiTi_2O_4$ [20,21]. While in the real structure, this band lies completely above $E_{\rm F}$ and causes the peak of the $d_{3z^2-r^2}$ partial DOS at 0.35 eV, it is stabilized in the ideal structure by the widening of the triangular octahedral faces, which point towards

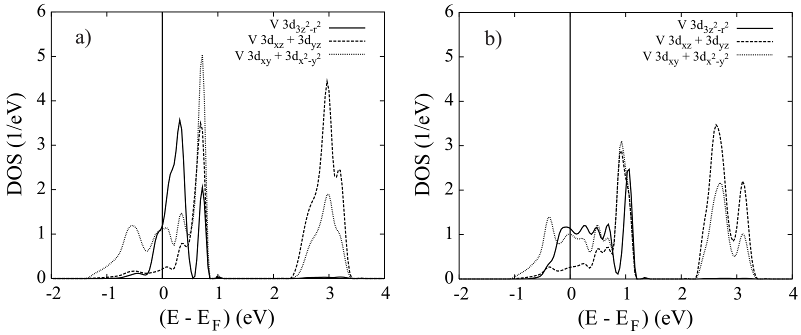

Fig. 2. – Partial densities of states of LiV_2O_4 for the (a) observed ($x_O = 0.26111$) and (b) ideal ($x_O = 0.25$) structure.

the $\langle 111\rangle$ direction. As a consequence, the electron count of these orbitals is slightly increased at the expense of the $d_{x^2-y^2}$ and d_{xy} electrons.

In conclusion, from their different response to the oxygen atom shifts we are able to clearly identify two groups of t_{2g} bands: The broad $d_{x^2-y^2}/d_{xy}$ states originate from strong σ-type V-V-overlap and are thus essentially unaffected by the change of the oxygen x_O parameter. In contrast, the much narrower $d_{3z^2-r^2}$ bands are involved in weak π-type V-O-overlap and depend sensitively on the oxygen position.

Motivated by the observed Curie-Weiss behaviour and disregarding for the time being possible geometric frustration effects in the spinel structure, we performed additional spin-polarized calculations. Both ferro- and antiferromagnetic order with a modulation of spins parallel to one of the cubic axes ($\mathbf{q} = (0, 0, 4\pi/a)$) were allowed for and, again, we considered both the observed and the idealized crystal structure. In all cases we obtained magnetic order with vanadium magnetic moments and total energy lowerings as summarized in table I. The latter are given relative to the respective non–spin-polarized solution. The vanadium magnetic moments result from almost equal contributions from the $d_{x^2-y^2}/d_{xy}$ and $d_{3z^2-r^2}$ orbitals; moments on all other atomic spheres are smaller than 0.025 μ_B. The main results are: For the antiferromagnetic states the rather small change of the ordered moment with respect to shifting the oxygen x_O parameter is contrasted with a considerable modification of the magnetic energy gain. In contrast, we witness a suppression of both the ferromagnetic moment *and* energy gain on going from the idealized to the observed structure. A detailed analysis revealed that this loss of magnetic moment affects all the t_{2g} states to a similar degree.

The afore-mentioned behaviour arises from two different mechanisms: i) The isotropic compression of the VO_6 octahedra in the observed structure as indicated by the 4.6% decrease of the V-O bond length, causes destabilization of both the ferromagnetic moment and order

Table I. – *Magnetic energy gain and vanadium magnetic moments.*

	$x_O = 0.26111$		$x_O = 0.25$	
	ferro	af	ferro	af
E_{tot} (m Ryd/f.u.)	−1.431	−3.655	−2.701	−1.170
m_V (μ_B)	0.590	0.877	1.108	0.768

as compared to the idealized structure. Furthermore, since the magnetic moments carried by the $d_{x^2-y^2}/d_{xy}$ and $d_{3z^2-r^2}$ orbitals are affected to a similar degree by the oxygen atom shift, we conclude that the polarization of the former orbitals is due to Hund's rule coupling rather than direct exchange interaction across the σ-type V-V bonds. ii) The deviation of the V-O-V bond angle from 90° for $x_\mathrm{O} = 0.26111$ supports antiferromagnetic superexchange interaction of the local vanadium magnetic moments via the occupied O $2p$ orbitals, while changing their size only little. The crossover from ferro- to antiferromagnetic order on increasing the oxygen x_O parameter and, in particular, the antiferromagnetic ground state of the observed structure thus arise from the combined effect of an increased overlap of the magnetic orbitals and a suppression of the ferromagnetic local vanadium moment. Still, the importance of ferromagnetic correlations has been recently revealed by neutron scattering experiments, which suggested to characterize $\mathrm{LiV_2O_4}$ as an itinerant d electron system close to weak ferromagnetism [22]. Similar conclusions have been drawn from the anomalous temperature dependence of the ^{7}Li NMR relaxation rate [11, 12]. Finally, the very small values of the magnetic energy gain as compared to other transition metal oxides and the almost linear variation of this energy gain with the magnetic moment for the ferromagnetic states result from the minor role of a direct d-d exchange interaction as well as the small superexchange coupling due to π-type p-d overlap. Thus, without the geometric frustration, we would find an antiferromagnetic ground state, in which the well-localized vanadium magnetic moments are coupled by weak superexchange interaction via the O $2p$ states.

Nevertheless, the geometric frustration inherent in the spinel structure with only nearest-neighbour interactions does prohibit long-range antiferromagnetic order as it leads to an energetical degeneracy of different antiferromagnetic configurations. Perhaps, in the states with large band width from the direct V-V overlap, the frustration of the magnetic interactions allows large-amplitude spin fluctuations to occur. This could explain the $T^3 \ln T$ behaviour of the specific heat observed at low temperatures, as well as the strong field dependence of the magnetic susceptibility below 30 K [23]. These spin fluctuations can result in large quasi-particle mass enhancements and thus mimic a heavy-fermion state. Alternatively, in the absence of magnetic ordering, the states, in which the small overlap of the d with the O $2p$ orbitals occurs, could place the orbitals at the brink of a transition to a localization and the local spin fluctuations could be responsible for the observed heavy-fermion behaviour.

To summarize, the electronic properties of $\mathrm{LiV_2O_4}$ as resulting from electronic structure calculations are dominated by a combination of broad and narrow bands near the Fermi energy, which originate from strong metal-metal and rather weak metal-oxygen overlap, respectively. While the direct V-V bonding does not contribute to magnetic ordering, the antiferromagnetic as well as the slightly unstable ferromagnetic state result from weak superexchange interaction. However, long-range magnetic order is suppressed by the geometric frustration inherent in the spinel structure; hence only large spin fluctuations survive, which provide a clue to an understanding of the observed specific heat and susceptibility data. The picture emerging from the present calculations is different from that usually used for f electron systems, where the hybridization between localized and the partially occupied itinerant states causes local spin fluctuations responsible for the HF behaviour, and when magnetic magnetic ordering occurs it is usually due to the RKKY interaction.

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