Electronic structure of spinel-type LiV$_2$O$_4$

J. Matsuno, A. Fujimori and L. F. Mattheiss
Department of Physics, University of Tokyo, Bunkyo-ku, Tokyo 113-0033, Japan
(February 12, 2022)

The band structure of the cubic spinel compound LiV$_2$O$_4$, which has been reported recently to show heavy Fermion behavior, has been calculated within the local-density approximation using a full-potential version of the linear augmented-plane-wave method. The results show that partially-filled V 3d bands are located about 1.9 eV above the O 2p bands and the V 3d bands are split into a lower partially-filled t$_{2g}$ complex and an upper unoccupied e$_g$ manifold. The fact that the conduction electrons originate solely from the t$_{2g}$ bands suggests that the mechanism for the mass enhancement in this system is different from that in the 4f heavy Fermion systems, where these effects are attributed to the hybridization between the localized 4f levels and itinerant spd bands.

PACS numbers: 71.27.+a, 71.20.-b, 71.15.Mb

The recent discovery of heavy Fermion (HF) behavior in LiV$_2$O$_4$ by Kondo et al.[8] has significant importance because this is the first d-electron system that shows HF characteristics, a phenomenon that has previously been observed only in f-electron systems. Kondo et al. have reported a large electronic heat coefficient of $\gamma \approx 0.42$ J/mol K$^2$ and a crossover with decreasing temperature $T$ from local moment to renormalized Fermi-liquid behavior.[8] Recently Takagi et al. have reported that the electrical resistivity $\rho$ of single crystals exhibits a $T^2$ temperature dependence $\rho = \rho_0 + AT^2$ (Ref. 9) with an enormous $A$, which is another HF characteristic. The Curie-Weiss law at high temperatures implies that each V ion has a local moment and their coupling is antiferromagnetic although no magnetic ordering is observed down to 0.02 K.[9]

The purpose of the present study is to determine from first principles the electronic band properties of LiV$_2$O$_4$, with particular emphasis on features near the Fermi level $E_F$. This provides a reference framework for evaluating the magnitude of the heavy Fermion mass-enhancement effects in this material. In addition, a simple tight-binding model[10] which captures the essential features of the LiV$_2$O$_4$ electronic structure is presented. In heavy Fermion systems, the enhanced electron mass manifests itself in terms of an exceptionally large value of the density of quasi-particles at $E_F$. Experimentally, this high density is reflected in the large specific-heat $\gamma$ and the large spin susceptibility $\chi_{spin}$ which is nearly $T$-independent. The calculated band DOS at $E_F$ $D(E_F)$ can be compared directly with the experimental results, and the ratio of the experimental and calculated band $D(E_F)$ values then provides a direct measure of the enhancement factors.

LiV$_2$O$_4$ forms with the well known cubic spinel structure in which the Li ions are tetrahedrally coordinated by oxygens while the V sites are surrounded by a slightly-distorted octahedral array of oxygens. The spinel structure features a face-centered-cubic Bravais lattice and a nonsymmorphic space group ($Fd\overline{3}m$) which is identical with that of the diamond structure. The primitive unit cell contains two LiV$_2$O$_4$ formula units (14 atoms). One can construct the spinel structure by an alternate stacking along [100]-type directions of the two different kinds of cubes shown in Fig. 1. 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 the 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 $x = 0.2611$. The VO$_6$ octahedra are trigonally distorted in the spinel structure unless the parameter $x$ is equal to the “ideal” value 0.25.

The present band-structure calculations for LiV$_2$O$_4$ have been carried out in the local-density approximation (LDA) using a full-potential, scalar-relativistic implementation[11] of the linear augmented-plane-wave (LAPW) method. The LAPW basis has included plane waves with a 14-Ry cutoff ($\sim$60 LAPW/s/atom) and spherical-harmonic terms up to $l = 6$ inside the muffin tins. The
valence electrons per cell in a perfectly stoichiometric material. The point symmetry at the V sites is \( D_{3d} \). In the fully localized limit, this allows the cubic \( t_{2g} \) crystal-field-type states to be split into \( a_{1g} \) and \( e_g \) levels. As discussed below, tight-binding estimates of this splitting show that it is quite small (~0.14 eV) in LiV_2O_4, about 6% of the octahedral \( e_g-t_{2g} \) splitting (~2.5 eV). The 0.14-eV difference between the \( a_{1g} \) and \( e_g \) orbital energies is small compared to the overall \( t_{2g} \) bandwidth (~2.2 eV). As a result, this splitting of the \( a_{1g} \) and \( e_g \) orbital energies does not produce effects which are readily discernible in the band-dispersion curves for LiV_2O_4.

In order to provide a convenient starting point for future investigations of electron-correlation effects in the present LiV_2O_4 system, we have applied a simple tight-binding (TB) model to fit the present LAPW results at six symmetry points in the BZ. This TB model has included the V 3d as well as the O 2s and 2p orbitals. Using 12 independent TB parameters, a moderately accurate (rms error = 0.17 eV) fit has been obtained to the 52 LiV_2O_4 valence and conduction bands. The fitting has involved two-center energy as well as overlap parameters. The TB parameters are listed in Table I. The TB representation of the LiV_2O_4 bands is shown in Fig. 3(b). It is clear that, although the agreement is not perfect, the TB model captures the essential features of the LAPW results.

A different TB model excluding the oxygen orbitals has been applied to the LAPW V 3d band results in order to obtain estimates of the orbital energies for the individual \( a_{1g} \) and \( e_g \) subbands in this system. (Note that the TB parameters in Table I include only a single V 3d orbital energy \( E_d \).) These TB orbital energies represent the mean band energy for each subband. They are in fact the crystal-field levels that come into play in the limit where the V 3d electrons are localized by electron-correlation effects. According to the present analysis, the mean band energy for the upper \( e_g \) complex is 2.82 eV while those for the \( t_{2g} \)-derived \( a_{1g} \) and \( e_g \) manifold are 0.43 and 0.29 eV, respectively. Thus, crystal-field splitting that arises from the octahedral coordination of oxygens (2.48 eV) is more than an order-of-magnitude larger than that originating from the trigonal distortion (~0.14 eV). This TB model, which also involved a total of 12 parameters, yielded a moderate fit (rms error = 0.15 eV) to the V 3d-band states. The effective \( d-d \) hopping integrals [(\( d\sigma \), (\( d\pi \)), (\( d\delta \))] over three shells of V-V neighbors [\( d_1 = 2.91 \text{ Å}, d_2 = 5.04 \text{ Å}, d_3 = 5.82 \text{ Å} \)] that have been included in this fit have values (in eV) [~0.425, 0.008, 0.152], [~0.034, 0.026, ~0.021], and [~0.060, 0.064, ~0.026], respectively. These parameters may provide a useful starting point for future studies of electron-electron correlation effects in this system.

A more detailed view of the \( t_{2g} \) portion of the LAPW V 3d energy-band results for LiV_2O_4 is shown in Fig. 3. The six LiV_2O_4 valence electrons per cell are sufficient to fill, on average, three of the 12 \( t_{2g} \) conduction bands. In fact, the calculated LAPW band dispersion produces several partially-filled bands, leading to a rather compli-
cated Fermi-surface topology in this system. While two bands are completely filled, the third conduction band contains holes near the X and L symmetry points (h3) and electron pockets at Γ (e4 and e5) and W (e4). Since the unit cell contains an even number of electrons, compensation requires that there exist equal numbers (i.e. BZ volumes) of electrons and holes. The existence of Fermi-surface sheets with both electron and hole character in LiV$_2$O$_4$ provides a ready explanation for the experimental observation that the Hall coefficient changes sign with temperature in accordance with a two-carrier model.

The total DOS and the projected contributions to the DOS from various muffin-tins are shown in Fig. 4. The dominant contribution to the DOS over this energy range originates from the O 2p and V 3d states. The O 2p bands are filled by electrons transferred from the Li 2s and V 3d orbitals so the system can be described by the ionic configuration Li$^+$($V^{3.5+}$)$_2$(O$^{2-}$)$_4$. Previous photoemission-spectra data are in general agreement with these results. However, the calculated band DOS and the photoemission spectra do not agree with each other in the V 3d band region near $E_F$. In particular, the photoemission intensity at $E_F$ is an order of magnitude lower than the calculated DOS. On the other hand, the density of quasi-particles at $E_F$ derived from the specific heat is much higher than the calculated $D(E_F)$. According to our results, the calculated $D(E_F) = 7.1$ states/(eV·formula-unit) corresponds to $\gamma_{\text{cal}} = 17$ mJ/mol K$^2$; this is $\approx 25$ times smaller than the experimental value of $\gamma = 0.42$ J/mol K$^2$. It is well-known that electron-phonon interactions enhance the electronic specific heat as in the closely-related spinel compound LiTi$_2$O$_4$, where band calculations indicated strong electron-phonon-coupling effects, yielding a coupling parameter $\lambda = 1.8$ and hence a mass enhancement factor of $1 + \lambda = 2.8$. In the present case, however, the deduced enhancement factor of $\approx 25$ suggests that a different mechanism such as electron-correlation effects would be responsible for the observed HF behavior in LiV$_2$O$_4$.

In comparison with the band structures of typical 4f-electron HF systems, our result show similar behavior in that the calculated density of states at $E_F$ is much smaller than those obtained from the analysis of experimental specific-heat data. For example, the ratio $\gamma_{\text{exp}}/\gamma_{\text{cal}}$ is $\approx 100$ for CeCu$_2$Si$_2$ and $\approx 70$ for CeAl$_3$. Also, the band structures of the f-electron HF and LiV$_2$O$_4$ systems are similar in that there is a sharp DOS peak just above $E_F$ ($\approx 0.3$ eV for CeCu$_2$Si$_2$ and $\approx 0.1$ eV for LiV$_2$O$_4$, see inset of Fig. 4). In order to explain the high density of quasi-particles deduced from the electronic specific heats, a renormalized band picture was proposed, in which a strong renormalization of the
$f$ band due to the strong correlation at the $4f$ site was taken into account. In the renormalized band picture, it is considered that electrons with two different degrees of wave function localization, namely, the itinerant $sd$ conduction electrons and the well localized $f$ electrons hybridize with each other. In the case of $\text{LiV}_2\text{O}_4$, however, all the conduction bands crossing $E_F$ consist of $\text{V} t_{2g}(3d)$ orbitals, i.e., electrons with the same degrees of localization, and therefore the mechanism of the mass enhancement may be totally different from the $f$-electron systems. The narrowing of the energy bands due to electron correlation within the $t_{2g}$ bands is likely. Given a high-temperature local moment behavior in a metallic system, a prerequisite for a HF behavior is that the local moments do not show long-range order at low temperatures. In the $4f$-electron HF systems, long-range order is prohibited by weakness of the coupling between the $4f$ local moments. In the case of $\text{LiV}_2\text{O}_4$, the long-range order is disfavored by the magnetic frustrations originating from the spinel structure. This phenomenological consideration remains to be justified by microscopic theories.

In conclusion, the results of LAPW band calculations for the spinel-type compound $\text{LiV}_2\text{O}_4$ show that the $\text{O} 2p$, $\text{V} 3d$ ($t_{2g}$) and $\text{V} 3d$ ($e_g$) bands as well as the high-lying $sp$ conduction band are well separated from each other and that the Fermi level lies within the $t_{2g}$ bands. The electronic structure of $\text{LiV}_2\text{O}_4$ can be well described by electrons in the triply-degenerate $t_{2g}$ bands, thereby indicating that the mechanism of the mass enhancement in this compound should be different from that in the $f$-electron heavy Fermion systems. Further experimental studies on various physical properties at low and high temperatures are necessary to characterize the nature of the heavy Fermion behavior in $\text{LiV}_2\text{O}_4$. High-resolution photoemission studies would be especially useful for clarifying the renormalization of quasi-particles in this system.

The authors would like to thank Prof. Y. Ueda for valuable discussions. This work was supported by a Special Coordination Fund for Promoting Science and Technology from the Science and Technology Agency of Japan. L. F. M. is grateful to Yamada Science Foundation for supporting his visit to the University of Tokyo. J. M. acknowledges support from the Japan Society for the Promotion of Science for Young Scientists.

1. S. Kondo et al., Phys. Rev. Lett. 78, 3729 (1997).
2. Until the discovery of the heavy Fermion behavior in $\text{LiV}_2\text{O}_4$, the largest electronic specific heat in $d$-electron systems had been $\gamma = 0.150$ J/mol K$^2$ for $\text{Y}_{1-x}\text{Sc}_x\text{Mn}_2$ with $x = 0.03$ [H. Wada, M. Shiga, and Y. Nakamura, Physica B 161, 197 (1989).]
TABLE I. Tight-binding parameters for LiV₂O₄ (rms error = 0.17 eV). Parameters in braces \{ \ldots \} have been approximated using simplifying relations (i.e., \((dd\pi) = 0.5(dd\sigma)\), etc.), leaving 12 independent parameters.

| Site/interaction | Distance (Å) | Parameters          | Value (eV)                  |
|------------------|--------------|---------------------|----------------------------|
|                  |              | Energy              |                            |
| V                | ...          | \(E_d\)             | −0.569                     |
| O                | ...          | \(E_{2s}, E_p\)     | −18.715, −4.390            |
| V-V              | 2.91         | \((dd\sigma), (dd\pi)\), \(dd\delta\) | −0.524, \{0.262\}, \{−0.052\} |
| V-O              | 1.97         | \((s\sigma), (p\sigma), (p\pi)\) | −2.278, −2.190, \{1.095\} |
| O-O              | 2.65         | \((s\sigma), (s\pi), (p\pi)\), \(pp\pi\) | −0.239, \{0.413\}, 0.711, \{−0.284\} |
| O-O              | 2.91         | \((s\sigma), (s\pi), (p\pi)\), \(pp\pi\) | −0.110, \{0.229\}, 0.479, \{−0.192\} |
| V-O              | 1.97         | \[s\sigma\], \[p\sigma\], \[p\pi\] | 0.046, 0.051, \{−0.026\}   |

Overlap