

Electronic structure of spinel-type LiV_2O_4

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The band structure of the cubic spinel compound LiV_2O_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. [S0163-1829(99)00627-X]

The recent discovery of heavy Fermion (HF) behavior in LiV_2O_4 by Kondo *et al.*¹ 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.* reported a large electronic heat coefficient of $\gamma \approx 0.42$ J/mol K² and a crossover with decreasing temperature T from local moment to renormalized Fermi-liquid behavior.² Recently Takagi *et al.* reported that the electrical resistivity ρ of single crystals exhibits a T^2 temperature dependence $\rho = \rho_0 + AT^2$ (Ref. 3) 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 antiferromagnetic⁴ although no magnetic ordering is observed down to 0.02 K.¹

The purpose of the present study is to determine from first principles the electronic band properties of LiV_2O_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 model⁵ which captures the essential features of the LiV_2O_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 quasiparticles at E_F . Experimentally, this high density is reflected in the large specific-heat γ and the large spin susceptibility χ^{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_2O_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 ($Fd\bar{3}m$) which is identical with that of the diamond structure. The primitive unit cell contains two LiV_2O_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 sub-

structure is the same as the $C15$ structure AB_2 , where the local moments at the B sites are highly frustrated.² The observed lattice constant of the LiV_2O_4 is 8.22672 Å at 4 K.⁶ 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_2O_4 have been carried out in the local-density approximation (LDA) using a full-potential, scalar-relativistic implementation⁷ of the linear augmented-plane-wave (LAPW) method.⁸ The LAPW basis has included plane waves with a 14-Ry cutoff (~ 60 LAPW's/atom) and spherical-harmonic terms up to $l = 6$ inside the muffin tins. The crystalline charge density and potential have been expanded using ~ 7300 plane waves (60 Ry cutoff) in the interstitial region and lattice harmonics with $l_{\text{max}} = 6$ inside the muffin-tin spheres ($R_{\text{Li}} \approx 1.98$ a.u., $R_{\text{V}} \approx 2.16$ a.u., $R_{\text{O}} \approx 1.54$ a.u.). Brillouin-zone (BZ) integrations have utilized a ten-point \mathbf{k} sample in the $1/48$ irreducible wedge. Exchange and correlation effects have been treated via the Wigner interpolation formula.⁹ The atomic $\text{Li}(2s^1)$, $\text{V}(3d^44s^1)$, and $\text{O}(2s^22p^4)$ states were treated as valence electrons in this study whereas the more tightly bound levels were included via a frozen-core approximation.

The results of the present LAPW calculations for LiV_2O_4 are plotted along selected BZ symmetry lines in Fig. 2(a).

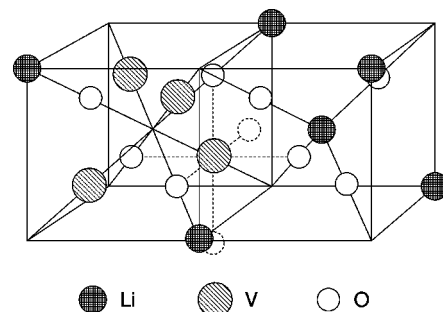


FIG. 1. A portion of the unit cell for the spinel-type LiV_2O_4 , where a is the lattice parameter for the face-centered-cubic Bravais lattice (see text).

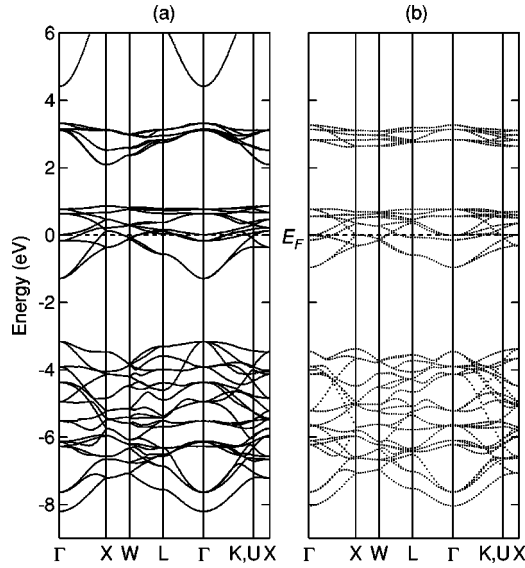


FIG. 2. Comparison of the LAPW (a) and tight-binding (b) energy-band results for LiV_2O_4 .

The O $2s$ states, which are not shown, form narrow (~ 1 eV) bands and are situated about 19 eV below the Fermi level E_F . The lowest band complex shown in this figure evolves from the O $2p$ states: it contains 24 bands, and has an overall width of ~ 4.8 eV. The 20 V $3d$ bands lie above the O $2p$ bands, separated by a 1.9-eV gap. A broad plane-wave conduction band evolves from the Γ point above 4.4 eV. These general features are quite similar to those exhibited by previous results for the closely related isostructural compound LiTi_2O_4 .^{11,12}

The octahedral crystal field at the V sites in the spinel structure splits the 20 V $3d$ bands into twelve partially filled t_{2g} bands and eight e_g states. The Fermi level lies within the t_{2g} complex, and thus the transport properties of LiV_2O_4 are solely associated with t_{2g} bands. The formal valence of vanadium is $3.5+$, yielding exactly six 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) model⁵ 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. 2(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 [$(dd\sigma)$, $(dd\pi)$, $(dd\delta)$] over three shells of V-V neighbors [$d_1=2.91$ Å, $d_2=5.04$ Å, $d_3=5.82$ 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.

TABLE I. Tight-binding parameters for LiV_2O_4 (rms error = 0.17 eV). Parameters in braces $\{\dots\}$ 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_s, 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 | $(sd\sigma), (pd\sigma), (pd\pi)$ | -2.278, -2.190, {1.095} |
| O-O | 2.65 | $(ss\sigma), (sp\sigma), (pp\sigma), (pp\pi)$ | -0.239, {0.413}, 0.711, {-0.284} |
| O-O | 2.91 | $(ss\sigma), (sp\sigma), (pp\sigma), (pp\pi)$ | -0.110, {0.229}, 0.479, {-0.192} |
| Overlap | | | |
| V-O | 1.97 | $[sd\sigma], [pd\sigma], [pd\pi]$ | 0.046, 0.051, {-0.026} |

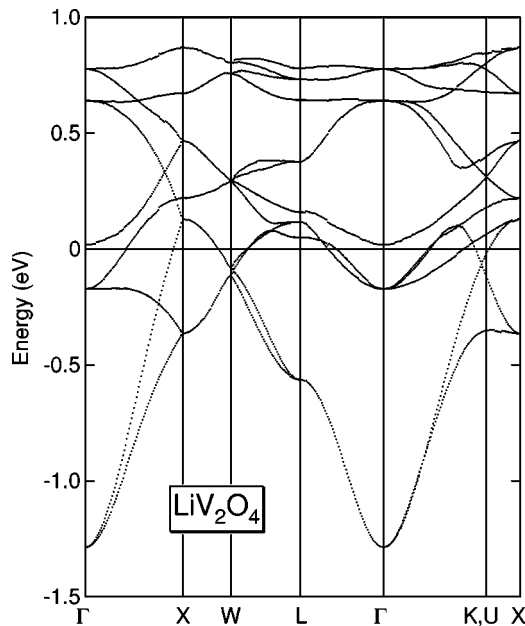


FIG. 3. Expanded plot of the LAPW t_{2g} bands for LiV_2O_4 .

A more detailed view of the t_{2g} portion of the LAPW $3d$ 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 complicated 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 (h_3) and electron pockets at Γ (e_4 and e_5) and W (e_4). 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_2O_4 provides a ready explanation for the experimental observation that the Hall coefficient changes sign with temperature³ 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 $\text{Li}^+(\text{V}^{3.5+})_2(\text{O}^{2-})_4$. Previous photoemission-spectra data are in general agreement with these results.¹⁰ 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 quasiparticles 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 ~ 25 times smaller than the experimental value of $\gamma \approx 0.42$ 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_2O_4 , where band calculations indicated strong electron-phonon-coupling effects,

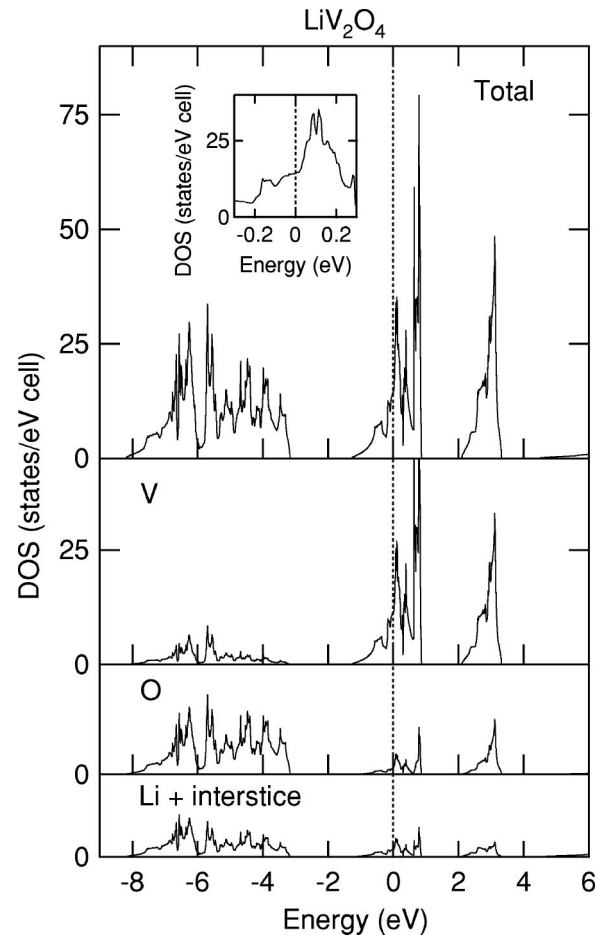


FIG. 4. Total and muffin-tin projected DOS results for LiV_2O_4 . The inset shows an enlarged view of the total DOS near E_F .

yielding a coupling parameter $\lambda = 1.8$ and hence a mass enhancement factor of $1 + \lambda = 2.8$.¹² In the present case, however, the deduced enhancement factor of ~ 25 suggests that a different mechanism such as electron-correlation effects would be responsible for the observed HF behavior in LiV_2O_4 .

In comparison with the band structures of typical $4f$ -electron HF systems, our result shows 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 ~ 100 for CeCu_2Si_2 and ~ 70 for CeAl_3 .¹³ Also, the band structures of the f -electron HF and LiV_2O_4 systems are similar in that there is a sharp DOS peak just above E_F (~ 0.3 eV for CeCu_2Si_2 and ~ 0.1 eV for LiV_2O_4 , see inset of Fig. 4). In order to explain the high density of quasiparticles 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.¹⁴ 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 LiV_2O_4 , however, all the conduction bands crossing E_F consist of 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.¹⁵ In the case of LiV_2O_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 LiV_2O_4 show that the O $2p$, V $3d$ (t_{2g}) and V $3d$ (e_g) bands as well as the higher-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 LiV_2O_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 LiV_2O_4 . High-resolution photoemission studies would be especially useful for clarifying the renormalization of quasiparticles in this system.

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