Electronic structure of the superconducting oxide spinel LiTi$_2$O$_4$

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We examine the electronic band structure of LiTi$_2$O$_4$ in the cubic spinel structure by performing a local-density calculation using the linear muffin-tin orbitals method. The Fermi energy lies in the Ti $3d$ bands with only one-half of an electron per Ti atom occupying this band. The next-lower O $2p$ bands occur about 2.4 eV below the Ti $3d$ bands in good agreement with the photoelectron spectra. However, enhanced specific heat and differences with photoemission spectra near E_f suggest effects beyond the band results. If the specific-heat enhancement is assumed to arise from phonons, we find $\lambda \sim 1.8$ indicating a strong electron-phonon coupling. The nature of electron states is also consistent with the possibility of resonating-valence-bond superconductivity.

Superconductivity among the compounds forming in the spinel structure is rather rare. Among the 300 or so of the known transition-metal ternary compounds in the spinel structure, only four, viz., LiTi$_2$O$_4$, CuRh$_2$S$_4$, CuV$_2$S$_4$, and CuRh$_2$Se$_4$, are known to show superconducting properties.[1-5] Of these, LiTi$_2$O$_4$ with the highest T_c of 12.4 K seems to be anomalous. The other three spinels have a T_c in the range of 3.5–4.8 K.

The recent discovery of high-T_c superconductivity in the oxides[6] of the types La-Ba-Cu-O and La-Y-Cu-O has raised the possibility of novel mechanisms for superconductivity. The possibility of superconductivity in LiTi$_2$O$_4$ by the resonating-valence-bond (RVB) mechanism has been raised by Anderson and co-workers.[7] Earlier Edwards et al.[8] tentatively suggested the presence of strong coupling of electrons to lattice vibrations leading to the formation of small polarons. In view of this, it is relevant to examine the nature of one-electron states in LiTi$_2$O$_4$. In this note, we report the results of a local-density calculation of the energy-band structure of the LiTi$_2$O$_4$ spinel.

The spinel crystal structure is face-centered cubic consisting of two formula units (14 atoms) in the unit cell. The lattice constant of the LiTi$_2$O$_4$ spinel compound[9] is 8.40 Å. The space group is $Fd3m$, which is the same as that of Si in the diamond structure: The Li atoms occupy the Si positions in the diamond structure with the Ti and O atoms placed around Li atoms in various interstitial positions. The structure can be conveniently thought of as made up by alternate stacking of two different types of cubes, as shown in Fig. 1. The oxygen atoms form a cubic close-packed array with the metal atoms occupying the interstitial positions. There are two such interstitial sites: the tetrahedral or A sites and the octahedral or the B sites. There are two A sites and four B sites in the unit cell. Li atoms occupy the A sites and Ti atoms the B sites.

The band structure was calculated within the local-density approximation using the self-consistent linear muffin-tin orbitals method[10] in the atomic spheres approximation (LMTO–ASA). The scalar-relativistic Kohn-Sham-Schrödinger equation with von Barth-Hedin[11] exchange correlation was solved; i.e., the spin-orbit coupling term was not included. In addition to the 14 atoms in the unit cell, we included 18 empty spheres. The positions

and sphere radii of various atoms as well as the empty spheres are given in Table I. Only muffin-tin orbitals of angular momentum s, p, and d for the atoms and s and p orbitals for the empty spheres were retained. Two panels were used. Electrons up to and including Li $1s$, Ti $3p$, and O $1s$ were treated as frozen-core electrons. Self-consistent potential was obtained with 16 k points in the irreducible $\frac{1}{48}$ th Brillouin zone and the one-electron densities of states displayed here were calculated with 104 k points.

The calculated one-electron bands are shown in Fig. 2. The O $2s$ states (not shown in the figures) from narrow bands which are 1 eV wide, occurring 19.4 eV below the Fermi energy E_f. The lowest bands shown are the O $2p$ bands which have a width of about 5.0 eV. The Ti d bands which are the next higher are separated from the O $2p$ bands by 2.4 eV. The octahedral component of the crystal field is strong enough that the t_{2g} and e_g orbitals originating from the Ti $3d$ orbitals form two separate and nonoverlapping bands. The further splitting of the t_{2g} orbital into $a_{1g}+e_g$ orbitals caused by the tetragonal component of the crystal field is small compared to the width of the t_{2g} band. These a_{1g} orbitals, four per unit cell, span

Cubic spinel structure
● Li   ■ Ti   ○ O
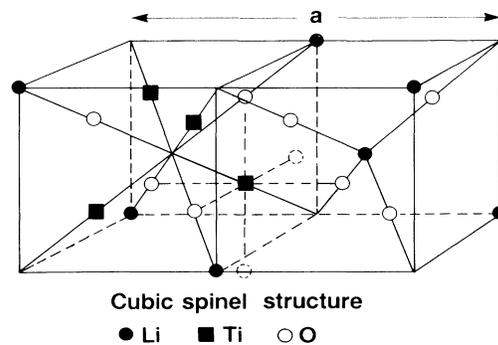
FIG. 1. The cubic spinel structure of LiTi$_2$O$_4$. The atoms shown here form the basis of a face-centered-cubic Bravais lattice with "a" being the lattice constant. The crystal consists of alternate stacking of the two different types of cubes shown in the figure. The stacking is such that cubes of one type are surrounded entirely by cubes of the other type.

TABLE I. Atom positions and the sphere radii used in the calculation. E denotes an empty sphere and x denotes the internal position parameter. The atom positions refer to the tables of Henry and Lonsdale (Ref. 12).

Atom	Core	Atom positions	Sphere radius (Å)
Li	[He]	8a	1.10
Ti	[Ar]	16d	1.15
O	[He]	$32e(x=0.3876)$	1.20
$E(1)$	···	16c	0.91
$E(2)$	···	8b	0.69
$E(3)$	···	$48f(x=0.25)$	0.91

$\Gamma_1 + \Gamma_{25'}$ irreducible representations of the O_h group, and therefore at the Γ point they do not contribute to the lowest Ti $3d$ band which has Γ_{12} symmetry. The charge density of the Γ_{12} state has about 71% Ti d + 10% O d character with the remaining 19% contributed mainly from muffin-tin orbitals centered on the empty spheres. Above the Ti $3d$ bands begins a free-electron-like band, with a large portion of its charge density located in the interstitial empty parts of the crystal where no atoms are lo-

cated.

In Fig. 3 we show the one-electron density of states (DOS) and the contribution to the DOS from various muffin-tin orbitals. As seen from this figure, the dominant contribution to the DOS in the energy range shown comes from the O $2p$ and the Ti $3d$ orbitals. The empty-sphere orbitals as well as the Li orbitals contribute very little to the DOS in this energy range. The O $2p$ shell is filled by electrons transferred from the Li $2s$ orbital and the rest from the Ti $3d$ orbitals so that the electron occupation may be roughly represented as Li^{+1} $(Ti^{+3.5})_2$ $(O^{-2})_4$. In the photoemission data of Edwards et al.,[8] the O $2p$ bands are about 5 eV wide and are separated from the Ti $3d$ bands by about 3 eV, in agreement with our results. From our calculation, the DOS has a peak at the E_f with the magnitude of the DOS at E_f $\rho(E_f) = 3.3$ states/eV/formula unit. From the photoemission experiments,[8] this value is estimated to be about 0.25 units, while a peak in the spectrum appears about 1 eV below E_f. Edwards et al. have suggested that this could come about by the presence of an electron-phonon interaction or an interaction among electrons which is included only in a mean-field sense in our calculation. The $\rho(E_f)$ extracted from
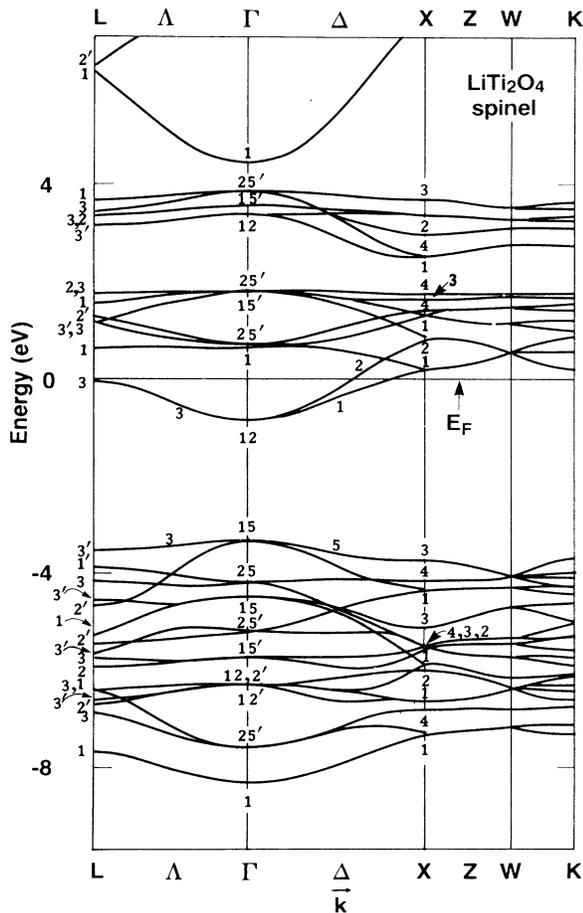
FIG. 2. Energy-band structure of $LiTi_2O_4$ calculated by the LMTO method in the local-density approximation. The O $2p$ bands are full and there is only half of an electron per Ti atom occupying the Ti $3d$ bands.
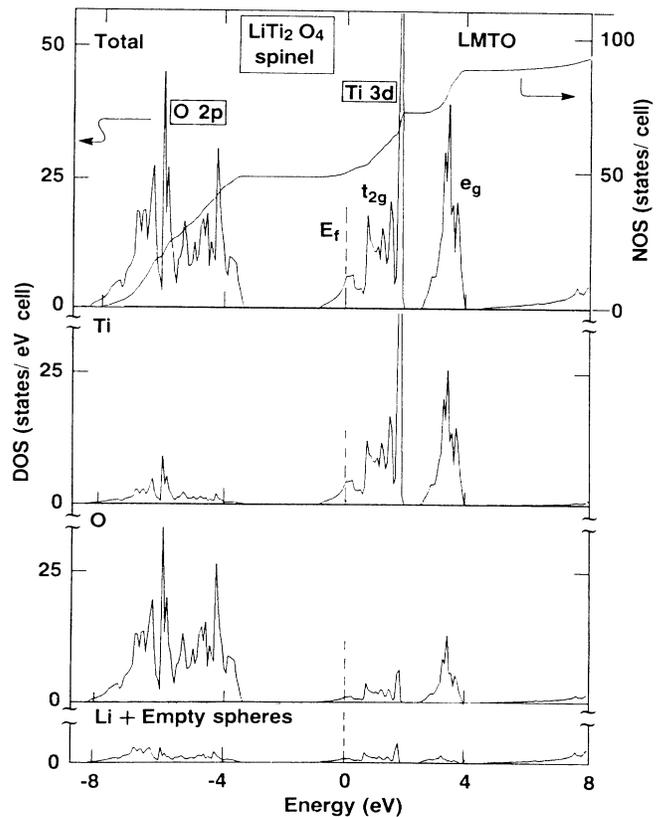
FIG. 3. One-electron total and partial densities of states (DOS) as well as the number of states (NOS) obtained by integrating the total DOS. The O $2p$, Ti $3d(t_{2g})$, and Ti $3d(e_g)$ form three nonoverlapping bands, with the Fermi energy E_f occurring at the lower part of the Ti $3d(t_{2g})$ bands. The contribution of orbitals centered on Li atoms and the empty spheres to the DOS is small.

the linear part of the measured normal-state specific heat[8,13] is 9.2 states/eV/formula/unit compared to the calculated value of 3.3. Assuming that this enhancement is purely due to electron-phonon coupling, we get the electron-phonon coupling parameter $\lambda = 1.8$. This is rather large compared with the typical λ value of about 0.5–1.0 for the weak-coupling transition-metal superconductors. From the magnetic susceptibiltiy measured by Johnston,[1] we obtain[14] $\rho(E_f) = 3.5$ states/eV/formula unit if we assume the susceptibility $\chi = \mu^2 \rho(E_f)$. This value is roughly the same as our calculated $\rho(E_f)$. It is well known[15] that the electron-phonon interaction, while enhancing the electronic specific heat, does not renormalize spin susceptibility. These results are thus consistent with the presence of a strong electron-phonon coupling which could be responsible for the rather high value of T_c.

The most suggestive feature in the bands of $LiTi_2O_4$ is that there is only a small pocket of electrons in the Ti $3d$ bands and, as already indicated, these bands lie about 2–3 eV above the next lower O $2p$ bands. Such a clear separation of ligand-p and metal-d bands is not a general feature of all transition-metal spinels. Band calculations,[16] for instance for the superconducting CuV_2S_4, show that Cu $3d$, V $3d(t_{2g})$, and S $3p$ orbitals form a joint band, 8 eV wide, crossing E_f. In $LiTi_2O_4$ there is only one-half of an occupied electron per Ti atom in the Ti $3d$ bands. Since there are twice as many Ti sites as the number of $3d$ electrons, this could lead to potential ordering in the ground state of these "extra" electrons on the Ti lattice due to exchange and Coulomb interaction between them. However, ordering of the electrons on the Ti sublattice is "frustrated" because the topology of the sublattice leads to an infinite degeneracy[17] of states with the lowest energy if only nearest-neighbor interactions are present.

The situation is reminiscent of the case of magnetite (Fe_3O_4), which undergoes the Verwey insulator-to-metal transition[18] at about 120 K. Below this temperature there occurs a complicated ordering of Fe^{2+} and Fe^{3+} ions on the octahedral B sites (Ti sites) of the spinel structure. The case of magnetite, however, may not be directly appli-cable to $LiTi_2O_4$ since in the former compound, the exchange interaction between iron electrons is ferromagnetic. In fact, in the model of Cullen and Callen,[19] for the Verwey transition in magnetite the "extra" electrons move in the spin-up band. In contrast to this, the exchange interaction between Ti electrons may be antiferromagnetic. Some time ago, Anderson[20] pointed out that the RVB state might be the ground state of a spin-$\frac{1}{2}$ system on certain lattices exhibiting "frustration." He and his co-workers[7] have recently hypothesized a RVB ground state for the new high-T_c superconductors and have alluded to the fact that $LiTi_2O_4$ may indeed be a candidate for this mechanism. Since the Ti sublattice of the spinel structure allows a high degree of frustration, we think that Anderson's RVB-type ground state is probable in the $LiTi_2O_4$ spinel.

In conclusion, a first-principles local-density calculation of electron band structure of the superconducting $LiTi_2O_4$ spinel compound was performed to gain insight into the nature of electron states. The calculated bands agree with the positions and widths of bands in the measured photo-emission spectra; however, there are differences in the spectral weights, particularly near E_f. If enhancement in the electronic specific heat over the prediction of the band theory is attributed to electron-phonon coupling, we find a rather strong coupling situation corresponding to $\lambda \sim 1.8$. The conduction-band states are largely Ti $3d$ states, with half an electron per Ti atom occupying this band. This band is well separated in energy from the O $2p$ bands, a feature not present in all ternary transition-metal spinels. This leads to a unique, and at the same time simple, picture of electron states for the $LiTi_2O_4$ spinel. Whether or not this feature plays a dominant role in superconductivity, for instance by RVB mechanism, remains to be investigated.

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