Role of Electron–Phonon Interaction in Lattice Dynamics and Superconductivity of Oxide Spinel LiTi$_2$O$_4$

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The lattice dynamics of an oxide spinel LiTi$_2$O$_4$ is studied by taking account of the electron–phonon (EP) interaction derived on the basis of the realistic tight-binding bands fitted to the first-principles bands. Due to the characteristic dependences of the EP interaction on wavevectors and vibrational modes, a remarkable frequency renormalization of the O vibrational modes, which hybridize with the Ti vibrational modes, is obtained over a wide region of the Brillouin zone. The overall features of the calculated phonon density of states are in agreement with those observed by the inelastic neutron scattering measurements. By using the EP interaction and the renormalized phonon frequencies we have calculated the EP spectral function $\alpha^2 F(\omega)$. The superconducting transition temperature, gap function, and tunneling spectra are calculated by solving the Eliashberg equation. The results agree well with the observations.

KEY WORDS: LiTi$_2$O$_4$; electron–phonon interaction; lattice dynamics; spectral function $\alpha^2 F(\omega)$; Eliashberg equation.

1. INTRODUCTION

Among a large number of oxide spinels, only LiTi$_2$O$_4$ becomes a superconductor, with transition temperature $T_c=12$ K [1]. LiTi$_2$O$_4$ has a normal spinel-type structure, in which Li and Ti atoms occupy the tetrahedral and octahedral sites, respectively. By substituting Li for Ti, Li$_{1+x}$Ti$_{2-x}$O$_4$ becomes insulating for $0.1 \leq x \leq 1/3$ [1].

Recently much effort has been made to clarify the mechanism of superconductivity in LiTi$_2$O$_4$ from both the experimental and the theoretical side, particularly in connection with the high-$T_c$ copper oxide superconductors. Judging from several experimental results such as specific heat [2,3] and tunneling spectra [4–6], it seems that the superconductivity of LiTi$_2$O$_4$ may be understood within the usual BCS-type mechanism.

Electronic band structure calculations based on the local-density approximation have been performed for LiTi$_2$O$_4$ by Satpathy and Martin [7] with the use of the linear-muffin-tin orbital (LMTO) method and by Massidda et al. [8] with the use of the full-potential linearized augmented-plane-wave (FLAPW) method. Furthermore, Massidda et al. investigated the electron–phonon (EP) interaction on the basis of the rigid-muffin-tin approximation (RMTA) [9]. They estimated the dimensionless EP coupling constant $\lambda$ and $T_c$ by using the empirical McMillan formula [10]. However, their estimation of $\lambda$ and $T_c$ is insufficient because they related the averaged phonon frequency to the Debye frequency and dealt with it as a parameter.

In the present paper we study, first, the lattice dynamics of LiTi$_2$O$_4$ by taking account of the EP interaction derived microscopically on the basis of the realistic tight-binding bands fitted to the first-principles bands [7,8]. Second, in order to study the superconductivity of LiTi$_2$O$_4$ in the framework of the usual phonon-mediated pairing mechanism, we calculate the EP spectral function $\alpha^2 F(\omega)$ by utilizing the EP coupling and the renormalized phonon frequencies. Then, $T_c$, gap function, and tunneling spectra are calculated by solving the Eliashberg equation. The
results are compared with the observations and are discussed in connection with those obtained for Ba$_2$K$_{1-x}$BiO$_3$ (BKB) and La$_{2-x}$Sr$_x$CuO$_4$ (LSC) [11-15].

2. ELECTRON-PHONON INTERACTION AND LATTICE DYNAMICS

According to the results of the first-principles band calculations [7,8], partially filled two-conduction bands, which are separated by an energy gap of 2.6 eV from the O 2p valence bands, consist predominantly of the Ti 3$d_5$ states hybridizing with the O 2p states through $d_{p\pi}$ bonds. This nature of the conduction bands is in sharp contrast to the case of high-$T_c$ cuprates, in which the conduction band consists of the Cu 3$d_{x^2-y^2}$ states hybridizing with the O 2p states through $d_{p\sigma}$ bonds. The overall features of the electronic density of states (DOS) for LiTi$_2$O$_4$ show good correspondence with the photoemission [16] and X-ray absorption [17] spectra. The dispersion curves and the DOS of the conduction bands in LiTi$_2$O$_4$ are well reproduced by the tight-binding model using the Slater–Koster transfer integrals, $t(d_{dc})$, $t(d_{dt})$, $t(d_{do})$, etc. for the nearest neighboring Ti–Ti, Ti–O, and O–O pairs.

In the tight-binding approximation the EP coupling arises from modulation of transfer integrals due to atomic displacements [18]. For the derivatives of the transfer integrals the following values are used: $t'(d_{p\pi}) = -7.0$, $t'(d_{dc}) = 0.39$, $t'(d_{dt}) = -0.23$, $t'(d_{do}) = -0.14$ in eV Å$^{-1}$. These parameter values are deduced from the difference between the electronic band structure in the real distorted crystal structure of LiTi$_2$O$_4$ and that in an ideal spinel-type structure and/or from the strength of the EP coupling calculated on the basis of the RMTA [8]. The EP coupling shows remarkable dependences on wavevectors and phonon modes. In particular, the EP coupling for vibrations which alter the nearest neighboring Ti–O bond length is stronger than those for the other vibrations. It is noted that contributions arising from $t'(d_{p\pi})$ are much larger than those arising from the other derivatives of the transfer integrals.

The lattice dynamics of LiTi$_2$O$_4$ has been studied by taking account of effective long-range interatomic forces caused by the EP interaction. For short-range interatomic forces we have considered six kinds of stretching-type forces for Li–O, Ti–O, Ti–Ti, and O–O neighboring pairs and determined them by referring to the force constants determined for other oxide spinels [19,20], because no sufficient data for phonons of LiTi$_2$O$_4$ are available so far.

![Fig. 1. The phonon density of states calculated for LiTi$_2$O$_4$ including the effect of renormalization due to the electron-phonon interaction.](image-url)