^{6}Li-^{7}Li isotope effect in superconducting LiTi$_2$O$_4$

R. G. Goodrich

Department of Physics and Astronomy, Louisiana State University, Baton Rouge, Louisiana 70803-4001

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The superconducting transition temperatures in isotopically pure samples of ^{6}LiTi$_2$O$_4$ and ^{7}LiTi$_2$O$_4$ have been determined from ac-susceptibility measurements. The transition temperatures and transition widths for the two samples are found to be identical within experimental accuracy.

Superconductivity with a transition temperature, T_c, near 12 K in the cubic spinel compound LiTi$_2$O$_4$ was first reported by Johnston et al.[1] in 1973. This material is believed to be a standard phonon-mediated BCS superconductor[2] in which the conduction electrons exist in titanium d bands.[3] In LiTi$_2$O$_4$, the titanium atoms are in an octahedral coordination with the O atoms, the same as exists in the ideal perovskite structure, and the lithium atoms occupy tetrahedral sites. In LiTi$_2$O$_4$, the titanium d band is separated in energy from the oxygen $2p$ band by several eV resulting in only weak hybridization.[3] In the case of LiTi$_2$O$_4$, the small masses of the lithium isotopes suggest that it would be interesting to investigate the isotope effect in this material because the percentage mass change between the two isotopes 6 and 7 is large.

In a recent article by Carbotte,[4] the theory of the isotope effect and, in particular, the contributions to an overall isotope effect in compounds having more than one constituent, is reviewed. While most of the analysis for multicomponent systems concerns oxygen isotope replacement in high-temperature superconductors, the overall conclusion from Ref. 4 is that the very low and very high energy phonons having the same electron-phonon coupling in multicomponent materials contribute less to the total isotope effect than those phonons having energies in the range of approximately $5-10k_B T_c$.[5]

Samples of nearly isotopically pure ^{6}LiTi$_2$O$_4$ and ^{7}LiTi$_2$O$_4$ were prepared by the method given by Mousa and Grimes.[6] In this method, the following chemical reaction is carried out at 860 °C for 72 h on pressed pellets of well-mixed starting materials:

$$Li_2CO_3 + 4TiO_2 + H_2(gas) = 2LiTi_2O_4 + CO_2\uparrow + H_2O\uparrow \ .$$
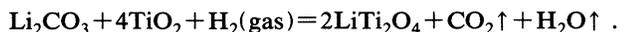
The ^{6}Li$_2$CO$_3$ and ^{7}Li$_2$CO$_3$ starting materials were obtained from Isotec, Inc. and had stated isotopic enrichments of 95% ^{6}Li and 99% ^{7}Li. Both the ^{6}Li and the ^{7}Li samples were reacted and fired at the same time under identical conditions. The final samples were pellets 13 mm in diameter and 2 mm thick, and x-ray-diffraction patterns of the pellets did not reveal any impurity phases. After the susceptibility measurements were completed, ^{6}Li and ^{7}Li NMR measurements on portions of the samples reflected the initial isotopic compositions.[7]

ac-susceptibility measurements were made at 2 MHz using a marginal oscillator circuit with the sample insert-

ed into the resonant tank coil. The frequency of the oscillator was recorded as a function of temperature with the temperature being measured from a calibrated 100 kΩ bismuth ruthinate chip resistor glued to one side of the sample. The tank circuit, sample, and thermometer were contained in a double-wall vacuum can cryostat immersed in liquid helium. A pressure of 100 μm of ^{4}He gas was maintained inside the inner can containing the sample, and a high vacuum was maintained between the cans. A heater wound on the outside of the inner can was used to control the temperature. This system improves the thermal contact between the sample and thermometer and allows the temperature to be swept at slow speeds — 2 h from 8 to 15 K.

The frequency shift of the oscillator versus temperature for both samples is shown in Fig. 1, and an expanded view of the frequency shift data near the onset of the transition is shown in Fig. 2. As can be seen from this data, the onset of superconductivity (the beginning of the large sustained frequency shift) occurs between 12.15 and
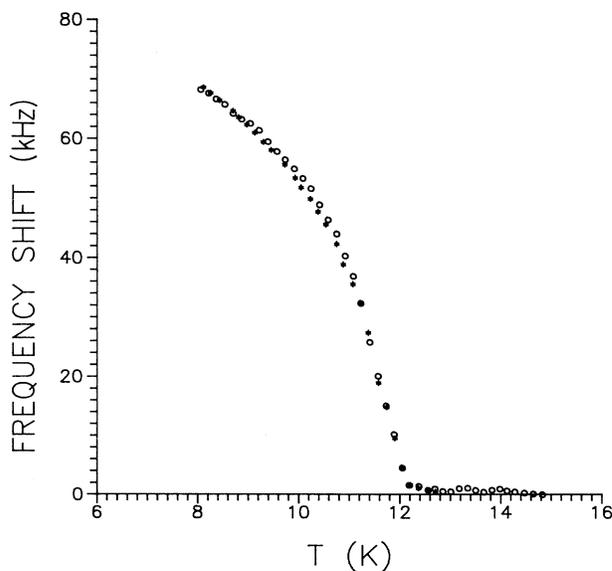
FIG. 1. Oscillator frequency shift vs temperature for two samples of superconducting LiTi$_2$O$_4$ showing the superconducting transition: $\bigcirc$, ^{6}LiTi$_2$O$_4$ and $\times$, ^{7}LiTi$_2$O$_4$.
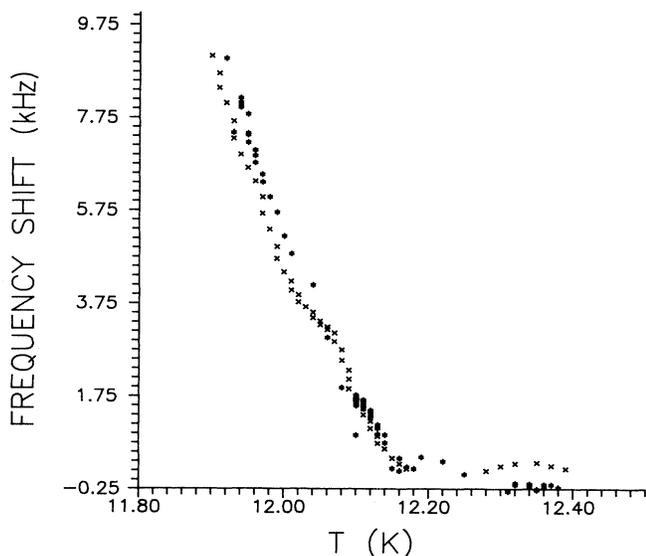
FIG. 2. Oscillator frequency shift vs temperature for two samples of superconducting $LiTi_2O_4$ near the onset of superconductivity: ●, $^6LiTi_2O_4$ and ×, $^7LiTi_2O_4$.

Thus, the high-energy phonons due to the light lithium atoms do not contribute significantly to the overall isotope effect. This result is consistent with the analysis of the isotope effect in the multicomponent systems of Rainer and Culetto.[6] The question of whether the null result is due to zero coupling between the lithium atoms and the Ti-O bands or is due to thier phonon energies being outside the region of effective coupling cannot be answered by this measurement alone. However, Massidda, et al.[3] have calculated the electron-phonon coupling strength for lithium in $LiTi_2O_4$ and find it to be zero. Our result is entirely consistent with this calculation. The lithium atoms appear to be completely ionized in this compound and function as impurity donors to the Ti-O network.[8] Thus, in this case, lithium may act in the opposite extreme for the isotope effect to the replacement of Y ($M=89$) in $YBa_2Cu_3O_7$ by Gd ($M=157$) with little change in T_c. In these materials, the heavy Y and rare-earth elements would have low-energy phonons again outside the $5-10k_BT_c$ energy range, or there may be no coupling between these isovalent, and completely ionized, heavy elements and the Cu-O conduction bands as energy band-structure calculations indicate.[3]

12.16 K for both isotopes, and the shift in T_c between isotopes is less than the scatter in the data of approximately 25 mK. Taking 25 mK as the maximum lithium isotope shift that is observed, the exponent β in the equation $^6T_c = {}^7T_c[7/6]^\beta$ gives a value of $\beta \leq 0.013$. Note that, for $\beta = 0.5$, the shift would be 0.97 K for a 12.15-K transition temperature.

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