EXPERIMENTAL STUDY OF THE SUPERCONDUCTING SPINEL SYSTEM Li1+xTi2-xO4

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EXPERIMENTAL STUDY OF THE SUPERCONDUCTING SPINEL SYSTEM $Li_{1+x}Ti_{2-x}O_4$

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Abstract. – We present new experimental results about the spinel system $Li_{1-x}Ti_{2-x}O_4$. Specific heat data and transport properties show the high quality of the samples prepared by new routes. If stoichiometric compound satisfies BCS theory the mechanism of superconductivity seems to be more complex when off-stoichiometric compounds are considered, due to the vicinity of a metal-insulator transition.

A tremendous amount of experimental and theoretical works have been reported on new high T_c superconductors but the understanding of the observed critical temperatures and the relevance of attractive theoretical models are still debated [1].

For a better understanding of the relative role of the factors leading to high T_c superconductivity (vicinity of a metal-insulator transition, low dimensional character, ...) the study of spinel compounds and especially $LiTi_2O_4$ seems to be attractive. This three-dimensional mixed valent system has unusual T_c value (T_c=12.7 K) and the off-stoichiometric compounds $Li_{1+x}Ti_{2-x}O_4$ ($0 < x < 1/3$) exhibit a metal-insulator transition for $x = 0.2$, i.e. before the complete emptying of the titanium "d" band [2].

We studied systematically the physical properties of $LiTi_2O_4$ and of the off-stoichiometric related compounds obtained by substituting lithium to titanium. In this first paper, we report new results about preparation, transport and magnetic properties.

Preparation and structural data

Samples were prepared by solid state reaction in two steps. First, a lithium titanate compound was synthesized under oxygen, then mixed to titanium and sintered under vacuum. Titanium oxides was obtained by hydrolysis of an alcoholic solution of titanium ethoxide, alcohol washed, air dried and calcinated 2 hours at 750 °C. This method gives a fine powder, extremely reactive and easy to reduce. The predried constituents, $Li_2(CO_3)$ and the ex-alkoxide TiO_2, were ground together for 1 hour under argon. The mixture was then heated at 750 °C under oxygen for 1 hour, in order to eliminate CO_2.

The appropriate amount of Ti was added to the prefired pellet and thoroughly ground. The mixture was then pressed at 275 MPa and heated under vacuum before being sealed in quartz tube. The sample was finally hold at 800 °C for 48 hours.

a) $(1+x)/2\ Li_2(CO_3) + (7-x)/4\ TiO_2 \rightarrow$ "$Li_{1+x}Ti_{(7-x)/4}O_4$" $+ (1+x)/2\ CO_2$

b) "$Li_{1+x}Ti_{(7-x)/4}O_4$" $+ (1-3x)/4\ Ti \rightarrow$ $\rightarrow Li_{1+x}Ti_{2-x}O_4$.

X-ray powder diffraction analysis of the samples, made by using the $CuK\alpha$ radiation, has not allowed to detect any impurity phase. The lattice parameter a of the face-centered-cubic spinel structure has been determined and its variation with the rate of lithium is displayed in figure 1. A linear decrease of a is observed over all the concentration range, in agreement with Johnston [2] results.

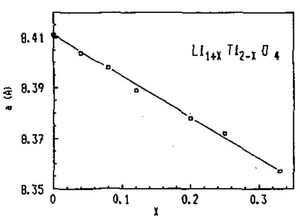

Fig. 1. – Lattice parameter *versus* composition for $Li_{1+x}Ti_{2-x}O_4$.

Electronic properties

On close examination of the specific heat of $LiTi_2O_4$ (Fig. 2), it appears that the transition is very sharp (ΔT_c= 0.32 K), indicating a very good homogeneity of the sample. This result is very satisfying, compared to that obtained for less homogeneous samples (Tab. I) or that reported by Johnston, ΔT_c=1.2 K. Note, on the other hand, that $\Delta C/\gamma T_c$, calculated from the specific

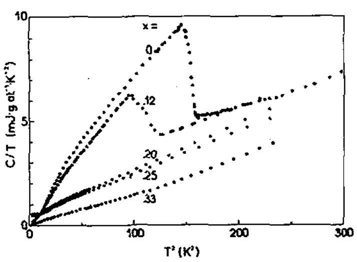

Fig. 2. – Specific heat of $Li_{1+x}Ti_{2-x}O_4$ for the temperature range 1.5-17 K.

Table I. – *Specific heat data.*

Compounds	γ ($mJgat^{-1}\ K^{-2}$)	θ_D (K)	T_c (K)	T_c onset (K)	ΔT_c (K)	$\Delta C/kT_c$	λ
$LiTi_2O_4^*$	2.55	490	12.9	13.4	0.60	1.4	0.74
$LiTi_2O_4$	3.14	535	12.4	12.6	0.32	1.57	0.71
$Li_{1.12}Ti_{1.88}O_4$	2.15	480	10.4	11.1	1.24	1.39	0.70
$Li_{1.20}Ti_{1.80}O_4$	0.38	432	< 1.5				
$Li_{1.25}Ti_{1.75}O_4$	0.31	441	< 1.5				
$Li_{4/3}Ti_{5/3}O_4$	0.05	518	/				
$Li_{0.98}Mg_{0.02}Ti_2O_4$	3.70	555	11.8	12.6	0.84	1.39	0.69

*Inhomogeneous sample.

heat jump at the transition and the electronic term in the normal state, which is quite high, agrees with prediction of BCS theory. Further, upon cooling down to zero, it can be observed that C_{el} is nearly zero (while it is non-zero for an inhomogeneous sample). The obtained value for the electron-phonon parameter, $2\Delta/kT_c$=3.8, is in good agreement with recent tunneling results yielding 4.00 and quite comparable to the BCS value, 3.53. Accordingly, we can assume that $LiTi_2O_4$ is a good bulk superconductor, without detectable impurity phase, and which verifies BCS theory.

Examine now the behavior of off-stoichiometric samples $Li_{1+x}Ti_{2-x}O_4$. It appears, for increasing x, that T_c and ΔC decrease, while in turn $\Delta C/\gamma T_c$ stays constant and ΔT_c raises as displayed for $Li_{1.12}Ti_{1.88}O_4$ in figure 2. This variation is, in fact, not regular as noticed by Johnston [2]; it exists a turning value of x corresponding to a transition from superconducting to insulating state. Low γ values are reported for x ranging in between 0.2 and 1/3, but without noticeable transition above 1.5 K, while $\gamma = 0$ is only obtained for $x = 1/3$. Note that the non-superconducting fraction in $Li_{1+x}Ti_{2-x}O_4$ increases with x, and corresponds, according to $\gamma = 0$, to a pure insulating species. Finally, for the limiting value $x = 1/3$, giving a pure Ti^{4+} phase, the behavior plotted in figure 2 presents, as expected, the signatures of an insulating system.

The variation of the electrical resistivity ρ with temperature shows a nearly temperature independent behavior, but with an unexplained wide bump around 200 K for the stoichiometric sample (Fig. 3). For off-stoichiometric compounds, ρ increases in the normal state upon cooling down; furthermore, the resistivity at the transition increases rapidly when x is raised ($\rho = 1.35\ \Omega$ cm at T_c^{onset} for $x = 0.12$ instead of $4.7 \times$

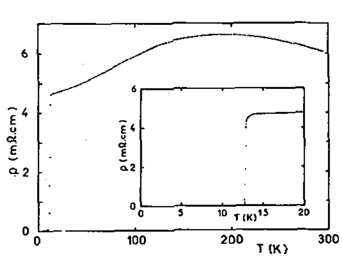

Fig. 3. – Electrical resistivity of $LiTi_2O_4$ for 4.2 K $<T<$ 300 K.

$10^{-3}\ \Omega$ cm for $x = 0$). The same findings have been observed by Johnston [2] and more recently by Watanabe *et al.* [3] but with resistivity larger by a factor 100. In addition, let us point out that the critical current is of the order of 10 A/cm^2 at 4.2 K, for $x = 0$, and decreases for increases x. In view of these results, a careful investigation of the influence of grain boundaries and intergranular regions has to be planned.

The magnetization curve of $Li_{1+x}Ti_{2-x}O_4$ exhibits the typical variation of superconductors reported so far. In the normal state, the magnetic susceptibility is weakly temperature dependent and its value is varying slowly with Li substitution. This behavior can be analyzed either through a band model (Pauli susceptibility) or in a mixed valence framework. In the specific case of Ti^{3+} which contains one unpaired electron, the behavior results from the combined effect of spin-orbit coupling and local distorsion stabilyzing a four fold degenerate level. Accidentally, this low-lying level is non-magnetic to first order. On close examination of the results, we can assume that the behavior for $x = 0$ obeys Pauli susceptbility with a superimposed contribution due to localized Ti^{3+} ions. Small amount of these last seems also to be present in the insulating phase ($x = 1/3$).

Concluding remarks

From the above results, it appears that our samples are of good quality, especially the stoichiometric compound $LiTi_2O_4$ whose specific heat variation shows a very narrow transition and no residual linear contribution below T_c. This sample verifies all features of a BCS weak coupling superconductor with typical parameters, $\Delta C/\gamma T_c$=1.4, $2\Delta/kT_c$=3.8,λ = 0.7 and a high γ value. Moreover, while T_c decreases with substitution of Li to Ti, γ falls to zero for the insulating material $Li_{4/3}Ti_{5/3}O_4$. Therefore, $LiTi_2O_4$ can be considered as a conventional BCS-type superconductor.

These preliminary results show that we have now to focus on the concentration range x = 0.2 to 0.3 where low γ values are obtained but no superconductivity is observed (at least above 1.5 K). This critical domain is now being studied in detail, including NMR studies. The important difference between theory and our experimental results concerning γ values variation has also to be explained. Further experimental studies will also concern the spinel system $Li_{1+x}Ti_{2-x}O_4$ where the ratio Ti^{3+}/Ti^{4+} is larger than 1.

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