

Evolution of Structure and Superconductivity with Lithium content in $\text{Li}_{1-x}\text{Ti}_2\text{O}_4$

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Abstract

The superconducting properties and crystal structure of the $\text{Li}_{1-x}\text{Ti}_2\text{O}_4$ compound have been studied as a function of lithium stoichiometry. We show that the presence of a maximum in the $T_c(x)$ curve is the result of the competition between the effects of the decrease in lithium stoichiometry and those induced by a gradual increase in Ti network disorder.

1. Introduction

The LiTi_2O_4 compound (spinel structure, space group $Fd3m$, $a \approx 8.41 \text{ \AA}$, $Z=8$) is known to be superconducting with $T_c \approx 11 \text{ K}$. In the spinel oxides containing lithium, it has been observed that the small Li^+ cations can move easily through vacant sites generated by the titanium-oxygen network. Therefore, by removing or inserting lithium, the stoichiometry of the compound can be varied. In the case of LiTi_2O_4 , we have previously shown [1] that it is possible to extract lithium in a "soft" and controlled way by immersion in an HCl solution.

Since the rate of lithium extraction strongly depends on the size, geometry and surface state of the grains, studies carried out on powder samples are hindered by the dispersion in lithium stoichiometry. Therefore, we have used single crystals to carry out a detailed study of the physical properties and crystal structure as a function of x in the $\text{Li}_{1-x}\text{Ti}_2\text{O}_4$ compound.

Preliminary results [1] indicated that the cell parameter a decreased monotonically from $\approx 8.41 \text{ \AA}$ to $\approx 8.30 \text{ \AA}$ with time of treatment in HCl, after which a plateau was reached. χ_{ac} measurements indicated that T_c initially increased to $\approx 14 \text{ K}$, and then decreased. When the cell parameter has reached its plateau, the sample is no longer superconducting. X-ray diffraction measurements performed on a single crystal with $a = 8.30 \text{ \AA}$ indicated that, as lithium was removed, part of the titanium atoms might have been displaced to occupy octahedral sites normally empty in the spinel structure.

The aim of the present study was to investigate detailed structural modifications induced by the removal of lithium and to correlate these modifications to the evolution of T_c . We have restricted our work to the small values of x for two main reasons: first, the region where T_c reaches a maximum is of particular interest, and second, the disorder of the Ti network caused by lithium extraction must be small enough not to hinder precise structure determination by x-ray single crystal analysis. In order to confirm the existence of a Ti network disorder, we have also performed electron diffraction experiments on samples with large x values.

2. Experimentals

2.1 Sample Preparation, Physical measurements

The single crystals used were prepared by electrolysis of molten salts, the bath used being a mixture of borates [2]. The octahedral-shape single crystals obtained were then ground into spheres, 0.1 mm in radius. A sphere was selected by checking its diffraction pattern with a precession camera. The following set of experiments was then carried out repeatedly with this sphere: lithium extraction, T_c measurement and structure determination using x-ray single crystal analysis.

Lithium was removed by immersing the spheres in a 1M HCl solution for a given time. T_c and the superconducting volume were obtained by magnetization measurements in a SQUID magnetometer.

2.2. Electron Diffraction Study

In order to verify the existence of a Ti cation network disorder, crystals treated in HCl solution for several days to create large lithium deficiencies ($a \approx 8.30 \text{ \AA}$) have been studied by electron diffraction. A Philips EM 400T microscope operating at 120KV was used.

Besides Bragg reflections, the presence of pronounced diffuse scattering was readily observed, and its geometry was studied by tilting around a^* and a^*+b^* directions from the [001] zone axis. Figure 1a and b shows examples of the diffuse scattering observed on [001] and [035] zone axes photographs, respectively.

To interpret the diffraction patterns we have applied the theory of invariant clusters proposed by Brunel et al. [3] and developed by Sauvage et al. [4]. This theory establishes that, if the diffuse scattering is confined to a geometric locus in reciprocal space, the ordering state can be described by the regular arrangement of identical polyhedra having the average composition of the sample. In the present case, we suppose that the diffuse scattering is due to the substitution disorder of Ti ions over the two types of octahedral sites in the spinel structure (16d and 16c), the displacement of Ti ions from a full 16d site to an empty 16c one being possible after the departure of the two neighboring Li ions.

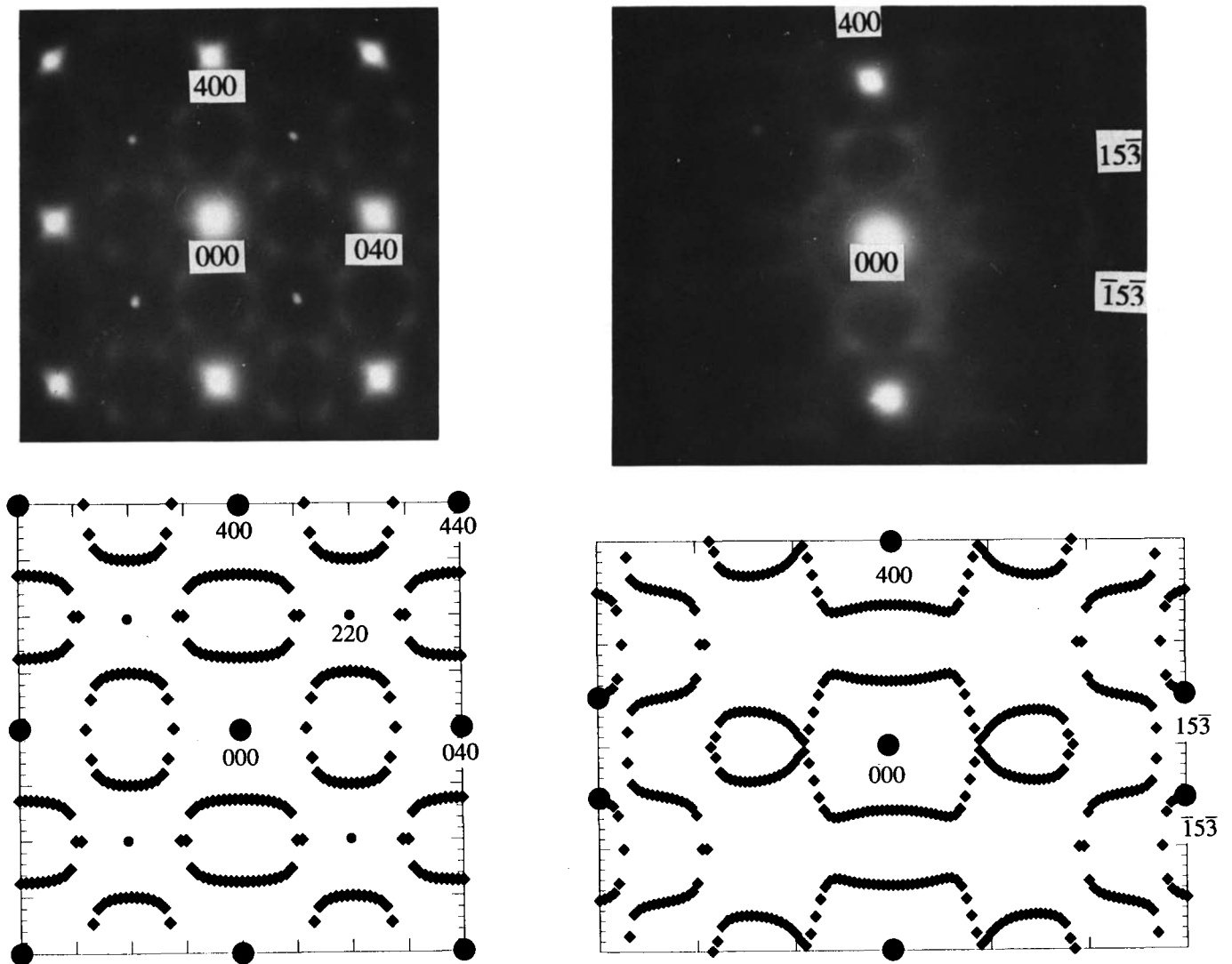


Figure 1. Electron diffraction photographs along the [001] (a) and [035] (b) zone axes showing the diffuse scattering due to Ti cation network disorder. The intersections of the diffuse scattering surface calculated with the model described in the text and the corresponding reciprocal planes are shown below.

Then, the relevant polyhedron is a cube of edge dimension $a/2$ whose corners and centers of the faces correspond to the center of the octahedral sites occupied either by a Ti atom or by a vacancy. The composition of the sample implies that the numbers of vacancies and Ti atoms in one such cube are equal. With this description, the equation of the surface of diffuse intensity is given by :

$$\cos(\pi h/2) + \cos(\pi k/2) + \cos(\pi l/2) + 4\cos(\pi h/2)\cos(\pi k/2)\cos(\pi l/2) = 0$$

The calculated intersections of this surface with different reciprocal planes are in agreement with the experimental diffraction patterns as shown in Figure 1a and b. This observation confirms the presence of a Ti cation disorder between the 16d and 16c octahedral sites in the case of large lithium deficiencies.

2.3. X-ray Diffraction Structural Analysis

The x-ray diffraction data were obtained with a CAD4 diffractometer using graphite monochromatized $\text{AgK}\alpha$ radiation. Cell parameters were obtained by absolute

measurement of the θ angles of 24 high angle reflections. The whole sphere in reciprocal space was collected up to $\theta=30^\circ$. It was noticed that the width of the Bragg reflections consistently increased as the lithium content was decreased. This effect is probably related to the presence of disorder in the cation network. Care was taken to choose sufficient scan widths in the ω -scan mode in order to correctly measure the reflection intensities.

The x-ray data were corrected for Lorentz-polarisation and isotropic absorption effects and averaged in the m3m point group. Internal consistency factors of the average were always of the order of 1%. The structure refinements were carried out with the MXD program [5] with the following atomic positions : Li 8a (1/8 1/8 1/8), Ti 16d (1/2 1/2 1/2) and O 32e (x x x, $x \approx 0.25$). The x parameter of the O atom and anisotropic thermal parameters for all atoms were refined together with the Li and Ti occupancy factors. The refinements were improved by allowing some of the Ti cations to be present on the 16c (0 0 0) octahedral site, which is normally empty in the spinel structure. In that case, the total Ti stoichiometry was constrained to unity and the thermal parameters of the Ti cation in the 16c position were constrained to be equal to those of the Ti cation in the 16d position.

Low angle reflections are known to be generally affected by various effects, such as non spherical contribution of valence electrons, extinction, etc...which can influence the values obtained for the Li stoichiometry. Thus, refinements were carried out with reflections having $\sin\theta/\lambda > 0, 0.4, 0.5$. Since better R factors and standard deviations for all parameters were obtained in the latter case, the final refinement cycles were carried out with reflections having $\sin\theta/\lambda > 0.5$, with all parameters varied simultaneously. For all experiments, the R factors were about 1% and the Li stoichiometry was determined with a $\approx 2\%$ precision.

3. Results and Discussion

Three sets of experiments have been carried out, corresponding to the as-grown crystal, and lithium-extracted crystal after 35' and 90' treatment in HCl solution. Figure 2 shows the magnetization curves obtained in the three cases. It can be seen that T_c is 11.5K for the as grown crystal, increases up to 13.2K after 35' treatment and then decreases down to 11.4K after 90' treatment. This confirms the behaviour of T_c found in our preliminary studies.

The results of the x-ray single crystal analyses are reported in Table 1 together with the principal interatomic distances. The Ti cation valences also reported in Table 1 were calculated by using the bond strength-bond length empirical relation with the constants given by Brese and O'Keeffe for Ti^{3+} cations [6].

The lithium stoichiometry decreases when the time of treatment (t) increases, as expected, but a really significant amount of cationic substitution ($\approx 2\%$) is only detected when $t=90'$. This is due to the short distance

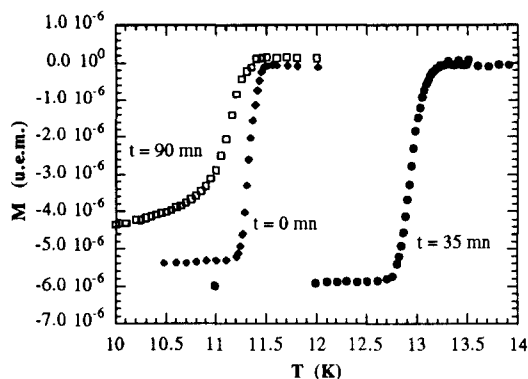


Figure 2. Magnetization curves as a function of time of treatment in HCl for $Li_{1-x}Ti_2O_4$.

between the 16c (000) sites and the two adjacent 8a (1/8 1/8 1/8) and (7/8 7/8 7/8) normally occupied by lithium : occupation of a 16c site by a Ti cation is only possible when these two adjacent Li sites are vacant, which is statistically unlikely to occur for small x values. Therefore, for very small x values ($t \leq 35'$) the evolution of the structure is only governed by the effects of lithium extraction : the cell parameter decreases from 8.398Å to 8.387Å and the oxygen positional parameter is not changed on going from $t=0'$ to $t=35'$. Consequently, the Ti-O distance decreases by 0.003Å and the Ti cation valence increases by 0.03 v.u.

When $t=90'$, $\approx 2\%$ of the Ti cations occupy the 16c site. This has several consequences on the evolution of the structure with x. First, the presence of Ti cations on the 16c site can hinder the Li diffusion through the crystal. The rate of Li extraction as a function of t is thus slightly decreased. Second, the Ti-O distances in the 16c site are too large ($\approx 2.20\text{Å}$) for the Ti cations. Thus, the occupation of a 16c site will lead to a local decrease of the Ti-O distances for this site. The oxygen positional parameter, which is now a spatial average between occupied and vacant 16c sites, decreases accordingly. As a consequence, the Ti-O distances of the 16d site increase, leading to a decrease of the Ti valence, and the Li-O distances decrease. Then, no change of cell parameter is necessary to accommodate the decrease of x due to Li extraction.

As shown above, our structural results can be interpreted in terms of a competition between the effects of lithium extraction and progressive occupation of the 16c sites by the Ti cations. An important observation is that the maximum of $T_c(x)$ corresponds with the maximum of the Ti cation valence. For small x values ($t \leq 35'$), almost no Ti network disorder exists and the Ti valence increases due to Li extraction, as expected ; T_c increases. When Li is further extracted, Ti cations begin to occupy the 16c sites, and the Ti valence on the 16d site decreases ; T_c decreases. The Ti cations on the 16c sites and the vacancies created on the 16d one could play the role of defects and trap the charge carriers, progressively leading to the disappearance of superconductivity when x

Table 1. Results of the single crystal x-ray diffraction analyses of $\text{Li}_{1-x}\text{Ti}_2\text{O}_4$ as a function of time of treatment in a HCL solution

Treatment in HCl	0 mn	35 mn	90 mn
a (Å)	8.398(1)	8.387(1)	8.386(1)
$x(\text{O})$	0.26261(3)	0.26267(4)	0.26220(5)
$U_{11}(\text{O})$ (Å ²)	0.00614(6)	0.00698(8)	0.0077(1)
$U_{12}(\text{O})$ (Å ²)	-0.00032(6)	-0.00020(8)	0.00000(9)
$p(\text{Li})=1-x$	0.93(1)	0.89(2)	0.86(2)
$U_{11}(\text{Li})$ (Å ²)	0.0110(5)	0.0120(7)	0.0108(8)
$p(\text{Ti}_{16d})$	0.9978(5)	0.9925(7)	0.9816(9)
$U_{11}(\text{Ti})$ (Å ²)	0.00584(2)	0.00689(3)	0.00802(4)
$U_{12}(\text{Ti})$ (Å ²)	-0.00083(2)	-0.00084(8)	-0.00074(3)
R	0.72%	1.05%	1.19%
χ^2	0.624	0.574	0.999
$d(\text{Li-O})$ (Å)	2.0016(3)	1.9999(3)	1.9928(4)
$d(\text{Ti}_{16d}\text{-O})$ (Å)	1.9992(3)	1.9962(3)	1.9994(4)
$d(\text{Ti}_{16c}\text{-O})$ (Å)	2.2105(3)	2.2081(3)	2.2036(4)
$v(\text{Ti}_{16d})$ (v.u.)	3.418	3.446	3.416
T_c (K)	11.5	13.2	11.4

continues to increase.

It could also be possible that the extraction of lithium in the solution takes place through an exchange reaction with creation of hydroxyl groups in the crystal. The presence of the very small amounts of protons involved in such a process would be extremely difficult to detect by x-ray diffraction techniques. However, it could have important consequences on the charge balance and physical properties of the compound. Additional experimental work is underway to check the validity of this hypothesis.

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