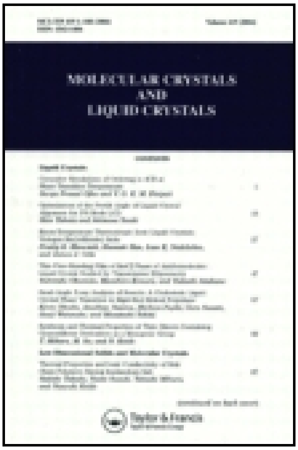

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Li Intercalation in $Tl_2Ba_2CuO_{6+\delta}$ Superconductor and Effective Charge of Migrating Li Ion

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Li Intercalation in $Tl_2Ba_2CuO_{6+\delta}$ Superconductor and Effective Charge of Migrating Li Ion

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Li intercalation into $Tl_2Ba_2CuO_{6+\delta}$ superconductor was shown to decrease doping level, leading to T_C increase for this overdoped material. By studying redistribution of intercalated atoms under flow of longitudinal electrical current, effective charge of migrating Li ion was determined as 1.1±0.3.

Keywords: intercalation; superconductivity; effective charge; electromigration

INTRODUCTION

Crystal lattices of $Bi_2Sr_2Ca_{n-1}Cu_nO_y$ and $Tl_2Ba_2Ca_{n-1}Cu_nO_y$ (n = 1 to 3) high temperature superconductors can be considered as formed of blocks of n CuO_2 layers, sandwiched by n+1 Sr(Ca)-O [or Ba(Ca)-O] layers. The blocks are terminated by Bi-O (Tl-O) buffer layers and are weakly coupled by Van der Waals force, enabling an intercalation of guest atoms and molecules [1,2].

The intercalation increases interlayer distance [1-6] and leads to the change of the doping level [7,8]. Therefore it can be an effective tool for modification of superconducting properties via charge transfer between the guest atom and host material. Until now intercalation was shown mostly to decrease T_C. This decrease is probably due to the decrease of the doping level [8], since in most of the compounds additional treatment is needed to increase a hole density for T_C increase (underdoped materials). $Tl_2Ba_2CuO_{6+\delta}$ is one of the few naturally overdoped materials. In this report we present evidence that Li intercalation increases superconducting T_C of the material by doping level decrease.

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EXPERIMENTAL

High-density (95% of theoretical value) ceramic samples of $Tl_2Ba_2CuO_{6+\delta}$ were obtained by hot-pressing technique. Structural identification was carried out by powder X-ray diffraction and all samples were confirmed to be single phase. The diffraction patterns were successfully described using tetragonal unit cell with $a=b=3.87$ Å and $c=23.17$ (±0.01) Å. The electronic properties of the samples were characterized by measuring temperature dependencies of resistance R(T) by a four-probe technique and of the Seebeck effect S(T) by an alternating gradient technique [9]. The superconducting T_C was determined as R(T) transition midpoint. Seebeck coefficient value at room temperature S_{RT} was used for the doping level characterization [10].

Li intercalation was done according to the procedure of Ref. 4. $LiClO_4$ in PC was used as an electrolyte. The intercalation leads to a formation of a product, which can be formally represented by the formula $Li_x{:}Tl_2Ba_2CuO_{6+\delta}$, with x up to 0.1, according to the Coulometric analysis data. The intercalation was reversible, at least during several first cycles.

After intercalation the pellet was treated in dry helium gas atmosphere. It was sectioned into parallel bars, on which T_C and S_{RT} were determined. Some of the samples were subjected to the post-intercalation treatment by a high-density electrical current to obtain longitudinal intercalant distribution change, similar to that obtained in pristine samples [11,12]. Effective charge of migrating atoms was determined from steady-state distribution profile [13].

RESULTS AND DISCUSSION

Intercalation

Fig.1 shows R(T) of pristine and intercalated samples. In the pristine sample T_C was 20 K and the transition width ΔT_C was typically 2 K. This T_C value indicates overdoping of the as-grown samples. Similar conclusion can be made from $S_{RT}= -6.2$ μ V/K and lattice parameter c [10]. Intercalation leads to general T_C increase and transition broadening. After de-intercalation the T_C of the sample comes approximately back to the initial value, however, ΔT_C essentially increases, and residual R appears below T_C. Dependence of the T_C and S_{RT} on the intercalated charge (per formula unit) is shown in Fig.2. The lattice parameter change is very close to our experimental resolution, except for the samples with Li content 0.07 and 0.1, in which $c=23.19$ Å. The data indicate a tendency for c-axis lattice expansion, though this point requires more precise measurement. Intercalation of 0.1 Li ion into compound can lead to T_C increase almost up to that of the optimally doped material (T_C=90 K) [10]. On contrary, the increase is actually limited to ca 40 K, and further intercalation leads to rapid residual R increase. These facts indicate that besides intercalation into matrix material (most probably Li atoms come to the interstitials

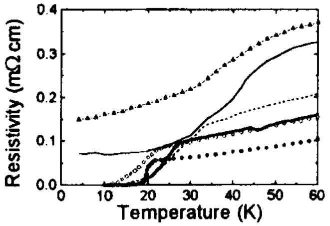

Fig.1

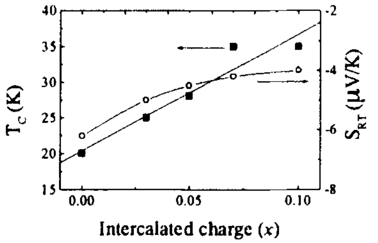

Fig.2

FIGURE 1 R(T) in the vicinity of the superconducting transition for as-grown material (solid dots); intercalated to x=0.03 (solid line); exfoliated after x=0.03 intercalation (open dots); intercalated to x=0.05 (thick dashes), x=0.07 (thin solid line) and x=0.10 (up triangles + full line).

FIGURE 2 Dependence of the superconducting transition temperature T_C (squares) and thermopower at room temperature S_{RT} (circles) on intercalated charge

between Tl-O layers, similar to excess oxygen atoms [14]), reaction leads to a decomposition of the material. Some new phases seem to be precipitated in the grain boundary region, since with intercalation $x \geq 0.07$ residual R increases much more rapidly than S_{RT}, which is almost saturated. This conclusion is supported by the facts that S is still equal to zero below T_C and no new phases are detected within the resolution of the X-ray studies.

Electromigration

Intercalated samples were subjected to a treatment with DC electrical current. This treatment is known to change T_C in pristine samples in a different way in the cathode and anode regions due to migration of oxygen [11]. Similar to pristine samples, current flow in x=0.03 samples created a gradient of T_C and S_{RT}, with both increasing in the cathode and decreasing in the anode region. However, in this case the changes are observed at essentially lower current densities [11,12]. The distribution becomes stable after 24 hrs of ≈ 10 Acm^{-2} current passage at 77 K, enabling determination of effective charge of migrating atom, according to the formula $\mathit{grad}[\ln(x)]=(ZeEF)/(fkT)$ [13], where concentration x gradient is created along current flow direction, Z is effective charge of migrating atom, e- electron charge, E is electric field strength, k is Boltzman constant, f and F are solute correlation and vacancy flow factors, respectively. For small *x* we can take both *f* and *F*=1, and simplify the relation to $\Delta x/x = ZeU/kT$, where U is voltage between probed points. Distribution of Li atoms was determined by sectioning long (30 mm) sample into 20 pieces, measuring for each piece T_C and S_{RT}, and determining *x* according to Fig.2. The distribution is approximately linear (Fig.3), as expected for small concentration gradients, and from its slope and voltage drop in the sample U we can extract Z as 1.1±0.3. Since the electromigration rate is notably increased in the intercalated samples, it is natural to take this charge as that of Li ion, and not of the migrating interstitial oxygen atoms [11].

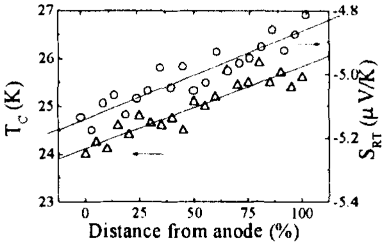

FIGURE 3 Distribution of T_C (triangles) and S_{RT} (circles) along the sample after passing 10 Acm^{-2} current for 24 hrs, *x*=0.03 sample.

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