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Transport properties of Li intercalated $KCa_2Nb_3O_{10}$

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Abstract

Superconductivity was observed in Li intercalated $KCa_2Nb_3O_{10}$ with a triple-layered perovskite structure. Although pure $KCa_2Nb_3O_{10}$ is electrically insulating, during Li intercalation electrical resistivity is dramatically reduced. The temperature dependence of resistivity of the sample, after 4 months of intercalation, shows metallic behavior below 50 K and a superconducting transition around 2 K (onset).

Keywords: Superconductivity; $KCa_2Nb_3O_{10}$; Insulator; Intercallation

Ten years have passed since the great discovery of the high-Tc superconductor $La_{2-x}Ba_xCuO_4$ [1]. Since that time, many high-Tc superconducting cuprates having two-dimensional CuO_2 layers have been synthesized. However, currently there is no widely accepted theory generally accorded to the high-Tc superconducting mechanism. In this situation, for further investigation, synthesis of new copper-free oxide superconductors with a layered perovskite structure are required. Contrary to our expectation, there have been only a few reports of the discovery of noncopper superconducting oxides with layered structure, e.g., Sr_2RuO_4 [2] and Li_xNbO_2 [3]. Here we describe the discovery of a new copper-free superconductor, Li intercalated $KCa_2Nb_3O_{10}$, with a layered perovskite structure. Fig. 1 shows a schematic of the crystal structure of $KCa_2Nb_3O_{10}$. It has a crystal structure of triple-layered NbO_6 octahedra [4] analogous to superconducting cuprate.

$KCa_2Nb_3O_{10}$ was synthesized by a standard solid-state reaction. An appropriate mixture of K_2CO_3, $CaCO_3$ and Nb_2O_5 was calcined in air. 10% excess K_2CO_3 was added to compensate for the loss due to devolatilization. Fired samples were reground and pelletized, and then calcined again at 1150°C for 10 h in air. The samples obtained were analyzed by X-ray powder diffractometer and confirmed to be a single phase. To introduce electron carriers, Li was intercalated into the samples by placing them in vials with an n-butyl lithium n-hexane solution. Prior to intercalation, Au electrodes, for resistivity measurements, were attached to the samples with Au paste and soldered with indium. The electrical resistivity was measured by a standard four-probe method in the temperature range 300–0.85 K. Low-temperature measurements were carried out using a ^3He refrigerator.

The starting samples, pure $KCa_2Nb_3O_{10}$, were white in color and electrically insulating. However, during Li intercalation of the samples in n-butyl lithium n-hexane solution, the room-temperature resistivity was dramatically reduced by approximately more than 3 orders of magnitude. Fig. 2 displays the temperature dependence of electrical

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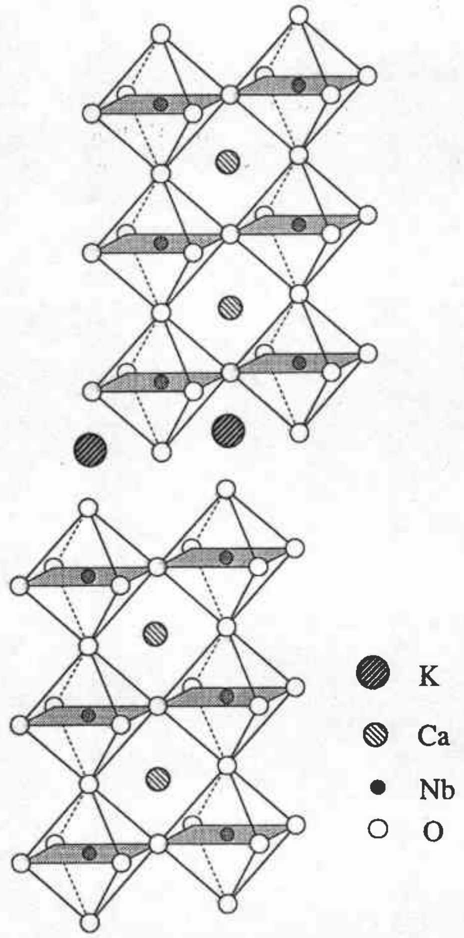

Fig. 1. Schematic of the crystal structure of $KCa_2Nb_3O_{10}$.

resistivity of $KCa_2Nb_3O_{10}$ after various intervals of intercalation. While initially semiconducting, the temperature dependence of resistivity approached metallic behavior over time. Activation energies for the semiconducting samples, those intercalated for less than two months, were estimated from the assumable temperature range and found to be between 5 and 32 meV. For the samples intercalated more than one month, the resistivities were found to increase with decreasing temperature to ~6 K whereupon they dropped in a manner that could suggest partial superconductivity. The temperature dependence of resistivity down to 0.85 K of the sample intercalated for 4 months is shown in Fig. 3. The resistivity exhibits metallic behavior below 60 K and drops rapidly around 2 K which corresponds to the onset of a superconducting transition. The broadness of the

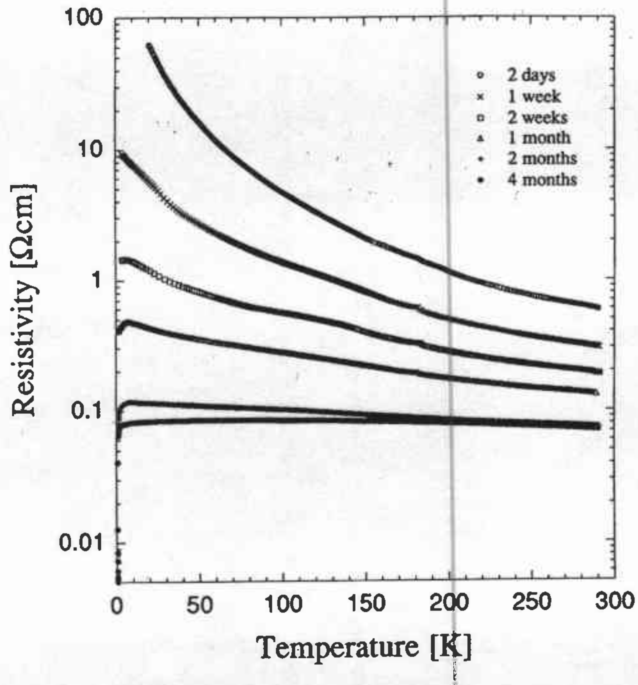

Fig. 2. The temperature dependence of electrical resistivity of $KCa_2Nb_3O_{10}$. Times indicated in the figure mean the duration of Li intercalation.

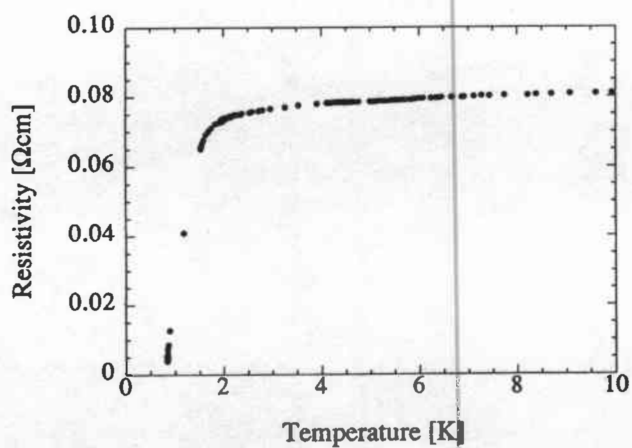

Fig. 3. Temperature dependence of resistivity below 10 K for the sample intercalated for 4 months.

transition is associated with inhomogeneity in the density of Li ions.

In summary, we observed that Li intercalation induced superconductivity in the triple-layered perovskite niobium oxide, $KCa_2Nb_3O_{10}$. This discovery of superconductivity in this copper-free layered perovskite compound is significant for elucidation of the mechanism of high-Tc superconductivity.

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