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SUPERCONDUCTING PROPERTIES OF LAYERED PEROVSKITE $KCa_2Nb_3O_{10}$ AND $KLaNb_2O_7$

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$KCa_2Nb_3O_{10}$ and $KLaNb_2O_7$ have triple and double layered perovskite structures, respectively. Although they are electrically insulating, Li intercalation drastically reduces resistivity and induces an insulator–metal transition. The Li intercalated $KCa_2Nb_3O_{10}$ exhibits a superconducting transition around 1 K. However, $KLaNb_2O_7$ shows no superconducting signal down to 0.5 K. © 1997 Elsevier Science Ltd

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Since the great discovery of high-T_c superconductivity [1], many superconducting cuprates with layered perovskite structure have been synthesized. All of the high-T_c superconducting cuprates have Cu–O layers and show superconductivity near an insulator–metal transition. Recently a report of the superconductivity in the Sr_2RuO_4 isostructural with $La_{2-x}Ba_xCuO_4$ demonstrated that the presence of copper is not a prerequisite for superconductivity in the layered perovskite [2]. In this situation, transport and intercalation properties of niobium oxide were studied by several authors [3–9]. Also, interesting interlayer reactions were reported in $KCa_2Nb_3O_{10}$ and $KLaNb_2O_7$ having a layered perovskite structure similar to the Ruddlesden–Popper series [3–7]. Here we present the discovery of superconductivity in the Li intercalated $KCa_2Nb_3O_{10}$ [10] and absence of superconductivity in the Li intercalated $KLaNb_2O_7$.

The $KCa_2Nb_3O_{10}$ and $KLaNb_2O_7$ [3, 4] were prepared from the starting materials of K_2CO_3, $CaCO_3$, La_2O_3 and Nb_2O_5. 10% of excess K_2CO_3 was added to compensate for the loss due to devolatilization. Pressed pellets of appropriate mixtures of starting materials were fired at 1150°C in the ambient atmosphere. Although the samples obtained were white in color and electrically insulating, during Li intercalation into the sample using the *n*-butyl lithium *n*-hexane solution, room temperature resistivity was drastically decreased. Samples were analyzed by the power X-ray diffractometer using Cu K_α radiation and confirmed no change in structure between before and after Li intercalation.

The temperature dependence of resistivity of $KCa_2Nb_3O_{10}$ and $KLaNb_2O_7$ after various intervals of Li intercalation are shown in Figs 1 and 2, respectively. Times indicated in these figures mean the duration of Li intercalation. While initially semiconducting, resistivity properties approached metallic behavior. For $KCa_2Nb_3O_{10}$, with decreasing temperature, resistivity begins to decrease weakly at 5 K and drops suddenly to zero around 1 K corresponding to a superconducting transition [Fig. 3]. The a.c. magnetic susceptibilities of the samples intercalated for various durations are shown in Fig. 4. The Meissner signal was observed below 5 K and becomes stronger over time. The superconducting volume fraction is estimated at ~6% from susceptibility data at 0.5 K for a sample intercalated for 4 weeks.

Contrary to our expectation, for $KLaNb_2O_7$ intercalated for 5 weeks, the temperature dependence of resistivity exhibits metallic conduction and superconductivity is not observed down to 0.5 K. Figure 5 shows the logarithm of resistivity vs $T^{-1/3}$ for the lightly intercalated sample. That this fit is close to a straight line

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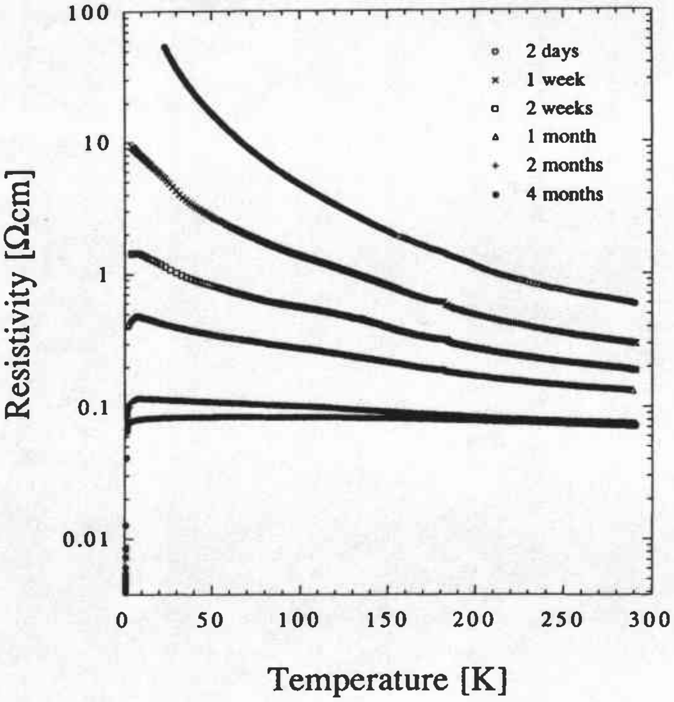

Fig. 1. Temperature dependence of electrical resistivity of Li intercalated $KCa_2Nb_3O_{10}$.

indicates that a variable range hopping (VRH) model describes well the low temperature properties of the material.

Superconductivity is realized in Li intercalated $KCa_2Nb_3O_{10}$. On the other hand, $KLaNb_2O_7$ can exhibit metallic behavior without any superconducting transition. Why the superconductivity is suppressed in $KLaNb_2O_7$ is the question we must ask. Li was intercalated into the alkali-metal layers sandwiched between perovskite sheets. For low concentration of intercalant of Li, Li enters inhomogeneously in the alkali-metal layers creating a random potential near the layers. This randomness affects the Nb–O layers of $KCa_2Nb_3O_{10}$ and $KLaNb_2O_7$. In the case of $KLaNb_2O_7$, both Nb–O layers are adjacent to alkali-metal layers, explaining why VRH conduction is

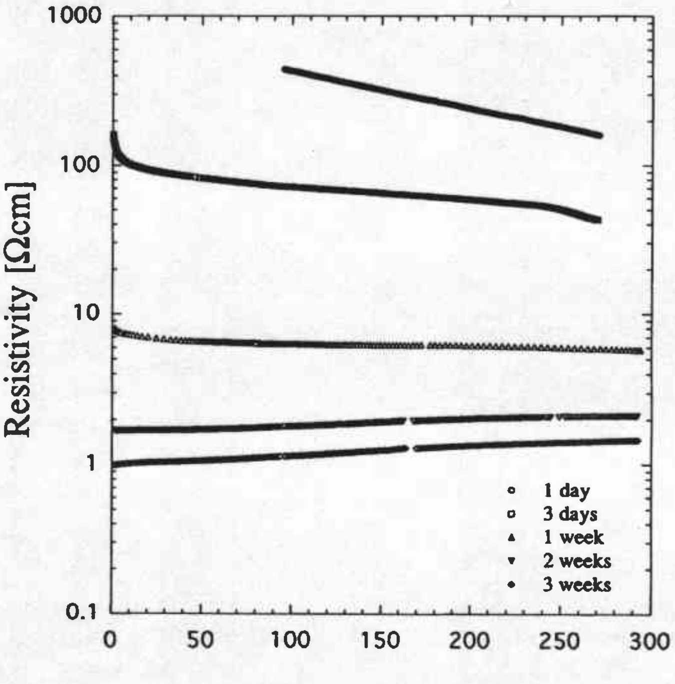

Fig. 2. Temperature dependence of electrical resistivity of Li intercalated $KLaNb_2O_7$.

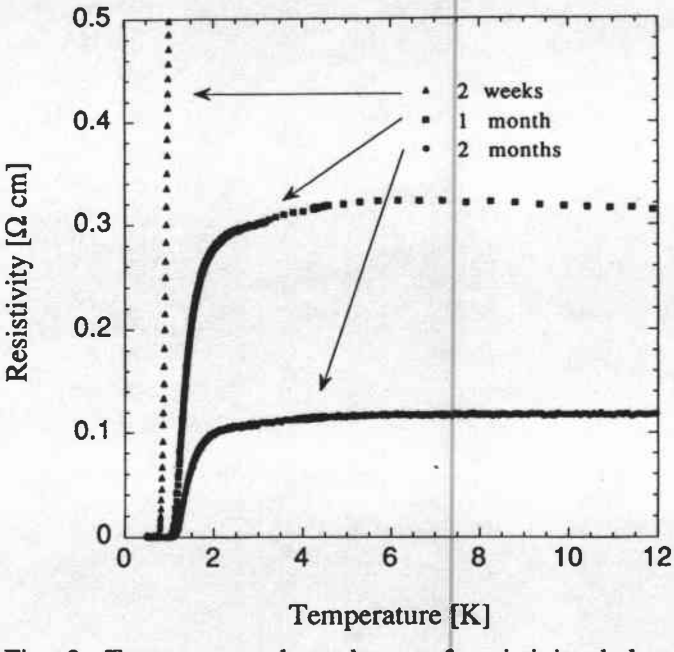

Fig. 3. Temperature dependence of resistivity below 12 K of $KCa_2Nb_3O_{10}$ intercalated for 2 weeks, 1 and 2 months.

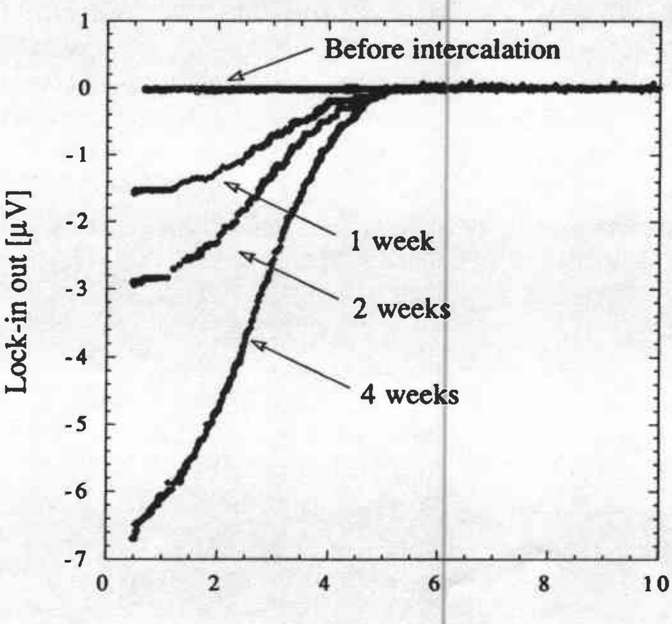

Fig. 4. Temperature dependence of a.c. magnetic susceptibility for Li intercalated $KCa_2Nb_3O_{10}$.

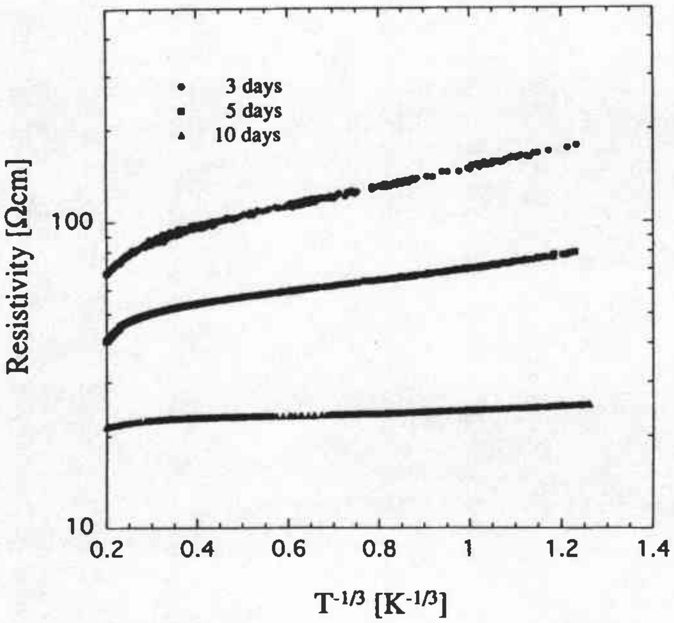

Fig. 5. Logarithm of resistivity as a function of $T^{-1/3}$ for Li intercalated $KLaNb_2O_7$.

observed. However, for $KCa_2Nb_3O_{10}$ the center Nb–O layer is far from the alkali–metal layers and thus is only weakly affected by the random potential. It seems likely that this middle layer is responsible for the superconducting behavior.

In summary, superconductivity was observed in the niobium oxide having a triple layered perovskite structure similar to high-T_c superconducting cuprates. However, the double layered analogue exhibits metallic conduction down to 0.5 K. We think that this difference is closely related to the effect of the random potential of Li. This new superconductor may provide clues to an elucidation of the mechanism of high-T_c superconductivity.

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