LBL-37360
UC-404

Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

Materials Sciences Division

National Center for Electron Microscopy

To be presented at the Microscopy Society of America, Kansas City, MO, August 13–17, 1995, and to be published in the Proceedings

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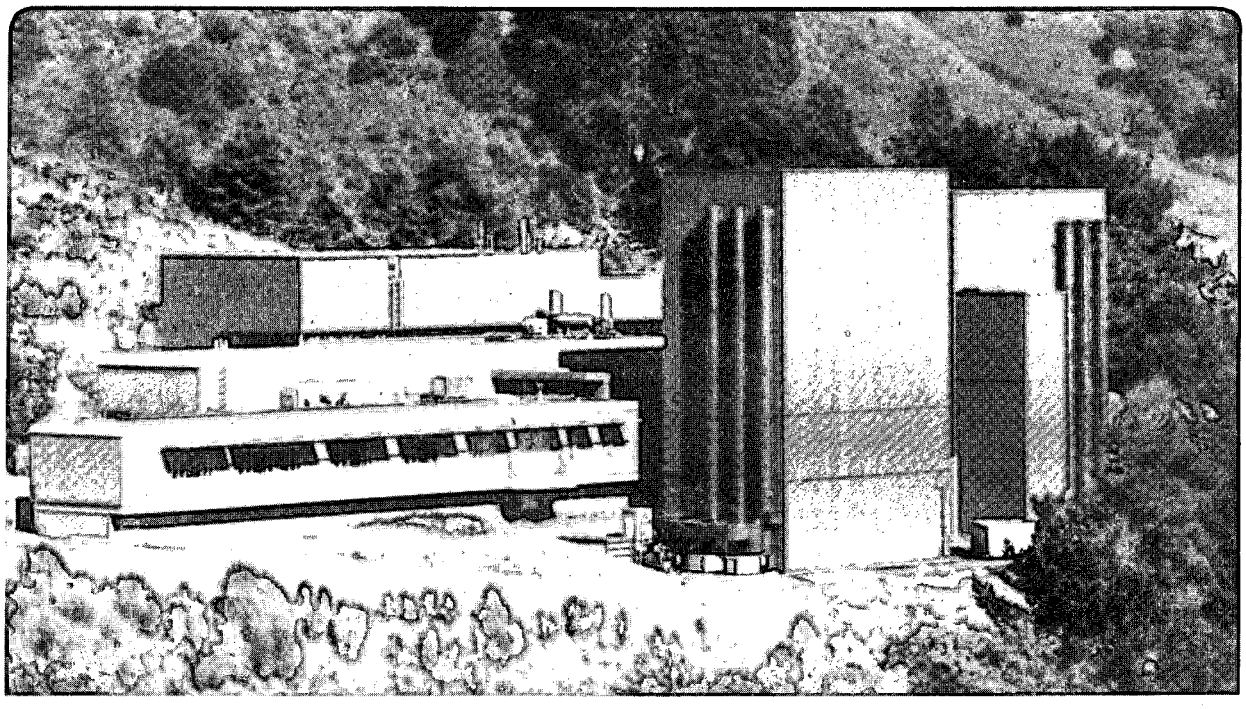
April 1995



Prepared for the U.S. Department of Energy under Contract Number DE-AC03-76SF00098

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Microscopy Society of America
Kansas City, MO., 8/13-8/17/95

This work was supported in part by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Science Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

SUPERCONDUCTIVITY AND OBSERVATION OF ORDERED STRUCTURES IN DEINTERCALATED Li_xNbO_2

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The prevalence of layered structures among the copper oxide superconductors has led us to search for new oxide superconductors with anisotropic structures to evaluate the relationship between structural anisotropy and superconductivity. Because of its layered structure,[1] we identified the dichalcogenide $LiNbO_2$ as a promising candidate for further study. The Nb oxidation state can be readily altered by deintercalation of Li, and we have reported magnetic measurements showing that the resulting Li_xNbO_2 ($x<1$) is a superconductor with transition temperature T_c=5.5K.[2] Interestingly it is the *Meisner fraction* rather than T_c, which changes as x is varied in this compound. This suggests that as a result of deintercalation, the material separates into two distinct phases, one superconducting and one non-superconducting, although powder x-ray diffraction shows no clear evidence of differences between $LiNbO_2$ and deintercalated material. This type of behavior is often associated with the transition to the superconducting state as the composition is varied in transition metal oxides.[3]

Since x-ray diffraction was unable to distinguish the two phases revealed by magnetic measurement, in the present study we use transmission electron microscopy (TEM) to examine Li_xNbO_2 materials. Because electrons are much more strongly scattered by a solid than are x-rays, electron diffraction will be better able to identify subtle changes in the crystal structure produced during deintercalation. TEM specimens were prepared by crushing the starting powders, suspending the finer particles in dry hexane, and then dispersing on a copper mesh grid with holey carbon film.[4] Except where otherwise indicated, all TEM work was performed using a room-temperature specimen holder. Diffraction patterns were obtained using an accelerating voltage of 100kV, while high-resolution imaging was carried out at 200kV and 800kV.

For material that was not deintercalated (hence $x\approx1$), selected area diffraction (SAD) patterns taken along the [001] axis show 6-fold symmetry and the expected lattice parameter $\mathbf{a_0}$=2.9Å (Fig. 1). In some areas, this sample yielded SAD patterns with extra reflections (also with 6-fold symmetry) corresponding to an extremely large lattice parameter ($a\approx41$Å), as shown in Fig. 2. In deintercalated materials with x ranging from 0.8 down to 0.65, two additional types of extra reflections were observed. The most prevalent of these corresponds to a tripling of the unit cell along <110> directions (yielding $a=\sqrt{3}\mathbf{a_0}$), (Fig. 3) and less frequently, a doubling along <100> (yielding $a=2\mathbf{a_0}$) also appeared (Fig. 4). Corresponding images of the "perfect" structure and the $2\mathbf{a_0}$ structure are presented in Figs. 5 and 6. Preliminary results with samples cooled to 98K indicate that the 41Å reflections disappear, the tripling along <110> and doubling along <100> remain stable, and no additional reflections appear at this temperature. (NOTE: All diffraction patterns are shown with the same scale.)

The occurrence of the extra reflections in these diffraction patterns can be explained either by the presence of charge density waves in Li_xNbO_2, or by ordering of Li-vacancies after deintercalation. Creation and subsequent ordering of oxygen vacancies can be ruled out because neutron diffraction indicates that deintercalated material is fully stoichiometric in oxygen (i.e., oxygen site occupation does not change upon deintercalation).[5] Furthermore, significant changes in niobium occupation would be detected by x-ray diffraction. Of the remaining two possibilities, Li-vacancy ordering is much more probable, since charge density waves are not expected to be stable in a sample at room temperature.[6] The fact that no additional periodicities seem to develop in a cooled sample tends to support this hypothesis. The large periodicity found in some areas of the $LiNbO_2$ sample can possibly be explained by small deviations from exact stoichiometry (x slightly less than 1), possibly beam-induced, with ordering of the small number of corresponding Li vacancies present in this case.

In summary, we have observed the appearance of extra reflections in [001] diffraction patterns obtained from deintercalated Li_xNbO_2 materials, and attribute this to the ordering of vacancies created as Li is removed from the host structure. The ordering of Li, apparently with two preferred periodicities, may be related to the phase separation revealed by magnetic measurement. Due to its sensitivity to scattering from light elements and ability to provide structural information from very small areas, transmission electron microscopy is proving to be an important tool in the study of the Li_xNbO_2 system.[7]

References

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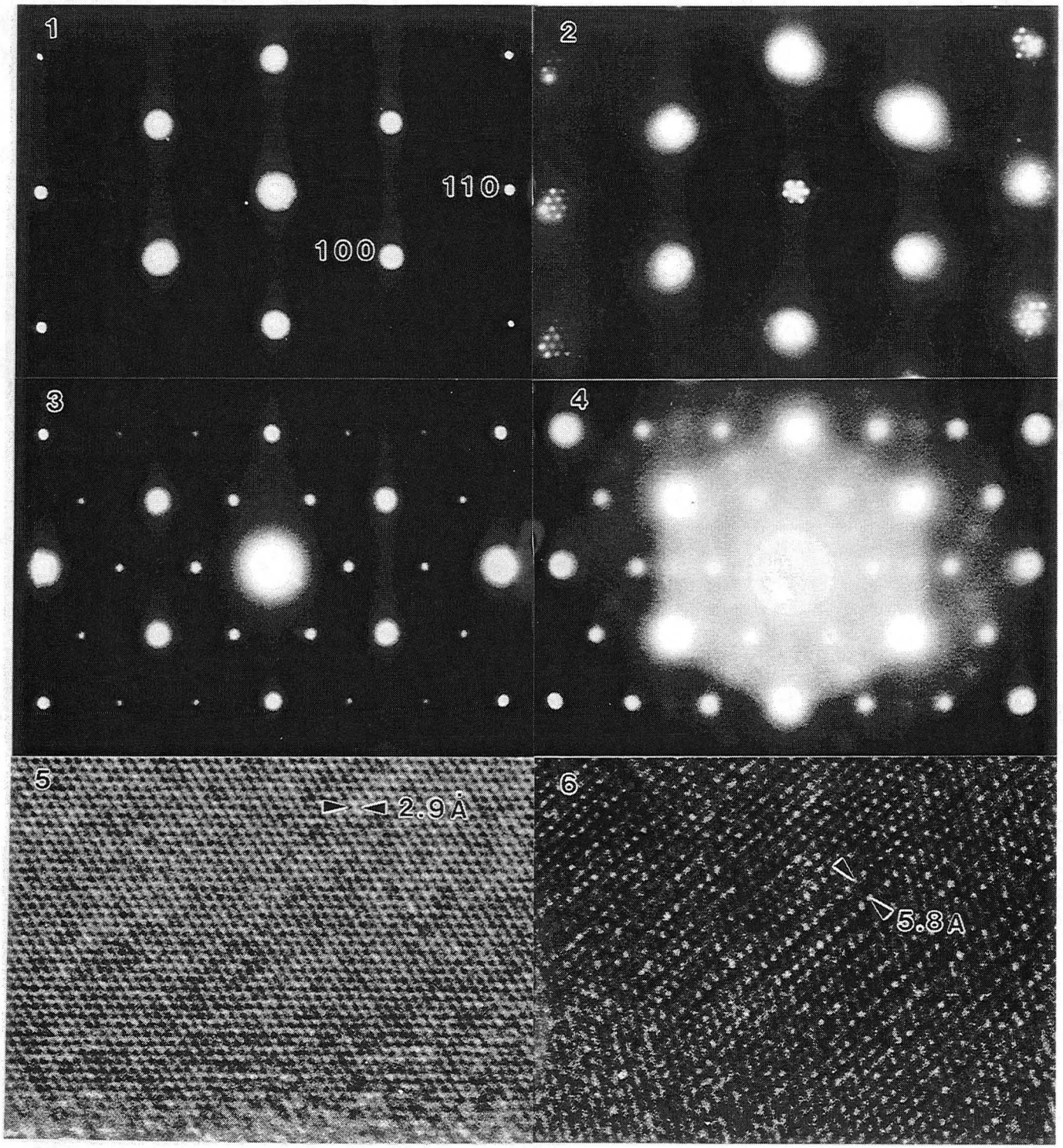

FIG. 1. -- [001] SAD pattern from stoichiometric $LiNbO_2$, showing 6-fold symmetry and $\mathbf{a_o}$≈2.9Å.
FIG. 2. -- [001] pattern from another $LiNbO_2$ particle, illustrating extra reflections with d≈41Å.
FIG. 3. -- [001] pattern from deintercalated Li_xNbO_2 showing tripling along <110> directions; here x≈0.65.
FIG. 4. -- [001] $Li_{0.65}NbO_2$ pattern showing doubling along <100> as well as tripling along <110>.
FIG. 5. -- High-resolution TEM image of "perfect", stoichiometric $LiNbO_2$ structure.
FIG. 6. -- High-resolution image from $Li_{0.8}NbO_2$, showing $2\mathbf{a_o}$ structure in central area of figure.

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