Comparison of the electronic structures of two non-cuprate layered transition metal oxide superconductors

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Abstract

Comparison is made of the electronic structure of the little-studied layered transition metal oxide LiNbO$_2$ with that of Na$_x$CoO$_2$, which has attracted tremendous interest since superconductivity was discovered in its hydrate. Although the active transition metal d states are quite different due to different crystal fields and band filling, both systems show a strong change of electronic structure with changes in the distance between the transition metal ion layer and the oxygen layers. The niobate is unusual in having a large second-neighbor hopping amplitude, and a nearest-neighbor hopping amplitude that is sensitive to the Nb–O separation. Li$_x$NbO$_2$ also presents the attractive simplicity of a single band triangular lattice system with variable carrier concentration that is superconducting.

1. Motivation

Among the various areas of research that were stimulated by the discovery of high temperature superconductors (HTS) nearly two decades ago is that of two-dimensional (2D) (or nearly so) transition metal oxides (TMOs). A second surprise appeared in 2001 with the discovery [1] of $T_c = 40$ K in MgB$_2$, where the physics is entirely different but the 2D character is crucial [2,3] for the surprisingly high value of critical temperature $T_c$. A further stimulus for study of superconductivity in 2D TMOs was provided in 2003 with the discovery [4] of hydrated Na$_x$CoO$_2$ at 4.5 K. These discoveries suggest a more general look at superconducting 2D TMOs besides the cuprates, to try to identify trends (or perhaps lack of trends).

Being isostructural to the first HTS (La,Sr)$_2$CuO$_4$, the ruthenate Sr$_2$RuO$_4$ has a special status in this class. Its electronic structure is quite distinct from that of HTS, however, and $T_c$ is only around 1 K. There is now a very large literature on Sr$_2$RuO$_4$. It is a different and very perplexing superconductor, but we will not pursue it in this paper.

What we focus on here is the little-noticed layered TMO superconductor Li$_x$NbO$_2$, with brief comparison with the cobaltate system Na$_x$CoO$_2$. This niobate was discovered [5] in 1990 when the community was absorbed with the new HTS materials, and has not yet attracted the attention that it deserves. While its $T_c = 5.5$ K is quite close to that of the hydrated cobaltates (4.5 K) it is the contrasts that we will focus on. These differences revolve mainly on: 4d versus 3d ion, trigonal versus octahedral coordination by six oxygen neighbors, and single band versus multiband character. We expose one similarity: z-displacement of the oxygen layers, which modulates the TM–O distance, has a strong influence on the electronic structure.

2. Layered lithium niobate

The compound LiNbO$_2$ itself is a band insulator with gap $\sim 2$ eV. The de-lithiated phase Li$_x$NbO$_2$ was found by the Berkeley group to be superconducting [6], with the few reports to date suggesting superconductivity sets in around $x \approx 0.8$ (i.e., when 20% of the Li is removed) beyond which $T_c$ does not depend much on the Li content $x$. The structure of LiNbO$_2$ consists of a triangular lattice of both the Li cations and the transition metal (niobium) ions, separated by layers of oxygen atoms, similar to Na$_x$CoO$_2$ except for the TM coordination. The trigonal prismatic coordination of niobium atoms by oxygen ions provides a
big distinction. The trigonal crystal field results in an
inertonic lowering of the Nb d_{z^2} states with respect to the
other 4d states by about 4 eV, leaving the system with only
a single band per formula unit to consider. This valence-
conduction band is also well separated from the O 2p
bands below (see Fig. 1).

Removal of the lithium has the effect of adding holes to
the conduction band made up of Nb d_{z^2} states. Super-
conductivity appears, as it does when holes are introduced
into NaCoO2 (followed by hydration), and at a very similar
temperature (5 K), but apparently at quite different carrier
concentrations and for very different electronic structures.

Since the Li content is variable, this compound becomes a
clean representation of a single band triangular lattice
system which can be compared rather directly with
Hubbard model results. As part of our study of this
system, we obtain a tight-binding (TB) representation of
the band to allow the subsequent study of possible
correlation effects within the Hubbard model. We return
to these issues below.

Structure. LiNbO2 takes on a hexagonal structure [6–8]
(a = 2.90 Å, c = 10.46 Å) having space group P6_3/mmc
(No. 194), with sites Li [2a(0, 0, 0), 3m], Nb
[2d(1/3, 1/3, 0), 6m2], and O [4f(1/3, 1/3, zO), 3m]. The oxygen
internal parameter zO specifies the Nb–O bond length and
due to the stacking type there are two LiNbO2 layers per
cell. The distance between Nb atoms, a, is almost identical
to bond length 2.86 Å in elemental BCC Nb, so direct
Nb–Nb overlap should be kept in mind. Experimental
values [6–9] of the internal parameter range from 0.125 to
0.129. Our optimization by energy minimization using the
abinit code gives the value zO = 0.125 (lattice constants held at the experimental values).

Electronic structure and tight-binding representation. The
band structure of LiNbO2 pictured in Fig. 1 is similar to
that given earlier by Novikov et al. [10] and indicates a Nb
d_{z^2} bandwidth of 1.9 eV. The Nb d_{z^2}-O 2p bands can be fit
straightforwardly to a TB model based on orthonormal
Wannier functions on the two Nb atoms per cell (one Nb
per layer). A full description of the results will be given
elsewhere, but we provide a synopsis here. There are three
important features of the TB fit that we emphasize here.
First, a good fit requires rather long range hoppings, up to
fourth neighbors within the layer and to three neighbors in
the layers above and below. Second, with oxygen ions at
their equilibrium position, the second-neighbor (in-plane)
hopping amplitude t_2 ~ 100 meV is much larger than the
nearest-neighbor hopping t_1 ~ 60 meV. The smaller value
of t_1 may reflect interference between direct Nb–Nb
interaction and the standard O-mediated Nb–O–Nb
processes. The same trend has been observed for 2H–TaS_2
[11], where the small value of t_1 was traced to phase
cancellation in the hopping integral when Wannier func-
tions are on nearest neighbors. This t_2 > t_1 feature may
have important implications for the microscopic under-
standing of the properties of Li_xNbO_2, since if t_2 were the
only non-zero hopping, the system decomposes into three
decoupled triangular lattices with lattice constant \sqrt{3}a; t_1
then becomes the “perturbation” that couples the three
sublattices, breaks symmetry and removes degeneracy.
Thirdly, the nearest-neighbor hopping t_1 is very strongly
modulated by oxygen displacement. We find that t_1
increases strongly as the O layers “squash” against the
Nb layers, as in the A_2 Raman mode. This modulation may
provide the largest contribution to electron–phonon
coupling in this compound.

Effective charges. We have evaluated the Born effective
charge tensor as described by Gonze and Lee [12] using the
abinit code [13]. Given in Table 1 are the two distinct
elements of the effective charge tensor for each atom type,
calculated in the relaxed atomic structure together with the
formal charges. Z^*_{Li}(Li) (Z^*_O = Z^*_N) is close to the formal
charge of Li indicating primarily ionic type bonding for
motion in the x–y plane, consistent with its propensity for
de-intercalation. The charge tensor for Li shows similar
anisotropy to that of LiBC [14] which is similar structurally
and electronically (if some Li is de-intercalated) to the 40 K
superconductor MgB_2. In LiBC Z^*_{Li}(Li) = 0.81,
Z^*_N(Li) = 1.46, and it was concluded that Li is involved in
electronic coupling (not only ionic, but covalent)
between consecutive B–C layers. Similar Li involvement
might be expected in LiNbO_2, and indeed the band
structure shows clear effects of interlayer coupling. The
difference from the formal charges for the Nb ions
(formally Nb^{5+}, O^{2–}) indicate substantial covalent char-
ter to the bonding which appears to be especially strong
for z displacement of the Nb ion.
The angular average \( Z_z \) is also displayed. Note the unexpected deviations from the formal values \( Z_0 \) of the effective charges for Li and Nb in the \( z \)-direction (larger for Li, smaller for Nb). For O in LiNbO\(_2\), the effective charges are nearly isotropic. Overall, the anisotropies are rather similar in NaCoO\(_2\), but somewhat more pronounced.

The Born effective charges have been reported [15] for NaCoO\(_2\), and since we investigate O squashing in this compound in the next section, we have included the NaCoO\(_2\) effective charges in Table 1 for comparison. Indeed there are several similarities, as noted in the table caption.

### 3. Layered sodium cobaltates

There is already a substantial literature on the electronic structure of the Na\(_x\)CoO\(_2\) system. Briefly: the \( t_{2g} \) bands are broken in symmetry by the layered structure and by the squashing of the CoO\(_2\) layers away from ideal cubic coordination by the six O ions. The bands are doped with \( 1 - x \) holes, with all the evidence indicating the holes go, at least initially, into \( a_g \) states rather than \( e_g' \) states. Using the observed structure, it is found that this results from the somewhat larger \( a_g \) bandwidth, because the band centers remain indistinguishable.

We address here the effect of the height of the O ions above/below the Co layer. In the calculations, the full-potential non-orthogonal local-orbital minimum-basis scheme (FPLO) was used [16]. For specific doping levels and treatments of the Na ions, the height has been optimized by a number of groups [17–21], revealing that there is some sensitivity of the O position to the environment. To clarify the question of the effect of squashing without reference to a specific doping level, we display in Fig. 2 the \( t_{2g} \) bands for O height (from the Co layer) of 1.14 Å (corresponding to undistorted CoO\(_6\) octahedra), 0.96 Å (typical value for intermediate values of \( x \)), and 0.88 Å (the smallest value reported). For orientation, we note that Johannes et al. [18] using the virtual crystal approximation for the Na concentrations \( x = 0.3, 0.5 \) and 0.7, obtained the heights 0.88, 0.90, 0.93 Å, respectively. The corresponding projected densities of states are shown in Fig. 3. For these calculations we used \( x = 0.5 \), treated within the virtual crystal model. To avoid unphysical O–O interactions across the layers as the O layer position was varied, the \( c \) axis was artificially increased by 20% for these calculations.

Simple crystal field arguments would suggest: (1) for the cubic octahedron \( z_0 = 1.14 \) Å the \( a_g \) and \( e_g' \) DOS should be the same, and (2) as the O ions are squashed down, the \( e_g' \) states should squash relative to the \( a_g \) states. The first expectation is severely violated in the region just below

### Table 1

Born effective charges for LiNbO\(_2\), together with a comparison with NaCoO\(_2\) calculated by Li et al. [15].

<table>
<thead>
<tr>
<th></th>
<th>LiNbO(_2)</th>
<th>NaCoO(_2)</th>
</tr>
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<tbody>
<tr>
<td>( Z_{xx} )</td>
<td>1.10</td>
<td>0.87</td>
</tr>
<tr>
<td>( Z_{yy} )</td>
<td>1.69</td>
<td>1.37</td>
</tr>
<tr>
<td>( Z_{zz} )</td>
<td>1.31</td>
<td>1.87</td>
</tr>
<tr>
<td>( Z_{t} )</td>
<td>+1</td>
<td>+1</td>
</tr>
</tbody>
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$E_F$ due to the dispersion being only 2D (presuming crystal fields from ions beyond nearest O ions are negligible). In addition, the effects of squashing are much more complex than suggested by the crystal field model. There is minor change in the mean energies of the $a_g$ and $e_g'$ states (they remain essentially equal, see Fig. 3), the main change is an increase in the $a_g$ bandwidth compared to that of the $e_g'$ states upon squashing. For $z_o = 1.14$ Å, doped holes initially would go equally into each band. At the highly squashed end, $~0.4$ holes/per Co can go into the $a_g$ band before encountering the $e_g'$ states. We emphasize that this is a model, constrained result; self-consistency and geometrical relaxation will change the details. There is also the question of decreasing interaction with the O 2p states upon squashing. This change which is of course also included in the changes shown in Figs. 2 and 3, may affect the $a_g$ and $e_g'$ states differently. The changes in the band structure, Fig. 2 are more instructive. At $\Gamma$, the $a_g$ state is almost 0.5 eV below its maximum for the cubic octahedron $z_o = 1.14$ Å, the maxima occurring midway along both $\Gamma$–M and $\Gamma$–K lines. The additional structure, and the associated decrease in bandwidth reflects longer range hopping, and most likely a strong change in the ratio $t_2/t_1$, analogous to the changes in LiNbO$_2$ but with additional complications due to the presence of the $e_g'$ bands. The shift with squashing motion in the $e_g'$ bands is noticeable not only at $\Gamma$, where the state increases in energy, but also in the degeneracy at the K point, which rises to the top of the $t_2g$ bands for the symmetric CoO$_6$ octahedron.

4. Summary

In this paper we have briefly compared and contrasted the electronic structure of the little-studied layered TMO LiNbO$_2$ to that of Na$_x$CoO$_2$, which has attracted tremendous since superconductivity was discovered in its hydrate. Although the active states are quite different, both systems show a strong change of electronic structure with changes in the TM–oxygen distance. The niobate is unusual in having a large second-neighbor hopping amplitude, and it also presents the attractive simplicity of a single active band on a triangular lattice. One of the primary questions to address is whether electronic correlations are important in the delithiated system, and whether the origin of superconductivity is of electronic or lattice origin.

Acknowledgments

We acknowledge stimulating comments from D. Khomskii and R. J. Cava on the effect of oxygen “squashing” in the Na$_x$CoO$_2$ system, and clarification from M. D. Johannes on calculations relating to this question. This work was supported by National Science Foundation Grant DMR-0421810.

References