Comparison of the Electronic Structures of Two Non-cuprate Layered Transition Metal Oxide Superconductors

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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.

I. 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 of $T_c = 40$ K in MgB$_2$, where the physics is entirely different but the 2D character is crucial 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 of superconductivity in 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 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: 4$d$ versus 3$d$ 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-oxygen distance, has a strong influence on the electronic structure.

II. LAYERED LITHIUM NIOBATE

The compound LiNbO$_2$ itself is a band insulator with gap $\approx$2 eV. The de-lithiated phase Li$_x$NbO$_2$ was found by the Berkeley group to be superconducting, 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 energetic lowering of the Nb $d_{z^2}$ states with respect to the other 4$d$ 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 2$p$ 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. Superconductivity appears, as it does when holes are introduced into NaCoO$_2$ (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. LiNbO$_2$ takes on a hexagonal
structure \([\text{R} \text{R} \text{R}]\) \((a=2.90 \text{ Å}, c=10.46 \text{ Å})\) having space group \(P6_3/mmc\) (No. 194), with sites Li \([2a (0,0,0), 3m]\), Nb \([2d (\frac{1}{2}, \frac{1}{2}, 0), 6m2]\), and O \([4f (\frac{1}{2}, \frac{1}{2}, z_0), 3m]\). The oxygen internal parameter \(z_0\) specifies the Nb-O bond length, and due to the stacking type there are two LiNbO\(_2\) 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.

**Electronic structure and tight-binding representation.** The band structure of LiNbO\(_2\) 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 \(d_{z^2}-O\) 2\(p\) 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 \(t_2\) \(\approx\) 100 meV is much larger than the nearest neighbor hopping \(t_1\) \(\approx\) 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.

**Table I: Born effective charges for LiNbO\(_2\), together with a comparison with NaCoO\(_2\).** The angular average \(Z_{\text{av}}^m\) is also displayed. Note the unexpected deviations from the formal values \(Z\) 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.

| LiNbO\(_2\) | NaCoO\(_2\) |
|---------|---------|
| \(Z_{\text{av}}^m\) | \(Z_{\text{av}}^m\) |
| Li       | Nb      | O      | Na      | Co      | O      |
| 1.10     | 1.69    | -1.68  | 0.87    | 2.49    | -1.68  |
| 1.30     | 1.94    | -1.62  | 1.04    | 1.95    | -1.49  |

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 functions are on nearest neighbors. This \(t_2 > t_1\) feature may have important implications for the microscopic understanding of the properties of Li\(_2\)NbO\(_2\), since if \(t_2\) were the only nonzero 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 \(A_g\) 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 I 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. \(Z_{\text{av}}^m\) \((Z_{xy}^m = Z_{xz}^m)\) 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\(_2\), which is similar structurally and electronically (if some Li is de-intercalated) to the 40 K superconductor MgB\(_2\). In LiBC \(Z_{\text{av}}^m\) \((\text{Li})=0.81, Z_{\text{av}}^m\) \((\text{Li})=1.46\), 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\(^{3+}\), O\(^{2-}\)) indicate substantial covalent character to the
FIG. 2: The $t_{2g}$ bands (which lie above -1.5 eV in these figures) of paramagnetic Na$_{0.5}$CoO$_2$ for three values of the O height $z_0$. The value 1.14 Å corresponds to symmetric CoO$_6$ octahedra. The thickened line emphasizes the $a_g$ character. The changes in the $t_{2g}$ bands are discussed in the text. Note also the changes in the O 2p bands just below the $t_{2g}$ bands.

bonding, which appears to be especially strong for $z$ displacement of the Nb ion.

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 I for comparison. Indeed there are several similarities, as noted in the table caption.

III. 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 nonorthogonal 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, 18, 19, 20, 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., 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 $z_O = 1.14$ 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 rise relative to the $a_g$ states. The first expectation is severely violated in the region just below $E_F$ due to the dispersion being only two-dimensional (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.

IV. 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$_2$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.

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