Electronic structure and disorder in $\text{Na}_x\text{CoO}_2$ and $\text{SrRh}_2\text{O}_4$

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Abstract

We discuss the electronic structure of $\text{Na}_x\text{CoO}_2$ from the point of view of first principles electronic structure calculations. The band structure contains low spin Co ions, with average charge $5 + x$ leading to a nearly full Co $t_{2g}$ manifold. The bands corresponding to this manifold are narrow and separated from the O 2p bands and from the $e_g$ bands, which are also narrow. There are two main sheets of Fermi surface, a large section derived from $a_g$ symmetry states and small hole pockets. We find significant effects due to Na disorder on these small sections, with the result that they should be localized. This is discussed in relation to recent photoemission experiments. For comparison, we present a virtual crystal band structure of beta-$\text{SrRh}_2\text{O}_4$. Like $\text{Na}_x\text{CoO}_2$ it shows a large crystal field gap between narrow $t_{2g}$ and $e_g$ manifolds, but because of its stoichiometry is a semiconductor rather than a high carrier density metal.

Keywords: Electronic structure; Fermi surface; $\text{Na}_x\text{CoO}_2$; $\text{SrRh}_2\text{O}_4$; Disorder

The layered Co oxide, $\text{Na}_x\text{CoO}_2$ shows remarkable properties that have stimulated considerable experimental and theoretical work. Although a high carrier density oxide metal, it has been shown to be an excellent thermoelectric [1], and furthermore upon hydration it becomes a superconductor, possibly with an unconventional order parameter [2]. Furthermore, the material shows a rather intriguing magnetic phase diagram with varying Na concentration, $x$, and correlated with Na orderings. This includes an insulating phase near $x = 0.5$ and ordered magnetism at high $x$ [3].

The hexagonal crystal structure consists of hexagonal Co sheets, coordinated above and below (along the $c$-axis) with hexagonal O sheets to produce an octahedral coordination of the Co. These CoO$_2$ blocks are stacked in alternating fashion. That is, considering the stacking $\ldots$O$\cdots$Co$\cdots$O$\cdots$Co$\cdots$O$\ldots$, one has $\ldots$ABC$\cdots$CBA$\ldots$ which yields two different types of trigonal prismatic sites between one over the Co ions (B) and the other over the O in the layer on the opposite side of the Co sheet. These are both partially occupied by Na, as shown in Fig. 1. We denote the Na sites above Co as Na$_{\text{Co}}$ and those above the holes as Na$_{\text{h}}$. Here there is one Na$_{\text{Co}}$ and one Na$_{\text{h}}$ site per Co, with a total Na filling of $x$ per Co, or $x/2$ per site. However, the number of available sites is smaller because occupation of a Na$_{\text{Co}}$ site next to an occupied Na$_{\text{h}}$ site or vice versa would be highly unfavorable due to the short Na$-$Na distance of 1.64 Å that would result. Furthermore, although the Na$_{\text{Co}}$ site is disfavored by repulsion between the Na and Co cations, both types of Na site are partially occupied, presumably because this allows more flexible Na arrangements that better minimize the Na$-$Na electrostatic interactions [4–6].

The band structure [7] of $\text{Na}_x\text{CoO}_2$ ($x = 0.5$) as calculated within the local density approximation (LDA), using a virtual crystal approximation, shows well separated manifolds of O 2p, Co $t_{2g}$, and Co $e_g$ bands, with the Fermi energy near the top of the $t_{2g}$ manifold as may be expected. This is shown in

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Fig. 2. The size of the gap, 1.3 eV, between the Co t\textsubscript{2g} and e\textsubscript{g} deserves mention. The crystal field splitting in oxides is mainly due to hybridization between transition metal and O states. Since, with geometrical factors, the same type of hybridization contributes to band widths (which then narrow the gaps), it is unusual to have such large crystal field gaps. The layered structure of Na\textsubscript{x}CoO\textsubscript{2}, which consists of edge shared octahedra, with near 90-degree Co–O–Co bonds, favors narrow bands [8] even though there is substantial hybridization. Within kinetic transport theory, the resulting narrow bands lead to high Seebeck coefficients, in accord with the observed thermoelectric properties [7], but also to magnetic instabilities [7,10,11]. These are in accord with the A-type antiferromagnetism (ferromagnetic CoO\textsubscript{2} sheets, stacked antiferromagnetically) observed at high x [12,13], but not with the paramagnetism observed elsewhere in the phase diagram. One possible explanation for this discrepancy is that quantum fluctuations suppress the ferromagnetism in the CoO\textsubscript{2} sheets at other doping levels. If correct, this would favor triplet (p or f) superconductivity in the hydrated compound [10].

The band structure [7] of the t\textsubscript{2g} manifold is shown with an expanded energy scale in Fig. 3. As may be seen, there are two types of bands crossing the Fermi energy. In the hexagonal structure, there is a secondary lifting of degeneracy in the t\textsubscript{2g} manifold, which is into a single degenerate a\textsubscript{g} symmetry and a two-fold degenerate e\textsubscript{g} symmetry, denoted as e\textsubscript{g}\textsuperscript{0} here to distinguish it from the higher lying e\textsubscript{g} manifold produced by the primary crystal field. The a\textsubscript{g} derived band yields large hole sections of Fermi surface around the zone center (note that there are two CoO\textsubscript{2} sheets per unit cell, and therefore two sets of bands; there are degenerate in the k\textsubscript{z} = 1/2 plane, and split into even and odd combinations in the k\textsubscript{z} = 0 plane). Meanwhile, the e\textsubscript{g}\textsuperscript{0} bands yield small hole pockets along the Γ-K directions. This basic structure persists over a wide range of x [8] and in the hydrated compound as well [9]. While the
small $e_g'$ sections have low velocities and therefore are not expected to have significant direct contributions to transport, they would contribute to thermodynamic quantities, susceptibility and other phase space dependent properties, especially at low $x$, where they are two dimensional and highly nested [14]. As mentioned, one possible explanation for the absence of magnetic ordering over much of the phase diagram, when LDA calculations predict ferromagnetism (or more precisely A-type antiferromagnetism), is that quantum fluctuations suppress the ordering. This suppression involves a phase space for fluctuations, and so it may be that the antiferromagnetic fluctuations caused by nesting of the small sections are sufficient to destroy ferromagnetism. We note that optical spectra show a narrowing with respect to the LDA electronic structure, which is consistent with a system having fluctuations [15]. This is consistent with the observation that magnetism appears at high $x$, where the $e_g'$ contribution disappears. In any case, these sections and the fluctuations associated with them would produce scattering that would be important for transport of the main $a_g$ carriers, and could be relevant either as a pairing interaction in the superconducting state or in suppressing superconductivity.

However, while the small sections are clearly present in LDA calculations, they have not been observed in photoemission. Rather angle resolved photoemission (ARPES) experiments see a large section of Fermi surface, consistent with the $a_g$ sheets, and a dispersive band that approaches the Fermi level ($E_F$), but then shows a kink-like feature and continues below $E_F$ [16,17]. This discrepancy between LDA predictions and ARPES measurements is likely the result of Na disorder [18].

As mentioned, Figs. 2 and 3 are based on virtual crystal calculations. In particular, one of the Na sites (Na$_0$) was left empty, and the other (Na$_C$) was fully occupied by an artificial ion of charge $Z = 10 + x$ instead of occupation $x$ with an ion of charge 11 (Na). However, calculations occupying the other Na site, and supercell calculations in which real Na ions and empty sites, all showed the same electronic structure, specifically the presence of both $a_g$ and $e_g'$ sections [8,9,18], in spite of the fact that placing the Na in different sites does change the potential on the Co. The explanation is that the $a_g$ and $e_g'$ sections have very similar (Co t$_{2g}$) orbital character, and so potential shifts affecting the Co atoms would not be expected to change the relative occupations. However, these shifts can be quantified, using core level positions [18], and when this is done it is found that the corrugation in the potential produced by Na disorder is larger than the energy difference between the top of the $e_g'$ band and $E_F$. This means that the $e_g'$ carriers are Anderson localized [18]. This is consistent with what is observed in ARPES, and would be confirmed by the observation of corresponding spectral weight above $E_F$ in the region of the zone where the $e_g'$ pockets are predicted, for example, by inverse photoemission. As mentioned, the hydrated compound has similar $e_g'$ Fermi surfaces, but differs from the non-hydrated compound in that it contains Na$^+$ ions each coordinated by four H$_2$O molecules instead of bare Na$^+$ ions. Because of the large size of these units, they are better ordered on the lattice and the center of charge is farther away from the CoO$_2$ sheets, corresponding to the larger $c$-axis lattice parameter. We speculate that the effect is to reduce scattering by Na disorder to the extent that the small $e_g'$ sections become delocalized. At this doping level, these sections are two-dimensional [9] and strongly nested [14].

We now return to the electronic structure of the non-hydrated compound. As mentioned, both the $t_{2g}$ and $e_g$ manifolds are narrow in Na$_3$CoO$_2$, leading to a large crystal field gap. While Na$_3$CoO$_2$, invariably has $x < 1$, a similar structured rhodate, SrRh$_2$O$_4$, exists [9]. This compound has RhO$_2$ sheets, isostructural to the CoO$_2$ sheets of Na$_3$CoO$_2$, and stacked in the same way. Similar to the Na ions in Na$_3$CoO$_2$, the Sr ions are distributed over the two trigonal prismatic sites in between the layers. Based on the Sr stoichiometry, this material will be an interesting semiconductor with a possibly sizable $t_{2g} - e_g$ gap if the electronic structure is similar to that of Na$_3$CoO$_2$. Although the virtual crystal approximation for Sr and vacancies is more suspect than the same approximation for Na and vacancies (note that Sr is divalent), we did calculations keeping either the Sr$_h$ or the Sr$_c$ sites empty and fully occupying the other sites with Na, which has the $x = 0.5$ virtual crystal ion for Sr and vacancies. These were done within the LDA using the general potential linearized augmented planewave (LAPW) method [20] as implemented in the WIEN2k code [21]. LAPW sphere radii of 2.2, 1.9 and 1.7 bohr were used for Rb, Rh and O, respectively, with standard well converged zone samplings and basis sets. The calculations are based on the structural parameters measured by Hector and co-workers [19].

The band structures are shown in Fig. 4. The calculated band gaps for these two virtual crystals differed by 0.14 eV, indicating that supercell calculations with real Sr ions will be needed to properly establish the electronic structure. Nonetheless, two features of the virtual crystal band structure may be expected to persist. These are the sizeable band gaps and the narrowness of the $t_{2g}$ and $e_g$ manifolds. It is not clear how strong the effect of scattering due to Sr disorder will be, but if it is not too large, this band structure makes SrRh$_2$O$_4$ an interesting semiconductor, both because of its sizable d–d band gap, which is relevant to photoelectrode applications, and because of its narrow bands. In fact, in analogy with Na$_3$CoO$_2$, it can be seen that very high thermopowers are expected within kinetic transport theory for heavily doped SrRh$_2$O$_4$. Realizing a high thermoelectric figure of merit based on this would require not only control of the carrier concentration, but also control of scattering in order to obtain high conductivity. This relates to the Sr disorder. One avenue may be to search for alternate structures, analogous to the misfit cobaltate thermoelectrics [22,23], in which the Na layers of Na$_3$CoO$_2$ are replaced by ordered stable oxide layers. In this regard, Klein and co-workers [24] have recently reported a thermopower $S = 95 \mu V/K$ in p-type [Bi$_{1-x}$Ba$_x$Rh$_2$O$_{12}$][RhO$_2$]$_{1/8}$ ceramics, while Okada and co-workers have found high values in SrRh$_2$O$_4$ [25,26]. It will be of interest to determine if properties superior to Na$_3$CoO$_2$ can be achieved in crystalline samples, especially in relation to doped SrRh$_2$O$_4$. Furthermore,
since the conduction $e_g$ bands are also very narrow, a high thermopower is also expected in n-type layered rhodates with this structure, if these can be synthesized.

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