Three-dimensional magnetic interactions in Na$_x$CoO$_2$: First-principles calculations and analysis of exchange mechanisms

M. D. Johannes,[1] I. I. Mazin,[1] and D. J. Singh[2]

[1]*Code 6391, Naval Research Laboratory, Washington, D.C. 20375, USA*
[2]*Condensed Matter Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6032, USA*

The puzzle of three-dimensional magnetic interactions in the structurally two-dimensional layered-oxide Na$_x$CoO$_2$ is addressed using first-principles calculations and an analysis of the exchange mechanisms. The calculations agree with recent neutron results, favoring the antiferromagnetic stacking of ferromagnetic planes. The superexchange via direct O-O hopping and through intermediate Na sp^2 hybrids couples each Co to its nearest and six *next*-nearest interplanar neighbors via equivalent paths. The individual exchange constants are rather two-dimensional, like the lattice itself, but due to multiple c-axis exchange paths, the magnetism becomes effectively three-dimensional.

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I. INTRODUCTION

The layered transition metal oxide (TMO), Na$_x$CoO$_2$ is attracting considerable interest because of its unusual magnetic and transport properties and the recently discovered superconductivity in its derivative, Na$_{1/3}$CoO$_2$(4/3H$_2$O). Although singlet pairing has not been definitively excluded[1] experimental signatures of triplet pairing[2–4] have lead to suggestions that spin fluctuations[5–9] mediate the superconductivity, in analogy with other layered superconducting TMO's like high-T_c cuprates and Sr$_2$RuO$_4$, both of which are close to magnetic instabilities, as is Na$_x$CoO$_2$.[5,10] However, in contrast to those materials where not only the electronic structure, but also the magnetic interactions are strongly two-dimensional (2D), recent neutron measurements of the magnon dispersion[11,12] in Na$_x$CoO$_2$, $x \simeq 0.8$, indicate that the antiferromagnetic (AFM) exchange between CoO$_2$ planes is nearly as strong as the ferromagnetic (FM) in-plane exchange. Since dimensionality plays a key role in unconventional superconductivity, it is important to understand the microscopic physics behind the apparent three-dimensional (3D) character of the magnetic interactions observed in Refs. 11 and 12 and to clarify the relationship of the magnetic properties of the parent compound to those of the superconducting hydrate. We address these issues here.

Na$_x$CoO$_2$ has an unusual magnetic-phase diagram as a function of x, which itself poses interesting, unresolved questions. For most x, Na$_x$CoO$_2$ is a metallic paramagnet, but in a very small range, around $x = 0.5$, a charge-ordered, insulating, and possibly antiferromagnetic (AFM) region emerges.[13] Surprisingly, the metallic states on either side of this region are quite different. For $x < 0.5$ the susceptibility is Pauli-paramagnet-like with a weak T dependence, while for $x > 0.5$ it is Curie-Weiss-like, suggesting local moments. Finally, for x greater than ~ 0.75 a spin-density wave condenses,[14–17] with clear antiferromagnetism, $T_N \sim 22$ K at $x = 0.82$. While this and the negative Weiss constant[14,18–20] suggest antiferromagnetic interactions, the experiments also show a characteristically ferromagnetic hysteresis[14] as well as predicted[5] in-plane ferromagnetic fluctuations.[21]

These varied data are reconciled by neutron-scattering experiments,[11,12] which attribute the $T_N = 22$ K transition to an A-type AFM ordering (FM planes stacked antiferromagnetically along the c axis). By fitting magnon-dispersion curves to a linear-spin wave model, both groups conclude that in-plane and perpendicular magnetic-exchange constants are of comparable magnitude, indicating magnetic isotropy, despite considerable structural two-dimensionality. We will show here that this quasi-isotropy does not imply comparable magnitudes of the nearest-neighbor exchange constants in-plane and out-of-plane, but rather unexpectedly large couplings to next-nearest neighbors across the planes, assisted mainly by Na sp^2 hybrid orbitals.

II. DENSITY FUNCTIONAL APPROACH

Our first-principles local density approximation (LDA) calculations were done using the augmented plane wave plus local orbital (APW+lo) and linearized augmented plane wave (LAPW) methods[22–24] implemented in two codes.[25,26] The experimental lattice parameters, $a = 2.828$ Å, $c = 10.94$ Å, and the LDA-relaxed oxygen height $z_O = 0.0859$ were used for all calculations.[27] The partial occupation of Na was treated both by virtual crystal approximation (VCA) and in supercells. In VCA, each $2d$ Wyckoff position of the $P6_3/mmc$ cell was occupied by a fictitious atom, atomic number $Z = 10 + x$, to model a partial occupancy of x. We also made some calculations with Na at the $2b$ positions. The supercell calculations were made at selected x with real Na at some $2d$ or $2b$ positions.

Prior calculations show that there is a FM solution in the LDA[10] for Na$_x$CoO$_2$ for all x in the experimentally relevant range. Our calculations for tripled $x = \frac{2}{3}$ supercells show that the A-type AFM order recently revealed by neutrons is actually the preferred LDA ground state. AFM stacking of the ferromagnetic layers is favored by 2.3 meV/Co for Na in the $2b$ site (Na on top of Co) in a $\sqrt{3} \times \sqrt{3}$ supercell and by 1.7 meV/Co in the $2d$ site. This is consistent with a recently measured[28] metamagnetic AFM-to-FM transition at the relatively low field of 8 T. We find very similar results in VCA:

1.4 meV/Co with Na in site $2d$ and 2.2 meV/Co with Na in site $2b$. The total-spin moment inside the Co APW spheres for the A-type AFM ordering is only $\sim 0.02 \ \mu_B$ less than that in the FM case, which is half metallic. In other words, the Co is maximally spin polarized for the doping level x, consistent with the $\sim 0.2 \ \mu_B$ limit from neutron[29] and muon spin-relaxation[15] experiments at $x \sim 0.8$. However, note that at $x = \frac{2}{3}$, the samples are paramagnetic; the LDA-ordered ground state is presumably suppressed by quantum critical fluctuations that are potentially important for superconductivity.[5]

III. TIGHT-BINDING PICTURE

We now turn to the relative magnitude of in-plane and perpendicular-exchange constants. Since the band structure is metallic, antiferromagnetic superexchange competes with ferromagnetic double exchange (the former depends on hopping linearly and the latter depends on hopping quadratically). The large in-plane dispersion leads to a net FM in-plane interaction, while the net interplane coupling, due to the smaller c-axis dispersion, is AFM. As mentioned, nearly isotropic three-dimensional (3D) magnetic interactions are unexpected in layered compounds. Still this is not inconsistent, considering the large bonding-antibonding splitting of the a_{1g} band in LDA calculations[30] at large x. At the Γ point, we will call this a_{1g} splitting Δ and use it as a measure of coupling between planes. At $x = \frac{2}{3}$, Δ reaches a value of 0.21 eV, i.e., 15% of the full t_{2g}-bandwidth.

The band structure can be mapped onto an effective Co-only model, using the three t_{2g} states as a basis. In this scheme, there is no first-order splitting for the two e'_g bands (consistent with the LDA-band structure), and $\Delta = 12t_\perp$, where $t_\perp$ is the effective interplanar-hopping amplitude, which includes interactions not only between first neighbors, but also between *all* more distant interplanar neighbors. Using $\Delta = 0.21$ meV, we derive $t_\perp \approx 15$ meV. If only nearest-neighbor hopping across the planes is allowed, as assumed in Refs. 11 and 12 (we will argue that this is *not* a good approximation), then $t_c = t_\perp = 15$ meV is the coupling between the nearest interplanar Co ions. Although the t_{2g}-t_{2g} in-plane hopping is nearly one order of magnitude larger, this still gives less anisotropy than would be anticipated for a layered material.

IV. HOPPING MECHANISMS

To gain further insight, we proceed to investigate the physics of the interlayer coupling. The hopping must proceed via O p states, which, in turn, requires either direct O p_z-p_z hopping or hopping assisted by diffuse unoccupied Na s and p orbitals. In the latter case the details of Na placement may be important. Moreover, it is significant that the energy separation between the unoccupied Na $3s$ and $3p$ states in Na$_x$CoO$_2$ is found to be rather small, smaller in fact than the corresponding bandwidth. This allows the s and $p_{x,y}$ orbitals of a Na atom, sitting inside an O$_6$ prism, to combine and form bands that may be described as coming from sp^2 hybrid orbitals, specifically, $h_1 = (s - \sqrt{2}p_y)/\sqrt{3}$, $h_{2,3} = (s \pm \sqrt{3/2}p_x$

$+ p_y/\sqrt{2})/\sqrt{3}$. These are asymmetric, orthonormal, and directed to the midpoints of the O prism edges. So the Na-assisted part of the O-O hopping goes from one O to another O above it via one, two, or three Na sp^2 hybrids, depending on how many of the three nearby Na sites are occupied. Note that if only Na s states were involved, the hopping amplitude to a second nearest-neighbor O in the next plane via a specific Na atom would be the same as that of hopping to the O directly on top. Thus Na p participation changes interlayer coupling in an essential way.

Besides the Na-assisted hopping, direct O-O hopping may be important. Considering the rhombohedral O-site symmetry, the relevant hopping is from Co a_{1g} to O p_z. Further, in Na$_x$CoO$_2$, the O atoms in adjacent CoO$_2$ sheets are directly on top of each other, favoring interlayer hopping via the opposing O p_z orbitals. To estimate this contribution we suppressed the Na-assisted hopping in three ways. First, we looked at CoO$_2 + xe^-$, i.e., a compound without Na, but with the correct number of valence electrons compensated by a uniform background charge. At $x = \frac{2}{3}$, the resulting Δ^O (a_{1g} splitting due to direct O-O hopping at Γ) is 0.12 eV or $\approx 70\%$ of the total effective coupling in Na$_{2/3}$CoO$_2$. We verified that this is independent of the amount of extra valence charge in the system, by doing calculations with 0.82, 0.75, and 0.4 extra e^-. Second, for $x = \frac{2}{3}$, we put Ne in the Na sites, again adding electrons with a compensating background. Finally, we made calculations for $\widetilde{\text{Na}}_{2/3}CoO_2$, where $\widetilde{\text{Na}}$ denotes Na with its s and p orbitals artificially shifted to higher energies. The results change very little between the three cases, indicating that Δ^O is ~ 0.12 eV. Thus, the effective interplanar coupling can be written as $t_\perp = t_\perp^{Na}(x) + t_\perp^O$, where $t_\perp^{Na}(x)$ is a function of doping, $t_\perp^O$ is constant, and the ratio $t_\perp^{Na}(x)/t_\perp^O$ varies from 0.48 to 0.78 in the range $0.6 \lesssim x \lesssim 0.9$ (see Fig. 1).

The Na-assisted hopping can be assessed using VCA or supercell calculations. These differ in two ways. First, in VCA, all Na sites are occupied regardless of x, while in a supercell and in reality a portion, 1-x are empty. The number of effective hopping paths via Na, and, correspondingly, the effective hopping between the planes, should therefore be reduced in this proportion relative to the VCA. Second, the VCA nuclear charge is $Z = 10 + x$, so the unoccupied Na s and p energies are moved up. This will reduce the Na-O hybridization, which is inversely proportional to the energy separation between Na $3s(p)$ and O $2p$ bands. This implies an artificial monotonic increase of Na-assisted hopping with x in the VCA. These two effects are in opposite directions and should at least partially cancel. To assess this, we performed VCA calculations for $0 \leq x \leq 1$ and supercell (real Na) calculations for $x = 0, \frac{1}{2}, \frac{2}{3}$, and 1. The calculated VCA a_{1g} splitting at Γ depends on x nonlinearly, and the supercell calculations give quite similar results with slightly larger splittings (Fig. 1). We verified that the deviation from this linearity for the supercell calculations has the same origin as in the VCA; the Na $3s$ and $3p$ levels shift in energy with changing x, though to a lesser degree than in the VCA. (The shift is due to the changing Coulomb potential as a function of doping.) This is seen in the charge density of the bonding a_{1g} state at Γ
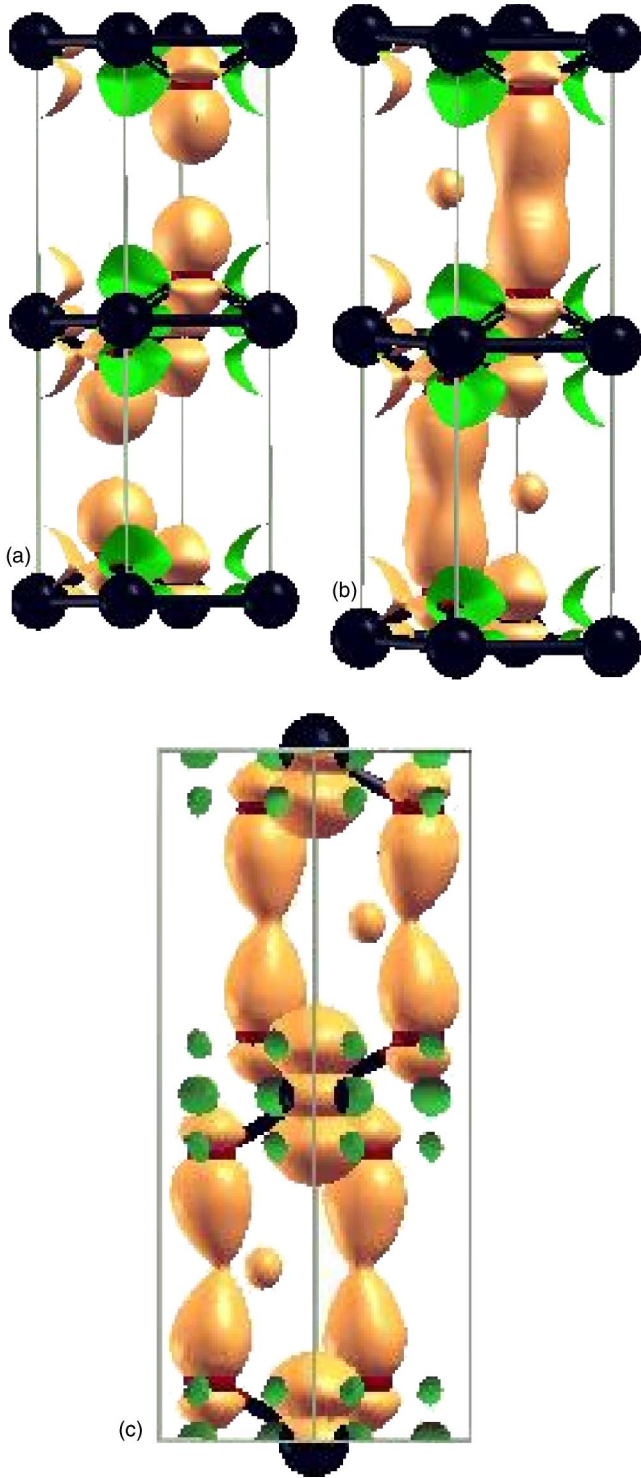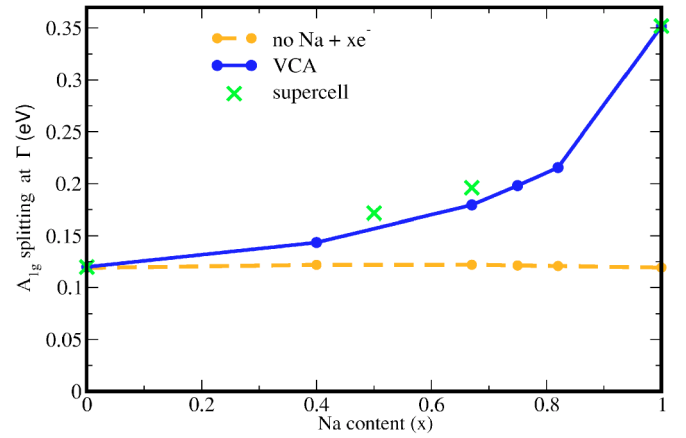
(a)

(b)

FIG. 2. (Color online) A comparison of VCA and supercell a_{1g} splitting at the Γ point, with the same structural parameters (see text), showing a monotonic increase with x. Calculations without Na orbitals, but with the proper valence charge show that the O-O hopping contribution is independent of x.

(c)

FIG. 1. (Color online) Charge density of the a_{1g} bonding orbital in $X_{2/3}CoO_2$ with $X=e^-$ (left), $X=$VCA Na (middle), and $X=$real Na (right). The Na ions facilitate O-O bonding and thus superexchange. The VCA and supercell calculations differ in the asymmetry of the Na sp^2 hybrid.

(Fig. 2). The relatively weak O p_z-p_z overlap is augmented in the VCA by a composite state in the middle of the O-O bond, consisting of the three Na sp^2 hybrids; the removal of one of these with the corresponding Na atom in the $Na_{2/3}CoO_2$

supercell makes the O orbitals tilt towards the remaining Na ions (Fig. 2, right panel).

A somewhat counterintuitive consequence of the above analysis is the fact that the nearest-neighbor approximation is invalid for interplane hopping. Neither a Co-O-Na-O-Co path nor a Co-O-O-Co path needs to end on the Co site directly above the one where it started. There are nine different Na-containing paths connecting nearest-neighbor Co ions in different planes,[31] and three connecting one Co with each of the six second neighbors.[32] For paths without Na, there are three that connect nearest neighbors and one that connects second neighbors. Assuming that each Na-containing path contributes τ to the effective interplanar hopping amplitude and each O-only path contributes τ', we find that

$$t_\perp^{Na}(x, \mathbf{k}) = \tau(9 + 6\cos \mathbf{ak} + 6\cos \mathbf{bk} + 6\cos \mathbf{ck}) \cdot x$$

$$t_\perp^{O}(\mathbf{k}) = \tau'(3 + 2\cos \mathbf{ak} + 2\cos \mathbf{bk} + 2\cos \mathbf{ck}), \quad (1)$$

where $\mathbf{a}$, $\mathbf{b}$, and $\mathbf{c}$ are the three vectors connecting a given Co ion with each of its unique neighbors. Then the a_{1g} splitting at the Γ point due to O-O interaction is $\Delta^O = 12(9\tau')$ $= 0.12$ eV, independent of Na content. For Na-assisted hopping, $\Delta^{Na} = 12(27\tau x)$. For $x = 0.82$, this gives $\tau = 0.4$ meV and $\tau' = 1.1$ meV, the latter holding for all values of x. Finally, we use the number of τ and τ' paths connecting a Co ion to its first and second neighbors to calculate t_c and t_c', the hopping integrals for the first- and second-neighbor Co interplanar couplings, respectively.

$$\frac{J_c}{J_c'} = \frac{t_c^2}{t_c'^2} = \left(\frac{9\tau x + 3\tau'}{3\tau x + \tau'}\right)^2 = 9 \quad (2)$$

V. SPIN-WAVE DISPERSION

We now revisit the interpretation of the spin-wave dispersion observed in Refs. 11 and 12, including second-neighbor-assisted hopping. A straightforward generalization of Eq. (2) in Ref. 11 yields
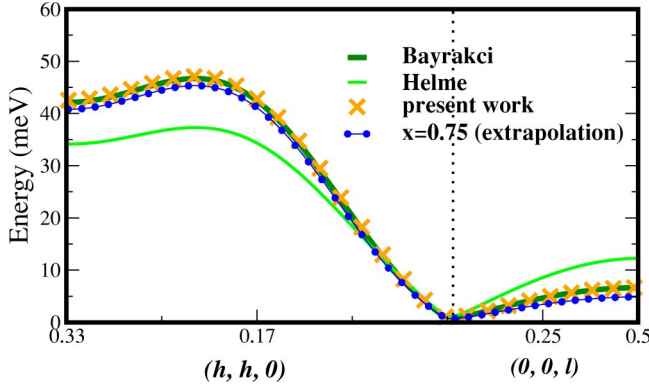
FIG. 3. (Color online) Magnon dispersion of Na_xCoO_2 along high-symmetry lines shown for $x=0.75$ and $x=0.82$. The results of two experiments in which data were fit to a nearest-neighbor interaction model are compared to our dispersion, which includes second-nearest out-of-plane neighbors. The parameters were fit to the data of Ref. 11 for $x=0.82$, adjusted for Na content (see text), and used to get the dispersion for $x=0.75$ *without* refitting.

$$E = 2S \sqrt{\left\{ \widetilde{\mathcal{J}}_\perp(0) - \mathcal{J}_\parallel(0) + \mathcal{J}_\parallel(\mathbf{q}) + \left(\frac{D}{2S}\right) \right\}^2 - \{\widetilde{\mathcal{J}}_\perp(\mathbf{q})\}^2},$$

where, following their notation, hkl is the wave vector in the units of the reciprocal lattice vector, and the following definitions apply:

$$\widetilde{\mathcal{J}}_\perp(\mathbf{q}) = 2f_\perp(\mathbf{q})[J_c + J_{c'}f_\parallel(\mathbf{q})],$$

$$\mathcal{J}_\parallel(\mathbf{q}) = 2J_{ab}f_\parallel(\mathbf{q}),$$

$$f_\perp(\mathbf{q}) = \cos(\pi l),$$

$$f_\parallel(\mathbf{q}) = 2\{\cos(2\pi h) + \cos(2\pi k) + \cos[2\pi(h+k)]\}.$$

Using the measured magnon energy at $\mathbf{q}=(0,0,\frac{1}{2})$, we can extract $J_c=1.98$ meV and $J_c'=0.22$ meV. This fits experiment[11] well with $J_{ab}=-4.5$ meV. Bayrakci *et al.*, using nearest neighbors only, found $J_c=3.3$ meV and $J_{ab}=-4.5$ meV, leading to the conclusion of magnetic isotropy. Figure 3 shows that our model produces results that are completely indistinguishable from the nearest-neighbor model used in Ref. 11, however, the parameters are more physically reasonable and compatible with the highly anisotropic, electronic structure of the compound.

Finally, we address the differences in the magnon dispersions obtained in Ref. 11 and 12, both shown in Fig. 3. Using VCA calculations at $x=0.75$, we recalculate τ to be 0.3 meV. Using the expression for J_c given in Eq. (2), we calculate the ratio $J_c^{0.75}/J_c^{0.82}$ to be 0.73. This gives $J_c^{0.75}=1.45$ meV and $J_{c'}^{0.75}=0.16$ meV as the new interplanar-exchange constants. We leave the in-plane hopping unchanged, in agreement with experiment, and plot the extrapolated magnon dispersion for $x=0.75$ in Fig. 3. The dispersion in the z direction is reduced, because less Na is available to mediate interplanar hopping.

In contrast, the measured dispersion[12] in the z direction is

much *larger* at $x=0.75$ than at $x=0.82$. In units consistent with the rest of this paper and Ref. 11 (a factor of two difference exists between the definition of J in Ref. 11 and Ref. 12), the exchange constants observed at x = 0.75 are $J_{ab}=-3$ and $J_c=6.1$. Since the calculated exchange parameters decrease smoothly with x (both in the VCA and supercell approaches), other effects, not accounted for in our calculations, must be operative. One possibility is a different pattern of Na ordering. Indeed, in our $x=\frac{2}{3}$ supercell calculations placing all the Na at the $2b$ sites instead of at the $2d$ sites yields a $\sim35\%$ increase in the interlayer coupling. While this number must certainly depend on the exact Na arrangement, it does indicate sensitivity to the ordering of a size sufficient to explain the observed increase in dispersion. In comparison with experiment, it should also be noted that Co disproportionation, seen by NMR studies[33] around $x=0.7$, would change the spin arrangement of the lattice and therefore the magnon dispersion. Co ions with formal valency $(4-x)^+$ split proportionally into nonmagnetic Co^{3+} and $S=\frac{1}{2}Co^{4+}$. The particular arrangement is unknown, but the exchange interaction may be changed. Note that the phase boundary of the charge order is not yet clearly defined and calculations[34] suggest that, near the crossover, there is a region where two distinct magnetic ions exist. Another consideration is that the spin-wave model adopted here and in Refs. 11 and 12 assumes a rigid spin moment of $S=\frac{1}{2}$, which may not be a good approximation for the weak magnetism in this compound. The actual moment, both measured and calculated, is smaller and grows with increasing x. Finally, the FM and AFM interactions in the system are in competition with each other, so that the relative effect of the doping changes on magnetism is magnified.

VI. SUMMARY AND CONCLUSIONS

In summary, we find that interplane coupling to second neighbors plays an important role in the out-of-plane magnetism of Na_xCoO_2. Heisenberg-type models including only one nearest-neighbor exchange across the plane are insufficient; exchange between the six next-nearest neighbors in adjacent planes is needed. Fortunately, the ratio of the two exchange constants can be accurately estimated, making it possible to extract them from experiment without increasing the number of fitting parameters. The resulting exchange constants provide a magnon spectrum that matches experiment extremely well and yields a physically realistic picture of magnetic interactions in this layered material. The LDA energy difference between the FM and the A-type AFM ordering for Na content $x=\frac{2}{3}$ is ~2 meV/Co, which is reasonable, considering the exchange coupling deduced from the experimentally measured spin-wave dispersion (6.6 meV and 12.1 meV/Co in Refs. 11 and 12, respectively). We note that superexchange drops with the distance more strongly than other coupling mechanisms, such as double exchange. Thus, although the interplanar coupling is surprisingly strong in Na_xCoO_2, yielding a three-dimensional magnetic character, it would be expected to be very weak in the hydrated superconducting compound. It is even possible that a crossover from AFM to FM coupling occurs with hydration due to the

suppression of the superexchange interaction. Dimensionality plays an important role in spin-fluctuation-mediated superconductivity.[35–37] If the magnetic interactions were to become effectively 2D in the hydrated compound, fluctuations would be enhanced, possibly revealing superconductivity associated with a nearby magnetic quantum critical point.

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