

Comment on “Low-Lying States and Hidden Kinematic Collective Charge Instabilities in Parent Cobaltate Superconductors”

Qian *et al.* [1] recently reported angular-resolved photoemission spectroscopy (ARPES) measurements for $\text{Na}_{0.8}\text{CoO}_2$ that show two concentric Fermi surfaces (FS) split by a δk_F that varies by a factor of 3 around the Brillouin zone (BZ). The surfaces occupy $70 \pm 5\%$ of the full 2D BZ and were interpreted as the bonding and antibonding splitting (BAS) of the a_{1g} bands, with an unspecified effect of magnetic ordering. Below we show that this interpretation is not possible, and, in fact, no valid interpretation of the observed spectra in terms of the *bulk* electronic structure of $\text{Na}_{0.8}\text{CoO}_2$ can be found.

The two formulas per unit cell of Na_xCoO_2 double all bands in the BZ, including the observed a_{1g} band. Symmetry mandates that the BAS is zero at $k_z = \pi/c$, but does not prescribe its k_z and $k_{x,y}$ dependence. The crystal structure, however, allows for sizeable hopping between Co planes only via connecting O-O dumbbells. This fact and the d_{z^2-1} symmetry of the orbitals give rise to two corollaries: (a) the BAS is proportional to $\cos k_z c$ and (b) the $k_{x,y}$ dependence of the BAS is, to high accuracy, proportional to $t_{\text{O-O}} t_{\text{Co-O}}^2 \sum_i \cos \mathbf{A}_i \cdot \mathbf{k}_{xy}$, where \mathbf{k}_{xy} is the in-plane vector and \mathbf{A}_i are the three nearest-neighbor Co-O vectors. This functional form is not related to LDA or any other approximation (the value of the prefactor is), but only to the symmetry of the underlying Hamiltonian. At the edge of the first BZ this expression provides a maximum BAS angular anisotropy of $\delta k_F / \langle \delta k_F \rangle < 15\%$ while at the k_F measured in Ref. [1] $\delta k_F / \langle \delta k_F \rangle < 2\%$, to be compared with an observed factor of 3. The discrepancy of 3 orders of magnitude leaves no doubt that the observed splitting is not the bulk BAS.

Contrary to a claim in Ref. [1], it is not AFM ordering that “leads to canonical doubling of the unit cell”; it is doubled already without magnetism. The total splitting is $\sqrt{\tau^2 + \Delta_{\text{ex}}^2}$, where τ is the nonmagnetic BAS and Δ_{ex} is the exchange splitting, which may depend on \mathbf{k}_{xy} . This interpretation can also be safely excluded: doubly degenerate AFM FSs would contain 0.7 holes/formula, not 0.2. Qian *et al.* argue that “the 2D Luttinger count is not applicable to the FS of highly doped cobaltates.” But, for practical purposes, it is: the cosine dependence of the BAS mandates that without AFM the Luttinger theorem (LT) is satisfied at each k_z separately. With AFM it is satisfied within $\tau^2 / \Delta_{\text{ex}}^2$, and to explain the large splitting anisotropy one has to assume that $\tau \ll \Delta_{\text{ex}}$.

Thus, the FS observed in Ref. [1] cannot represent the bulk FS. However, it is consistent with measurement of a spin-split surface layer. Since a polar surface cannot be stable [2], the termination layer in Na_xCoO_2 is not Na_x , as in the bulk, but Na_y ($0 \leq y \leq x$). Conditions of nonpolarity and total neutrality then imply that the top CoO_2 layer has a

charge of $z = -(x/2 + y)$, or $1 - x/2 + y$ holes. The implicit assumption in Ref. [1] that the outermost CoO_2 layer has the bulk hole concentration, CoO_2^{-x} , requires the surface Na concentration to be $y = x/2$. As we have argued, this assumption leads to a severe violation of the LT. Moreover, since the termination layer is now $\text{Na}_{x/2}$, the first and second CoO_2 layers see different Na potentials. If ARPES were probing the top two CoO_2 layers, two spin-split bands would be observed for each layer (four total) for $x = 0.8$, and two bands for $x < 0.6$. That neither is the case proves that only one CoO_2 layer is probed.

For $x = 0.8$, the ARPES hole count is incompatible with $\text{Na}_{x/2}$ termination. It is, however, approximately compatible with $y = 0$ termination (no Na on the surface) where the top layer is $\text{CoO}_2^{-0.4}$ (0.6 holes), roughly agreeing with 0.70 ± 0.05 . The observed splitting may then be ascribed to exchange, perhaps explaining the angular anisotropy. Although the measured magnetic moment of 0.13 ± 0.02 (at $x = 0.82$, Ref. [3]) implies a larger FS splitting, the surface layer may be less polarized than the bulk. The *bulk* LT is fulfilled for the data in Fig. (2d) of Ref. [1] for $x \leq 0.6$, compatible (assuming only the top layer is probed), with $\text{Na}_{x/2}$ termination and a CoO_2^{-x} surface layer. While the electronic structure of this layer will not be identical to the bulk, its doping level is.

To summarize, the observed [1] Fermi surfaces cannot represent the bulk electronic structure due to severe restrictions on the BAS anisotropy imposed by the crystal symmetry, and the impossibility of satisfying the LT, either with or without the AFM spin density wave. We point out that creating a nonpolar surface while maintaining the bulk Na concentration on the surface is impossible. The ARPES data of Ref. [1] appear to be fully understandable under the assumption that only the top CoO_2 layer is probed, with a magnetically ordered surface with *no* Na termination for bulk doping $x \geq 0.6$, and a nonmagnetic surface with *half* Na termination, $\text{Na}_{x/2}$, for $x \leq 0.6$. The two observed FSs at $x = 0.8$ then correspond to the two spin directions. We emphasize that while observation of magnetic surface states is a consistent interpretation, the main purpose of our Comment is to show what the data *cannot* be, rather than to definitely answer what it *can* be.

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