

Aspects of the Correlation Effects, Antiferromagnetic Order, and Translational Symmetry of the Electronic Structure of NiO and CoO

Z.-X. Shen,⁽¹⁾ C. K. Shih,⁽²⁾ O. Jepsen,⁽³⁾ W. E. Spicer,⁽¹⁾ I. Lindau,⁽¹⁾ and J. W. Allen⁽⁴⁾

⁽¹⁾Stanford Electronic Laboratory, Stanford University, Stanford, California 94305

⁽²⁾Department of Physics, University of Texas, Austin, Texas 78712

⁽³⁾Max-Planck-Institute for Solid State Research, Stuttgart, Federal Republic of Germany

⁽⁴⁾Department of Physics, University of Michigan, Ann Arbor, Michigan 48109-1120

(Received 12 February 1990)

We have performed angle-resolved photoemission experiments and density-functional band calculations for NiO and CoO. The measured oxygen bands are in excellent agreement with the calculation, but the measured cation $3d$ dispersion is only about 25% of the calculated one. We have also demonstrated the effects of the antiferromagnetic order on the electronic structure of these materials.

PACS numbers: 72.80.Ga, 71.30.+h, 75.20.Hr, 79.60.-i

For years, the electronic structure of transition-metal mono-oxides like NiO and CoO has been a focal point in condensed-matter physics.^{1,2} This problem has drawn more attention as a result of the discovery of high-temperature superconductors,³ since it is widely believed that a key to the understanding of the high-temperature superconductivity is the electronic structure of transition-metal oxides. There are three interesting aspects of the electronic structure of NiO and CoO: correlation effects, antiferromagnetic (AF) order, and translational invariance. The correlation effects, caused mainly by the strong Coulomb interactions, are well known in these materials. They are stated by many as the main cause of the breakdown of the one-electron picture in these materials, which resulted in the introduction of the now famous Mott-Hubbard picture of insulators.⁴⁻⁶ The AF order is also an interesting correlation phenomenon occurring in these oxides. NiO and CoO are AF insulators below their Néel temperatures (T_N) at 525 and 289 K, respectively. From the standpoint of the one-electron band theory, it is essential to include the AF order in the calculation.^{7,8} As a crystalline material, the translational invariance plays an interesting role in the electronic structure. Among these aspects, the correlation effect is the most extensively discussed and controversial issue.⁴⁻¹⁰ Spectroscopically, Sawatzky and Allen concluded that the correlation effects are very strong in NiO, so that it is not a band insulator.⁹ However, Brookes *et al.* recently concluded that CoO is a band insulator.¹⁰ Unlike the issue of the correlation effect, the aspects of the AF order and translational symmetry have remained basically unexplored experimentally except for the recent effort on CoO.¹⁰

In this paper, we explore all three aspects of the electronic structure of NiO and CoO by performing angle-resolved photoemission experiments as well as density-functional band calculations with and without AF order. Our results can be summarized as follows: (a) Oxygen bands are very well described by the band theory for the

AF state, but not for the paramagnetic state. (b) The states of mainly $3d$ origin show some dispersion, but it is less than 25% that of the band calculation, indicating that one has to go beyond the one-electron picture to describe the $3d$ bands. On the other hand, this dispersion is large enough to suggest a real need to extend the cluster model to include the lattice effect. Based on these results, we argue that NiO and CoO are not band insulators.

The angle-resolved photoemission experiments were performed on the Seya-Naminoka beam line III-2 with a VG ADES 400 system. The photoelectrons were collected at normal emission, and 45° photon incident angle is used. The NiO and CoO were cleaved *in situ* (pressure $< 2 \times 10^{-10}$ Torr), with their [001] surface verified by LEED. The experiments were carried out at room temperature which is well below the T_N of NiO, and slightly above the T_N of CoO as described in a longer paper.¹¹ The first-principles density-functional band-structure calculations used the local potential of von Barth and Hedin.¹² The calculations were performed by the scalar-relativistic self-consistent linear-muffin-tin-orbital method of Andersen¹³ in the atomic-spheres approximation including the combined correction term and with a minimal basis set in the standard way.¹⁴

Figure 1 presents results of normal-emission data from the NiO [001] surface. Four prominent features are observed in the experimental data, which are assigned as *A*, *C*, *D*, and *E*, respectively. The features *E* and *D* show strong dispersions and intensity modulations as a function of photon energy, which is consistent with the earlier assignment that these are oxygen features.¹⁵ The feature *E* starts at lowest energy near 17–19-eV photon energies, then shifts monotonically towards higher energy until near 26 eV, where its behavior becomes complicated. At photon energies of 27 and 28 eV, it shows some backbending (moves to lower energy), and the backbending peaks fade very quickly (circled points). This bending point cannot be a critical point as will be

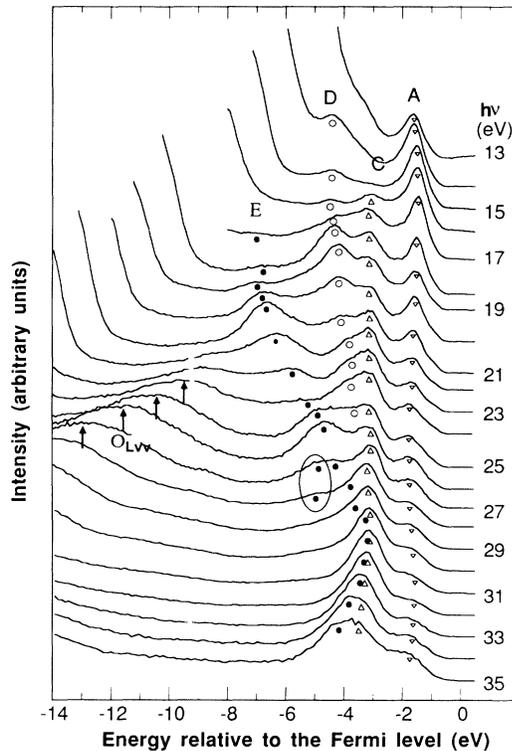


FIG. 1. Normal-emission data from the NiO [001] surface recorded at photon energies between 13 and 35 eV.

justified later and another branch of this feature continues to shift to higher energy after 26-eV photon energy (as indicated), where it merges with the features *C* and *D*. The other oxygen feature *D* starts at photon energy of 15 eV and shifts monotonically towards higher energy until it merges with the feature *C*, which remains basically nondispersive. The feature *A* shows a small dispersion of about 0.3 eV but a strong intensity modulation.

Using an effective mass of $0.95m_e$ and an inner potential of -8 eV,¹⁶ we obtain an experimental E vs k relation which is presented in Fig. 2(a) together with the calculated paramagnetic bands. The data points in the form of crosses are obtained from off-normal-emission data to be published in a follow-up paper. In a normal-emission experiment, one can only observe the $\Delta 1$ and $\Delta 5$ bands with fourfold symmetry surface.¹⁷ Hence, the features *E* and *C* correspond to $\Delta 1$ and $\Delta 5$ oxygen bands, respectively, and they are in excellent agreement with the calculated bands. Our calculated oxygen bandwidth ($\Delta 1$) is significantly (1.6 times) larger than that of earlier calculation.¹⁸ The k value of the feature *E* at 26-eV photon energy is about $0.2\Gamma X$, so that the backbending of the feature *E* (points circled) at photon energies of 27 and 28 eV are not caused by reaching the zone edge. To understand this, in Fig. 2(b) we show results of our self-consistent calculation with the AF magnetic order incorporated. For the oxygen bands of $\Delta 1$ and $\Delta 5$ symmetry (dark curves), an effect of the AF order on oxygen band

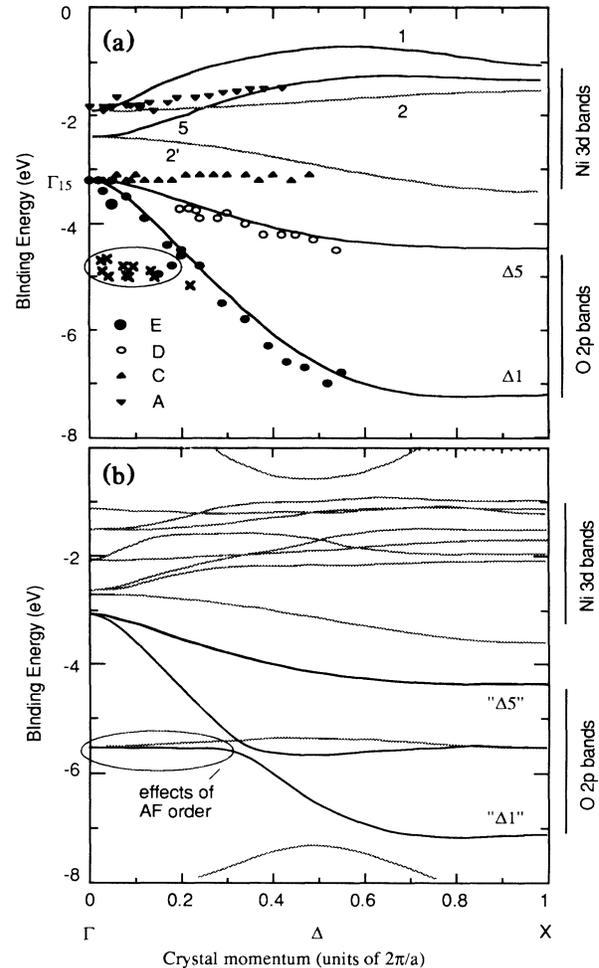


FIG. 2. (a) The experimental E vs k relation together with results of a nonmagnetic self-consistent density-functional band calculation; the data points in the cross form are obtained from off-normal-emission data not included in Fig. 1. (b) The results of the band calculation but with the AF order incorporated.

is the small splitting of the " $\Delta 1$ " bands caused by the repelling between the two $\Delta 1$ bands, as indicated by the circle. The backbending of the feature *E* (circled) is most likely caused by this magnetic splitting, which may also explain why it fades away so quickly. This assignment is further supported by the data points (crosses) from the off-normal-emission measurements. The position of the backbending point in k space, which is basically the crossing point of the $\Delta 1$ band and a folded flat band, does not agree exactly with the theory. This discrepancy is most likely caused by the fact that the flat band is pushed too low because its hybridization with the 3d bands is overestimated by the band calculation due to neglected correlation effects. Nevertheless, this result is an excellent demonstration of the effects of the AF order on the electronic structure, which is usually very hard to

observe. Because we can observe the effect of the AF order on the oxygen bands, it is very reasonable to expect that the effects of the AF order on the cation 3d bands are strong.

We now turn to features *A* and *C* which are Ni-3d derived bands. The first possible explanation is that the feature *A* is due to the emission from the 1 and 5 bands while the feature *C* is due to one-dimensional density of states (ODDS) associated with the critical point at *X* for the 2' band.¹⁹ The experimentally observed energy dispersion (~ 0.3 eV) is only about 25% of that of the calculated energy dispersion (~ 1.2 eV). This we attribute to correlation effects which include the large on-site Coulomb interaction and the AF order. Interestingly, the measured critical point appears to coincide with the Γ point of the calculation. As pointed out earlier, the data should, in principle, be compared to the AF 3d bands which are very complicated. The AF bands are basically a superposition of the paramagnetic bands of Fig. 2(a) with the folded bands from $\pi/a(111)$ to $\pi/a(311)$, which is then modified near the crossing points of the bands. Not all the bands are allowed to be seen at normal emission by their symmetries. Similar to the oxygen data, the total dispersion of the " $\Delta 1$ " and " $\Delta 5$ " bands, which are the ones that can be seen in photoemission, is approximately unchanged. Hence, the conclusions we have drawn are still correct. The problem with this interpretation, however, is that the feature *C* is too strong. Another possible explanation of the features *A* and *C* can be found in a cluster calculation, which gives two peaks at approximately correct energies due to photoemission final states of $d^8\bar{L}$ and $d^9\bar{L}^2$.²⁰ This localized picture can explain very well the valence-band satellite which is clearly a difficulty for the band theory,^{9,20} but it ignores the lattice effect completely. In essence, we are comparing our data with results from two different theoretical approaches, delocalized bands theory and completely localized cluster calculation. Even though we cannot pin down the exact origin of the features *A* and *C*, the general conclusion of the discussion is clear: The observed *d*-band dispersions are about 25% or less than the predictions from the band calculation, but they are large enough to suggest a real need of extending the cluster model to the Anderson lattice Hamiltonian.

In Fig. 3 we present the experimental and theoretical *E* vs *k* relations for paramagnetic CoO, with some of the experimental spectra as an inset. Similar to the NiO case, the oxygen bands are in excellent agreement with the calculation, while the *d* bands are significantly narrower. This conclusion differs from that of Brookes *et al.*, even though our experimental data are consistent with theirs.¹⁰ We can still see the magnetic backbending at 27 eV (circled point), though the long-range AF order has been destroyed. This is caused by the effects of a local AF order that defines "local bands," as is supported

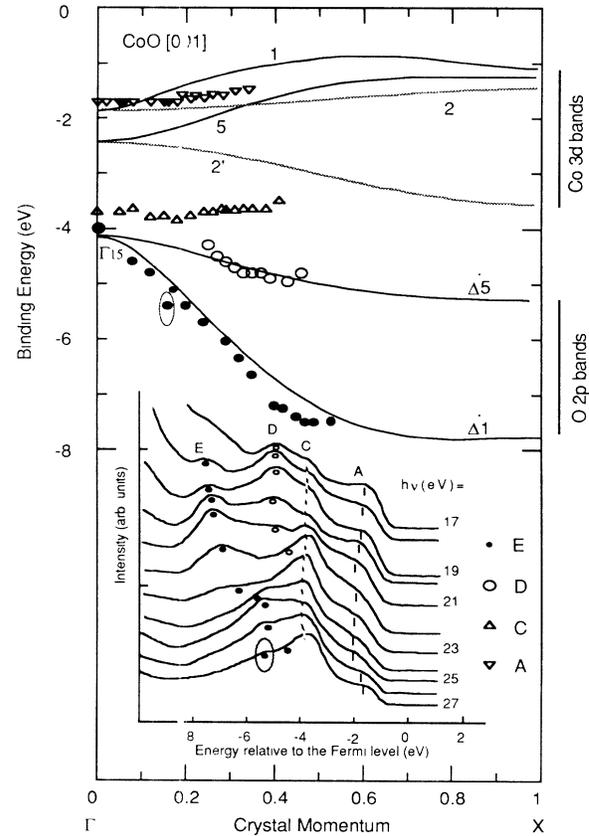


FIG. 3. Experimental *E* vs *k* relation together with results of a nonmagnetic band calculation for CoO.

by many of other experimental observations.¹¹ Such a local magnetic order has also been observed by photoelectron diffractions from MnO and other Mn compounds.²¹

Finally, we discuss the implications of our result on the current research of these oxides as well as high- T_c superconductors. The most important implication of our results is that it sets a boundary condition for future theoretical efforts to calculate the bands of highly correlated materials like NiO and CoO, which has become a major task in condensed-matter physics research with the discovery of the high- T_c superconductors.²² If one starts with the results of the band calculation and then modifies the bands by a self-energy correction or renormalization as one would do in simpler materials,²³ this correction must be such that the 3d-band dispersions are reduced by a factor of 4 or so, while the O 2p bands remain essentially unchanged. On the other hand, one may also start with the cluster calculation and then incorporate in the lattice effects, then one has to obtain about 0.3- and 4-eV dispersions for 3d and 2p states, respectively. The effects of the AF order on electronic structure is also of great relevance in the field of high-temperature superconductivity, where a growing amount

of experimental evidence suggests that the local magnetic order persists in the superconducting phase and its implications on the electronic structure have also been explored theoretically.²⁴⁻²⁶

To summarize, we have performed angle-resolved photoemission and density-functional band calculations for NiO and CoO to explore some aspects of correlation effects, AF order, and translational symmetry of the electronic structure. We show the following: (a) The oxygen states agree very well with the AF band calculation, but not the paramagnetic band calculation. (b) The states of mainly 3d origin show some dispersion, but its magnitude is only 25% that of the band calculation, indicating that one has to go beyond the one-electron band picture to explain the 3d bands. On the other hand, this dispersion is large enough to suggest a real need to extend the cluster model to include the lattice effect.

We thank Dr. P. A. P. Lindberg for many discussions, and many colleagues for experimental help. One of us (Z.X.S.) is grateful to Dr. R. Kasowsky for providing his NiO bands before publication. The experiments were performed at Stanford Synchrotron Radiation Laboratory (SSRL) which is funded by the DOE under Contract No. DE-AC03-82ER-13000, Office of Basic Energy Sciences, Division of Chemical and Materials Sciences. This work was supported by NSF Grant No. DMR-89103478, and by the Joint Services Electronic Program Contract No. DAAG 29-85-K-0048.

¹B. H. Brandow, *Adv. Phys.* **26**, 651-808 (1977).

²P. W. Anderson, in *Frontiers and Borderlines in Many Particle Physics*, International School of Physics "Enrico Fermi," Course CIV, edited by R. A. Broglia and J. R. Schrieffer (North-Holland, Amsterdam, 1988).

³J. G. Bednorz and K. Z. Müller, *Z. Phys. B* **64**, 189 (1986).

⁴N. F. Mott, *Proc. Roy. Soc. London A* **42**, 416 (1949).

⁵J. Hubbard, *Proc. Roy. Soc. London A* **276**, 238 (1963).

⁶P. W. Anderson, *Phys. Rev.* **115**, 2 (1959).

⁷J. C. Slater, *Phys. Rev.* **82**, 538 (1951).

⁸K. Terakura, T. Oguchi, A. R. Williams, and J. Kübler, *Phys. Rev. B* **30**, 4734 (1984).

⁹G. A. Sawatzky and J. W. Allen, *Phys. Rev. Lett.* **53**, 2339 (1985).

¹⁰N. B. Brookes, D. S.-L. Law, D. R. Warburton, P. L. Wincott, and G. Thornton, *J. Phys. Condens. Matter* **1**, 4267-4272 (1989).

¹¹Z.-X. Shen *et al.* (to be published).

¹²U. von Barth and L. Hedin, *J. Phys. C* **5**, 1629 (1972).

¹³O. K. Andersen, *Phys. Rev. B* **12**, 3060 (1975).

¹⁴O. K. Andersen, O. Jepsen, and D. Götzels, in *Highlights of Condensed Matter Physics*, International School of Physics "Enrico Fermi," Course LXXXIX, edited by F. Bassani, F. Fumi, and M. P. Tosi (North-Holland, Amsterdam, 1985).

¹⁵D. E. Eastman and J. L. Freeouf, *Phys. Rev. Lett.* **34**, 395 (1975).

¹⁶The -8-eV inner potential is obtained from a LEED study on CoO (see Ref. 10). The inner potential for NiO should be very similar.

¹⁷W. Eberhardt and F. J. Himpsel, *Phys. Rev. B* **21**, 5572 (1980).

¹⁸L. F. Mattheiss, *Phys. Rev. B* **5**, 290 (1972).

¹⁹This is possible only because the photoelectron energy analyzer has finite angular resolution.

²⁰A. Fujimori and F. Minami, *Phys. Rev. B* **30**, 957 (1984).

²¹B. Sinkovic, B. Hermsmeier, and C. S. Fadley, *Phys. Rev. Lett.* **55**, 1227 (1985); B. Hermsmeier, J. Osterwalder, D. J. Friedman, and C. S. Fadley, *Phys. Rev. Lett.* **62**, 478 (1989).

²²W. E. Pickett, *Rev. Mod. Phys.* **61**, 443 (1989), and references therein.

²³E. Jensen and E. W. Plummer, *Phys. Rev. Lett.* **55**, 1918 (1985).

²⁴P. C. Hammel, M. Takigawa, R. H. Hoffner, Z. Fisk, and K. C. Ott, *Phys. Rev. Lett.* **63**, 1992 (1989).

²⁵R. J. Birgeneau and G. Shirane, in *Physical Properties of High Temperature Superconductors*, edited by D. M. Ginsberg (World Scientific, Singapore, 1989).

²⁶A. Kampf and J. R. Schrieffer, *Phys. Rev. B* **41**, 6399 (1990).