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LETTER TO THE EDITOR

Transition-metal monoxides: band or Mott insulators? Angle-resolved photoemission results for CoO

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Abstract. Evidence of itinerant (band-like) behaviour of the Co 3d states in paramagnetic CoO has been observed in CoO(001) angle-resolved photoemission spectra. Two d bands are identified, which disperse 0.4 eV and 1.7 eV between Γ and X. In broad terms the results are consistent with a recently proposed model of the electronic structure in which the insulating gap arises largely from an exchange potential perturbation of the one-electron band structure.

The nature of the electronic structure and the origin of the insulating gap in the transition-metal (TM) monoxides has been a controversial subject for many years [1, 2]. However, it has become generally accepted that the ≈ 4 eV band gap of MnO, FeO, CoO and NiO arises from Mott–Hubbard (correlation) localisation of electrons in partly filled d bands [1, 2]. Such a model is appropriate when $U/W > 1$, where U and W are the d–d Coulomb repulsion energy and d-band width, respectively. Recently, it has been suggested that hybridisation of the localised d levels and O 2p bands is of critical importance and that the insulating gap is actually of the charge-transfer type [3–5]. Despite the apparent breakdown in band theory that this approach represents, one-electron models have been successful in correctly determining the lattice spacings and ground-state antiferromagnetic (AF) order [6–9]. Furthermore, recent theoretical work [7–9] has revived the idea [10] that the principal origin of the band gap is the inherent AF order. In this itinerant 3d-electron model of the TM monoxides, exchange perturbation of the one-electron band structure opens a d–d gap. Added impetus to resolve this conflict of ideas comes from the likely involvement of magnetic and/or correlation effects in the superconducting mechanism of the new high- T_c oxide materials (see, e.g., [11]).

In seeking a means of determining whether the TM monoxides are band or Mott insulators, it seems natural to turn to photoemission techniques. They have played a major role in testing electronic structure models of a wide variety of materials including oxides [12], finding in many cases good agreement between experiment and the one-electron band structures although correlation effects often need to be included. Until recently, however, only angle-integrated photoemission (AIP) studies of the TM monoxides have been reported [3, 13–16]. Thus far, angle-resolved photoemission (ARP), by

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far the most powerful technique with which to examine the electronic structure of materials, has only been applied in a limited way to the TM monoxide problem [17, 18]. In principle, ARP should be able to distinguish between localised and itinerant (band-like) 3d states by the observation (or not) of peak dispersion with photon energy. The recent angle-resolved study [18] of MnO(001) supports the localised approach since little dispersion (<0.2 eV) of the d bands was observed, although sample charging may have played a role. In the present work we have recorded ARP data from CoO(001). The spectra show evidence of 3d-band dispersion and hence support the itinerant-electron model.

The ARP experiments were carried out using the toroidal grating monochromator ($17 \leq h\nu \leq 95$ eV) on station 6.2 at the SRS, Daresbury Laboratory. The experimentally determined [19] degree of polarisation of the monochromator (in the horizontal plane) varies from ≈ 0.8 at 20 eV to ≈ 0.6 at 60 eV. A Vacuum Generators ADES 400 system was used, the base pressure during this work being $\approx 9 \times 10^{-11}$ mbar. The electron energy analyser had an angular acceptance of about $\pm 2^\circ$, the combined analyser and monochromator resolution being 140 meV. The CoO sample ($10^{-10} \Omega^{-1} \text{cm}^{-1}$) was cleaved *in situ* to expose a clean unreconstructed (001) surface, as determined by Auger spectroscopy and LEED. Normal-emission spectra were recorded in the range $19 \leq h\nu \leq 90$ eV at two angles of incidence, $\theta_i = 30^\circ$ and $\theta_i = 70^\circ$ with respect to the sample normal in the (horizontal) [110] azimuth. Measurements were carried out with the sample at 393 K ($T_{\text{Néel}} = 292$ K [2]) to prevent sample charging. At this temperature the surface was found to stay clean for extended periods. The binding energy (BE) scale of the ARP spectra shown below is referenced to the Fermi energy (E_F) recorded from the Cu sample holder.

In figure 1 we compare an $h\nu = 30$ eV AIP spectrum of CoO(001) from [13] with normal-emission ARP spectra recorded at $h\nu = 30$ and 55 eV. On the basis of photon energy-dependent cross section behaviour [13, 14], the spectra can be divided into O 2p- and Co 3d-derived features. The Co 3d (O 2p) features lie above (below) about 4 eV BE. The broad peak at about 10 eV BE seen in the spectra of figure 1 has been assigned to a multi-electron satellite [20].

The presence of the satellite shows that correlation effects play an important role in determining the photoemission spectra, just as they do in Ni metal [16]. The initial assignment of such satellites in the spectra of TM oxides was to an O 2p \rightarrow TM 3d shake-up feature [21]. The corresponding assignment of the valence band 3d emission structure to unscreened $3d^{n-1}$ hole states, as indicated on the AIP spectrum in figure 1, follows from the assumption of correlation-localised 3d electrons in the ground state [13, 14] (i.e. the Mott–Hubbard model). More recently, resonant photoemission studies [15] have shown that this assignment cannot be correct for NiO, which has led to a re-interpretation of the photoemission spectra in terms of a modified Mott correlation picture [3–5]. In this model the satellite represents unscreened d^{n-1} states, the valence band 3d emission arising from the formation of mainly $d^n L^{-1}$ states, the initial d hole having been screened by charge transfer from the ligand (L^{-1} signifies a hole on a ligand site). Such models explicitly assume that the d levels are totally localised (i.e. the dispersion band width is zero) and that the translational symmetry can be ignored. This approach, which has also been used to interpret photoemission spectra of the high- T_c superconducting oxides [22], would also be appropriate for CoO since it displays resonance behaviour [23] similar to that of NiO.

Within these localised descriptions of the valence band d electrons, there is little reason to expect the 3d-electron wavevector to be conserved in the photoemission

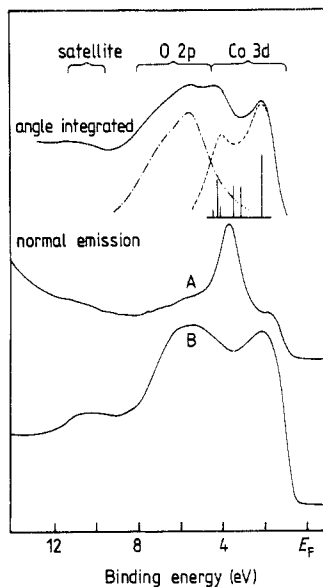


Figure 1. A comparison of a CoO(001) ARP spectrum recorded at $h\nu = 30$ eV (after [13]) with normal emission, $\theta_i = 70^\circ$ ARP spectra recorded at photon energies of (A) 30 and (B) 55 eV. On the ARP spectrum the O 2p (---) and Co 3d (---) contributions are shown and the vertical lines indicate the calculated positions and intensities of localised d^6 final states (after [13]).

process. Hence, the Co 3d profile in ARP spectra is expected to be unchanged with photon energy and just vary in intensity following the photoemission cross section. In contrast, the larger bandwidth of the O 2p bands is expected to reduce correlation effects such that their contribution to ARP spectra can be interpreted on the basis of a one-electron model [24]. Hence, O 2p structure should disperse in ARP spectra in a manner reasonably consistent with the one-electron band structure. Indeed, the difference in the O 2p relative intensity in the $h\nu = 30$ eV ARP spectrum of figure 1 compared with the ARP spectrum is probably due to band-structure effects. While the differences between the two normal-emission spectra shown in figure 1 are in line with expectations regarding the O 2p features, the Co 3d structure cannot easily be accounted for within a purely localised model. In particular, the disappearance in the photon energy range $h\nu = 45$ to 55 eV of the intense 3.5 eV BE peak in the $h\nu = 30$ eV spectrum is anomalous. It is extremely unlikely that these changes arise from a redistribution of Co 3d emission intensity into different final-state channels through changes to the component asymmetry parameters, since such large effects are usually associated with threshold phenomena [25]. The alternative origin of the spectral change involves peak movement and is evidence for band-like (itinerant) behaviour of the Co 3d electrons.

In figure 2 we show a representative selection of our normal-emission ARP data, recorded over the range $25 \leq h\nu \leq 55$ eV. Within an itinerant-electron model ARP features represent direct transitions from the Γ - Δ - X direction in the bulk Brillouin zone. Selection rules [26] only allow initial states of Δ_1 and Δ_5 symmetry— Δ_1 when the photon E vector lies perpendicular to the surface, Δ_5 when it is parallel. Analysis of peak dispersion in the normal-emission spectra allows the determination of the band structure along Γ - X [12]. Figure 3 shows the results of such an analysis based on an extensive data set which includes spectra recorded at $\theta_i = 30^\circ$ and $\theta_i = 70^\circ$. Spectra in the range $57 \leq h\nu \leq 74$ eV were not used because of Co 3p resonance effects and we note that the important changes shown in figure 3 occur well away (≥ 10 eV) from threshold. A nearly free-electron final state was assumed, of the form $E = \hbar^2 k^2 / 2m_{\text{eff}} - E_0$, where E is

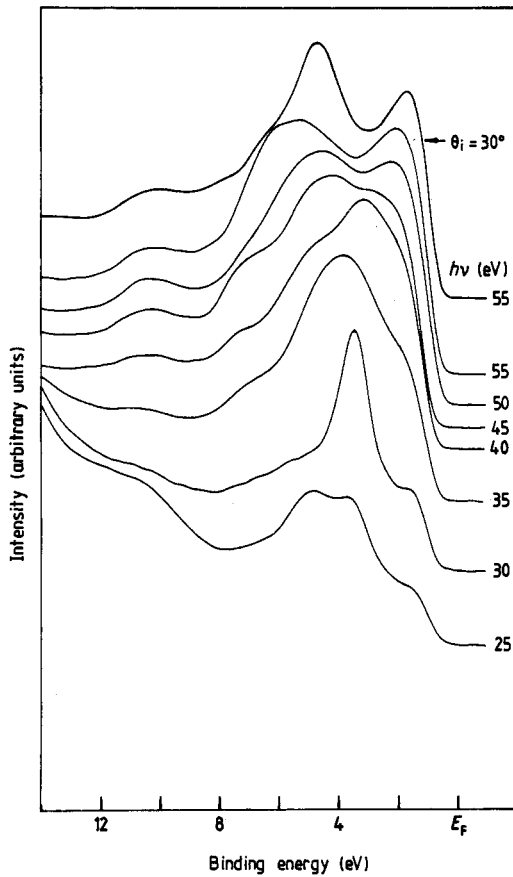


Figure 2. Selected normal-emission spectra of CoO(001) ($T = 393$ K, $\theta_i = 70^\circ$). An $h\nu = 55$ eV spectrum recorded at $\theta_i = 30^\circ$ is included to illustrate the polarisation dependence of the ARP data.

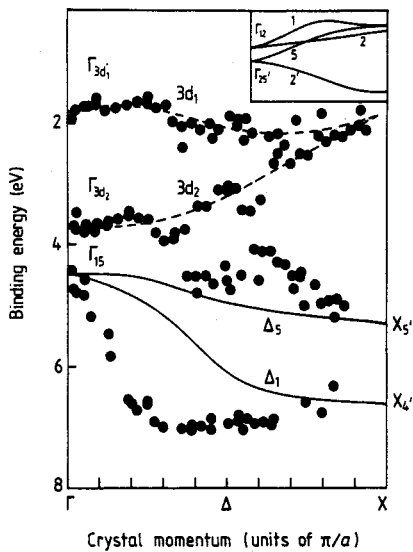


Figure 3. The empirical Δ -line band structure of CoO in the reduced-zone scheme (\bullet) derived from ARP data including those shown in figure 2. The full curves are the O 2p bands calculated by Mattheiss [28]—the inset shows the corresponding 3d bands, where the Γ_{12} – $\Gamma_{25'}$ separation is 0.41 eV. The empirical Co 3d band dispersion is highlighted by the broken curve.

referenced to E_F , and k is the electron wavevector [12]. A value of $E_0 = 8$ eV was used, being derived from the inner potential obtained in a low-energy electron diffraction (LEED) study [27]. The effective electron mass, m_{eff} , was adjusted to give symmetric dispersion of bands about Γ and X. This is achieved when $m_{\text{eff}} = 1.15m$, m being the free-electron mass.

The calculated O 2p Δ -line band structure for paramagnetic CoO [28] is also shown in figure 3, the theoretical results being rigidly shifted to match experiment at Γ_{15} . In general, the behaviour of the O 2p bands is consistent with the one-electron calculations. The polarisation dependence, an example of which is shown in figure 2, shows the high- β E peak to be Δ_1 -derived and the predicted dispersions of the Δ_1 and Δ_5 bands, 2.2 eV and 0.7 eV, respectively, are in reasonable agreement with the observed values of 2.5 eV and 0.5 eV. The empirical d bands in figure 3 also show itinerant behaviour. The features marked $3d_1$ and $3d_2$ disperse 0.4 eV and 1.7 eV, respectively, between Γ and X. Only a weak polarisation dependence of the Co 3d bands is observed.

While comparison of the empirical O 2p bands with theory is relatively straightforward, the d bands present a fundamental problem. The inset in figure 3 shows the calculated d bands of Mattheiss [28]. Since there are formally only seven d electrons per Co atom in CoO, a simple band-structure picture predicts that these d bands are partially occupied with no insulating gap. Similar problems arise for MnO and NiO. From a band-structure perspective some perturbation of the band structure is required to create the insulating gap; in the model of Oguchi and co-workers [7–9] this is the exchange potential. While their model predicts that the AF order along [111] induces an exchange potential gap in MnO (between the majority e_g and minority t_{2g} bands) and NiO (between the majority and minority e_g bands), for CoO E_F lies within the minority t_{2g} band. Although at first sight this casts severe doubts on the veracity of the AF band-structure model, it has been argued that this discrepancy arises from inaccurate treatment of correlation and the exchange potential within the theoretical method employed [7–9]. As for a band-model description of the paramagnetic phase band gap, it has been suggested that short-range magnetic order could maintain the exchange potential gap [7–9]. Recent spin-polarised photoelectron diffraction studies [29] have shown that short-range magnetic order in MnO persists up to $\approx 4.5T_{\text{Néel}}$. Although in principle, the model of Oguchi and co-workers [7–9] provides a means of reconciling the presence of dispersing d bands in the TM monoxides with their insulating character, there is as yet no calculation of the band structure. Consequently, it does not provide us with a ready assignment of the bands $3d_1$ and $3d_2$. Furthermore, since the experiment reflects an excited state the results should be compared with the calculated quasi-particle band structure.

While there are clearly many problems associated with the band structure picture, this work shows that such an approach can still not be ruled out. As for the localised approach, while it can readily explain the insulating nature of the monoxides it cannot explain the 3d-electron dependence on k observed in our data. It is conceivable that a correct description of the electronic properties could come from a theoretical approach that starts from the localised (charge-transfer model) limit and includes the translational properties of the solid. At present there is no such model. As to the origin of the optical gap, we believe that the resolution of this problem lies in achieving a proper theoretical description of the electronic structure, which we hope will be assisted by the results presented here.

In summary, we have shown that the 3d electrons in the paramagnetic phase of CoO have itinerant character. Although a full understanding of the data awaits further theoretical work, this result can be understood within a previously proposed electronic

structure model of the TM monoxides [7–9, 30]. In this model the antiferromagnetic nature of the monoxides gives rise to their insulating gaps, with local magnetic order maintaining the gap above $T_{N\text{eel}}$. While the understanding of the electronic properties of the TM monoxides is in itself of considerable interest, these results may also have a significant bearing on models of high- T_c superconductivity that are couched in terms of band structure [31] and/or magnetic effects [11].

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References

- [1] Brandow B H 1977 *Adv. Phys.* **26** 651
- [2] Adler D 1968 *Solid State Phys.* **21** 1 (New York: Academic)
- [3] Sawatzky G A and Allen J W 1984 *Phys. Rev. Lett.* **53** 2339
- [4] Zaanen J, Sawatzky G A and Allen J W 1985 *Phys. Rev. Lett.* **55** 418
- [5] Davis L C 1982 *Phys. Rev. B* **25** 2912
Fujimori A and Minami F 1984 *Phys. Rev. B* **30** 957
- [6] Anderson O K, Skriver H L, Nohl H and Johansson B 1979 *Pure Appl. Chem.* **52** 93
Yamashita J and Asano S 1983 *J. Phys. Soc. Japan* **52** 3514
- [7] Oguchi T, Terakura K and Williams A R 1983 *Phys. Rev. B* **28** 6443
- [8] Terakura K, Oguchi T, Williams A R and Kübler J 1984 *Phys. Rev. B* **30** 4734
- [9] Terakura K, Williams A R, Oguchi T and Kübler J 1984 *Phys. Rev. Lett.* **52** 1830
- [10] Wilson T M 1968 *Int. J. Quantum Chem. Symp.* **2** 269
- [11] Anderson P W, Baskaran G, Zou Z and Hsu T 1987 *Phys. Rev. Lett.* **58** 2790
Emery V J 1987 *Phys. Rev. Lett.* **58** 2794
- [12] Brookes N B, Law D S-L, Padmore T S, Warburton D R and Thornton G 1986 *Solid State Commun.* **57** 473
- [13] Eastman D E and Freeouf J L 1975 *Phys. Rev. Lett.* **34** 395
- [14] Grenet G, Jugnet Y, Tran Minh Duc and Kibler M 1979 *Chem. Phys. Lett.* **62** 125
- [15] Thuler M R, Benbow R L and Hurych Z 1983 *Phys. Rev. B* **27** 2082
- [16] Hüfner S and Riesterer T 1986 *Phys. Rev. B* **33** 7267
- [17] McKay J M and Henrich V E 1984 *Phys. Rev. Lett.* **53** 2343
- [18] Ladd R J and Henrich V E 1988 *Phys. Rev. B* **38** 10860
- [19] Law D S-L 1986 unpublished results
- [20] Wertheim G K and Hüfner S 1972 *Phys. Rev. Lett.* **28** 1028
- [21] Kim K S 1974 *Chem. Phys. Lett.* **26** 234
- [22] Fuggle J C, Weijs P J W, Schoorl R, Sawatzky G A, Fink J, Nücker N, Durham P J and Temmerman W M 1988 *Phys. Rev. B* **37** 123
- [23] Brookes N B, Law D S-L, Warburton D R, Wincott P L and Thornton G 1989 in preparation
- [24] Koiller B and Falicov L M 1974 *J. Phys. C: Solid State Phys.* **7** 299
- [25] Berkowitz J 1979 *Photoabsorption, Photoionisation, and Photoelectron Spectroscopy* (New York: Academic)
- [26] Eberhardt W and Himpfel F J 1980 *Phys. Rev. B* **21** 5572
- [27] Felton R C, Prutton M, Tear S P and Welton-Cook M R 1979 *Surf. Sci.* **88** 474
- [28] Mattheiss L F 1972 *Phys. Rev. B* **5** 290; 1972 *Phys. Rev. B* **5** 306
- [29] Hermsmeier B, Osterwalder J, Freidman D J and Fadley C S 1989 *Phys. Rev. Lett.* **62** 478
- [30] Kübler J and Williams A R 1986 *J. Magn. Magn. Mater.* **54–57** 603
- [31] Weber W 1987 *Phys. Rev. Lett.* **58** 1371