Transition-Metal Monoxides: Band or Mott Insulators

K. Terakura[(a)] and A. R. Williams
IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598

and

T. Oguchi
Institute for Solid State Physics, The University of Tokyo, Roppongi, Minato-ku, Tokyo, Japan

and

J. Kübler
Fachgebiet Theoretische Physik, Institut für Festkörperphysik, D-6100 Darmstadt, West Germany

(Received 24 February 1984)

We argue that the widely held view that MnO, FeO, CoO, and NiO are Mott insulators is incorrect. Intra-atomic potential energies do not dominate interatomic kinetic energies, to the extent commonly believed; both are 1–2 eV in magnitude. A measure of the importance of interatomic effects is our finding that both the crystal structure and the magnetic structure of these materials are crucial to their insulating behavior.

PACS numbers: 71.30.+h, 75.10.Lp, 75.30.Et, 75.50.Ee

The transition-metal monoxides MnO, FeO, CoO, and NiO occupy a special place in condensed-matter physics, because they are regarded as prototypes of the Mott-insulator[1] concept. These materials are antiferromagnetic, electrically insulating, ionic compounds forming in the rocksalt structure. The oxygen p states are fully occupied; the metal s states are empty, and the metal d states are partially occupied. It is the apparent incompatibility of the insulating behavior with the partial occupation of the d shell that makes these materials especially interesting. The Mott-insulator concept resolves this incompatibility, but requires the intra-atomic Coulomb interaction to be unscreened to a degree that is difficult to reconcile with other experimental observations.[2] That the d states are not too localized to participate in interatomic bonding is already clear from the variation of the lattice constant across the monoxide series. The large lattice-constant jump at MnO[3] reflects the onset of magnetism, caused by the filling of majority-spin d states, whose contribution to covalent bonding is thereby lost (causing the lattice constant to increase). The similarity and the strength of the lattice-constant variation[3] in the first and second halves of the monoxide series suggest that the minority-spin d states add a significant covalent contribution to the fundamentally ionic bonding.

MnO is the simplest of the monoxides; it is an insulator simply because the exchange splitting of the d bands is greater than the d-band width (Fig. 1), which together with the valence (5) of the Mn^{++} ion, makes MnO an insulator. The new information[4] that we bring to the discussion of MnO is that the dominance of intra-atomic exchange over interatomic hopping is so marginal that *MnO is an insulator only when the magnetization is permitted to assume the particular antiferromagnetic spin structure that is observed experimentally.* Our energy-band calculations[5] reveal that the significance of the [111] spin structure (Fig. 2) is that only in this structure does the σ bonding of the e_g (cigar shaped) d states via collinear oxygen p states couple *exclusively* exchange-split d states. In this way the strongest interatomic interaction, which would otherwise lead to a large bandwidth and metallic behavior, is dissipated, causing only an enhancement of the spin splitting. (Our calculated total energy for the observed [111] antiferromagnetic order is 0.3 eV lower than that for the otherwise identical system in which the magnetization varies in the [100] direction.)

Progressing through the monoxide series, the minority-spin d band fills, causing the magnetic moment and the exchange splitting to decrease. (For NiO, it is ~ 1.3 eV.) In contrast to MnO, two independent gaps (Fig. 1) are required to make NiO an insulator: the exchange/sigma-bond gap described above for MnO, and the ligand-field gap separating minority-spin e_g and t_{2g} states. The [111] spin variation is crucial to both gaps, because it causes the width of the e_g and t_{2g} bands to be determined by π rather than σ bonding. Figure 1 also indicates the aspect of our band picture of NiO that is in stark disagreement with the prevailing understanding of the monoxides, namely, the pres-

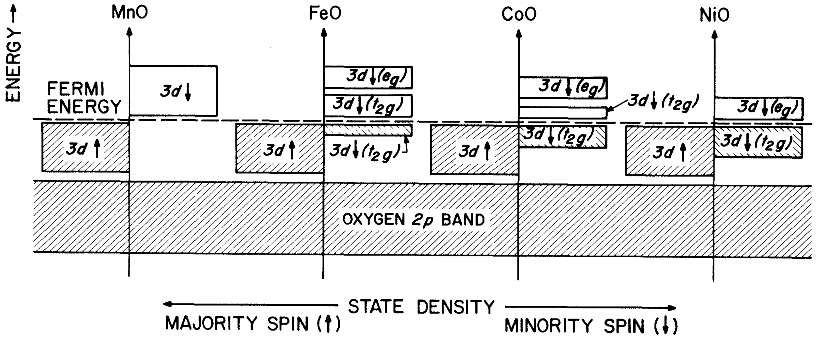

FIG. 1. Band picture of the monoxides. The qualitative difference between this picture and the commonly accepted one is the energy position of the empty d states. To quantify the state-density information, we find the width of the Mn $3d$ and the O $2p$ bands to be 3 eV and 5 eV, respectively. The band centers are separated by ~ 5 eV. The gaps in MnO and NiO are 0.4 and 0.3 eV, respectively.

ence of empty d states just above ϵ_F. Using inverse photoemission, which is the most direct probe of such states (Figs. 1 and 3), Scheidt *et al.*[6] have observed states located at energies where our calculations put the empty Ni d (e_g) states. Appearance-potential measurements[6] also detect these states. (The data for states near ϵ_F are very similar to those for pure Ni.)

The measurement figuring most prominently in many discussions of NiO is optical absorption.[7,8] The strong absorption beginning at ~ 4 eV is usually ascribed to transitions from $3d$ states to the $4s$ conduction band (not shown in Figs. 1 and 3). Resonant-Raman measurements[9] indicate, however, that the absorption edge is due instead to transitions out of the oxygen $2p$ states, for which the empty d states just above ϵ_F are the only available final states. Our calculations support this interpretation of the absorption edge in a second, independent way: Transitions out of the Ni d states must go to the Ni $4p$ component of the conduction-band states. We find this component of the state density to rise too slowly from threshold to account for the absorption rise. The band picture also accounts for the undetectability of photoconductivity near threshold.[10] If absorption is due to transitions into empty d states, then current carrying O $2p$ holes will be filled by Auger transitions from occupied d states. If (as we do not believe) the absorption is due to transitions out of filled d states, then the empty d states will serve as conduction-killing trap states. Either way, the carriers will be in d states in which conduction will be poor and probably polaronic, because of the ionic character of the compound and the very large effective mass of the d bands.

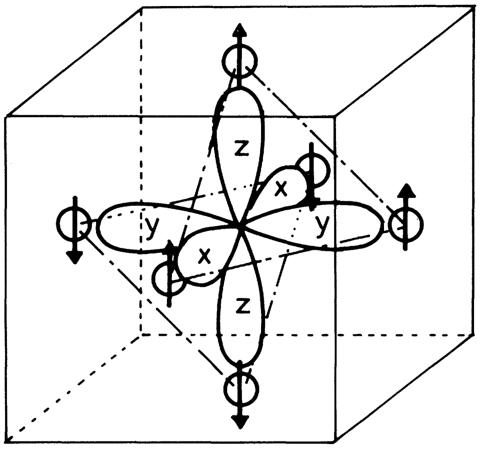

FIG. 2. Special significance of the [111] type of antiferromagnetic order observed in the monoxides. The figure depicts the arrangement of O (cube center) and Mn (cube faces) atoms in the rocksalt structure. In this crystal/spin structure the O p orbitals couple only oppositely magnetized Mn ions.

The weak absorption below threshold is generally ascribed to dipole-forbidden transitions between Ni d states. Unlike most ionic insulators, the states on either side of the gap in the monoxides are concentrated on the same atoms. Therefore, the electron-hole interactions accompanying d-to-d excitations across the gap will be so strong that the band picture is probably a poor starting point from which to analyze these excitations. This observation is consistent with the similarity of the data for NiO to those for Ni impurities in MgO,[11] and with the success of ligand-field theory in interpreting these data.[8]

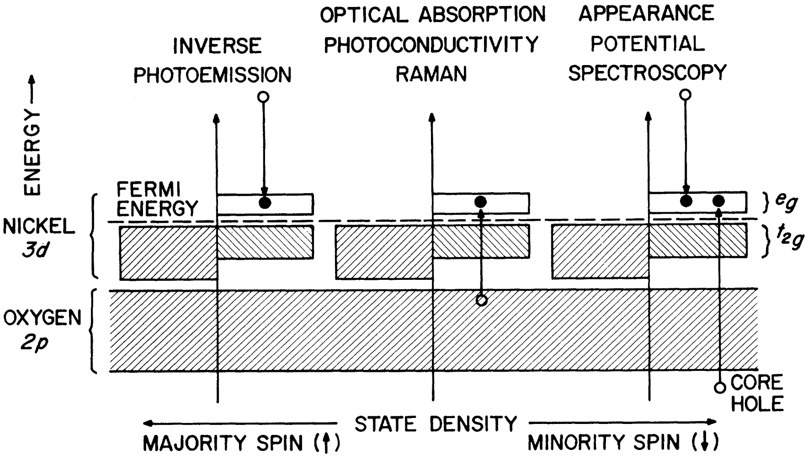

FIG. 3. Measurements (Refs. 6–10) indicating the existence of empty *d* states close to the top of the valence band in NiO.

Hall-coefficient measurements indicate hole conduction in NiO,[12] which is consistent with the greater bandwidth of the t_{2g} valence band, relative to that of the e_g conduction band. Also, the activation energy for carrier creation[13] is very similar to the magnitude of the gap that we find separating the valence and conduction bands (0.3 eV). The observation that the mobility of thermally produced carriers is much smaller than that of band electrons and holes[13] is also consistent with our inference (see above) that *d*-state conduction in NiO is polaronic.

FeO and CoO raise an additional issue. Our band calculations *do not* exhibit the gap shown in Fig. 1 for FeO and CoO. We believe that this deviation from experiment reflects a previously established[14,15] failure of the local-density treatment of exchange and correlation, on which our calculations are based. The exchange interaction, if treated properly, causes the energy of a single-particle level to fall as the level is occupied. This has the natural effect of separating occupied levels from unoccupied ones. The local-density approximation causes just the reverse to occur; levels rise as they are filled, and fall as they are emptied. This effect can force the minimum-energy state to be metallic, *even in a free atom.* (In a "metallic" free atom two or more degenerate levels are partially occupied.) This failure of the local-density approximation becomes more severe with increasing orbital localization,[14] and first seriously corrupts calculations for free atoms in the 3*d* transition series. Two facts support this explanation of the gap in FeO and CoO. First, the appropriate exchange energy, when calculated in the Hartree-Fock approximation, is more than adequate (several electronvolts) to create the gap, as a result of the flatness of the bands. Second, the measured magnetic moment in CoO ($\sim 3.4\mu_B$)[16] is larger than can be generated by spin alone. We infer that CoO has a substantial orbital moment, which implies a preferential occupation of $m_l = 1$ states over the $m_l = -1$ states in the t_{2g} manifold. Such an orbital moment is consistent with the observed direction of the magnetization in CoO, which is determined by the spin-orbit interaction.[17] (The difficulty of making sufficiently pure and stoichiometric FeO has thus far prevented the determination of the orbital moment in FeO.)

The monoxides remain insulating above the Néel temperature. Our coherent-potential-approximation calculations[18] show that the insulating gap survives even the complete disordering of the magnetic moments in MnO, whereas such complete disorder closes the calculated band gap in NiO. This might reflect the persistence of short-range magnetic order above the Néel temperature, or an underestimate of the gap due to our use of the local-density approximation, or the onset of Anderson localization. (Recall that the monoxides exhibit very poor mobility at low temperatures, which can only be worsened by magnetic disorder.)

between the band and localized-electron pictures of the monoxides, we mention the variation of the strength of the interatomic exchange coupling across the monoxide series. In the traditional picture ("superexchange"[19]), this coupling is inversely proportional to the Coulomb-repulsion parameter *U*. This dependence is difficult to reconcile with the monotonic *rise* of the Néel temperature by a factor of 5 across the monoxide series, from MnO to NiO. In our band picture, this rise is naturally predicted,[18] because the parameter U is replaced by the exchange splitting in the denominator of the expression for the exchange coupling (second-order perturbation theory). Whereas U is either constant or increases across the series, the exchange splitting decreases linearly toward zero, causing the exchange coupling and the Néel temperature to increase sharply.

This work was supported in part by a Grant in Aid for Cooperative Research from the Ministry of Education, Science, and Culture of Japan.

---

[a] Permanent address: Institute for Solid State Physics, University of Tokyo, Roppongi, Minato-ku, Tokyo, Japan.

[1] N. F. Mott, Proc. Phys. Soc., London, Sec. A **62**, 416 (1949); D. Adler and J. Feinleib, Phys. Rev. B **2**, 3112 (1970); B. H. Brandow, Int. J. Quantum Chem., Symp. No. 10, 417 (1976), and Adv. Phys. **26**, 651 (1977); B. Koiller and L. M. Falicov, J. Phys. C **7**, 299 (1974), and **8**, 695 (1975); A. B. Kunz and G. T. Surratt, Solid State Commun. **25**, 2989 (1978); A. B. Kunz, Int. J. Quantum Chem., Symp. No. 15, 487 (1981).

[2] S. Hüfner and G. K. Wertheim, Phys. Rev. B **7**, 5086 (1973). These authors deduce a value for the intra-atomic Coulomb interaction U from a variety of photoemission experiments. Their value of ~2 eV is much smaller than assumed in Refs. 1.

[3] O. K. Andersen, H. L. Skriver, H. Nohl, and B. Johansson, Pure Appl. Chem. **52**, 93 (1979); J. Yamashita and S. Asano, J. Phys. Soc. Jpn. **52**, 3506 (1983); K. Schwarz, private communication.

[4] T. M. Wilson, Int. J. Quantum Chem. IIIS, 757 (1970), obtained results similar to ours. In a subsequent extensive energy-band analysis, L. F. Matheiss, Phys. Rev. B **77**, 290, 606 (1972), concluded that band theory could not account for the observed insulating behavior.

[5] Exchange and correlation are treated in the local-spin-density approximation, and the single-particle equations are solved by using the augmented- spherical-wave method described by A. R. Williams, J. Kübler, and C. D. Gelatt, Jr., Phys. Rev. B **19**, 6094 (1979). A. R. Williams and U. von Barth, in *The Inhomogeneous Electron Gas,* edited by S. Lundqvist and N. H. March (Plenum, New York, 1983), present a review of this kind of analysis.

[6] H. Scheidt, M. Glöbl, and V. Dose, Surf. Sci. **112**, 97 (1981). See also, F. J. Himpsel and Th. Fauster, Phys. Rev. Lett. **49**, 1583 (1982).

[7] R. J. Powell and W. E. Spicer, Phys. Rev. B **2** 2182 (1970); G. W. Pratt and R. Coelho, Phys. Rev. **116**, 281 (1959); D. R. Huffman, R. L. Wild and M. Shinmei, J. Chem. Phys. **50**, 4092 (1969).

[8] R. Newman and R. M. Chrenko, Phys. Rev. **114**, 1507 (1959).

[9] R. Merlin, T. P. Martin, A. Polin, M. Cardona, B. Andlauser, and D. Tannhauser, J. Magn. Magn. Mater. **9**, 83 (1978).

[10] J. E. Keem and M. A. Wittenauer, Solid State Commun. **26**, 213 (1978).

[11] W. Low, Phys. Rev. **109**, 247 (1958).

[12] A. J. Bosman and H. J. van Daal, Adv. Phys. **19**, 53 (1970).

[13] J. E. Keem, J. M. Honig, and L. L. van Zandt, Philos. Mag. **37**, 537 (1978).

[14] J. F. Janak and A. R. Williams, Phys. Rev. B **23**, 6301 (1981).

[15] Williams and von Barth, Ref. 5.

[16] D. C. Khan and R. A. Erickson, Phys. Rev. B **1**, 2243 (1970).

[17] J. Kanamori, Prog. Theor. Phys. **17**, 177, 197 (1957).

[18] T. Oguchi, K. Terakura, and A. R. Williams, Phys. Rev. B **28**, 6443 (1983).

[19] P. W. Anderson, in *Solid State Physics,* edited by F. Seitz and D. Turnbull (Academic, New York, 1963), Vol. 14, p. 99.