substance: NiO
property: band structure

There is no literature consensus on the detailed electronic structure of NiO or the interpretation of the UV absorption spectra. The results of three different calculations of dispersion in the ΓX direction are shown in Fig. 1. A complete band structure calculation at the non-self-consistent Hartree-Fock level is shown in Fig. 2. At the other extreme, the results of a local SCF – Xα cluster calculation are given in Fig. 3. A large number of phenomenological electronic structures have been proposed and are shown in Figs. 4...6. These differ primarily in the widths and positions of the d^8 and d^9 Ni bands. The extremes are represented by [70A], who places a very narrow d^9 band some 15 eV above the d^8 band which in turn is placed below the O $2p^6$ band, and [81D] who places a much broader d^9 band 3.6 eV above the O 2p and 2.2 eV above the Ni d^8 level. In this model the extinction coefficient for charge exchange between Ni^{2+} ions is assumed to be extremely small near threshold.

References:

69M McNatt, J. L.: Phys. Rev. Lett. 23 (1969) 915.
70A Adler, D., Feinleib, J.: Phys. Rev. B2 (1970) 3112.
72M1 Mattheiss, L. F.: Phys. Rev. B5 (1972) 290, 306.
72M2 Messick, L., Walker, W. C., Glosser, R.: Phys. Rev. B6 (1972) 3941.
72S Slater, J. C., Johnson, K. H.: Phys. Rev. B5 (1972) 844.
73J Johnson, K. H., Messmer, R. P., Lonnolly, J. W. D.: Solid State Commun. 12 (1973) 313.
75C Collins, T. C., Kunz, A. B., Ivey, J. L.: Int. J. Quantum Chem. Symp. 9 (1975) 519.
78K Kunz, A. B., Surratt, G. T.: Solid State Commun. 25 (1978) 9.
81D Dare-Edwards, M. P., Goodenough, J. B., Hamnett, A., Nicholson. N. D.: Faraday Trans. Chem. Soc. II 77 (1981) 643.

Fig. 1.

NiO. Band calculations (a) [78K], (b) [72M1], (c) [75C] along the ΓX-axis in *k*-space; (d) comparison with the experimental density of states from photoemission spectra [78K].

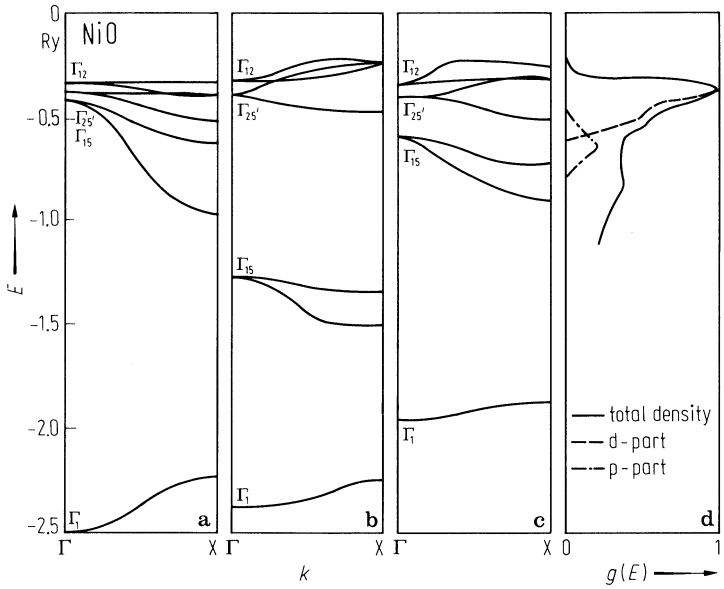

Fig. 2.

NiO. LCAO energy bands obtained by fitting APW results at symmetry points [72M1].

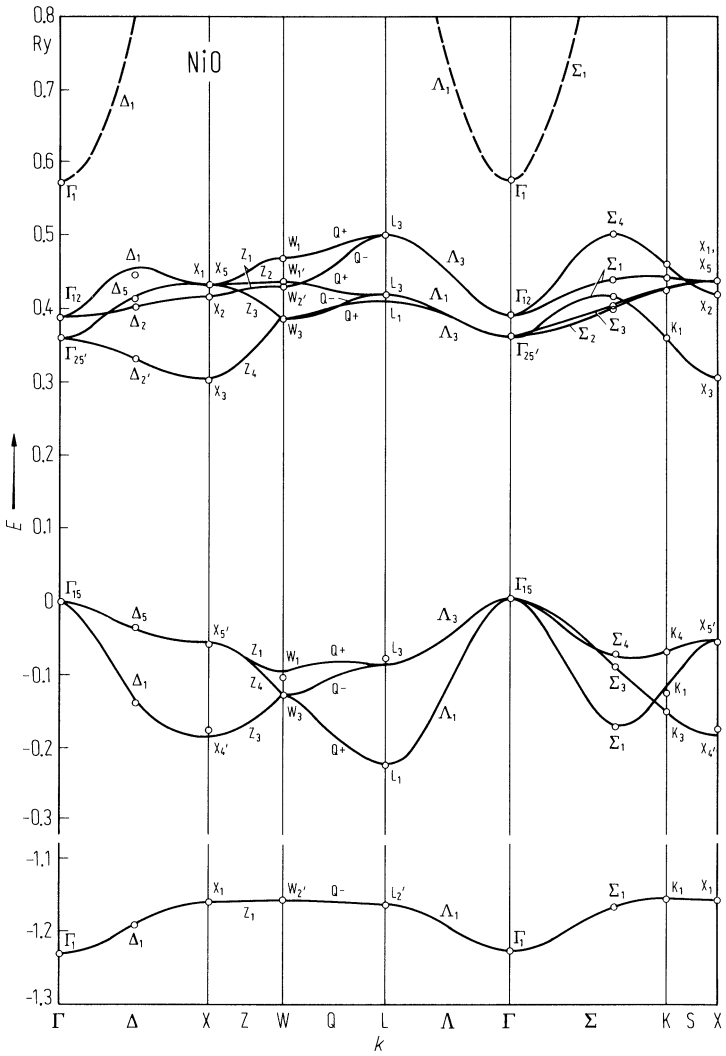

Fig. 3.

NiO. Ground-state spin-polarized SCF-Xα electronic levels of an NiO_6^{10-} cluster. Also shown are the corresponding spin-restricted SCF-Xα free-atom energy levels for O and Ni (in $3d^8 4s^2$ configuration) [73J]. For discussion of self consistent field cluster method, see [72S].

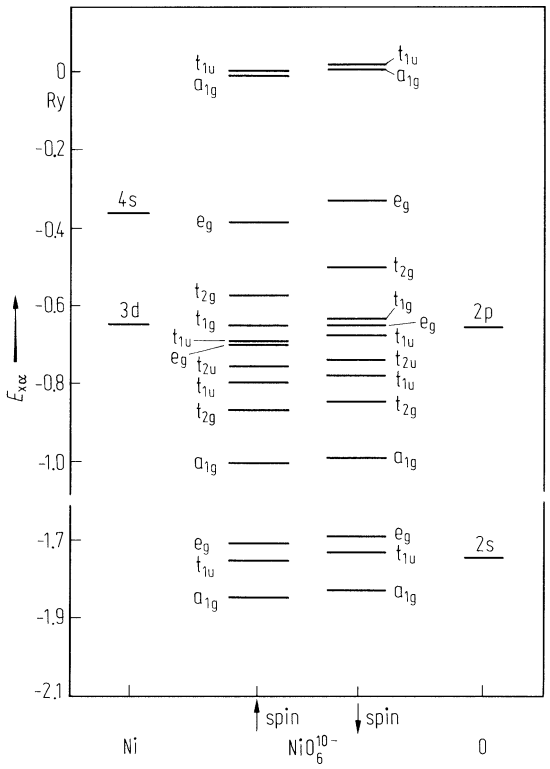

Fig. 4.

NiO. Various models for the electronic structure of NiO (a) one electron density of states (b) many electron states (c) energy band structure [69M].

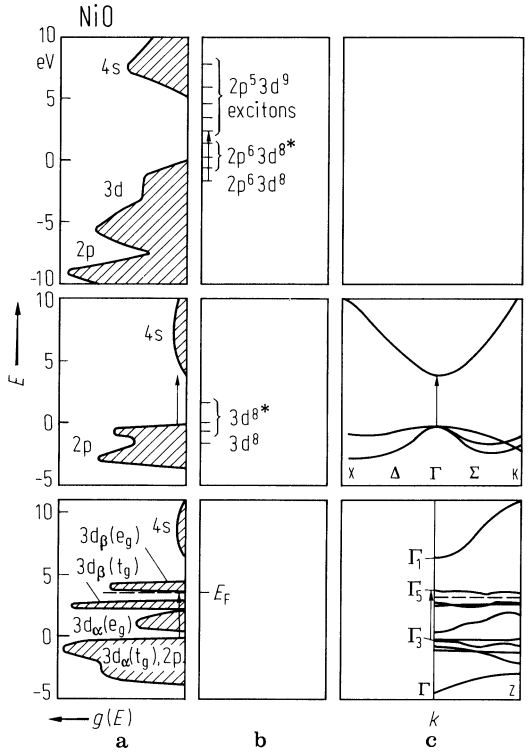

Fig. 5.

NiO. Electronic states from RT data. Left: band states, right: localized states I: $d^7(t_\alpha^3 t_\beta^3 e_\alpha)$ + 4s, II: $d^7(t_\alpha^2 t_\beta^3 e_\alpha^2)$ + 4s, III: $d^7(t_\alpha^3 t_\beta^2 e_\alpha^2)$ + $d^9(t_\alpha^3 t_\beta^2 e_\alpha^2 e_\beta)$, IV: $d^7(t_\alpha^3 t_\beta^3 e_\alpha)$ + $d9(t_\alpha^3 t_\beta^3 e_\alpha^2 e_\alpha)$, V: $d^7(t_\alpha^2 t_\beta^3 e_\alpha^2)$ + $d^9(t_\alpha^3 t_\beta^3 e_\alpha^2 e_\beta)$ [72M2].

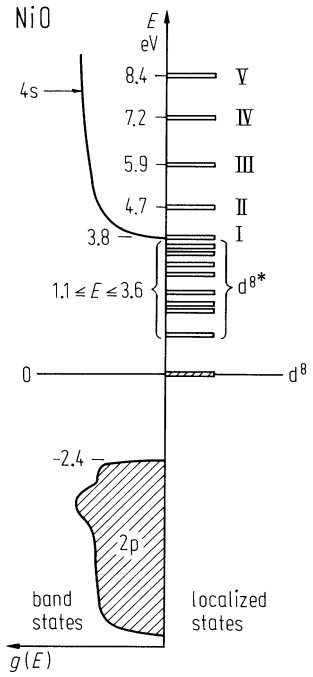

Fig. 6.

NiO, 0.5 at% Li doped. Phenomenological band structure from photoelectrochemical measurements at 295 K; the ordinate is the band energies relative to vacuum; I and II correspond to surface states detected electrochemically [81D].