

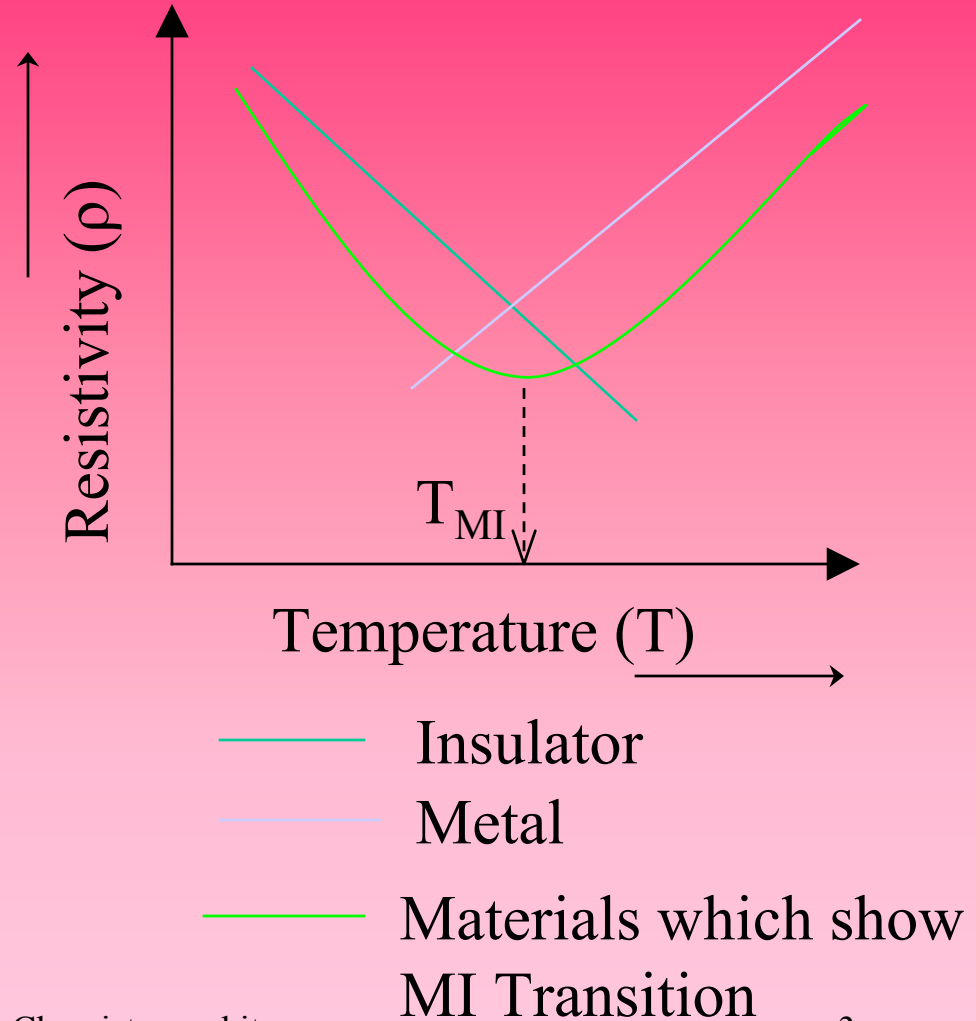
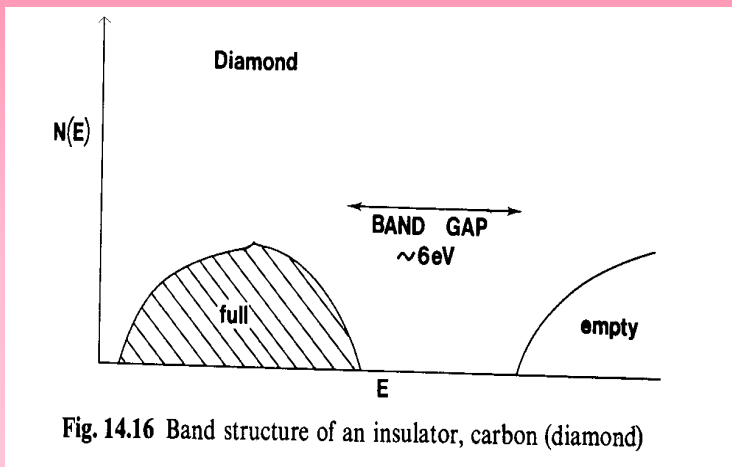
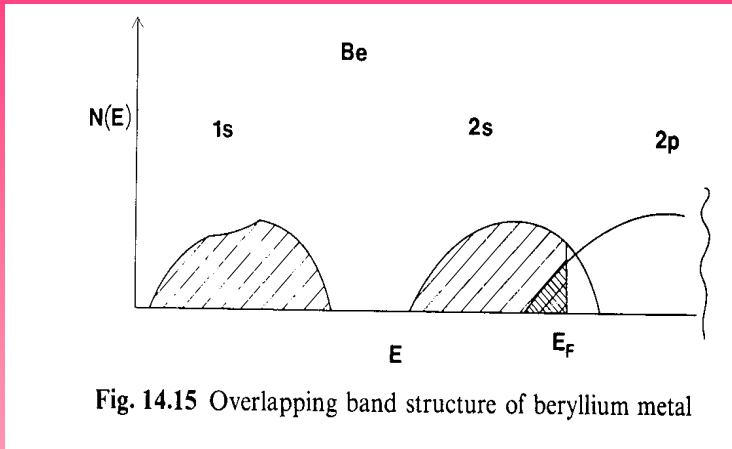
Photoelectron spectroscopy through the metal-insulator transition

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Introduction

- Materials are either conductors or semiconductors or insulators.
- Metals are conductors which have electrons in valence band and conduction band.
- Semiconductors have a energy gap which is about 1 eV.
- Insulators have energy gap greater than 6 eV.
- Materials can be made to conduct or insulate by various electronic transitions which would change the relative populations of the valence and core levels.

Band Structure of metals and insulators



Materials

- Various oxides of transition metals like Ni, Cu, V, Fe etc...
- Transition metal compounds.e.g., $(\text{NbSe}_4)_3\text{I}$
- Rare earth bimetallic oxides e.g., RNiO_3
- Some metallic mono layers on specific surfaces.
e.g., Ba

NiO

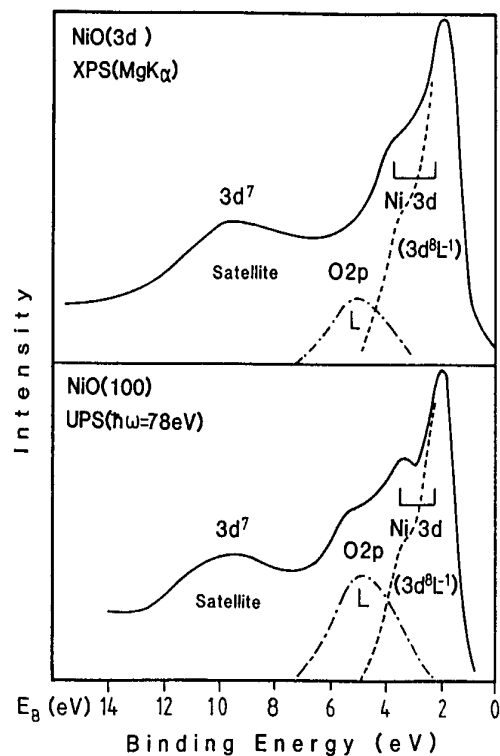


Fig.5.34. Comparison of XPS and UPS spectra of NiO [5.65]. In the XPS spectrum the O 2p contribution was estimated from a comparison of XPS spectra with those of other transition-metal oxides (see also Fig.5.25); in the UPS spectrum the O 2p band is visible. In both cases a distinct satellite is evident. Its assignment to a $3d^7$ final state (NiO has a $3d^8$ initial state) is discussed in the text [5.65]. The zero is the experimental Fermi energy, which is close to the top of the valence band

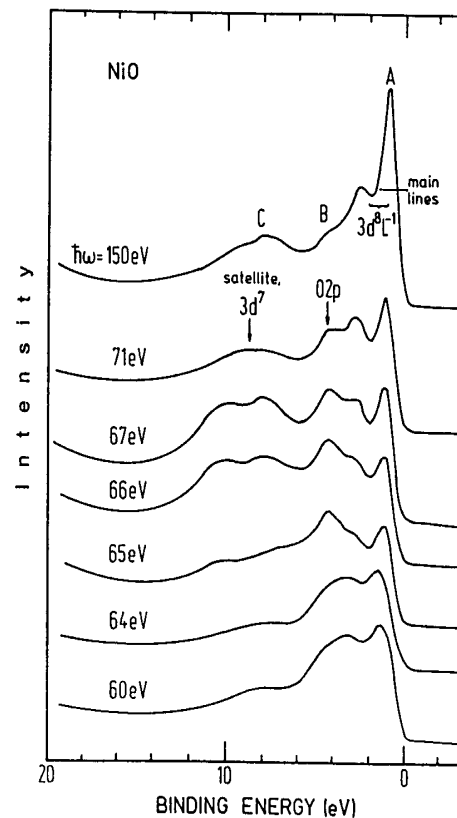


Fig.5.35. Resonance PE spectra of NiO [5.66,67]. A is the "main 3d structure", B the O 2p valence band and C the satellite. Resonance enhancement of the satellite occurs via the reaction: $3p^6 3d^8 + \hbar\omega \rightarrow 3p^5 3d^9 \rightarrow 3p^6 3d^7$, indicating that the satellite is a $3d^7$ final state

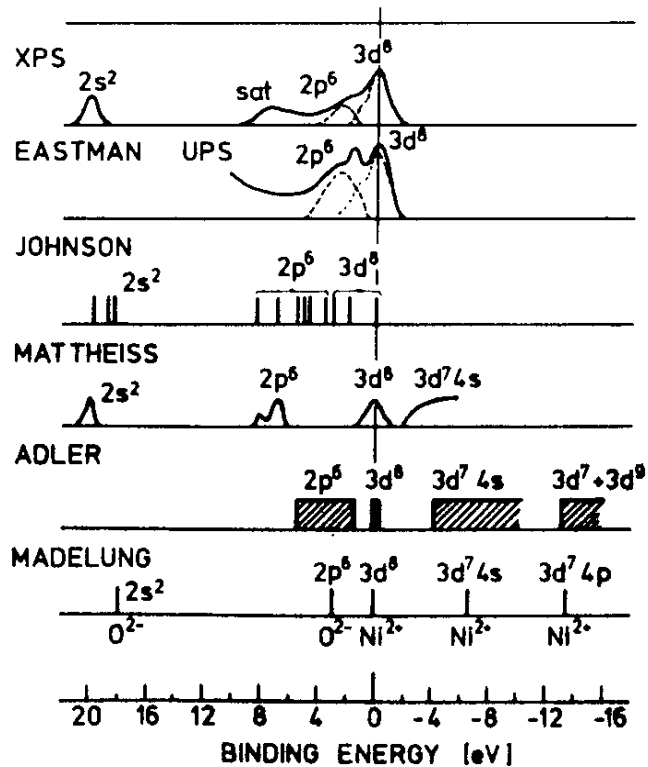


Fig. 3.11. Experimental and theoretical results for the valence band structure of NiO. In every case the zero of energy has been made to coincide with the center of the 3d band

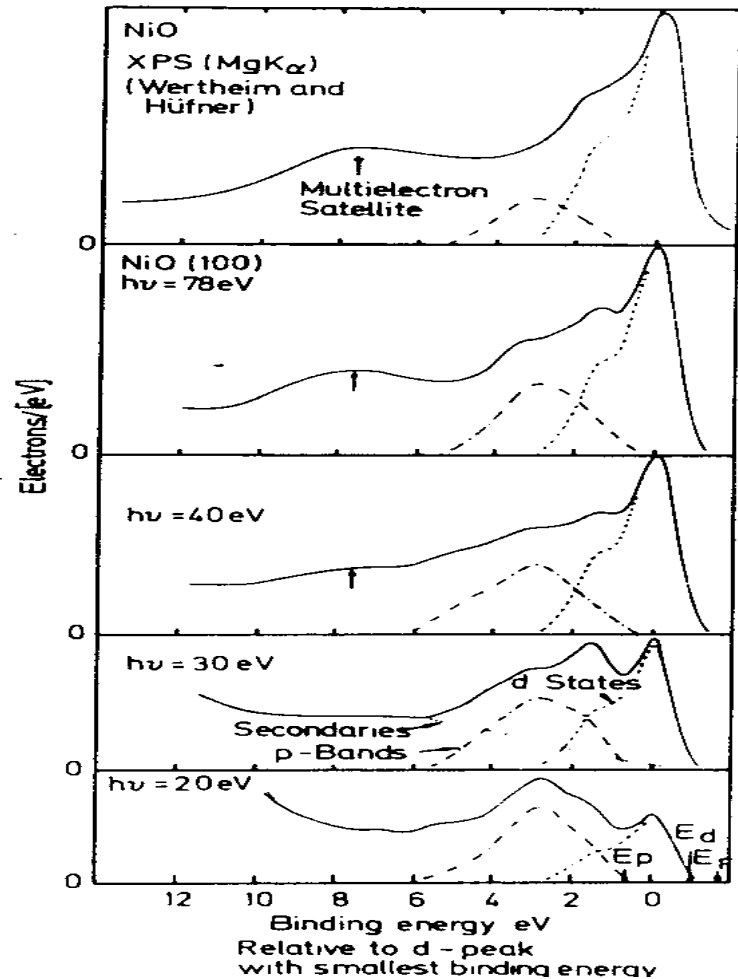
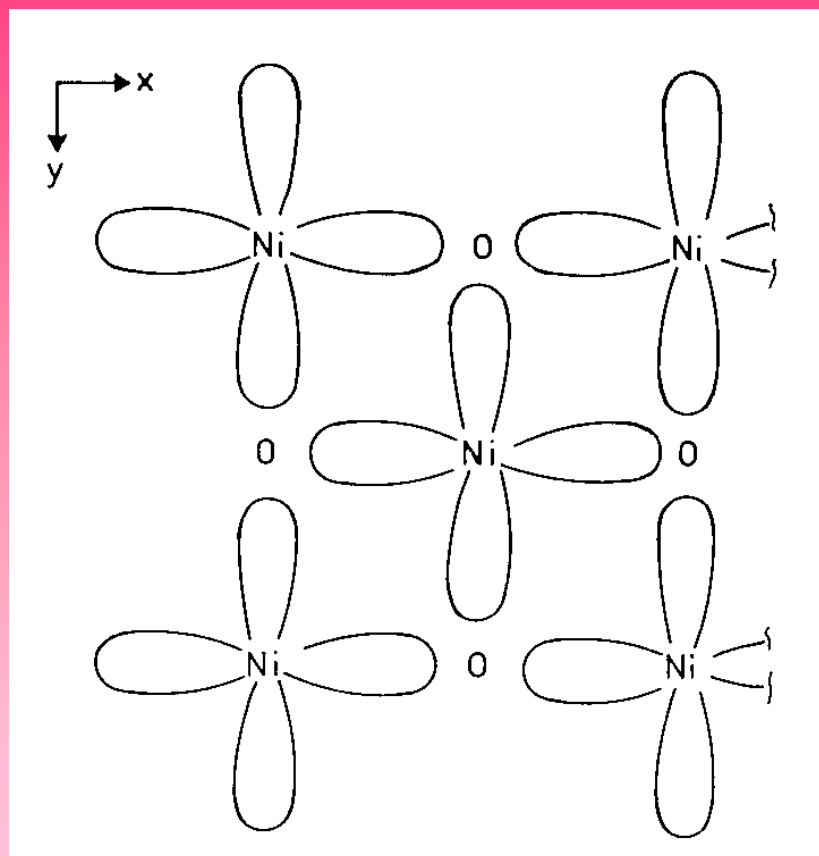


Fig. 3.10. Photoelectron spectra for NiO taken with various photon energies between 20 and 78 eV and with Mg K_{α} radiation. The zero of energy is placed at the d -state peak and E_F , E_d , and E_p are the Fermi energy, d -state edge, and p -band edge. Partial d -state emission intensities (dashed lines) and p -band intensities (broken lines) are shown (see text) [3.44]

NiO Structure



MNiO₃ (M = Pr, Sm, Eu, Nd)

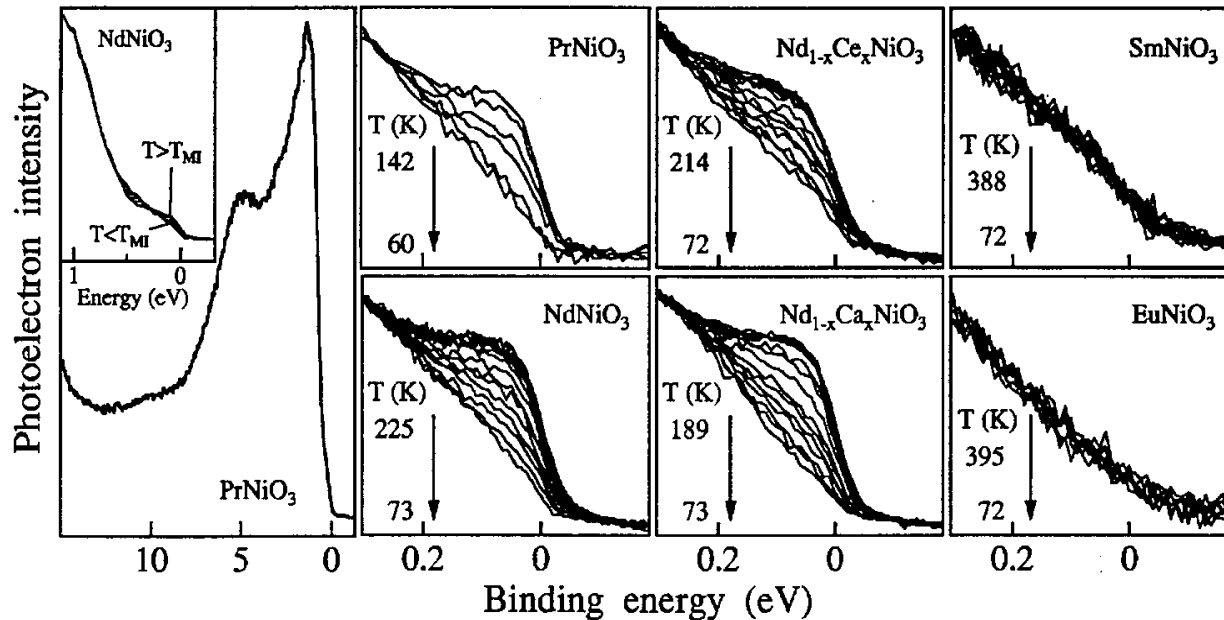


FIG. 1. First panel: Valence band of PrNiO₃ ($h\nu = 1486.6$ eV); Inset: The zoom-in into the energy interval of ~ 1 eV of E_F (NdNiO₃ with $h\nu = 21.2$ eV) showing the spectral weight transfer to higher binding energies below T_{MI} ; Remaining panels: spectra recorded at different temperatures for PrNiO₃, NdNiO₃, electron doped Nd_{0.98}Ce_{0.02}NiO₃, hole doped Nd_{0.99}Ca_{0.01}NiO₃, SmNiO₃, and EuNiO₃ ($h\nu = 21.2$ eV).

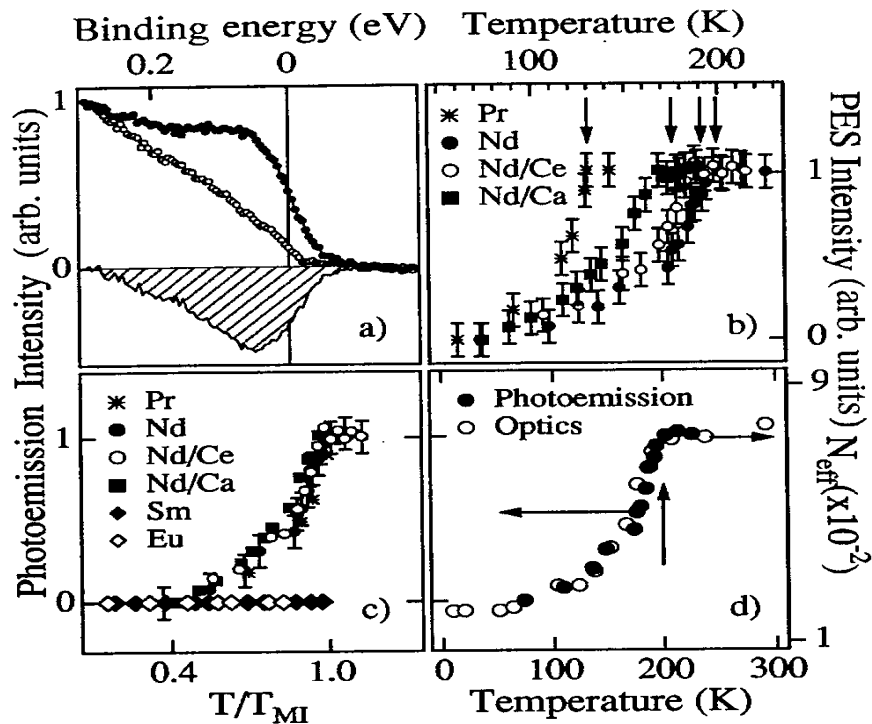


FIG. 2. (a) PES spectra of NdNiO₃ at 200 K (full symbols) and 73 K (open symbols) together with their difference. (b) Temperature dependence of the integrated area of the difference curves for PrNiO₃, NdNiO₃, Nd_{0.98}Ce_{0.02}NiO₃, Nd_{0.99}Ca_{0.01}NiO₃, normalized to the maximum value. (c) The same as (b) versus the reduced temperature (T/T_{MI}) and together with the results for SmNiO₃ and EuNiO₃. (d) The optics result from Katsufuji *et al.* (open symbols; right axis) together with our result from (b) for NdNiO₃ (closed symbols; left axis). The vertical arrows mark the MI transition temperatures.

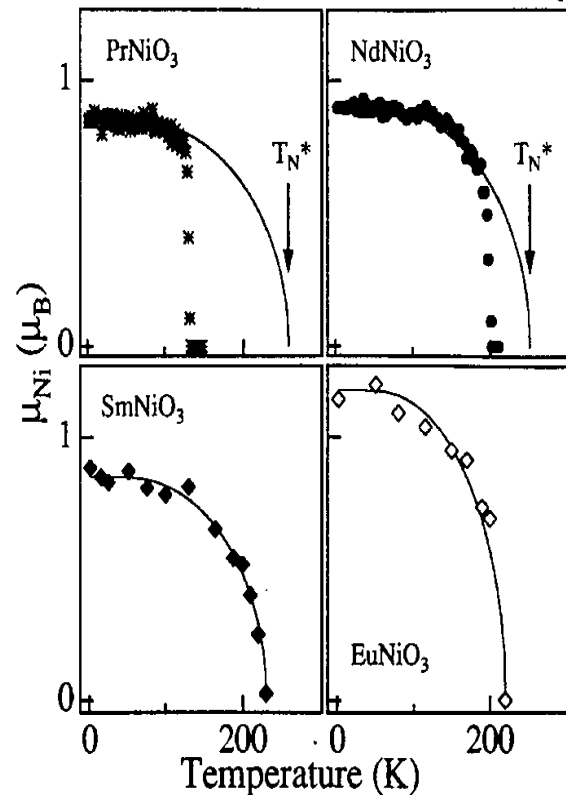


FIG. 3. The evolution of the Ni magnetic moments with temperature for PrNiO₃, NdNiO₃, SmNiO₃, and EuNiO₃. The lines are an attempt to fit the data with Brillouin function. The arrows mark the virtual Néel temperatures (T_N^*) for PrNiO₃ and NdNiO₃.

Ba (3x1) on Si(111)

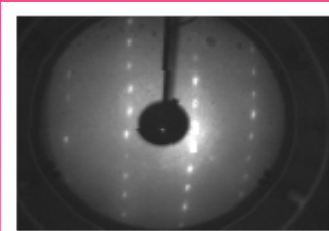


Figure 2:
LEED image of the single-domain
(3x1) reconstruction, recorded at
84 eV.

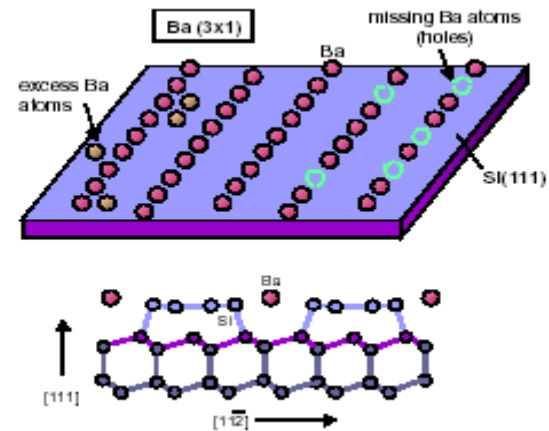


Figure 1:
Schematic of the Ba(3x1)/Si(111) reconstruction. It is possible to prepare the system with excess or missing Ba atoms (top). The chain-channel model is currently discussed in the literature as the most likely one. Removal of Ba atoms does not involve bond breaking and leaves a hole-doped one-dimensional chain (bottom).

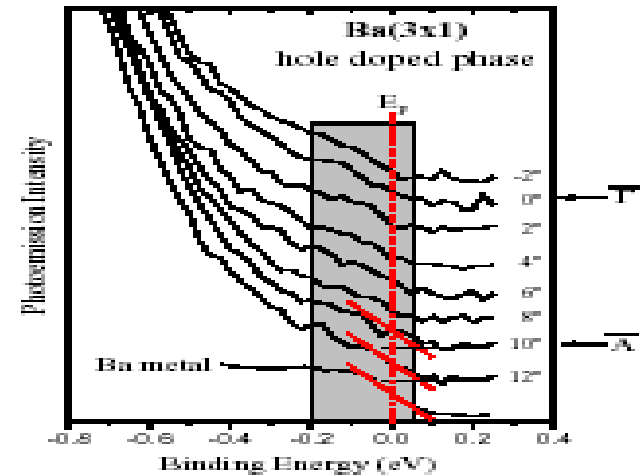
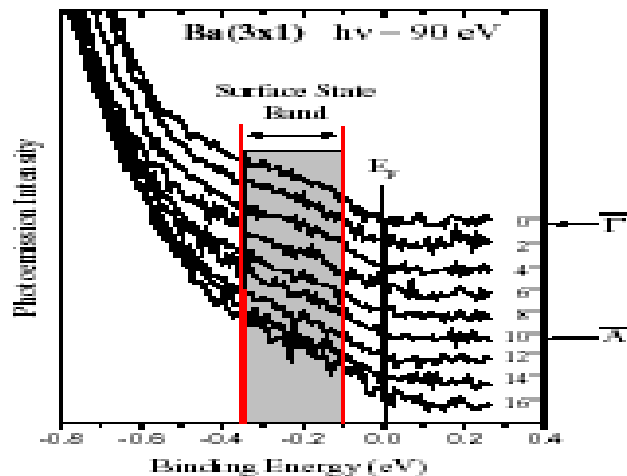


Figure 3:

The left panel shows the surface state band of the Ba(3x1) reconstruction under typical preparation conditions. A weakly dispersing band is identified around ~ 0.3 eV below E_F . Upon sufficient Ba desorption (right panel), the band is shifted upward by about 0.2 eV such that the band crosses E_F .

$(\text{NbSe}_4)_3\text{I}$

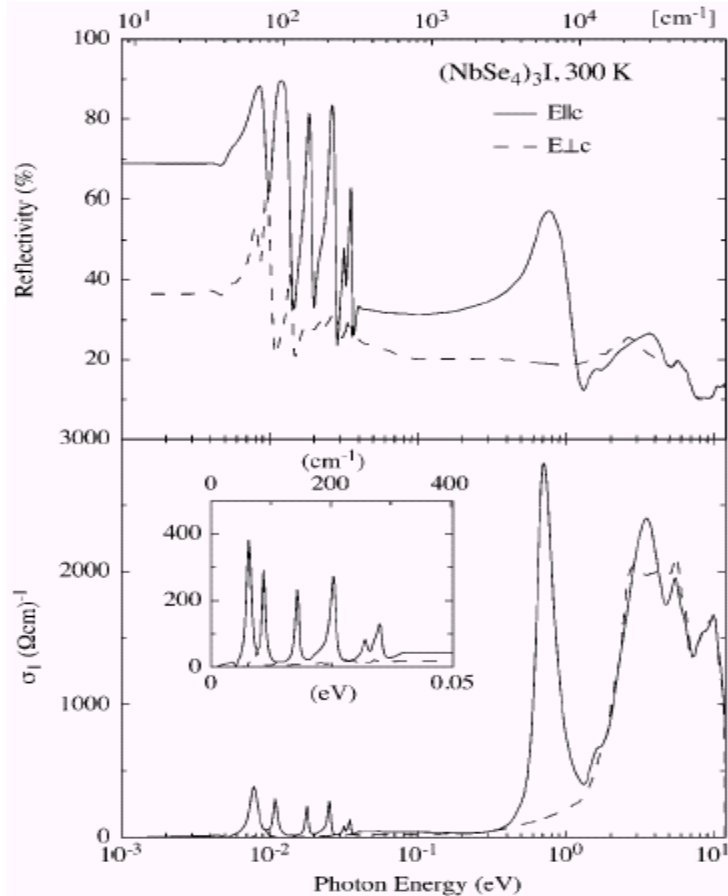


FIG. 1. Reflectivity and real part of the optical conductivity of $(\text{NbSe}_4)_3\text{I}$ at 300 K and for light polarized along and perpendicular to the c axis. The inset is an enlargement of the far-infrared spectral range, showing the phonon modes.

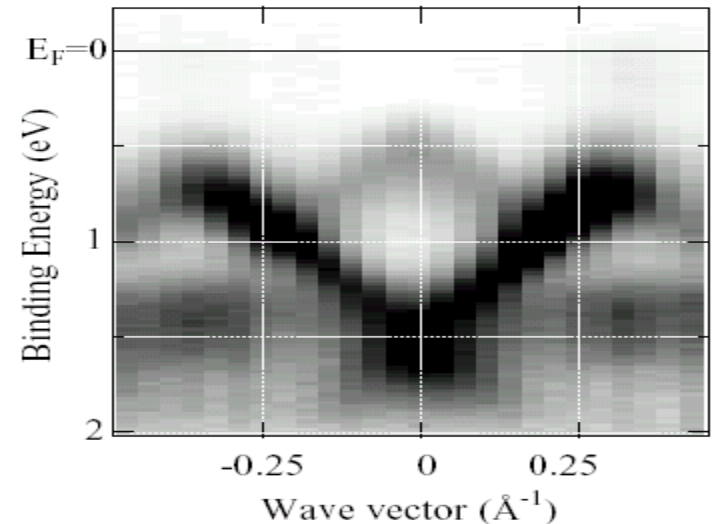


FIG. 2. ARPES intensity map ($h\nu = 21.2$ eV; $T = 300$ K) of $(\text{NbSe}_4)_3\text{I}$. Each column represents the intensity of an ARPES spectrum collected at the indicated wave vector along the 1D (FZ) chain direction.

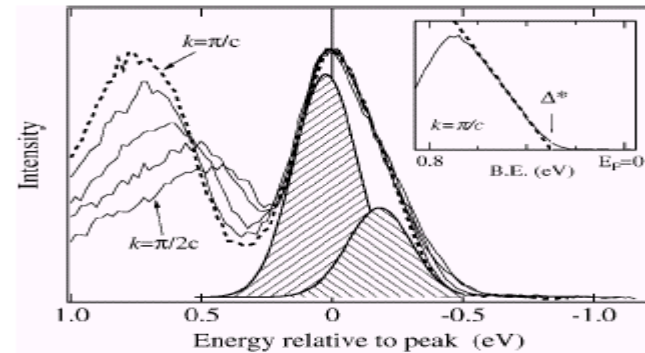
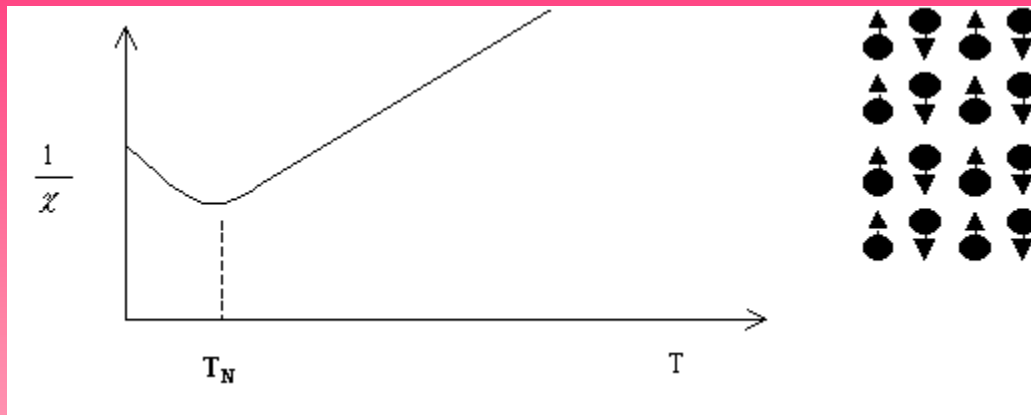


FIG. 4. ARPES spectra of $(\text{NbSe}_4)_3\text{I}$ for wave vectors $\pi/2c < k < \pi/c$. The peak intensities and energy positions have been normalized to those of the $k = \pi/c$ spectrum to illustrate the k -independent line shape. A satisfactory fit is tentatively obtained by two Gaussian peaks of equal width (FWHM = 0.29 eV) and 5:2 intensity ratio, separated by 0.20 eV. Inset: a linear extrapolation of the $k = \pi/c$ spectrum identifies a baseline intersection $\Delta^* = 0.3$ eV.

Magnetic transitions



T_N Néel Temperature



Louis Néel

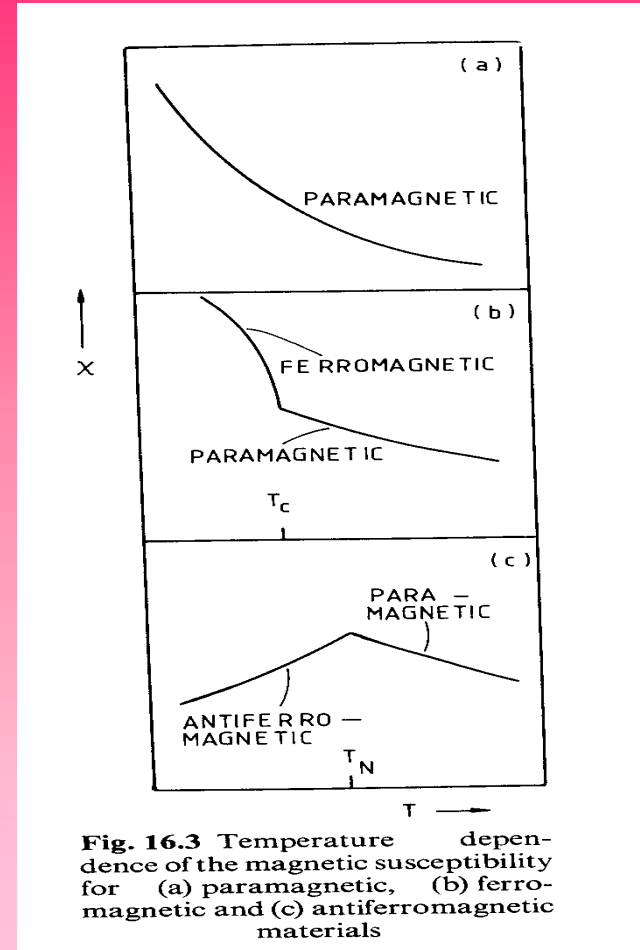


Fig. 16.3 Temperature dependence of the magnetic susceptibility for (a) paramagnetic, (b) ferromagnetic and (c) antiferromagnetic materials

VO₂

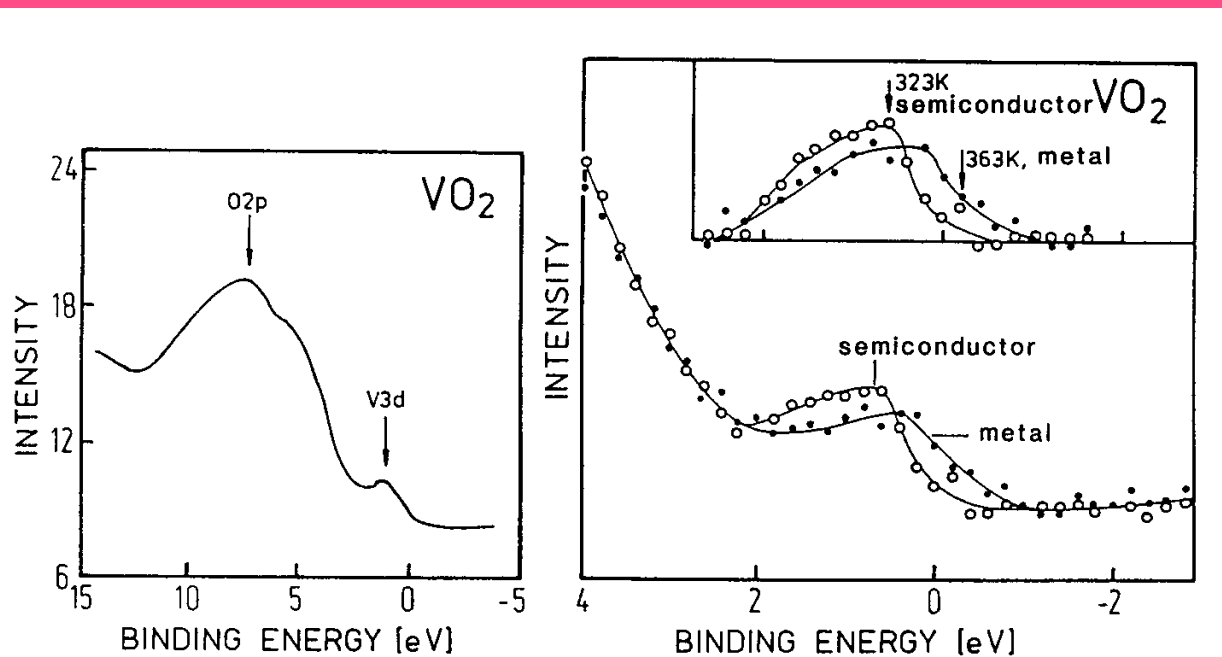


Fig.5.51. XPS valence band spectra of the metal-nonmetal transition in VO₂ [5.107, 108]. The left panel gives the complete valence band. The right panel gives the 3d structure above (363K), and below (323K) the metal-nonmetal transition ($T_N = 340K$). In going through the transition the 3d band moves towards the Fermi energy to intersect it

Conclusion

- The metal insulator transitions are studied using PES
- XPS, UPS, AES, ARPES are all tools which help in studying the transitions.
- As the molecule gets bigger the electronic structure gets more complicated and is tough to study.