

**substance: binary transition-metal oxides**

**property: placement of d bands and formal valence**

The binary oxides and chalcogenides contain a broad bonding band of primarily anion-p character separated by an energy gap from a broad antibonding band of primarily cation-s character. In oxides, the gap is large and the Fermi energy generally lies within it. Therefore we may use formal valence states, assuming  $O^{2-}$  ions, to obtain a count of the number of d electrons per transition-metal atom. Compounds may contain the same transition-metal atom in either a single or a mixed valence state, the latter occurring where the number of d electrons per transition-metal atom is non integral. In general, only two different valence states are present simultaneously, but exceptional cases are known where three quite different crystallographic sites stabilize three different valence states of the same atom in one structure. On the other hand, if two different valence states occupy crystallographically equivalent sites, valence transfer may be so rapid that available measuring techniques are unable to realise two distinguishable ions; in this case it is more meaningful to assign each atom an average, non integral valence state. Such is certainly the case in the itinerant-electron limit.

Although the situation is similar for the binary transition-metal chalcogenides of lower valence state, caution must be exercised in the interpretation of apparent higher valence states. Attempts to create higher valence states on the transition-metal ions of a chalcogenide may introduce holes into the broad, primarily anion-p bands instead of into the d states. These broad-band holes either render the compound metallic or become trapped in polyanion antibonding orbitals as in an  $(S_2)^{2-}$  unit. Polyanion formation can generally be detected from the structure; it is classically illustrated in the pyrite and marcasite structures of  $FeS_2$ .

The location of the Fermi energy relative to the edge of the broad anion-p bands clearly reflects the position of the d bands relative to this band edge. The d bands are more stable the higher the formal valence state on the transition-metal atom and, for a given valence state, the further to the right in any long series.