

4.3. ELECTRON DIFFRACTION

Wilkins, 1982). Core-loss spectroscopy, however, imposes specific conditions on the accessible final state: the overlap with the initial core wavefunction involves a projection in space on the site of the core hole, and the dominant dipole selection rules are responsible for angular symmetry selection. When extending the band-structure calculations to energy states rather high above the Fermi level, more elaborate methods, combining the conceptual advantage of the tight-binding method with the accuracy of *ab initio* pseudopotential calculations, have been developed (Janssen & Sankey, 1987). This self-consistent pseudo-atomic orbital band calculation has been used to describe ELNES structures on different covalent solids (Weng, Rez & Ma, 1989; Weng, Rez & Sankey, 1989).

The most promising description at present is the multiple scattering method developed for X-ray absorption spectra by Durham, Pendry & Hodges (1981) and Vvedensky, Saldin & Pendry (1985). It interprets the spectral modulations, in the energy range 10 to 30 eV above the edge, as due to interference effects, on the excited site, between all waves back-scattered by the neighbouring atoms (see Fig. 4.3.4.29). This multiple scattering description in real space should in principle converge towards the local point of view in the solid-state band model, calculated in reciprocal space (Heine, 1980). As an example investigated by EELS, the oxygen and magnesium *K* edges in MgO have been calculated by Lindner, Sauer, Engel & Kambe (1986) and by Weng & Rez (1989) for increased numbers of coordination shells and different potential models (representing variable ionicities). Fig. 4.3.4.30 shows the comparison of an experimental spectrum with such a calculation. Another useful idea emerging from this model is the simple relation, expressed by Bianconi, Fritsch, Calas & Petiau (1985):

$$(E_r - E_b)d^2 = C, \quad (4.3.4.48)$$

where E_r is the energy position of a given resonance peak attributed to multiple scattering from a given shell of neighbours (d is the distance to this shell), and E_b is a reference energy close to the threshold energy. This simple law, advertised as the way of measuring 'bond lengths with a ruler' (Stohr, Sette & Jonson, 1984), seems to be quite useful when comparing similar structures (Lytle, Gregor & Panson, 1988).

Other effects, generally described as multi-electron contributions, cannot be systematically omitted. They all deal with the presence of a core hole on the excited atom and with its influence on the distribution of accessible electron states. Of particular importance are the intra-atomic configuration interactions for white lines, as explained by Zaanen, Sawatzky, Fink, Speier & Fuggle (1985) for L_3 and L_2 lines in transition metals and by Thole, van der Laan, Fuggle, Swatzky, Karnatak & Esteve (1985) for $M_{4,5}$ lines in rare-earth elements.

(c) *The extended fine structures* (EXELFS) are equivalent to the well known EXAFS oscillations in X-ray absorption spectroscopy (Sayers, Stern & Lytle, 1971; Teo & Joy, 1981). Within the previously described multiscattering theory, it corresponds to the first step, the single scattering regime (see Fig. 4.3.4.29a). These extended oscillations are due to the interference on the excited atom between the outgoing excited

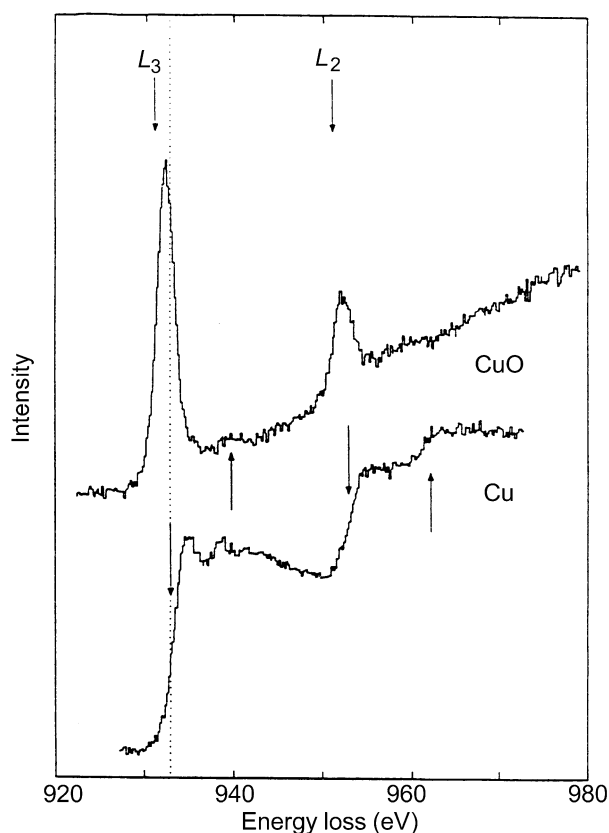


Fig. 4.3.4.28. The dramatic change in near-edge fine structures on the L_3 and L_2 lines of Cu, from Cu metal to CuO. The appearance of the intense narrow white lines is due to the existence of vacant d states close to the Fermi level [courtesy of Leapman *et al.* (1982)].

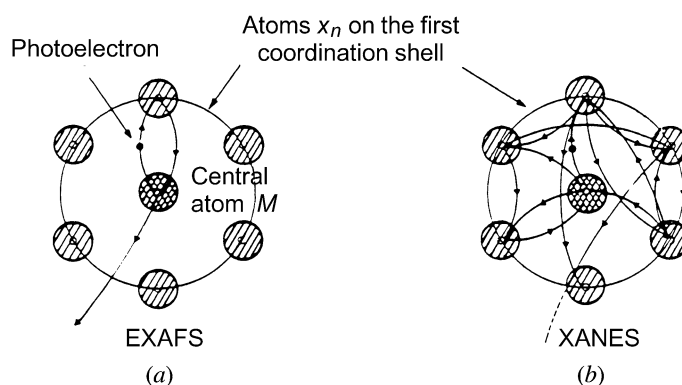


Fig. 4.3.4.29. Illustration of the single and multiple scattering effects used to describe the final wavefunction on the excited site. This theory is very fruitful for understanding and interpreting EXELFS and ELNES features, respectively equivalent to EXAFS and XANES encountered in X-ray absorption spectra.

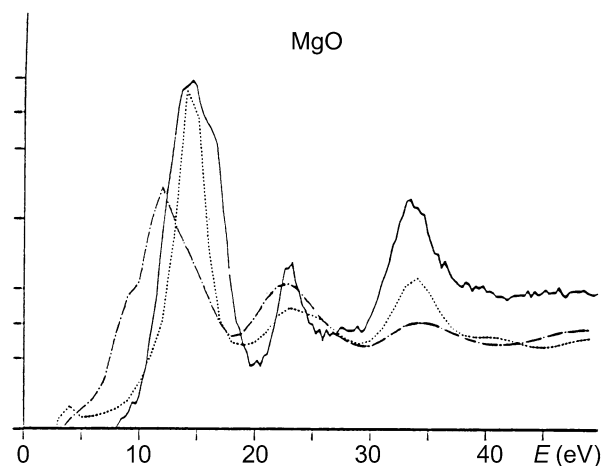


Fig. 4.3.4.30. Comparison of the experimental O *K* edge (solid line) with calculated profiles in the multiple scattering approach [courtesy of Weng & Rez (1989)].