Kroning Theory of Extended X-Ray Absorption Fine Structure

Kronig considered the extended fine structure appearing on the high-energy side of x-ray absorption edges. He suggest that such structure observed in gases were due to transitions of the ejected electron to the discrete energy states of an atom (or molecule) which becomes a, continuum of states above a characteristic energy and that for crystalline material, assuming zone theory breaks up into allowed and forbidden energies. Thus, an electron ejected in a given direction of the crystal can undergo transitions only to certain energy zones given by

$$E_n = \frac{h^2}{8m} \frac{n^2}{a^2},$$

(1)

where h is Planck's constant, m is the electron's mass, n is an integer, and a is the length of the period in the propagation direction. The maxima in the absorption edge then correspond to such allowed transitions whereas the minima correspond to forbidden transitions, a process which can be likened to the reflection of electrons by crystallographic planes. Kronig ascribed the breadth of the observed maxima to the multiplicity of directions in which an electron could travel and to the "broadening" of the allowed zones by thermally induced vibrations of the atoms. This model is developed considering the ejected electron as a plane wave function known as a Bloch function. Although no numerical calculations were presented in this first paper of Kroning, it was suggested that the temperature dependence of absorption spectra, a shifting of the peaks in Fe closer to the "main" edge and a decrease in their magnitude at larger energies with increasing temperature, was consistent with an increase of a in (1) and a temperature-induced broadening of the allowed zones, the more distant ones being subject to greater broadening. It should be noted here that most absorption-edge curves published to date are not amenable to quantitative interpretation unless corrected for instrumental effects' so that some of the "successes" of this and other theories may be coincidental rather than real.

In his second paper, "Kronig presented a detailed analysis of the behaviour of the ejected electron by representing it by a Bloch function solution of the time-independent Schrodinger equation. The Hamiltonian contains a periodic potential function having the periodicity of the lattice which has the effect of producing discontinuities in the allowed energy values whenever

$$E = \frac{h^2}{8m} \frac{(\alpha^2 + \beta^2 + \gamma^2)}{a^2 \cos^2 \varphi}$$

(2)

where α, β, γ are integers and φ is the angle between the electron's direction of propagation and the normal to a "boundary" plane. (φ is the compliment of the Bragg angle theta) When one integrates over all possible propagation directions, it can be shown that the discontinuities occur when

$$E = \frac{h^2}{8m} \frac{(\alpha^2 + \beta^2 + \gamma^2)}{a^2}$$

(3)

Kronig also estimated the energy at which an electron becomes "free" given by

$$E_0 = \frac{h^2}{8m} \left(\frac{3N}{a^3}\right)^{\frac{2}{3}}$$

(4)

where N is the total number of electrons contained in a unit cell. [(4) is the usual expression for calculating the Fermi energy in a metal except that N then represents the number of valence electrons in a^3] On this basis he concluded that formula (3) should be valid beyond 67 eV in Cu and beyond 11 eV in Fe. Incidentally, the energy values in (3) must be corrected before comparing them with experiment by subtracting the average inner potential of the absorber.

Kronig plotted a bar graph of height n [=multiplicity of the α, β, γ indices] and width 2, as a function of $\alpha^2 + \beta^2 + \gamma^2$. This bar graph shows maxima and definite minima [absence of maxima] permitting the establishment of "regions" in which boundary planes produce energy discontinuities whose midpoints should correspond with the values determined in (3). According to Kronig, the "reflecting" planes marked in Fig. 1 do not represent allowed or forbidden energy regions but the boundary planes separating them (Brillouin-zone boundaries).
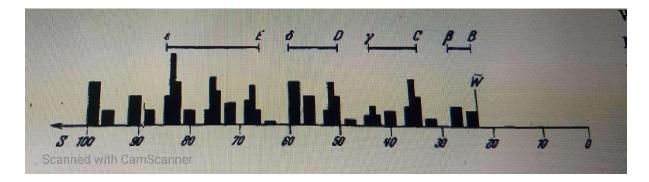

Fig.1 A bar graph showing the relative effectiveness of the reflecting planes in a crystal in producing discontinuities in the absorption curve

On the long-wavelength side of this energy value lie the allowed energies [absorption maxima in Fig. 2] and on the other side the forbidden energies [absorption minima, in Fig.2]. As can be seen in Fig. 1, the energy discontinuities are determined for groups of α, β, and γ values since Kronig believed that the contributions of individual αβγ boundary planes could not be resolved. A comparison between the centres of the energy "regions" calculated from Fig. 1 and those observed in the absorption curve of Cu, Fig. 2, results in a good agreement [~8%].
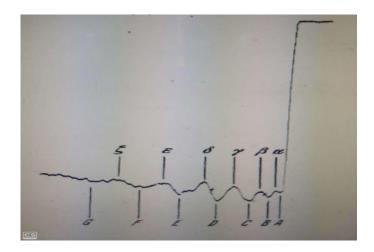

Fig.2 K edge of copper measured by Coster and Veldkamp

In his third paper, "Kronig analyzed the case of a diatomic molecule. By considering the potential field of the molecule as a whole, he reduced the treatment to a one-electron problem for which it is possible to calculate the transition probabilities from an initial state i to a final state i' according to

$$P(i,i') = \int \psi_i^* \ (xyz) \ V_{\alpha\beta\gamma} \ \psi_{i'} \ (xyz) \ dx \ dy \ dz \qquad (5)$$

where ψ^* represents the complex conjugate of ψ and $V_{\alpha\beta\gamma}$ is the appropriate matrix element. This analysis was extended by Petersen, Hartree, Kronig. "Their analysis consisted of representing the ejected electron by a plane wave and calculating the effect of scattering this wave by the surrounding atoms. Such calculations require a knowledge of the atomic fields of each scattering atom and a solution of the wave equation for an electron of positive energy in such fields; particularly, the determination of the asymptotic phase of the wave at large distances. The fine structure is then given by the ratio $\chi(E)$ of the absorption coefficient for an atom A, bound in a diatomic molecule AB, to that of an isolated atom."

$$x(E) - 1 = \tfrac{1}{2} \int_0^\pi \sin\theta \, d\theta \, [(q + q^*)\cos\theta + q \, q^*]$$

(6)

where

$$q = [C(r,\theta)/r] \exp [i(2E)^{\frac{1}{2}}r(1 - \cos\theta)]$$

(7)

and r is the interatomic distance in the molecule, $C(r,\Theta)/r$ is the amplitude of elastic scattering at a distance r from the nucleus of B, and Θ is the scattering angle for the plane wave of energy E. A simplified form of this equation, expressed in terms of the phase angles has been derived by Petersen" who also showed that the fine structure due to each B atom surrounding A can be added directly, i.e., the fine structures superpose linearly. Hartree et al. found a good agreement between the predictions of (6) and experimentally determined absorption curves and suggested that this type of analysis should be useful in determining the charge distributions of the atoms coordinating the A atom. They also pointed out that, although such analyses are much more complicated than those of x-ray or electron diffraction, they allow the study of the individual atoms separately.

References:

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