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Theory of Extended Fine Structure of X-Ray Absorption Edges*

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CONTENTS

I. INTRODUCTION

THE fine structure appearing on the high-energy side of an x-ray absorption edge can be explained by determining the availability of unoccupied quantum states for the ejected electron and the probability that the electron can undergo transitions to such states. The first theory explaining the fine structure extending for hundreds of electron volts on the short-wavelength side of an x-ray absorption edge in crystalline solids was proposed by Kronig in 1931. Several extensions of this theory have appeared since and some of them have been reviewed already.[1–6] Even the most recent review by Parratt,[6] however, does not discuss all of the theories proposed to date so that a critical comparison of these theories is necessary in order to gain a complete insight into the current state of the theory.

Fundamentally, all the theories predict that the energies at which the absorption extremities occur in cubic crystals are proportional to $(h^2 + k^2 + l^2)/a^2$ where h, k, l are the Miller indices of crystallographic planes and a is the length of the unit-cell edge. This suggests that a relation between the x-ray absorption process and a diffraction phenomenon obeying Bragg's law should exist. Kronig suggested that Bragg reflections of the ejected electrons are responsible for the discontinuities in what would be a monotonic absorption curve for a free atom. He further assumed that the transition probabilities did not vary significantly with energy so that the main features of the extended structure in solids could be explained by the density of states distributions grouped in allowed and forbidden energy bands.

In a later extension of his theory, Kronig considered the case of a small molecule and assumed that the ejected electrons were scattered by the neighboring atoms in the same molecule; a process that bears certain similarities to electron diffraction by gases. By suitably combining the wave functions of the initial and final states, he showed how the transition probabilities can be calculated. Thus, Kronig suggested that the extended fine structure can be examined in two somewhat different ways, namely, by considering variations in the allowed density of states or by calculating the transition probabilities after determining the final states of electrons scattered by neighboring atoms. Since the distance traveled by an ejected electron in a crystal is probably quite small, several authors have attempted to extend the second approach to large crystals (infinite molecules). Their theories differ primarily in how the scattering effects are calculated. At least one author (Hayasi) has attempted to extend the band-theoretical approach. A certain success has been claimed for all theories presented although a closer examination shows that the agreement between experiment and theory is by no means exact. In the following discussion, the essential features of each theory and its "successes" in interpreting experimental curves are presented. This is done in chronological order of their appearance in the scientific literature. Some of their shortcomings are pointed out at the same time, although a more general evaluation and comparison is postponed to the concluding sections.

II. KRONIG THEORY

In his first paper,[7] Kronig considered the extended fine structure that appears on the high-energy side

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* This work was supported by a grant from the National Science Foundation.

[1] Y. Cauchois, *Les Spectres de Rayons X et La Structure Electronique de la Materiere* (Gauthier-Villars, Paris, 1948).

[2] H. Niers, Ergeb. Exakt. Naturw. **23**, 359 (1950).

[3] C. H. Shaw, in *Theory of Alloy Phases* (American Society for Metals, Cleveland, 1956), p. 13.

[4] A. E. Sandström, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1957), Vol. 30, p. 78.

[5] D. H. Tomboulian, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, 1957), Vol. 30, p. 246.

[6] L. G. Parratt, Rev. Mod. Phys. **31**, 616 (1959).

[7] R. de L. Kronig, Z. Physik **70**, 317 (1931).

of x-ray absorption edges observed by others. In agreement with an earlier suggestion by Kossell,[8] the relatively short extent of such structure observed in gases was attributed by Kronig 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. For a crystalline material, Kronig assumed that this continuum breaks up into zones of allowed and forbidden energies as predicted by the then recently discovered zone theory of solids. Thus, an electron ejected in a given direction of the crystal can undergo transitions only to certain energy zones delimited by

$$E_n = \frac{h^2}{8m}\,\frac{n^2}{a^2}\,, \tag{1}$$

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 as first demonstrated by Germer and Davisson. Kronig attributed 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 based, of course, on the assumption that the ejected electron can be described by a plane-wave function known as a Bloch function. Although no numerical calculations were presented in this first paper, it was suggested that the temperature dependence of absorption spectra observed by Hannawalt,[9] namely, 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. Similarly, the larger maxima observed by Coster and Veldkamp[10] in Cu as compared to Zn were attributed to larger vibrational amplitudes in Zn, a proposition since shown to be invalid. Although an evaluation of this and other theories is postponed to a later section, it should be noted here that most absorption-edge curves published to date are not amenable to quantitative interpretation unless corrected for instrumental effects[6] so that some of the "successes" of this and other theories may be fortuitous rather than real.

In his second paper,[11] Kronig presented a detailed analysis of the behavior of the ejected electron by representing it by a Bloch function solution of the time-independent Schrödinger 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

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

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 θ.) When one integrates over all possible propagation directions, it can be shown that the discontinuities occur when

$$E = \frac{h^2}{8m}\,\frac{(\alpha^2+\beta^2+\gamma^2)}{a^2}\,. \tag{3}$$

Next, Kronig estimated the energy at which an electron becomes "free" by means of

$$E_0 = \frac{h^2}{8m}\left(\frac{3N}{a^3}\right)^{\frac{2}{3}}, \tag{4}$$

where N is the total number of electrons contained in a unit cell. [Note that (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.

Lastly, Kronig constructed a bar graph in which he plotted rectangles 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 [reproduced from his paper in Fig. 1(a) for Cu] 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). [This is an important point which is often overlooked in the discussion of Kronig's theory by some authors. According to Kronig, the "reflecting" planes marked in Fig. 1(a) do not represent allowed *or* forbidden energy

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[8] W. Kossel, Z. Physik **1**, 119 (1920); **2**, 470 (1920).

[9] J. D. Hannawalt, Phys. Rev. **37**, 715 (1931); Z. Physik **70**, 293 (1931).

[10] D. Coster and J. Veldkamp, Z. Physik **70**, 306 (1931).

[11] R. de L. Kronig, Z. Physik **75**, 191 (1932).

regions but the boundary planes separating them (Brillouin-zone boundaries).] On the long-wavelength side of this energy value lie the allowed energies [absorption maxima in Fig. 1(b)] and on the other side the forbidden energies [absorption minima in Fig. 1(b)]. As can be seen in Fig. 1(a), the energy discontinuities are determined for groups of α, β, and γ values since Kronig believed that the contributions of individual $\alpha\beta\gamma$ boundary planes could not be resolved. A comparison between the centers of the energy "regions" calculated from Fig. 1(a) and those observed in the absorption curve of Cu, Fig. 1(b), results in a good agreement [±8%].

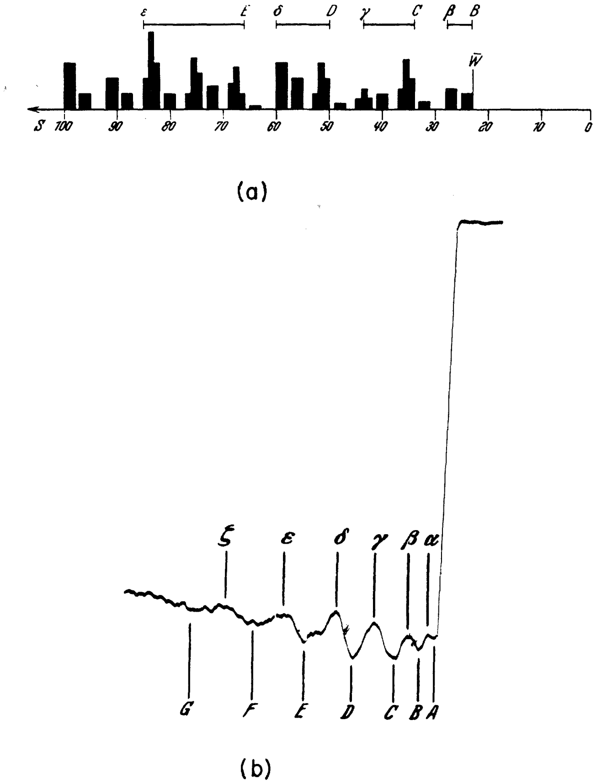

FIG. 1. Original Kronig theory (Ref. 11). (a) A bar graph showing the relative effectiveness of the reflecting planes in a crystal in producing discontinuities in the absorption curve plotted against $s = h^2 + k^2 + l^2$. Note that Kronig grouped these planes and used their mean energy value as an indication as to where the transition from a maximum to a minimum should occur in the absorption curve. (b) K edge of copper measured by Coster and Veldkamp (Ref. 10) photographically.

In his third paper,[12] 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

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

where ψ^* represents the complex conjugate of ψ and $V_{\alpha\beta\gamma}$ is the appropriate matrix element. This analysis was extended by Petersen[13] and applied to $GeCl_4$ by Hartree, Kronig, and Petersen.[14] 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.[12]

$$\chi(E) - 1 = \tfrac{1}{2} \int_0^\pi \sin\theta\, d\theta\, [(q + q^*) \cos\theta + q\, q^*]\,, \quad (6)$$

where

$$q = [C(r,\theta)/r] \exp [i(2E)^{\frac{1}{2}} r(1 - \cos\theta)] \quad (7)$$

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[13] 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.*[14] found a good agreement between the predictions of (6) and experimentally determined absorption curves for[15] $GeCl_4$ and suggested that this type of analyis 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.

It should be noted at this point that Petersen[13] applied this theory to explain the absorption curve of chlorine but subsequent experimental measurements by Lindh and Nilsson[16] deviated appreciably from his theoretical calculations. Also, recent meas-

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[12] R. de L. Kronig, Z. Physik **75**, 468 (1932).

[13] H. Petersen, Z. Physik **80**, 258 (1933).

[14] D. R. Hartree, R. de L. Kronig, and H. Petersen, Physica **1**, 895 (1934).

[15] D. Coster and G. Klamer, Physica **1**, 888 (1934).

[16] A. Lindh and A. Nilsson, Ark. Mat. Astron. Fys. **29A**, 17 (1943).

urements on[17–19] $GeCl_4$ do not agree with the above discussed predictions of Hartree *et al.* A theoretical recalculation by Corson[20] showed a better agreement with Shaw's[17] measurements, however.

III. KOSTAREV THEORY

In a preface to the presentation of his theory, Kostarev[21] scoffs at Kronig's original theory for failing to explain the "general features" of the absorption curves of all materials. He argues that a more general theory should be based on the consideration of nearest-neighbor atoms only and cites the success of Hartree *et al.*[14] in explaining the absorption-edge structure of $GeCl_4$ in support of this contention. The gist of Kostarev's argument is that the ratio $\chi(E)$ in (6) is determined by the transition probabilities from the initial K state to the final state F according to

$$\chi(E) = \frac{\overline{|P_{KF}|^2_{\text{solid}}}}{\overline{|P_{KF}|^2_{\text{free atom}}}} \tag{8}$$

and is independent of the variations in the density of allowed states underlying Kronig's theory for solids. In order to calculate the transition probabilities P_{KF}, Kostarev used the approximate method of Wentzel–Kramers–Brillouin (WKB) which, interestingly, Hartree *et al.*[14] decided to be inapplicable in their study of $GeCl_4$ absorption curves.

The main difficulty in such a calculation arises when the wave function describing the final state of the ejected electron in the solid is sought. Kostarev assumed a potential distribution based on the well-known Wigner–Seitz model and derived an expression analogous to (6) for polycrystalline copper

$$\chi(E) = \left\{1 + \frac{6.259}{k(k^4 + 3.222k^2 + 2.523)} \times \sin\left[9.16k + 2\delta(k) - \arctan\frac{0.213k}{k^2 + 1.589}\right]\right\}^{-1}, \tag{9}$$

in which k is the wave vector and $\delta(k)$ is the phase of the scattered wave calculated by the WKB approximation. The numerical coefficients in (9) were calculated by assuming spherical symmetry about the absorbing atom (the surrounding atoms are considered to lie in concentric shells about the absorbing atom) and considering only its twelve nearest-neighbor atoms, i.e., only the first shell. Although Kostarev admitted that the contributions of atoms lying in concentric shells outside the first coordination sphere may contribute to $\chi(E)$ terms as large as 70% of the first term, he ignored them on the grounds that their contribution is too difficult to assess quantitatively and the predicitions of (9) appeared to agree sufficiently well with experiment not to require further refinements. In fact, Kostarev did not attempt to apply (9) to explain the actual shape of an absorption curve, but instead calculated the values of k at which minima and maxima in the absorption curve should occur. This is clearly the case (in polycrystalline Cu) when the argument of the sine in (9) equals $\frac{1}{2}(2n - 1)\pi$ where n is any integer. Using the values of k thus determined for $n > 8$ (this limit being imposed by the approximations used), he then calculated the energies separating the expected absorption maxima and minima in Cu according to

$$h^2k^2/2m - |U_0| + A\,, \tag{10}$$

where U_0 is the average potential in the crystal and A is the electron work function. Finally, Kostarev compared his theoretically predicted energy separations to the experimental values for Cu obtained by Coster and Veldkamp[22] and ignored the more recent and different values reported by Beeman and Friedman[23] on the grounds that they were less reliable. Kostarev's calculations agree with this data within a few percent whereas Kronig's values differ by as much as 10%.

In a later reexamination of his theory,[24] Kostarev used a simplified version of (9)

$$\chi(E) = \left\{1 + \frac{2}{k}\sum_{i=1}^{\infty} z_i \int_0^{\infty} \overline{u_i(r)} \sin 2[kr + \delta(k)]dr\right\}^{-1}, \tag{11}$$

where r is the radial distance from the absorbing atom; k is the wave vector, and $\delta(k)$ the phase of the ejected electron wave; z_i is the number of atoms in the ith spherical shell about the absorbing atom and $u_i(r)$ is the potential energy of the electron in the field of an atom in the ith shell, averaged over all values of r. He calculated the phases with the aid of the WKB approximation as before, and used (presumably) a Hartree self-consistent field calculation to determine the values of $u_i(r)$ for each shell. Then Kostarev calculated and tabulated separately the energy positions of the maxima and minima pre-

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[17] C. H. Shaw, Phys. Rev. **70**, 643 (1946).

[18] S. T. Stephenson, Phys. Rev. **71**, 84 (1947).

[19] H. Glaser, Phys. Rev. **82**, 616 (1951).

[20] E. M. Corson, Phys. Rev. **70**, 645 (1946).

[21] A. I. Kostarev, Zh. Eksperim. i Teor. Fiz. **11**, 60 (1941).

[22] D. Coster and J. Veldkamp, Z. Physik **74**, 191 (1932).

[23] W. Beeman and H. Friedman, Phys. Rev. **56**, 392 (1939).

[24] A. I. Kostarev, Zh. Eksperim. i Teor. Fiz. **19**, 413 (1949).

dicted by (11) for all odd i layers surrounding a copper atom. (The contributions of even layers were considered to be smaller than experimental errors.) It turns out that each coordination shell predicts maxima and minima at somewhat different energy values but these can be combined into groups agreeing fairly well with an experimental curve shown in Kostarev's paper. Moreover, the possible occurrence of maxima and minima (for different shells) at nearly the same energy value serves to indicate the approximate magnitudes of each. It should be noted that Kostarev associated minima labeled β and γ in his curve each with only one predicted minimum. Several other predicted minima and maxima lie near these values but are not used. They may, however, account for a barely visible ultrafine structure in his curve.

IV. HAYASI THEORY

In his original theory[11] Kronig suggested that the monotonic absorption curve of a free atom is interrupted by maxima and minima due to transitions to allowed and forbidden states, respectively, in a solid. A different interpretation was offered by Hayasi who suggested that the maxima are superimposed on the free-atom curve, that is, that they are additive. In his first paper,[25] he argued that the ejected electron is reflected backward ($\theta = 90°$) by certain crystallographic planes which prevent it from moving very far from the absorbing atom. The conditions for such a reflection can be analyzed with the aid of the reciprocal-lattice concept and show that, for a transition to a state having p-type (twofold) symmetry, a standing-wave pattern is set up in the vicinity of the absorbing atom by total reflection from such planes in a perfect crystal. Hayasi called these quasistationary states and suggested that the amplitudes of the reflected waves are directly proportional to some power of the number s of atoms coordinating the absorbing atom and lying in the reflecting planes, and inversely proportional to some power of the distance r to these atoms. Finally, from the Bragg reflection law $n\lambda = 2d$, he concluded that such reflections will occur for electrons having energies (in eV) given by

$$E_{hkl} = \frac{(h^2 + k^2 + l^2)}{4a^2} 150\,, \tag{12}$$

where h, k, l are the Miller indices of the reflecting planes and a (in angstroms) is the length of the unit-cell edge in a cubic crystal.

In his second paper,[26] Hayasi extended this theory in an attempt to reproduce the exact shape of actual absorption curves, on the assumption that the breadth of an absorption maximum is due to a natural breadth, equal to twice the corresponding Fourier coefficient of the crystal potential (matrix element of the transition) plus a broadening due to the thermal motion of the atoms which he calculated using Einstein's specific-heat theory. By fitting a (presumably) Gaussian curve to the breadth thus determined and fixing its height by making it proportional to s, Hayasi attempted to reconstruct the observed absorption curves of copper and nickel. Immediately adjacent to the "main" edge, the calculated maxima are broader than the observed ones. Beginning with the third maximum the breadths of the observed and calculated maxima appear to be commensurate, however, the energy positions predicted by (12) for some of the calculated maxima do not coincide with the observed ones. If these maxima are shifted by arbitrarily small amounts, a fairly good agreement is achieved. Since these shifts and the heights of individual maxima cannot be justified rigorously, Hayasi contented himself by pointing out the agreement between the observed and calculated breadths.

In general, the agreement between Hayasi's predictions and experimental curves for Cu and Ni, although not exact, is as good as that of the other theories. Similarly to Kronig, Hayasi assumed that the transition probabilities vary monotonically with energy and, therefore, need not be evaluated in detail. In comparing his theory to that of Kronig, it should be noted that Kronig claimed that his relation (3) predicted the midway point between a maximum and minimum, whereas Hayasi's identical relation (12) predicts the energies of the quasistationary states (lying in the forbidden-energy regions) and, hence, the positions of absorption maxima. A direct comparison of these two theories is rather difficult at present because it is not possible to establish the correct location of the "main" edge with sufficient precision. In a third paper,[27] Hayasi reconstructed the simpler absorption curve of lithium quite accurately. A similar comparison in aluminum has been carried out by Johnston and Tomboulian[28] and by Fujimoto[29] who both found a good agreement to exist. It is particularly noteworthy that the agreement is fairly good for the maxima located close to

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[25] T. Hayasi, Sci. Repts. Tôhoku Univ. **33**, 123 (1949).

[26] T. Hayasi, Sci. Repts. Tôhoku Univ. **33**, 183 (1949).

[27] T. Hayasi, Sci. Repts. Tôhoku Univ. **34**, 185 (1950).

[28] R. W. Johnston and D. H. Tomboulian, Phys. Rev. **94**, 1585 (1954).

[29] H. Fujimoto, Sci. Repts. Tôhoku Univ. **39**, 189 (1956).

the main edge, a region where Kronig believed his theory to be invalid.

More recently, Hayasi[30] has elaborated the theoretical basis of his quasistationary states and showed that they are simply the consequence of a triply periodic potential containing a "hole." Although his actual calculations are based on a one-dimensional model, they can be generalized to three dimensions in the usual way. The significance of the one-dimensional calculation is that it predicts the appearance of a set of discrete states (the so-called quasistationary states) one lying in each of the forbidden-energy bands of a perfect crystal. The energy levels of these states are predicted by (12). On this basis, Hayasi suggested that the absorption spectrum consists of two parts: a continuous absorption curve due to the transitions to the allowed energy states in a perfect crystal and absorption maxima produced by transitions to the quasistationary states. He then applied this theory to the $L_{\mathrm{II,III}}$ spectra of aluminum with fair success and extended this discussion in a subsequent paper[31] in which the reflecting planes (*hkl*) in (12) were selected on the basis of their reflecting power (akin to electron diffraction), but without taking into account the actual transition probabilities.

V. SAWADA THEORY

In analyzing the original Kronig theory, Shiraiwa, Ishimura, and Sawada[32] decided that its chief limitation was the failure to take into account the transition probabilities for the ejected electron. Assuming that the density of states varies $\propto E^{\frac{1}{2}}$, they concluded that the absorption coefficient

$$\chi(E) \propto E^{\frac{1}{2}}P(E)\,, \tag{13}$$

where $P(E)$ is the transition probability. Shiraiwa *et al.* further assumed that the ejected electron undergoes elastic and inelastic scattering by the other atoms and that the scattering cross sections σ are additive. This means that the amplitude of the electron wave is attenuated by $\exp\left[-\frac{1}{2}(\sigma_{\mathrm{el}}+\sigma_{\mathrm{inel}})\rho r\right]$, where ρ is the density of atoms and r the distance traveled from the absorbing atom. A simple-minded calculation then shows that the ejected electron travels only several lattice spacings before the amplitude becomes nearly zero. This is another way of saying that the lifetime of the ejected electron is severely limited by scattering processes.

Having thus concluded that only the nearest neighbor atoms can influence the absorption process, Shiraiwa *et al.* developed a method based on that of Kronig[12] and Petersen,[13] but modified by including the amplitude attenuation due to scattering. The time-dependent Schrödinger equation was used to determine the electron's wave function and a wave packet was formed in the vicinity of the absorbing atom by combining this wave with waves scattered by the neighboring atoms. This wave packet complied with the Pauli uncertainty principle, spreading out with time, and the potential field existing within the wave packet was used in the Schrödinger equation calculation. In a second paper,[33] Shiraiwa used tabulated Hartree self-consistent-field values to determine the field of the scattering atoms, required in calculating the phases of the scattered waves. The transition probabilities were then calculated by an expression similar to that of Petersen[13] (modified to include the amplitude attenuation) by summing over the nearest neighbors of the absorbing atom. The contribution of each set of equidistant neighbors was assumed to be proportional to s/r^2, where s and r represent the number and radial distance of equidistant neighboring atoms. The absorption curve finally was constructed by multiplying the transition probabilities by the density of states which Shiraiwa assumed to be proportional to $k[=2\pi(E/150)^{\frac{1}{2}}]$.

In his first paper,[32] Sawada compared the calculated absorption curves to those measured for Cu, Ni, and Fe in his laboratory. In the second paper,[33] similar comparisons were made for curves of Cu and of Ti in the metal and in two polymorphic modifications of $\mathrm{TiO_2}$. In both papers, absorption curves were calculated for several values of $(\sigma_{\mathrm{el}}+\sigma_{\mathrm{inel}})$. Their agreement with the observed absorption curves of the metals, particularly in the second paper is good, whereas that for both modifications of $\mathrm{TiO_2}$ is not as good.

VI. OTHER THEORIES

The recently published "Theory of the Fine Structure of Absorption Spectra" by Kozlenkov[34] is not so much a new theory as a recapitulation of the theoretical treatments of Petersen,[13] Kostarev,[24] and Shiraiwa *et al.*[32] In his discussions, however, Kozlenkov brings out several interesting features of this approach. As also noted by others, it is possible to distinguish these theories from the early Kronig theory[11] by realizing that the Kronig theory (also Hayasi[30]) is based on the existence of long-range

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[30] T. Hayasi, Sci. Repts. Tôhoku Univ. **44**, 87 (1960).

[31] T. Hayasi and T. Sagawa, Sci. Repts. Tôhoku Univ. **44**, 126 (1960).

[32] T. Shiraiwa, T. Ishimura, and M. Sawada, J. Phys. Soc. Japan **13**, 847 (1958).

[33] T. Shiraiwa, J. Phys. Soc. Japan **15**, 240 (1960).

[34] A. I. Kozlenkov, Izv. Akad. Nauk SSSR **25**, 957 (1961).

order (lro) in a crystal whereas the other theories consider only the nearest-neighbor atoms, i.e., the short-range order (sro). This makes the sro theories more general in that they should apply equally well to small molecules or infinitely large ones (e.g., a crystal) whereas lro exists only in crystals. [It is correct that the two kinds of theories utilize the concept of lro or sro in their formulation but their validity cannot be ascertained by qualitative analyses based on this consideration alone. The reverse is also true, i.e., it is not possible to cite the appearance of the observed structure as supporting evidence for either kind of theory. This is discussed further in the next section because such qualitative tests have been suggested by several authors.] Since the basic formulas of all the sro theories are the same, they differ mainly in how the potentials of the scattering atoms are calculated and the formalism used in determining the phases of the scattered waves. Kozlenkov demonstrated that the assumption of a simple square-well potential for an atom permits the calculation of the phases with an accuracy not worse than that obtained in more rigorous calculations. The various relations for calculating the absorption curves $\chi(k)$ proposed by others [13,24,32] are essentially equivalent to

$$\chi(k) \propto -\sum_i \frac{s_i}{r_i^2} \sin (2kr_i + 2\delta) , \qquad (14)$$

where the subscript i denotes the atoms in the ith shell about the absorbing atom and the other symbols have their previously defined meanings. Using this relation and phases determined by noting the mean values of tabulated phases,[35] or by extrapolation from these values, Kozlenkov calculated the absorption-edge structures for Ti, Zn, Fe, Al, and Cu and compared them to plots of experimental absorption curves. The agreement appears to be of the same order as that observed in the other theories.

One of the main experimental observations supporting Kronig's (and Hayasi's) lro theory in metals has been the fact that the energy values at which the maxima and minima occur in cubic crystals having the same lattice type are inversely proportional to a^2. Kozlenkov showed that this result also can be derived from the approximate equation (14) and suggested, therefore, that it is not really supporting evidence for Kronig's theory. In addition, Shmidt[36] showed how (14) can be used also to explain the temperature dependence of the fine structure in terms of the Debye theory. Although other explanations of the absorption-edge fine structure also have been proposed (cf. discussions in Refs. 1–6) they have dealt primarily with the Kossel[8] structure occurring within 20–30 eV from the "main" edge. For example, Borovskii and Shmidt[37] have suggested that the ejected electrons can interact with conduction electrons in a metal by generating plasma oscillations. This mechanism of energy absorption is not likely to explain the absorption of higher energy electrons but the possibility of some energy losses due to plasma oscillations cannot be ruled out even though it has not been considered in any of the theories discussed above.

VII. COMPARISONS WITH EXPERIMENTAL OBSERVATIONS

Before attempting a quantitative evaluation of the relative successes with which the various theories can explain experimentally observed fine structures, it is natural to inquire whether qualitative considerations can be used to determine which theoretical approach is more valid. Kostarev[21] suggested that hcp and fcc cobalt could serve to distinguish between the validity of the lro and sro theories because the nearest neighbors are the same in both closest packings whereas the lattice types are different. Sawada *et al.*[38] used the similarity of the absorption-edge fine structures of these two modifications of Co as proof of the validity of his sro theory. Unfortunately this proof is not very convincing. As first observed by Hull,[39] the interplanar spacings of the strongly reflecting planes are the same for both modifications so that the main discontinuities (Brillouin-zone boundaries) should occur at the same energy values. An apparently more promising comparison should be possible between two polymorphs having pronounced structural differences while retaining the same nearest-neighbor configurations, for example, the two modifications of TiO_2, anatase and rutile. The K absorption curves of Ti for both modifications were recorded by Shiraiwa[33] and show two similar maxima near the edge but somewhat dissimilar structures at higher energies. Qualitatively this supports the principles underlying the lro theory since the short-range order is only modified for the more distant neighbors. The absorption curves calculated for both modifications by Shiraiwa using the sro theory show about the same order of similarity with each other as they do with

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[35] N. F. Mott and H. S. W. Massey, *Theory of Atomic Collisions* (Clarendon Press, Oxford, 1933).

[36] V. V. Shmidt, Izv. Akad. Nauk SSSR **25**, 977 (1961).

[37] I. B. Borovskii and V. V. Shmidt, Izv. Akad. Nauk SSSR **24**, 428 (1960).

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the experimental curves. This doesn't "prove" that the sro theories are less valid than the lro theories, but merely points out the difficulties in making qualitative comparisons that have been suggested by several authors as being decisive. Nevertheless, several other investigators have expressed their belief that nearest neighbors rather than lro have a predominant influence on absorption-edge fine structure, cf. Coster and Kiesta,[40] a viewpoint supported primarily by the presumably short mean free path of the ejected electron.

Obashi recorded the fine structures of the K absorption edges of iron and cobalt in the same Fe–Co alloy[41] and of nickel and cobalt in the same Ni–Co alloy.[42] He claimed that the similarity of the extended structure for both atoms in the same alloy supports the sro viewpoint because the nearest neighbor configurations and separations are the same. Conversely, Coster and Smoluchowski[43] concluded from their examination of several Cu–Zn alloys that the similarities in the extended fine structures of the K absorption edges of Cu and Zn support the Kronig lro theory. Since both sro and lro are the same in these alloys, it is hardly possible to draw final conclusions when the fine structures of both elements are the same. Research currently in progress in this author's laboratory on Cr–Ni solid solutions indicates that the extended structure of Cr and Ni are different even though both atoms presumably have similar environments in the same crystal structure. Borovskii and Ronami[44] compared the structures of the K edge of copper and the L edge of platinum in a 50–50 alloy CuPt at 20°C and 500°C. The authors found that the height of the fine structure of the Pt L edge was decreased at 500°C far more than that of the Cu K edge and cite this as proof supporting Kostarev's sro theory's predictions of temperature dependence.[45] (For an alternate discussion of temperature dependence see Hayasi.[26]) What the authors overlooked, however, is that the room-temperature structures of both edges are different in that the absorption maxima are more widely spaced in the extended structure of the platinum L edge. Finally, Stephenson[46] examined a number of binary ionic compounds and found that the absorption-edge structures for the pairs of elements comprising each salt differed out to 150 eV, i.e., the limit of his measurements. These observations certainly dispute the claim that lro determines the characteristics of the extended fine structure although it is not obvious just how they can be explained by the sro theories proposed so far, since the immediate coordinations of both absorbing atoms are similar.

Other experiments also have been proposed. Stephenson[47] suggested that the absorption of polarized x rays should show a dependence on crystal orientation if Kronig's theory is valid. The results of several experimental studies[48–51] using partially polarized x rays showed that some variations did occur but not of sufficient magnitude to permit definite conclusions. Recently, Boster and Edwards[52] passed 82.4% polarized x rays through a copper foil whose plane was parallel to (100) and compared the extended fine structures (measured to 350 eV) for four different angular positions of the foil relative to the plane of polarization. Although differences as large as 5% in the positions of peaks lying more than 230 eV from the "main" edge were observed, it is not possible to assign a real meaning to these observations because the experimental errors in locating these positions are as large as 2% and no significant changes in the peak heights were detected. Similarly, Dr. H. Fujimoto examined three single-crystal foils of copper in our laboratory using 70% polarized x rays. Although the crystal foils were, respectively, parallel to (100), (110), and (111), no significant differences were observed in the fine structure. It is planned to repeat these measurements in the near future using 100% polarized x rays, primarily to establish what the directional dependence is, if any.

In view of the foregoing, it is clear that the only kind of meaningful comparison that can be made between the various theories is to compare the agreement between the predicted and observed positions of the maxima in an absorption curve. The fine structure of the K absorption edge of Cu has been chosen for this purpose. The experimental curve used is that determined by Krogstad,[53] Fig. 2, which is one of the most accurately measured absorption

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[40] D. Coster and C. Kiesta, Physica **14**, 175 (1948).

[41] M. Obashi, Sci. Repts. N. Coll. Osaka Univ. **6**, 55 (1957).

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[52] T. A. Boster and J. E. Edwards, J. Chem. Phys. **36**, 3031 (1962).

[53] R. S. Krogstad, Ph.D. thesis, Washington State College, 1955 (unpublished).

curves available. It has not been corrected for all the factors suggested by Parratt[6]; however, such corrections affect primarily the structure close to the "main" edge and are not of much significance to the present comparisons since the above theories presumably are not valid in this region anyway. Copper is also convenient to use because it is one of the test cases employed by each innovator and their own calculated values can be utilized in making the comparison. Because of the uncertainty in locating the reference zero of energy (position of "main" edge and true value of inner potential in copper), each calculated set of peak positions has been "normalized" by lining up the strong peak occurring at 103 eV in the experimental curve. The actual "shift" in the calculated values is noted for each theory below.

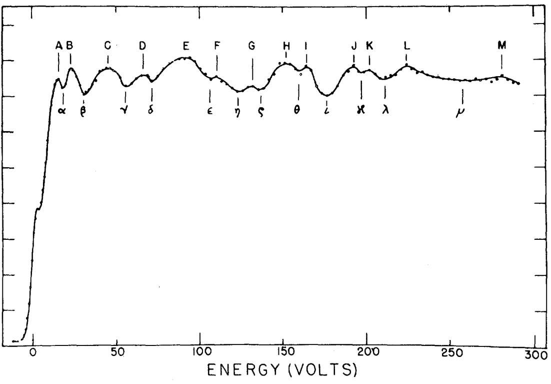

FIG. 2. *K* edge of copper measured by Krogstad (Ref. 52) using a two-crystal spectrometer.

In making a comparison to Kronig's theory, it is necessary to use a somewhat different procedure since Kronig described how the positions of inflection points and not peaks can be determined. Thus, the discontinuities in Kronig's plot shown in Fig. 1(a) were grouped in conformity with the observed structure and their average E determined. The energies at the maxima and minima in Krogstad's curve shown in Fig. 2 were similarly used to determine their median separation. The comparison between the observed and calculated values is given in Table I. Note that this comparison differs slightly from the one made by Krogstad[52] who assumed that Kronig's theory predicted the positions of the minima.

The experimental values listed in Table I are the actual values measured from Krogstad's curve (from his Table 2) to which 11 eV has been added, since this represents the best available value for the energy separating the Fermi level from the inner potential level. As can be seen, the agreement is fair; the largest deviations are less than 10%.

The positions of the maxima and minima in Krogstad's curve [after adding 11 eV] are compared to the values predicted by the other theories in Table II. Hayasi's and Kostarev's values were read from tables in their papers and have been increased by 11 eV and 19 eV, respectively. Sawada's and Kozlenkov's values were read off a plotted curve and are subject to reading errors of ±3 eV because of the small scale used in their publications. Two things of interest to the present discussion stand out from this comparison: (1) The agreement between observed and calculated values appears to be excellent for some of the maxima predicted by all four authors, but not for all maxima; (2) The approximate equation used by Kozlenkov agrees as well, if not better, than the more exact calculations of the others.

VIII. DISCUSSION

To date, essentially three distinct mechanisms have been proposed to explain the extended fine structure occurring on the high energy side of an x ray absorption edge:

(I) The original lro theory of Kronig.[7,11]

(II) The lro Hayasi theory[25,26] involving transitions to quasistationary states.

(III) The sro theory originally formulated by Kronig[12] and modified by others.[13,14,21,24,32–34]

Theories (I) and (II) do not provide a "formula" predicting the exact shape of the experimental absorption curve. Instead, theoretical arguments are used to justify the prediction that anomalies should occur in the absorption curve for energies proportional to $(h^2 + k^2 + l^2)/a^2$, provided that the energies are measured with respect to the average inner potential in the crystal, i.e., from the "main" absorption edge. Kronig predicted that these energies should correspond to discontinuities in the allowed energy values that an electron can have in a crystal, whereas Hayasi predicted that these are the energies of maxi-

TABLE I. Comparison of Kronig theory with experimental curve for Cu.

	$A-\alpha$	$B-\beta$	$C-\gamma$	$D-\delta$	$E-\epsilon$	$F-\eta$	$G-\zeta$	$H-\theta$	$I-\iota$	$J-\kappa$	$K-\lambda$	$L-\mu$
Experiment	28	38	62	83	110	128	146	167	181	206	219	252
Theory	...	...	69	78	103	122	149	166	196	208	218	241

mum overlap between the ejected electron's wave and waves scattered by neighboring atoms back toward the absorbing atom. The discontinuities predicted by Kronig are fundamental to the band theory of solids. In metals, however, the allowed bands are believed to overlap so that one would not expect necessarily to observe absorption maxima and minima extending for hundreds eV in metals, despite the fact that the presence of such discontinuities does contribute to electron scattering.

TABLE II. Comparison of experimental and theoretical values of the absorption maxima and minima of copper (energy in eV).

Peak	Experiment	Hayasi	Kostarev	Sawada[a]	Kozlenkov[b]
A	26.2	23	24	10	21
α	30.00		29	28	25
B	34.3	34	34	39	31
β	41.7		44	51	41
C	56.5	57	52	63	52
γ	67.0		60	67	64
D	77.6	80	80	77	75
δ	82.9		91	89	88
E	103.0	103	103	103	103
ϵ	117.8		120	111	117
F	122.0	115	125[c]	121	122
η	134.7		134[c]	132	136
G	143.2	126	...	147	149
ζ	148.5		150[c]	152	153
H	163.3	...	161[c]	165	168
θ	170.7		169[c]	178	182
I	176.0	172	182[c]	...	
ι	187.6		192	...	
J	203.5		...	...	209
κ	208.8		...	...	209
K	213.0	219	210	211	217
λ	222.5		228	222	225
L	235.2	...	241	231	242
μ	269.0		274[c]	254	264
M	282.3	287	308	286	298

[a] These values were read off a curve computed for the weighted scattering factor equal to 0.138^{-1}.

[b] These values were read off a curve computed for seven-nearest-neighbor spheres.

[c] Values based on one or two predicted values only.

By comparison, the model underlying Hayasi's theory appears to be physically more reasonable. For example, he recognizes the fact that simple transitions to allowed energy bands in metals should not lead to a specific structure but to a monatonic absorption curve. The fact that his theory predicts the absorption maxima positions at slightly larger energy values than those predicted by Kronig is of little practical significance because neither the true inner potentials in crystals nor the exact energy value of the "main" absorption edge can be determined with sufficient accuracy. In fact, Kozlenkov[34] has suggested that the relative positioning of the predicted and observed maxima should be adjusted by trial and error, preferably in the 100–150 eV range. This proposal is not as arbitrary as it sounds in view of the above mentioned difficulties and also has been used by others.[28,29] The present limitations of Hayasi's theory are that it does not appear to predict correctly the entire absorption curve, including both the position and the breadths of all absorption maxima, and it does not predict the heights of the maxima. Also, in its present form it is limited to perfect crystals and does not include calculations of actual transition probabilities to the quasistationary states.

Although the sro theories (III) attempt to calculate a continuous absorption curve, the predicted shapes do not agree with experimental curves as well as do the predicted positions of the maxima and minima. There are several possible reasons for this lack of fit, for example, the various approximations used in determining the phases of scattered waves may not be sufficiently accurate, the methods used for averaging the potential field acting on the ejected electron may be inappropriate, etc. Of even greater significance is the fact that the possible contributions to absorption of multiple-vacancy states and energy losses by plasma oscillations are not considered, even though it is not certain how large an effect these processes have at energies lying more than a few tens eV from the edge.

There is one recent observation that strongly supports the sro approach. Nelson, Siegel, and Wagner[54] measured the extended fine structure of the germanium K edge in amorphous GeO_2 out to 350 eV and compared it to that of two crystalline polymorphs. They found that the extended structures of amorphous and hexagonal GeO_2 were very similar but differed notably from that of tetragonal germanium dioxide. Since it is not likely that an extensive long-range periodicity exists in GeO_2 glasses, it is necessary to conclude that the fine structure is most strongly influenced by the arrangement of neighboring atoms about germanium. The immediate coordination of Ge, however, is the same in both crystalline polymorphs also so that, unlike the beliefs expressed by Kostarev and later proponents of the sro theories, it is necessary to consider the influence of next-nearest, and further neighbors as well.

It is not possible to draw any really definite conclusions from the above analyses except that the theories proposed so far do not appear to explain the observed fine structures in full detail. Although the matching procedure used in making the comparison in Table II is not necessarily the best possible, it is evident from the randomness of the observed differ-

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[54] W. F. Nelson, I. Siegel, and R. W. Wagner, Phys. Rev. **127**, 2025 (1962).

ences that any other comparison procedure would not alter the preceding statement. By way of suggesting future lines of attack, it is worth pointing out the similarity between Kozlenkov's relation (14) and a very similar expression underlying the intensity of x-ray scattering by disordered alloys. It can be shown that when short-range order only is present, the intensity

$$I \propto \sum_i \alpha_i \frac{\sin kr_i}{kr_i}, \qquad (15)$$

where α_i is a coefficient dependent on the scattering power and number of atoms in the ith shell about a central atom and $k = (2\pi/\lambda)\ 2 \sin \theta$. The close relation between absorption and diffraction has already been pointed out above and suggests that a consideration of the ejected electron's diffraction by the atomic arrays may lead to a more convenient formulation of the absorption process. If successful, such an approach also would have the advantage of making absorption-edge studies amenable to the investigation of the structure of solids. A more rigorous theory, however, doubtlessly also will require more exact experimental measurements than are generally available at the present time.

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Thermal Conductivity of Multicomponent Mixtures of Inert Gases

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I. INTRODUCTION

THE proper understanding of the process of thermal conduction in monatomic gases is not only important in itself but is also basic for the more complicated case of polyatomic gases. The investigations during the last five years have thrown considerable light on this problem. In this paper we discuss all the experimental and theoretical work with a view to get an over-all assessment.

Three different groups of workers have reported the experimental thermal conductivity data of binary and ternary mixtures of inert gases. These are: (a) Saxena (1956, 1957) and Srivastava and Saxena (1957a, 1957b), who determined the thermal conductivity of six binary gas systems and of two ternary gas systems at 38°C as a function of composition; (b) von Ubisch (1959), who measured the thermal conductivity of all the ten possible binary systems of the five stable inert gases, and of the ternary system He–Kr–Xe for different proportions of the constituents at 29° and 520°C; and (c) Thornton (1960, 1961) who reported on the thermal conductivity of seven binary gas pairs at 18°C and again as a function of composition.

The *rigorous* treatment of the phenomenon of thermal conduction in gases was given by Enskog (1911) and Chapman (1917) and is adequately described by Chapman and Cowling (1952), and Hirschfelder, Curtiss, and Bird (1954). Recently Muckenfuss and Curtiss (1958) have derived an equation for the complete second approximation to the thermal conductivity of multicomponent gas mixtures. Mason (1958) gave a somewhat simpler expression and Mason and Saxena (1959) have investigated the relative accuracies of both these formulations. Muckenfuss' and Curtiss' (1958) formula for the thermal conductivity of an n-component mixture can be written after the modification suggested by Mason and Saxena (1959) in the following form:

$$\lambda_{\text{mix}} = \begin{vmatrix} L_{11} & \cdots & L_{1n} & x_1 \\ \vdots & & \vdots & \vdots \\ L_{n1} & \cdots & L_{nn} & x_n \\ x_1 & \cdots & x_n & 0 \end{vmatrix} \div \begin{vmatrix} L_{11} & \cdots & L_{1n} \\ \vdots & & \vdots \\ L_{n1} & \cdots & L_{nn} \end{vmatrix}, \qquad (1)$$

where

$$L_{ii} = -\frac{4x_i^2}{[\lambda_i]_1} - \frac{16T}{25p} \sum_{\substack{k=1 \\ k\neq i}}^{n} \frac{x_i x_k[\frac{15}{2} M_i^2 + \frac{5}{2} M_k^2 + 4M_i M_k A_{ik}^*]}{(M_i + M_k)^2 D_{ik}}, \qquad (2)$$

$$L_{ij}\ (i \neq j) = \frac{16T x_i x_j M_i M_j (10 - 4A_{ij}^*)}{(M_i + M_j)^2 D_{ij}}. \qquad (3)$$