PHYSICAL REVIEW B VOLUME 11, NUMBER 8 15 APRIL 1975

Quantitative comparison of Kronig's theory of x-ray absorption with experiments for polycrystalline copper, cadmium, and gallium

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(Received 29 October 1974)

The K-absorption fine structures of polycrystalline copper, cadmium, and gallium have been calculated from Kronig's early theory of the extended x-ray absorption fine structure of solids, summing algebraically all absorption irregularities within 70 and 500 eV (copper), 90 and 400 eV (cadmium), and 40 and 280 eV (gallium). The disagreement of this theory with measured K fine structures of copper, cadmium, and gallium is obvious.

I. INTRODUCTION

In the explanation of the extended x-ray absorption fine structure of crystalline solids Kronig's[1,2] early theory is still used instead of other theories. The agreement with experiment as regards location and relative magnitude of fine-structure features turns out to be excellent,[3] good,[4] reasonably good,[5] insufficient,[6] or bad.[7,8] In the cited publications the spectra have been calculated according to the procedure used by Kronig himself or a slightly different one. In the present paper the individual absorption irregularities are summed directly with the aid of a plotter. A comparison of these results with experiments shows complete disagreement. A preliminary summary of this work has been given elsewhere.[9]

II. THEORY

Long ago, Kronig[1,2] gave his well-known theory of the extended x-ray absorption fine structure of crystalline absorbers. In this theory the photoelectron is Bragg reflected by the crystal-lattice planes; making use of a plane electron wave as an unperturbed eigenfunction Kronig calculated the state density $N(E)$ of the "nearly free" electron from second-order perturbation theory. Since the transition probability is considered to be constant, the variations of $N(E)$ to be calculated reflect the variations of the x-ray absorption. It is found that each set of lattice planes with reflection indices $\alpha\beta\gamma$ for which the cell-structure factor does not vanish produces an irregularity in the absorption curve, as shown in Fig. 1. In this theory the shape of the unperturbed absorption curve is presupposed; the shape of an "irregularity" is given by Kronig's[2] equations (19)–(21):

$$\overline{K}(E)=k(E)(1-f(E_{\min})\{E-E_{\min}-[(E-E_{\min})^2-\Delta^2]^{1/2}\})\quad \text{for } E>E_{\min}+\Delta,$$

$$\overline{K}(E)=k(E)[1-f(E_{\min})(E-E_{\min})]\quad \text{for } E_{\min}+\Delta>E>E_{\min}-\Delta,$$

$$\overline{K}(E)=k(E)(1+f(E_{\min})\{E_{\min}-E-[(E_{\min}-E)^2-\Delta^2]^{1/2}\})\quad \text{for } E<E_{\min}-\Delta.$$

Here $k(E)$ is the "atomic"-mass absorption coefficient, $\overline{K}(E)$ is the actual-mass absorption coefficient as a function of the electron energy E, $E_{\min}$ is the electron energy for which the Bragg condition is fulfilled for a reflection $\alpha\beta\gamma$ for normal incidence, $f(E_{\min})$ is the distribution function of the photoelectrons for $E=E_{\min}$, and $\Delta=|V_{\alpha\beta\gamma}|$ is the modulus of the Fourier coefficient $\alpha\beta\gamma$ in the Fourier-expansion series of the crystal-field potential.

From Kronig's equations (19)–(21) it follows that the energy width of an irregularity amounts to about $5|V_{\alpha\beta\gamma}|$; the amplitude is given by $2k(E_{\min})\times f(E_{\min})|V_{\alpha\beta\gamma}|$, where $k(E_{\min})$ is the atomic-mass absorption coefficient for $E=E_{\min}$. When the absorber consists of polycrystalline material (and to this case Kronig applied his theory), so that the ejected electrons may be assumed to be distributed evenly over all directions with respect to the crystal axes, one has $f(E_{\min})=1/2E_{\min}$. Further, when the microcrystals of the absorber have cubic symmetry, Kronig's equation (14) holds,

$$E_{\min}=\frac{h^2}{8m}\,\frac{\alpha^2+\beta^2+\gamma^2}{a_0^2},$$

where m is the electron mass and a_0 is the lattice constant. For a hexagonal crystal

$$E_{\min}=\frac{h^2}{8m}\,\frac{4(\alpha^2+\alpha\beta+\beta^2)/3+a_0^2\gamma^2/c_0^2}{a_0^2}$$

[Kronig's equation (14a)], and when the crystallites are orthorhombic

$$E_{\min}=\frac{h^2}{8m}\left(\frac{\alpha^2}{a_0^2}+\frac{\beta^2}{b_0^2}+\frac{\gamma^2}{c_0^2}\right)$$

[Kronig's equation (14b)].

In Sec. III we apply Kronig's theory to polycrystalline absorbers of copper (fcc), cadmium (hcp), and gallium (orthorhombic).

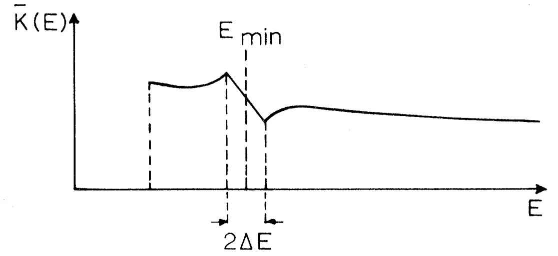

FIG. 1. Reflection $\alpha\beta\gamma$ of the electron wave gives rise to an irregularity in the absorption curve.

III. COMPARISON WITH EXPERIMENT

A. Copper

1. *Data.* Since the amplitudes of the absorption irregularities within a few tens of electron volts from the main edge become very large, we stick to Kronig's original value of $S=\alpha^2+\beta^2+\gamma^2=24$ for the first irregularity in the theoretical copper $K(L, M\ldots)$ absorption spectra. The data for all irregularities up to 287 eV are collected in Table I of Kronig's[2] paper; our Table I gives them for 288 up to 507 eV. The values of $E_{\min}$ are obtained from $E_{\min}=2.88S$, taking in Kronig's equation (14) $a_0=3.14$ Å. The values of $|V_{\alpha\beta\gamma}|$ in the table[10] do not differ very much from the values given in Kronig's[2] original paper; the increase of these coefficients at low temperatures[11] (see below) we did not take into account.

2. *Method.* Since the width of an irregularity is $5|V_{\alpha\beta\gamma}|$ in first approximation, most of the irregularities overlap. It is not possible, therefore, to explain the observed absorption maxima and minima by a small number of calculated irregularities (or main irregularities) neatly linked together. For that reason, Kronig[2] in his explanation of the copper K-absorption spectrum made use of a histogram in which he plotted the calculated absorption irregularities as rectangles of height s and a constant width of 2×2.88 eV. In that histogram Kronig distinguished groups of bars, each corresponding to one single maximum and minimum in the observed spectrum; the energy position of the center of gravity of such a group was expected to correspond to the position of the midpoint between the maximum and minimum in question. This procedure was followed in most papers in which Kronig's theory was applied to observed spectra. Hayasi[12] pointed out that in Kronig's way of grouping the irregularities there is an element of arbitrariness. Kurylenko[13] introduced a slightly modified form of Kronig's diagram, replacing each bar by a triangle with height and base proportional to $s|V_{\alpha\beta\gamma}|$ and $|V_{\alpha\beta\gamma}|$, respectively; this procedure was also used by Brümmer *et al.*[3] in their paper on the K spectra of bcc and hcp chromium.[14] In the present paper we prefer an algebraic summation of all absorption irregularities, making use of Kronig's equations (19)–(21). The unperturbed copper K-absorption curve was calculated from Jönsson's[15] formulas.

3. *Result and comparison with experiment.* In Fig. 2 the solid curve represents the theoretical copper K fine structure from 69 up to 507 eV. The separate absorption irregularities are calculated for a total energy width of $(2+2\times 30)\,|V_{\alpha\beta\gamma}|$. Since in Kronig's theory the influence of tempera-

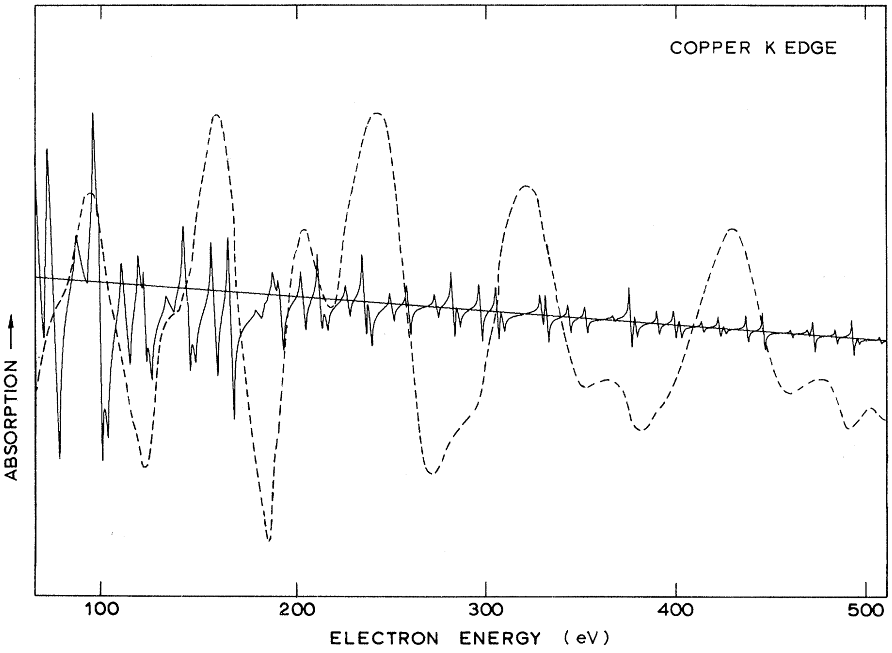

FIG. 2. Copper K-absorption fine structure, calculated from Kronig's theory (solid line) and measured at 9 K (dashed line) by Lytle (Ref. 7). We have reproduced Lytle's original curve with increasing absorption along the Y axis. The straight line through the core of the calculated spectrum is the "unperturbed" copper K-absorption spectrum, calculated from Jönsson's formulas (Ref. 15).

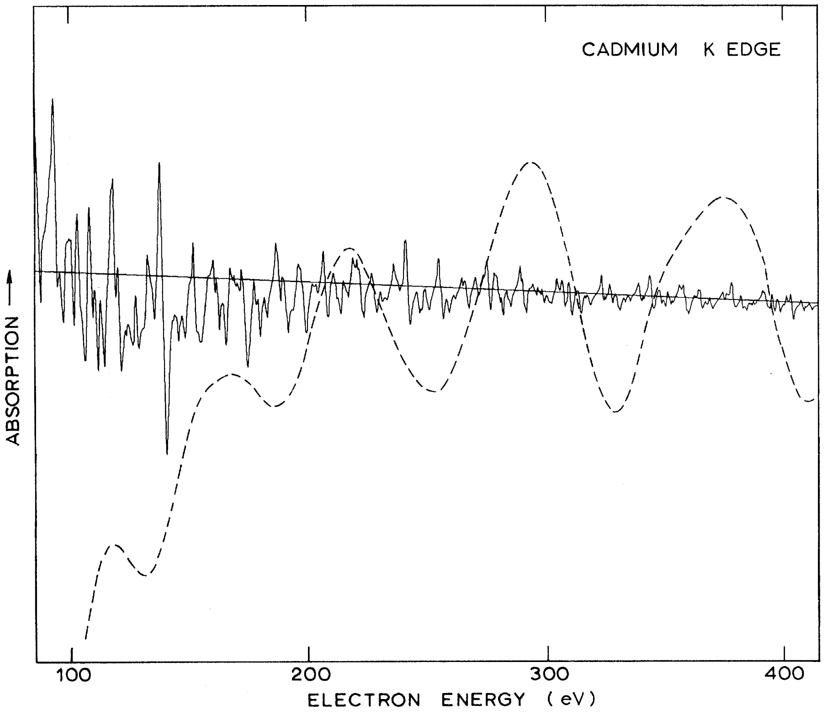

FIG. 3. Cadmium K-absorption fine structure, calculated from Kronig's theory (solid line) and measured at 83 K (dashed line) by Weber (Ref. 16). The experimental spectrum is drawn from a microphotometer record.

ture is not accounted for, the calculated copper K fine structure should be compared with an experimental spectrum taken at a temperature near 0 K. For that reason, we have drawn as a dashed curve in the same figure the corresponding part of the K-absorption spectrum of a polycrystalline copper foil, measured at 9 K by Lytle.[7] Obviously, there are only a few accidental concurrences of the positions of the absorption maxima and minima in the theoretical and experimental spectra. Further, the amplitudes of the maxima and minima in the calculated spectrum decrease with increasing energy, so that the fine-structure amplitudes above 300 eV from the main absorption edge become far too small in comparison with the experimental copper fine structure, which is still measurable at 900 eV, showing maximal absorption variations in the region 150–300 eV. We must conclude, therefore,

TABLE I. Electron energies, multiplicities, and Fourier coefficients of the crystal potential for electron reflections in copper.[a]

$\alpha\beta\gamma$	E_{min} (eV)	s (of pairs)	$\lvert V_{\alpha\beta\gamma}\rvert$ (eV)	$\alpha\beta\gamma$	E_{min} (eV)	s (of pairs)	$\lvert V_{\alpha\beta\gamma}\rvert$ (eV)	$\alpha\beta\gamma$	E_{min} (eV)	s (of pairs)	$\lvert V_{\alpha\beta\gamma}\rvert$ (eV)
860	288	12	1.19	971	377	24	0.93	(12)22	438	12	0.81
(10)00	288	3	1.19	(11)31	377	24	0.93	975	446	24	0.80
862	300	24	1.14	882	380	12	0.92	(11)53	446	24	0.80
(10)20	300	12	1.14	(10)44	380	12	0.92	(12)40	461	12	0.77
773	308	12	1.11	866	392	12	0.90	991	469	12	0.76
951	308	24	1.11	(10)60	392	12	0.90	886	472	12	0.76
666	311	4	1.10	973	400	24	0.88	(10)80	472	12	0.76
(10)22	311	12	1.10	(11)33	400	12	0.88	(12)42	472	24	0.76
953	331	24	1.04	(10)62	403	24	0.88	(10)82	484	24	0.75
864	334	24	1.04	884	415	12	0.86	993	492	12	0.74
(10)40	334	12	1.04	(12)00	415	3	0.86	(11)55	492	12	0.74
(10)42	346	24	1.00	777	423	4	0.84	(11)71	492	24	0.74
775	354	12	0.98	(11)51	423	24	0.84	(13)11	492	12	0.74
(11)11	354	12	0.98	(12)20	426	12	0.83	(10)66	495	12	0.74
880	369	6	0.95	(10)64	438	24	0.81	(12)44	507	12	0.73
955	377	12	0.93								

[a] The data for all reflections with E_{min} from 69 up to 287 eV are to be found in Ref. 2.

that Kronig's theory does not reproduce the observed extended copper K-absorption fine structure.

B. Cadmium

The electron energies $E_{\rm min}$ corresponding to the absorption irregularities in the hexagonal crystal structure of metallic cadmium were computed from Kronig's equation (14a), with $a_0 = 2.964$ Å and $c_0 = 5.564$ Å (at 83 K). Values for $|V_{\alpha\beta\gamma}|$ for 51 crystallographic nonequivalent reflections $\alpha\beta\gamma$ corresponding to energies $E_{\rm min}$ between 85 and 411 eV were borrowed from Radi's[10] paper. Since the quantity

$$\frac{|V_{\alpha\beta\gamma}|}{|\sum_j \exp(-i\vec{g}\cdot\vec{R}_j)|} = \frac{|V_{\alpha\beta\gamma}|}{\{2+2\cos\pi[(1/3)(4\alpha+2\beta)+\gamma]\}^{1/2}}$$

(where $\vec{g}$ is a reciprocal-lattice vector, $\vec{R}_j$ is the position vector of the jth atom in the unit cell, and $|\sum \exp(-i\vec{g}\cdot\vec{R}_j)| = 1, 2$ or 1.732) decreases monotonously with increasing electron energy, the remaining 216 values for $|V_{\alpha\beta\gamma}|$ for $E_{\rm min}$ between 85 and 411 eV could easily be evaluated. The multiplicity s is 1, 3, 6, or 12 here.

Figure 3 shows the result of the summation of all 267 absorption irregularities for an energy width of $(2+2\times 30)\Delta$ of each of them (full curve). For comparison, we have shown an experimental curve of the extended cadmium K-absorption fine structure, obtained in Groningen at a temperature of 83 K of the absorber (dashed curve).[16] Although a periodic structure appears in the calculated curve, it is obvious from the figure that this structure has no similarity with the fine structure of the experimental cadmium spectrum.

C. Gallium

For the case of an orthorhombic gallium absorber 1796 values for $E_{\rm min}$ were calculated from Kronig's equation (14b) with $a_0 = 4.510$ Å, $b_0 = 4.486$ Å, and $c_0 = 7.646$ Å (at 4.2 K); the electron energy region mounted from 40 up to 280 eV. The corresponding values of Fourier coefficients $|V_{\alpha\beta\gamma}|$ were calculated from the formula

$$\begin{aligned}|V_{\alpha\beta\gamma}| &= \frac{e^2}{\epsilon_0 V_c g^2}\sum_j\left[Z_j - f_j\left(\frac{g}{4\pi}\right)\right]|\exp(-i\vec{g}\cdot\vec{R}_j)| \\ &= \frac{e^2}{\epsilon_0 V_c g^2}\left[Z - f\left(\frac{g}{4\pi}\right)\right]\left|\sum_j \exp[-2\pi i \right. \\ &\quad \left.\times(\alpha x_j + \beta y_j + \gamma z_j)]\right| ,\end{aligned}$$

given in Radi's[10] paper. Here e is the electron charge, ϵ_0 is a constant $= 8.859\times 10^{-12}$ F/m, V_c is the volume of the unit cell, $g = 2\pi/d$ is the reciprocal-lattice constant, and Z is the atomic number. The quantity f denotes the atomic x-ray scattering amplitude as a function of $g/(4\pi) = \sin\theta/\lambda$ (Å^{-1}); $f(g/4\pi)$ for metallic gallium was evaluated with the aid of Ref. 17. The coordinates x_j, y_j, z_j of the eight atoms in the gallium unit cell are given by[18]

$$\begin{array}{llll} \text{i:} & (u,\ 0,\ v), & \text{v:} & (\tfrac{1}{2}+u,\ \tfrac{1}{2},\ -v), \\ \text{ii:} & (-u,\ 0,\ -v), & \text{vi:} & (\tfrac{1}{2}-u,\ \tfrac{1}{2},\ v), \\ \text{iii:} & (u,\ \tfrac{1}{2},\ \tfrac{1}{2}+v), & \text{vii:} & (\tfrac{1}{2}+u,\ 0,\ \tfrac{1}{2}-v), \\ \text{iv:} & (-u,\ \tfrac{1}{2},\ \tfrac{1}{2}-v), & \text{viii:} & (\tfrac{1}{2}-u,\ 0,\ \tfrac{1}{2}+v), \end{array}$$

with $u = 0.0785$ and $v = 0.1525$. As regards the

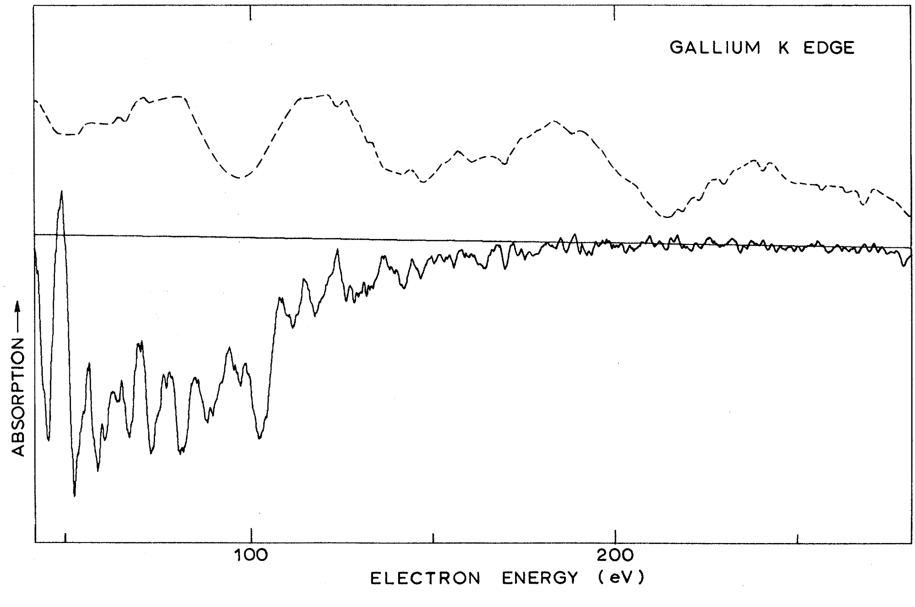

FIG. 4. Gallium K-absorption fine structure, calculated from Kronig's theory (solid line) and measured at 88 K (dashed line) by Weber and Brinkman (Ref. 19). The experimental spectrum is drawn from a microphotometer record.

multiplicity s of a reflection in this crystal structure, it is easily seen that $s=1$, 2, or 4.

In Fig. 4 we show the result for all 1796 absorption irregularities for an energy width of $(2+2\times 20)\Delta$. Comparison with an experimental gallium K-absorption spectrum, taken at 83 K,[19] demonstrates complete disagreement. This result is at variance with Smoluchowski's[20] calculation of the extended gallium K-absorption fine structure from Kronig's theory.

IV. DISCUSSION

In his original paper, Kronig[2] compared his calculated copper and iron K spectra with experimental spectra obtained by Coster and Veldkamp.[21] In his comparison Kronig pointed out that the hill and well of each absorption irregularity should be rounded and broadened by the effect of collisions of photoelectrons and conduction electrons and by periodic alterations in the interplanar spacings as a result of the lattice vibrations. In the same way the peaks in the calculated curves of the absorption fine structures of copper, cadmium, and gallium, given in the present paper, should be rounded and broadened, but this does not change essentially our comparison.

As for the discrepancy between Kronig's theory and the experiments, measurements of the electron range for energies of some hundreds of eV, among others by Steinhardt, Hudis, and Perlman[22] and Palmberg and Rhodin,[23] have shown that the range amounts to only a few interatomic distances. Therefore it may be assumed that the range of the x-ray photoelectron is reduced so strongly by inelastic collisions with electrons of the surrounding atoms and with conduction electrons that only atoms in comparatively few cells around the absorbing atom influence the absorption process. In conformity with this assumption, good results for the extended fine structures of polycrystalline absorbers are obtained by the "short-range theories," given by Kostarev,[24] Shiraiwa *et al.*,[25] Kozlenkov,[26] Izraileva,[27] Lytle,[28] and Sayers *et al.*[29] In the energy region up to a few eV from the main absorption edge, i.e., for very small electron energies, where the electrons can travel over distances of hundreds of Å before scattering, long-range effects like those considered in Kronig's theory of crystalline solids may be of importance. In Kronig's[30] early theory of a molecular gas, based on the same fundamental idea of interference of coherent electron waves, the calculated x-ray fine structure was in reasonable agreement with experiment in the case of the $\mathrm{GeCl_4}$ molecule.[31]

ACKNOWLEDGMENTS

The author is indebted to Professor H. de Waard for his critical reading of the manuscript and to Professor R. Kronig for his comments. The computational portions of this investigation were performed at the Rekencentrum der Rijksuniversiteit, Groningen, with the Cyber 74-16 computer.

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[17] The quantities $f(g/4\pi)$ were evaluated by interpolation from Table 3.3.1A in *International Tables for X-ray Crystallography* (Kynoch, Birmingham, England, 1962), Vol. III.

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