x.u. the separation between the nearest tungsten line and the K edge of Ga would have to be 24 percent greater than that observed.

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A Theoretical Investigation of the Fine Structure of X-Ray Absorption Edge of Gallium

R. Smoluchowski, *Institute for Advanced Study, Princeton*

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The fine structure of x-ray absorption edge of gallium is calculated theoretically on the basis of Kronig's theory. A method given by the author in a previous paper of calculating the fine structure in complicated crystals is applied for the first time to a non-cubic crystal (orthorhombic-pseudotetragonal). A quantitative comparison with experimental results shows a good agreement.

CHARACTERISTIC x-ray absorption is connected with the transferring of an electron from one of the inner shells of the atom to the outside of the occupied electronic levels; the minimum energy necessary for this act corresponds to the absorption edge. Quanta of higher energy than this minimum value eject the electron into the region of the so-called "free electrons," the probability of such a transition however is not a continuous function of the electronic energy (i.e., of the absorbed quantum). Namely on account of the presence of (a) unoccupied atomic levels and, for higher energies, of (b) forbidden and allowed energy zones, which arise in crystals (and in molecular gases) there appear in the energy spectrum of electrons regions of higher and lower transition probability. These give rise to the so-called Kossel[1] (case a) and Kronig[2] (case b) fine structure of x-ray absorption limits. In his theory, which has been checked in many ways on a quite extensive experimental material,[3] Kronig considers the ejected electron moving in a certain direction in the periodic field of the crystal lattice. For a certain direction not every energy value is allowed and the energy spectrum consists of alternate allowed and forbidden zones. In wave-mechanical picture this fact corresponds to the scattering of the wave associated with the ejected electron on the atoms of the lattice and the resulting interference of primary and of scattered waves. As a result of this the x-ray absorption coefficient for each direction is finite in certain intervals and zero in between. Since the position of these intervals depends upon direction of the movement of the electron one must take the average over all directions whereby only fluctuations ("discontinuities") of the absorption coefficient remain. A set of $(\alpha\beta\gamma)$-planes (α, β, γ-Miller indices) gives rise in this way to a minimum and a maximum of absorption coefficient, the first occurring on the short wave-length side and the latter at the same distance on the long wave-length side of the energy

$$W=(h^2/8\mu d^2)(\alpha^2+\beta^2+\gamma^2) \qquad (1)$$

(μ-mass of an electron) measured from the mean potential of the crystal (assumed to be cubic with the lattice constant d).

If we represent the potential in the crystal

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[1] W. Kossel, Zeits. f. Physik **1**, 119 (1920).

[2] R. de L. Kronig, Zeits. f. Physik **70**, 317 (1931); **75**, 191 (1932); **75**, 468 (1932).

[3] D. Coster and J. Veldkamp, Zeits. f. Physik **70**, 306 (1931); **74**, 191 (1932); J. Veldkamp, Zeits. f. Physik **77**, 250 (1932); **82**, 776 (1932); Dissertation Groningen 1934; D. Coster and R. Smoluchowski, Physica **2**, 1, 1935; R. Smoluchowski, Dissertation Groningen, 1935; Zeits. f. Physik **94**, 775 (1935); **95**, 588 (1935); and others.

lattice as a Fourier series then the magnitude (intensity of electron wave reflection) of a discontinuity is proportional to

$$I_{\alpha\beta\gamma}=H_{\alpha\beta\gamma}(V_{\alpha\beta\gamma})^2, \tag{2}$$

where $H_{\alpha\beta\gamma}$ is the abundance factor of the $(\alpha\beta\gamma)$-planes and $(V_{\alpha\beta\gamma})$ is the Fourier coefficient of the potential in the crystal. The occurrence of many closely lying discontinuities and the neglected interaction of electrons and of thermal agitation of the nuclei make it impossible for each discontinuity to show up individually in the absorption curve. One must rather find the accumulation centers ("gravity center") of the discontinuities in the energy scale and only these can be used for comparison with experiment.

It has been shown by the author[4] that in case of an alloy and of a complicated arrangement of atoms in the unit cell of the crystal the fine structure has to be calculated with the $V_{\alpha\beta\gamma}$ given by the formula

$$\begin{aligned}&V_{\alpha\beta\gamma}=[ed^2/\pi(\alpha^2+\beta^2+\gamma^2)]\\&\sum_j[\exp -2\pi i(\alpha x_j+\beta y_j+\gamma z_j)]\cdot Z_j(1-F_j),\end{aligned} \tag{3}$$

where x_j, y_j, z_j are coordinates of the atom j in the unit cell, Z_j is its atomic number and Z_jF_j the atomic form factor in the Fermi approximation for heavier elements. This formula was found in good agreement with experimental investigations on several alloys with complicated structure (e.g., γ-brass) or very different atomic numbers of constituents (e.g., Cu Be).[5] In case of pure metals it simplifies and one can finally calculate only with the so-called structure factor

$$K_{\alpha\beta\gamma}=\sum_j[\exp -2\pi i(\alpha x_j+\beta y_j+\gamma z_j)]. \tag{4}$$

The factor $1/(\alpha^2+\beta^2+\gamma^2)$ in (3) and the slow change of F_j with (α, β, γ) can be omitted since they make $V_{\alpha\beta\gamma}$ decrease monotonically with increasing energy a fact which has no appreciable influence on the final results. All quantitative comparison of theoretical fine structure with experiment was done up until now only for cubic crystals. This paper is the first attempt to make a theoretical calculation of fine structure for a non-cubic crystal, namely for the orthorhombic pseudotetragonal (space group $V_h{}^{18}$ in Shoenflies' system[6]) type of crystal lattice. The fine structure of the K absorption edge of gallium which according to Laves[7] crystallizes in this lattice was recently investigated by Mutch[8] so that a direct comparison with experiment is possible.

The unit cell of gallium contains 8 atoms of which the positions are given by means of two parameters $p=0.080$ and $m=0.153$ and the identity periods are $a=b=4.506\text{A}$, $c=7.642\text{A}$. Formula (4) retains its validity in this case, in the application of formula (2) however one must be careful with the abundance factor $H_{\alpha\beta\gamma}$ since the permutation of indices does not always give equivalent planes. Taking this into account the main change occurs in formula (1) which has to be substituted by

$$W=(h^2/8\mu)[(\alpha^2+\beta^2)/a^2+\gamma^2/c^2]. \tag{5}$$

Mutch's measurements were made in −140°C and −67°C so that one should calculate with lattice constants at these temperatures, these however are not known. Fortunately the thermal linear expansion coefficient α for Ga at room temperature is rather low (18×10^{-6}) so that even not taking into account the fact that α in general is smaller at low temperatures[9] the correction can be shown as negligible in view of

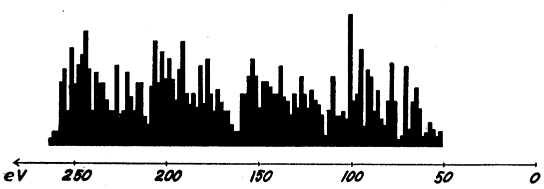

FIG. 1. Intensity of electron wave reflection *vs.* energy.

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[4] R. Smoluchowski, Diss. Groningen, 1935; Zeits. f. Physik **94**, 775 (1935); **95**, 588 (1935).

[5] R. Smoluchowski, references 3, 4.

[6] See R. W. G. Wyckoff, *The Structure of Crystals*.

[7] F. Laves, Zeits. f. Kristallographie **84**, 256 (1933).

[8] W. W. Mutch, Phys. Rev. **50**, 197 (1936) (preceding paper).

[9] See, e.g., G. Borelius, *Handbuch der Metallphysik*, vol. I, part 1, page 224 (the value of α for Ga given there is wrong since 55 is the volume expansion coefficient for gallium).

TABLE I.

Group	Exper.	Theor.
$A-\alpha$	74	86
$B-\gamma$	142	139
$D-\delta$	190	191
$E-\epsilon$	230	236

the accuracy of comparison with measurements and of the experimental error. Moreover as can be seen comparing the fine structure at −67°C and −140°C the position of the maxima and minima which can be reasonably used as check of Kronig's theory that is, which are sufficiently far from the main edge are within experimental error the same in both curves (B and γ).

For actual calculation the formula (4) simplifies for this crystal lattice to

$$K_{\alpha\beta\gamma}=\cos\left[2\pi m\alpha+\pi/2(\alpha+\beta)\right]\cdot\cos\left[2\pi p\gamma-(\pi/2)(\alpha+\beta)\right],\qquad(6)$$

where m and p are the parameters mentioned above. The values $I_{\alpha\beta\gamma}$ obtained with help of formula (2) and (6) for a set of planes which give rise to discontinuities lying between 50 and 260 volts and plotted against energy as given by (6) are shown in Fig. 1. One can distinguish four groups denoted $(A-\alpha)$, $(B-\beta)$, $(D-\delta)$, $(E-\epsilon)$ and obtain their centers of gravity (see above). In order to compare these with experimental results one must add to the values given by Mutch the energy difference between the mean potential in the crystal lattice and the first empty level. Since the experimental data necessary to calculate this magnitude are not known for Ga the value accepted is 10 volts which is the usual magnitude found experimentally in other metals and often applied with good results in similar cases.[10]

The maximum β occurring in Mutch's measurements has not been taken into account in our comparison since it is not very pronounced and the theoretical group $(B-\gamma)$ has sufficient breadth to account for the comparatively large distance between B and γ. The experimental and theoretical values (in eV) are compared in Table I. We see that the agreement is quite good if one takes into account the many approximations underlying the theoretical values. The group $(A-\alpha)$ is here as well as in all other comparisons not to be taken into consideration since the basic assumption of the theory (approximation from "free" electrons) is not valid in this region of fine structure.

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[10] From measurements of electronic reflection we know how low the mean potential in the crystal lies in comparison with the outside potential; from the Richardson potential in the photoelectric effect we can obtain the energy necessary to remove from the crystal electrons of greatest energy. The difference between these two values gives us the desired quantity. See J. Veldkamp, Diss. Groningen 1934 and R. Smoluchowski, references 4.