ON THE THEORY OF THE SHORT-WAVELENGTH REGION OF X-RAY K-ABSORPTION SPECTRA OF SINGLE CRYSTALS AND POLYCRYSTALLINE SAMPLES

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Abstract

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ON THE THEORY OF THE SHORT-WAVELENGTH REGION OF X-RAY K-ABSORPTION SPECTRA OF SINGLE CRYSTALS AND POLYCRYSTALLINE SAMPLES

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The fine structure of x-ray K-absorption spectra of molecules and polycrystalline metal samples in the region from about ten to several hundred electron volts from the edge is successfully interpreted in a number of works [1–4] on the basis of a one-electron model, the principal features of which are as follows:

1. Reduction of the problem to a centrally symmetric one by averaging the true potential of the system $V(\mathbf{r})$ over the surface of a sphere centered at the chosen atom;
2. Division of the averaged potential $\overline{V}(r)$ into two parts $\overline{V}(r) = V_a(r)+V'(r)$, of which the potential $V_a(r)$, which gives the behavior of the true potential $V(\mathbf{r})$ inside the atom in the system sufficiently well, is taken into account exactly, while the remaining part $V'(r)$ is treated within perturbation theory. The physical cause of the fluctuations of the absorption coefficient τ_k in this model is the scattering of the electron wave in the field $V'(r)$ and, as a consequence of this, the nonmonotonic dependence of the amplitude of the photoelectron wave function in the region of localization of the initial $1s$ state [1–3].

In work [5] the absorption coefficient of a single crystal was determined for the case of polarized radiation for a specific model of the crystalline field, in which an effective polyhedron charge is introduced. The potential of one polyhedron $V_a = Ze/|\mathbf{r}-\mathbf{R}_a|$ was taken into account exactly, as in [1–3], while the potentials of the others were treated as a perturbation, but, in contrast to [1–3], were not averaged over the surfaces of spheres. A shortcoming of approximation [5] is the neglect of the phase η_l introduced by the field V_a, which, according to [3], substantially affects the dependence of the absorption coefficient on photon energy. Below, an expression will be obtained for the absorption coefficient of a single crystal τ_k in the short-wavelength region in the case of polarized or oriented radiation, taking the phase into account and suitable for any crystalline

field. It will also be shown that τ_k for a polycrystalline sample with arbitrary orientations of the crystallites automatically turns out to depend only on the mean value of the crystal potential on the surface of a sphere centered at the chosen atom. The latter may be regarded as a justification of the model [1–3].

The absorption coefficient of the $1s$ band, taking into account the quasi-atomic character of the $1s$ states, their localization near the nuclei ($\chi r_{1s} \ll 1$, where χ is the wave vector of the photon, r_{1s} is the radius of the $1s$ state), and the translational symmetry of the crystal, can be written in the form:

$$\tau_k \simeq \sum_i \left| \int \psi_i(x,y,z)\, \mathbf{E}^0 \mathbf{r} \psi_{1s}(r)\, d\mathbf{r} \right|^2, \tag{1}$$

where ψ_{1s} is the atomic wave function of the $1s$ state; $\mathbf{E}^0$ is the direction of polarization of the radiation; the summation in (1) is carried out over the final states of the photoelectron belonging to the energy $\mathcal{E}_i = \mathcal{E}_{1s} + \hbar\omega$, and $\cdots$

the integration actually extends over the region $|\mathbf{r}| \lesssim r_{1s}$ around the selected atom. Thus, the problem of calculating $t_k(\omega)$ reduces to finding the wave function of the photoelectron $\psi_i(x,y,z)$ in the region $|\mathbf{r}| \lesssim r_{1s}$. For large photoelectron energies $\mathcal{E}_i > 0$ ($\mathcal{E}_i$ is measured from the average potential of the crystal) we use perturbation theory. Let us represent the "true" potential of the crystal in the form of a sum $V(\mathbf{r}) = V_a(r) + V'(\mathbf{r})$, where for $r < r_0$ ($r_0 > r_{1s}$) $V_a(r) \approx V(r)$, $V'(\mathbf{r}) \ll V_a(r)$; as $r \to \infty$, $V_a(r) \to 0$, $V'(\mathbf{r}) \to V(\mathbf{r})$. In the equation for the wave function of the photoelectron

$$\Delta\psi + \frac{2m}{\hbar^2}\left[\mathcal{E} - V_a(r) - V'(\mathbf{r})\right]\psi = 0 \tag{2}$$

we shall take the potential $V_a(r)$ of the "quasiatom" into account exactly, and $V'(\mathbf{r})$ as a perturbation. As solutions of the unperturbed equation ($V'(\mathbf{r}) \equiv 0$) for $\mathcal{E} > 0$, we choose a system of wave functions of the continuous spectrum characterized by a definite value of the photoelectron momentum $\hbar\mathbf{p}$:

$$\psi_p^0(\mathbf{r}) = \frac{1}{4\pi p} \sum_{l=0}^{\infty} i^l (2l+1) e^{i\delta_l(p)} R_{pl}(r) P_l\left(\frac{\mathbf{nr}}{r}\right). \tag{3}$$

Then, for those $\mathcal{E}$ for which perturbation theory for nondegenerate states is applicable, the solution of (2), accurate to first-order terms, will have the form [6]

$$\psi_p(\mathbf{r}) = \psi_p^0(\mathbf{r}) + \psi_p'(\mathbf{r}) = \psi_p^0(\mathbf{r}) - \frac{2m}{\hbar^2} \int G_E(\mathbf{r},\mathbf{r}') V'(\mathbf{r}') \psi_p^0(\mathbf{r}')\, d\mathbf{r}'. \tag{4}$$

Here

$$G_E(\mathbf{r},\mathbf{r}') = \sum_{n,l,m} \frac{\psi^0_{nlm}(\mathbf{r})\psi^{0*}_{nlm}(\mathbf{r}')}{-p_n^2 - p^2} + \int \frac{\psi^0_{p'}(\mathbf{r})\psi^{0*}_{p'}(\mathbf{r}')\, d\mathbf{p}'}{{p'}^2 - p^2 - i0}$$

$$\left(p^2 = \frac{2m}{\hbar^2}\mathcal{E}, \quad p_n^2 = -\frac{2m}{\hbar^2}\mathcal{E}_n\right) \tag{5}$$

is the Green' s function of equation (2) for $V'(\mathbf{r}) \equiv 0$. Note that $\psi_p(\mathbf{r})$ is normalized in the same way as $\psi^0_p(\mathbf{r})$, accurate to first-order small terms.

In the zeroth approximation the matrix element M^0_{1sp} of the probability of the transition $1s - \mathbf{p}$ upon absorption of x-ray radiation with frequency $\omega = (|\mathcal{E} - \mathcal{E}_{1s}|)\, 1/\hbar$ and polarization $\mathbf{E}^0$ is equal to

$$M^0_{1sp} \sim \int \psi^0_p(\mathbf{r})\, \mathbf{E}^0\mathbf{r}\, \psi_{1s}(\mathbf{r})\, d\mathbf{r} = \cos\hat{\mathbf{p}}\mathbf{E}^0\, \frac{ie^{i\delta_1(p)}}{p} M_{1s}(p), \tag{6}$$

where

$$M_{1s}(p) = \int_0^\infty dr\, r^3 R_{p1}\psi_{1s}. \tag{6'}$$

As is seen from (6), M^0_{1sp} is different from zero only for the term of series (3) with $l = 1$. Similarly, in the matrix element of first-order smallness

$$M'_{1sp} = \int \psi'_p \mathbf{E}^0\mathbf{r}\psi_{1s}\, d\mathbf{r}$$

there will be a contribution from the term in (5) with $l = 1,\ m = 0$, if the direction of polarization $\mathbf{E}^0$ is chosen as the quantization axis. Substituting series (3) into (5), carrying out the integration over the directions of $\mathbf{p}'$, and extracting from (5) the term with $l = 1,\ m = 0$, it will be equal to

$$G_{p1}(r,r')Y_{10}(\theta,\varphi)Y^*_{10}(\theta',\varphi') =$$

$$= \left[\sum_n \frac{R_{n1}(r)R_{n1}(r')}{-p_n^2 - p^2} + \int \frac{R_{p'1}(r)R_{p'1}(r')\, dp'}{{p'}^2 - p^2 - i0}\right] Y_{10}(\theta,\varphi)Y^*_{10}(\theta',\varphi') \tag{7}$$

(θ, θ' are the angles between $\mathbf{E}^0$ and $\mathbf{r}, \mathbf{r}'$).

The expression in square brackets in (7) is, as is not difficult to see, the Green' s function $G_{p1}(r,r')$ of the equation arising from (2) for $V'(r) = 0$ and $l = 1$:

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\left[p^2-\frac{2}{r^2}-\frac{2m}{\hbar^2}V_a(r)\right]R=0. \tag{8}$$

The Green' s function (8) can also be written [6,7] as the product of two different particular solutions of (8), one of which, $R_{p1}(r_<)$, is regular at zero, while the other, $\Phi_{p1}(r_>)$, is not regular ($r_<, r_>$ are respectively the smaller and larger of r, r'):

$$G_{p1}(r,r')=\frac{\pi}{2p}R_{p1}(r_<)\Phi_{p1}(r_>). \tag{9}$$

The coefficient in the product in (9) is determined from the condition that $G_{p1}(r,r')$ for $V_a(r)\equiv 0$ pass directly into the corresponding expression $pj_1(pr_<)n_1(pr_>)$ for free motion with $l=1$ [6].

Taking into account relations (7), (9), the matrix element M_{1sp} of the probability of transition to the state (3) is equal to

$$M_{1sp}=M^0_{1sp}+M'_{1sp}=M^0_{1sp}-\frac{2m}{\hbar^2}\int d\mathbf{r}'\,\psi^0_p(\mathbf{r}')V'(\mathbf{r}')\int d\mathbf{r}\,G_\varepsilon(\mathbf{r},\mathbf{r}')\,\mathbf{E}^0\mathbf{r}\,\psi_{1s}(\mathbf{r})$$

$$=M^0_{1sp}-\frac{m\pi}{\hbar^2 p}\int d\mathbf{r}'\,\psi^0_p(\mathbf{r}')V'(\mathbf{r}')P_1\left(\frac{\mathbf{E}^0\mathbf{r}'}{r'}\right)\int_0^\infty dr\,r^3R_{p1}(r_<)\Phi_{p1}(r_>)\psi_{1s}(r). \tag{10}$$

In order to obtain the absorption coefficient τ_k for the $1s$-band, it is necessary, according to (1), to sum the transition probability $|M_{1sp}|^2$ over all states with energy $\mathcal{E}=\hbar^2p^2/2m$, i.e., over all directions $\mathbf{p}$. To accuracy including terms of first order in smallness, τ_k will be equal to

$$\tau_k=\int|M_{1sp}|^2\,d\Omega=\int|M^0_{1sp}|^2\,d\Omega+2\,\mathrm{Re}\int d\Omega\,M^{0*}_{1sp}M'_{1sp}. \tag{11}$$

The first term in (11) is the absorption coefficient of the "quasiatom" τ^0_k. In the second term of (11), the product $\cos\mathbf{p}\wedge\mathbf{E}^0P_l(\mathbf{nr}'/r')$ ($l=0,\ldots,\infty$) depends, according to (10), (6), and (3), on the direction of the momentum $\mathbf{n}=\mathbf{p}/p$; let us carry out in (11) the integration over $\mathbf{n}$. The potential $V'(\mathbf{r}')\sim 0$ for $|\mathbf{r}'|\le r_{1s}$; therefore we replace $R_{p1}(r_<)\Phi_{p1}(r_>)\to R_{p1}(r)\Phi_{p1}(r')$; in this case (11) reduces to the form

$$\tau_k=\tau^0_k\left\{1-\frac{2m\pi}{\hbar^2p}\int R_{p1}(r')\Phi_{p1}(r')V'(\mathbf{r}')\frac{3}{4\pi}\left[P_1\left(\frac{\mathbf{r}'\mathbf{E}^0}{r'}\right)\right]^2 d\mathbf{r}'\right\}. \tag{12}$$

Formula (12) is the final expression for the absorption coefficient τ_k of the $1s$-band of a single crystal in the case of polarized radiation, suitable, as already noted, in the short-wavelength region.

Expanding $V'(\mathbf{r})$ in a series in spherical functions ($\mathbf{E}^0$ is the quantization axis):

$$V'(\mathbf{r}) = V'(r) + \sum_{l\neq 0,\, m} V_{l,m}^{E^0}(r) Y_{l,m}(\theta,\varphi) \tag{13}$$

and substituting (13) into (12), we obtain that τ_k of a single crystal for the $1s$-band depends only on the components $V'(r)$ and $V_{20}^{E^0}(r)$ of the crystal potential:

$$\tau_k^{E^0} = \tau_k^0 \left\{ 1 - \frac{2m\pi}{\hbar^2 p} \int_{r_0}^{\infty} dr'\, r'^2 R_{p1}(r') \Phi_{p1}(r') \left[V'(r') - \frac{1}{\sqrt{5\pi}} V_{20}^{E^0}(r') \right] \right\}. \tag{14}$$

The absorption coefficient of a single crystal $\tau_k^{\vec{x}}$ in the case of unpolarized oriented radiation is obtained from (12) as the result of averaging the expression

$$\left[P_1(\mathbf{r}'\mathbf{E}^0/r') \right]^2 = \cos^2 \mathbf{r} \wedge \mathbf{E}^0 = \sin^2 \chi_{r'}^{\hat{\vec{x}}} \cos^2 \varphi_{E^0}. \tag{15}$$

in a plane perpendicular to $\vec{\varkappa}$, over φ^{E^0}. Substituting series (13) into (12), where the direction $\vec{\varkappa}$ is now taken as the quantization axis, we obtain, analogously to the preceding case, that $\tau_k^{\vec{\varkappa}}$ depends only on the components $V'(r)$ and $V_{20}^{\vec{\varkappa}}(r)$ of the crystal potential:

$$\tau_k^{\vec{\varkappa}} = \frac{1}{2\pi} \int \tau_k^{E^0}\, d\varphi = \tau_k^0 \left\{ 1 - \frac{2m\pi}{\hbar^2 p} \int_{r_0}^{\infty} dr'\, r'^2 R_{p1}(r') \Phi_{p1}(r') \left[V'(r') + \frac{1}{2\sqrt{5}} V_{20}^{\vec{\varkappa}}(r') \right] \right\}. \tag{16}$$

Finally, on averaging (12) over all polarizations, we arrive at an expression for the absorption coefficient $\bar{\tau}_k$ of a polycrystalline specimen:

$$\bar{\tau}_k = \frac{1}{4\pi} \int \tau_k^{E^0}\, d\Omega = \tau_k^0 \left\{ 1 - \frac{2m\pi}{\hbar^2 p} \int_{r_0}^{\infty} dr'\, r'^2 R_{p1}(r') \Phi_{p1}(r') V'(r') \right\}. \tag{17}$$

As is seen from (17), $\bar{\tau}_k$ depends only on the mean value of the crystal potential

$$V'(r) = \frac{1}{4\pi} \int V'(r)\, d\Omega$$

on the surface of a sphere centered at the selected atom; in other words, on the zero component of series (13). Thus, models[1–3] in which, from the very beginning, $V'(r)$ was averaged over the surface of spheres are entirely legitimate for polycrystalline specimens and also, obviously, for molecular gases. For a single crystal, formulas (14) and (16) differ from formula (17) by additional terms depending on another component of the crystal potential, $V_{20}(r)$. Information about it can be obtained from the K absorption spectrum of a single crystal, if the dependence of the spectrum on the polarization or orientation of the incident beam is established experimentally.

In the energy region of photoelectrons $pr_0 \gg 1$, the wave functions $R_{p1}(r)$, $\Phi_{p1}(r)$ in formulas (14)–(17) may be replaced by their asymptotic expressions

$$R_{p1} \sim \sqrt{\frac{2}{\pi}} \frac{\sin(pr - \pi/2 + \eta_1)}{r}, \qquad \Phi_{p1} \sim \sqrt{\frac{2}{\pi}} \frac{\cos(pr - \pi/2 + \eta_1)}{r},$$

then formula (17) for a polycrystalline specimen passes into the known expression[3]

$$\bar{\tau}_k = \tau_k^0 \left\{ 1 + \frac{2m}{\hbar^2 p} \int_{r_0}^{\infty} dr \, \sin(2pr + 2\eta_1) V'(r) \right\}, \tag{18}$$

while formulas (14) and (16) will have the form

$$\tau_k^{E^0} = \tau_k^0 \left\{ 1 + \frac{2m}{\hbar^2 p} \int_{r_0}^{\infty} dr \, \sin(2pr + 2\eta_1) \left[V'(r) - \frac{1}{\sqrt{5\pi}} V_{20}^{E^0}(r) \right] \right\}, \tag{19}$$

$$\tau_k^{\vec{\varkappa}} = \tau_k^0 \left\{ 1 + \frac{2m}{\hbar^2 p} \int_{r_0}^{\infty} dr \, \sin(2pr + 2\eta_1) \left[V'(r) + \frac{1}{2\sqrt{5\pi}} V_{20}^{\vec{\varkappa}}(r) \right] \right\}. \tag{20}$$

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Note: Figure translations are in progress. See original paper for figures.