LIMITS OF APPLICABILITY OF THE THEORY OF K-ABSORPTION SPECTRA OF POLYCRYSTALLINE SAMPLES

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Abstract

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LIMITS OF APPLICABILITY OF THE THEORY OF K-ABSORPTION SPECTRA OF POLYCRYSTALLINE SAMPLES

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For calculations of the K-absorption spectra of molecules in the short-wavelength region, a method was proposed in (^{1}), which was subsequently developed and refined as applied to the K-absorption spectra of metals (^{2}, ^{3}). A feature of the method (^{1}) is that, when it is used, the potential of the system $V(\mathbf{r})$ is averaged over the surface of a sphere centered at the absorbing atom. In other words, only the zero component is retained in the expansion of $V(\mathbf{r})$ in a series in spherical functions $V_0(r)$:

$$V(\mathbf{r}) = V_0(r) + \sum_{l\neq 0,\ m} V_{l,m}(r) Y_{l,m}(\theta, \varphi), \tag{1}$$

$$V_0(r) = \frac{1}{4\pi} \iint V(\mathbf{r}) d\Omega. \tag{2}$$

Further, in finding the wave function of the final state of the photoelectron, the part $V_0(r)$—the potential inside the absorbing atom in the system $V_a(r)$—was taken into account exactly, while the difference $V'(r) = V_0(r) - V_a(r)$, or the "potential of the surrounding atoms" (^{2}, ^{3}), was treated as a perturbation. In (^{4}) it was shown that the sphericity of the initial $1s$ state and the averaging of the absorption coefficient τ_k over the polarization of the radiation, which in fact occurs in experiments with molecules and polycrystalline samples, leads to the result that for these objects τ_k does indeed depend only on the component $V_0(r)$ of the potential, but only for those photoelectron energies for which perturbation theory for nondegenerate states is applicable (^{5}). This condition is violated in the case of a periodic $V(\mathbf{r})$ for electrons with quasimomenta $\mathbf{k}$ satisfying the Wulff-Bragg condition $(\mathbf{k} - 2\pi\mathbf{g})^2 = k^2$ ($\mathbf{g}$ is a reciprocal-lattice vector) (^{6}). Let us show how this fact is reflected in the results of (^{2}, ^{3}).

For simplicity we restrict ourselves to the case of a crystal with a center of symmetry and expand $V(\mathbf{r})$ in a Fourier series

$$V(\mathbf{r}) = \sum_g V_g \cos(2\pi \mathbf{g}\mathbf{r}). \tag{3}$$

Let us average (3) over θ, φ in order to obtain $V_0(r)$ (2). Passing in the integration to variables χ, ψ, where $\chi = \hat{\mathbf{g}}\mathbf{r}$, and ψ is the angle in the plane normal to $\mathbf{g}$, we obtain:

$$V_0(r) = \frac{1}{4\pi} \iint V(\mathbf{r}) d\Omega = V_{\text{cp}} + \sum_{g \neq 0} V_g \frac{1}{4\pi} \int_0^{\pi} \int_0^{2\pi} \cos(2\pi g r \cos\chi) \sin\chi \, d\chi \, d\psi =$$

$$= V_{\text{cp}} + \sum_{g \neq 0} V_g \frac{\sin 2\pi g r}{2\pi g r}, \tag{4}$$

where V_{cp} is the mean potential of the crystal. The formula for the relative absorption coefficient (with ionization of the $1s$ shell) in the model $(^3)$ has form:

$$\tau_k / \tau_0 = 1 + 2 \left(I' \cos 2\eta_1 + I'' \sin 2\eta_1 \right), \tag{5}$$

where $\eta_1(k)$ is the phase of the electron wave in the field $V_a(r)$ for $l = 1$,

$$I' = \frac{m}{\hbar^2 k} \int_{r_0}^{\infty} V'(\xi) \sin 2k\xi \, d\xi,$$

$$I'' = \frac{m}{\hbar^2 k} \int_{r_0}^{\infty} V'(\xi) \cos 2k\xi \, d\xi,$$

$$V'(r) = V_0(r) - V_{\text{av}} \quad \text{for } r > r_0.$$

We have not restricted the region of integration in I' and I'' to some value R, but have extended the integration to the entire crystal, i.e., formally to ∞. Substituting series (4) into the integrands I' and I'' and assuming that $V'(\xi)$ is measured in units of e^2/a (a is a certain characteristic lattice parameter), ξ, r_0 in units of a, and k in units of $1/a$, after elementary transformations we obtain:

$$I' = \frac{a/a_0}{ka} \sum_{g \neq 0} \frac{V_g}{4\pi g} \left[\operatorname{ci} 2(k + \pi g) r_0 - \operatorname{ci} 2|k - \pi g| r_0 \right], \tag{6}$$

$$I'' = \frac{a/a_0}{ka} \sum_{g \neq 0} \frac{V_g}{4\pi g} \left[\frac{\pi}{2} - \operatorname{si} 2(k + \pi g) r_0 + \operatorname{sign}(\pi g - k) \left(\frac{\pi}{2} - \operatorname{si} 2 r_0 |k - \pi g| \right) \right], \tag{7}$$

where

$$\operatorname{si}(x) = \int_0^x \frac{\sin t}{t}\, dt \quad \text{and} \quad \operatorname{ci}(x) = -\int_x^\infty \frac{\cos t}{t}\, dt$$

are the sine and cosine integrals, and a_0 is the Bohr radius.

From expression (6) it is immediately evident that, since $\operatorname{ci} x \sim C + \ln x$ as $x \to 0$, I' tends to ∞ as $k \to \pi g$, and near such a k, $I' \sim \ln|k - \pi g|$. Together with I', the first-order correction to the photoelectron wave function defined in (3) also diverges. This means that the model ([2,3]), based on perturbation theory for nondegenerate states, is inapplicable for polycrystalline samples at photoelectron energies

$$\mathcal{E} = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2}{2m} (\pi g)^2.$$

For k close to πg, in the nearly-free-electron approximation one obtains a fluctuation of the density of states ([6,7]). We shall show that in the model ([2,3]) a fluctuation of the absorption coefficient may be observed in this region. Let $\zeta = |k - \pi g| > 0$ ("resonance deficiency" ([6])). Assuming that there exist $\zeta \ll \pi g_1 - \pi g_2$ (g_1, g_2 are successive reciprocal-lattice vectors) for which the theory ([2,3]) is still applicable, and neglecting ζ in comparison with πg, we obtain from (6) and (7):

a) for $k = \pi g_1 - \zeta$

$$I' \approx \frac{a/a_0}{ka} \sum_{|g| \neq 0} \left[\operatorname{ci} 2(\pi g_1 + \pi g) r_0 - \operatorname{ci} 2\zeta r_0 \right] \frac{1}{4\pi g} \sum_{|g| = \text{const}} V_g, \tag{8}$$

$$I'' \approx \frac{a/a_0}{ka} \left\{ \sum_{|g| \neq 0, g_1} \left[\pi - \operatorname{si} 2(\pi g_1 + \pi g) r_0 - \operatorname{si} 2|\pi g_1 - \pi g| r_0 \right] \frac{1}{4\pi g} \sum_{|g| = \text{const}} V_g + \right.$$

$$\left. + \left[\pi - \operatorname{si}(4\pi g_1 r_0) - \operatorname{si}(2\eta r_0) \right] \frac{1}{4\pi g_1} \sum_{|g| = g_1} V_g \right\}; \tag{9}$$

b) for $k = \pi g_1 + \zeta$

$$I'' \simeq \frac{a/a_0}{ka} \left\{ \sum_{|g| \neq 0, g_1} [\pi - \operatorname{si} 2(\pi g_1 + \pi g) r_0 - \operatorname{si} 2|\pi g_1 - \pi g| r_0] \frac{1}{4\pi g} \sum_{|g| = \mathrm{const}} V_g + [-\operatorname{si}(4\pi g_1 r_0) + \operatorname{si}(2\zeta r_0)] \frac{1}{4\pi g_1} \sum_{|g|=g} \right. \tag{10}$$

I' does not change in comparison with (8).

According to (9), (10), upon passing through the value $k = \pi g_1$, I'' changes by a finite amount:

$$I''(\pi g_1 - \zeta) - I''(\pi g_1 + \zeta) \simeq \frac{a/a_0}{ka} \frac{\sum_{|g|=g_1} V_g}{4g_1}. \tag{11}$$

The change in I'' will lead, in accordance with (5), to a finite change $\Delta\tau$ in the relative absorption coefficient:

$$\Delta\tau = \tau(\pi g_1 - \zeta) - \tau(\pi g_1 + \zeta) = 2 \frac{a/a_0}{ka} \frac{\sum_{|g|=g_1} V_g}{4g_1} \sin 2\eta_1(\pi g_1) = \frac{\frac{e^2}{a} N_{g_1} V_{g_1}}{\frac{\hbar^2}{2ma^2} (\pi g_1)^2} \frac{\pi}{4} \sin 2\eta_1(\pi g_1) \tag{12}$$

(in the last expression (12), for simplicity, we have put $V_g = V_{|g|}$, N_{g_1} is the number of reciprocal-lattice points on the sphere of radius g_1).

Thus, just as in the approximation (^{6,7}), the magnitude of the fluctuation of the absorption coefficient near $k = \pi g$ is proportional to

$$\frac{N_g V_g}{E_g} \left(E_g = \frac{\hbar^2}{2ma^2} (\pi g)^2 \right),$$

but, in addition, it also depends on the phase $\eta_1(\pi g_1)$ of the field of the absorbing atom in the crystal.

Let us estimate the energy interval ΔE near E_g, outside which the theory (^{2,3}), and hence formulas (5)–(12), are still valid. For this, for $E < E_g - \Delta E$, $E > E_g + \Delta E$, the condition

$$I' \sim \frac{\frac{e^2}{a} N_{g_1} V_{g_1}}{\frac{\hbar^2}{2ma^2} (\pi g_1)^2} \frac{1}{8} \ln 2\zeta r_0 < 1, \tag{13}$$

must be satisfied, where $\zeta = |k - \pi g|$, and ΔE is related to ζ as follows:

$$\Delta E = E - E_{g_1} = \frac{\hbar^2}{2ma^2}(\pi g_1 + \zeta)^2 - \frac{\hbar^2}{2ma^2}(\pi g_1)^2 \sim \frac{E_{g_1}}{\pi g_1} 2\zeta. \tag{14}$$

For a KCl crystal in the region from $E_g = 11.7$ eV ($g = \sqrt{12}/2$) to $E_g = 31.2$ eV ($g = \sqrt{32}/2$), the interval ΔE is largest for $E_{g_1} = 19.5$ eV ($g_1 = \sqrt{20}/2$) and is ~ 0.5 eV. The estimate was made using formulas (13), (14); $N_{g_1} = 24$, $r_0 = 0.5a$, $a = 5.9a_0$; $V_{g_1} = -0.57e^2/a$ was calculated from known atomic factors of the ions K^+ and Cl^- (8). Since the region $2\Delta E \lesssim 1$ eV, where the theory (2,3) is not valid for KCl, proves comparable with the width of the K-level itself ($\gamma_K \sim 0.65$ eV for K and $\gamma_K \sim 0.60$ eV for Cl (9)), and for a number of values of g is considerably smaller, it may be assumed that in many cases its presence is insignificant and does not show up when comparing the results (2,3) with experiment. However, in each specific-

in that case a special estimate of the quantity ΔE is necessary for different g.

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