QUANTUM THEORY OF SCATTERING X-RAYS.
4. THEORY OF X-RAY RAMAN SCATTERING

By F. A. Babushkin

Department of Physics, Komi Government Pedagogical Institute*

Inelastic scattering of X-rays by localized K-electrons in solids is treated theoretically. The excited electron is considered in the OPW-approximation. We obtain a Compton-like angular dependence for the differential cross-section.

Das Gupta [1] and Suzuki [2] have informed about the Raman scattering of X-rays by solids of light elements, such as metalic lithium, beryllium, boron, graphite. However, one may point out to Weiss' work [3], in which the Raman scattering of X-rays has not been discovered in the repeated Das Gupta's measurements.

The quantum-mechanical theory of the Raman scattering is given in the work by Mizuno and Ohmura [4]. They have obtained the result, that the differential cross-section in the dipole-approximation is proportional to

$$\nu_0^2 \cdot t(\nu_0 - \nu) \cdot (1 + \cos^2 \vartheta) \cdot \sin^2 \frac{\vartheta}{2} \tag{1}$$

where ϑ is the scattering angle, ν_0 and ν are respectively the frequencies of the incident and scattered X-rays, and $t(\nu_0 - \nu)$ is the matrix element, which they do not calculate.

In this paper we give the quantum theory of the Raman scattering, which is free from the defficiency of the above work [4] (we are interested in the general case, not in the dipole--approximation, and calculate the matrix element).

The double differential cross-section of the X-ray scattering by the crystal is defined by the well known formula:

$$\frac{d^2\sigma}{d\varepsilon_f \cdot d\Omega} = \sigma_0 \cdot \frac{k_f}{k_i} \sum_{f,i} \varrho_i \left| \left\langle n_{\boldsymbol{q},s}, \varphi' \left| \sum_{\alpha} \exp(i\boldsymbol{K}\boldsymbol{r}_\alpha) \right| n_{\boldsymbol{q},s}, \varphi \right\rangle \right|^2 \cdot \delta(E_f - E_i) \tag{2}$$

where

$$\sigma_0 = \frac{1 + \cos^2 \vartheta}{2} \cdot \left(\frac{e^2}{mc^2} \right)^2, \quad \boldsymbol{K} = \boldsymbol{k}_i - \boldsymbol{k}_f$$

* Address: Department of Physics, Komi Government Pedagogical Institute, Siktivkar, USSR.

$\langle \varphi |$ is the wave function of the electronic subsystem, $\langle n_{q,s} |$ is the wave function of the lattice subsystem in the representation of the occupation numbers, $n_{q,s}$ is the number of the phonons with the wave vector $\boldsymbol{q}$ for the s-th vibration branch.

$\sum\limits_{\alpha}$ means the summation over all electrons of the scattered system.

For the lattice, which is in the thermal equilibrium state at the temperature T, ϱ_i is defined with the help of Gibbs' distribution.

For the case of the Raman scattering: $n'_{q,s} = n_{q,s}$, $|\varphi\rangle$ is the wave function of the electronic subsystem, which is in the ground state,

$\langle \varphi' |$ is the wave function of the electronic subsystem for the case, when one of K-electrons jumps to an unoccupied state,

In the one-electron approximation the wave function $|\varphi\rangle$ is given as a Slater Determinant and the present approximation reduces the matrix element in the expression (2) to a simple integral

$$\langle n_{q,s}, \varphi' | \sum_{\alpha} \exp(i\boldsymbol{K}\boldsymbol{r}_\alpha) | n_{q,s}, \varphi \rangle = \sum_{j} \exp(i\boldsymbol{K}\boldsymbol{n}_j^0) \langle n_{q,s} | \exp(i\boldsymbol{K}\delta n_j) | n_{q,s} \rangle \times$$

$$\times \langle \varphi' | \sum_{\nu} \exp(i\boldsymbol{K}\boldsymbol{r}_\nu) | \varphi \rangle = \sum_{j} \exp(i\boldsymbol{K}\boldsymbol{n}_j^0) \langle n_{q,s} | \exp(i\boldsymbol{K}\delta n_j) | n_{q,s} \rangle \times$$

$$\times 2 \int \psi_k^* \exp(i\boldsymbol{K}\boldsymbol{r}) \psi_K d\boldsymbol{r}. \tag{3}$$

The formula (3) is obtained for the primitive lattice, when

$$\boldsymbol{r}_\alpha = \boldsymbol{n}_j^0 + \delta \boldsymbol{n}_j + \boldsymbol{r}_\nu, \qquad \sum_{\alpha} = \sum_{j=0}^{N-1} \cdot \sum_{\nu=1}^{Z} \tag{4}$$

where:

n_j^0 is the vector of the lattice,

r_ν is the coordinate of the ν-th electron in the j-th cell,

$\delta\boldsymbol{n}_j$ the replacement of the j-th atom from the equilibrium position as the result of the thermal movement.

The generalization for the lattice with basis is simple.

ψ_K is the K-electron wave function, which is well localized around the j-th lattice site.

The electrons in the excited state shall be described with the help of the orthogonalized plane wave (OPW-approximation) [5]

$$\psi_k = \frac{1}{\sqrt{V}} \cdot e^{ikr} - \sum_{l} \mu_{kl} \cdot \varphi_{kl}(\boldsymbol{r}) \tag{5}$$

where

$$\varphi_{kl} = \frac{1}{\sqrt{N}} \sum_{n_j^0} e^{ikn^0_j} \cdot u_l(\boldsymbol{r} - \boldsymbol{n}_j^0) \tag{6}$$

here:

$u_l(\boldsymbol{r})$ are the localized wave functions,

l is the three quantum numbers (n, l, m),

V is the crystal's volume,

N is the number of the cell units in the crystal.

The coefficients μ_{kl} are defined with the help of the orthogonality

$$\int \varphi_{kl}^{*}(\boldsymbol{r}) \cdot \psi_{k}(\boldsymbol{r}) \cdot d\boldsymbol{r} = 0 \tag{7}$$

and with the assumption of the non-overlap of the localized wave functions are given in the formula

$$\mu_{kl} = \frac{1}{\sqrt{v}} \int e^{ikr} \cdot \mu_{l}^{*}(\boldsymbol{r}) d\boldsymbol{r} \tag{8}$$

where v is the cell unit's volume and the integration is carried out in all the crystal volume.

We consider the Raman scattering of X-rays by solids of light elements (Li, Be...) and the localized wave functions are the K-electron's wave functions, which in the nonrelativistical approximation may be defined as

$$u_{l}(\boldsymbol{r}) = \frac{1}{\sqrt{\pi}} \cdot \left(\frac{Z}{a_0}\right)^{3/2} \cdot e^{\frac{Zr}{a_0}} \tag{9}$$

In order to calculate the integration in (8), we shall choose the axis $z \| k$ and make use of the table integrals [6]

$$\int\limits_{0}^{\infty} r^{a-1} \cdot e^{-br} \cdot \sin cr \cdot \omega r = \frac{\Gamma(a)}{(b^2+c^2)^{a/2}} \cdot \sin\left(a \cdot \text{arctg } \frac{c}{b}\right). \tag{10}$$

We have the result

$$\mu_{kl} = \frac{1}{\sqrt{\pi v}} \cdot \left(\frac{Z}{a_0}\right)^{3/2} \cdot \int dr \cdot e^{\frac{Zr}{a_0}+ikr} = 8\sqrt{\frac{\pi}{v}} \cdot \left(\frac{a_0}{Z}\right)^{3/2} \cdot \left[1+\left(\frac{a_0 k}{Z}\right)^2\right]^{-2} \tag{11}$$

Substituting ψ_k for (3), we have

$$\int \psi_k^* \cdot e^{iKr} \cdot \psi_K \cdot dr = e^{-ikn^0j} \cdot \left(\frac{a_0}{Z}\right)^{3/2} \cdot 8\sqrt{\frac{\pi}{v}} \cdot \left\{\left[1+\left(\frac{a_0(\boldsymbol{K}-\boldsymbol{k})}{Z}\right)^2\right]^{-2} - \right.$$

$$\left. - \left[1+\left(\frac{a_0 k}{Z}\right)^2\right]^{-2} \cdot \left[1+\left(\frac{a_0 K}{2Z}\right)^2\right]^{-2}\right\}. \tag{12}$$

The expression

$$\sum_{i} \varrho_i |\langle n_{q,s}|e^{iK\delta n_j}|n_{q,s}\rangle|^2 \tag{13}$$

is the well known Debye-Waller's thermal factor e^{-2W}.

The summation over the final states $\sum\limits_{R}$ in the formula (2) is the summation of all the ways of averaging $\boldsymbol{k}$ of the electron, which is to jump to an unoccupied state, the latter may

be for the integration by $d\boldsymbol{k} \cdot 2Nv/(2\pi)^3$ and it is not difficult to do, if we make use of the substitution of the interferometric function (the structure sum) for the δ-function

$$\left| \sum_j e^{i(\boldsymbol{K}-\boldsymbol{k})\boldsymbol{n}^0_j} \right|^2 = (2\pi)^3 \cdot \frac{N}{v} \cdot \delta[(\boldsymbol{K}-\boldsymbol{k})-\boldsymbol{\tau}] \tag{14}$$

where $\boldsymbol{\tau}$ is the vector of the reciprocal lattice.

Making use of the δ-function from the energy $\delta(E_f-E_i)$ we may take the integral over energy and thus obtain the final expression of the following kind for the differential cross-section

$$\frac{d\sigma}{d\Omega} = \sigma_0 \cdot \frac{k_f}{k_i} \cdot e^{-2W} \cdot \frac{2^9 \cdot N^2 \cdot \pi}{V} \left(\frac{a_0}{Z} \right)^3 \cdot A^2. \tag{15}$$

The angular dependence of the Raman scattering is defined by

$$(1+ \cos^2 \vartheta) \cdot A^2 \tag{16}$$

where

$$A = \left[1+ \left(\frac{a_0\tau}{Z} \right)^2 \right]^{-2} - \left[1+ \left(\frac{a_0k}{Z} \right)^2 \right]^{-2} \cdot \left[1+ \left(\frac{a_0K}{2Z} \right)^2 \right]^{-2}. \tag{17}$$
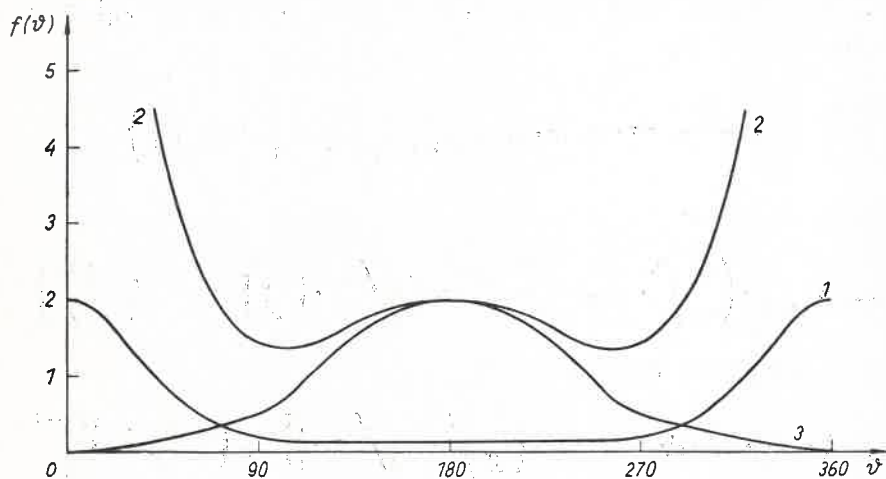

Fig. 1

For the crude estimation by angular dependence we may take

$$\frac{a_0\tau}{Z} \approx \frac{a_0K}{2Z} \approx \sin \frac{\vartheta}{2} \qquad \frac{a_0k}{Z} \approx 1 \tag{18}$$

which will bring us to

$$\frac{1+ \cos^2 \vartheta}{\left(1+ \sin^2 \dfrac{\vartheta}{2} \right)^4}. \tag{19}$$

The present dependence is the Compton-like, which can be seen from Fig. 1 (curve *1*), where the angular dependence of the Compton scattering for the comparison [4] (curve *2*)

$$\frac{1 + \cos^2 \vartheta}{\sin^2 \dfrac{\vartheta}{2}} \tag{20}$$

and the angular dependence of the Raman scattering, which has been obtained by the Japan physicists [4] in the dipole approximation (curve *3*) are represented.

The formula (15) holds true also for the case of the scattering by polycrystals also, as in (15) we have the dependence on the absolute value of the vector of the reciprocal lattice only, and not on its direction.

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