Energy-Dispersive Analog of the Zernicke–Prins Method for Determining the Atomic Radial Distribution Function

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Abstract—A modification of the Zernicke–Prins method is proposed for determining the radial distribution of atoms in a solid. The modification consists in measuring the spectra of scattered broadband X-ray radiation instead of the angular distribution of a quasi-monochromatic radiation scattered from the probed sample. It is shown that, according to the proposed approach, it is possible to eliminate the principal difficulty of the traditional Zernicke–Prins method, which is related to a limited region of variation of the argument in the measured angular distribution of scattered radiation.

The well-known Zernicke–Prins (ZP) method of determining the radial distribution of atoms in an X-ray probed medium consist in reconstructing the unknown radial distribution function (RDF) from an integral equation that relates this function to the experimentally measured angular distribution of a quasi-monochromatic X-ray radiation scattered from the probed sample [1]. A solution to this equation is obtained by inversion of the integral Fourier transform. However, this procedure encounters a difficulty, which is related to the fact that the magnitude of momentum transfer in the scattering event is limited from above. This principal difficulty cannot be eliminated within the framework of the traditional ZP method. Apparent oscillations, which appear in the RDF as a result of this limitation, are conventionally reduced by special smoothening procedures [2].

In this Letter, we suggest to eliminate the aforementioned difficulty by using an energy-dispersive approach based on the spectral measurements of broadband radiation scattered from the sample. It will be shown that, within the framework of the proposed approach, the arguments of functions entering into the main integral equation are determined on the entire numerical axis, which eliminates distortions of the RDF function that are inherent in the traditional ZP method.

Consider the scattering of an X-ray wave on atoms of the probed medium. The Maxwell equations for the Fourier image of the electromagnetic field in the medium are as follows:

$$(k^2 - \omega^2)\mathbf{E}_{\omega\mathbf{k}} - \mathbf{k}(\mathbf{k}\mathbf{E}_{\omega\mathbf{k}}) = 4\pi i \omega \mathbf{J}_{\omega\mathbf{k}}$$
$$= -\omega^2 \int d^3 k' G(\mathbf{k}', \mathbf{k})\mathbf{E}_{\omega\mathbf{k}'}, \tag{1}$$

$$G(\mathbf{k}', \mathbf{k}) = \frac{1}{2\pi^2}\alpha(\mathbf{k}' - \mathbf{k}, \omega)\sum_l e^{i(\mathbf{k}' - \mathbf{k})\mathbf{r}_l},$$

$$\alpha = \alpha_0(\omega)F(|\mathbf{k}' - \mathbf{k}|)/Z, \quad \alpha_0 = \frac{e^2}{m}\sum_{n \geq 1}\frac{f_{n0}}{\omega_{n0}^2 - \omega^2},$$

where $\mathbf{J}_{\omega\mathbf{k}}$ is the Fourier image of the induced electron current density for all atoms in the medium, $G(\mathbf{k}', \mathbf{k})$ is the response function (calculated in the dipole approximation [3, 4]), $\alpha_0(\omega)$ is the dipole atomic polarizability, f_{n0} is the oscillator strength for the $|0\rangle \longrightarrow |n\rangle$ transition, $\omega_{n0} = E_n - E_0$ is the energy difference between atomic levels, $F(\mathbf{k}' - \mathbf{k})$ is the atomic form factor, Z is the number of electrons in the atom, and $\mathbf{r}_l$ is the radius vector of nucleus of the lth atom. Representing the response function $G(\mathbf{k}', \mathbf{k})$ as a sum of the average and fluctuation components,

$$G(\mathbf{k}', \mathbf{k}) = \overline{G}(\mathbf{k}', \mathbf{k}) + \tilde{G}(\mathbf{k}', \mathbf{k}),$$
$$\overline{G}(\mathbf{k}', \mathbf{k}) = \langle G(\mathbf{k}', \mathbf{k})\rangle = 4\pi n_0 \alpha_0(\omega)\delta(\mathbf{k}' - \mathbf{k}), \tag{2}$$

where n_0 is the number density of atoms in the target, we can eventually reduce Eq. (1) to the following form:

$$(k^2 - \omega^2 \varepsilon(\omega))\mathbf{E}_{\omega\mathbf{k}}$$
$$= -\omega^2 \int d^3 k' \tilde{G}(\mathbf{k}', \mathbf{k})\left(\mathbf{E}_{\omega\mathbf{k}} - \mathbf{k}\frac{\mathbf{k}\mathbf{E}_{\omega\mathbf{k}'}}{\omega^2 \varepsilon(\omega)}\right). \tag{3}$$

Here, in agreement with Eq. (2), the refractive properties of the medium are described by the dielectric permittivity defined as $\varepsilon(\omega) = 1 + 4\pi n_0 \alpha_0(\omega) = 1 + \chi(\omega)$ (where $\chi(\omega)$ is called the susceptibility of the medium).

A solution to Eq. (3) can be obtained by applying the method of iterations to $\mathbf{E}_{\omega\mathbf{k}} = \mathbf{E}_{\omega\mathbf{k}}^{(i)} + \mathbf{E}_{\omega\mathbf{k}}^{(S)}$), where the first term describes the incident wave that satisfies Eq. (3) in the zero-order approximation with respect to $\tilde{G}(\mathbf{k'}, \mathbf{k})$ and the second term describes the scattered field that obeys Eq. (3) in the first-order approximation with respect to $\tilde{G}(\mathbf{k'}, \mathbf{k})$. These terms can be written as follows:

$$\mathbf{E}_{\omega\mathbf{k}}^{(i)} = \mathbf{e}_i E_\omega \delta(\mathbf{k} - \omega\sqrt{\varepsilon(\omega)}\mathbf{n}_i), \quad \mathbf{e}_i \mathbf{n}_i = 0,$$

$$\mathbf{E}_{\omega\mathbf{k}}^{(S)} = -\frac{\omega^2}{k^2 - \omega^2\varepsilon(\omega)}E_\omega\left(\mathbf{e}_i - \mathbf{k}\frac{\mathbf{k}\mathbf{e}_i}{\omega^2\varepsilon(\omega)}\right) \quad (4)$$
$$\times \tilde{G}(\omega\sqrt{\varepsilon(\omega)}\mathbf{n}_i, \mathbf{k}),$$

where $\mathbf{e}_i$ is the vector of polarization of the incident nonmonochromatic wave, E_ω is the wave amplitude, and $\mathbf{n}_i$ is the unit vector of the wave propagation direction.

Formulas (4) lead to the following expression for the spectral and angular distribution density of scattered radiation:

$$\omega\frac{dN^{(S)}}{d\omega d\Omega} = 4\pi^4\omega^4|E_\omega|^2(1 - (\mathbf{n}_S\mathbf{e}_i)^2)$$
$$\times \langle \tilde{G}(\omega\sqrt{\varepsilon(\omega)}\mathbf{n}_i)\tilde{G}^*(\omega\sqrt{\varepsilon(\omega)}\mathbf{n}_S)\rangle, \quad (5)$$

where $\mathbf{n}_S$ is the unit vector in the direction of scattered wave propagation and angle brackets denote averaging with respect to the positions of all atoms in the target. This averaging is performed with allowance for the following formula:

$$\left\langle \sum_l \sum_m \exp(i\omega\sqrt{\varepsilon(\omega)}(\mathbf{n}_i - \mathbf{n}_S)(\mathbf{r}_l - \mathbf{r}_m))\right\rangle$$
$$= N + \sum_l \sum_{m \neq l} \int d^3r_l d^3r_m f_2(\mathbf{r}_l, \mathbf{r}_m) \quad (6)$$
$$\times \exp(i\omega\sqrt{\varepsilon(\omega)}(\mathbf{n}_i - \mathbf{n}_S)(\mathbf{r}_l - \mathbf{r}_m)),$$

where N is the total number of atoms in the target (assumed to be homogeneous), $f_2(\mathbf{r}_l, \mathbf{r}_m)$ is the two-particle atomic distribution function that can be presented as the product of a one-particle function $f_1(\mathbf{r}_l) = 1/V$ and a pair correlation function $g(|\mathbf{r}_l - \mathbf{r}_m|)$ (which decreases with increasing argument [5]), and V is the target volume. Substituting formula (6) into Eq. (5) leads to the following final expression for the density of scattered radiation

$$\frac{dN^{(S)}}{d\omega d\Omega} = \frac{N}{Z^2}(1 - (\mathbf{n}_S\mathbf{e}_i)^2)\omega^3|E_\omega|^2F^2$$

$$\times (2\omega\sqrt{\varepsilon(\omega)}\sin(\vartheta/2))|\alpha_0(\omega)|^2$$

$$\times \left[1 - \frac{2\pi}{\omega\sqrt{\varepsilon}\sin(\vartheta/2)}\right] \quad (7)$$

$$\times \int_0^\infty dr r(n_0 - n(r))\sin(2\omega\sqrt{\varepsilon}r\sin(\vartheta/2))\right],$$

where ϑ is the scattering angle defined by the relation $|\mathbf{n}_i - \mathbf{n}_S| = 2\sin(\vartheta/2)$ and $n(r)$ is the atomic RDF defined by the relation $n_0 g(r) = [n(r) - n_0]/V^2$ [6] (as the radius r increases, $n(r)$ tends to the average number density of atoms $n_0 = N/V$). It should be noted that, in the X-ray frequency range, the permittivity of substances only very slightly duffers from unity and, hence, we can put $\varepsilon(\omega) \approx 1$ in the right-hand side of Eq. (7).

Formula (7), which is considered as the integral equation for determining the RDF $n(r)$, is analogous to the ZP equation [1]. As was noted above, $n(r)$ is reconstructed according to the ZP method from the angular dependence of the scattered radiation density $dN^{(S)}/d\omega d\Omega$, which is experimentally measured at a fixed frequency ω. The argument $x = 2\omega\sin(\vartheta/2)$ of the measured function varies within finite limits $0 < x < 2\omega$. This leads to a distortion of the $n(r)$ function reconstructed by inversion of the integral Fourier transform, in which the integration must be performed over the infinite domain.

We propose to use the alternative possibility that follows from Eq. (7) for determining $n(r)$ from measurements of the spectra of scattered broadband radiation for a given initial spectrum $|E_\omega|^2$ and a fixed scattering angle ϑ. Indeed, since all quantities entering into Eq. (7) are determined as functions of ω (at present, data on the susceptibilities $\chi(\omega)$ measured in a broad frequency range are available for many substances [7]), the unknown function $n(r)$ can be determined from Eq. (7) according to the following formula:

$$n(r) - n_0 = \frac{1}{2\pi^2 r}\int_0^\infty dx x J(x)\sin(xr),$$
$$\quad (8)$$
$$J(x) = \frac{dN^{(S)}/d\omega d\Omega}{dN_0/d\omega d\Omega} - 1,$$

where the argument x is related to the frequency ω by the relation presented above ($x = 2\omega\sin(\vartheta/2)$ and the quantity $dN_0/d\omega d\Omega$ coincides with the coefficient at the square bracket in the right-hand side of Eq. (7). This coefficient describes the spectral and angular distribution of radiation scattered by atoms in the medium independently of each other, since it is obvi-

ous that the collective effects in the scattering decrease with increasing frequency ω and the measured value of $dN^{(S)}/d\omega d\Omega$ tends to $dN_0/d\omega d\Omega$. In contrast to the ZP approach, the integrand function $J(x)$ in Eq. (8) is determined on the entire numerical axis. This circumstance eliminates distortions of the unknown function $n(r)$, which are inherent in the traditional ZP method.

It should be noted that the scheme of spectral measurements at a fixed position of the X-ray detector is simpler than the scheme of angular measurements involved in the ZP method. On the other hand, the proposed approach implies the need in the knowledge of the susceptibility of a target and the spectrum of probing radiation. In view of the latter requirement, one of the most convenient sources of probing photons is the synchrotron, which ensures a high intensity of the radiation and makes possible exact calculation of its characteristics.

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