QUANTITATIVE XPS ANALYSIS OF DISPERSE SYSTEMS: MODELLING OF MIXED SYSTEMS

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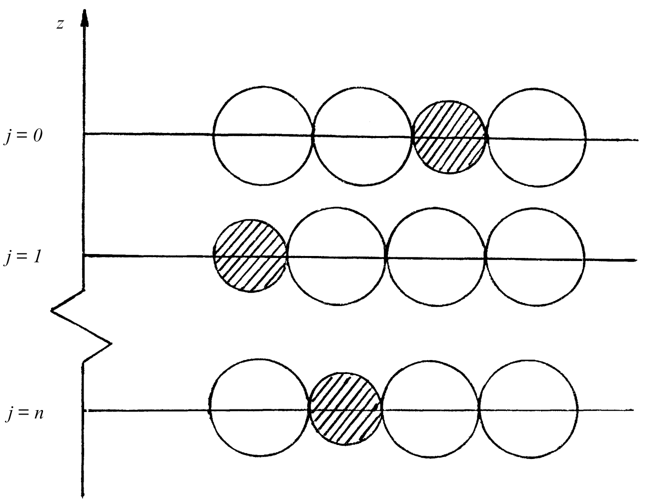
A mathematical formalism for modelling of mixed systems is developed. A method for quantitative analysis of XPS intensities for a mixed system consisting of two types of spherical particles is presented.

Questions concerning the quantitative analysis of ultradisperse systems by XPS technique have been subject of inquiry in numerous works (see, e.g., [1-4]). At the same time, some aspects of X-ray photoelectron spectroscopy have been elucidated insufficiently. This inference applies, in particular, to the problem of quantitative analysis of mixed systems by XPS technique. With due regard for the above-mentioned, we decided to undertake a task concerning the treatment of physical fundamentals of quantitative analysis and the development of approaches to simulation of mixed systems.

We next consider a mixed system consisting of two types of noninteracting spherical particles (see Figure). The sample under study is made up of several layers of particles, and it is assumed that the ratio of particles of different types within each layer is equal to their ratio in the bulk of the sample.



Schematic representation of the sample used to study systems consisting of particles of two types A (open circles) and B (hatched circles)

Henceforth, symbol f will denote the probability of finding a particle of the first type (A) in a layer of the sample. Accordingly, the probability of finding a particle of the second type (B) will be equal to $1-f$. Probability f can be written as

$$f = \frac{\frac{m_A/\rho_A}{4/3\pi R_A^3}}{\frac{m_A/\rho_A}{4/3\pi R_A^3} + \frac{m_B/\rho_B}{4/3\pi R_B^3}}, \tag{1}$$

where m_A – content of particles A in the sample (in units of wt.%); m_B – content of particles B in the sample (in units of wt.%) ($m_B = 100 - m_A$); ρ_A – density of the material of particles A; ρ_B – density of the material of particles B; R_A – mean radius of particles A; R_B – mean radius of particles B.

By simple manipulations, we get

$$f = \frac{\frac{m_A/\rho_A}{R_A^3}}{\frac{m_A/\rho_A}{R_A^3} + \frac{(100-m_A)/\rho_B}{R_B^3}}. \tag{2}$$

Let us find the numbers of photoelectrons emitted by particles A and B in direction $\mathbf{z}$ into a solid angle $d\Omega$. With allowance for the fact that the probability of finding particle A in the layer $j=0$ is equal to f, the number of photoelectrons emitted in direction z as a result of photoionization in volume dV at distance l from the surface of particle A can be defined as

$$dN_{A,j=0} = fI\frac{d\sigma_A}{d\Omega}d\Omega n_A \exp\left(-\frac{l}{\lambda_{AA}}\right) dV N_{\text{eff}}, \tag{3}$$

where I – intensity of X-radiation; n_A – concentration of the studied atoms in material A; $\frac{d\sigma_A}{d\Omega}$ – differential cross-section for ionization of the studied electronic level of A; N_{eff} – effective number of particles A and B in the analyzed layer; λ_{AA} – inelastic mean free path of photoelectrons of the studied element in particle A when crossing material A.

If a use is made of the system of cylindrical coordinates $dV = rdrd\varphi dz$ and $l = \sqrt{R_A^2 - r^2} - z$

and the distribution of atoms in the bulk of a particle is assumed to be constant, n_A = const, the required integration over the particle volume is written as

$$N_{A,j=0} = \iiint\limits_V fI\frac{d\sigma_A}{d\Omega}d\Omega n_A \exp\left(-\frac{l}{\lambda_{AA}}\right) dV N_{\mathrm{eff}}. \quad (4)$$

The integration of Eq. (4) yields

$$N_{A,j=0} = fI\frac{d\sigma_A}{d\Omega}d\Omega n_A 2\pi\lambda_{AA}\times$$

$$\times\frac{1}{2}R_A^2(1-\xi(R_A/\lambda_{AA}))N_{\mathrm{eff}}, \quad (5)$$

where the function

$$\xi(R_A/\lambda_{AA}) = \frac{1}{2}\left[\left(\frac{R_A}{\lambda_{AA}}\right)^2 - \right.$$

$$\left. -\exp\left(-\frac{2R_A}{\lambda_A}\right)\left(\frac{2R_A}{\lambda_{AA}}+\frac{R_A^2}{\lambda_{AA}}\right)\right]. \quad (6)$$

A similar expression for the number of photoelectrons emitted in direction **z** into a solid angle $d\Omega$ by particles B in the upper layer $j=0$ can be written as

$$N_{B,j=0} = (1-f)I\frac{d\sigma_B}{d\Omega}d\Omega n_B 2\pi\lambda_{BB}\times$$

$$\times\frac{1}{2}R_B^2(1-\xi(R_B/\lambda_{BB}))N_{\mathrm{eff}}, \quad (7)$$

where n_B – concentration of the studied atoms in material B; $\frac{\sigma_B}{d\Omega}$ – differential cross-section for ionization of the studied electronic level of B; λ_{BB} – inelastic mean free path of photoelectrons of the studied element in particle B when crossing material B.

Then, the ratio of the numbers of photoelectrons emitted by particles A and B in the upper layer $j=0$ is equal to

$$\frac{N_{A,j=0}}{N_{B,j=0}} = \frac{fI\frac{d\sigma_A}{d\Omega}d\Omega\pi R_A^2\lambda_{AA}n_A}{(1-f)I\frac{d\sigma_B}{d\Omega}d\Omega\pi R_B^2\lambda_{BB}n_B}\times$$

$$\times\frac{[1-\xi(R_A/\lambda_{AA})]N_{\mathrm{eff}}}{[1-\xi(R_B/\lambda_{BB})]N_{\mathrm{eff}}} =$$

$$= \frac{f\frac{d\sigma_A}{d\Omega}n_A R_A^2\lambda_{AA}[1-\xi(R_A/\lambda_{AA})]}{(1-f)\frac{d\sigma_B}{d\Omega}n_B R_B^2\lambda_{BB}[1-\xi(R_B/\lambda_{BB})]}. \quad (8)$$

Thus, by neglecting the differences in asymmetry parameters and the losses of the main peak due to satellites, the intensity ratio for XPS lines can be written as

$$\frac{I_{A,j=0}}{I_{B,j=0}} = \frac{f}{(1-f)}\frac{T_{E_{k,A}}}{T_{E_{k,B}}}\frac{\sigma_A}{\sigma_B}\times$$

$$\times\frac{n_A R_A^2\lambda_{AA}[1-\xi(R_A/\lambda_{AA})]}{n_B R_B^2\lambda_{BB}[1-\xi(R_B/\lambda_{BB})]}, \quad (9)$$

where T – spectrometer transmission; $E_{k,A}$ – kinetic energy of photoelectrons of the studied element in material A; $E_{k,B}$ – kinetic energy of photoelectrons of the studied element in material B; σ_A – cross-section for the photoionization involving the studied electronic level in atom A; σ_B – cross-section for the photoionization involving the studied electronic level in atom B.

It is easy to show that

$$\frac{n_A}{n_B} = \frac{c_A}{c_B}\frac{\rho_A(100-m_A)}{\rho_B m_A}, \quad (10)$$

where c_A – atomic concentration of the studied element of material A in the sample; c_B — atomic concentration of the studied element of material B in the sample.

Substituting the right sides of Eqs. (2) and (10) for f and n_A/n_B respectively in Eq. (9), we get

$$\frac{I_{A,j=0}}{I_{B,j=0}} = \frac{T_{E_{k,A}}}{T_{E_{k,B}}}\frac{c_A\sigma_A R_B\lambda_{AA}[1-\xi(R_A/\lambda_{AA})]}{c_B\sigma_B R_A\lambda_{BB}[1-\xi(R_B/\lambda_{BB})]}. \quad (11)$$

It should be noted that expression (11) is valid for one layer of particles (for a sample with a low specific surface area in the case of $R_A \ll \lambda_{AA}$, $R_B \ll \lambda_{BB}$).

Thus, the expression derived makes it possible to determine the mean radius of particles of one type under the condition that the mean radius of particles of other type is known and there are experimental data on the intensity ratios for XPS lines.

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КІЛЬКІСНИЙ АНАЛІЗ ДИСПЕРСНИХ СИСТЕМ МЕТОДОМ РФС: МОДЕЛЮВАННЯ ЗМІШАНИХ СИСТЕМ

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Р е з ю м е

Розроблено математичний формалізм для моделювання змішаних систем. Запропоновано метод для кількісного аналізу інтенсивностей спектрів РФС для системи, що складається з двох типів сферичних частинок.

КОЛИЧЕСТВЕННЫЙ АНАЛИЗ ДИСПЕРСНЫХ СИСТЕМ МЕТОДОМ РФС: МОДЕЛИРОВАНИЕ СМЕШАННЫХ СИСТЕМ

И.В.Плюто, А.П.Шпак

Р е з ю м е

Разработан математический формализм для моделирования смешанных систем. Предложен метод для количественного анализа интенсивностей спектров РСФ для системы, которая состоит из двух типов сферических частиц.