

METHOD FOR CONSTRUCTING THE RADIAL DISTRIBUTION CURVES

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A method for constructing the model radial distribution curves of electron density is described. The utility of this technique for the refinement of structure and phase composition for highly disperse materials is demonstrated by reference to several examples.

Keywords: radial distribution of electron density (RDED) method, highly disperse materials.

INTRODUCTION

Traditional X-ray phase analysis compares peak positions (interplanar distances) and intensities on the experimental diffractogram with known values for conjectural phases. For highly disperse materials, phase analysis has certain restrictions because the diffractograms of these substances consist of very diffuse peaks, causing difficulties in peak position and intensity determination. For nanoobjects including catalysts and catalyst supports, determining their phase composition is especially important in view of their high dispersity.

Any structure is characterized by certain interatomic distances r and coordination numbers (c.n.) of atoms. As is known, the crystallite size affects the values of c.n.: it decreases for small coherent scattering regions. In this case, however, at least short contacts are always possible. This fact may be used for phase analysis of X-ray amorphous substances and nanoobjects ($< 30 \text{ \AA}$).

To obtain the values of r and c.n. from diffraction data we employ the radial distribution of electron density (RDED) method [1, 2]. The coordination peaks on the RDED curves are generally described by modified Gaussians [2]. Thus from the values of r and c.n. one can construct a general **model** radial distribution curve. Because of the structural peculiarities of the materials and ambiguous information that may be derived by this technique, data obtained from RDED curves do not always coincide with structural data for known compounds. This necessitates comparison of the RDED curves obtained from the diffraction experiment with the model curves constructed for the assumed phase composition. Moreover, the model curves may be used for determining changes in the local structure of the highly disperse material.

RDED TECHNIQUE

The RDED technique is based on the dependence between the radial distribution of electron density $\rho(r)$ and the experimentally measured intensity of coherent X-ray scattering $i(s)$ corrected for background, polarization, absorption, and Compton scattering expressed in electron units:

$$4\pi r^2 \rho(r) = 4\pi r^2 \rho_0 + 2r / \pi \int_0^\infty si(s) \sin(sr) ds, \quad \rho(r) = \sum_a \sum_b n_a k_a k_b \rho_{ab}(r), \quad (1)$$

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where $\rho_{ab}(r)$ is the distribution of atomic density; n_a is the number of atoms a in the “effective” molecule (in the molecule obtained by calculation from the chemical composition) of the compound under study; k_a and k_b are the effective scattering abilities compared to the unit factor of scattering or the effective number of electrons in atoms a and b , respectively. The ability k_a may be evaluated in different ways. It is estimated here using Weinstein's formula [3]:

$$k_a^2 = \frac{\int_{S_{\min}}^{S_{\max}} f_a^2(s) s^2 ds}{\int_{S_{\min}}^{S_{\max}} f_L^2(s) s^2 ds}, \quad (2)$$

where f_a is the atomic scattering factor of atom a ; f_L is the atomic factor for the lightest atom in the system for which it is set that $k_L = 1$.

The unit atomic factor f_e is determined in the following way:

$$f_e = \frac{\sum_a n_a f_a(s)}{\sum_a n_a k_a}.$$

The density $\rho_0 = \frac{\sum_a (n_a k_a)^2 d N_A}{M}$ is the mean electron density in unit volume, where d is bottle density; N_A is the Avogadro number; M is molar weight; $s = 4\pi \sin(\theta/\lambda)$ is the vector of reciprocal space, where θ is the Wulff–Bragg angle; λ is radiation

wave length; $i(s) = \frac{J(s) - \sum_a n_a f_a^2(s)}{f_e^2(s)}$, where N is the number of accumulated atoms; $J(s) = \frac{J_0(s) - J_{\text{backgr}}(s)}{PA}$, where $J_0(s)$

is the measured intensity of coherent X-ray scattering, $J_{\text{backgr}}(s)$ is background intensity obtained under the same conditions; P is the polarization factor; and A is the absorption factor.

For RDED curve calculations one needs the following experimental and reference data for the substance. Experimental data: X-ray scattering intensities for the sample, background intensities, sample thickness, molding density (these data are relevant to systems of light atoms), chemical composition of the sample ($n_A \dots n_M$) recalculated for the “effective” molecule, bottle density. Reference data: the number of electrons in atoms, absorption coefficients of atoms for the given type of X-radiation, radiation wave length, atomic factors of atoms or ions. The RDED curve is generally plotted in spherical coordinates $4\pi r^2 \rho(r) = f(r)$, where the distance r is expressed in Å, and electron density $\rho(r)$, in $\text{el.}^2/\text{Å}$.

The quantitative parameters of the structure derived from RDED curves are the equilibrium interatomic distances (the values of r at which one can observe electron density peaks), c.n. (determined from the areas under the coordination peaks), mean square displacements of atoms (evaluated from the widths of the coordination peaks), and the distance at which correlation in the atomic arrangement vanishes (distance r starting from which $\rho(r) = \rho_0$). The latter circumstance may be used for evaluating the size of the coherent scattering region [4].

All X-ray diffraction patterns for constructing the experimental RDED curves were obtained on a high-resolution diffractometer (molybdenum radiation, $\lambda = 0.71 \text{ Å}$) at a synchrotron radiation station, Siberian Synchrotron Radiation Center (Institute of Nuclear Physics, Siberian Division, Russian Academy of Sciences) using Si (1.1.1) monochromator crystal on the diffraction beam. Scanning was performed within a wide range of 2θ angles, from 5° to 135° at a step of 0.1° by the point-by-point method; accumulation $\sim 15,000$ pulses at a maximum point.

Original software has been designed at the Institute of Catalysis (Siberian Division, Russian Academy of Sciences) for calculating, processing, and modeling the RDED curves. The curves are constructed and interpreted by selecting a mode in a dialog box. The menu reflects the key stages of calculation: 1) reading and editing the initial file (data from different diffractometers may be used); 2) primary treatment: measurements of the position, intensity, and integrated half-width of the diffraction peaks; 3) correcting the intensity curves by introducing various corrections; 4) data filtration (using Fourier-series expansion); 5) and normalization of the intensity curves by reducing them to electron units.

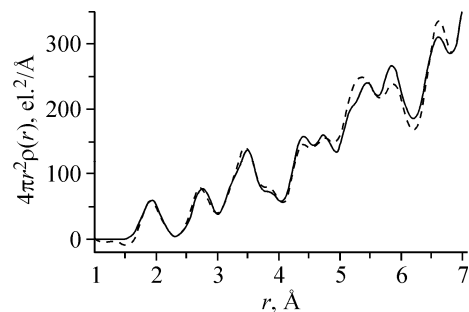


Fig. 1. Experimental (dashed line) and model (solid line) RDED curves of α - Al_2O_3 .

Double normalization (based on the area and long range of angles) and using the experimental scattering factors obtained by smoothing the experimental diffraction pattern are distinctions of our method for calculating the RDED curves [1, 5].

Comparison of the experimental RDED curves with model curves plotted for the hypothetical phase composition of the sample may be used for refining not only the phase composition (primarily, of X-ray amorphous and highly disperse materials), but also the structural features of phases in the material.

The chemical composition and sample preparation procedure suggest which known compounds are the individual phases of the sample. Available structural data (unit cell parameters, space group, atomic coordinates, and site occupancies) for each structure are used for calculating the interatomic distances and c.n. Having determined by formula (2) the required values of k_a , one can calculate the area under the coordination peaks for the same atoms:

$$S = n_a k_a^2 Z_{aa}, \quad (3)$$

and for different atoms:

$$S = n_a k_a k_b Z_{ab}, \quad (4)$$

where Z_{aa} , Z_{ab} is the c.n. for the same and different atoms, respectively.

As mentioned above, the experimental RDED curve may be represented as the sum of modified Gaussians. The same is true of the model curves. This may be represented as

$$4\pi r^2 \rho(r) = \sum_i \frac{S_i}{\sqrt{2\pi b_i^2 \left(1 + b_i^2 / r_i^2\right)}} \exp \left[\frac{(r - r_i)^2}{2b_i^2} \right] \left(\frac{r}{r_i} \right)^2, \quad (5)$$

where r_i is the equilibrium position of the i th maximum; b_i is the standard deviation; S_i is the area of the i th coordination maximum.

The model curves were calculated using the Mathcad-12 program. For model calculations we employed structural data from the ICSD/Retrieve card file [6]. The interatomic distances and coordination numbers were calculated with ICSD/Retrieve and "POLYCRYSTAL" (designed at the Institute of Catalysis) programs [7].

The model plotting procedure was tested on a reference sample of α - Al_2O_3 SRM-676 (powder) provided by the International Center on Diffraction Data (ICDD) [8]. The model curve [6, No. 75559] and the curve obtained by calculation from the experimental diffraction pattern of α - Al_2O_3 are presented in Fig. 1. They coincide with the R factor (6%) [9].

EXAMPLES OF APPLICATION OF THE METHOD

From formula (5) it can be seen that, in addition to the general curve, one can construct "partial" components of the RDED curve, corresponding to the distances between atoms of certain types.

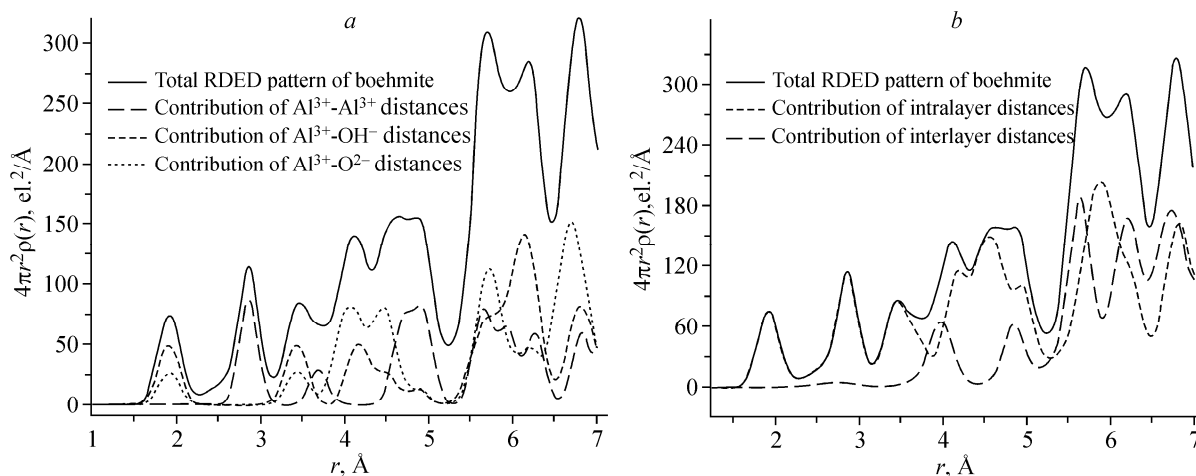


Fig. 2. RDED model curves with components, showing the contributions of several interatomic distances (a) and of intra- and interlayer interatomic distances (b).

Figure 2a shows an example of an RDED model curve for aluminum monohydroxide (crystalline boehmite AlOOH [6, No. 200599]) with “partial” curves corresponding to metal–metal, metal–oxygen, and metal–OH group distances. In the structure of crystalline boehmite, the aluminum atoms are surrounded by a deformed octahedral group of oxygen atoms. The distorted octahedra are linked by their edges and vertices, forming layers stacked along the b axis and linked by multiplet H bonds.

Moreover, for layered structures such as boehmite, the overall curve may be represented in the form of components that reflect contributions from the inter- and intralayer distances (Fig. 2b). This possibility was used in analyzing structural models of another kind of aluminum hydroxide — pseudoboehmite ($\text{AlOOH}\cdot n\text{H}_2\text{O}$, $n = 0.3\text{--}2.0$). As can be seen from the chemical formula, pseudoboehmite differs from crystallized boehmite in the water content in the structure. Pseudoboehmite has a disordered structure and high dispersity (crystallite size ~ 30 Å). This is the starting material for the preparation of one of the most important supports for industrial catalysts. Differences between the structures of crystallized boehmite and pseudoboehmite are revealed in [10].

For different polymorphic modifications, the RDED curves must be different; therefore phase analysis may be performed based on RDED curves if the phases are finely disperse. Figure 3 presents the RDED model curves of three ZrO_2 phases: monoclinic [6, No. 68782], cubic [6, No. 72955], and tetragonal [6, No. 68781]. From Fig. 3 it can be seen that the tetragonal and cubic phases cannot be differentiated from the viewpoint of the RDED method. The distinction of the RDED curves lies in the splitting of the first coordination peak and broadening of several coordination peaks belonging to the zirconium–oxygen distances in the tetragonal phase. The curve of the monoclinic phase, however, differs from the RDED curves of both cubic and tetragonal phases. The use of structural differences between the highly disperse zirconium oxide phases is treated in detail in [9].

The RDED method was employed for the refinement of the phase composition of highly disperse aluminum oxides and hydroxides. Pulsed thermal decomposition of gibbsite $\text{Al}(\text{OH})_3$ is one of the stages of the process for the preparation of aluminum oxides and hydroxides [6, No. 6162]. This stage may be performed as centrifugal thermal activation (CTA) of gibbsite [11] and results in X-ray amorphous aluminum hydroxo oxide. Analysis of the experimental RDED curves of CTA products (Fig. 4) revealed that the latter contain not only aluminum hydroxo oxide, but also a highly disperse bayerite phase, not showing itself as individual diffraction peaks on the diffraction pattern. The RDED curve of the CTA product (Fig. 4, curve 1) has a peak ($r = 5$ Å) at the site of the intense peak on the RDED curve of bayerite (curve 2). Note that this distance is not observed on curve 3 for boehmite. This conclusion about the phase composition of the CTA product of gibbsite explained why rehydration under mild conditions forms the bayerite phase, which is already present as a nucleus in the starting substance [12].

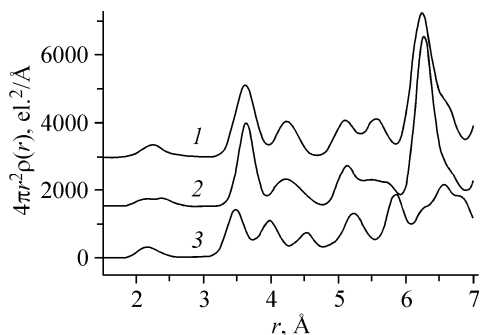


Fig. 3. RDED model curves for the cubic (1), tetragonal (2), and monoclinic (3) phases of zirconium oxide.

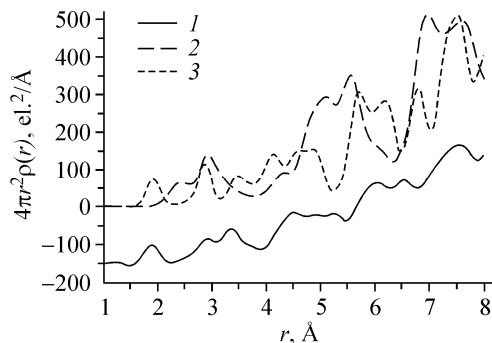


Fig. 4. Experimental RDED curves of highly disperse CTA products of gibbsite (1) and model curves of bayerite (2) and boehmite (3).

One can also construct RDED model curves for mixtures of noninteracting phases and for solid solutions. Comparison of the experimental and model RDED curves of a solid solution may reveal variation of the short-range structure and highly disperse or X-ray amorphous phases present in the substance but not detected on the diffraction pattern [13].

Thus modeling the RDED curves and comparison of the resulting experimental and model curves open up opportunities for more detailed investigation of both the phase composition and the local structure of highly disperse substances including catalysts.

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