

Surface Structure of Nanometer-Sized Zinc Ferrite Particles by the Anomalous X-ray Scattering (AXS) Method

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The atomic structure of nanometer-sized zinc ferrite particles has been studied with the anomalous x-ray scattering (AXS) method as well as the ordinary x-ray diffraction. The analysis of the peak broadening indicated that little microstrain exists in these nanometer-sized particles, and the average size of the particles is estimated to be 4 nm. Since the ratio of atoms located on the surface increases extremely in such fine particles, the contribution of these surface atoms to the x-ray scattering intensity was evaluated. The interference function $Q_i(Q)$ for the surface atoms appears to be similar to that of the zinc-ferrite glass. The experimental intensity is successfully explained by using a simple particle model consisting of the about 0.2 nm thick surface layer having a glass-like structure and the internal atoms having the ferrite crystalline structure.

Introduction

Various reactions occur on the surface of materials and are controlled by the surface structure. Therefore there is an increasing need for structural information about surfaces. Actually, many structural analyses of surfaces have been done by x-ray diffraction, such as the grazing incidence x-ray scattering (GIXS) method [1] and the off-Bragg peak method [2]. In addition to these sophisticated methods, there may be an alternative way to obtain some information on the surface structure of materials.

Gleiter and his colleagues [3] pointed out the extremely large contribution of the interfacial component comprising the atoms situated in the interfaces between nanometer-sized crystalline materials, and tried to determine this interfacial structure by x-ray diffraction in nanometer-sized crystalline iron particles. Because of the large fraction of the surface atoms, nanometer-sized particles show some peculiar features distinct from those in the bulk. The nanometer-sized zinc ferrite particles used in the present study show an extremely large magnetization compared to the value reported for the bulk [4]. In order to explain this characteristic magnetic property, information on the

atomic structure of the surface is required. This prompted us to report the x-ray scattering intensity from nanometer-sized zinc ferrite particles together with comments on their surface structure.

Experimental

Nanometer-sized particles of zinc ferrite crystals were prepared using the coprecipitation method. A 0.1 molar aqueous solution of ZnCl_2 and a 0.2 molar aqueous solution of FeCl_3 were prepared. While a mixture of 100 ml of each solution was being stirred, a 3 N NaOH aqueous solution was added at a fixed temperature to reach a certain pH-value. The precipitated ZnFe_2O_4 particles were dried and used for the x-ray analysis. Observation by transmission electron microscopy indicated that the size of these particles approximately follows a normal distribution function with an average size of 4 nm, 90% of the particles having a size between 2 and 6 nm [5]. Details of the experimental conditions for the preparation of various spinel-type ferrite nanometer-sized particles are found in [6]. For the x-ray measurements, these ultra-fine particles were mounted on a glass sample holder with a hole of 20 mm width and 0.5 mm depth. For comparison, a bulk sample of zinc ferrite was also prepared.

The anomalous x-ray scattering (AXS) measurements were carried out with synchrotron radiation at the Photon Factory of the National Laboratory for High Energy Physics, Tsukuba, Japan. Details of

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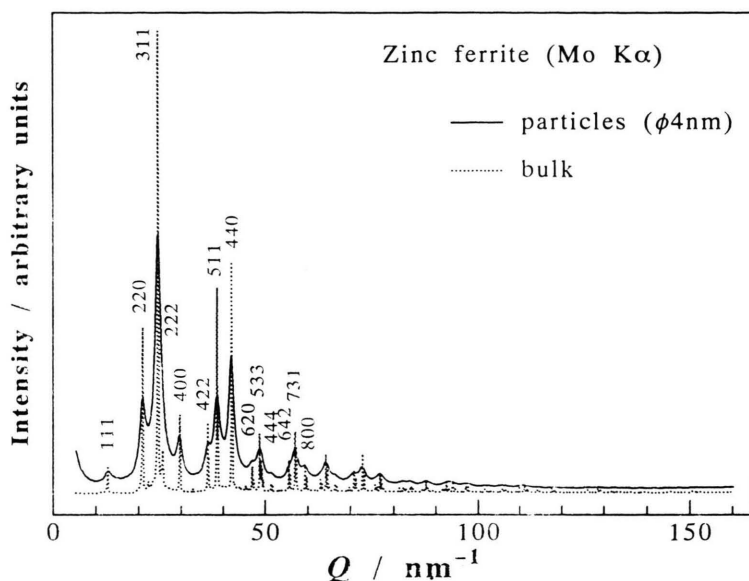


Fig. 1. Comparison of scattering intensities of the nanometer-sized particles (solid) and bulk sample (dotted) of zinc ferrite crystal.

the experimental setting were already explained in [7]. Because of particular near-edge phenomena, e.g. XANES (X-ray Absorption Near Edge Structure) and EXAFS (Extended X-ray Absorption Fine Structure), and very intense fluorescent radiation on the higher energy side of the absorption edge, only the lower energy side was used in the present AXS measurements. Scattering intensities were observed at 9.360 and 9.635 keV below the Zn K-absorption edge (9.660 keV), and 6.811 and 7.086 keV below the Fe K-absorption edge (7.111 keV). The Zn K β and Fe K β radiations overlapping with the elastic scattering in the measurements at 9.635 and 7.086 keV were corrected by a procedure [8] coupled with the measured intensity of Zn K α and Fe K α radiations and the intensity ratios of K α and K β radiations [9], respectively. Scattering intensities were collected with a pure Ge solid state detector in order to eliminate the fluorescent radiation from the sample. These observed intensities were converted to the absolute intensities using the monitor counts by a nitrogen-gas-flow-type ion chamber placed in front of the sample [10] and corrected for polarization, absorption and Compton scattering intensity with the Breit-Dirac recoil factor. The variation detected in the resultant coherent intensities below the Zn and Fe K-absorption edges is attributed only to a change of the real part of the anomalous dispersion terms f' of Zn and Fe, respectively. Therefore, the difference between two scattering

intensities at each absorption edge represents the environmental structure around each Zn or Fe atom.

The ordinary x-ray scattering intensity was also measured with monochromatic MoK α radiation obtained by a sealed molybdenum x-ray tube with a singly bent pyrolytic graphite monochromator in a diffracted beam. The scattering intensities were corrected with a scintillation counter in combination with a pulse height analyzer. The observed intensity was corrected for air scattering, polarization and absorption, and converted to the absolute intensity with the Krogh-Moe-Norman method [11], followed by the correction of the Compton scattering.

For these series of analyses, x-ray atomic scattering factors in the International Tables for X-ray Crystallography, Vol. IV [12] and the anomalous dispersion terms calculated [13] by Cromer and Liberman's scheme [14] and in the International Tables for X-ray Crystallography, Vol. IV [15] were used. For estimating the Compton scattering intensity, the values computed by Cromer *et al.* [16, 17] were employed.

Results

Scattering intensity profiles of the nanometer-sized particles and the bulk sample obtained with MoK α radiation are compared in Figure 1. The positions and relative intensities of the Bragg peaks show no

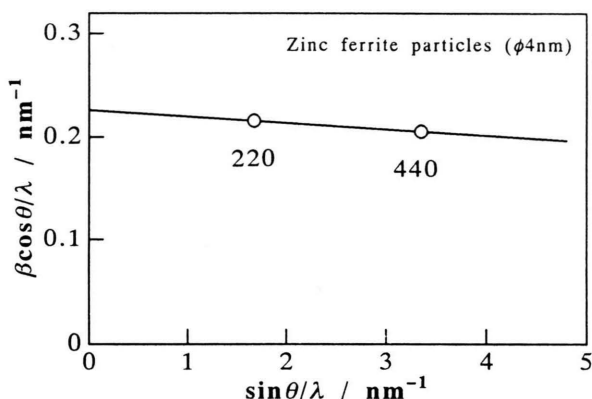


Fig. 2. Hall's plot of $\beta \cos \theta/\lambda$ vs. $\sin \theta/\lambda$ for the nanometer-sized zinc ferrite particles, where β is the integral breadth, θ the scattering angle and λ the wavelength.

difference between the samples although the peaks are extremely broadened for the nanometer-sized particles. This suggests that the fundamental atomic structures are identical in both samples. The peak broadening analysis proposed by Hall [18, 19] was applied to the relatively well separated two Bragg peaks 220 and 440 for the nanometer-sized particle sample in Figure 1. The product of the integral breadth of the peak β and $\cos \theta/\lambda$ is plotted as a function of $\sin \theta/\lambda$ in Figure 2, where θ is the scattering angle and λ is the wavelength of x-rays. According to Hall's theory, the average crystalline size is given by the inverse of the intercept with the ordinate, and the value of the microstrain is evaluated from the slope of the line in Figure 2. The average particle size is found to be 4 nm, which coincides with the value obtained by electron microscopy [5]. The very small value of the slope indicates that the microstrain present in these particles is negligibly small. Thus, the contribution of the microstrain was ignored in further analysis of the scattering intensity profiles.

The scattering intensities of the nanometer-sized zinc ferrite particles measured at 9.361 and 9.636 keV below the Zn K-absorption edge, and at 6.811 and 7.086 keV below the Fe K-absorption edge (7.111 keV) are shown in Figure 3. Their respective intensity differences are also illustrated in Figure 3.

Discussion

The scattering intensity of zinc ferrite crystalline particles with an average size of 4 nm was calculated,

using the following equation based on Warren's approach [20]:

$$I(Q) = \sum_{j=1}^N \sum_{k=1}^N f_j f_k \exp(-2M) \frac{\sin(Qr_{jk})}{Qr_{jk}}, \quad (1)$$

where N is the total number of atoms in a crystalline particle, f_j the x-ray atomic scattering factor of the element j and M the Debye-Waller factor. The Debye-Waller factor of the zinc ferrite particle was computed from the Debye temperature (630 K), which was estimated from the Debye temperatures of ZnO (600 K) and Fe_2O_3 (660 K). The contribution of the interparticle interference is not included in the calculation of the scattering intensity because it has been shown to yield a significant contribution only in the small angle region [21]. Figure 4 shows a comparison of the calculated intensity profile with the experimental one. The disagreement is clearly detected. The following points may also be added. The calculated peak intensities become closer to the experimental ones by choosing a smaller average particle size, but the relatively large background intensity cannot be reproduced by simply changing the particle size. Thus, another model is required for explaining the present experimental data of nanometer-sized ferrite particles.

More than 40% of the total number of atoms are located on the surface of nanometer-sized particles. It is well known that some properties, such as Debye-Waller factor [22], magnetization [4] and melting point [23] for such ultra-fine particles differ from those of the bulk. In a recent study of lead surfaces by the grazing incidence x-ray scattering method, it is found that a few nanometer thick surface has a glass-like structure well below the melting point of the bulk [24]. Molecular dynamics simulations also predicted disordering and melting of the surface of Ni below the melting point [25]. Therefore, let us assume a surface layer of about a mono-layer thickness, 0.2 nm, with a structure different from the bulk. This is schematically shown in Figure 5. The scattering intensity due to atoms inside the particle can be calculated as it is described with a dotted curve in Figure 6. The difference between the experimental and calculated intensities shown at the top of Fig. 6 is readily obtained. A glass-like intensity profile consisting of the broad first peak at about 25 nm^{-1} and the second and third broader and weaker peaks at about 40 and 65 nm^{-1} is obtained from this difference. On the assumption that atoms at the surface are randomly displaced against atoms inside the particle, the average phase shift between atoms

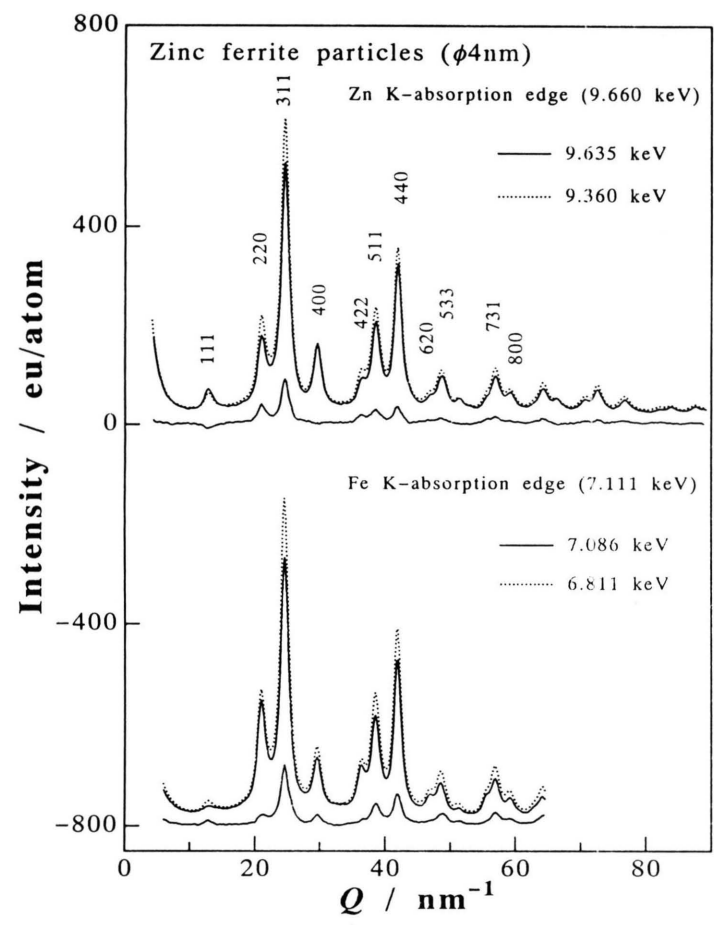


Fig. 3. Scattering intensity profiles and their differences of the nanometer-sized zinc ferrite particles observed at 9.361 and 9.636 keV below the Zn K-absorption edge (top), and at 6.811 and 7.086 keV below the Fe K-absorption edge (bottom). Data for the Fe K-absorption edge are shifted -800 along the y -axis.

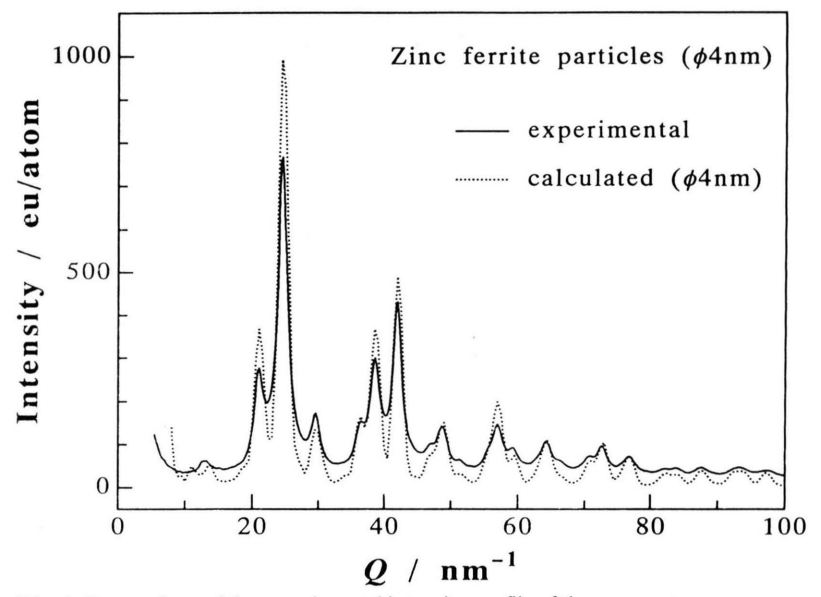


Fig. 4. Comparison of the experimental intensity profile of the nanometer-sized zinc ferrite particles with the intensity calculated with (1) for a 4 nm particle.

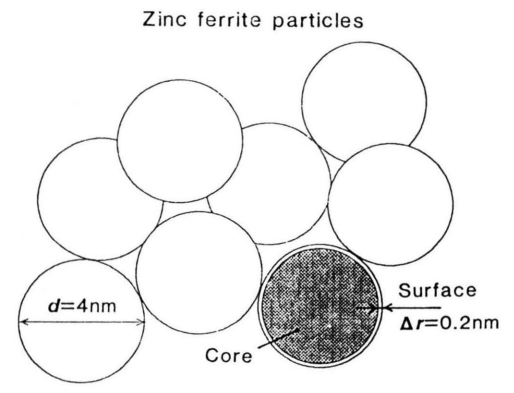


Fig. 5. Schematic diagram of the structural model of the nanometer-sized zinc ferrite particles used for the computation of the scattering intensities.

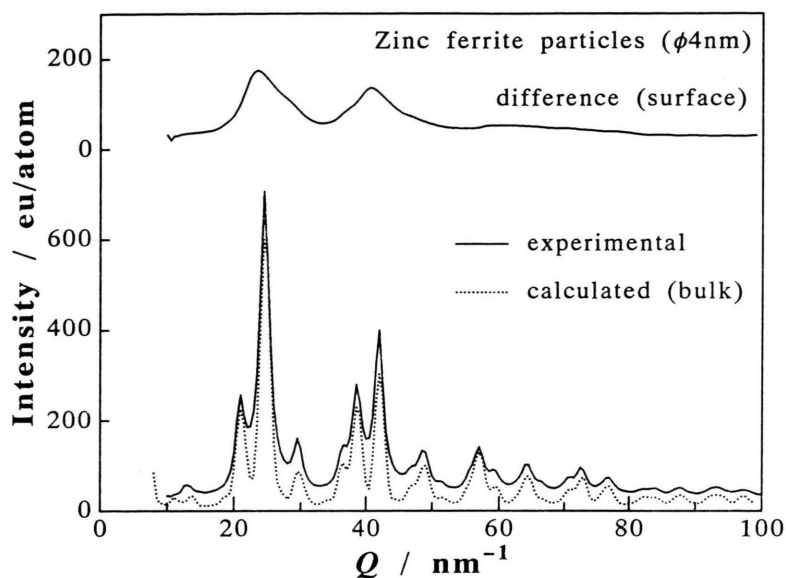


Fig. 6. Intensity difference (top) between the experimental (bottom, solid) and calculated (bottom, dotted) intensity profiles for the nanometer-sized zinc ferrite particles.

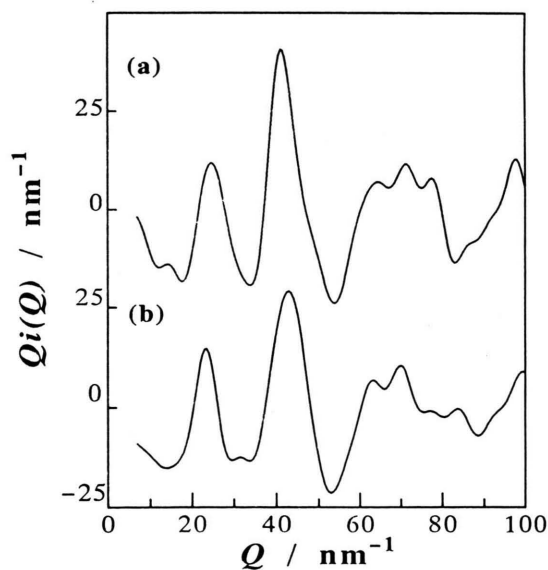


Fig. 7. The interference function $Q_i(Q)$ of (a) the difference between the experimental and calculated intensities for nanometer-sized zinc ferrite particles and (b) zinc ferrite glass grown on a silica glass slide [23].

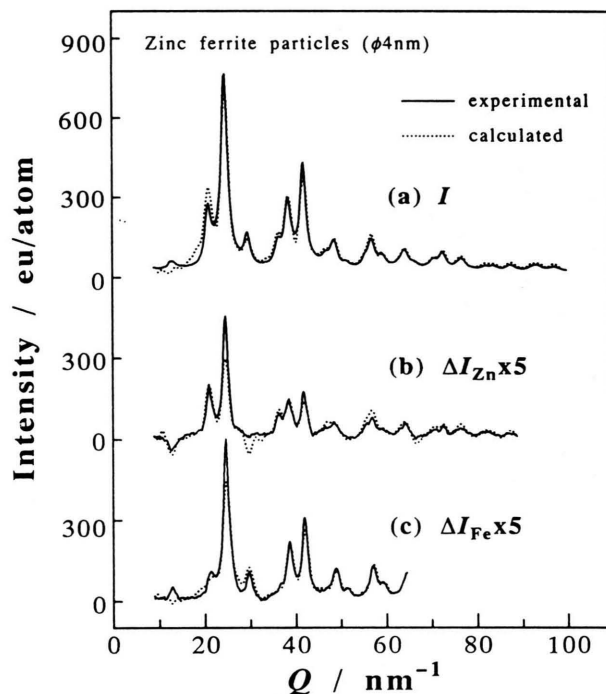


Fig. 8. The experimental (solid) and calculated (dotted) intensity profiles (a) obtained by the ordinary x-ray diffraction with MoK α -radiation and (b, c) by the AXS measurements below the Zn and Fe K-absorption edges, respectively.

at the surface and inside the particle in every direction around the particle becomes zero. Thus, the scattering intensity due to the cross term is considered to contribute much less to the total scattering intensity than those for atoms at the surface and inside the particle. Consequently, the difference in Fig. 6 is attributed to the atoms at the surface. In Fig. 7, the interference function $Q i(Q)$ determined from this intensity difference is compared with the interference function of the zinc ferrite glass grown on a silica glass substrate [26]. Although there are differences in detail, the similarity between these two profiles is readily recognized. This is consistent with the results by the grazing incidence x-ray scattering and by molecular dynamics simulations mentioned above. Although the details of the structure of the surface atoms cannot be deduced in the present study alone, the total scattering intensity was calculated by substituting the scattering intensity of the zinc ferrite glass for the intensity due to the surface component. This is also used for the calculation of the intensity differences in Fig. 3 which were determined in the AXS measurements at the Zn and Fe K-absorption edges. These scattering intensities are compared with the experimental ones in Figure 8.

Quite good agreement was obtained, including the background intensities and peak intensities.

Although the boundary between the surface and bulk components is sharp in the present model, a gradual change from the glass-like structure to the crystal might be more plausible. However, the presence of a glass-like structure on the surface is considered to be in a sense of the necessary condition for explaining the scattering intensities for the nanometer-sized zinc ferrite particles and for reproducing the three independent scattering intensity profiles shown in Figure 8. It would be interesting to extend the present model to other nanometer-sized particles in order to test its validity.

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