Anomalous Scattering Factors near the Zn *K* Absorption Edge Estimated from the Absorption Coefficient Measurement of $ZnFe_2O_4$

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ABSTRACT

The X-ray linear absorption coefficient for $ZnFe_2O_4$ was measured near the Zn K absorption edge in the energy region between 9 and 11 keV. The result was used for determining the imaginary part of the anomalous dispersion factors $f''(E)$ as a function of energy E. The real part of the anomalous scattering factor $f'(E)$ was also estimated from the $f''(E)$ data through the dispersion (Kramers-Krönig) relation. The experimental $f'(E)$ values agree almost within the error bars with the data calculated by the Cromer-Liberman scheme, except for the energy region about 400 eV above the absorption edge.

1. INTRODUCTION

The x-ray scattering amplitude f is known to consist of a photon energy independent f^o term, referred to as Thomson scattering, and the energy dependent real f' and imaginary f'' terms, referred to as anomalous scattering factors; then it can be given as follows /1/:

$$f(Q,E) = f^o(Q) + f'(E) + if''(E) \qquad (1)$$

where Q and E are the wave vector and the energy of the incident x-rays, respectively. Normally, the energy dependent terms of $f'(E)$ and $f''(E)$ are small because x-rays interact weakly with substances of interest and the refractive index is usually only slightly less than one. However, when the energy of the incident x-rays is close to an absorption edge of atom, the changes in f' and f'' terms can no longer be considered as insignificant. Such energy dependent x-rays provide increasingly important probes to study the fine structure or the electronic states of various materials /2/. This is strongly supported by making available the intense white radiation (continuous energy spectrum) from a synchrotron radiation source and thus enabling the use of an energy in which the anomalous scattering is the greatest. This has also led to an increasing need for the accurate values of anomalous scattering factors in the energy region of interest, because there are substantial differences between the experimental data and the relativistic calculation values of the Cromer-Liberman scheme in the energy region about several eV above the absorption edge mainly arising from the EXAFS. The anomalous scattering factors of x-rays are determined experimentally by various methods such as x-ray interferometry /3/, and Kramers-Krönig transformation of the absorption data /4/. There is no result which gives any definite conclusion regarding the superiority of any method to others at the present time. Nevertheless, it may be suggested for structural analysis of various materials that the combination method of the absorption measurement and the dispersion (Kramers-Krönig) relation is one way to determine the anomalous scattering factors of a desired sample, at least in cases when other methods are found to be technically difficult.

The main purpose of this work is to describe the anomalous scattering factors of Zn atoms in the energy region close to the Zn *K* absorption edge estimated from the x-ray absorption coefficient data for a $ZnFe_2O_4$ sample by applying the Kramers-Krönig relation.

2. PRINCIPLE

When an x-ray beam passes through a material, the incident beam intensity I_0 is reduced as follows:

$$I / I_o = \exp(-\mu(E)t) \tag{2}$$

where I is the intensity of the transmitted x-rays and t and $\mu(E)$ are the thickness of the sample and the linear absorption coefficient, respectively. The value of $\mu(E)$ depends upon the substance of interest, its density and the energy of x-rays. The imaginary part of the anomalous scattering factor $f''(E)$ at an energy of E is known to be proportional to the linear absorption coefficient through the following equation:

$$f''(E) = \frac{M\mu(E)}{2r_e N\lambda\rho} \tag{3}$$

where M is the atomic weight, ρ is the density, N is Avogadro's number, and r_e is the classical electron radius. It may be suggested that the $f''(E)$ profile refers to the oscillatory modulation of the x-ray absorption coefficient within a few hundred eV beyond an absorption edge, corresponding to the so-called EXFAS which has recently received much attention for determining the fine structure of materials.

The real part of the anomalous scattering factor $f'(E)$ can be connected with the $f''(E)$ values via the Kramers-Krönig relation as follows /1/:

$$f'(E_o) = \frac{2}{\pi}\int_0^\infty \frac{f''(E)E}{E^2-E_o^2}dE \tag{4}$$

The relativistic treatment of scattering factors is not simple, as recently discussed by Jensen /5/, and then the $f'(E)$ values estimated from the $f''(E)$ data using eq. (4) may not be sufficiently accurate in the strict sense. However, this is only one way to obtain experimentally the anomalous scattering factors of a desired sample without any devised apparatus, as proposed by Kawamura and Fukamachi /4/.

3. EXPERIMENTAL

The absorption measurements were made using an in-house x-ray facility at the Institute for Advanced Materials Processing, Tohoku University. For convenience, the experimental setup is schematically shown in Fig. 1. An 18 kW rotating anode x-ray generator (Rigaku Rotaflex RU-300) with molybdenum target was used as an x-ray source and the incident x-ray energy was selected using 400 reflection from a Ge(100) crystal monochromator in the Johansson configuration. The incidence of the energy between 9 to 11 keV with its band width of about 5 eV was used for the present measurement /6/. It may be added that the x-ray flux was over 10^5 photons/s at the sample position in the operation of 1 kW. An energy up to 36 keV can also be chosen by the higher order reflection of 800, although the incident x-ray beam intensity is reduced by less than two orders of magnitude.

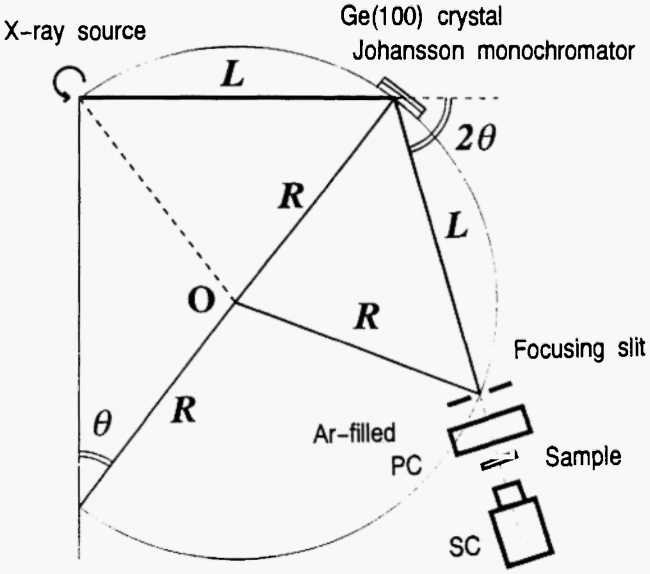

Fig. 1: Schematic diagram of the experimental setup for the present absorption measurements.

A sample was prepared from commercial zinc-ferrite powder of 99.9 mass% purity (Kojundo Chemical Laboratory Co., Ltd.) by heating at 1273 K for 5 days in air /7/. The x-ray diffraction pattern of the prepared sample agreed well with the compiled JCPDS data of No. 22-1021 and the measured lattice constant was $a = 0.84411$ nm. The $ZnFe_2O_4$ sample was diluted to 10 mass% in Li_2CO_3 in order to prepare a homogeneous sample for the following absorption measurement. The powders were sufficiently mixed by grinding in an agate mortar, and then 748 mg of the mixture was packed into a hole (20 x 18 x 1.5 mm^3) of an aluminium plate. The incident x-ray beam intensity was monitored by an Ar-filled proportional counter (PC) placed in front of the sample. The intensities through the sample were measured using a scintillation counter (SC). At each energy at least 800,000 counts and about 1,300,000 counts on average were accumulated. The value of $\mu_{sample}(E)$ can be obtained by comparing the measuring intensity data with and without the sample in the x-ray beam path.

4. RESULTS AND DISCUSSION

The measured intensities indicate marked variations near the *K* absorption edges due to the resonant anomalous scattering phenomena /1/. Figure 2 shows the energy dependence of $\mu_{sample}(E)$ calculated from the measured intensity for the $ZnFe_2O_4$ sample. In order to $\mu_{Zn}(E)$ from measured $\mu_{sample}(E)$, the contribution of factors of $\mu_M(E)$ (M = Fe, C, Li and O) should be considered. For this purpose, the theoretical values of $\mu_M(E)$(M = Fe, C, Li and O) were employed in the present calculation /8,9/. The estimated contributions of $\mu_M(E)$ are also illustrated in Fig. 2. As easily seen in eq. (4), the range of the integral is from zero to infinity, whereas the available experimental data are usually limited due to some technical reasons. However, the contribution of the $f''(E)$ values away from a desired energy is known to be extremely small because of the factor of $E/(E^2 - E_0^2)$. Therefore, the values of theoretical $\mu_{Zn}(E)$ are reasonably linked with measured $\mu_{Zn}(E)$ for the calculation of $f'(E)$ by the Kramers-Krönig relation of eq. (4). Particularly, the full profile of $f''(E)$ for the calculations of $f'(E)$ is shown in Fig. 3.

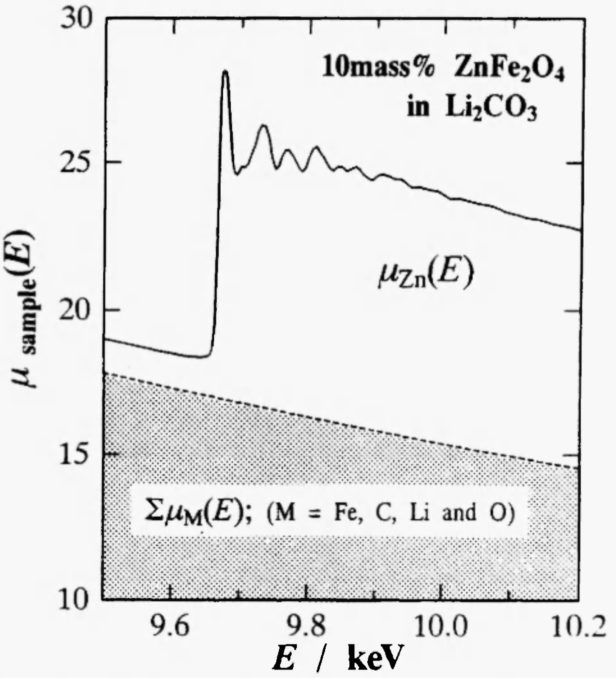

Fig. 2: Measured value of $\mu_{sample}(E)$ as a function of energy.

The resultant $f''(E)$ and $f'(E)$ values for Zn near the Zn *K* absorption edge are illustrated in Fig. 4. The theoretical anomalous scattering factors by the Cromer-Liberman scheme /8,9/ are also given in this figure for comparison. It should be stressed here that the calculated value of $f'(E)$, more or less, includes some errors because of the limited range of the integral between a lower value E_{min} and an upper value of E_{max}. Such a point has readily been confirmed by the results of Fig. 4, estimated from the $f''(E)$ data with three different energy ranges. Of course, when only very limited $f''(E)$ data are used for integration, one can find some different features such as a positive shift of 0.5 electron from the theoretical values (see Fig. 4), although the profile itself is unchanged.

The fine structures are found in the experimental $f''(E)$ curve at the higher energy side of the absorption edge, which corresponds to EXAFS. Such fine structures are not reproduced by the Cromer-Liberman theory for an isolate atom without any solid state effects including the solid-state-induced EXAFS oscillations. There is a systematic relation that $f'(E)$ behaves like a differential value of $f''(E)$. Namely, the $f'(E)$ curve shows the fine structures in the energy region about

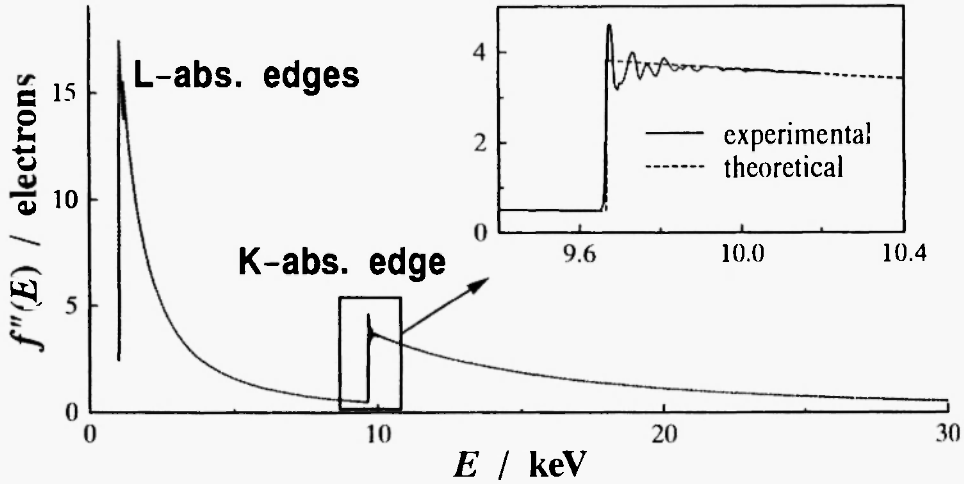

Fig. 3: The full profile of $f''(E)$ for the calculation of $f'(E)$. The dotted lines denote the theoretical values /8,9/.

several hundred eV above the absorption edge. It is also mentioned here that the near edge values of $f'(E)$ depend mainly upon the form of the $f''(E)$ curve in the energy region where the drastic change appears.

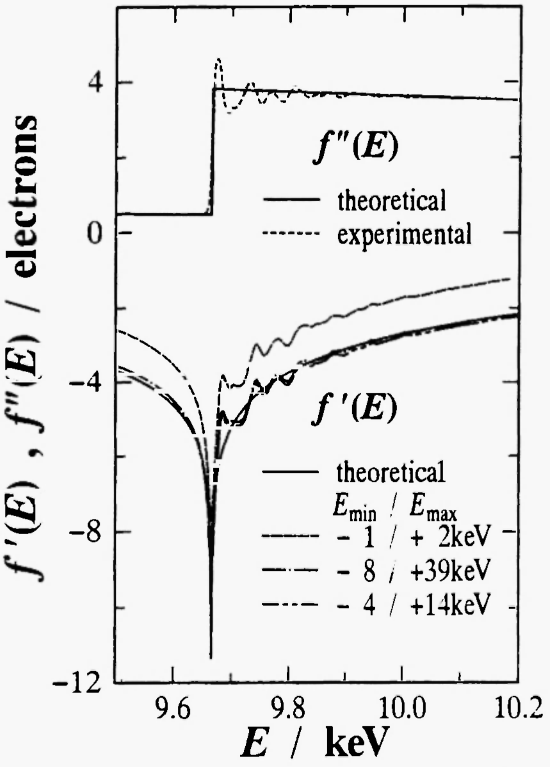

Fig. 4: Energy dependence of anomalous scattering factors $f'(E)$ and $f''(E)$ for Zn in $ZnFe_2O_4$. The solid lines denote the theoretical values calculated by the Cromer-Liberman scheme /8,9/.

The agreement between the experimental data of $f'(E)$ and $f''(E)$ and the theoretical values of the Cromer-Liberman scheme is, in the authors' view, rather surprisingly good because characteristic behavior of the theoretical anomalous scattering factors includes a relatively narrow and deep minimum in $f'(E)$ or a sharp increase in $f''(E)$ near the absorption edge. However, the free-atom assumption of the theoretical values limits their applicability to the structural studies using the anomalous x-ray scattering, mainly because of the neglect of solid state effects such as white lines /10,11/. White lines are known to be strong and sharp maxima in f'' at the higher energy site of the absorption edge which results from transitions to a high density of unoccupied states. This suggests the following point: In the near edge region, particularly in the higher energy region of about 400 eV above the absorption edge, we requested to check the difference between the experimental data of f' and f'' and the theoretical values before structural studies are processed. On the other hand, at the lower energy side of the absorption edge, the solid state effects are less important and the theoretical anomalous scattering factors may reasonably be allowed for use in structural analysis.

The accurate determination of the absolute values for the anomalous scattering factors is not yet established and the experimental values of f' and f'' may be less accurate in some cases than those required for structural analysis. Nevertheless, it may be concluded that the combination method of the absorption measurement and the dispersion relation is one way to obtain the anomalous scattering factors of a desired sample experimentally. In addition, this method is fairly simple and useful for both crystalline and non-crystalline systems.

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