Acta Crystallographica Section A
Foundations of Crystallography
ISSN 0108-7673

Received 7 September 2004
Accepted 24 August 2005

Anomalous scattering factor determined by semicircle fitting near the *K*-absorption edge of Ge

Masami Yoshizawa,[a]* ShengMing Zhou,[b] Riichirou Negishi,[a] Tomoe Fukamachi[a] and Takaaki Kawamura[c]

[a]Saitama Institute of Technology, Fusaiji, Okabe, Saitama 369-0293, Japan, [b]Shanghai Institute of Optics and Fine Mechanics, Chinese Academy of Science, Tacheng Road 295, Jiading, Shanghai, People's Republic of China, and [c]University of Yamanashi, Kofu, Yamanashi 400-8510, Japan. Correspondence e-mail: yoshizaw@sit.ac.jp

It is shown that the locus of the $f' + if''$ plot in the complex plane, f' being determined from measured f'' by using the dispersion relation, looks like a semicircle very near the absorption edge of Ge. The semicircular locus is derived from a quantum theory of X-ray resonant scattering when there is a sharp isolated peak in f'' just above the *K*-absorption edge. Using the semicircular behavior, an approach is proposed to determine the anomalous scattering factors in a crystal by fitting known calculated values based on an isolated-atom model to a semicircular focus. The determined anomalous scattering factors f' show excellent agreement with the measured values just below the absorption edge. In addition, the phase determination of a crystal structure factor has been considered by using the semicircular behavior.

1. Introduction

The anomalous scattering factor ($f' + if''$) of an atom varies remarkably with respect to X-ray energy near its absorption edge. This variation can be utilized in many ways such as in a phase determination of a crystal structure factor and a study of X-ray magnetic scattering (Materlik *et al.*, 1994). However, it is not easy to calculate accurately the anomalous scattering factors very near an absorption edge owing to several factors such as the conduction band structure and the intermediate state lifetime of the scattering process. For this reason, the crystal structure analysis by multiwavelength anomalous diffraction is carried out in most cases at energies far from the absorption edge. If more accurate anomalous scattering factors are available very near the absorption edge, the structure analysis should be much improved.

In this paper, we report on the semicircular behavior of the $f' + if''$ plot by analyzing the values of $f' + if''$ across Ge *K*-absorption edge and its application to the correction of well known calculated anomalous scattering factors. Semicircular behavior is obtained when the values of f'' are obtained by measuring *K*-edge XANES of Ge and those of f' are calculated from these f'' using the dispersion relation (Kawamura & Fukamachi, 1978). We show that we can derive semicircular behavior of an $f' + if''$ plot by assuming an isolated peak in f'' just above the absorption edge. As an application, we show that the calculated values of the anomalous scattering factor in a crystal are determined from those based on an isolated-atom model (Sasaki, 1989) by using the semicircular behavior. The results are compared with the values obtained by two other methods: calculation based on an isolated-atom model and use of the dispersion relation. We also discuss a potential application to the determination of the phase of a crystal structure factor by using the semicircular behavior.

2. Experiment

The experiment was carried out using X-ray synchrotron radiation (SR) at BL-15C, Photon Factory, KEK, Japan. The X-rays from SR were monochromated by an Si 111 double-crystal monochromator. The energy resolution in this optical set-up was about ± 0.5 eV. The sample Ge crystal was first mechanically polished and then chemically polished to remove the strained layer due to the mechanical polishing. It was a parallel plate with a thickness of approximately 27 μm. The values of f'' in Fig. 1 were obtained by measuring the absorption coefficient (XANES) around the Ge *K*-absorption edge with an energy step of 0.5 eV. The errors of the measured values were within 1%. The ordinate f'' was scaled by adjusting the values of XANES spectra far from the *K* edge to coincide with those calculated by Sasaki (1989) using the method of Cromer & Liberman (1970) (CLS). The values of f' in Fig. 1 were determined from measured f'' by using the dispersion relation. The resultant values are listed in Table 1.

3. Correction by semicircle fitting

Fig. 2 shows the locus of the anomalous scattering factor $f' + if''$ when the X-ray energy is changed across the Ge *K*-absorption edge. The abscissa represents f' and the ordinate f''. The dashed line shows the values evaluated by CLS, the solid line those calculated by the formula of Parratt &

Hempstead (1954) using the oscillator strength from Cromer (1965) (PH), and the filled circles the experimental values in Fig. 1. In Fig. 2, there are distinct differences between the loci of $f' + if''$ obtained by CLS and by PH, although both methods are based on an isolated-atom model. One difference is that the lifetime $\tau = \hbar/\Gamma$ (Γ is the natural width of the spectrum) of the intermediate state is taken into account in PH but not in CLS. The experimental values agree with the values of PH better than with those of CLS. This shows the importance of taking the lifetime into account in the calculation of the anomalous scattering factor around the absorption edge. It is noted that the locus of $f' + if''$ with f' determined by using the dispersion relation from f'' obtained by measuring XANES looks like a semicircle in the energy region near the K edge as shown in Fig. 2. A similar semicircular locus of $f' + if''$ has been reported by Sakamaki *et al.* (1980) near the K edge of Zn in hemimorphite.

According to a quantum theory of X-ray resonant scattering (Fukamachi & Hosoya, 1975), the anomalous scattering factor is given by

$$f' + if'' = -\sum_n \frac{\omega_{n0} g_{0n}}{2}\left(\frac{1}{\omega_{n0} - \omega + i\Gamma_{0n}/2} + \frac{1}{\omega_{n0} + \omega}\right) \quad (1)$$

under the dipole approximation. Here the atomic unit ($\hbar = m = e = 1$) is used. The suffix n expresses the nth excited state with energy E_n, $n = 0$ being the ground state with energy E_0. ω is the incident X-ray energy and $\omega_{n0} = E_n - E_0$. Γ_{0n} is the spectral width of the excited state. g_{0n} is given by

$$g_{0n} = (2/\omega_{n0})|\langle\varphi_n|\mathbf{e}\cdot\mathbf{P}|\varphi_0\rangle|^2, \quad (2)$$

where φ_n and φ_0 are the wavefunctions of the excited and the ground states, respectively, **e** is the polarization vector and **P** is the momentum vector of an electron. When only one excited state (n) is dominant in the energy region (ω) very close to ω_{n0}, equation (1) can be written as

$$f' + if'' = \frac{\omega_{n0} g_{0n}}{2}\frac{1}{\omega - \omega_{n0} - i\Gamma/2} + f'_b + if''_b, \quad (3)$$

where $f'_b + if''_b$ is assumed to be constant within $\pm\Gamma/2$ ($= \Gamma_{0n}/2$) around ω_{n0}. If we put the first term of the right-hand side of equation (3) as

$$\frac{\omega_{n0} g_{0n}}{2}\frac{1}{\omega - \omega_{n0} - i\Gamma/2} = \Delta f' + i\Delta f'' = \frac{\Delta f''_M \Gamma/2}{\omega - \omega_{n0} - i\Gamma/2}, \quad (4)$$

with $\Delta f''_M \Gamma$ being equal to $\omega_{n0} g_{0n}$ and constant, we obtain the relation

$$(\Delta f')^2 + \left(\Delta f'' - \frac{\Delta f''_M}{2}\right)^2 = \left(\frac{\Delta f''_M}{2}\right)^2. \quad (5)$$

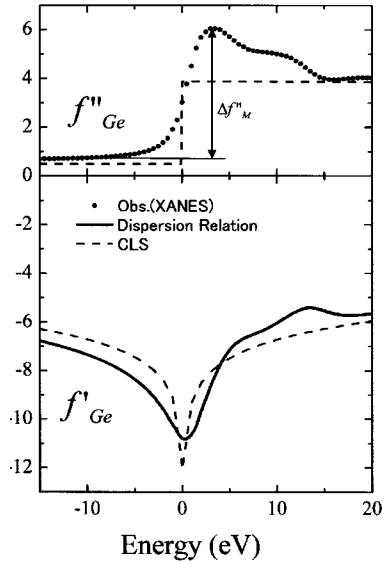

Figure 1
Measured anomalous scattering factors near the Ge K-absorption edge. The values of f''_{Ge} (filled circles) are obtained by measuring the absorption coefficients and those of f'_{Ge} (solid line) are obtained from f''_{Ge} by using the dispersion relation. The dashed lines are the values calculated by CLS.

Table 1
Values of f' and f'' of Ge as a function of X-ray energy near the K-absorption edge .

The second column shows f' obtained from measured absorption coefficient f'' by using the dispersion relation. The fourth and fifth columns show f' and f'' obtained by the semicircle correction.

	Dispersion relation		Semicircle correction	
Energy (keV)	f'_{Ge}	f''_{Ge}	f'_{Ge}	f''_{Ge}
11.088	−6.78	0.70	−6.84	0.60
11.089	−6.88	0.70	−6.94	0.61
11.090	−6.98	0.71	−7.05	0.63
11.091	−7.09	0.72	−7.18	0.64
11.092	−7.22	0.73	−7.31	0.66
11.093	−7.35	0.74	−7.46	0.69
11.094	−7.50	0.76	−7.62	0.73
11.095	−7.67	0.78	−7.80	0.77
11.096	−7.87	0.81	−8.01	0.82
11.097	−8.09	0.85	−8.25	0.90
11.098	−8.36	0.90	−8.52	1.00
11.099	−8.68	0.99	−8.84	1.13
11.100	−9.08	1.13	−9.22	1.34
11.101	−9.60	1.38	−9.66	1.64
11.102	−10.2	1.92	−10.2	2.12
11.103	−10.8	3.01	−10.7	2.88
11.104	−10.6	4.51	−10.7	4.04
11.105	−9.66	5.68	−9.71	5.37

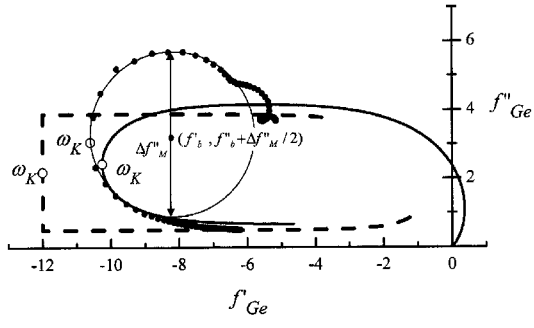

Figure 2
Plot of f'_{Ge} *versus* f''_{Ge}. The dashed line and the solid line are the values calculated by CLS and PH, respectively. The filled circles are the values of f'_{Ge} and f''_{Ge}, with f'_{Ge} obtained from the measured f''_{Ge} by using the dispersion relation.

The locus of $f' + if''$ is a circle as a function of ω, with its center at $(f'_b, f''_b + \Delta f''_M/2)$ and the radius $\Delta f''_M/2$.

In the following, we assume that ω_{n0} is the energy corresponding to the initial peak position of $\Delta f''$, and that $\Delta f''_M$ is the diameter of the circle as shown in Fig. 2 and corresponds to the peak height without background as shown in Fig. 1. In order to determine the values of $f' + if''$ in equation (3), it is necessary to determine the values of $f'_b + if''_b$. We used the calculated values of $f'_b + if''_b$ based on an isolated-atom model, as it is known that they show good agreement with the experimental values except for the energy region near an absorption edge. By using the measured results, $\Delta f''_M$ and $\Gamma/2$ in equation (4) are determined to be 5.38 and 2.8 ± 0.5 eV, respectively. The value of $\Gamma/2$ contains the error due to the resolution of the optical system (± 0.5 eV). In order to make the $\Delta f'' + f''_b$ curve fit better to the measured f'' (XANES) curve, the value of $\Gamma/2$ is adjusted to be 2.5 ± 0.5 eV. It is five times larger than that calculated by the classical damping (0.5 eV) and corresponds to a lifetime of 0.13 ± 0.03 fs. $\Delta f'$ and $\Delta f''$ thus obtained are shown in Fig. 3. As the values of f' determined by measuring *Pendellösung* fringes due to resonant scattering are in good agreement with those calculated by CLS in the energy range of 50–300 eV below the Ge *K*-absorption edge (Fukamachi *et al.*, 1990), the calculated values by CLS are employed as $f'_b + if''_b$. In order to avoid the divergence in the real part of the anomalous scattering factor by CLS at the absorption edge, a fixed value at $\omega_{0n} - \Gamma/2$ is assumed in the range between $\omega_{0n} - \Gamma/2$ and $\omega_{0n} + \Gamma/2$. The resultant values of $\Delta f'$ and $\Delta f''$, f' and f'' are obtained as shown in Figs. 3 and 4 and are listed in Table 1.

4. Results and discussion

The following results are obtained in the above experimental and theoretical investigations.

1. The semicircular locus of $f' + if''$ near the *K*-absorption edge of Ge is obtained. This is because f'' increases rapidly and forms a sharp peak just above the edge.

2. The semicircular locus of $f' + if''$ is utilized to determine the values of $f' + if''$ in a crystal from the calculated values based on an isolated-atom model (referred to as the semicircle correction). The natural width of the excited state has been obtained.

3. The anomalous scattering factors after the semicircle correction are in good agreement with previously determined experimental values (Fukamachi *et al.*, 1990; Katoh *et al.*, 1985) as shown in Fig. 4.

4. The f' spectrum obtained by using the dispersion relation is asymmetric with fine structures on the higher-energy side of the *K* edge and the values on the low-energy side down to -30 eV below the edge are approximately 10% smaller than those based on an isolated-atom model. The difference can be explained by the contribution of the $\Delta f'$ term given by the semicircle correction as shown in Fig. 4.

In the semicircle correction, the precise measurement of the first peak height ($\Delta f''_M$) above the absorption edge (ω_K) is important. However, the energy resolution in the present experiment was approximately ± 0.5 eV for measuring $\Delta f''_M$. The resolution of the optical system must be improved by several times in order to determine the width Γ more accurately. It may look a coarse approximation that f'_b is constant in the energy range between $\omega_{0n} - \Gamma/2$ and $\omega_{0n} + \Gamma/2$. But if we

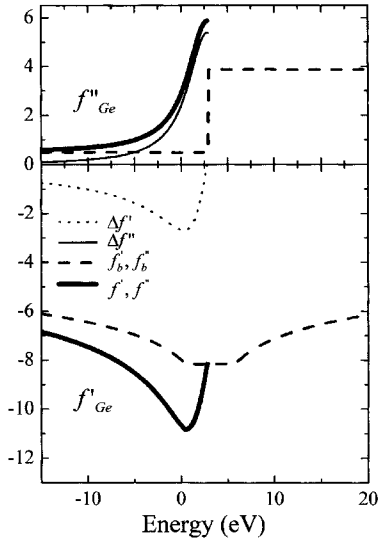

Figure 3
Anomalous scattering factors of Ge with semicircle correction near the Ge *K*-absorption edge. The thick solid lines f'_{Ge} and f''_{Ge} are the real and imaginary parts of the anomalous scattering factor after semicircle correction, respectively. The thin solid line and the dotted line are the values of $\Delta f'$ and $\Delta f''$, respectively. The dashed lines are the values calculated with CLS.

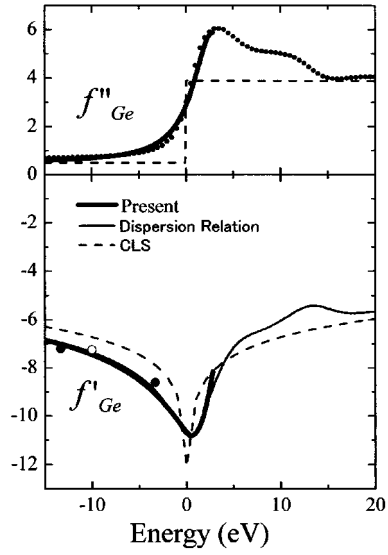

Figure 4
Anomalous scattering factors near the Ge *K* edge. The thick solid line represents the values after semicircle correction to values calculated by CLS. The dashed line represents the values calculated by CLS. The thin solid line represents values obtained by using the dispersion relation. For f'', the filled circles represent values obtained using the dispersion relation. For f', the open circle shows the experimental value from the *Pendellösung* beat method (Fukamachi *et al.*, 1990) and the filled circles show the experimental values from the prism method (Katoh *et al.*, 1985).

consider the influence of the lifetime corresponding to the natural width of the spectrum (approximately several electronvolts) on the calculation of f'_b near the absorption edge (Fukamachi *et al.*, 1993), the error in f'_b should be very small. We can justify the assumption.

We can apply the result of the semicircle fitting to the phase determination of a crystal structure factor. When there is one resonant atom in a unit cell, the crystal structure factor $F_h(\omega)$ can be written as

$$F_h(\omega) = |F_h^0| \exp(\phi_h) + f'(\omega) + if''(\omega),$$

assuming the resonant atom is at the origin of the unit cell. Here $|F_h^0| \exp(\phi_h)$ is the crystal structure factor without the anomalous scattering. As shown above, we are able to obtain the values of $f'(\omega) + if''(\omega)$ using the semicircle behavior. Suppose that we choose two energies ω_1 and ω_2 (here $\omega_1 < \omega_K$ and $\omega_2 > \omega_K$) at which the condition $f'(\omega_1) = f'(\omega_2)$ is satisfied. In Fig. 5, the two points are given by $f'(\omega_1) + if''(\omega_1)$ and $f'(\omega_2) + if''(\omega_2)$, and indicated by filled circles. We use equation (4) to choose the energies. When the integrated intensities at ω_1 and ω_2 are measured, $|F_h(\omega_1)|$ and $|F_h(\omega_2)|$ are obtained.

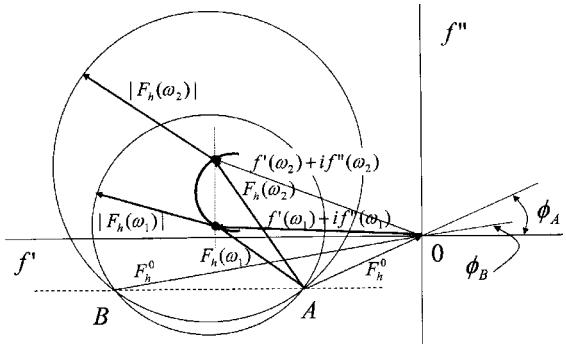

Figure 5
Schematic diagram of phase determination of a crystal structure factor using semicircular behavior of the anomalous scattering factor across the absorption edge. The abscissa represents f' and the ordinate represents f''.

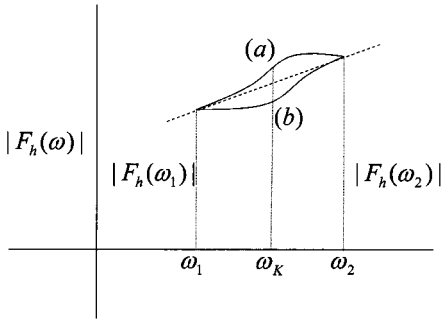

Figure 6
Values of $|F_h(\omega)|$ as a function of X-ray energy around the absorption edge. Curve (*a*) represents the locus of $|F_h(\omega)|$ ($\omega_1 < \omega < \omega_2$) corresponding to point *A* in Fig. 5 and curve (*b*) represents the locus corresponding to point *B*.

As shown in Fig. 5, if we plot two circles, one with radius $|F_h(\omega_1)|$ and its center at $f'(\omega_1) + if''(\omega_1)$, and the other with radius $|F_h(\omega_2)|$ and its center at $f'(\omega_2) + if''(\omega_2)$, we have two crossing points (*A* and *B*). The line connecting these two points is parallel to the abscissa f'. Either vector $\overrightarrow{AO}$ or $\overrightarrow{BO}$ corresponds to the crystal structure factor to be determined. One of these points (*A* or *B*) should be chosen. In experiments using SR, it is easy to measure the integrated intensities in the energy region between ω_1 and ω_2 simultaneously by tuning the energy width of the incident X-rays to the region across the absorption edge. If the measured curve of $|F_h(\omega)|$ ($\omega_1 < \omega < \omega_2$) shows the value above the dashed line [the straight line from $|F_h(\omega_1)|$ to $|F_h(\omega_2)|$] as curve (*a*) in Fig. 6, the vector $\overrightarrow{AO}$ is chosen as the right structure factor. If $|F_h(\omega)|$ shows the value below the dashed line as curve (*b*), the vector $\overrightarrow{BO}$ is chosen as the right structure factor. We can determine the phase of the crystal structure factor uniquely.

As shown above, the values of $f' + if''$ vary remarkably within the energy range approximately several electronvolts around the absorption edge. If the diffracted intensity is measured by tuning X-ray energy across the absorption edge of a resonant atom in a crystal after improving the energy resolution up to 0.1 eV, it is possible to determine the phase of the crystal structure factor precisely by utilizing the semicircular locus of $f' + if''$.

The authors are particularly indebted to Professor M. Tokonami of Saitama Institute of Technology (SIT) and Professor T. Fujikawa of Chiba University for valuable discussions. They are also grateful to Dr K. Hirano of the Photon Factory at KEK, and Dr I. Matsumoto and Mr T. Akagawa of SIT for their help in some experiments. This work was partly supported by the 'High-Tech Research Center' Project for SIT: matching fund subsidy from MEXT (Ministry of Education, Culture, Sports, Science and Technology), 2000–2004.

References

Cromer, D. T. (1965). *Acta Cryst.* **18**, 17–23.
Cromer, D. T. & Liberman, J. (1970). *J. Chem. Phys.* **53**, 1891–1898.
Fukamachi, T. & Hosoya, S. (1975). *Acta Cryst.* A**31**, 215–220.
Fukamachi, T., Negishi, R., Yoshizawa, M., Ehara, K., Kawamura, T., Nakajima, T. & Zhao, Z. (1993). *Acta Cryst.* A**49**, 573–575.
Fukamachi, T., Yoshizawa, M., Ehara, K., Kawamura, T. & Nakajima, T. (1990). *Acta Cryst.* A**46**, 945–948.
Katoh, H., Shimakura, H., Ogawa, T., Hattori, S., Kobayashi, Y., Umezawa, K., Ishikawa, T. & Ishida, K. (1985). *J. Phys. Soc. Jpn*, **54**, 881–884.
Kawamura, T. & Fukamachi, T. (1978). *Jpn. J. Appl. Phys.* **17**, Suppl. 17-2, 224–226.
Materlik, G., Sparks, C. J. & Fischer, K. (1994). *Resonant Anomalous X-ray Scattering*. Amsterdam: Elsevier Science.
Parratt, L. G. & Hempstead, C. F. (1954). *Phys. Rev.* **94**, 1593–1600.
Sakamaki, T., Hosoya, S. & Fukamachi, T. (1980). *Acta Cryst.* A**36**, 183–189.
Sasaki, S. (1989). KEK Report 88-14 M/D, pp. 1–136.