

15.4-3 ATOMIC POSITIONS OF K-SHELL ELECTRONS OBSERVED BY SR X-RAY ANOMALOUS SCATTERING. By Satoshi SASAKI and Katsuhiko TSUKIMURA*, Photon Factory, National Laboratory for High-Energy Physics, Oho-machi, Ibaraki 305, Japan and *Geological Survey of Japan, Yatabe-machi, Ibaraki 305, Japan.

The synchrotron radiation with continuous spectrum is of great advantage to use the anomalous scattering effect for most atoms. We propose here an analysis method of diffraction where only the electrons at some specific energy levels are observable instead of a mass of electrons. With this new method for x-ray diffraction data at some wavelengths, one can utilize x-ray anomalous scattering to truly pinpoint the atoms of a specific kind as if x-rays interact only with electrons around the atoms.

We define the shell structure factor in order to extract the x-ray intensity by anomalous scattering from the total integrated intensity:

$$S^{hkl} = \sum_i \langle a_{ij}^{-1} \rangle (F^{hkl}(\lambda_j) - F^{hkl}(\lambda_0)) = \sum_i \exp 2\pi i (h x_i + k y_i + l z_i) \exp(-W_i)$$

where λ_j and λ_0 are wavelengths near the K-absorption edge of an atom and far from the edge, respectively, and the matrix element of $\langle a \rangle$ is given by

$$a_{ij} = f'_i(\lambda_j) - f'_i(\lambda_0) + i(f''_i(\lambda_j) - f''_i(\lambda_0))$$

and its inverse matrix is written as $\langle a^{-1} \rangle$.

An orthopyroxene with the composition of (Co,Ni,Zn)SiO₃ (Co:Ni:Zn = 1:1:1; Pbcn; a = 18.209(1), b = 8.915(1), c = 5.2182(4) Å) has been chosen to observe independently each of Co, Ni, and Zn atoms in the two crystallographic sites. The site occupancy of M1 and M2 sites were preliminarily determined using anomalous scattering (Table 1). X-ray intensity data for a spherical crystal were measured by using four wavelengths: Mo K α ($\lambda = 0.7107$ Å) and wavelengths longer than Co, Ni, and Zn absorption edges by 0.01 Å ($\lambda = 1.6168, 1.4968, \text{ and } 1.2926$ Å). Complete intensity profile data near K absorption edges were collected using a vertical type four-circle diffractometer at the BL-10A station of Photon Factory. The matrix $\langle a \rangle$ was obtained from the anomalous scattering factors calculated with Cromer and Liberman's method. Atomic coordinates from the K-shell electrons can be obtained by means of the least-squares method by minimizing the residual factor of shell structure factors.

The atomic positions for Co, Ni, and Zn atoms in the M1 and M2 sites based on K-shell electrons are listed in Table 1. Because the positional shift on the ab plane in the M2 site is dominant, the distributions have been schematically drawn in Fig. 1. The Ni atoms in the M2 sites were found to have a deviation of 0.16 Å from the average position. The second largest deviation by 0.1 Å is for the Zn atoms in the M1 sites. It is observed above that the atoms less likely occupy each site when their displacement becomes larger. This view is consistent with a crystal structure framed by flexible oxygen positions and the layers of MO₆ polyhedra.

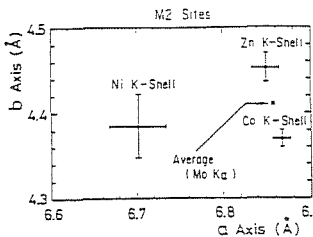


Fig. 1,

Table 1,

	Occupancy	x(Å)	y(Å)	z(Å)
M1 Sites				
Co	0.27(1)	6.86(1)	5.82(1)	4.57(1)
		[0.02]	[-0.01]	[-0.02]
Ni	0.53(2)	6.85(1)	5.84(1)	4.60(1)
		[0.01]	[0.01]	[0.01]
Zn	0.20	6.94(4)	5.80(4)	4.59(4)
		[0.10]	[-.03]	[0.00]
Average	6.8414(4)	5.8266(3)	4.5910(4)	
M2 Sites				
Co	0.39	6.87(1)	4.37(1)	1.92(1)
		[0.01]	[-0.04]	[-0.02]
Ni	0.14	6.70(3)	4.38(4)	1.95(4)
		[-.16]	[-.03]	[0.01]
Zn	0.46	6.85(2)	4.45(2)	1.95(2)
		[-.01]	[0.04]	[0.01]
Average	6.8565(5)	4.4102(4)	1.9433(4)	

15.5-1 PROFILE ANALYSIS ON THE BASIS OF THE ENERGY DISPERSIVE SPECTRA AT HIGH PRESSURE AND TEMPERATURE USING SYNCHROTRON RADIATION. By T. Yamanaka and K. Ogata, Mineralogical Institute, Faculty of Science, University of Tokyo, 3-1 Hongo, Tokyo 113, Japan. Production Engineering Research Laboratory, Hitachi Ltd., 292 Yoshida-cho, Totsuka, Yokohama 244, Japan.

X-ray diffraction experiments with polychromatic photons (white X-ray radiation) can be made by means of energy dispersive (ED) measurements under the condition of a fixed optical geometry. Synchrotron X-radiation (SR) has the following excellent properties for ED measurements: a) Smooth wave-length distribution without any characteristic X-rays; b) high intensity through wide energy range; c) highly collimated beam providing high energy resolution. These advantages of SR have been reported for ED powder diffraction studies. The ED method also enables us to undertake quick spectrum measurements and time dependent studies such as phase transformations at elevated temperature and/or under high pressure.

Profile of the ED spectra. The diffraction intensity $y(E_i)$ by the ED method is expressed by the following equation, in consideration of the relation, $E_{hkl} = 12.983/2d_{hkl} \sin \theta$ (KeV) at the Bragg angle θ ,

$$y(E) = \frac{I_0(E)}{16\pi} \left[\frac{e^2}{4\pi\epsilon_0 mc} \right]^2 h^2 c^4 \frac{1}{E_j} \left[\frac{N^2 Z V}{r} \right] \left[P |F_{hkl}|^2 \exp(-2B \frac{E^2 \sin^2 \theta}{h^2 c^2}) A(E) \right]$$

Since the number of photons varies with the energy E_i , a source brightness calculated by the second order Bessel function directly contributes to the intensity $I_0(E_i)$. Mass absorption coefficient as a function of energy $A(E_i)$ is calculated from Victoreen (1948, 1949). An intrinsic Ge SSD has a large dynamic range from 2 KeV to 100 KeV. The counting efficiency at each channel has been tested in advance by an isotope source.

The correction of the counting loss caused by the dead time of the linear amplifier has been made. An absorption edge of Ge is present at 11.1 KeV, at which the counting efficiency indicates a discontinuity. A photon counting correction is made for the escape peaks at the energy $E_i - E_f$, where E_f is an energy of the X-ray fluorescence of Ge. Compton peaks caused by the X-ray recoil are subtracted from the ED spectrum, which is eminent especially at high energies under the condition of light elements in the sample. An ED spectrum after the intensity data process including the subtraction of the background is expressed by the pseudo-Voigt function, which is a sum of Gaussian and Lorentzian function. The variation of FWHM of the diffraction peaks with energy is taken into account.

A computer program for ED spectrum least-squares fitting considers the following parameters: lattice constant, structure factor, modified pseudo-Voigt shape function, FWHM parameters (UVW), asymmetry parameters of the profile, and background.

ED profile fitting of GeO₂ at high pressures and temperatures. ED measurements were made for powder diffraction under high pressures and temperatures using a diamond anvil pressure cell. A platinum ring heater and thermocouple are installed in the cell, which easily generates pressures and temperatures up to 20 GPa and 550°C. NaCl powder is also placed in the cell for an internal standard of the pressure calibrant. In order to avoid the effect of grain growth on the diffraction intensity, the diamond anvil is oscillated around the incident beam.

ED pattern fitting experiments for GeO₂ polymorphs, trigonal (P3₂, z=3) and tetragonal (P4₂/mmm, z=2) phases, have been performed at high temperatures and pressures. Structure variations were elucidated with a high accuracy. The kinetics of the transition at high temperatures and pressures were also examined.