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Structural strain in pyrites evaluated by X-ray powder diffraction

K. SASAKI, H. KONNO, M. INAGAKI
Faculty of Engineering, Hokkaido University, Sapporo 060, Japan

Two parameters for measuring the structural strain, the effective Debye–Waller parameter, B_{eff}, and lattice strain, ε, were evaluated on a natural pyrite (FeS_2) after grinding. The effective Debye–Waller parameter, B_{eff}, which depends on the displacement of atoms in the crystal, was calculated for the overall crystal, $B_{eff}(FeS_2)$, and for sulphur, $B_{eff}(S)$, from the intensities of the X-ray diffraction lines. The $B_{eff}(S)$ increased markedly with increasing grinding time, while $B_{eff}(FeS_2)$ did not change significantly. The lattice strain, ε, was not recognized. These observations suggest that the displacement of sulphur atoms preferentially takes place by grinding. The relations between these B_{eff} values and crystallite size, L, were observed to be common for two different methods of grinding. This tendency was considered to be an inherent property of pyrite. The value of $B_{eff}(S)$ is a useful index to estimate mechanically caused strain in pyrite.

1. Introduction

The chemical and biological decomposition of sulphide minerals has been studied [1–4], in relation to environmental problems and also to the establishment of a new process for recovering natural resources. The biological oxidation of sulphide minerals has been developed in the field of mining to recover useful metals from low-grade ores; this is termed bacterial leaching. During the experiments, it was inferred that the grinding may alter the properties of both surface and bulk sulphide minerals and affect the solubility in acidic solutions. It was also reported that the pretreatment of ground pyrite (FeS_2) affects the oxidation rate and the reproducibility of the data [5, 6]. This suggests the necessity to evaluate the strain in the crystals of minerals which is induced by mechanical treatment.

Two parameters have been proposed to measure the strain in crystalline powders caused by mechanical force; the effective Debye–Waller parameter, B_{eff}, and lattice strain, ε. The former depends on the displacement of constituent atoms of the crystal from their equilibrium positions and is measured from the diffraction intensities of X-rays. Inagaki *et al.* studied the changes of B_{eff} with grinding on different crystals [7–12]. On certain crystal structures, it is possible to calculate the B_{eff} values for each constituent atom, for example those of lead and sulphur for lead sulphide, PbS [10, 11]. The lattice strain, ε, of PbS may be determined from the slope of the relation between width and diffraction index of X-ray diffraction lines, according to Hall's equation [13]. A simple calculation shows that this lattice strain, ε, is mainly due to the fluctuation of interlayer spacing in the crystal [13].

Pyrite (FeS_2) has a cubic structure based on the NaCl type: the sodium site is occupied by iron and the chlorine site by the mid-point of the couple S_2. Because of this structure, it was found that only the B_{eff} values for sulphur in the crystal could be evaluated in addition to that for the overall crystal. The strain in pyrite crystals has not been measured, as far as we know.

In the present work, the changes in the effective Debye–Waller parameters, B_{eff}, for sulphur and the overall pyrite crystal, and also in lattice strain, ε, in pyrite caused by the two different grinding methods, were evaluated.

2. Experimental procedure

2.1. Pyrites sample and grinding methods

The sample pyrite was supplied from Yanahara Mines (Okayama, Japan). The metal composition in the sample was determined by inductively coupled plasma–atomic emission spectroscopy (ICP–AES), after decomposition in a 5:1 mixture of HNO_3 and HF at 150 °C for 2 h [14], as shown in Table I. No diffraction lines other than FeS_2 were observed with this sample, except for a very weak single line of SiO_2 ($d = 0.388$ nm).

The sample was ground by the following two methods, using a cell and balls made of tungsten carbide.

Method 1. Grinding was performed in one step using a Blender mill 3800 (Pitchford Co. Ltd, USA). The sample was ground for 2–30 min under the following conditions: rotation rate, 2850 r.p.m.; fractional packing volume of balls, 0.153; weight of feed, 5.0 g; feed size, d_{50}, 3.0 mm.

Method 2. Grinding was performed in two steps using a planetary-type ball mill P-5 (Fritsch Co. Ltd, Germany). First, the sample was ground for 15 min under the following conditions: rotation rate,

TABLE I Composition (mg g^{-1}) of the pyrites from Yanahara (Japan)[a]

Na	Al	Si	P	K	Ca	Mn	Fe	Cu	Zn	Unknown residues
0.046	1.38	12.0	0.806	1.05	1.36	0.055	458	2.10	2.22	520.983

[a] Owing to the decomposition of pyrite, an accurate content of sulphur was not obtained [14].

TABLE II Structure factor, F, and multiplicity, p, of pyrites and the theoretical relative intensities, I_{cal}, calculated for pyrites

$(h\,k\,l)$	F	p	I_{cal}
(5 1 1)	$4f_{Fe} + 4.12f_s$	24	32.46
(4 2 2)	$4f_{Fe} - 0.14f_s$	24	13.86
(3 3 2)	$3.63f_s$	24	4.45
(4 2 1)	$5.01f_s$ $0f_s$	24 24	8.98
(4 2 0)	$4f_{Fe} - 1.06f_s$	24	14.03
(3 3 1)	$4f_{Fe} - 1.80f_s$	24	12.20
(3 2 1)	$5.01f_s$ $2.84f_s$	24 24	20.72
(2 3 0)	$6.64f_s$ $0f_s$	12 12	15.89
(2 2 2)	$4f_{Fe} + 0.02f_s$	8	16.30
(3 1 1)	$4f_{Fe} + 2.49f_s$	24	100.00
(2 2 0)	$4f_{Fe} + 0.15f_s$	12	51.70
(2 1 1)	$-3.92f_s$	24	43.25
(2 1 0)	$5.20f_s$ $0f_s$	12 12	50.85
(2 0 0)	$4f_{Fe} + 1.10f_s$	6	95.69
(1 1 1)	$4f_{Fe} - 3.43f_s$	8	38.79

2000 r.p.m.; fractional packing volume of balls, 0.251; weight of feed, 160 g; feed size, d_{50}, 3.0 mm. It was then reground for 10–60 min under the following conditions: rotation rate, 2000 r.p.m.; fractional packing of balls, 0.261; weight of feed, 40 g.

Specific surface area, S_{BET}, of the ground samples was determined by the nitrogen adsorption BET method with a Quantasorb QS-13 (Yuasa Ionics Co. Ltd, Japan).

2.2. X-ray diffraction analysis

The X-ray diffraction patterns of the ground samples were collected by an XRD 3063 diffractometer (Rigaku, Japan) with a monochromator under the following conditions: radiation, CuK_α, 30 kV, 20 mA; time constant, 1 s; scanning rate, 0.5 in 2θ, deg $\min^{-1}$; chart speed, 40 mm $\min^{-1}$. The diffraction angle was corrected with the peaks from NaCl [15].

The effective Debye–Waller parameter, B_{eff}, was determined from the following equation [7, 8]

$$\ln\{I_{obs}(h\,k\,l)/I_{cal}(h\,k\,l)\} = \ln k - 2B_{eff}\sin^2\theta/\lambda^2 \quad (1)$$

where $I_{obs}(h\,k\,l)$ is an integrated intensity observed on the $h\,k\,l$ line of pyrite, $I_{cal}(h\,k\,l)$ the theoretical intensity of $h\,k\,l$ line, k a scale factor, λ the wavelength of the X-ray used ($\lambda = 0.15405$ nm), and θ the Bragg angle. The theoretical intensity, I_{cal}, was calculated from

$$I_{cal}(h\,k\,l) = \mathrm{LP}|F(h\,k\,l)|^2 pA \quad (2)$$

where LP is the Lorentz-polarization factor, $F(h\,k\,l)$ the structure factor, p the multiplicity, and A the absorption factor. In the present work, A was assumed to be constant over the experimental range of $\sin^2\theta/\lambda^2$ because of the high mass absorption coefficient of pyrite (191 $cm^2\,g^{-1}$) and thick specimen (1 mm). The structure factor, F $(h\,k\,l)$, of pyrite was calculated from the atomic scattering factors of each atom, f_{Fe} and f_s, and their equivalent positions in a unit cell.

Fe: $(0, 0, 0)$, $(0, 1/2, 1/2)$, $(1/2, 0, 1/2)$, and

$(1/2, 1/2, 0)$.

S: (x, x, x), $(1/2 + x, 1/2 - x, -x)$,

$(-x, 1/2 + x, 1/2 - x)$, $(1/2 - x, -x, 1/2 + x)$,

$(-x, -x, -x)$, $(1/2 - x, 1/2 + x, x)$,

$(x, 1/2 - x, 1/2 + x)$,

and $(1/2 + x, x, 1/2 - x)$

where x is known to be 0.386 [16]. When diffraction indices, $h\,k\,l$, are all even or all odd, $F(h\,k\,l)$ depends on both f_{Fe} and f_S, and in the other cases $F(h\,k\,l)$ depends only on f_S, as summarized in Table II. In this table, the multiplicity, and theoretical intensity for each diffraction line of pyrite are also listed.

The lattice strain, ε, was evaluated from the following equation

$$\beta_{obs}\cos\theta/\lambda = K/L + 2\varepsilon\sin\theta/\lambda \quad (3)$$

where β_{obs} is the observed full-width at half maximum, FWHM, of a diffraction peak, K a shape factor, equal to 0.89 in the present case, L the crystallite size, and ε a lattice strain. The β_{obs} values were determined for Cu$K_{\alpha1}$ by computer fitting using a Cauchy function. By plotting $\beta_{obs}\cos\theta/\lambda$ against $\sin\theta/\lambda$, both the lattice strain, ε, and crystallite size, L, were obtained.

3. Results and discussion

The effective Debye–Waller parameter was calculated from the slope of a linear relation between $\ln\{I_{obs}(h\,k\,l)/I_{cal}(h\,k\,l)\}$ and $\sin^2\theta/\lambda^2$ according to Equation 1. Fig. 1a is for the diffraction lines with all even and all odd indices, and Fig. 1b for those with mixed indices. From Fig. 1a, the effective Debye–Waller parameter for the overall crystal, $B_{eff}(FeS_2)$, was calculated for each ground sample and that for sulphur, $B_{eff}(S)$, from Fig. 1b. These two values, $B_{eff}(FeS_2)$ and $B_{eff}(S)$, measured on the samples ground by the two methods are listed in Table III, as a function of the grinding time, t_G. A large scattering of experimental points on the sample ground for a short

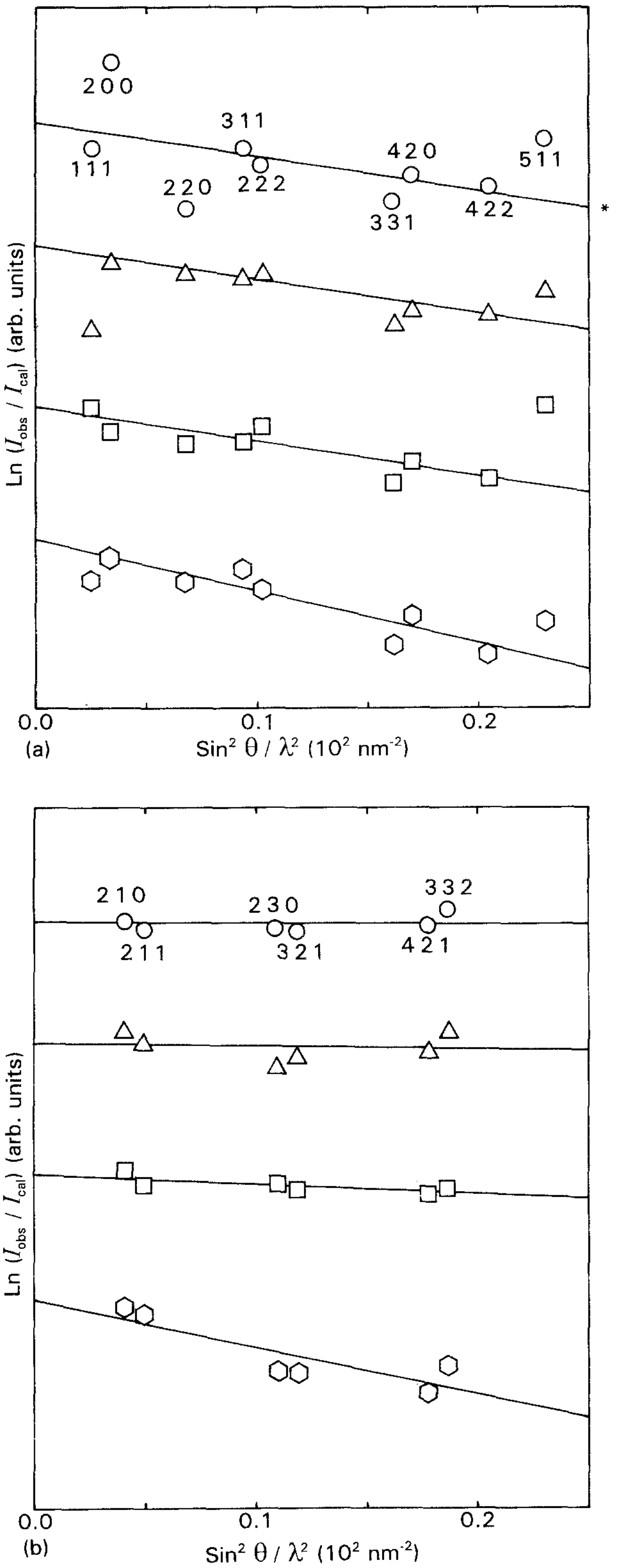

Figure 1 Plots of $\ln(I_{obs}/I_{cal})$ against $\sin^2\theta/\lambda^2$ to evaluate the effective Debye–Waller parameter, B_{eff}, in grinding Method 1. (a) Miller indices are all even or all odd. (b) Miller indices are sets of both even and odd. t_G: (○) 2 min, (△) 10 min, (□) 20 min (⬡) 30 min.

TABLE III Changes of the effective Debye–Waller parameter, B_{eff}, the crystallite size, L, and the specific surface area, S_{BET}, with the grinding time, t_G, in the two methods

Method	t_G (min)	$B_{eff}(FeS_2)$ (nm^2)	$B_{eff}(S)$ (nm^2)	L (nm)	S_{BET} (m^2g^{-1})
1	2	7.3×10^{-3}	4.3×10^{-4}	81	2.5
	10	7.8×10^{-3}	6.6×10^{-4}	63	5.5
	20	7.8×10^{-3}	2.1×10^{-3}	54	7.5
	30	1.0×10^{-2}	1.1×10^{-2}	46	6.8
2	$15^a + 0^b$	$-^c$	$-^c$	46	0.85
	$15^a + 10^b$	7.0×10^{-3}	1.8×10^{-3}	49	2.0
	$15^a + 20^b$	6.5×10^{-3}	6.4×10^{-3}	45	3.2
	$15^a + 60^b$	7.8×10^{-3}	7.7×10^{-3}	41	6.0

[a] In the first step.
[b] In the second step.
[c] Cannot be estimated.

time (* in Fig. 1) is probably due to large grains of pyrite crystal.

In Table III, $B_{eff}(S)$ increases with increasing t_G, and $B_{eff}(FeS_2)$ does not show a marked change in either grinding method. At the beginning of grinding by Method 1 the value of $B_{eff}(S)$ is much smaller than $B_{eff}(FeS_2)$, increases about two orders of magnitude after 30 min grinding, and becomes very close to the B_{eff} (FeS_2) value. This change in B_{eff} is also recognized in the results with grinding Method 2. This suggests that sulphur atoms in pyrite tend to be displaced from the equilibrium positions by grinding, while the displacement of iron atoms is not so large.

The plots of $\beta_{obs} \cos\theta/\lambda$ versus $\sin\theta/\lambda$ for 10 and 30 min ground samples by Method 1 are shown in Fig. 2, as examples. The slope of an approximately linear relation was negligibly small on all ground samples, so that the value of ε was calculated to be very small in the present samples. The result suggests that there is no noticeable lattice strain, in other words, no appreciable scattering in spacings in the pyrite samples ground. The intercept on the y-axis by extrapolating the linear relation increases with increasing t_G; that is, the crystallite size, L, decreases with t_G. The crystallite size, L, measured on each ground sample is listed in Table III.

The BET surface area, S_{BET}, is also shown in Table III; the area increases with grinding. The changes in L and S_{BET} suggest that the two grinding methods exert different effects on pyrite.

It was reported for diatomic crystals that B_{eff} values for the overall crystals were close to those for the heavy atoms [10]. With lead sulphide, for example, $B_{eff}(PbS)$ was almost equal to $B_{eff}(Pb)$, and $B_{eff}(S)$ was

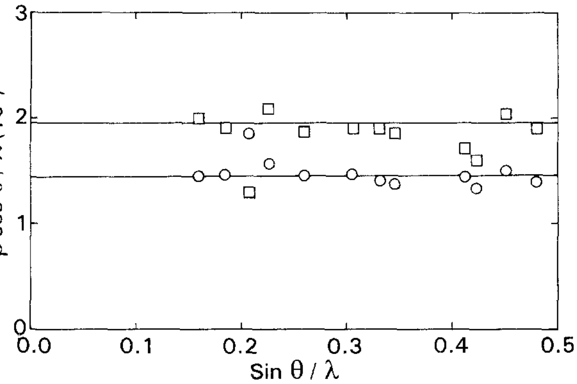

Figure 2 Plots of $\beta \cos\theta/\lambda$ against $\sin\theta/\lambda$ to evaluate the crystallite size, L, and a lattice stain, ε, in grinding Method 1. t_G: (○) 10 min, (□) 30 min.

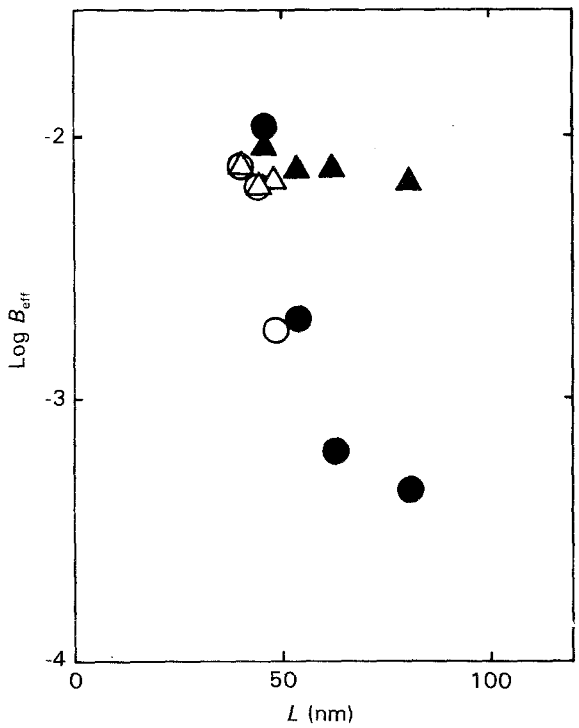

Figure 3 Relationship between B_{eff} and L. (▲, △), $B_{eff}(FeS_2)$; (●, ○), $B_{eff}(S)$, for methods (▲, ●) 1 and (△, ○) 2.

very small in comparison with $B_{eff}(Pb)$ [11]. Although B_{eff} values for iron, $B_{eff}(Fe)$, cannot be evaluated for pyrite, it is supposed that the heavy atom, iron, governs the B_{eff} values of the overall crystal $B_{eff}(FeS_2)$; in other words, the contribution of $B_{eff}(S)$ to $B_{eff}(FeS_2)$ is small, as shown for other diatomic crystals such as PbS [10]. On grinding, however, $B_{eff}(S)$ increases markedly; that is, mainly the displacement of sulphur occurs, probably due to rotation of S_2 couples. The plots of $B_{eff}(FeS_2)$ and $B_{eff}(S)$ against L (Fig. 3) show clearly the mutual relation between two B_{eff} values mentioned above. Fig. 3 also shows that the relations between these three parameters are common for the two grinding methods, in spite of results indicating that the two methods exerted different effects on pyrites, as mentioned above.

In pyrites, the displacement of sulphur atoms from their equilibrium positions by grinding was observed, but the fluctuation of interlayer spacing was not recognized. This is considered to be an inherent property of pyrite; due to the presence of S_2 couples. With longer grinding time than used in the present experiments, there is a possibility that displacement of heavy iron atoms and also lattice strain may occur in pyrite. However, after 60 min grinding with Method 1, the surface of pyrite spontaneously ignited when exposed to air. This is the reason why the sample with the longer grinding time was abandoned in the present work.

The evaluation of the structural strain in pyrites was found to give important information on the structural changes with grinding, and so was valuable for understanding the solubilities of pyrite in acidic solutions. Further details will be reported elsewhere [4].

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