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Determination of Fe/Ni Distribution in Pentlandites

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Abstract

The Fe/Ni distributions in the octahedral and tetrahedral sites of natural and heated pentlandites, $Fe_{4\cdot40}Ni_{4\cdot57}Co_{0\cdot03}S_8$, and synthetic pentlandite, $Fe_{5\cdot00}Ni_{4\cdot00}S_8$, have been determined by the X-ray powder method employing the anomalous dispersion of Fe $K\beta$ and Cu $K\alpha$ radiations. In order to eliminate the effect of preferred orientation the ratio of structure factors for the two radiations was used for the structure refinement. The Fe/(Fe + Ni) ratio in the octahedral sites of natural pentlandite is determined as $0\cdot84 \pm 0\cdot11$ ($R = 4\cdot11\%$), that of the heated one as $0\cdot30 \pm 0\cdot09$ ($R = 3\cdot32\%$) and that of the synthetic one as $0\cdot39 \pm 0\cdot04$ ($R = 1\cdot42\%$).

Introduction

A unit cell of pentlandite [$Fm3m$ (No. 225), $a_o \sim 10\cdot1$ Å] contains four formula units of $(Fe, Ni)_9S_8$. S atoms form an almost cubic-close-packed framework, and metal atoms occupy four of the octahedral sites, $M(O)$, and 32 of the tetrahedral sites, $M(T)$, within the S framework (Lindqvist, Lundqvist & Westgren, 1936). Recently the crystal structure was refined by Hall & Stewart (1973) and Rajamani & Prewitt (1973), but the cation distribution between $M(O)$ and $M(T)$ sites was not determined because of the similarity between the X-ray scattering factors of Fe and Ni.

Indication of the cation ordering has, however, been noticed in lattice-parameter measurements and Mössbauer studies. Knop, Ibarahim & Sutarno (1965) observed that the lattice parameters of pentlandite increase by ~0·5% on heating *in vacuo* or in argon atmosphere and that the expansion of the unit cell, which takes place between 423 and 473 K, is not prevented by argon pressure up to 0·2 GPa. A Mössbauer study by Knop, Huang & Woodhams (1970) showed an enrichment of Fe in $M(O)$ sites for natural pentlandite and migration of Fe to $M(T)$ sites on heating. Vaughan & Ridout (1971) reported, however, almost disordered distribution of Fe and Ni for natural pentlandites on the basis of their Mössbauer work.

Determination of the Fe/Ni distribution of pentlandites is significant for studying the genesis of Ni ore deposits because the site preference in the crystal may reflect the thermodynamical conditions of the surroundings. If the Fe/Ni distribution does differ between natural and heated pentlandites, the natural crystal may have grown or been metamorphosed under conditions different from those of the heated one.

In this study we determine the Fe/Ni distribution in pentlandites by the X-ray diffraction technique employing the anomalous-dispersion effect. The degree of ordering is compared with the previous results of the Mössbauer study.

Experimental

Selection of X-ray wavelengths

The X-ray anomalous-dispersion effect is well known to increase the difference in the atomic scattering factors for two cations with neighbouring atomic numbers. With the appearance of synchrotron radiation as a tunable X-ray source, the effect has been widely applied to the determination of cation ordering, for example, in cobalt ferrite by Yakel (1980), $Cr_{48}Fe_{52}$ by Yakel (1983) and $Fe_xV_{3-x}S_4$ by Nakazawa, Tsukimura, Hirai & Wada (1983).

In this study the diffraction intensities are measured by the powder method, as samples are easy to obtain. The powder method has, however, the serious problem that the observed intensities are influenced by preferred orientation which is not completely avoidable in mounting the samples and makes the determination of the Fe/Ni distribution in pentlandite difficult. To solve this problem the ratios of the structure factors for the two X-ray wavelengths are used for structure refinement. The technique has been applied to determine the Mn/Fe distribution in ferrites (Skolnick, Kondo & Lavine, 1958; Rieck & Driessens, 1966; Yamanaka & Nakahira, 1973).

The selection of the two X-ray wavelengths is based on the following consideration. As pentlandite is centrosymmetric, the imaginary dispersion correction has

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only a minor contribution to the structure factor. The values of f_0+f' should, therefore, be considered in selecting the appropriate X-ray wavelengths. To determine cation ordering by the ratio of structure factors, the two wavelengths, λ_1 and λ_2, must be chosen to give a large value for

$$|[f'(\lambda_1, \mathrm{Fe})-f'(\lambda_2, \mathrm{Fe})]-[f'(\lambda_1, \mathrm{Ni})-f'(\lambda_2, \mathrm{Ni})]|,$$

where $f'(\lambda, M)$ is the real part of the anomalous-dispersion correction of the M atom by the X-rays of wavelength λ. Thus, Fe $K\beta$ ($\lambda_1 = 1{\cdot}757$ Å) and Cu $K\alpha$ ($\lambda_2 = 1{\cdot}542$ Å) radiations have been selected in this experiment.

Sample

Three samples with different thermal histories are used in this study. One is a natural pentlandite separated from the Sudbury Fe–Ni ore. Another is the same natural specimen, but heated and annealed at 523 K for 1 d. The other is a synthetic pentlandite prepared at 773 K by a gas mixing method (H_2–H_2S). The chemical compositions of these samples analysed by EPMA and atomic absorption spectrophotometry are $Fe_{4\cdot40}Ni_{4\cdot57}Co_{0\cdot03}S_8$ (natural) and $Fe_{5\cdot00}Ni_{4\cdot00}S_8$ (synthetic).

Intensity measurement

Integrated X-ray powder diffraction intensities for the three samples were measured by a conventional powder diffractometer (Rigaku RAD-rA) equipped with a diffracted-beam graphite monochromator. Radiations employed were Fe $K\beta$ and Cu $K\alpha$. The reflections measured were 111, 200, 220, 311, 222, 400, 331 and 440. The full width at half maximum of each reflection was in the range from 0·2 to 0·3° in 2θ. Intensities were measured by step counting at every 0·01° for 4 s for Fe $K\beta$ radiation and for 1 s for Cu $K\alpha$. Backgrounds were measured for the same period as the integral step-scan time. Statistical counting errors in the intensity measurements are in the range from 0·47 to 5·5% for Cu $K\alpha$ radiation and from 0·50 to 11·5% for Fe $K\beta$.

Refinement of cation ordering

After corrections of multiplicity and Lp factor, the observed structure factors were calculated from the intensity data for Fe $K\beta$ and Cu $K\alpha$ radiations and the results are listed in the column F_{obs} in Table 3.

The calculated structure factors for Fe $K\beta$ and Cu $K\alpha$ radiations were obtained for two extreme models of the site preference: (1) the $M(O)$ sites are entirely occupied by Fe, and (2) they are entirely occupied by Ni. As the variation of the structure factor of pentlandite having a given chemical composition should be linear with the change of Fe/(Fe + Ni) ratio in $M(O)$ sites, the structure factor of any intermediate states can be derived by proportional allocation of the structure factors for the above two extreme models.

Table 1. *Atomic parameters for pentlandite* [*after Rajamani & Prewitt* (1975)]

		Natural	Heated
4(b) $M(O)$	B (Å^2)	0·55 (4)	0·77 (4)
32(f) $M(T)$	x	0·12608 (4)	0·12632 (4)
	y	0·12608 (4)	0·12632 (4)
	z	0·12608 (4)	0·12632 (4)
	β_{11}	0·00106 (9)	0·00184 (5)
	β_{12}	0·00008 (4)	0·00008 (3)
	B_{eq} (Å^2)	0·42 (3)	0·75 (2)
8(c) S(1)	B (Å^2)	0·58 (4)	0·83
24(e) S(2)	x	0·2632 (1)	0·2604 (2)
	β_{11}	0·0009 (1)	0·0015 (1)
	β_{22}	0·0011 (1)	0·0019 (1)
	B_{eq} (Å^2)	0·42	0·73 (3)

Table 2. *Anomalous-dispersion corrections*

	f'(Fe $K\beta$)	f''(Fe $K\beta$)	f'(Cu $K\alpha$)	f''(Cu $K\alpha$)
Fe	−5·21	0·00	−1·50	2·99
Ni	−2·25	0·00	−3·57	0·00
S	0·33	0·66	0·30	0·51

The calculation is based on the following assumptions: the atomic parameters of natural and heated pentlandites are the same as those determined by Rajamani & Prewitt (1973, 1975) (Table 1); the atomic scattering factors are after Cromer & Mann (1968); the anomalous-dispersion corrections are evaluated by the method described by James (1967) (Table 2); the chemical composition of natural pentlandite remains unchanged after heating; and the synthetic pentlandite is assumed to have the same atomic parameters as the heated natural one. No vacancies in $M(O)$ and $M(T)$ sites are assumed.

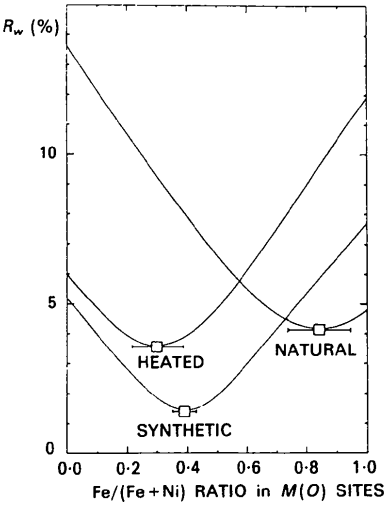

Fig. 1. Variations of R_w values for three samples against Fe/(Fe + Ni) ratios in the $M(O)$ site. The most probable cation distribution should have the smallest R_w value.

Table 3. *Observed and calculated structure factors*

h k l	F_{obs} Fe $K\beta$	F_{obs} Cu $K\alpha$	FR_{obs}	FR_{calc}	w ($\times 10^3$)
Natural					
1 1 1	59·2	38·1	1·55	1·52	2·50
2 0 0	24·0	17·9	1·34	1·29	0·15
2 2 0	31·5	23·4	1·34	1·29	0·33
3 1 1	112·8	80·1	1·41	1·39	2·50
2 2 2	138·9	87·0	1·60	1·57	2·50
4 0 0	53·1	35·9	1·47	1·33	0·13
3 3 1	68·5	46·6	1·47	1·51	2·07
4 4 0	306·4	231·0	1·33	1·43	2·50
			$R = 4{\cdot}1\%$		
Heated					
1 1 1	62·0	45·6	1·36	1·28	2·50
2 0 0	28·3	19·3	1·46	1·41	0·22
2 2 0	34·3	23·8	1·44	1·40	0·43
3 1 1	115·6	86·3	1·34	1·34	2·50
2 2 2	140·9	101·8	1·38	1·43	2·50
4 0 0	47·2	42·4	1·11	1·05	0·10
3 3 1	63·3	50·5	1·25	1·30	1·88
4 4 0	316·0	240·6	1·31	1·35	2·50
			$R = 3{\cdot}3\%$		
Synthetic					
1 1 1	60·1	44·8	1·34	1·32	2·50
2 0 0	28·5	19·5	1·46	1·45	0·23
2 2 0	32·5	22·7	1·43	1·44	0·37
3 1 1	110·7	78·9	1·40	1·42	2·50
2 2 2	142·3	96·0	1·48	1·51	2·50
4 0 0	40·5	41·4	0·98	1·02	0·06
3 3 1	60·1	45·4	1·32	1·34	1·47
4 4 0	311·0	221·5	1·40	1·40	2·50
			$R = 1{\cdot}4\%$		

The Fe/Ni distribution in the $M(O)$ and $M(T)$ sites is determined by the following procedures. In order to eliminate the effect of preferred orientation, the ratio of the observed structure factors, FR_{obs} $(=F^{obs}_{\text{Fe}\,K\beta}/F^{obs}_{\text{Cu}\,K\alpha})$, is used for the refinement of site preference, where $F^{obs}_{\text{Fe}\,K\beta}$ and $F^{obs}_{\text{Cu}\,K\alpha}$ are the observed structure factors for Fe $K\beta$ and Cu $K\alpha$ radiations. The ratio of the calculated structure factors, FR_{calc} $(=F^{calc}_{\text{Fe}\,K\beta}/F^{calc}_{\text{Cu}\,K\alpha})$, is derived from the calculated $F_{\text{Fe}\,K\beta}$ and $F_{\text{Cu}\,K\alpha}$ with division of 0·01 of the Fe/(Fe + Ni) ratio in the $M(O)$ sites. With these FR_{calc} and FR_{obs} the 'reliability' factor,

$$R_w = [\sum w(|FR_{obs}| - |FR_{calc}|)^2 / \sum w|FR_{obs}|^2]^{1/2},$$

was calculated as illustrated in Fig. 1. For the scale fitting between FR_{obs} and FR_{calc} by the least-squares method and the calculation of R_w, the weight w is assumed as follows:

$$w = 2{\cdot}50 \times 10^3 \qquad \text{when } \sigma(FR_{obs})/FR_{obs} \leq 0{\cdot}02;$$

$$w = [FR_{obs}/\sigma(FR_{obs})]^2 \text{ when } \sigma(FR_{obs})/FR_{obs} > 0{\cdot}02,$$

where $\sigma(FR_{obs})$ is the statistical counting error of FR_{obs}.

In this treatment the most probable cation distribution should give the lowest R_w value. As seen in Fig. 1, the Fe/(Fe + Ni) ratio in the $M(O)$ sites of the natural pentlandite is determined as 0·84 ± 0·11 (R = 4·11%), that of the heated one as 0·30 ± 0·09 (R = 3·32%) and that of the synthetic one as 0·39 ± 0·04 (R = 1·42%). The refined FR_{calc} and w are listed together with FR_{obs} in Table 3.

Discussion

The present results are consistent with the Mössbauer study of Knop *et al.* (1970) which indicates that the Fe occupancy in $M(O)$ sites is 0·75 ± 0·075 in a natural pentlandite and 0·30 ± 0·03 in the heated sample. Although the metal occupancy, (Fe + Ni)/(Fe + Ni + □), in the $M(O)$ or $M(T)$ site cannot be determined directly in this study, small amounts of vacancy have little influence on the determination of the Fe/Ni distribution, because the contribution of the vacancy to each structure factor is cancelled out in the ratio of the structure factors. Rajamani & Prewitt (1973) reported the existence of 1·5% vacancy in the $M(T)$ sites. In such a case, for example, the deviation of the Fe/(Fe + Ni) ratio in the $M(O)$ sites, determined by the present method, is less than 0·01 even if no vacancy is assumed in the calculation of the structure factors. In the present analysis, the atomic parameters are taken to be the same as the single-crystal results of Rajamani & Prewitt (1973), because the number of the parameters is too large compared with the number of observable reflections. Slightly high R values, 4·11% for the natural and 3·32% for the heated pentlandites, might be attributed to the possible deviation of atomic parameters due to the slight difference in chemical composition between the sample of Rajamani & Prewitt (1973) and ours.

As the results from the two independent methods, Mössbauer and X-ray diffraction, are consistent with each other, it seems certain that Fe atoms are concentrated in $M(O)$ sites for natural pentlandite and in $M(T)$ sites for heated and synthetic samples. Although the Fe/Ni distribution of any given pentlandite crystal must be related to temperature and pressure, it is unclear at the moment how the distribution is controlled by the thermodynamic parameters. An annealing experiment at various temperatures and pressures coupled with thermodynamical consideration is needed for further understanding of the present results and their possible implication to the genesis of natural pentlandites.

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Time-of-Flight Neutron Diffraction Study of a Single Crystal of Yttria-Stabilized Zirconia, $Zr(Y)O_{1 \cdot 862}$, at High Temperature and in an Applied Electrical Field

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Abstract

Single-crystal time-of-flight neutron diffraction techniques have been applied to the analysis of oxygen behavior in the structure of yttria-stabilized cubic zirconia, $Zr(Y)O_{1 \cdot 862}$. Reflection data were collected at room temperature, at 1040 K, and at 1040 K with a 7·8 DC voltage across the (100) and ($\bar{1}00$) crystal faces, which generated a 9–10 mA ionic current. On the difference Fourier maps derived from high-temperature data, residual peaks due to interstitial mobile oxygen ions were observed along ⟨100⟩ under the condition of an applied DC voltage. Residual peaks attributed to large anharmonic thermal vibrations along ⟨111⟩ were also observed.

Introduction

Single crystal time-of-flight (TOF) neutron diffraction is a particularly powerful technique for the study of crystal structures under special environmental conditions. In this paper we report on the application of this technique to the study of oxygen motion in yttria-stabilized cubic zirconia at high temperatures.

Yttria-stabilized zirconia (YSZ), in which the cation is partially substituted by Y, crystallizes in a cubic structure (fluorite type) at high temperatures. This cubic structure is oxygen deficient owing to the statistical substitution of ZrO_2 by Y_2O_3 and is stable over a wide temperature range. This material is a very good O^{2-}-ion conductor at temperatures exceeding 900 K. In order to elucidate the O-atom motion in the structure, YSZ has been studied extensively using X-ray and neutron diffraction techniques (Steel & Fender, 1974; Faber, Mueller & Cooper, 1978; Morinaga, Cohen & Faber, 1979). However, most of these studies have been made on products quenched from high temperatures.

Neutron diffraction is more advantageous than X-ray diffraction for determining the oxygen behavior in these structures because the ratio of the scattering amplitude of O to Zr and Y is much larger (1 : 1·22 : 1·36) and the absorption due to Zr and Y is much less for neutrons. Furthermore, the TOF technique combined with a position-sensitive area detector (Schultz, Srinivasan, Teller, Williams & Lukehart, 1984) minimizes the motion of the specimen and permits the collection of diffracted intensities with the simultaneous measurement of ionic conductivities at high temperatures.

In this work, we investigated the crystal structures of yttria-stabilized cubic zirconia at room temperature, at 1040 K, and at 1040 K with a 7·8 DC voltage applied across the (100) and ($\bar{1}00$) crystal faces, which generated ~9–10 mA ionic current. The single crystal used in this study has the chemical composition $0 \cdot 84ZrO_2.0 \cdot 16Y_2O_3$. Data were measured using the TOF single-crystal diffractometer

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