

Superstructure of tetrataenite from the Saint Severin meteorite

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Abstract. The superstructure of tetrataenite, FeNi from the Saint Severin meteorite was determined using X-ray diffraction data from a conventional X-ray source and synchrotron radiation. Lattice constants of tetrataenite show clearly tetragonal symmetry; $a = 3.581(2) \text{ \AA}$, $b = 3.582(2) \text{ \AA}$, $c = 3.587(2) \text{ \AA}$, $\alpha = 90.03(3)^\circ$, $\beta = 90.04(3)^\circ$ and $\gamma = 90.00(3)^\circ$. The structure, however, is monoclinic. The space group may be Pm . The atomic coordinates and the temperature were determined by data from conventional X-ray diffraction. The ordering of Fe/Ni was determined by refinement of site occupancies of the atoms applying the difference of anomalous scattering factors of Fe and Ni with synchrotron radiation $\lambda = 1.746 \text{ \AA}$. The tetrataenite from the Saint Severin meteorite does not show perfect ordering of Fe and Ni. It still contains 15% disorder of Fe/Ni on average.

Introduction

The iron-nickel minerals commonly found in meteorites are kamacite and taenite. Kamacite is characterized by a low Ni-content of less than 7 wt% and has a body-centered cubic structure. Taenite shows a Ni-content of up to about 55 wt% and has a face-centered cubic structure. Albertsen et al. (1978a, b, c) found a new phase with chemical composition of about FeNi by means of X-ray diffraction and Mössbauer spectroscopy. They assumed the new phase to be the ordered FeNi phase. Clarke and Scott (1980) observed this phase optically in 60 slow-cooled meteorites and named it tetrataenite due to the tetragonal distortion of face-centered cubic taenite. This tetragonal phase can also be obtained by neutron- or electron-irradiation of Ni–Fe alloys at temperatures below the critical order-disorder transition temperature of $T_c = 593 \text{ K}$ (Pauleve et al., 1962; Gros, Pauleve, 1970; Chamberod et al., 1979). From the distribution of tetrataenite (clear taenite) in cloudy taenite (exsolved taenite/kamacite) and the diffusion of Ni in kamacite and taenite, it is concluded that the ordering of Fe/Ni takes place

during extremely slow cooling (c.g. 0.1–100 K/m.y.) at a temperature below 573 K (Albertsen, 1981; Clarke, Scott, 1980). However, it is not yet well understood how this superstructure is formed.

Reuter et al. (1985, 1989) performed electron irradiation experiments and proposed a low temperature Fe–Ni phase diagram.

Mehta et al. (1980) applied various electron-optical techniques to tetrataenite from the Esterville meteorite to resolve spatially the ordered FeNi phase. They confirmed the presence of a superstructure in clear taenite.

The structure of tetrataenite can be derived from that of taenite by ordering of Fe and Ni (Albertsen, 1981).

The ordering of Fe and Ni in tetrataenite has mainly been confirmed by the presence of a quadrupole splitting in Mössbauer spectra arising from the non-cubic environment of Fe atoms in the structure (Danon et al., 1979). Albertsen (1981) found some weak superstructure reflections in the X-ray diffraction and he determined precisely the lattice of tetrataenite, which show tetragonal symmetry.

In this study, the structure of tetrataenite was determined using conventional X-ray and synchrotron radiation data and the ordering of Fe/Ni is discussed.

Sample

Tetrataenite specimens could be separated from the Saint-Severin meteorite. The Saint Severin meteorite fell on June 27, 1966 in Charente, France. It is classified as olivine-hypersthene chondrite (LL6). Danon et al. (1979) confirmed Fe/Ni-ordering of tetrataenite from the meteorite using Mössbauer spectroscopy. The tetrataenite grains in the meteorite sample showed optical anisotropy. The chemical composition of the sample was determined to be $\text{Fe}_{1.00(1)}\text{Ni}_{1.00(1)}$ by means of the electron probe microanalysis. The meteorite sample was roughly crushed and then treated in fluoric acid. With this treatment, tetrataenite specimens of some mm– μm size could be separated. The separated ones had a very irregular shape since they often showed a vein-like texture occupying the vacant space of the silicate minerals.

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X-ray diffraction

The separated specimens were investigated by conventional X-ray methods. Most specimens showed elongated diffraction spots in the X-ray diffraction diagram due to misoriented aggregates of the small crystals. Finally, a fairly good crystal about 30 μm in diameter with irregular form could be selected but it included very small other crystals of different orientations. In the following experiment, the selected crystal was considered as a single crystal.

In order to confirm the lattice symmetry, lattice constants were determined on the assumption of triclinic symmetry on the diffractometer using MoK_α radiation as: $a = 3.581(2)\text{ \AA}$, $b = 3.582(2)\text{ \AA}$, $c = 3.587(2)\text{ \AA}$, $\alpha = 90.03(3)^\circ$, $\beta = 90.04(3)^\circ$, $\gamma = 90.00(3)^\circ$. The lattice constants show clearly the tendency of tetragonal symmetry within experimental error.

In the course of the phase transition from taenite to tetrataenite, which can be interpreted as an ordering process of Fe/Ni, the symmetry is changed from cubic (face-centered cubic structure, abbrev. to f.c.c. structure) to tetragonal. In such transition, the cubic symmetry elements are sometimes retained as the twin operations in the tetragonal structure, namely the threefold twinning along [111] of taenite. It is difficult to confirm the existence of the threefold twinning along [111] by X-ray diffraction methods because the deviation from cubic symmetry is very small. The threefold twinning could not be detected even by the high resolution diffraction method (Tagai, 1992). The lattice constants could not be precisely determined on the diffractometer because of the fairly large mosaic spread of the graphite monochromator. However, if the crystal is twinned by threefold rotation along [111], it would not show the tetragonal symmetry of the lattice constants. The selected crystal was, therefore, assumed to be practically free from threefold twinning in the course of the following structure determination.

Diffraction data were collected on a four circle diffractometer using MoK_α radiation with 40 kV and 100 mA. A total of 1484 reflections was measured within the range of $2\theta \leq 150^\circ$ and 696 independent reflections ($\geq 1\sigma$) were used for structure determination. The absorption correction was not carried out because of the complex form of the crystal.

The same crystal was, then, supplied to a diffraction experiment using synchrotron radiation. The crystal was mounted on a four circle diffractometer of vertical type on beam line BL10a at Photon Factory, Laboratory for High Energy Physics, Tsukuba, Japan. The electron storage ring was operated at 2.5 GeV and the diffraction data were collected with a ring current of 135–85 mA. The X-ray beam from the bending magnet of the storage ring is horizontally polarized. It was monochromatized by a Si(111) perfect crystal (with a mosaic spread of about 0.02 mrad.) and was led to the four circle diffractometer through a He-pass. The diffracted intensity was measured by a scintillation detector and the higher harmonics were sufficiently cut off by a discriminator. The diffraction data were collected at $\lambda = 1.746\text{ \AA}$. The correction parameter for anomalous scattering for this wave length are: for Fe:

$f' = -6.299$, $f'' = 0.469$ and for Ni: $f' = -1.740$, $f'' = 0.638$ (Sasaki, 1984). A large difference in f' and the small values in f'' are adequate to determine the site occupancies of Fe and Ni in the structure because of little absorption effect. 25 independent reflections were collected with $2\theta \leq 100^\circ$. The intensities of standard reflections measured at intervals of five reflections were used to correct the decreasing intensity of the primary X-ray.¹

Structure determination

According to Clarke and Scott (1980) and Albertsen (1981), the tetrataenite structure can be derived from the taenite structure by ordering of Fe and Ni atoms. If Fe atoms occupy the positions of 0, 0, 0 and 1/2, 1/2, 0 and Ni atoms occupy the positions of 1/2, 0, 1/2 and 0, 1/2, 1/2 of the f.c.c. cell in the course of ordering, the ordered structure should have the space group $P4/mmm$ with cell constants of about $a = b = 2.5\text{ \AA}$ and $c = 3.5\text{ \AA}$ according to the following transformation matrix:

$$\begin{pmatrix} a_p \\ b_p \\ c_p \end{pmatrix} = \begin{pmatrix} 1/2 & 1/2 & 0 \\ -1/2 & 1/2 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} a_f \\ b_f \\ c_f \end{pmatrix}$$

(p: primitive tetragonal cell and f: face-centered cubic cell) (Figs. 1a, b).

In this space group, all atoms occupy special positions and the intensities of the superstructure reflections, therefore, should be interpretable only by the difference of scattering factors of Fe and Ni.

When the primitive tetragonal cell is adopted, Fe atoms occupy 0, 0, 0 and Ni atoms occupy 1/2, 1/2, 1/2 in the perfectly ordered FeNi structure with $P4/mmm$ (Fig. 1b). Then the structure factor can be written as

$$F(hkl) = f_{\text{Fe}} + f_{\text{Ni}}\{\exp \pi i(h + k + l)\}.$$

The intensities of the substructure reflections (for $h + k + l = \text{even}$) are, therefore, proportional to $(f_{\text{Fe}} + f_{\text{Ni}})$ and those of superstructure reflections are proportional to $(f_{\text{Fe}} - f_{\text{Ni}})$. In the $\sin \theta/\lambda$ range from 0.0 to 1.0, the structure factors of the superstructure reflections were found to be about 10–20% of those of the substructure reflections. The calculated $(f_{\text{Fe}} - f_{\text{Ni}})/(f_{\text{Fe}} + f_{\text{Ni}})$ in the same $\sin \theta/\lambda$ range is about 2–6%. The perfectly ordered structure model in space group $P4/mmm$ does not give sufficient intensity for the superstructure reflections. It is, therefore, most probable that tetrataenite has a lower symmetry than $P4/mmm$.

If tetrataenite has a symmetry of $P422$, all atoms should occupy special positions: 0, 0, 0 for Fe atoms and 1/2, 1/2, 1/2 for Ni atoms. The structure models with this

¹ Additional material to this paper can be ordered referring to the no. CSD 57568, names of the authors and citation of the paper at the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany. The list of F_o/F_c -data is available from the author up to year after the publication has appeared.

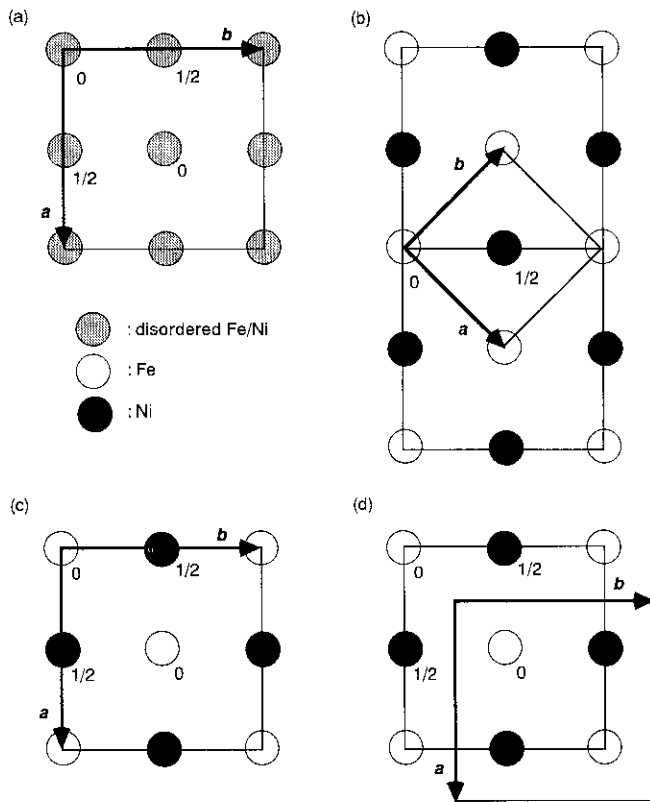


Fig. 1. Cell relations among (a) the disordered Fe/Ni structure, (b) the ordered $P4/mmm$ structure, (c) the ordered structure of lower symmetry and (d) the structure (c) with different setting of unit cell. 0 and 1/2 in the figure indicate z -coordinates.

symmetries cannot give sufficient intensity of the superstructure reflections. If the symmetry is $P4mm$ or $P4$, then only the z -coordinates of all atoms can be varied. The intensities of superstructure reflections of $(hk0)$, however, should remain unchanged since the projection of the structure on (001) is the same as that of the $P4/mmm$ structure.

If tetrataenite has a lower symmetry than tetragonal, the atom positions 0, 0, 0 and 1/2, 1/2, 0 in the f.c.c. cell are no more equivalent and the new primitive cell

$$\begin{pmatrix} a_n \\ b_n \\ c_n \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} a_f \\ b_f \\ c_f \end{pmatrix}$$

(n : new primitive cell and f : face-centered cubic cell) (Fig. 1c) is adopted for the following discussions. In this

new cell, Fe atoms occupy 0, 0, 0 and 1/2, 1/2, 0 and Ni atoms 1/2, 0, 1/2 and 0, 1/2, 1/2.

Then it is assumed that tetrataenite has an orthorhombic or a monoclinic symmetry. If it has a symmetry $Pmmm$ or $P222$, all atoms should occupy special positions; 0, 0, 0 and 1/2, 1/2, 0 for Fe and 1/2, 0, 1/2 and 0, 1/2, 1/2 for Ni. In the case of $Pmm2$ only the z -coordinates of all atoms can be varied. As discussed in the cases of tetragonal symmetry, these orthorhombic models cannot give sufficient intensity for the superstructure reflections. If tetrataenite has a monoclinic or a triclinic symmetry, we should consider the following cases;

A) $P2/m$, $P2$, Pm , $P\bar{1}$ and $P1$ with Fe atoms at 0, 0, 0 and 1/2, 1/2, 0 and Ni atoms at 1/2, 0, 1/2 and 0, 1/2, 1/2
 B) $P2/m$, $P2$, Pm , $P\bar{1}$ and $P1$ with Fe atoms at 1/4, 1/4, 0 and Ni atoms at 3/4, 1/4, 1/2 (1st setting) (Fig. 1d).
 The cases of $P2/m(A)$ and $P\bar{1}(A)$ correspond to those of $P222$ and $Pmmm$. The case of $P2(A)$ corresponds to that of $Pmm2$.

Therefore, it can be concluded that tetrataenite has a symmetry $P2/m(B)$, $P2(B)$, $Pm(A)$, $Pm(B)$, $P\bar{1}(B)$ or $P1(A/B)$. In the structure models of $P2/m(B)$, $Pm(A)$ and $Pm(B)$, all atoms are on the mirror planes and the x and y coordinates of the atoms can be varied. All these models were considered in the following discussion.

When the symmetry of tetrataenite is monoclinic, the true Laue symmetry should be determined using weak superstructure reflections, because strong substructure reflections are due to the f.c.c. structure. From the intensity distribution of the superstructure reflections, one of three axes was assigned to the twofold axis.

Because of the very small number of reflections collected with synchrotron radiation, the positional parameters and temperature coefficients were determined using MoK_α data. For structure determination the least squares program of RFINE II (Finger, 1969) was used. After several cycles the least squares refinement to the structure model of $Pm(A)$ converged to an R -factor of 7.3% (for 6969 observed reflections). The R -factor is 18.7% for 333 weak superstructure reflections. The tetragonal $P4/mmm$ model resulted in an R -factor of 10.5%, whereby the R -factor was 39.8% for superstructure reflections. The structure models of $P2/m(B)$, $Pm(B)$ and $P2(B)$ gave R -factors of 9–10%.

Then the Fe and Ni occupational probabilities were refined using synchrotron data with the converged atomic coordinates and temperature factors of the $Pm(A)$ model

Table 1. Final atomic coordinates and temperature factors.

Atom Occup.	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ni1 0.84(7) (Fe 0.16)	0.0	0.0	0.0	0.009(2)	0.004(2)	0.002(2)	0.0	-0.002(1)	0.0
Ni2 0.85(8) (Fe 0.15)	0.482(3)	0.0	0.493(4)	0.002(2)	0.002(3)	0.004(2)	0.0	-0.001(1)	0.0
Fe1 0.85(8) (Ni 0.15)	0.508(3)	0.5	0.994(4)	0.003(2)	0.003(2)	0.006(2)	0.0	0.003(1)	0.0
Fe2 0.87(7) (Ni 0.13)	0.011(5)	0.5	0.520(5)	0.014(4)	0.044(8)	0.033(7)	0.0	0.010(3)	0.0

fixed. The sum of Fe and Ni in every site was constrained to 1.0. Final results are shown in Table 1. It can be concluded that Ni and Fe positions are averagely 15–16% ordered as $\text{Ni}_{0.85}\text{Fe}_{0.15}$ and $\text{Ni}_{0.16}\text{Fe}_{0.84}$, respectively. The positional shifts of the atoms are less than 0.05 Å from the positions of the f.c.c. structure. The selected bond distances and angles are summarized in Table 2.

Table 2. Selected bond distances of the Ni and Fe atoms.

Ni(1)	—	Ni(2)	2.470(13)
			2.508(13)
			2.564(13)
			2.597(13)
	average		2.535
Ni(1)	—	Fe(1)	2.512(7)
			2.512(7)
			2.553(7)
			2.553(7)
	average		2.533
Ni(1)	—	Fe(2)	2.485(13)
			2.485(13)
			2.586(13)
			2.586(13)
	average		2.536
Ni(2)	—	Fe(1)	2.534(14)
			2.534(14)
			2.539(14)
			2.539(14)
	average		2.537
Ni(2)	—	Fe(2)	2.462(14)
			2.462(14)
			2.608(15)
			2.608(15)
	average		2.535
Fe(1)	—	Fe(2)	2.461(22)
			2.478(22)
			2.595(22)
			2.608(22)
	average		2.536

Under the assumption of space group $P1(A)$, the structure determination was carried out as well. This model converged to 7.1%. The better R -factor may be due to the larger number of parameters. The results show that the converged parameters are the same as those of $Pm(A)$ model within an error of 3σ . $P\bar{1}(B)$ model converged to 9.0%. Therefore, the $Pm(A)$ structure model was adopted in the present study.

In order to conform the Laue symmetry, other possibilities to assign an axis to twofold one were tried. All other models gave R -factors of about 8.5% for the symmetry independent reflections.

Discussion

The ideal full ordered structure of tetrataenite can be described in space group $P4/mmm$ but this model cannot satisfy the intensity distribution of the superstructure reflections. The other possible tetragonal and orthorhombic structure models cannot explain the intensity distributions of the superstructure reflections as well,

since all atoms still occupy special positions 0, 0, 0, 1/2, 1/2, 0, 1/2, 0, 1/2 and 0, 1/2, 1/2 or since the projected structure of tetrataenite on (001) is the same as that of taenite on (001). If tetrataenite has a monoclinic or a triclinic symmetry, we should consider:

- A) $P2/m$, $P2$, Pm , $P\bar{1}$ and $P1$ with Fe atoms at 0, 0, 0 and 1/2, 1/2, 0 and Ni atoms at 1/2, 0, 1/2 and 0, 1/2, 1/2
 B) $P2/m$, $P2$, Pm , $P\bar{1}$ and $P1$ with Fe atoms at 1/4, 1/4, 0 and Ni atoms at 3/4, 1/4, 1/2 (Fig. 1d).

The structure models of $P2/m(A)$, $P2(A)$ and $P\bar{1}(A)$ were excluded for the same reason as in the orthorhombic models. The results of the least squares refinements of the other structural models indicated that the tetrataenite structure can best be described by the monoclinic model with symmetry Pm . The deviation from the substructure (f.c.c), however, is not large. When the symmetry of tetrataenite is monoclinic, the true Laue symmetry should be determined using weak superstructure reflections, because strong substructure reflections are due to the f.c.c. structure. From the intensity distribution of the superstructure reflections, one of three axes was assigned to the twofold axis. This structure model was confirmed to be true by the results of the least squares refinement of the other structure models by different assignments of the axes to the twofold one.

The anisotropic temperature factors of Fe(2) are very large, which may indicate the possibility of a domain structure formation with positional disorder in Fe(2) site. Therefore, a structure model with split Fe(2) position was calculated applying equal occupation of 0.5 in each position, but the refinement of the model converged only to an R -factor of about 10%. One of the split Fe atoms showed extremely large temperature factors.

The convergence of the least squares refinements was not satisfactory. This may be due to the quality of the selected crystal, the existence of the small amount of threefold twinning and the irregular form of the crystal used for the diffraction experiments.

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