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# Pyrrhotite: The *nA* (or 2*A*, 3*C*) superstructure reviewed

CARL A. FRANCIS AND JAMES R. CRAIG

*Department of Geological Sciences, Virginia Polytechnic Institute & State University*
*Blacksburg, Virginia 24061*

## Abstract

The *nA* superstructure is developed in sulfur-rich pyrrhotites and $(Fe,Ni)_{1-x}S$ analogues. Precession photographs show slightly offset 'c' reflections and weak 001 and $00\bar{1}$ reflections. In electron diffraction patterns 'b' and 'd' reflections as well as 'c' reflections are doublets with relative separation distances: $\Delta h_b \simeq 2\Delta h_d \simeq 3\,\Delta h_c$. Direct lattice repeats on the order of 250-700 Å in the (001) plane are required to explain the observed separation distances of 'c' reflections. A regular stacking sequence of full and vacancy-containing metal layers may be inferred from the integral 3*C* repeat. High resolution transmission electron microscopy is the most promising technique for the ultimate solution of the *nA* superstructure problem.

## Introduction

The pyrrhotite minerals, $Fe_{1-x}S$, are widespread and locally abundant in terrestrial, lunar, and meteoritic rocks. Crystallographic studies by numerous investigators have shown that the pyrrhotite group consists of several distinct phases, each an ordered superstructure of the hexagonal ($P6_3/mmc$) NiAs structure which all pyrrhotites possess at high temperatures (>300°C). Pyrrhotite superstructures are designated following the convention of Wuensch (1963) in which dimensions of the supercell, denoted by lower case letters, are expressed as multiples of the subcell dimensions, which are denoted by capital letters. Usually the *c* cell dimension is characteristic of the superstructure and is the only dimension reported. For example, troilite, stoichiometric FeS, is designated 2*C* because its cell dimensions are $a = \sqrt{3}A$ and $c = 2C$.

Especially enigmatic among pyrrhotite superstructures is one which closely approximates a 2*A*,3*C* supercell but is nonintegrally related to the subcell in the a direction. The designation *nA* was proposed by Nakazawa and Morimoto (1971:p. 351) "to indicate the non-integral character of the *a* axis." Our interest in the *nA* superstructure was prompted by its discovery in quenched samples of the synthetic $(Fe,Ni)_{1-x}S$ monosulfide solid solution (mss) (Francis, 1974). In this brief contribution, new electron diffraction data are presented and discussed within the context of a review of the crystallography of the *nA* superstructure.

## Experimental procedures

The samples used in this study were synthesized from high purity (99.999%) iron, nickel, and sulfur in evacuated silica tubes (see Kullerud, 1971). Crystallization of single mss crystals up to 0.1 mm in diameter was accomplished by sublimation of powered mss and subsequent condensation in thermal gradients of 5–14°/cm at temperatures ranging from 850°–950°C. Prior to quenching, crystals were annealed at 600°C for at least twenty-four hours to minimize possible effects due to differences in temperature of crystallization. Unit-cell parameters were determined on a Philips Norelco diffractometer using monochromatized Cu*Kα* radiation and an internal standard ($BaF_2$, $a$ = 6.1971 Å). Superstructure types were determined by the precession method using Zr-filtered Mo*Kα* radiation and by electron diffraction on an 100 kV Siemens Elmskop I-A transmission electron microscope. Compositions were determined on an ARL electron microprobe using synthetic troilite (FeS) and millerite (NiS) as standards.

## Results

Experimental conditions and results of all runs in which the *nA* superstructure was encountered are reported in Table 1. In the following discussion the effect of nickel on the development of the *nA* superstructure was not considered, although we realized that the presence of nickel may modify the size and position of the superstructure's stability field in *T-P-*

TABLE 1. Synthesis Data

| Run # | Composition (weight percent) | | | | | | | Temperature of Crystallization | Run Duration (hours) | Run Products[5] | Structure Type | Cell Dimensions | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Starting | | | Microprobe | | | | | | | | | | |
| | Fe | Ni | S | Fe | Ni | S | Σ | | | | | a | c | $d_{102}$ |
| 102 | 24.66 | 36.91 | 38.42 | 24.30 | 35.59 | 38.77 | 98.66 | 940 | 170 | mss$_1$+mss$_2$ | NA, 1C? | 3.41, 5.41; | 3.44, 5.54[1] | 2.004[2] |
| 103 | 45.31 | 15.60 | 39.09 | 44.42 | 14.02 | 39.59 | 98.03 | >900 | --- | mss+pn | NA | 3.428(1)[3] | 5.600(3) | 2.037 |
| 104 | 30.05 | 31.47 | 38.48 | 29.52 | 31.02 | 38.42 | 98.96 | >900 | --- | mss | NA | 3.418(1) | 5.435(3) | 2.002 |
| 105 | 30.50 | 31.69 | 37.81 | 30.06 | 31.34 | 37.91 | 99.31 | 940 | 170 | mss | NA | 3.440(2) | 5.590(10) | 2.039 |
| 112 | 60.08 | ----- | 39.92 | 59.83 | ----- | 40.42 | 100.25 | 940 | 170 | mss | NA + 4C[4] | 3.434(1) | 5.682(1) | 2.054[2] |
| 122 | 54.03 | 7.26 | 38.71 | ----- | ----- | ----- | ----- | 875 | 338 | mss+pn | NA | 3.441(1) | 5.691(2) | 2.058 |

[1] measured from uncalibrated precession photograph
[2] average value
[3] one estimated standard deviation in parenthesis
[4] two phases distinguished only in TEM image
[5] pn = pentlandite

X space and the intensity of the superstructure reflections.

## Discussion

The *nA* superstructure was discovered almost simultaneously by Corlett (1968), Fleet (1968), and Morimoto and Nakazawa (1968). Corlett investigated a heated Lake Superior pyrrhotite while the others studied synthetic pyrrhotite. The *nA* superstructure has since been observed in quenched natural crystals from the Broadlands, New Zealand, geothermal field as well as in synthetic crystals by Kissin (1974).

The stability field of the *nA* superstructure in the Fe-S system has been determined by Nakazawa and Morimoto (1971). More recently, Kissin (1974) adapted a $Ag|AgI|Ag_{2+x}S$ electrochemical cell to a precession camera, thereby permitting the measurement, at temperature, of the sulfur activity and hence determination of the pyrrhotite composition. His phase diagram (Fig. 1) is considered more reliable and is adopted for the purposes of the present discussion. It is clear from Figure 1 that the metal-deficient phases, intermediate pyrrhotite (*nC*) and monoclinic pyrrhotite (*4C*), develop from the *nA* superstructure. Thus the *nA* superstructure represents one stage in the progressive ordering of metal vacancies with decreasing temperature.[1]

The salient features of the X-ray diffraction record are shown in a schematic diagram of the $a^*$-$c^*$ reciprocal lattice plane (Fig. 2). Morimoto and Nakazawa (1968) recognized three distinct classes of reflections and named them 'a'-, 'b'-, and 'c'-type reflections. A fourth class has been reported by Fleet (1968) and is here named the 'd'-type reflection. These four classes of reflections are conveniently described in terms of indices based on the NiAs reciprocal lattice as follows:

'a'-type reflections: $h, k, l$
'b'-type reflections: $h + 1/2, k, l$
$h, k + 1/2, l$
'c'-type reflections: $h + 1/2 \pm 1/2\,\Delta h, k, l \pm 1/3$
$h, k + 1/2 \pm 1/2\,\Delta h, l \pm 1/3$
$h + 1/2, k + 1/2, l \pm 1/3$
'd'-type reflections: $h, k, l \pm 1/3$

The strong 'a'-type reflections are the subcell (NiAs structure) reflections; the others, all much weaker, are the superstructure reflections. The 'b'-type reflections lie within rows of subcell reflections parallel to [100]* while 'd'-type reflections lie within rows of subcell reflections parallel to [001]*. The 'c'-type reflections lie within the subcell defined by the 'a' reflections. In precession photographs the 'c'-type reflections appear to be slightly offset from their ideal Bragg positions. Both Fleet (1968) and Morimoto and Nakazawa (1968) have recognized these reflections as doublets. One of the pair is strong while the other is so weak as to escape detection without careful scrutiny. The 'b' and 'd' reflections are much weaker than 'c' reflections. Neither were reported by Corlett (1968) and Kissin (1974), nor were they observed in the precession photographs of the present study.

The separation ($\Delta h$) of the 'c' reflections was quantitatively investigated by Nakazawa and Morimoto (1971) who defined the parameter $n = 2A^*/\Delta h$. They found that $n$ varied continuously from 90 to 40 with decreasing temperature. Although Kissin (1974) reported a value of $n$ as high as 105, he found little systematic variation in the value of $n$.

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[1] This being true and by analogy with the alkali feldspars, clarification of the ordering mechanism may result in a structural explanation for twinning which is universally present in monoclinic pyrrhotite (*4C*).

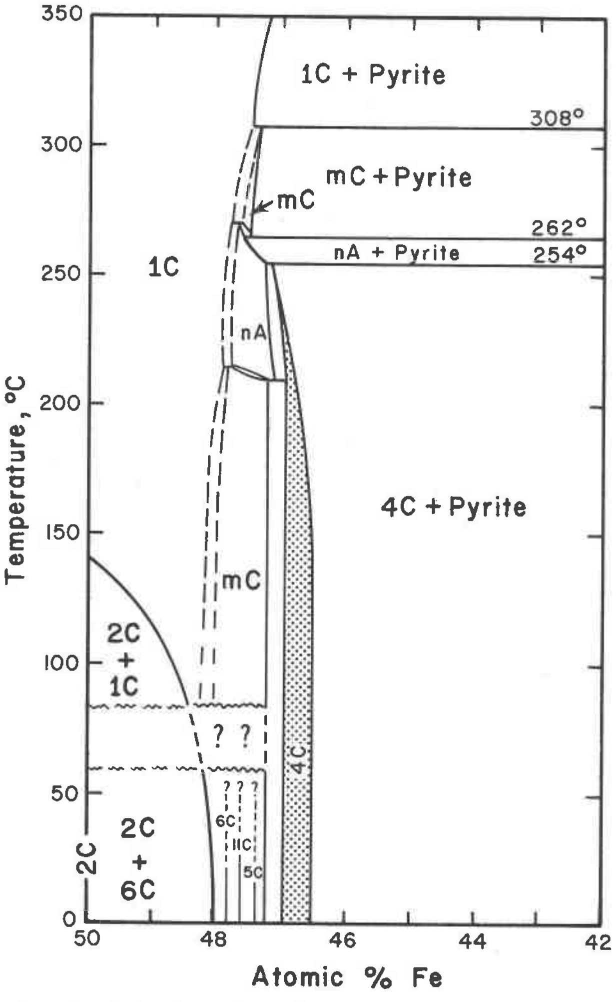

FIG. 1. Equilibrium phase diagram of the pyrrhotite region of the Fe-S system (after Kissin, 1974; also in Scott, 1974).

The intensity distribution of the 'c' reflections (doublets) in the *h0l* plane (Fig. 2) is peculiar and merits emphasis. The more intense of the two spots occur alternately on either side of the reciprocal lattice row corresponding to the 2*A* repeat, and the intensity distribution is repeated by reflection across each subcell boundary. It should be noted that only single, intense, centered 'c' reflections are observed in [110]*[001]* precession photographs because the film plane is perpendicular to their separation direction.

Selected area electron diffraction patterns (Fig. 3a) of the *a**-*c** reciprocal lattice plane show the 'b' and 'd' reflections to be doubtlets. The separation distance of the 'b' reflections is greater than that of the 'd' reflections which in turn is greater than that of the 'c' reflections. The relative displacements are approximately: $\Delta h_b \simeq 2\Delta h_d \simeq 3\Delta h_c$. The 'b' reflections are much weaker than the 'd' reflections (too weak to survive reproduction) and are shown schematically in Figure 3b.

Curiously the superstructure reflections occur only as doublets rather than as extensive rows of regularly spaced reflections. The similarity to 'e' and 'f' reflections of plagioclase feldspars has already been noted by Morimoto and Nakazawa (1968).

Extinctions of the subcell reflections on precession photographs superficially resemble those expected for the NiAs space group ($P6_3/mmc$). Exceptions are 001 and $00\bar{1}$, whose presence violates the $6_3$ screw axis and implies the nonequivalence of adjacent metal layers. Reflections which violate the *c*-glide are present in 200-hour exposures. The *nA* superstructure was assigned to the space group $P6_222$ (or $P6_422$) (Fleet, 1968; Morimoto and Nakazawa, 1968) on the basis of the apparent extinction condition: 00*l* present when $l = 3n$. Selected area diffraction patterns (Fig. 3) have 'd' reflections which violate this extinction condition. The space group assignment is further complicated by the apparent pseudosymmetry which was encountered during a crystal structure refinement of the *nA* superstructure.

Fleet (1971) undertook a refinement of this phase on the basis of 167 intensities collected by film methods. The unit-cell size is dictated by the supercell reflections, which, ignoring the doublet character of these reflections, define a 2*A*,3*C* cell. Such a cell consists of three layers of four NiAs subcells stacked parallel to the *c* axis and has an ideal composition of $M_{24}S_{24}$. The *nA* superstructure, however, is developed only in the metal deficient region of the mss corresponding approximately to $M_{21}S_{24}$. In Fleet's model of the structure, the three metal vacancies are ordered into alternate metal layers. The resulting

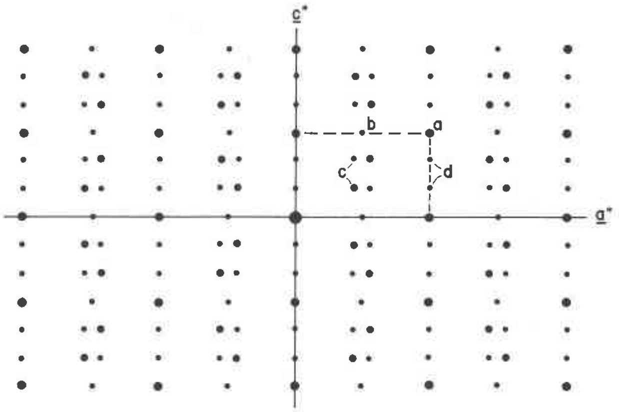

FIG. 2. Diagram of the *a**-*c** reciprocal lattice plane of the *nA* superstructure illustrating the various classes of reflections.

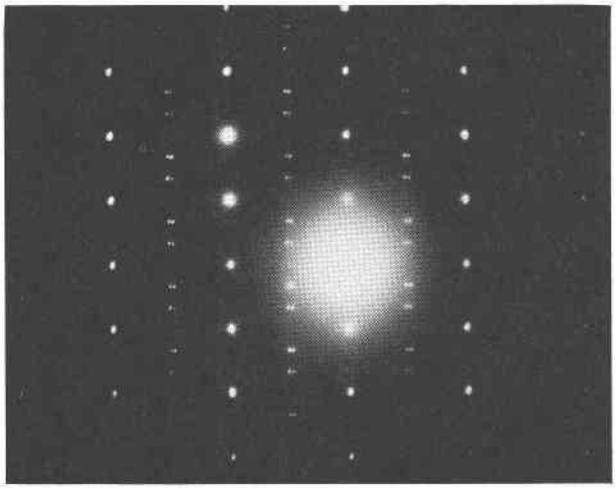

FIG. 3a. Selected area diffraction pattern of the $a^*$-$c^*$ reciprocal lattice plane of the *nA* superstructure (mss #104) showing the 'b' and 'd' reflections to be doublets.

structure has $P3_1$ (or $P3_2$) symmetry rather than $P6_222$ symmetry. However, during refinement certain classes of reflections (*e.g.*, $h0l$ and $\bar{h}0l$) were observed to have equal intensities where no equivalence should exist in space group $P3_1$. These equivalencies were attributed to a two-fold twinning operation about the *c* axis, but the evidence for twinning is not compelling. This apparent pseudosymmetry is more plausibly explained by true six-fold symmetry about the *c* axis as originally proposed and is consistent with Corlett's observation that the positions and intensities of 'c' reflections in the $a^*$-$c^*$ plane are identical for every sixth turn about $c^*$. For lack of evidence to the contrary the *nA* superstructure is here assigned to the fully symmetric hexagonal space group $P6/mmm$.

The refinement of *nA* pyrrhotite appears to be questionable because the number of intensity data is small, the proposed model for ordering of metal vacancies does not uniquely satisfy the diffraction data, and the separation of the 'c' reflections is neglected. However, crystal structure analysis is probably not the best method for determining the detailed nature of this superstructure because such analysis only provides a space-time average of the atomic arrangement. Direct imaging of pyrrhotites by high resolution electron microscopy has already provided new insight into the nature of the *nC* superstructure (Pierce and Buseck, 1974; Nakazawa, Morimoto, and Watanabe, 1974) and will likely be the key to illuminating the nature of the *nA* superstructure.

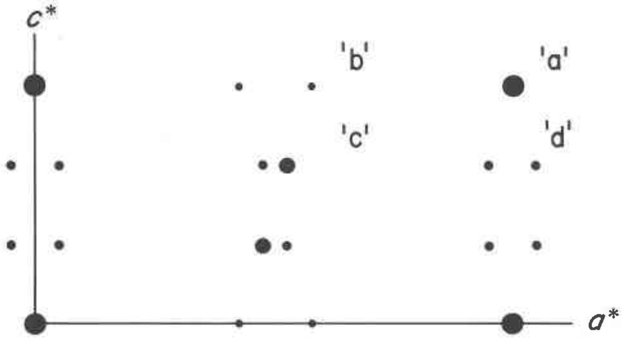

FIG. 3b. Schematic diagram of Figure 3a.

Ordering of metal vacancies distinguishes the various pyrrhotite superstructures (except troilite) from the disordered high-temperature 1*C* phase (NiAs structure) and the determination of these ordering schemes is the essential problem of pyrrhotite crystal chemistry. The sequence of filled and vacancy-containing metal layers stacked along [001] determines the symmetry and *c* cell parameters of all metal-deficient pyrrhotite superstructures, integral or not. Ordering is best understood in monoclinic pyrrhotite (4*C*) which has a composition approximating $Fe_7S_8$. Crystal structure analysis (Tokonami, Nishiguchi, and Morimoto, 1972) has shown that the vacancies are ordered into alternate metal layers as proposed by Bertaut (1953). Structure images obtained by high resolution electron microscopy have been interpreted on the basis of this ordered structure (Nakazawa, Morimoto, and Watanabe, 1975).

Direct imaging of *nC* pyrrhotite by high resolution electron microscopy has permitted ordered sequences of filled and vacancy-containing metal layers to be observed. The non-integral *c* parameters inferred from the irrational positions of the superstructure reflections are attributed to the X-ray averaging of irregular sequences of anti-phase domains, the domains being ordered sequences of filled and vacancy-containing metal layers (Pierce and Buseck, 1974). The integral 3*C* repeat of the *nA* superstructure shows that the ordering sequence of metal layers is regular and the presence of the 001 and $00\bar{1}$ reflections requires adjacent metal layers to be non-equivalent. However, the ordering sequence proposed by Fleet cannot be considered to be established because that scheme does not uniquely satisfy the diffraction data.

The separation of superstructure reflections into doublets signals a second aspect of ordering, which is unique to the *nA* superstructure. Morimoto and Nakazawa (1968) suggested that the separation could be accounted for by the three orthorhombic crystals with the unlikely cell dimensions of $a = A$, $b = 45\sqrt{3}A$, $c = 3C$ twinned about [001]. They also considered domain development but found no change in the X-ray patterns after crystals were slowly cooled from 350° to 250°C in a magnetic field of 15,000 gauss. Our attempts to image domain structure by electron microscopy were fruitless. Although the ultimate cause of the separation of superstructure reflections remains unexplained, it is clear from the measured values of $\Delta h_c$ (or $n$) that a repeat on the order of 250–700 Å must exist in the (001) plane.

## Summary

1. The *nA* superstructure is readily recognized in precession photographs by slight offset of the 'c'-type reflections from the ideal Bragg position and the presence of weak 001 and $00\bar{1}$ reflections.
2. The absence of systematic extinctions suggests that *nA* pyrrhotite crystallizes in space group $P6/mmm$ rather than $P6_222$ as previously proposed.
3. New electron diffraction data show that 'b' and 'd' reflections as well as 'c' reflections are doublets with separation distances $\Delta h_b \simeq 2\Delta h_d \simeq 3\Delta h_c$.
4. A regular stacking sequence of full and vacancy-containing metal layers with non-equivalent adjacent layers may be inferred from the integral $3C$ repeat.
5. A direct lattice repeat of 250 to 700 Å in the (001) plane is required to explain the observed separation distances of the 'c' reflections.
6. High resolution transmission electron microscopy probably represents the most promising technique for future research into the *nA* superstructure problem.

## Note added in proof

A paper by J. M. Parker (1972) entitled "The domain structure of nepheline" (*Z. Kristallogr.* **136**, 255–272) has just come to our attention. It bears directly on the *nA* pyrrhotite problem. Nepheline and other compounds exhibit paired, non-Bragg reflections analogous to those described above. To account for them, Parker proposed a domain model in which "domain boundaries are not planar but fluctuate with quite large amplitude about a well-defined mean position." We believe a similar model could profitably be applied to *nA* pyrrhotite.

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