Phys Chem Minerals (1982) 8:175–179

PHYSICS AND CHEMISTRY OF MINERALS

Transmission Electron Microscopy on Meteoritic Troilite

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Abstract. Phase transitions and associated domains of meteoritic troilite (FeS) have been studied by means of *transmission electron microscopy* (TEM). Three polymorphs have been found, two of which can be described by superstructures of the NiAs-type structure (A, C subcell). The $P\bar{6}2c$ ($\sqrt{3}A, 2C$) polymorph, stable at room temperature, displays antiphase domains with the displacement vector $1/3<\bar{1}10>$. In situ heating experiments showed that the $P\bar{6}2c$ polymorph changes at temperatures of 115°–150° C into an orthorhombic pseudohexagonal transitional phase with the probable space group $Pmcn$ ($A, \sqrt{3}A, C$). It contains antiphase domains with the displacement vector 1/2 [110] and twins with a threefold twin-axis parallel c. When heated above 210° C the transitional phase transforms into the high-temperature modification with NiAs structure ($P6_3/mmc$). All observed phase transitions are reversible. The occurrence of antiphase and twin domains, respectively, agrees with the symmetry reductions involved in the subsolidus phase transitions. This is demonstrated by group-subgroup relationships among the space groups $P6_3/mmc$, $Pmcn$, and $P\bar{6}2c$.

Introduction

Troilite (FeS) is a common mineral in lunar and meteoritic samples. It is formed under strong reducing conditions. The chemistry is assumed to be very close to stoichiometry. Three modifications of FeS exist at different temperatures. At room temperature FeS crystallizes in a superstructure of the NiAs-type structure. The NiAs-type is the high temperature form (Haraldsen 1941a, b). A transitional phase exists between the high and room temperature modification (Putnis 1974; King and Prewitt 1978).

The crystal structure of FeS at room temperature was first determined by Bertaut (1956) using synthetic FeS, and later refined on lunar troilite by Evans (1970). X-ray diffraction yielded the space group $P\bar{6}2c$ with $a = 5.962$ Å and $c = 11.750$ Å (Evans 1970). These lattice parameters can be described by $a = \sqrt{3}A$ and $c = 2C$, whereby A and C are the lattice parameters of the NiAs subcell (cf. Fig. 1). The superstructure of FeS at room temperature is due to a distortion of the ideal NiAs structure, in which the sulfur atoms are arranged in a hexagonal closed packing with iron atoms occupying the octahedral sites. This structure displays alternating sulfur and iron planes.

Haraldsen (1941a, b), Andresen (1960), Sparks et al. (1962), and Andresen and Torbo (1967) studied the transformational behaviour of troilite by means of X-ray and neutron powder diffraction. They reported a phase transition occuring between 138° and 185° C. The variation of the transition temperature is assumed to be due to small deviations from the precise stoichiometry.

Putnis (1974) first observed the transitional phase. During electron microscopic studies the transition of troilite to the high temperature form was induced by focusing the electron beam. By defocusing the beam, the high temperature phase was transformed into a transitional one, which then changed into the room temperature troilite modification. In this case, the temperatures necessary for the transition were generated by the heat of the electron beam. Putnis described the transitional structure with a hexagonal $2A$, $1C$ cell.

King and Prewitt (1978) studied the transitional behaviour by single-crystal X-ray-diffraction in situ heating techniques. They found that troilite transforms into a transitional phase at about 150° C. They described the new structure as probably orthorhombic with a multiple twinned cell and proposed a MnP structure.

The high temperature transition to the NiAs-type structure has not been thoroughly investigated. As far as we know, electron microscopy on FeS has been carried out

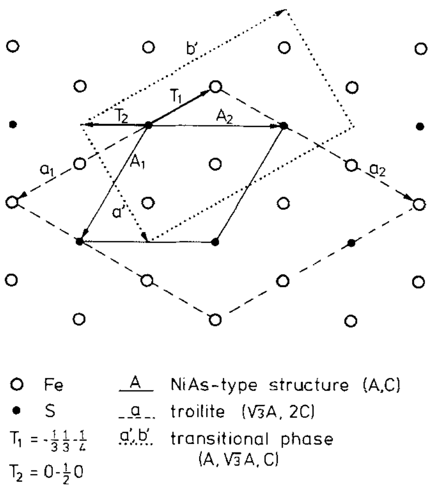

Fig. 1. c-Axis projection of subcell and supercells of FeS. Vector T_i describes the origin shifts

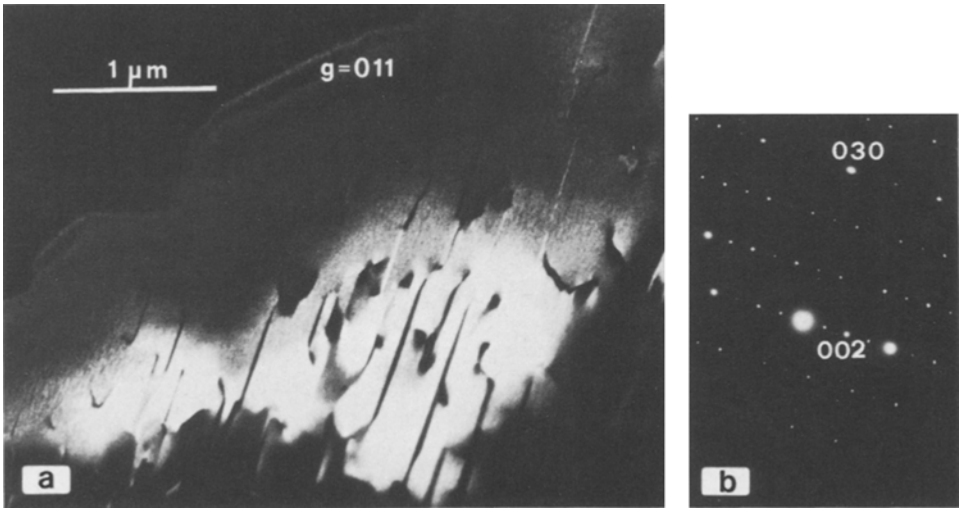

Fig. 2
a Antiphase domain boundaries in troilite at room temperature, the displacement vector of the antiphase domains is $1/3 <\bar{1}10>$, dark field image with g = 011 and **b** diffraction pattern

only by Putnis (1974). Fe$_{1-x}$S (pyrrhotite), which is characterized by an iron deficiency, has been studied by high resolution electron microscopy (Pierce and Buseck 1974; Nakazawa et al. 1975; Morimoto 1978a, b). Van Landuyt and Amelinckx (1972) reported a variety of defects in Fe$_7$S$_8$.

The phase diagram proposed by Nakazawa and Morimoto (1971) and Morimoto (1978a, b) shows a field with two phases between 100° C and 150° C, 2*C* (troilite) and 1*C* (NiAs-type structure), in the range of FeS to Fe$_{0.945}$S.

Materials and Techniques

Troilite from the unequilibrated ordinary chondrites Chainpur (LL3), Mezö-Madaras (L3), and Tieschitz (H3) and from the equilibrated ordinary chondrite Etter (L-H6) has been studied by means of *transmission electron microscopy* (TEM). The opaque mineral is part of the matrices and also covers the chondrules by forming "dark rims" (Ashworth 1977).

The TEM observations were made with the aid of a JEOL JEM 100B electron microscope equipped with a side entry goniometer. To observe phase transitions at elevated temperatures in situ, a commercially available heating holder was used. Suitable thin specimens for TEM with 100 kV acceleration voltage were prepared from conventional petrographic thin sections by ion bombardment (Bach 1964; Barber 1970; Tighe 1976). With regard to the relatively low transition temperature of FeS, one specimen (Etter) was kept below 90° C during preparation. Information on chemical composition was obtained by the characteristic X-ray spectrum excited in the specimen by the incident electron beam of an attached energy-dispersive X-ray spectrometer (König 1976; Lorimer and Cliff 1976). The accuracy of the analysis lies between ±2% to 3%. Within this limitation, the specimens studied represent troilite close to stoichiometry. Traces of Ni were not observed.

Observations and Results

Antiphase Domain Boundaries at Room Temperature

In all specimens under investigation, troilite displayed *antiphase domain boundaries* (APB) as characteristic crystal defects, predominantly oriented parallel to (001) (Fig. 2) and ending at dislocations. They were only visible in the dark field mode with superstructure reflections of the type $h-k \neq 3n$. They were out of contrast with reflections of the basic NiAs-type structure. Contrast experiments (cf. Amelinckx and Van Landuyt 1976) showed that the displacement vector of the APB is $1/3 <\bar{1}10>$. The observed electron diffraction pattern is in agreement with the space group $P\bar{6}2c$ (Bertaut 1956; Evans 1970).

Heating Experiments and Phase Transition

Controlled heating experiments with the commercial heating holder were performed on troilite inside the electron microscope. When troilite ($P\bar{6}2c$) is heated to 115°–150° C it inverts to a transitional phase, and at about 210° C a second transformation to the NiAs-type structure occurs. All observed phase transitions are reversible, i.e., the transitional phase is generated by heating as well as by cooling. The transition went back and forth within a temperature change of a few degrees in the furnace. The precise temperatures of the transitions cannot be given because they were not measured directly at the specimen area under observation. Only the furnace temperature of the heating stage was accurately obtained by a 13% Pt Rh-Pt thermocouple. By slightly focusing or defocusing the electron beam, both phase transitions could be produced.

The transitions could easily be detected in the electron diffraction mode. At the first transition point (troilite $P\bar{6}2c$ to the transitional phase), reflections of the type $h-k \neq 3n$ and $l \neq 2n$ (indices referring to the space group $P\bar{6}2c$) disappeared and other reflections characterizing the transitional phase occurred. From the diffraction pattern it was not clear whether this phase had a hexagonal or pseudohexagonal orthorhombic multiple twinned unit cell. However, dark field images operating with superstructure reflections demonstrated that the transitional phase was twinned and the threefold twin axis lies parallel to *c*. The intensity of the twin reflections was often very different, indicating that one twin orientation was preferred (Fig. 3a, b). An indexing of the diffraction pattern of the twinned transitional phase is shown in Fig. 4. Dark field images proved twin domains of different sizes. The observations indicated an orthorhombic pseudohexagonal cell with the lattice parameters $A, \sqrt{3A}, C$.

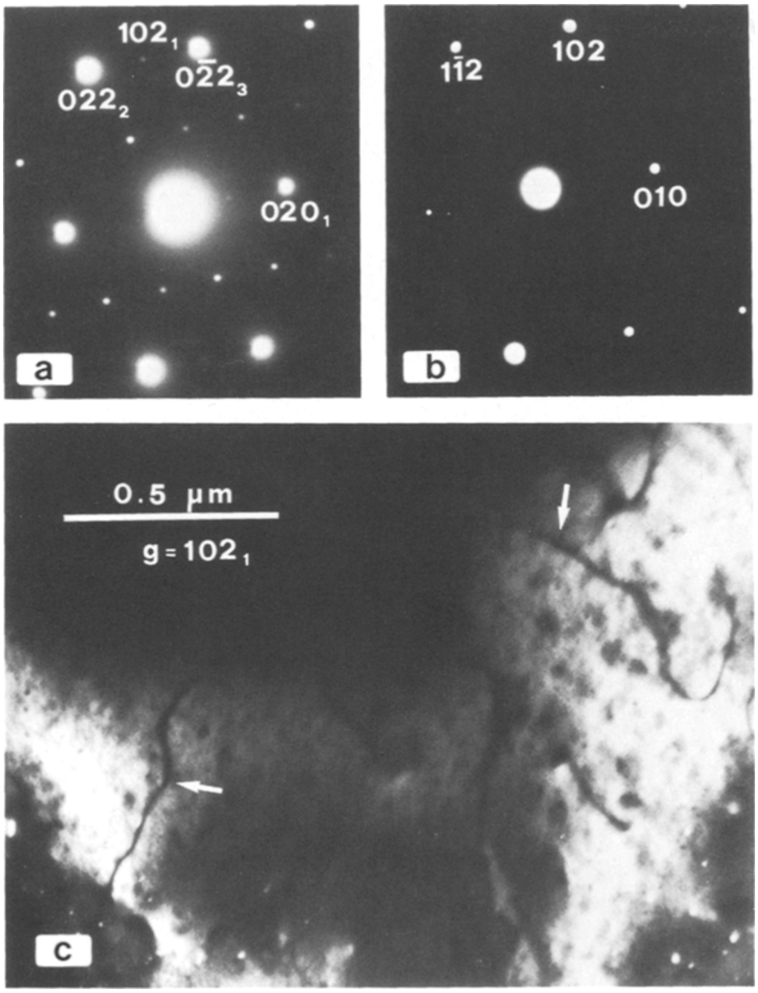

Fig. 3
a Diffraction pattern of the transitional phase, ($T \approx 200°$ C), showing twin and superstructure reflections
b At $T \approx 230°$ C the additional reflections have vanished and only the main reflections corresponding to the NiAs-type structure occur
c The crystal defects present in the transitional phase are APB (*arrow*) with the displacement vector 1/2 [110] referring to the orthorhombic pseudohexagonal cell with A, $\sqrt{3}A$, C dark field image at $T \approx 200°$ C

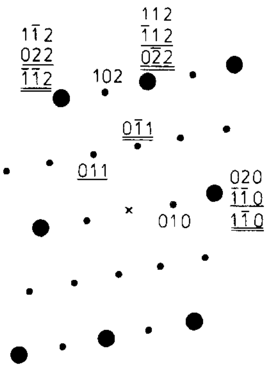

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Fig. 4. Indexing of the diffraction pattern in Fig. 3a. The reflection of the three twin individuals are indicated by underlining

The transitional phase contained additional antiphase domains (Fig. 3c). Their displacement vector, as determined by contrast experiments was 1/2 [110], referring to the orthorhombic setting. This Burgers vector indicates a primitive orthorhombic cell.

In the $h0l$ electron diffraction pattern of the transitional phase, reflections of the type $h0l$, $l \neq 2n$ are systematically absent which is caused by a (010) glide plane with the translation $1/2c$. In addition to previous studies (Töpel-Schadt and Müller 1979) the inspection of the $hk0$ diffraction pattern shows only reflections with $h+k=2n$, indicating a (001) glide plane with the component $1/2[a+b]$. In these crystal orientations the common phenomenon of multiple diffraction in electron diffraction can be excluded (Gard 1976). Assuming centrosymmetry, the space group *Pmcn* is the most probable one to describe the transitional phase. The $hh\overline{2h}l$ diffraction pattern of the high temperature phase shows systematic absence of reflections of the type $hh\overline{2h}l$, $l \neq 2n$. This result is in agreement with the space group $P6_3/mmc$ (NiAs structure), the probable space group of the high temperature phase.

The high temperature phase and the transitional phase could in no case be quenched to room temperature; all phase transitions were reversible.

No difference could be detected between the shape of the APB of the specimen that was kept below 90° C during preparation (Etter) and the other samples.

Discussion

Space-Group Relationships and Occurrence of Twin and Antiphase Domains

Group-theoretical considerations based on symmetry relations may help to understand the correlation between the space groups of the troilite modifications at room temperature in the transitional and in the high temperature phase. Symmetry relations of domains, e.g., twin laws or the displacement vector of antiphase domains, allow conclusions regarding the structure of the parent phase and possibly on the character of the transition. Several authors applied those considerations in the field of material science and mineralogy (Van Tendeloo and Amelinckx 1974; Bärnighausen 1975a, b, 1980; Amelinckx and Van Landuyt 1976; Wondratschek and Jeitschko 1976; Müller 1977; Töpel-Schadt et al. 1978).

Inspections of the tables "Maximal subgroups of the space groups" (Neubüser and Wondratschek, 1969) show that $P\bar{6}2c$ (troilite) and *Pmcn* (transitional phase) are both subgroups of $P6_3/mmc$ (high temperature phase), but lie on different branches of the "family tree" (Bärnighausen 1975a, 1980). The possible group-subgroup relationships are shown in Fig. 5. The symmetry reduction from $P6_3/mmc$ to $P\bar{6}2c$ can be obtained in two equivalent ways, which were proposed independently by Bertaut (1979) and Töpel (1980).

Twins are expected by "klassengleiche" and ABP by "translationengleiche" symmetry reduction. Therefore $P\bar{6}2c$ (troilite) may display APB with the displacement vector $R = 1/3 < \bar{1}10 >$ and $R = 1/2[001]$ caused by the loss of translational symmetries. Only the first kind of APB has been observed. The symmetry reduction t2 occurring here is connected with the loss of centrosymmetry. During the symmetry-reducing steps, the transitional phase loses point group and translational symmetry operations, namely the threefold twin axis parallel to c and the translational symmetry operation $1/2(a+b)$. Three orientation variants with the threefold twin axis parallel to c and antiphase domains with the displacement vector 1/2[110] are possible in the transitional phase and have been observed. A shift of the origin of the space groups $P\bar{6}2c$ and $Pmcn$ is necessary (Fig. 1). The vector $T_1 = -\frac{1}{3}\frac{1}{3}-\frac{1}{4}$ transforms the origin of the $P6_3/mmc$ to the $P\bar{6}2c$ cell and the vector $T_2 = 0-\frac{1}{2}0$ describes the origin shift from the subcell to the $Pmcn$ cell.

The vectors defining the unit cell of $P\bar{6}2c$ are $a'_1 = a_1 - a_2$, $a'_2 = a_1 + 2a_2$, $c' = 2c$, whereby a_1, a_2, and c are the basic vectors of the NiAs subcell. The vectors describing the cell of the transitional phase are $a'' = a_1 + a_2$, $b'' = -a_1 + a_2$, $c'' = c$.

The transitional phase can be described by the MnP structure type according to King and Prewitt (1978). The structural relationship between NiAs and MnP types is obvious and has been discussed by Bärnighausen (1980) and Bertaut (1979).

Conclusion

The crystal defects in troilite observed in this study originate from subsolidus phase transitions. The following sequence of transitions is proposed:

$$P6_3/mmc \xrightleftharpoons{\approx 215°\ C} Pmcn \xrightleftharpoons{115°-150°\ C} P\bar{6}2c.$$

The range of stability of troilite is in agreement with values given in the literature. The superlattices result from a distortion of the NiAs-type structure. Therefore, group-theoretical considerations were a useful tool in describing the space-group relations.

The combination of electron diffraction and imaging of characteristic crystal defects with respect to the group-theoretical considerations revealed the space group $Pmcn$ to be the most probable one for the transitional phase.

This result is in agreement with the presumption of King and Prewitt (1978), based on X-ray diffraction at elevated temperatures. To exclude unequivocally the acentric space group $P2_1cn$ displaying the same diffraction symbol as $Pmcn$, an X-ray structure analysis at high temperature is necessary. The acentric space group $P2_1cn$ also fits the "family tree", e.g., $P2_1cn$ is a maximal "klassengleiche" subgroup of $Pmcn$ (cf. Fig. 5).

Since neither $P\bar{6}2c$ or $Pmcn$ are subgroups of each other, but lie on different branches of the family tree (cf. Fig. 5), this phase transition is of first order, while the transition $Pmcn \rightleftharpoons P6_3/mmc$ between super and subgroups is a phase transition of second order according to (Bärnighausen 1975b). Putnis (1974) regarded both phase transitions as second order because he assumed hexagonal symmetry of the transitional phase.

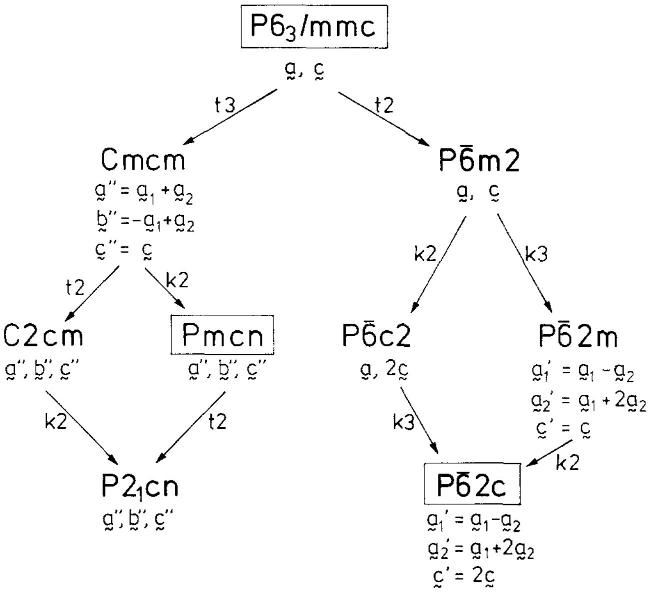

Fig. 5. Possible group-subgroup relationships between the three FeS modifications with the space groups $P6_3/mmc$, $Pmcn$ ($P2_1cn$), and $P\bar{6}2c$ displayed in a "family tree". The unit cell transformations are given in terms of the basic vectors a and c of the fundamental NiAs-type structure ($P6_3/mmc$). The symmetry-reducing step is symbolized by an arrow connecting the space group with its maximal subgroup. The letters t or k indicate that the subgroup has the same translational or point group symmetry, respectively, as the parent space group. The numbers give the indices of reduction, e.g., t3 means that the subgroup has the same translational symmetry as the parent space group, but has lost the point symmetry of the threefold axis. Formalism after Bärnighausen (1975a, 1980)

This study on FeS completes the phase diagram proposed by Morimoto (1978a, b) who worked on FeS only at room temperature, while $Fe_{1-x}S$ was studied at elevated temperatures. An orthorhombic pseudohexagonal structure with the lattice parameters A, $\sqrt{3}A$, C like the transitional phase has not been observed in the vicinity of stoichiometric composition. It is of further interest to investigate whether such a transitional phase only occurs for FeS or if it also exists in phases with small deficiencies or excesses of iron at 100°–300° C.

Acknowledgements. We thank H. Fuess and G. Miehe for helpful discussions, M. Korekawa for encouragement, G. Kurat and the Natural History Museum, Vienna (Austria), for supplying the meteorite samples. Support of the Deutsche Forschungsgemeinschaft is gratefully acknowledged (grant Ko 413/9).

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Received August 17, 1981