Reports

Electron-Optical Observations on the α-Transformation in Troilite

Abstract. *The transformation from high to low troilite occurs via a transitional structure. The transformation to this transitional state is continuous, whereas that to the low-temperature form is discontinuous. This illustrates alternative metastable behavior in a system when nucleation of the low-temperature phase may be impeded.*

The α-transformation at 140° ± 5°C (*1*) in troilite (FeS) is a transformation from a NiAs-type structure at high temperature to a closely related superstructure (*2*). Bertaut (*3*) has derived an atomic arrangement to account for this superstructure which involves small displacements (0.2 Å) of sulfur atoms along the *c* axis and of iron atoms perpendicular to the *c* axis. The transformation is characterized by marked discontinuities in the thermal expansion coefficient and in the lattice parameters with an associated volume change of about 0.22 Å^3 per mole of FeS (*4*).

Although this transformation has been observed by various methods, the mechanism and kinetics of the phase change have yet to be described. In the work reported here the transformation has been followed electron-optically and a number of new observations pertinent to the mechanism have been made.

Under heating by the electron beam, the transformation can be observed both in the transmission image and in the diffraction pattern. In suitable grains the temperature can be controlled quite sensitively by small shifts of the beam, and it is found that the transformation to the low troilite structure is rapid and reversible. It is not possible to quench the high-temperature phase even with the most rapid cooling rates. Nucleation of the low structure can be observed along grain boundaries and at dislocations and subsequent growth of this phase spreads rapidly. The difference in the lattice parameters of the phases indicates some measure of noncoherence with associated strain energy, so that some degree of hysteresis might be expected.

Observations of the changes in the diffraction pattern on very slow cooling of the high-temperature NiAs phase show the existence of a transitional state between the high and low structures. Figure 1 shows the stages in the transformation as seen in a [211] axis diffraction pattern. The transitional structure (Fig. 1a) shows diffracted intensity at points corresponding to the existence of a $2a,1c$ supercell. These diffraction spots grow continuously from zero intensity to a maximum value with slow continuous undercooling, until the spontaneous appearance of the $3^{1/2}a$, $2c$ low troilite superstructure spots (Fig. 1b). The intensity of the diffraction spots due to the transitional structure can be continuously increased or decreased by slight variations in temperature, whereas the intensity of the low troilite spots cannot be varied and their appearance and disappearance occur as a distinct discontinuity. The transitional phase is fully coherent with the high-temperature matrix and does not seem to be associated with any discontinuities in lattice spacing, there being no evidence in the image that a transformation has occurred, whereas the strain associated with the subsequent nucleation and growth of the low-temperature structure can be seen as diffraction contrast in the transmission image. The behavior observed in both the diffraction pattern and the image is considered to be evidence that the phase change from the high to the intermediate structure is of continuous type, and that the change to the low

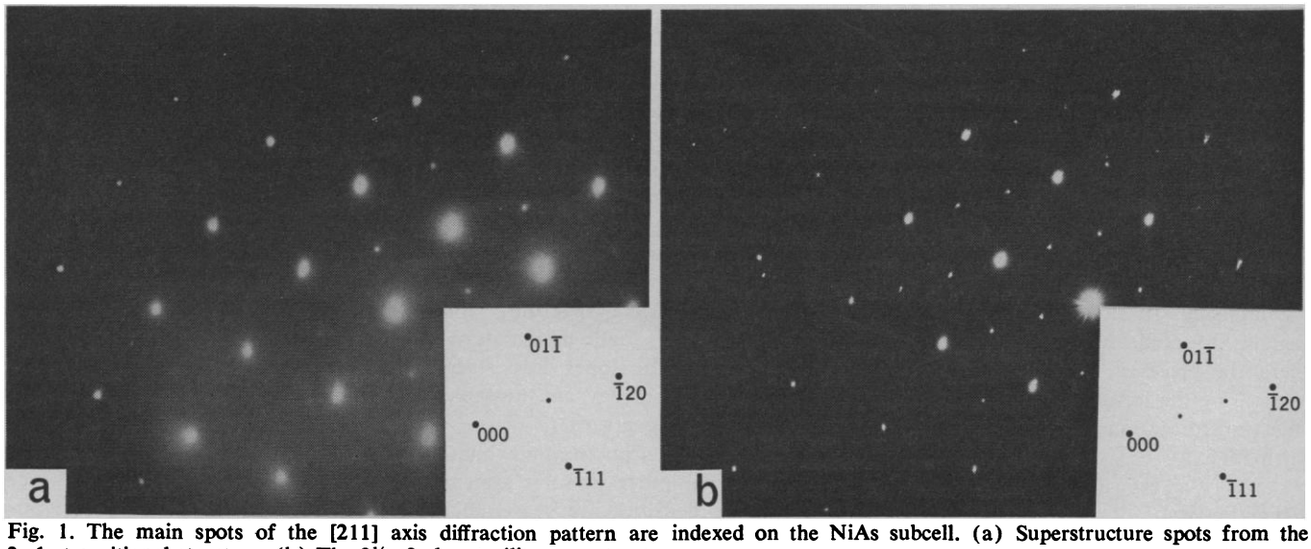

Fig. 1. The main spots of the [211] axis diffraction pattern are indexed on the NiAs subcell. (a) Superstructure spots from the $2a,1c$ transitional structure. (b) The $3^{1/2}a,2c$ low troilite superstructure.

structure is essentially of discontinuous type.

On heating the low-temperature phase the transitional state is not observed, indicating that this phase does not have a stability field. It is considered that the formation of the transitional state represents an alternative continuous process in a situation where hysteresis occurs in the formation of the equilibrium low-temperature structure. Such a metastable transitional phase would be subject to symmetry constraints such that its structural state is compatible with the symmetry of the parent state. The definition of the operative constraints on behavior of this kind is discussed by McConnell (*5*).

The nature of the α-transformation can be considered according to Landau's general theory of phase transformations (*6*) in which the conditions for second-order transformations are derived from group theory. The transitional phase can be characterized in reciprocal space by the vector $\mathbf{k} = (\frac{1}{2}\ \frac{1}{2}\ 0)$ for which the proper symmetry group (the group of rotations and reflections that leave $\mathbf{k}$ invariant) contains symmetry planes and axes intersecting at a point. Thus $(\frac{1}{2}\ \frac{1}{2}\ 0)$ is a "singular point" and a second-order transformation is possible from the high to the transitional phase. For the low structure the reciprocal lattice is characterized by the vectors $\mathbf{k}_1 = (\frac{1}{3}\ \frac{2}{3}\ \frac{1}{2})$ and $\mathbf{k}_2 = (\frac{1}{3}\ \frac{2}{3}\ 0)$, and hence the structure can be described only by a linear combination of functions corresponding to at least two irreducible representations. This precludes the possibility of a second-order transformation from the high to the low structure. The experimental observations outlined above are in accord with the predictions of Landau's theory, which provides a theoretical basis for the operative symmetry constraints on continuous transformations.

The transformation in troilite illustrates the general principles of behavior in a system in which the nucleation of a true equilibrium phase may be impeded. In stoichiometric FeS the barrier to nucleation of the low-temperature phase is small, although on increasing the iron deficiency in $Fe_{1-x}S$ the transformation becomes more sluggish (*7*).

A. PUTNIS

Department of Mineralogy and Petrology, University of Cambridge, Cambridge CB2 3EW, England

References and Notes

1. H. Haraldsen, *Z. Anorg. Allg. Chem.* **231**, 78 (1937).
2. G. Hagg and I. Sucksdorf, *Z. Physik. Chem. Abt. B* **22**, 444 (1933).
3. E. F. Betraut, *Bull. Soc. Fr. Mineral. Cristallogr.* **79**, 276 (1956).
4. L. A. Taylor, *Carnegie Inst. Wash. Year* **68**, 259 (1970).
5. J. D. C. McConnell, *Mineral. Mag.* **38**, 1 (1971).
6. L. D. Landau and E. M. Lifschitz, *Statistical Physics* (Pergamon, London, 1962), chap. 14.
7. F. Gronvold and H. Haraldsen, *Acta Chem. Scand.* **6**, 1452 (1952).
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The Temperature Gradient in the Solar Nebula

Abstract. *The available compositional data on planets and satellites can be used to place stringent limits on the thermal environment in the solar nebula. The densities of the terrestrial planets, Ceres and Vesta, the Galilean satellites, and Titan; the atmospheric compositions of several of these bodies; and geochemical and geophysical data on the earth combine to define a strong dependence of formation temperature on heliocentric distance. The pressure and temperature dependences of the condensation process are separable in the sense that the variation of the deduced formation temperatures with heliocentric distance is insensitive to even very diverse assumptions regarding the pressure profile in the nebula. It is impossible to reconcile the available compositional data with any model in which the formation temperatures of these bodies are determined by radiative equilibrium with the sun, regardless of the sun's luminosity. Rather, the data support Cameron's hypothesis of a dense, convective solar nebula, opaque to solar radiation, with an adiabatic temperature-pressure profile.*

Theoretical studies have been made of the chemistry of solar material in order to elucidate conditions in the solar nebula at the time of condensation of meteoritic and planetary material (*1–3*). With this knowledge of the stability fields of condensed minerals and ices and some basic information on the bulk chemical composition of solar system bodies, it is possible to constrain the temperature and pressure conditions present in the nebula at the time of condensation.

Figure 1 contains the results of calculations of the condensation temperatures of a variety of compounds of abundant elements from a gas having the same composition as the sun. Also given are several radically different types of temperature-pressure profiles through the nebula, including isobaric (constant pressure), isopycnic (constant density), and isentropic (adiabatic) sections. It can be seen that the sequence of chemical reactions going from high temperatures to low temperatures is insensitive to very widely divergent assumptions regarding the pressure. Note that all temperature-pressure plots with slopes less steep than that of an adiabat are unstable against convective overturn.

I will place limits on the bulk compositions of a number of solar system bodies whose densities are reasonably well determined, then use this information in conjunction with Fig. 1 to constrain the conditions under which the dominant materials of these bodies condensed.

1) Mercury has a zero-pressure density of 5.3 g cm^{-3}, which requires that it be made of material very rich in metal. Iron-nickel alloy must make up at least 60 to 65 percent of the planet. No atmosphere has been detected. The density of Mercury is directly explained if it formed at a temperature so high that $MgSiO_3$ was not fully condensed (*2*). This is radically different from the proposal by Ringwood (*3*), who attributed the high density of Mercury to secondary volatilization of silicates from the planet by a putative highly luminous phase of the sun.

2) Venus has a zero-pressure density slightly less than that of the earth. Despite very high surface temperatures of 750°K, no sulfur-bearing gases have been detected in its dense and very dry atmosphere (*4*). Venera 8 has measured the potassium abundance in a small sample of the surface of Venus and found it to be ~ 4 percent (*5*). This requires formation within the stability field of alkali feldspar, but probably above the formation temperatures of FeS and hydrous silicates.

3) The earth has a mantle FeO content of ~ 10 percent and a liquid outer core significantly less dense than pure iron, presumably containing ~ 15 percent sulfur (*2*, *6*). The earth's hydro-