

## New observations on natural pyrrhotites: magnetic transition in hexagonal pyrrhotite

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### Abstract

Quenching hexagonal pyrrhotite,  $\text{Fe}_9\text{S}_{10}$ , from 225°C retains the high temperature ferrimagnetic phase. The rate of loss of magnetism when the sample is annealed at temperatures below the ferrimagnetic stability range allows the determination of an activation energy for vacancy diffusion. The measured value of 50.2 kJ/mol agrees closely with that of Fryt *et al.* (1979).

In the course of a study of hexagonal pyrrhotites by means of a magnetic thermobalance (Bennett and Graham, 1980), it was observed that the anti-ferro-magnetic ferri-magnetic transition which usually occurs at about 210°C can be delayed by quenching the ferri-magnetic phase from 225°C to room temperature in a current of air. If the sample is then annealed at temperatures between about 70°C and the transition temperature of 210°C, it loses its magnetism at a rate which depends on temperature. This work is related to that of Marusak and Mulay (1979, 1980), but because it is following the demagnetization reaction, our work extends over a much wider temperature range.

We believe that the high temperature ferri-magnetic structure is stabilized by a vacancy superlattice which develops above the transition temperature, and that the transition to the low temperature antiferro-magnetic structure depends on a vacancy reordering process; this view is reinforced by the results described below. However, following Nakazawa and Morimoto (1971) and Kissin (1974), we understand the high temperature phase to have an "nA" ordered structure, and the low temperature phase the "mC" structure. As suggested by Morimoto, Nakazawa and Wantanabe (1974) these structures are probably partly ordered and/or intimately intergrown rational superlattices. The temperature at which the naturally occurring "5C" structure forms is still not well known, if indeed it can be formed in the laboratory after heat treatment.

The results in the present paper were all derived from a single sample of natural pyrrhotite from

Nairne in South Australia. The sample consisted of about 50 mg of pyrrhotite sealed *in vacuo* in a silica capsule. A series of curves was obtained for the rate of loss of magnetism at different temperatures, of which six are shown in Figure 1, corrected and scaled to show the main trends. There is a maximum reaction rate at about 200°C. Below this temperature the reaction slows because of lower diffusion rates, and at higher temperatures the rate slows because the free energy for the change to the low temperature structure decreases as the transition temperature is approached.

There are several problems in accurately quantifying the kinetic data. Because the sample was sealed in silica to avoid oxidation, it reached annealing temperatures slowly, and a zero of time was indeterminate. The initial decrease in magnetic susceptibility in a raw demagnetization curve (Fig. 2) is due to thermal demagnetization as the sample heats to ambient furnace temperature. The magnitude of this decrease can be predicted for a given temperature by reference to the demagnetization curve of monoclinic pyrrhotite, the Curie temperature of which is only ~50°C above that of the hexagonal phase. The rate of temperature rise of the sample can be inferred from the curve in Figure 2; it is easier to determine accurately at the lower temperatures, where demagnetization due to vacancy movement does not interfere because it is too slow. There is an initial rapid fall in magnetization which is accomplished in about 1 minute, but it is clear from Figure 2 and from runs above the transition temperature (Fig. 3) that the sample does not reach

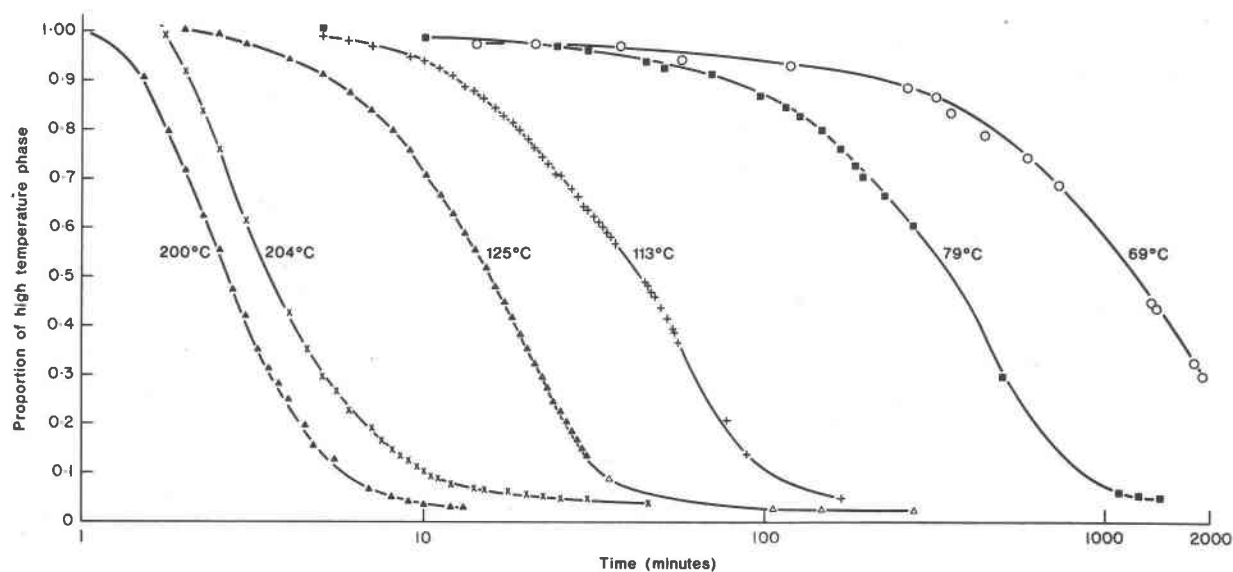


Fig. 1. Selected curves showing fraction of the high temperature phase remaining after annealing at specified temperatures. The raw data for intensity of magnetization have been corrected for thermal demagnetization and scaled to their initial value.

the desired temperature for 5–6 minutes. Even at the lowest temperatures where the initial few minutes are not so important, definitive curve fitting is precluded by this thermal lag time.

After allowing for thermal demagnetization, the initial magnetization of the sample is a function of the temperature of annealing; all the curves in Figure 1 have been given a common scale by taking

the ratio of the magnetization at time  $t$  to the initial magnetization at time  $t_0$ . This is approximately the fraction of the high temperature phase remaining. The curves do not seem to fit a power law, presumably because of a complex interaction between vacancy order and magnetic order.

At temperatures approaching the transition temperature ( $\sim 210^\circ\text{C}$ ) rates of reaction are strongly dependent on the small temperature excursions of the temperature controller which are believed to generate the main source of error after the initial temperature equilibration period. This is supported by the fact that a better curve was obtained when the temperature was arrived at by using a fixed stabilized voltage to power the furnace. A study of the transition region would require more sophisticated equipment.

Many chemical and physical rate processes are characterized by the Arrhenius equation,  $\text{Rate} = A \exp(-B/RT)$ , where  $B$  is the activation energy for the process and  $T$  is the absolute temperature. Taking logarithms,  $\log(\text{rate}) = \log A - (B/RT)$ . If the logarithm of the rate is plotted against  $1/T$ , the slope is a measure of the activation energy.

The rates were derived from the demagnetization curves by taking the time required to reach 1/10, 1/4, 1/2, 3/4 and 9/10 of the transition. The resulting Arrhenius plots for 1/10 and 3/4 are shown in Figure 4. The low temperature part of each of the curves approaches the activation energy of 50.2 kJ/mole characteristic of vacancy migration in pyrrhotite

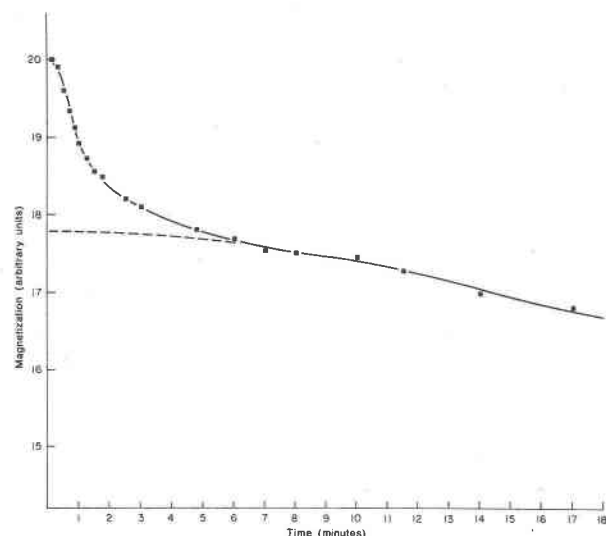


Fig. 2. Initial part of the transformation curve at a furnace temperature of  $96^\circ\text{C}$ . The portion of the curve above the dashed line is due to thermal demagnetization and gives an idea of the rate at which the specimen itself reaches the annealing temperature. Loss of magnetization due to the transformation is probably represented by the dotted curve and its continuation.

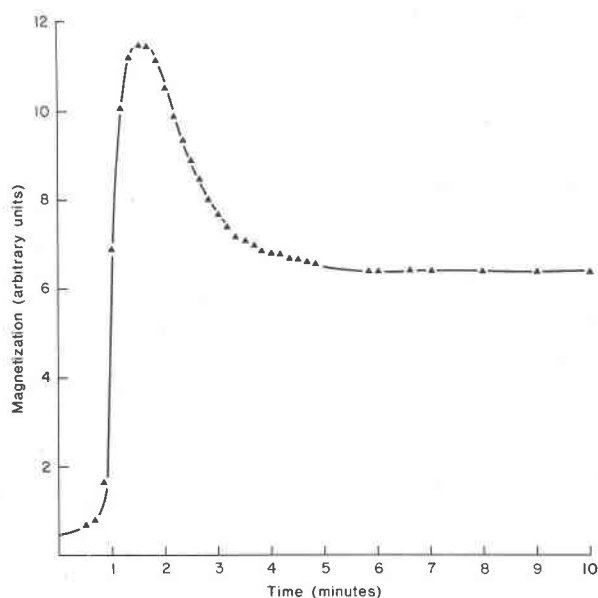


Fig. 3. The shape of the transformation curve at a furnace temperature of 245°C, above the transformation temperature. The initial increase in magnetization is due to the formation of the high temperature superlattice as the specimen heats above 210°C. At higher temperatures, however, thermal demagnetization occurs, so that as the specimen heats further its magnetization drops to the equilibrium value for 245°C

(Fryt *et al.*, 1979). Deviations from this value became extreme as the transformation temperature is approached, and at this temperature the two superlattices become equally stable. We may infer that the curved Arrhenius plots are due to competition between the forward and reverse ordering processes. The exact shape of the Arrhenius plots in this region is uncertain because of heating lag times, but the general shape is as shown. The temperature range 440–480°K in which Marusak and Mulay (1980) made their observations corresponds to the extreme left hand side of Figure 4 ( $1000/T = 2.08$ – $2.27$ ). Apparent activation energies here are much lower than at temperatures further from the transition temperature. This may explain the low values of activation energy obtained by Marusak and Mulay, but there are discrepancies in detail.

At temperatures slightly above the transition temperature the reverse (magnetization) reaction can be observed by plunging an unmagnetized sample into the furnace set to the desired temperature. Temperatures are so high here, however, that heating lag times cause severe problems (see Fig. 3), except very close to the transition temperature where rates are slow due to other causes. As shown

in Figure 3 the magnetic transformation is complete long before the specimen has actually reached its annealing temperature, and the magnetic phase is then subject to thermal demagnetization. Times involved in these transitions are consistent with an extrapolation of the straight part of the Arrhenius plot through the transition region; negative deviations occur just above as well as below the transition temperature. At 210°C the transition is not complete in an hour, during which the specimen gains magnetism approximately linearly with time.

It is interesting that these transitions involving vacancy diffusion can be observed at temperatures 200°C lower than those of published macroscopic diffusion effects (Ewers, 1972) and that the experiments still only take hours at 70°C. This is because only nearest neighbor exchanges are involved. The magnetization of the sample is extremely sensitive to vacancy order. Any order/disorder or order/

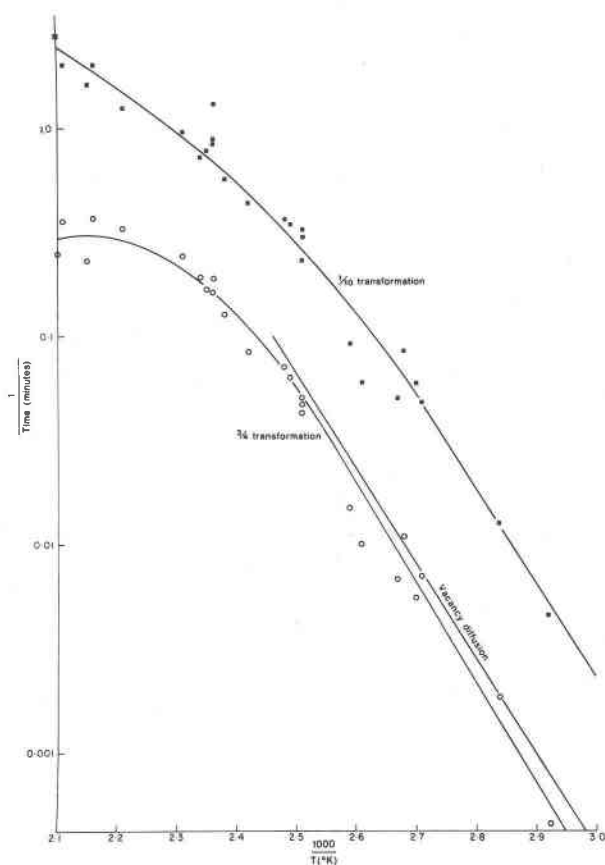


Fig. 4. Arrhenius plots for rate of annealing out the high temperature magnetic phase. These curves show the inverse of times for  $1/10$  and  $3/4$  of the reaction to occur. The line labelled "vacancy diffusion" has the slope characteristic of vacancy diffusion at high temperatures ( $1000/T < 1.15$ ).

order transition will occur in similar times so that the well known "metastability" of hexagonal and monoclinic pyrrhotites cannot be explained in terms of a transition of this type. Nucleation difficulties are only likely to be a major factor where the phases are of a different basic structure, *e.g.*, pyrite exsolution. Difficulties in the occurrence of transitions between NiAs-based phases in the Fe-S system must therefore be due to additional effects such as long-range diffusion of vacancies (phase separation) or stabilizing impurities. The ease with which vacancy ordering occurs probably contributes to equilibration difficulties by reducing the energy available for the formation of equilibrium phases.

It is possible to derive a relationship between the exchange field coefficients for hexagonal and monoclinic pyrrhotites from the equation  $T_c = n\mu^2\alpha/3k$  (Craik, 1971). The exchange field coefficient,  $\alpha$ , is the degree of coupling between the unpaired spins, and  $n$  is the number of magnetic dipoles of moment  $\mu$ . For the hexagonal structure  $n = 1/10$  of the number of sulphur atoms, and for the monoclinic structure it is  $1/8$ . The Curie temperature  $T_c$  for the monoclinic material is 315°C and for hexagonal it is 255°C. It is apparent that  $\alpha$  is approximately 12% higher for hexagonal than for monoclinic pyrrhotite.

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#### References

- Bennett, C.E.G. and Graham, J. (1980). New observations on natural pyrrhotites Part III. Thermomagnetic experiments. *American Mineralogist*, 65, 800-807.
- Craik, D.J. Structure and properties of magnetic materials. Pion Limited, London, 1971.
- Ewers, W.E. (1972) Nickel-iron exchange in pyrrhotite. *Proceedings of the Australasian Institute of Mining and Metallurgy* No. 241, 19-26.
- Fryt, E. M., Bhide, V. S., Smeltzer, W. W. and Kirkaldy, J. S. (1979), Growth of the iron sulfide ( $Fe_{1-\delta}S$ ) scale on iron at temperatures 600°-1000°C. *Journal of the Electrochemical Society, Solid-State Science and Technology*, 126, 683-688.
- Kissin, S.A. (1974). Phase relations in a portion of the Fe-S system. Ph.D. thesis, University of Toronto.
- Marusak, L. A. and Mulay, L. N. (1979). Mössbauer and magnetic study of the antiferro- to ferrimagnetic phase transition in  $Fe_9S_{10}$  and the magnetokinetics of the diffusion of iron atoms during the transition. *Journal of Applied Physics*, 50, 1865-1867.
- Marusak, L. A. and Mulay, L. M. (1980). Polytypism in the cation-deficient iron sulphide,  $Fe_9S_{10}$ , and the magnetokinetics of the diffusion process at temperatures about the antiferro- to ferrimagnetic ( $\lambda$ ) phase transition. *Physical Review B*, 21, 238-244.
- Morimoto, N., Nakazawa, H. and Watanabe, E. (1974). Direct observation of metal vacancy in pyrrhotite,  $Fe_{1-x}S$ , by means of an electron microscope. *Proceedings of the Japan Academy*, 50, 756-759.
- Nakazawa, H. and Morimoto, N. (1971). Phase relations and superstructures of pyrrhotite,  $Fe_{1-x}S$ . *Materials Research Bulletin*, 6, 345-358.

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