LETTERS TO THE EDITOR

EXOELECTRON EMISSION DURING PHASE TRANSFORMATIONS OF MAGNETIC PYRITES

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In this communication we present the results of measurements of exoelectron emission from magnetic pyrites which in the temperature range from 300°K to 650°K undergo magnetic transitions as well as non-magnetic phase transitions.

The exoelectron emission technique can be used for investigating both the allotropic phase transformations of iron alloys (Bogachev, et.al. 1967) and the magnetic transformations of nickel, chromium and oxides coating these metals (Biernacki *et al.* 1967; Sujak *et al.* 1969).

Obtaining a thin layer of pyrrhotite, $Fe_{1-x}S$, of a predetermined stoichiometric composition is not easily accomplished, and it is even more difficult to maintain this composition during sample annealing to a temperature of the order of 650°K (Lotgering 1956). Because of this fact, measurements were performed on 25 bulk samples freely cut from a large block of the mineral. The samples had the shape of disks 1.6 cm in diameter and from 0.2 to 0.3 cm thick. Emission measurements were conducted in atmospheric air by means of a point counter with saturated quenching vapour over the free surface of the liquid, at least 24

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hours after the samples had been prepared. The time dependence of emission intensity, $N/t = f(t)$, and the furnace temperature $T = f(t)$, on which the examined samples were placed, were measured simultaneously. On the basis of the obtained results the intensity of electron emission was presented as a function of temperature, $N/t = f(T)$. The heating rate was always about 15°K/min, and the cooling rate was of the same order. The measuring arrangement applied has been described in detail earlier (Sujak *et al.* 1968).

As follows from the phase diagram given by Hansen and Anderko (1958), the FeS alloy displays two polymorphic transformation points: the low-temperature α phase transformation point and the high-temperature β point. For alloys containing up to 50 per cent of sulphur atoms the α point is at a temperature of about 411°K. With increased content of sulphur the temperature of the α phase transition point drops to about 323°K at 53 at. %. S. The high-temperature β phase transformation point lies at 580°K and, as quoted by Hansen and Anderko (1958), it does not depend on the sulphur content in the Fe-S alloy.

Alloys with 52–54 at. % sulphur are ferrimagnetic (Below 1959, Lotgering 1956). The magnetic transformation of pyrrhotite has a more complex character. Each stage of this transformation is usually described by giving four characteristic temperatures:

a) $Q_n \approx 490$°K, above this temperature the vacancies become ordered, which causes a rise in the unbalanced antiferromagnetism;

b) $Q_C \approx 575$°K, at this temperature there takes place a transition from the state of unbalanced antiferromagnetism to the antiferromagnetic state;

c) $Q_V \approx 595$°K, above this temperature the ordering of the vacancies becomes destroyed:

d) $Q_N \approx 615$°K, at this point there is antiferromagnetic transformation (Néel point).

The $N/t = f(T)$ curves for the 25 samples examined by us can be divided into three main groups presented respectively in Figs 1 to 3. Most of the curves had the character presented in Figs 1 and 2. In a few cases only the two extreme maxima were observed distinctly on the curves $N/t = f(T)$. Samples of powdered pyrrhotite do not have any maxima on the $N/t = f(T)$ curve even though the other measurement conditions are maintained.

Conducting a simplified graphical analysis of the $N/t = f(T)$ curves for the bulk samples we can distinguish 5 maxima:

1) The low-temperature maximum I of exoelectron emission intensity in the vicinity of 355°K corresponding to the α polymorphic transformation of those microregions of the examined samples in which the content of sulphur atoms exceeds 52% (Hansen and Anderko 1958);

2) The maximum II appearing distinctly on the experimental curves (≈ 420°K), due to the α transformation of those microregions of the examined samples in which the content of sulphur atoms is less than 50% (Hansen and Anderko 1958);

3) Maximum III (≈ 490°K) of exoelectron emission corresponding to the magnetic transformation of $Fe_{1-x}S$ at the point Q_n;

4) Maximum IV (≈ 565°K) corresponding to the temperature Q_C;

5) Maximum V (≈ 620°K) corresponding to the antiferromagnetic transformation (the Néel point of pyrrhotite).

In some cases the maxima IV and V may be recorded as one maximum.

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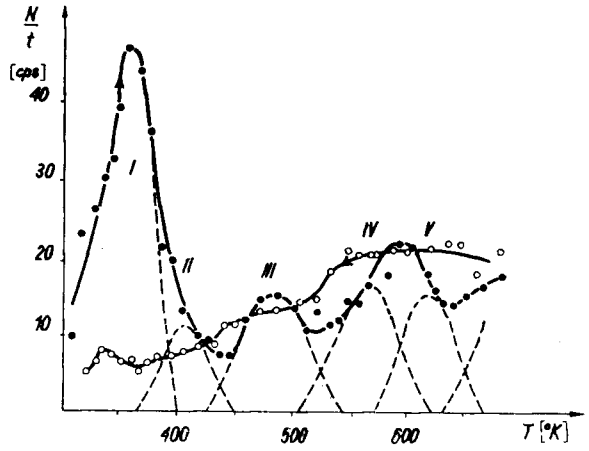

Fig. 1

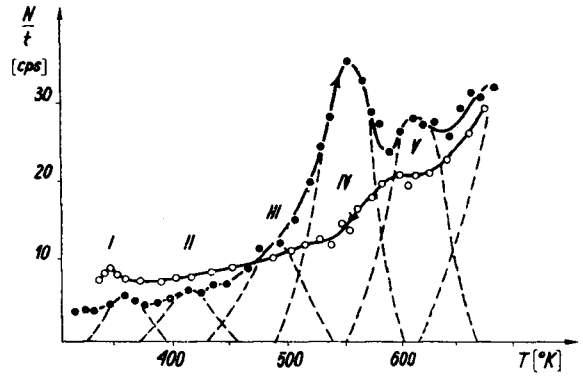

Fig. 2

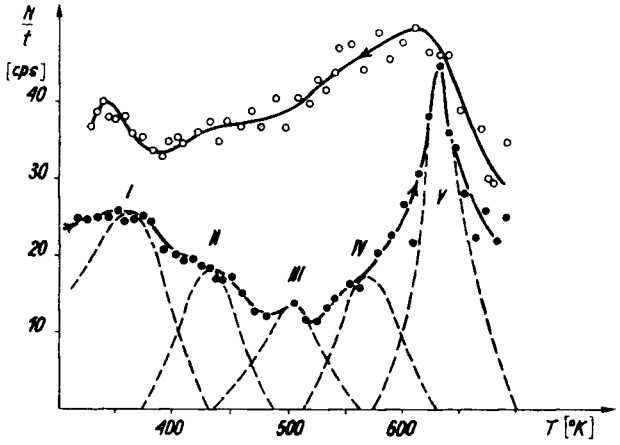

Fig. 3

Figs 1–3. Typical runs of photostimulated exoelectron emission intensity for different samples of pyrrhotite, $Fe_{1-z}S$. The full circles symbolize the values of measurement obtained during heating, whereas the open circles are the measurements values during cooling of the sample

The results presented here indicate the possibility of applying the exoelectron emission technique in investigations of the degree of homogeneity and the composition of complex materials, for which the position of the phase transformation points strongly depends on the stoichiometric composition. The method of exoelectron emission makes it possible to observe the "subtleties" of the magnetic transformation in pyrrhotite.

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