Order-Disorder Transitions in Iron-Nickel (50%-50%) Alloys from Iron Meteorites as Studied by Mössbauer Spectroscopy

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Iron meteorites contain an ordered FeNi (50%-50%) alloy. By study of the disordering process above the transition temperature $T_c \simeq 593$ K with Mössbauer spectroscopy, it is shown that the hyperfine parameters reflect the degree of order. This depends on the cooling rate of the meteorites. As the hyperfine parameters, and therefore the degree of order, vary from meteorite to meteorite, the ordered FeNi alloy contains information on the relative cooling rates of meteorites.

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Iron meteorites are interesting physical systems being iron-nickel alloys that have cooled with a cooling rate of about 1 K per 10^6 y. The meteorites often contain two phases, called kamacite and taenite.[1] It has recently been shown that the taenite phase, which is the object of our investigation, is composed of an ordered FeNi (50%-50%) alloy with $L1_0$ structure (see Fig. 1) and a disordered fcc iron-nickel alloy containing 25% of Ni or less.[2] The ordered phase forms domains of linear dimensions of the order of 1000 Å while the disordered phase fills up the space between the ordered domains.[2] The ordered FeNi phase is tetragonal, though the tetragonality is very small ($c/a = 1.0036$).[3]

Because of the extremely slow diffusion below the order-disorder transition temperature $T_c \simeq 593$ K,[4] it has not been possible to produce the ordered FeNi phase by thermal treatment of disordered alloys. The phase has, however, been produced as small ordered domains (linear dimensions about 100 Å) in neutron-irradiated iron-nickel alloys.[4] The reason why the ordered structure has formed in meteorites after all shall be sought in the extreme low cooling rates of the parent bodies of the meteorites.[1]

By Mössbauer spectroscopy the ordered FeNi phase has been identified both in iron meteorites and in the metal inclusions in stony meteorites, and it is found that the Mössbauer parameters of the ordered phase vary from meteorite to mete-

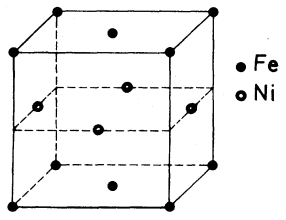

FIG. 1. The unit cell of the ordered FeNi (50%–50%) alloy, $L1_0$ structure.

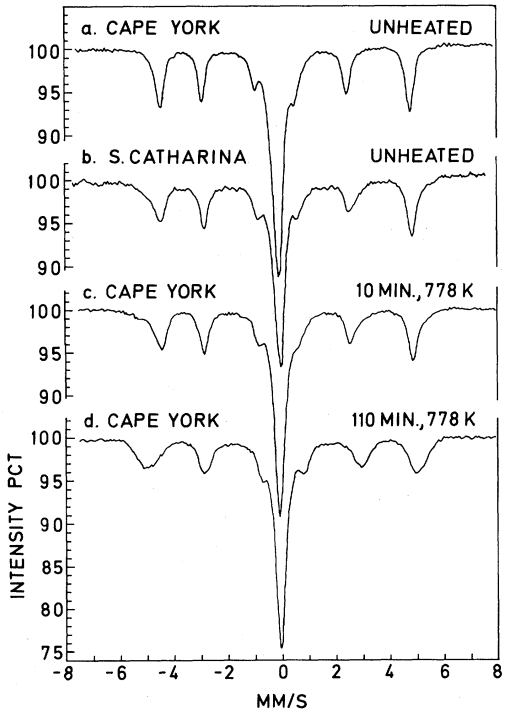

FIG. 2. (a) Mössbauer spectrum of taenite from the meteorite Cape York and (b) from the meteorite Santa Catharina. (c) Mössbauer spectrum of taenite from Cape York heated at 778 K for 10 min and (d) for 110 min. The spectra were all recorded at room temperature. Source: ^{57}Co in Rh.

orite.[5,6] With this in mind we have initiated a study of the order-disorder transition by means of Mössbauer spectroscopy.

In Figs. 2(a) and 2(b) we show the Mössbauer spectra of taenite from two iron meteorites, Cape York and Santa Catharina. The spectra are recorded at room temperature. They are both superpositions of two spectra[2]: (1) a central line from the disordered alloy, which is paramagnetic at room temperature; (2) an asymmetric six-line spectrum from the ordered phase, i.e., FeNi with the $L10$ structure. The ordered phase is ferromagnetic at room temperature. The asymmetry in the spectrum is due to a quadrupole splitting caused by the noncubic surroundings of the iron atoms.

From the spectra we find that the magnetic hyperfine field in Cape York is 288 ± 0.5 kG and the hyperfine field in Santa Catharina is 291 ± 0.5 kG. The magnetic hyperfine field is a function of the short-range order parameter.[4,7] Thus the difference in the hyperfine field of the two meteorites leads to the conclusion that their degree of order is not the same.

It is impossible to study the kinetics of the ordering process by thermal treatment. Therefore, we have studied the kinetics of the disordering process by heating an ordered FeNi (50%-50%) alloy at temperatures above the transition temperature. As a sample containing the ordered alloy we have used taenite from the Cape York meteorite. In the first series of experiments the taenite was heated in a reducing atmosphere at 758 K for 15 min and then rapidly cooled to room temperature. At room temperature a Mössbauer spectrum was recorded. This procedure was repeated in eighteen steps until the order in the alloy was almost destroyed.

A second series was like the first with the change that the taenite was heated at 778 K and the heating periods were 10 min repeated eleven times.

Figures 2(c) and 2(d) show selected spectra from experiments of the second series. For each experiment the hyperfine parameters were found by fitting the Mössbauer spectrum obtained with seven broadened Lorentz lines (the six lines corresponding to the ordered phase and the seventh to the central line). The main results of the two series of heating experiments may be read from Figs. 3(a)–3(c).

Figure 3(a) shows the room-temperature value of the magnetic hyperfine field H as a function of the heating time, at temperatures 758 and 778 K,

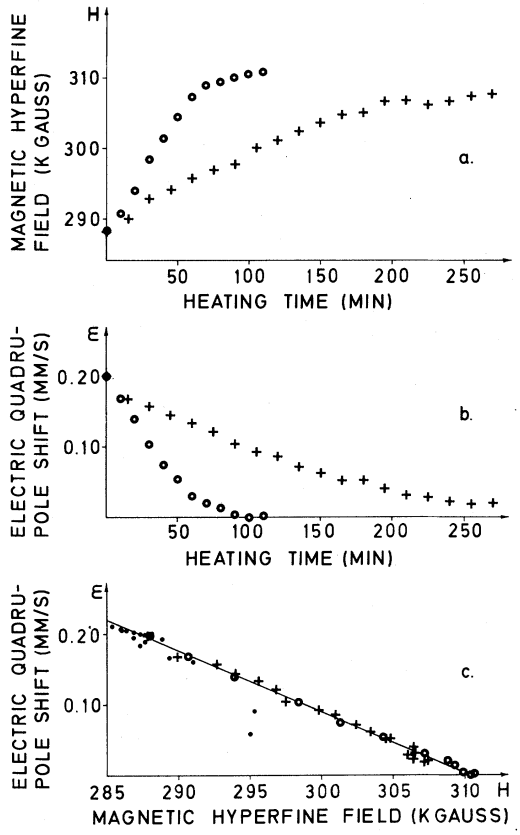

FIG. 3. Results from heating experiments of taenite from the meteorite Cape York. Crosses: the taenite was heated at 758 K; open circles: the taenite was heated at 778 K. The hyperfine parameters are room-temperature values after heat treatment (see text). (a) The magnetic hyperfine field H at the iron nucleus in the ordered FeNi (50%–50%) phase as a function of heating time. (b) The electric quadrupole shift ϵ in the Mössbauer spectra for the ordered FeNi phase as function of heating time. (c) The quadrupole shift ϵ as function of the magnetic hyperfine field H. [The solid points are (H,ϵ) values from sixteen meteorites, taken from Ref. 5.]

respectively. Figure 3(b) shows the room-temperature value of the electric quadrupole shift ϵ as a function of the heating time, at the two temperatures. It is seen that the magnetic hyperfine field increases and the electric quadrupole shift decreases with increasing heating time, i.e., with decreasing degree of order.

In Fig. 3(c) we show ϵ as a function of H for both series of experiments. We see that the results fall on a straight line. This is to be expected, because both hyperfine parameters are to a first approximation linear functions of the short-range order parameter which is proportional to

W^2, where W is the long-range order parameter.[7] The hyperfine field for the totally ordered alloy (long-range order parameter $W=1$) is close to 285 kG (Ref. 5) and the hyperfine field corresponding to $W=0$ (complete disorder) is measured to be 311 kG.

We have previously recorded the Mössbauer spectra of taenite from Cape York at increasing temperatures[8] in order to find the temperature, or temperatures, where the order dies out on a time scale conveniently measured in the laboratory. In that experiment a Mössbauer spectrum at each chosen temperature was run for 10 h. At temperatures up to 700 K the spectrum did not change (except for small changes caused by a decrease in the magnetization). At 732 K drastic changes in the spectrum occurred because of the breakdown of the ordered phase. Even though we were far above T_c ($\simeq 593$ K) the order needed about 20 h to disappear. This fact demonstrates the extremely sluggish kinetics of this order-disorder transition. At the temperatures at which the taenite was heated in the experiments presented in this Letter, i.e., 758 and 778 K, the order dies out on a time scale of about 100 min; see Fig. 3(a).

From Figs. 2(b) and 2(c) it is seen that unheated taenite from the meteorite Santa Catharina has a Mössbauer spectrum that closely resembles taenite from Cape York that has been heated for 10 min at 778 K. The degree of order in the unheated FeNi (50%-50%) phase is thus higher in Cape York than in Santa Catharina. This fact clearly demonstrates that the unheated taenite from Santa Catharina [Fig. 2(b)] is farther from thermal equilibrium[2] than the unheated taenite from Cape York [Fig. 2(a)].

In a previous paper we have shown the (H,ϵ) values for the ordered FeNi (50%-50%) phase from sixteen iron meteorites.[5] The values are marked in Fig. 3(c). It is seen that these points fit fairly well to the line drawn for the heating experiments on the ordered phase from Cape York. Two meteorites have (H,ϵ) values far from the line. This can be explained by an error in the fitting procedure for these two meteorites, but we have chosen to use the numbers from the published paper[5] without corrections.

The measurement of the hyperfine parameters of the ordered FeNi (50%-50%) phase from different meteorites is thus a method to study their relative degree of order. As the degree of order depends on the cooling rate of the meteorite, we can conclude that Mössbauer spectroscopy offers a tool for the study of the relative cooling rates of meteorites at temperatures below the transition temperature $T_c \simeq 593$ K. The hyperfine parameters of the ordered phase are frozen memories of the thermal history of the meteorites.

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