Relaxation and hysteresis of magnetization of antiferromagnetic FeCo$_3$

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The magnetic properties of FeCO$_3$ at 4.2°K are studied in a strong pulsed magnetic field that induces a transition from the antiferromagnetic to paramagnetic state. The observation of the relaxation and of the hysteresis leads to conclusions regarding the magnetic structure of the FeCO$_3$ in the vicinity of the transition.

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1. INTRODUCTION

An external magnetic field induces in antiferromagnetic FeCO$_3$ a transition to the paramagnetic state. The magnetic properties in the vicinity of this transition were investigated in detail in[3] The results of this investigation suggest that the energy of the surface tension between the antiferromagnetic and the paramagnetic phases in FeCO$_3$ is negative. Therefore the investigated transition is not a first-order transition. It proceeds gradually, starting in a field $H_1 = 148$ kOe and ending at $H_2 = 176$ kOe.

In this magnetic-field interval of width $\Delta H = 28$ kOe, an inhomogeneous periodic magnetic structure is realized.[3] It differs in its properties from the antiferromagnetic and paramagnetic phases and is similar in structure to the mixed type-II superconductor state. Investigations of the properties of the mixed state in antiferromagnetic FeCO$_3$ and a check on certain deductions concerning its magnetic structure are of definite interest and are the subject of the present paper.

We consider below the results of a study of the magnetic properties of FeCO$_3$ under nonstationary conditions, i.e., when the time of action of the magnetic field is comparable with the characteristic times of the relaxation processes in the sample, Such an experiment affords a comparative estimate of the relaxation times of the magnetic structures that appear upon magnetization, and also provides a check on the validity of the following hitherto-advanced[3] representations of the mixed state structure:

1) When the mixed state is magnetized, a number of magnetic structures with different periods are realized in succession. Each structure has a definite relaxation time. We can therefore expect the relaxation time in a field interval ΔH to have a nonmonotonic dependence on the magnetic field intensity.

2) The transition of FeCO$_3$ from the antiferromagnetic to the paramagnetic state proceeds via realignment of the spin structure of only one of the sublattices, which is directed initially opposite to the magnetic field. The relaxation time of this process should differ from the time required to establish equilibrium in the two sublattices.

2. MEASUREMENT PROCEDURE AND RESULTS

The magnetic properties of FeCO$_3$ single crystals were studied at a temperature 4.2°K in a pulsed magnetic field. Taking into account the possible sensitivity of the relaxation processes to the crystal-lattice defects and to the impurities contained in the sample, the measurements were made on several FeCO$_3$ samples taken from different sources. The experimental results described below were the same for all the investigated samples and were well reproducible from measurement to measurement.

The external magnetic field was produced by a pulsed solenoid and was oriented along a threefold symmetry axis or at an angle up to 10° to this axis. The rise of the magnetic-field in the pulse to the maximum value was 7×10^{-3} sec. By varying the pulse amplitude it is possible to vary the rate of change dH/dt of the magnetic field at any value of the field in the ΔH interval of interest to us, from 7×10^6 to 30×10^6 Oe/sec.

The measurements were made by an induction procedure, the details of which were described earlier.[4] The experimental curves obtained on an oscilloscope screen took the form of the magnetic-field dependence of the sample magnetization M or of its time derivative

$$dM/dt = \chi dH/dt.$$

The pulse procedure is such that, simultaneously with the magnetic field intensity H, its derivative dH/dt changes simultaneously in accordance with a certain law. The measured value of χ is independent of dH/dt at low values of dH/dt and is the static differential susceptibility χ_0. With increasing dH/dt, the susceptibility χ deviates from its static value, and this deviation is a reflection of the relaxation processes in the sample.

Figure 1 shows the magnetic susceptibility of the samples in the critical magnetic-field interval ΔH. In this interval, a transition from the antiferromagnetic to the paramagnetic state takes place. The magnetic susceptibility in the transition is on the average 2.7×10^{-2} cgs emu and has overshoots at the start and at the end of the transition. An analysis of the value of χ and of the magnetization jumps at the end points of the field interval ΔH is contained in an earlier paper.[3] The

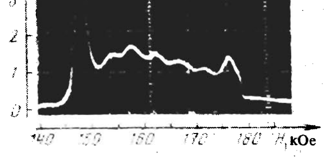

FIG. 1. Differential magnetic susceptibility in the critical magnetic-field interval $H_1 < H < H_2$. The magnetic-field growth rate dH/dt ranges from 3.5×10^7 Oe/sec at the start of the interval ΔH to 2.8×10^7 Oe/sec at its end.

differences between the experimental curves, due to the increased rate of change of the magnetic field, and the new experimental results, consist in the following:

1) Between the magnetic-susceptibility overshoots at the ends of the field interval ΔH (at H_1 and H_2) there are five smaller peaks that are clearly pronounced at large values of dH/dt. A careful study of these peaks has shown that they are well reproducible from pulse to pulse in all samples. This excludes any possible connection between them and individual blocks and inhomogeneous inclusions of the sample. The susceptibility peaks also remain when the external field is inclined to the crystal symmetry axis [111].

In magnetic-field pulses of varying amplitude, the time intervals between the individual pulses are different. However, the values of the magnetic fields $H^{(k)}$ at which each of the peaks appears remain the same. In all the investigated samples, the susceptibility peaks were equidistant when measured in terms of the magnetic field. The critical field-intensity values at which they appear are described by the empirical expression

$$H^{(k)}=H_1+k\Delta h,$$

where H_1 = 148 kOe, Δh = 4.7 kOe, and k = 0, 1, 2, 3, 4, 5, and 6.

2) The magnetic susceptibility inside the field interval ΔH can be characterized by two quantities. The arithmetic mean of the susceptibilities taken at the maximum and minimum points near each peak yields the smooth part of the susceptibility, $\chi_0(H) = \frac{1}{2}(\chi_{\max} + \chi_{\min})$. The ratio of the difference of these susceptibilities to the value of the smooth parts gives the relative amplitude of the peak.

Figure 2 shows the dependence of these quantities on the rate of change dH/dt of the field. Whereas the smooth part, as well as the amplitude of the first overshoot, is practically independent of dH/dt, the amplitudes of the five internal peaks decrease simultaneously with decreasing rate of change of the magnetic field. It appears that the modulation of the $\chi(H)$ curve by the internal peaks is due to the nonequilibrium character of the magnetization process, and disappears completely in the case of magnetization in the stationary regime.

3) The dependence of the sample magnetization on the magnetic field intensity is different when the field is increased and decreased, i.e., magnetic hysteresis is present and is characterized by the area of its loop (Fig. 3). The $\chi(H)$ curves differ both in shape and in the positions of the individual singularities on them (Fig. 4).

The hysteresis has a nonlinear dependence on the maximum magnetic field intensity $H_{\max}$ attained in the pulse. It is important that the critical quantity in this sense is the field $H_{\max} = H_2$. If $H_{\max} < H_2$, then the hysteresis is not strongly pronounced on the curves (Figs. 3a and 4a). On the other hand, if $H_{\max}$ exceeds H_2 by even 2%, i.e., if the sample becomes completely paramagnetic, the area of the hysteresis curve increases jumpwise (Fig. 3b) and the $\chi(H)$ curves becomes noticeably deformed (Fig. 4b).

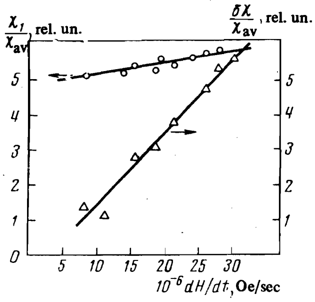

FIG. 2. Dependence of the amplitude of the first overshoot (○) and of the internal peaks (△) of the magnetic susceptibility on the rate of increase of the magnetic field.

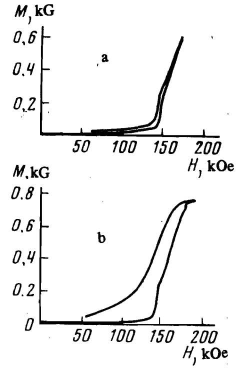

FIG. 3

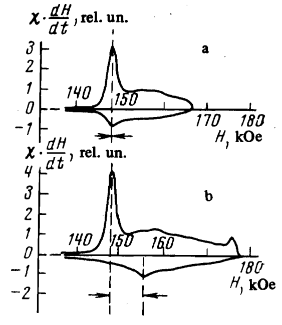

FIG. 4

FIG. 3. Magnetization curves obtained with two magnetic-field pulses of different amplitude: a) $H_{\max} < H_2$; b) $H_{\max} > H_2$.

FIG. 4. Magnetic susceptibility with increasing (dH/dt > 0) and decreasing (dH/dt < 0) magnetic field, obtained with two pulses of unequal amplitude: a) $H_{\max} < H_2$; b) $H_{\max} > H_2$. The arrows indicate the displacement of the singularity on the curve.

3. DISCUSSION

1) The dependence of the magnetization of the $FeCO_3$ samples on the rate of change of the magnetic field shows that the relaxation time of the equilibrium magnetic structure is quite large. This situation, generally speaking, is not typical of magnetic phase transitions in antiferromagnets. We note for comparison that in the sublattice-flipping phase transition in MnF_2, which we have investigated at the same values of dH/dt,[4] no pronounced traces of relaxation processes were observed.

The possible cause of the long relaxation time of the magnetic structures produced in $FeCO_3$ in the field interval between H_1 and H_2 is their complexity, which can be characterized by the large dimension of the unit cell. An important role in the formation of the structure of such a cell, which contains a large number of sites, is played by the weak long-range correlations between the ion spins, and this is the cause of the relatively long time needed to establish equilibrium.

The assumption that the unit cell in the $FeCO_3$ structure produced in the field interval ΔH is large was justified earlier in[3]. On the one hand, the process of $FeCO_3$ magnetization consists of a jumplike reorintation of the magnetizations of the individual sublattices. On the other hand, the rather smooth change of the magnetization can be explained only by introducing a large number of such sublattices. It is this circumstance which leads to the assumption of a magnetic unit cell of sufficiently large dimensions.

Thus, the long time required to establish equilibrium in the magnetic structures produced in $FeCO_3$ in the mixed state can be regarded as an indirect confirmation of the complexity of these structures and of the important role played in their formation by weak interaction between magnetic ions that are far from one another.

2) Let us consider from this point of view the cause of the nonmonotonic dependence of the relaxation rate on the magnetic field intensity. The periodic increase of the relaxation rate at certain values of the external field $H^{(k)}$ can be explained that at $H = H^{(k)}$ there are realized in the mixed state simpler magnetic structures. In other words, the flipped spins arrange themselves in the complex magnetic unit cell in such a way that the cell can be regarded as consisting of a number of periodically-repeating small-dimension subcells. The formation of the structure of the latter is governed only by the strong nearest-neighbor interactions, and the corresponding relaxation times are therefore small.

Let us determine the number of possible values of the critical fields $H^{(k)}$ in which the aforementioned simple structures are realized. Since only the spin configuration of the nearest environment is significant in the latter, the number of neighbors k with flipped spin should be the same for each site, with k varying in the range $0 < k < z$, where z is the coordination number. Therefore the total number of values that $H^{(k)}$ can assume is $z + 1$.

The total number of peaks on the experimental curve of Fig. 1 is seven, so that the coordination number is $z = 6$. The Fe^{2+} ion in the $FeCO_3$ lattice does indeed have six nearest neighbors in like sublattices; these neighbors lie in the (111) layer plane and are separated by a distance $r = 4.68$ Å. This agreement favors the validity of the proposed explanation of the peaks on the $\chi(H)$ curve. On the other hand, observation of such curves is a very interesting method of determining the coordination number via magnetic measurements.

Let us calculate the critical field $H^{(k)}$ in which a magnetic structure with a definite number of flipped neighbors is realized. According to the premises of the earlier paper,[3] the magnetization process proceeds as follows: The spins of one sublattice (I) of the initial antiferromagnetic structure, directed along the external magnetic field, maintain the same direction at all values of the external field. The spins of the other sublattice (II), initially directed opposite to the external field, reverse their direction in succession in the field interval ΔH. The effective field at the sites of sublattice II can be represented in the form of a sum of the following terms:

$$H_{\text{eff}}^{(\text{II})}=H+\gamma-\delta-\Delta H^{(k)}.$$

The first three terms describe the fields acting in the initial antiferromagnetic structure situated in the external field H. The second and third terms, $H_1 = \gamma - \delta$, describe the fields produced by sublattices I and II respectively. The field produced by sublattice II can be represented in the nearest-neighbor approximation as a superposition of equal fields $\Delta h/2$ acting from the direction of each of them: $-\delta = z\Delta h/2$. The last term represents the change produced in the effective field by the successive changes of the spin orientations at the sites of sublattice II:

$$\Delta H^{(k)}=k\Delta h.$$

Here k is the number of nearest neighbors whose spins were flipped; its range is $0 < k < z$, and therefore $0 < \Delta H^{(k)} < 2\delta$.

We assume that the spin in a given site of sublattice II becomes unstable and reverses its orientation when the effective field at the sign reverses sign as it passes through zero. Putting $H_{\text{eff}}^{(\text{II})} = 0$, we find the discrete series of external magnetic field values at which stability loss takes place in magnetic structures in which each ion has k nearest neighbors with flipped spins:

$$H^{(k)}=H_1+k\Delta h.$$

Thus, the equidistant series of critical fields $H^{(k)}$ begins with $H_1 = \gamma + \delta$ (at $k = 0$) and ends with $H_2 = -\gamma - \delta$, when each ion of the sublattice II has z flipped neighbors.

The obtained expression coincides with that obtained from experiment, where the critical fields mark the instants of the appearance of the peaks in the $dM(H)/dt$ curve. The comparison of these formulas is based on the assumption that each of the $z + 1$ magnetic structures realized in the field interval $H_1 < H < H_2$ has a short relaxation time, and this is indeed the cause of the peak on the experimental curve. The fact that the observed peaks are equidistant confirms the chosen model wherein the fields of the nearest neighbors make equal contributions to the field at the considered site. According to experiment, the change of the effective field following the flipping of the spin of each of the neighbors is $\Delta h = 4.7$ kOe.

Consider the simplest example of the series of magnetic structures that can be realized in the magnetic-field interval $H_1 < H < H_2$ and have lability fields $H^{(k)}$. In the absence of an external magnetic field, the spins of the magnetic ions in antiferromagnetic $FeCO_3$ in the plane of the layer (111) have the same orientation. Layers with mutually opposite orientations alternate in the [111] direction. Figure 5 shows one of the (111) layers, in which the spins are antiparallel to the external magnetic field when $H < H_1$.

Since the experimental $\chi(H)$ curve has seven peaks, the smallest number of sublattices needed for their description is 14, and each (111) layer contains sites belonging to seven sublattices. The number 1 labels the ions belonging to the first sublattices that reverses direction as a result of the first jump of the magnetic moment in the field H_1. These ions form in the (111) plane a regular triangular lattice; none of them has nearest flipped neighbors ($k = 0$). The number 2 designates the sublattice that is flipped after the second magnetization jump. Each ion of this sublattice has one flipped neighbor ($k = 1$), and its lability field amounts to $H_1 + \Delta h$.

With further flipping of the ions of the remaining sublattices, the number of flipped neighbors of each ion increases from zero to six, and the lability field of the corresponding magnetic structure increases. Even this very simple model describes correctly the equidistance of the seven magnetization jumps observed in the experiment. Its shortcoming is the inexact description of the change in the magnetization in each jump. It is possible

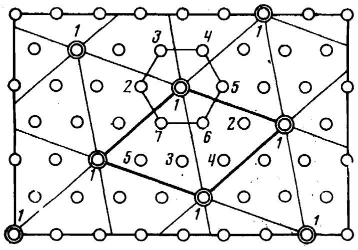

FIG. 5. Distribution of the ions over the sublattices in the (111) layer in a 14-sublattice model. The thick line outlines the unit cell.

to construct enough other more complicated models by increasing the dimensions of the magnetic unit cell and the number of introduced sublattices. We regard such constructions, however, as premature, since the large experimental errors do not make it possible to give final preference to any particular model.

It should be noted that the model in which only the nearest neighbors are considered describes a curve on which the changes of the magnetic moment occur only at definite values of the external field $H^{(k)}$. Actually, under conditions of equilibrium magnetization, the magnetic moment varies smoothly, i.e., changes in the spin orientation occur also in the intervals between the corresponding critical fields $H^{(k)}$ and $H^{(k+1)}$. In this case, apparently, magnetic structures are realized in which the average number of flipped neighbors at the sites of sublattice II is not an integer, but varies smoothly with increasing magnetic field. An important role is played in the formation of such structure by interaction not only between nearest neighbors, but also between more remote ones. From the point of view of the foregoing, all that matters is that the relaxation time of these structures must be longer than that described here. Therefore at sufficiently large values of dH/dt one should observe a decrease of the susceptibility in the intervals between the fields $H^{(k)}$ and $H^{(k+1)}$, as is indeed the case in experiment. Thus, the periodic increase of the relaxation rate upon magnetization of the mixed state can be understood by assuming that at definite values of the external magnetic field $H^{(k)}$ there are produced rather simple magnetic structures, in the formation of which only nearest-neighbor strong interactions are significant, and which therefore have a short relaxation time. Measurements of the nonequilibrium magnetization curve of $FeCO_3$ will make it possible, in the assumed interpretation, to determine the total number of neighbors $z = 6$ of each magnetic ion in the second coordination sphere, and to measure directly the effective magnetic field produced by each of them.

3. Let us consider the possible cause of the hysteresis on the $FeCO_3$ magnetization curve when the magnetic-field pulse amplitude exceeds $H_2 = 176$ kOe. We assume for this purpose that there exist two spin-relaxation mechanisms. The time τ_{11} characterizes the relaxation inside the ion layer (111) pertaining to one of the sublattices of the initial antiferromagnetic structure. We introduce the longer time τ_{12} to describe the establishment of the equilibrium between two neighboring layers.

It was shown earlier that as the $FeCO_3$ becomes magnetized the spin orientation changes only in layers that belong to one sublattice. If the maximum value of the magnetic field pulse does not exceed H_2, then the antiferromagnet retains the information on the initial distribution of the sites over the sublattices. Since the distance between the unflipped spins does not exceed the interaction radius, the relaxation process that occurs in the subsequent demagnetization affects only one sublattice. The characteristic time of this process, according to our estimates, is 10^{-4}—10^{-5} sec.

If the amplitude of the magnetic-field pulse exceeds H_2, when all the spins are oriented along the external field, the physical difference between the sublattices vanishes. With further decrease of the magnetic field, the spins belonging to different layers reverse their orientation with equal probability, so long as the distance between them exceeds the interaction radius. As they come closer together, the intersublattice relaxation mechanism comes into play. A unified distribution of the flipped spins over the layers is first reached in individual regions of the crystal. As a result of the displacement of the boundaries between these regions, a long-range order is established in the crystal. The characteristic time of this process, according to the experimental data, is $\tau_{12} = 10^{-2}$—10^{-3} sec.

It appears that the total time of establishment of the initial magnetic structure exceeds τ_{12}. The impurities in the crystal slow down the motion of the boundaries between the individual antiferromagnetic regions. In addition, these boundaries can form in the crystal three-dimensional grids that remain, not being thermodynamically favored, relatively stable when the magnetic field is completely turned off. These factors can lead, in particular, to appearance of remanent magnetization of the crystal.

Thus, an investigation of the relaxation phenomena and of the hysteresis confirm the earlier conclusions[3] concerning the magnetic structure of $FeCO_3$ in the region of the transition from the antiferromagnetic to the paramagnetic state. It appears that an inhomogeneous magnetic structure is realized in the field interval ΔH, and the changes of the magnetization in the field are due to the continuous realignment of the spins in one of the sublattices of the initial antiferromagnetic structure.

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