Investigation of the transition of $FeCO_3$ from the antiferromagnetic to the paramagnetic state under the influence of a strong magnetic field

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The magnetic properties of $FeCO_3$ have been studied near the transition that occurs over the field interval from H_1 = 148 kOe to H_2 = 176 kOe. The transition is described as the result of a continuous change of the modulus of the magnetization of that one of the sublattices that is opposite to the external magnetic field. This description is substantiated by the concept of removal of sublattice degeneracy and successive flipping of individual spins. In the field interval $H_1 < H < H_2$ these spins form a periodic magnetic structure. The transition is discussed from the point of view of energy of the interface between the antiferromagnetic and paramagnetic phases and is compared with the transition in which type-II superconductivity is destroyed by a magnetic field.

1. INTRODUCTION

Crystals of $FeCO_3$ have a rhombohedral structure with two magnetic Fe^{2+} ions per unit cell. Below T_n = 38 K[1] $FeCO_3$ is antiferromagnetic; the direction of the spontaneous magnetization coincides with a threefold axis. In the antiferromagnetic range, the anisotropy of the magnetic properties is anomalously large[2]. In a strong magnetic field directed along the axis of symmetry, there has been observed in antiferromagnetic $FeCO_3$ a magnetic transition to a state that has been identified as paramagnetic[3,4]. This transition proceeded smoothly over the field interval 150–200 kOe.

Theory describes the transition from the antiferromagnetic to the paramagnetic state under the influence of a magnetic field as a first-order phase transition accompanied by an abrupt jump of the magnetization[5]. Therefore the finite width of the experimentally observed transition and the magnetic structure of $FeCO_3$ in the transitional region have remained unexplained. On the other hand, it has been shown theoretically[6] and experimentally[7] that even when the phase transition in an infinite magnet is of first order, in specimens of finite dimensions the magnetization should change smoothly, and the transition should occur over a finite magnetic-field interval. In this interval the magnet is in an essentially nonuniform state, analogous to the intermediate state of type-I superconductors.

But the applicability of such a description to the explanation of the properties of $FeCO_3$ is by no means obvious. The occurrence of a domain structure in the transition region is possible only if the energy of surface tension between two phases is positive ($\sigma > 0$). If this energy has a negative sign, a first-order phase transition is impossible. In type-II superconductors, for example in the case $\sigma < 0$, there occurs a qualitatively different nonuniform state, which has received the name "mixed."

At present there is no comprehensive theory of the phase boundaries that separate antiferromagnetic and paramagnetic phases. For this reason, investigations of the properties of $FeCO_3$ and of its magnetic structure in the transition region, which are the subject of the present paper, are of obvious interest. Preliminary results of measurements of the peculiarities of the magnetic susceptibility[8] and of the transverse components of the magnetization of $FeCO_3$[9] in the critical magnetic-field interval were communicated earlier. The present paper studies in detail the magnetic properties of $FeCO_3$ in the vicinity of the critical field for transition to the paramagnetic state. The experimental data are discussed from the point of view of the possible magnetic structures realized in the critical magnetic-field interval.

2. EXPERIMENTAL RESULTS

The magnetic properties of $FeCO_3$ were studied at temperature 4.2 K in a pulsed magnetic field directed along the symmetry axis of the crystal. The rise time of the pulsed field was 7×10^{-3} sec, and its rate of change at each value of the magnetic field was varied over the range 5 to 30×10^6 Oe/sec. The components of the magnetization both longitudinal and transverse to the field were measured. Details of the induction method used were described earlier[7]. The angle between the direction of the magnetic field and the symmetry axis of the crystal was varied over the range 0–10°. The measurements were made on several specimens of natural origin, taken from different deposits. Specimens of various forms were used, from cylinders with axis parallel to [111] to disks whose plane was perpendicular to the symmetry axis. The measuring system had a sufficient pass band (up to 10^6 Hz) to insure reproduction of the most rapid changes of magnetization. Damping of the measurement channels prevented oscillations after reproduction of the abrupt jumps of magnetization.

The principal results of the measurements reduce to the following.

1) The dependence of the longitudinal magnetization of the specimens on the magnetic field intensity is shown in Fig. 1. The main changes of magnetization begin at field H_1 = 148 kOe and end at H_2 = 176 kOe. The mean magnetic susceptibility in this field interval is 2.7×10^{-2} cgs emu. Outside the interval $H_1 < H < H_2$, the magnetization changes little with magnetic field intensity.

2) If the magnetic field is oriented along the symmetry axis of the crystal, the components of magnetization perpendicular to this axis are zero within experimental error (~5%) for all values of the magnetic field. These components appear and increase in absolute value with increase of the angle ψ between the direction of

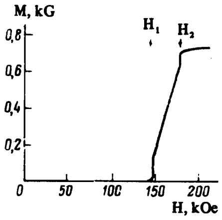

FIG. 1

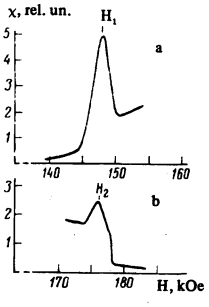

FIG. 2

FIG. 1. Dependence of the longitudinal magnetization of $FeCO_3$ on the intensity of a magnetic field directed along the axis of symmetry of the crystal.

FIG. 2. Differential magnetic susceptibility near the critical fields for: a) the beginning (H_1) and b) the end (H_2) of the magnetic transition.

the external field and the symmetry axis [111]. Their dependence on the magnetic field intensity exactly repeats Fig. 1 for the longitudinal component. The absolute value of the transverse components at arbitrary angles ψ ($0 < \psi < 10°$) remains such that the total magnetization vector of the specimen is oriented along the direction of the external magnetic field. Thus components of the magnetization perpendicular to the direction of the external field are absent for all fixed intensities and for all angles ψ.

3) Near the critical fields H_1 and H_2 the magnetization of the specimens changes more abruptly than inside the interval $H_1 < H < H_2$. Figure 2 shows in greater detail the dependence of the magnetic susceptibility on the magnetic field intensity near the critical fields. The maximum value of the susceptibility in these sections exceeds its value inside the interval $H_1 < H < H_2$ by almost a factor two. In specimens of cylindrical shape (diameter-to-height ratio $\beta = 0.2$), the susceptibility amplitude is 40% larger than in specimens of disk form ($\beta = 5$). The width of the magnetic-field interval $\Delta H = H_2 - H_1$ is practically independent of the specimen shape.

The abrupt change of the magnetic susceptibility (of the specimen as a whole) near H_2 (Fig. 2b) makes it possible to estimate an upper bound to the nonuniformity of the magnetic field in the specimen. It amounts to less than 1 kOe, which is appreciably less than the width of the characteristic singularities of the magnetization curve that will be the subject of discussion below.

The results enumerated were the same for all specimens of natural origin, taken from different deposits.

3. THE MAGNETIC SUSCEPTIBILITY IN A PHENOMENOLOGICAL TREATMENT

A phenomenological analysis of the magnetic properties of an antiferromagnet usually consists in an investigation of the thermodynamic potential, which contains the important interactions resulting from the presence of spontaneous magnetization of the sublattices. The results of this analysis[10] for crystals with a not very large anisotropy do not describe the experimental magnetization curve of Fig. 1.

In view of the strong anisotropy of the magnetic properties of $FeCO_3$, the experimental absence of transverse components of the magnetic moment, and the results of other papers[11-13], we shall include in the thermodynamic potential only the interactions due to the longitudinal components of the magnetization vectors of the sublattices. We shall initially treat the crystal under study as a two-sublattice antiferromagnet; for the sublattice magnetizations, we introduce the notation

$$\mathbf{m}_1 = \mathbf{M}_1/M_0, \quad \mathbf{m}_2 = \mathbf{M}_2/M_0.$$

Here M_0 is the spontaneous saturation magnetization, the same for both sublattices. We direct the external magnetic field $h = h_z = H_z/M_0$ along the symmetry axis of the crystal. Then the thermodynamic potential of the antiferromagnet can be described in the form

$$\Phi = -{}^1\!/_2\delta(m_1^2+m_2^2) - \gamma m_1 m_2 - (m_1+m_2)h, \tag{1}$$

where the variables $m_1 = m_{1z}$, $m_2 = m_{2z}$, and $m = m_1 + m_2$ vary within the bounds

$$-1 \leqslant m_1 \leqslant +1, \quad -1 \leqslant m_2 \leqslant +1, \quad -2 \leqslant m \leqslant +2.$$

The expression (1) is applicable for description of uniform states (with nonuniformities not exceeding the dimensions of the elementary cell), and also of nonuniform states; but in the latter case, the quantities m_1 and m_2 must be understood as the sublattice magnetizations averaged over regions whose dimensions exceed the dimensions of all possible nonuniformities.

In the absence of a magnetic field, the antiferromagnetic state corresponds to a minimum of (1) with the following relations among the constants:

$$\gamma < 0, \quad |\gamma| > |\delta|$$

or

$$h_1 = -(\gamma-\delta) > 0, \quad h_2 = -(\gamma+\delta) > 0.$$

Minimization of (1) with respect to m_1 and m_2, with attention to the limits on their variation, gives the following solutions for the sublattice magnetizations, the total magnetization, and the thermodynamic potential, for various magnetic field intensities:

A) $h < h_1$: $m_1 = +1$, $m_2 = -1$, $m = 0$, $\Phi_1 = -h_1$;

B) $h_1 < h < h_2$: $m_1 = +1$, $m_2 = -\dfrac{h+\gamma}{\delta}$, $m = -\dfrac{h+(\gamma-\delta)}{\delta}$,
$\Phi_2 = -h_1 - \dfrac{(h-h_1)^2}{h_2-h_1}$ (at $\delta < 0$);

C) $h > h_2$: $m_1 = +1$, $m_2 = +1$, $m = +2$, $\Phi_3 = h_2 - 2h$.

Solution A), realized in small fields, corresponds to the antiferromagnetic state. In strong fields, solution C) describes the paramagnetic state. The transition from one state to the other occurs near the critical field $h_t = {}^1\!/_2(h_1 + h_2) = -\gamma$. It is important to notice that in the transition process there is a change of magnetization of only one sublattice, while the other remains magnetized to saturation at all values of the magnetic field. The solutions given above show that the transitions from the antiferromagnetic to the paramagnetic state can be of two types, depending on the sign of the constant δ:

I) For $\delta > 0$, the field $h_2 < h_1$, and the change of orientation of the second sublattice occurs at field $h = h_t$ by a first-order phase transition. At this field the total magnetization changes discontinuously by the amount $\Delta m = 2$. In the field interval $h_2 < h < h_1$, there are metastable states, and hysteresis is possible (Fig. 3a).

II) For $\delta < 0$, the field $h_2 > h_1$, and the transition occurs smoothly in the field interval $\Delta h = h_2 - h_1$ (Fig.

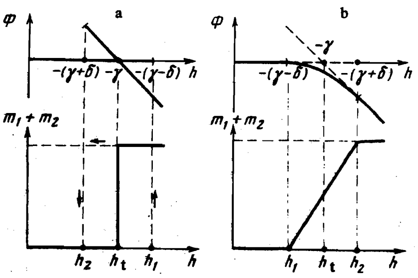

FIG. 3. Dependence of thermodynamic potential and total magnetization on magnetic field intensity near the transition from the antiferromagnetic to the paramagnetic state: 1) first-order transition ($\delta > 0$; b) second-order transition ($\delta < 0$).

3b). In this interval, solution B is realized. With increase of magnetic field, at $h = h_1$ there occurs a second-order phase transition, and the magnetic susceptibility changes discontinuously by the amount $\Delta\chi = 2M_0/(H_2 - H_1)$. The linear increase of magnetization ends at $h = h_2$, where there also occurs a second-order phase transition, and the magnetic susceptibility again drops to zero.

From the form of the first term in the thermodynamic potential, it can be deduced that the constant δ is the energy of intrasublattice exchange interaction. Its sign is determined primarily by the sign of J_{11}—the sign of the interaction of the ion under consideration with the ions of the first coordination sphere. If the sign of J_{11} promotes ferromagnetic ordering within a sublattice, the transition under study is a first-order phase transition, Such a situation occurs, evidently, in the layered antiferromagnets $FeCl_2$, $FeBr_2$, etc.[14,15]. But if sign J_{11} = sign J_{12}, the transition occurs smoothly, beginning and ending with second-order phase transitions.

Comparison of the experimental magnetization curve (Fig. 1) for $FeCO_3$ with the theoretical (Figs. 3a and b) shows that the transition in this antiferromagnet occurs according to type II. Therefore we must ascribe to antiferromagnetic $FeCO_3$ an intrasublattice interaction of the same sign as the intersublattice. The sign of the intrasublattice interaction of an antiferromagnet can also be determined approximately from molecular-field theory, by comparison of the Néel (T_N) and Weiss (Θ) temperatures. According to experiment[2] the Weiss temperature of $FeCO_3$ is negative: $\Theta = -14$ K; this does not contradict the supposition that the sign of the intrasublattice interaction is negative.

The experimental curve of Fig. 1 enables us to determine the ratio of the magnitude of the intrasublattice interaction to that of the intersublattice:

$$\frac{\delta}{\gamma}=\frac{h_2-h_1}{h_2+h_1}=+0.08.$$

We remark that if the treatment presented is actually applicable to the description of the magnetization curve of $FeCO_3$, measurement of this curve is the most accurate of the known methods for determining the value of the intrasublattice exchange interaction.

Thus the phenomenological thermodynamic potential (1), containing only interactions of the longitudinal components of the magnetizations of the sublattices, provides a classification of transitions from the antiferromagnetic to the paramagnetic state dependent on the sign of the constant δ of intrasublattice exchange interaction. For the negative sign of δ, it correctly describes the presence of two critical fields, h_1 and h_2, and also explains the finite value of the magnetic susceptibility inside the interval $h_1 < h < h_2$.

4. TRANSVERSE COMPONENTS OF THE MAGNETIZATION AND LIMITEDNESS OF THE TWO-SUBLATTICE MODEL

The phenomenological analysis presented imposes no limitations on the value of the transverse components of the magnetization. Although in our choice of the thermodynamic potential we supposed them absent, nevertheless the solutions are formally applicable also to the case in which transverse components are present but make no contribution to the interaction. Therefore in order to discuss their value, it is necessary to introduce additional considerations.

According to molecular-field theory, the dependence of the magnetization of the sublattices on field and temperature is described by the following relation:

$$M_i=M_0B_S(y_i),$$

where $B_S(y_i)$ is the Brillouin function for spin S, and where $y_i = H_i\mu_B gS/kT$. Consequently, at $T = 0$ a sublattice should be magnetized to saturation, $M_i(0) = M_0$, in an arbitrary nonvanishing magnetic field. In the magnetic-field interval $h_1 < h < h_2$ the longitudinal component of the magnetization of $FeCO_3$ changes smoothly. If the modulus of the sublattice magnetization meanwhile remains constant, the vector m_2 must perform a gradual rotation through angle π. The value of the transverse component of magnetization should reach a maximum value M_0.

Experimentally, however, transverse components of the magnetization are absent. This property persists even on application of transverse components of the magnetic field, which would be able to orient the transverse components of the magnetization if they existed but had different directions in different macroscopic regions of the crystal. It must be supposed, apparently, that the transverse components of the magnetization of the sublattice vanish identically, while the modulus of the magnetization changes with change of the magnetic field. This fact is contradictory to the deductions of the two-sublattice model.

An analogous difficulty, already encountered in Néel's[16] researches on the analysis of the ferrimagnetic state, was successfully circumvented by Yafet and Kittel[17]. Their assumption, also pertinent to the case of negative intrasublattice interaction, consists in the following: The sublattice under consideration actually splits into two, each of the new sublattices being magnetized to saturation at $T = 0$. But because they can be oriented at an angle to each other, the total magnetization can take an arbitrary intermediate value $-M_0 < M_i < M_0$. Such a treatment may serve as the key to understanding the state of a sublattice in the field interval $h_1 < h < h_2$.

But this interpretation is complicated by the fact that the magnetic Fe^{2+} ions in the crystal under study can apparently have only two orientations, parallel and antiparallel to the external magnetic field, and the transverse components must vanish even in the single-ion approximation. Analysis of the joint action of spin-orbit coupling and the crystalline field on the Fe^{2+} ion, whose spin is $\frac{4}{2}$, has shown that the lowest state of the ion is a doublet state, corresponding to two mutually opposite directions of the spin[18]. In this case one should ascribe to the ion an effective spin $S_{eff} = \frac{1}{2}$ and use the Ising model for describing the interactions between the ions. These ideas have now been confirmed by numerous experiments[11-13]. It may therefore be supposed that the sublattice in $FeCO_3$ are oriented in only two fixed directions. This fact, on the one hand, is the basis of the thermodynamic potential (1), Sec. 3. On the other hand, the explanation of an arbitrary intermediate value of the magnetization of the sublattice by separation of it into two sublattices is unsuccessful.

It may be supposed that the sublattice under study splits into a quite large number of sublattices. In a multisublattice model, with successive change of orientation of each of the sublattices the magnetization curve becomes one of many steps. But because the number of sublattices that can be introduced into consideration can be increased practically without limit, the magnetization curve may look sufficiently smooth to describe the experimental curve with arbitrary accuracy.

The physical reason for splitting of the sublattice consists in the following. As was shown in Sec. 3, when account is taken of the interaction of the sublattices with each other, minimum energy corresponds to parallel orientation of the spins in each of them. But if we consider one sublattice as an isolated subsystem, in which $\delta < 0$, minimum energy corresponds to a state in which it splits into several sublattices, with different spin orientations in each of them.

The characteristics of this problem are such that the external magnetic field h cancels the effective field of intersublattice interaction γm_1 in one of the sublattices:

$$h_{2\text{eff}} = h + \gamma m_1 + \delta m_2.$$

Therefore in a magnetic field the degeneracy of this sublattice is removed. It splits into n component sublattices, whose field can be described in the form

$$\sum_{j=1}^{n} \gamma_{ij} m_j = \delta + 2 \sum_{j=1}^{k} \gamma_{ij} = -\delta - 2 \sum_{j=k+1}^{n} \gamma_{ij}.$$

Here $m_j = M_j / M_{0j}$ is the reduced magnetic moment of the j-th subsublattice, which can take the values $m_j = \pm 1$ ($\Delta m_j = \pm 2$), and γ_{ij} are the corresponding molecular field coefficients. The total value of this field can vary over the range from $-\delta$ in the antiferromagnetic state (every $m_j = -1$) to $+\delta$ in the paramagnetic ($m_j = +1$ for every j). On the right sides of the equation, the summation extends only over those k (or n-k) subsublattices whose magnetization has changed (or has not changed) sign.

If the γ_{ij} are positive, flipping of the j-th sublattice decreases the effective magnetic field on the sites of the other sublattices. This explains why their changes of orientation occur not simultaneously but successively as the external magnetic field is increased.

Thus the result obtained in Sec. 3, describing a gradual change of the longitudinal magnetization, can be reconciled with the experimental absence of transverse components if we suppose that one of the sublattices splits into a large number of subsublattices, whose period far exceeds the dimensions of the originally chosen elementary cell. The magnetic state of the crystal in the field interval $h_1 < h < h_2$ can therefore be considered an inhomogeneous one, whose periodicity, caused by the periodicity of the subsublattices, can change with the magnetic field intensity.

5. PHASE TRANSITIONS AND SHORT-RANGE ORDER NEAR THE CRITICAL FIELDS h_1 AND h_2

Calculation of the whole magnetization curve M(H) in the multisublattice model is impossible, because the molecular-field coefficients γ_{ij} are unknown. It can be shown, however, that most of these are close to zero. This fact enables us to describe the sections of the magnetization curve and the magnetic structure near the critical fields h_1 and h_2.

It is known that the exchange interaction in a crystal falls off rapidly at distances r_0 of the order of a few interatomic distances. In the multisublattice model, the sublattice period d is large enough ($d \gg r_0$) so that its exchange field at a given point either is zero, when all the ions of the sublattice are located far from the point, or is produced by the one nearest ion. In other words, the coefficients γ_{ij} either are zero or are dependent on the distance r_{ij} of the nearest ion of the j-th sublattice from the i-th point. Therefore in the expression for the total field at a site of the i-th sublattice, one can go over to a summation over ions located near the site.

We shall suppose that the orientation of the ions of the i-th sublattice changes to the opposite orientation at that critical value h_i of the external field for which the total effective field acting on them vanishes:

$$h_i = -(\gamma - \delta) + 2 \sum_{j=1}^{k} \gamma_{ij}(r_{ij}).$$

Here the summation extends over ions located near the i-th site and that have changed their orientation. If all the coefficients γ_{ij} are positive, the magnetization process begins at the field $h_1 = -(\gamma - \delta)$ by a change of orientation of spins at individual sites located at distance r_0 from each other.

If $r_0 \to \infty$, a second-order phase transition should occur at $h = h_1$ in accordance with the results of the phenomenological analysis. Interaction of reversed spins with each other for $\gamma_{ij} > 0$ increases the total energy, which is equivalent to a repulsion between them. Therefore the ions with reversed spins have minimum energy if they form a regular close-packed structure (Fig. 4).[1)] The fine lines in Fig. 4 join points at which an ion produces equal effective exchange fields. With increase of the magnetic field, the period of such a lattice should decrease continuously.

From the value of the magnetization of the crystal one can calculate the mean distance between reversed spins. Therefore the experimentally measurable M(H) curve in principle enables us to obtain the interesting dependence of the effective exchange field on the dis-

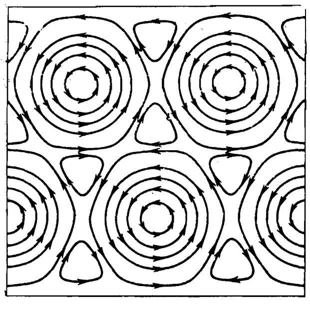

FIG. 4. Distribution of the effective exchange field produced by ions with reversed spins in the (111) plane.

tance between interacting spins, $H_{eff}(r)$. On the experimental magnetization curve (Fig. 1) there is observed near H_1 an abrupt rise, and on the magnetic susceptibility curve (Fig. 2a) an abrupt burst. In such cases it is difficult to guarantee that the form of the curves is free from the influence of appreciable experimental errors. Therefore we have not calculated the $H_{eff}(r)$ relation mentioned above. Estimating the actual experimental error of the curve near H_1, we compare with this section the model of an infinitely abrupt jump—a phase transition of the first kind. This jump is easily explained.

If the radius of interaction between reversed spins r_0 is finite, a finite number of spins flip simultaneously at field H_1. They should form a regular lattice in which the distances between them are equal to the radius of exchange interaction r_0. Here r_0 has the meaning of the minimum distance at which this interaction does not yet show up, with the given error, in the shape of the magnetization curve. From the experimental value of the change of magnetization near H_1, one can calculate that the concentration of abruptly reversed spins amounts to ~12.5%, which corresponds to a mean distance between them, in the (111) plane, $r_0 = 9.4$ Å. In order to discuss the magnetization jump observed experimentally at H_2, we express the critical field at a site in the form

$$h_i = -(\gamma+\delta) - \sum_{j=k+1}^{n} \gamma_{ij}(r_{ij}),$$

where the summation extends over ions whose spins have not yet changed their orientation. An analysis similar to that given above enables us to draw a conclusion about the presence of a magnetization jump and about the magnetic structure near the critical field $h_2 = -(\gamma + \delta)$, a structure analogous to that near h_1.

The set of reversed spins in the crystal at $h = h_1$ can be represented in the form of individual threads, parallel to the external magnetic field and carrying a quantum of additional flux of magnetic induction,

$$\Delta\Phi_0 = 4\pi\mu_B 4S/d \approx 0.2\cdot 10^{-10}\ \text{Oe cm}^2$$

where μ_B is the Bohr magneton, S is the spin of the Fe^{2+} ion (equal to $4/2$), and d is the distance between nearest reversed spins in the direction [111] (equal to 5×10^{-8} cm). The magnitude of this flux is 4 orders of magnitude smaller than the quantum of magnetic flux that occurs in a type-II superconductor.

Thus a calculation of the value of the field produced at a site by individual ions, and its dependence on distance, explain the experimental discontinuous changes of magnetization at $h = h_1$ and $h = h_2$. As a result of the first phase transition, the reversed spins form a close-packed structure with period $r_0 \sim 10^{-7}$ cm.

6. ENERGY OF THE INTERPHASE BOUNDARY, AND COMPARISON WITH THE TRANSITION IN WHICH TYPE-II SUPERCONDUCTIVITY IS DESTROYED BY A MAGNETIC FIELD

The transition from the antiferromagnetic state to the paramagnetic, described above, has much in common with the transition in which superconductivity is destroyed by a magnetic field. The classification of transitions in superconductors is based on consideration of the surface energy on the interface between the normal and the superconducting phases. If the surface energy σ is positive (type-I superconductor), the magnetization in an infinite medium changes discontinously at $h = h_t$, while the magnetic susceptibility is infinite; that is, a first-order phase transition occurs (Fig. 5a). If the sign of σ is negative (type-II superconductor), the transition occurs smoothly, beginning and ending with second-order phase transitions. The variation of the magnetization and of the magnetic susceptibility near h_t for this case is shown in Fig. 5b. In the field interval $h_1 < h < h_2$, there occurs in an infinite medium a mixed inhomogeneous state[19].

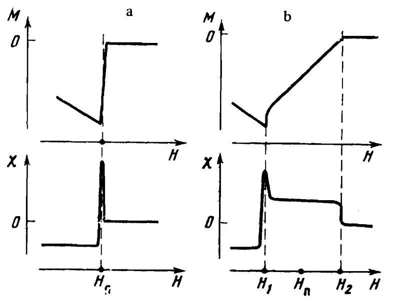

FIG. 5. Magnetization and magnetic susceptibility during the transition from the superconducting to the normal phase in a magnetic field: a) type-I superconductor ($\sigma > 0$); b) type-II superconductor ($\sigma < 0$).

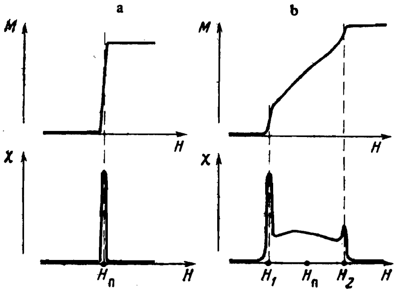

FIG. 6. Magnetization and magnetic susceptibility during the transition from the antiferromagnetic to the paramagnetic phase in a magnetic field: a) first-order transition ($\sigma > 0$); b) second-order transition, $FeCO_3$ ($\sigma < 0$).

The magnetization curves of type-I and type-II superconductors (Figs. 5a and b) are analogous to those obtained as a result of phenomenological analysis of first- and second-order transitions from the antiferromagnetic to the paramagnetic state (Figs. 6a and b). To intensify this analogy, we shall show that the energy of the interface between the antiferromagnetic and paramagnetic phases in the model described above is positive for a first-order transition and negative for a second-order transition.

It was shown above that individual spins in $FeCO_3$ can apparently have only two mutually opposite directions, and that intermediate orientations are excluded. Therefore we arrive directly at a specific form of sharp phase boundary, in which the transition from one phase to the other occurs over a single interatomic distance. In Fig. 7 the boundary is shown in the (111) plane perpendicular to it. On the left the crystal is in the antiferromagnetic state, on the right in the paramagnetic; the external magnetic field $h = h_t = -\gamma$ is parallel to the [111] axis.

To simplify the problem, we shall suppose that each ion interacts only with neighbors from the first and second coordination spheres. In the first coordination

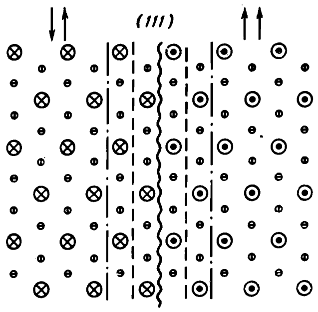

FIG. 7. Model of the interface between antiferromagnetic (left) and paramagnetic (right) phases. The large circles represent reversed (⊙) and unreversed (⊗) spins of a single (111) layer; the small circles represent magnetic ions of the two neighboring layers.

sphere, an Fe^{2+} ion in $FeCO_3$ has six nearest neighbors, located in neighboring (111) layers at distances 3.7 Å. We shall denote by J_{12} the energy of interaction with each of them for parallel orientation of the spins. In the second coordination sphere there are six ions, located in the plane of the same (111) layer at distances 4.7 Å; we shall denote the corresponding interaction energy by J_{11}. Then the interaction energy per magnetic ion in the antiferromagnetic phase, in the paramagnetic phase, and on the interface can be written, respectively,

$$E_A = +6J_{12} - 6J_{11},$$

$$E_P = -6J_{12} - 6J_{11} - \mu_0 H,$$

$$E_I = -4J_{11} - {}^1/_2\mu_0 H.$$

In the absence of a magnetic field, if $J_{12} < 0$ and $|J_{12}| > |J_{11}|$, the antiferromagnetic phase and the assumed distribution of ions with respect to sublattices possess the least energy. For $h \gg -\gamma$, the paramagnetic phase is thermodynamically stable. In external magnetic field $H_t = -12J_{12}/\mu_0$, the energies of the two phases are equal. The additional energy due to the presence of the interface, at field H_t, has the form

$$E_{At} = E_I - E_A = q2J_{11},$$

where q is the number of ions per unit area of the interface. Consequently, in this model the energy of surface tension may have either sign, depending on the sign of the energy of intrasublattice exchange interaction.

Thus the sign of the surface energy, which is uniquely related to the sign of the intrasublattice exchange interaction, directly indicates the type of transition of an antiferromagnet to the paramagnetic state in an external field.

For antiferromagnets, the traditional description is in terms of magnetic sublattices. But for describing the magnitude of the jumps on the magnetization curve at H_1 and H_2, the number of sublattices must already be appreciably larger than two. As was shown above, when the sign of the energy of surface tension is negative, an inhomogeneous periodic state is created in an antiferromagnet in the critical magnetic-field interval. Just as in type-II superconductors, an essential role in the formation of this state is played by the law of decrease of the interaction with distance, which is characterized by the correlation radius. But in contrast to type-II superconductors, where this radius amounts to $\sim 10^{-5}$ cm, in antiferromagnets it is $\sim 10^{-7}$ cm. Therefore in antiferromagnets the inhomogeneous state has a period smaller by three orders of magnitude.

Despite this difference, the magnetization curves considered for $FeCO_3$ and for type-II superconductors are in many respects similar. In both cases the transition from one state to the other occurs over a finite magnetic-field interval. The beginning of the transition is accompanied by a jump of the magnetization and a burst of the magnetic susceptibility. And finally, the curves have appreciable hysteresis. These formal features have served as justification for comparing transitions of different nature, in two objects, from the point of view of the general idea of considering the sign of the energy of the interface between two states of the crystal.

There is a definite similarity also in the physical processes that occur in the critical magnetic-field interval. We consider these processes in a plane perpendicular to the direction of the external magnetic field. The transition to a new state is accomplished initially at separate points. The distance between them at the instant of formation is infinite. With each point is connected a quantum of magnetic flux. The repulsion between them leads to the result that the points in a plane perpendicular to the field form a regular periodic structure. The interaction between them decreases exponentially; therefore with increase of the field, the points rapidly approach each other, and this leads to an infinite slope of the magnetization curve. If the interaction vanishes for $r > r_0$, the magnetization initially changes discontinuously. As a result of the jump, an inhomogeneous structure with period r_0 develops. Further approach of the points with increase of the magnetic field occurs more smoothly because of the appreciable interaction between them. The magnetization curve then has a finite slope, and the value of the magnetization increases until the specimen goes over completely to a new homogeneous phase.

Thus the transition of $FeCO_3$ from the antiferromagnetic to the paramagnetic state is similar to the transition in which a magnetic field destroys type-II superconductivity. The energy of the interface between the antiferromagnetic and paramagnetic states is negative. The transition occurs over a finite magnetic-field interval, where according to the model there is realized an inhomogeneous periodic magnetic structure, reminiscent of the mixed state of type-II superconductors.

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1) This structure, like the mixed state of superconductors [19], has the form of a triangular lattice in the (111) plane.

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