Noncollinear magnetic phases in a strongly anisotropic antiferromagnet CoF_2 with large Dzyaloshinskiĭ interaction

K. G. Gurtovoĭ, A. S. Lagutin, and V. I. Ozhogin

I. V. Kurchatov Institute of Atomic Energy

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The magnetization and differential magnetic susceptibilities are measured in a field H up to 500 kOe directed along the U_2 and C_4 axes of the tetragonal crystal CoF_2. Antiferromagnetic resonance in the wavelength range from 1 to 8 mm is also investigated at $\mathbf{H}\|C_4$. Softening of one of the AFMR modes in a field $H_{c1} = 210$ kOe is observed, as well as a jump of the magnetic moment in a field $H_{c2} = 255$ kOe when the field deviates from the C_4 axis by an angle not more than 30′. The phenomena are interpreted on the basis of a model in which it is assumed that at field strengths between H_{c1} and H_{c2} there exists a canted phase in which the sublattice moments make various angles with the C_4 axis. The magnetization curves for CoF_2, which has an exceptionally high single-ion magnetic anisotropy, are calculated on the basis of a semiphenomenological theory within the framework of the model in a longitudinal and a transverse field. Satisfactory agreement with the measured magnetization curves is obtained.

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1. INTRODUCTION

Antiferromagnetic cobalt fluoride ($T_N = 38$ K, space group $D_{4h}^{14} - P4_2/mnm$) is one of the most interesting magnetically ordered dielectrics because of the substantial influence of the not-fully-frozen orbital momentum of the cobalt ion on the magnetic properties of this crystal. The strong spin-orbit interaction, which is as a matter of fact typical of the Co^{2+} ion, leads to an unusually large magnetic anisotropy of crystals containing such ions. This makes difficult, particularly for CoF_2, both a theoretical description, owing to the lack of a small parameter (usually the ratio of the anisotropic and exchange interactions), and experimental studies, since a strong field applied along the hard magnetization axis (the tetragonal axis C_4) damages the crystal. This last circumstance explains the limited amount of experimental data for the field region $H > H_{c1} = 210$ kOe. In Refs. 1 and 2 they succeeded in observing antiferromagnetic resonance (AFMR) in this field region and in measuring the magnetization up to $H = 200$ kOe (Ref. 1).

Both a phenomenological[3] and a microscopic[4,5] approach were used to describe the magnetic properties of cobalt fluoride. The latter reference dealt in detail with the field regions $H < H_{c1}$ and $H \gtrsim 2H_E$ (H_E is the exchange field), which correspond to collinear phases. For the first of these intervals it was possible to explain qualitatively the dependence of the magnetization and of the AFMR frequencies on the magnetic field. It was also shown that a spin-flop state is possible in fields $H_{c1} < H < 2H_E$. In Ref. 5b was investigated, in addition, the feasibility of realizing in the indicated field region a state corresponding to a continuous (with increasing longitudinal field) deviation of the spins from the C_4 axis, but no such solution could be obtained within the framework of the model employed.

A phenomenological theory of model-free description of the properties of CoF_2 in a field $\mathbf{H}\|[001]$ was developed in Ref. 3, and the field region $H < H_{c1}$ was investigated in detail. The state in fields stronger than H_{c1} was not discussed in detail, and the resonance observed in this region was interpreted as AFMR in spin-flop state. Thus, for the field $\mathbf{H}\|[001]$ there were no reliable data on the behavior of the magnetic system of CoF_2 in strong fields.

At another orientation of the field relative to the C_4 axis, namely $\mathbf{H}\|[100]$, the situation turns out to be simpler. At this orientation the moments of the sublattices rotate around the magnetic field,[6] and in a field $H_{c1} = 125$ kOe a phase transition into a weakly ferromagnetic state takes place. With further increase of the field the angle between the sublattice magnetizations decreases gradually. In this case, the behavior of CoF_2 can be quantitatively described with the aid of a simple phenomenological theory.[7] If, however, the constants chosen for this purpose are used and a similar calculation is performed for a longitudinal field, the results do not agree with experiment.[2,3]

We have continued the investigation of the behavior of cobalt fluoride in strong magnetic fields, and observed at $\mathbf{H}\|[001]$ singularities that can be easily interpreted as the result of the onset of a canted phase in the interval 210 kOe $= H_{c1} < H < H_{c2} = 255$ kOe (Ref. 8). This phase was simultaneously observed also by a magneto-optic method.[9] It is shown in the present paper that within the framework of a semiphenomenological[1)] theory it is possible to describe satisfactorily the field dependences of the magnetization for both transverse and longitudinal fields, and to present a picture of the motion of the magnetic sublattices in the collinear and canted phases.

2. EXPERIMENTAL TECHNIQUE

The magnetization and the differential magnetic susceptibility were measured by an induction method. We used a system similar to that described in Ref. 10, consisting of two measuring and two compensating coils wound on a Plexiglas form. The measuring coils had approximately 1000

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turns each of PÉVL wire of 0.05 mm diameter. The sensitivity of the susceptibility measurements was 4×10^{-6} (at a sample volume $\sim10^{-3}$ cm^3). This corresponds to a sensitivity 0.02 G·cm^3 to the magnetic moment of the sample. The measuring insert together with a glass helium dewar was mounted on a specially constructed platform that moved over a cylindrical surface whose center coincided with the center of the solenoid that produced the magnetic field. The sample rocking plane relative to the field could be varied by rotating the sample holder in the measurement insert. This design made it possible to tilt the insert axis $\pm$ 3 deg relative to the solenoid axis, with an error not worse than 5′.

Measuring-coil signals proportional to the time derivative of the sample magnetic moment were amplified with a low-noise amplifier based on integrated circuit K140UD8A. The same integrated circuits were used in the integrators that shaped signals proportional to the sample magnetization and to the magnetic field.

Antiferromagnetic resonance was investigated in the frequency range from 37 to 300 GHz. We used for this purpose reflection spectrometer made up of standard waveguide parts for 8, 4, and 2 mm wavelengths. As an additional 4-mm band waveguide we used a fused-quartz rod of 4 mm diameter,[11] and the results obtained with it did not differ from those obtained with a waveguide insert made of thin-wall stainless steel. The microwave oscillators used backward-wave tubes of approximately 100 mW power, built by the Experimental Shop of the Institute of Radio and Electronics of the Ukrainian Academy of Sciences, as well as OV-13 and OV-14 tubes.[12] The microwave signal was detected either with an indium-antimonide receiver cooled with liquid helium or by standard D-407 point-contact diodes (at frequencies lower than 80 GHz).

The magnetization, susceptibility, and resonance were recorded by one of the channels of an S8-11 two-beam memory oscilloscope, whose second input received a signal proportional to the field (the inductive field sensor was placed alongside the sample). The field was calibrated against an EPR signal ($\nu = 120$ GHz) in diphenylpicrylhydrazine. The magnetic field was produced by discharging a capacitor bank rated 180 kJ (maximum voltage 5 kV) through an increased-reliability multiturn solenoid.[13] To decrease the noise pickup, T-630 thyristors were used as dischargers.

The solenoid winding was made up of a copper bus (cross section 2×3.5 mm) reinforced with NbTi-alloy filaments. The pulsed solenoid was cooled with liquid nitrogen, so that the superconducting bus was in the normal state and only its higher strength was used. The solenoid case, approximately 15 mm thick, was wrapped with Fiberglas impregnated with epoxy resin. The described design made it possible to receive repeatedly in a 15-mm diam opening a field of 500 kOe amplitude with half-wave duration of approximately 15 msec. All the measurements were made at liquid-helium temperature.

As already noted, the main experimental difficulty in the investigation of CoF_2 is that a strong magnetic field parallel to the C_4 axis damages the sample. It was stated in Ref. 2 that this damage takes place at sample thicknesses exceeding 0.5 mm in fields exceeding 210 kOe. This is attributed to accumulation of the shear strain between the domains of the flopped and unflopped phases, produced in a phase order transition between the indicated phases.

Our experiments have shown that the samples are damaged in a longitudinal field even at thicknesses $\delta\leqslant0.1$ mm and in fields not exceeding 200 kOe. The damage was caused by the forces that oriented the sample in such a way that its easy magnetization axis U_2 coincided with the field direction. We observed this in the course of investigations of resonance, when samples in the form of plates of varying thickness were secured with BF-2 adhesive to a small stainless steel base that short-circuited the waveguide insert placed in the pulsed solenoid. The samples were crumbled into particles smaller than 0.1 mm, and part of the plate of thickness 0.05–0.1 mm was left on the base. To prevent damage to the sample, we secured it by several methods. The CoF_2 crystal remained whole at field amplitudes up to 500 kOe if it consisted of a plate 0.15–0.8 mm thick secured with BF-2 adhesive between two fused-quartz plates 1–3 mm thick. The sample for the magnetization measurement at $\mathbf{H}\|[001]$ was a disk 0.8 mm thick and 3.5 mm in diameter, while in the case of $H\|[100]$ we used a cylinder 3.5 mm in diameter and 7 mm long, on which measurements were made in Refs. 1, 6, and 7. To measure the differential magnetic susceptibility at both field orientations we used disks of the indicated diameter and 0.4–0.8 mm thick, with cross section 3–6 mm^2.

3. EXPERIMENTAL RESULTS

A. Longitudinal field, H = (0,0, H)

The magnetization curve of a CoF_2 crystal in a field parallel to the tetragonal axis is shown in Fig. 1.

At $H<H_{c1}$ our results agree with those of Refs. 1 and 2. In fields $H>200$ kOe one observes a strong magnetization increase that slows down considerably on going into a new phase in fields $H>H_{c2}=255\pm5$ kOe. The dependence of the susceptibility on the field in CoF_2 (Fig. 2) in the field interval 150–300 kOe is similar to the $\chi(H)$ dependence in the canted phase of rare-earth iron garnets (see, e.g., Ref. 14), when the moments of the rare-earth and of the resultant iron sublattices are inclined at different angles to the external field direction. The phase transition in the field H_{c2} is accompanied by a susceptibility peak that can be reliably revealed, however, when the field is inclined away from the C_4 axis by an angle not larger than 30′ (see Fig. 2 and Fig. 3, oscillogram 1). Corresponding to this peak is a magnetiza-

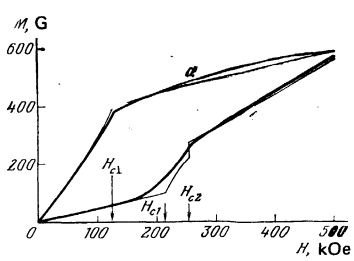

FIG. 1. Magnetization curves of CoF_2 single crystal at 4.2 K: thin lines—calculation, thick—experiment. a) $\mathbf{H}\|[100]$, b) $\mathbf{H}\|[001]$.

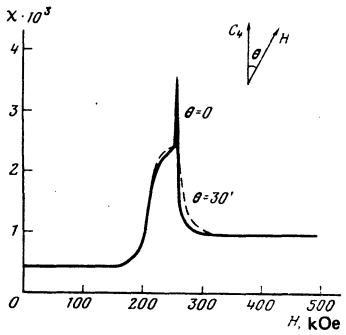

FIG. 2. Differential magnetic susceptibility $\tilde{\chi}$ vs the field in CoF_2 at 4.2 K, for different field orientations relative to the C_4 axis.

tion jump of approximately 2–3 G, which can naturally not be observed at the scale chosen for Fig. 1.

Generally speaking, a susceptibility peak of this amplitude ($\sim 10^{-3}$) still does not prove that a first-order transition took place in the field H_{c2}, inasmuch for a first-order transition the maximum measured susceptibility for a disk perpendicular to the field should be $1/N \approx 1/4\pi$ (10^{-1}), where N is the demagnetizing factor. The region where an intermediate state exists is in this case $\Delta H = 4\pi\Delta M$, where ΔM is the change of the magnetization in the first-order transition. If, however, ΔM is small, as in CoF_2, the width of the transition in terms of the field is determined already by the inhomogeneity of the solenoid field in the interior of the sample (in our case, 0.2–0.5 kOe in a 200-kOe field). Thus, the observed maximum of the susceptibility (3.5×10^{-3}) at $\Delta M \ll 20$ G is less than $1/4\pi$ and agrees in order of magnitude with the estimate ($\Delta M/\Delta H \sim 10^{-2}$) that takes into account the inhomogeneity of the solenoid field.

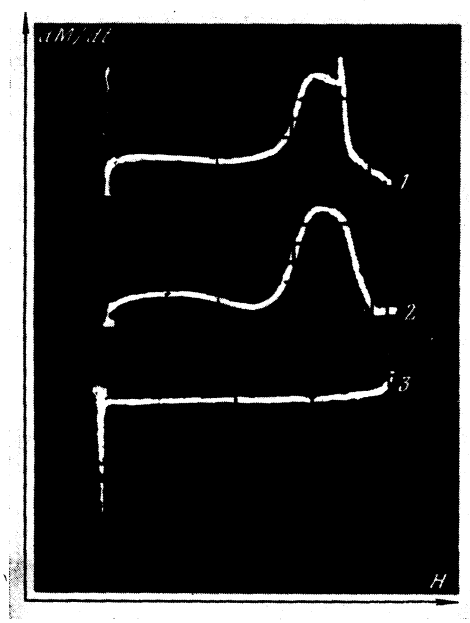

FIG. 3. Oscillograms of the time derivative of the magnetization as a function of the magnetic field, obtained at different inclination angles θ of the field away from the C_4 axis of the crystal: curve 1) $\theta = \pm 5'$, curve 2) $\theta = 30'$, curve 3) signal in the absence of a sample.

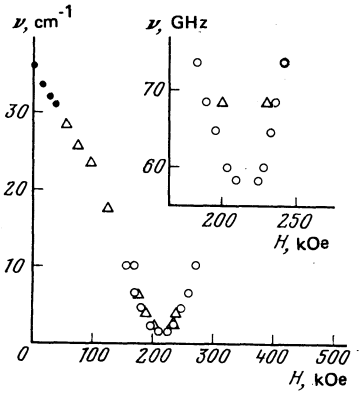

FIG. 4. AFMR frequency vs. longitudinal magnetic field ($T = 4.2$ K). Dark circles and triangles—results of Refs. 16 and 3; white circles—our data.

In fields $H > H_{c2}$ the magnetization is linear in the field and its extrapolation to zero field yields a zero magnetization. This behavior of the magnetization is typical of the flopped phase of antiferromagnets.[15]

The results of our AFMR experiments are shown in Fig. 4 together with the data of Refs. 3 and 16. In fields from 160 to 240 kOe our dependence of the resonance frequency on the field agrees well with the results cited in Ref. 3. Investigations at frequencies ν lower than in Ref. 3 have shown that the AFMR signals vanish at $\nu \leqslant 58$ GHz (see inset of Fig. 4). It was also found that the field dependence of the resonance frequency at $H > H_{c1} = 210 \pm 10$ kOe differs somewhat from that described in Refs. 2 and 3.

B. Transverse field, H = (H,0,0)

The experimental data obtained in a transverse field (see Fig. 1) agree up to 250 kOe with those previously obtained.[1,17] In the region $H > H_{c1} = 125$ kOe the $m(H)$ dependence is nonlinear, owing to the existence of a Dzyaloshinskiĭ interaction. This interaction makes it impossible to reach a state in which the sublattice magnetizations are parallel and directed along the field.[18] We have measured the differential magnetic susceptibility in a field close to that of the [100] axis, changing the orientation of the crystal relative to the field in small steps along two orthogonal direction in a range $\pm 3°$, in analogy with the procedure described above. At 4.2 K, however, we observed no susceptibility peak that might be evidence of a first order transition in the field H_{c1}.

4. SEMIPHENOMENOLOGICAL CALCULATION

A. Qualitative picture

The data obtained on the behavior of CoF_2 in a longitudinal field suggest the following new picture of the phenomena that take place in this antiferromagnet in strong magnetic fields $\mathbf{H} \| [001]$. In fields up to H_{c1} the magnetic structure is collinear and the difference between the magnetic moments of the sublattices increases with increasing field. This difference causes the susceptibility of the system to be large even as $T \to 0$ K (Refs. 4, 5). In the field H_{c1}, the sublattices begin to make different angles with the C_4 axis of the crystal, i.e., a second-order phase transition takes place into an asymmetric canted phase that exists in fields up to H_{c2}. In

this field, the angles between the tetragonal axis and the sublattice moments become jumpwise equal, i.e., a first-order phase transition takes place, but only at a very accurate orientation of the field along the tetragonal axis. With further increase of the magnetic field, the sublattices rotate gradually towards the field direction; this rotation is completed in the collapse field H_{c3}. Its value can be estimated by extrapolating the magnetization plot to the value $M = 2M_0$, where $2M_0 = 762$ G in the limiting case $H \gg 2H_E$ (the spin per site tends in this case to 3/2, Ref. 5). The field H_{c3} is determined in this manner to be 750 kOe. The CoF_2 in fields $H > H_{c3}$ is in a state of magnetic saturation.

In a field directed along the [100] axis, at $H < H_{c\perp}$, a phase is produced with rotation of the sublattices around the field direction, and at $H_{c\perp}$ a transition takes place into the weakly ferromagnetic phase.[6,7,17,19] The character of this transition will be discussed below.

B. Quantitative analysis

Phenomenological models for the description of the canted phase of antiferromagnets were proposed in a number of theoretical papers.[20–22] The existence of this state in a uniaxial antiferromagnet in a longitudinal magnetic field can be explained by using in the expression for the magnetic energy either only the bilinear terms that describe the anisotropy,[20] or also the biquadratic.[21,22] The difference between the expressions for the anisotropy energy leads to different dependences of the magnetic moment on the field in the canted phase. In the first case[20] this dependence is linear in the field, and in the second[21] it is nonlinear. In both cases the noncollinear state is bounded by second-order phase transitions. Introduction of one more parameter of the anisotropic interactions changes, generally speaking, the character of the transitions in these fields. Such a parameter can be the third anisotropy constant K_3 (the coefficient of the term of the type $K_3 l_z^6$ in the expansion of the energy[21]) or the Dzyaloshinskiĭ interaction.[22]

It should be noted that the theory developed in Ref. 22 is applicable only to the case of an antiferromagnet with a superweak Dzyaloshinskiĭ interaction and cannot be used for cobalt fluoride, where this interaction is comparable with the exchange interaction.

A universal phenomenological method of describing magnets is the model-free approach[3,23] based on the use of an integer rational basis of invariants of the symmetry group of the crystal. This makes it possible in principle to calculate completely the magnetic properties, particularly also of CoF_2, with any accuracy. The use of this method may possibly result in a better agreement between the calculated and experimental data than in the present paper. This, however, may call for very cumbersome calculations and for additional experimental data. We, on the other hand, propose the simplest form of a Hamiltonian that describes well the static properties of CoF_2 in magnetic fields $\mathbf{H} \| C_4$ and $\mathbf{H} \perp C_4$, and the additional conditions imposed on the connection between the sublattice magnetization components are substantially different from the usual ones.

We express the density of the magnetic energy of the antiferromagnet as $T \to 0$ K in the following form,[24] with an aim at applying the calculation results to CoF_2, which has, in the terminology of Turov's monograph,[10] an odd magnetic structure relative to the principal axis:

$$\mathcal{E} = 2M_0\mathcal{H}, \quad \mathcal{H} = {}^1/_2 E\mathbf{m}^2 + {}^1/_2 G(\mathbf{ml})^2 + D(m_x l_y + l_x m_y)$$
$$+ F(\mathbf{ml})l_x l_y - \mathbf{mH} + {}^1/_2 A_1(l_x^2 + l_y^2) + {}^1/_4 A_2(l_x^2 + l_y^2)^2. \qquad (1)$$

Here $\mathbf{m} = (\mathbf{M}_1 + \mathbf{M}_2)/2M_0$ and $\mathbf{l} = (\mathbf{M}_1 - \mathbf{M}_2)/2M_0$ are the ferro- and antiferromagnetic vectors, $\mathbf{M}_1$ and $\mathbf{M}_2$ are the sublattice magnetizations, $2M_0$ is a certain quantity measured in gausses (see above), E and G are exchange-interaction constants, D and F are Dzyaloshinskiĭ-interaction constants, A_1 and A_2 are uniaxial anisotropy constants, and $\mathbf{H}$ is the external field. According to the chosen notation, all these constants are the effective fields of the corresponding interactions and are measured in oersteds. The axis $z \| C_4$, while the axes x and y are directed along the edges of the basic square ($x \| U_2$). We impose on the vectors $\mathbf{m}$ and $\mathbf{l}$ the constraint

$$\mathbf{m}^2 + \mathbf{l}^2 = 1, \qquad (2)$$

which means that the moduli of the magnetic moments of the sublattices can vary in such a way that the sum of their squares is constant. The quantum-mechanical calculation of the changes of the sublattice spins with increasing field, carried out in Ref. 5b, justifies the use of this approximation for fields weaker than H_{c1} and stronger than H_{c2}. It must be noted, however, that the other customarily employed constraint $\mathbf{m} \cdot \mathbf{l} = 0$, which in conjunction with Eq. (2) is identical with the requirement that the moduli of the magnetic moments of each sublattice be separately conserved, is not applicable in the case of CoF_2. The reason is that the parallel susceptibility of cobalt fluoride differs from zero and is comparable with the perpendicular susceptibility, so that allowance for the inequality of the moduli of the sublattice-magnetization vectors is absolutely mandatory for the description of the properties of this crystal. We minimize expression (1) first with respect to $\mathbf{m}$ (so as to eliminate the explicit dependence of $\mathcal{H}$ on $\mathbf{m}$):

$$\partial\mathcal{H}/\partial\mathbf{m} = E\mathbf{m} + G(\mathbf{ml})\mathbf{l} - \mathbf{H} - \mathbf{H}_D = 0, \qquad (3)$$

where

$$\mathbf{H}_D = -\{l_y(D + Fl_x^2), \quad l_x(D + Fl_y^2), \quad Fl_x l_y l_z\}. \qquad (4)$$

Following the procedure described in Ref. 4, we find that

$$\mathbf{m} = \chi_\perp(\mathbf{H} + \mathbf{H}_D) - \Delta\chi\boldsymbol{\gamma}(\mathbf{H}\boldsymbol{\gamma} + \mathbf{H}_D\boldsymbol{\gamma}), \qquad (5)$$

where we have introduced for brevity the relative susceptibilities

$$\chi_\perp = \frac{1}{E}, \quad \chi_\| = \frac{1}{E + Gl^2}, \quad \Delta\chi = \chi_\perp - \chi_\|, \quad \boldsymbol{\gamma} = \frac{\mathbf{l}}{|\mathbf{l}|}.$$

Substituting (5) in (1) we obtain

$$\mathcal{H} = -{}^1/_2\chi_\perp(\mathbf{H} + \mathbf{H}_D)^2 + {}^1/_2\Delta\chi(\mathbf{H}\boldsymbol{\gamma} + \mathbf{H}_D\boldsymbol{\gamma})^2$$
$$+ {}^1/_2 A_1 l^2(1 - \gamma_z^2) + {}^1/_4 A_2 l^4(1 - \gamma_z^2)^2. \qquad (6)$$

B1. Longitudinal field H = (0,0,H)

Transforming to the polar coordinates of the vector γ, we obtain (θ and φ are the polar and the azimuthal angles of the vector γ)

$$\mathcal{H}_{\parallel}=-{}^{1}/_{2}\chi_{\perp}H^{2}+p\sin^{4}\theta\sin^{2}2\varphi+{}^{1}/_{2}\Delta\chi H^{2}\cos^{2}\theta$$
$$-\Delta\chi Hd^{*}\sin^{2}\theta\cos\theta\sin 2\varphi+{}^{1}/_{2}a_{1}^{*}\sin^{2}\theta+{}^{1}/_{4}a_{2}\sin^{4}\theta, \quad (7)$$

where

$$d=Dl, \quad f=Fl^{3}, \quad a_{1}^{*}=a_{1}-\chi_{\perp}d^{2}, \quad a_{1}=A_{1}l^{2}, \quad a_{2}=A_{2}l^{4},$$
$$d^{*}=d+{}^{1}/_{2}f-{}^{1}/_{2}f(\chi_{\perp}/\Delta\chi), \quad p={}^{1}/_{8}\Delta\chi(2d+f)^{2}-{}^{1}/_{8}\chi_{\perp}(4d+f)f. \quad (8)$$

We obtain the equilibrium conditions by minimizing (7) with respect to φ and θ:

$$\partial\mathcal{H}_{\parallel}/\partial\varphi=2\sin^{2}\theta\cos 2\varphi\,[2p\sin^{2}\theta\sin 2\varphi-\Delta\chi Hd^{*}\cos\theta]=0, \quad (9)$$

$$\partial\mathcal{H}_{\parallel}/\partial\theta=\sin\theta\{[-\Delta\chi H^{2}-2\Delta\chi Hd^{*}\cos\theta\sin 2\varphi$$
$$+4p\sin^{2}\theta\sin^{2}2\varphi$$
$$+a_{1}^{*}+a_{2}\sin^{2}\theta]\cos\theta+\Delta\chi Hd^{*}\sin^{2}\theta\sin 2\varphi\}=0. \quad (10)$$

Equations (9) and (10) admit of the existence of four solutions:

$\sin\theta=0$—antiferromagnetic phase (11a)

$\cos\theta=0$—flip-flop phase (11b)

$\sin\theta=w(H)$, $\cos 2\varphi=0$—canted phase A (11c)

$\sin\theta=u(h)$, $\cos 2\varphi=v(H)$—canted phase B, (11d)

where the function $w(H)$ is determined by equating to zero the content of the curly brackets in (10) at $\sin 2\varphi=\pm 1$ (this corresponds to two possible planes of rotation of the sublattice moments, (110) and $(1\bar{1}0)$; $u(h)$ and $v(H)$ are obtained by simultaneous solution of (9) and (10). The treatment that follows pertains to CoF_2.

It follows from neutron-diffraction data[26] that CoF_2 is antiferromagnetic in a zero magnetic field. When the field increases the magnetic system of the crystal undergoes, as we assume, a number of orientational phase transitions described at the beginning of this section. In particular, a transition from the antiferromagnetic to the canted phase takes place in the field H_{c1}. It can be seen from the equilibrium conditions (9) and (10) that two canted phases can exist: in one (A) the antiferromagnetism vector l moves in the (110) plane when the field is increased, and in the other (B) the vector l rotates without remaining in any fixed plane whatever. It was shown in Ref. 9 by a magnetooptic method that in CoF_2 a transition to the canted phase A takes place in the field H_{c1}. Some difference between the value of H_{c1} obtained by us from that given in the cited reference ($H_{c1}=180$ kOe) can be attributed to the rather large error (10% in our case and in Ref. 9) in the determination of this field from the experimental data. We obtain the value of H_{c1} from the condition that the energies of the antiferromagnetic (11a) and canted (11b) phases be equal:

$$\mathcal{H}_{\parallel}{}^{\parallel}-\mathcal{H}_{\parallel}{}^{\angle}=\sin^{2}\theta_{c1}[-{}^{1}/_{2}\Delta\chi H_{c1}{}^{2}-\Delta\chi H_{c1}d^{*}\cos\theta_{c1}$$
$$+a_{1}^{*}+a_{2}^{*}\sin^{2}\theta_{c1}]=0, \quad (12)$$

and from the equilibrium condition (10) with account taken of the equality $\cos 2\varphi=0$:

$$\partial\mathcal{H}_{\parallel}/\partial\theta=[-\Delta\chi H_{c1}{}^{2}-2\Delta\chi H_{c1}d^{*}\cos\theta_{c1}+a_{1}^{*}+a_{2}^{*}\sin^{2}\theta_{c1}]\cos\theta_{c1}$$
$$+\Delta\chi H_{c1}d^{*}\sin^{2}\theta_{c1}=0. \quad (13)$$

Here $a_{2}^{*}=a_{2}+4p$. The transition from the antiferromagnetic phase ($\sin\theta=0$) into the canted phase proceeds in accord with Eq. (12) when either $\sin\theta_{c1}=0$ or when the expression in the brackets vanishes ($\sin\theta_{c1}\neq 0$). The phase transition is of second order in the former case and of first in the latter. In CoF_2 this transition is of second order. This is attested to by the absence of a jump of the magnetic moment[8,9] and by the softening of one of the AFMR modes in the field H_{c1} (Ref. 8). Using the equilibrium condition (13) we obtain therefore

$$H_{c1}(\mathrm{II})=(a_{1}^{*}/\Delta\chi+d^{*2})^{1/2}-d^{*}. \quad (14)$$

We discuss now the transition from the canted phase A to the spin-flop phase. In the field H_{c2} corresponding to this transition we have observed, as mentioned above, a small jump of the magnetic moment. We consider therefore first the case when a first-order transition takes place in the field H_{c2} and is accompanied by a jump of the magnetic-moment projection $\Delta m_{\parallel}$ on the [001] axis. Using (5), we obtain an equation that connects $\Delta m_{\parallel}$ with the critical angle θ_{c2} at which the vector l goes over jumpwise into the basal plane:

$$\Delta m_{\parallel}=m_{\perp}-m_{\parallel}=\Delta\chi\cos\theta_{c2}(H_{c2}\cos\theta_{c2}-d^{*}\sin^{2}\theta_{c2}). \quad (15)$$

The value of the field H_{c2} is obtained from the condition that the energies of the canted and spin-flop phases are equal:

$$\mathcal{H}_{\parallel}{}^{\angle}-\mathcal{H}_{\parallel}{}^{\perp}={}^{1}/_{2}\Delta\chi H_{c2}{}^{2}\cos^{2}\theta_{c2}-\Delta\chi H_{c2}d^{*}\sin^{2}\theta_{c2}\cos\theta_{c2}$$
$$-{}^{1}/_{2}a_{1}^{*}\cos^{2}\theta_{c2}-{}^{1}/_{4}a_{2}^{*}\cos^{2}\theta_{c2}(1+\sin^{2}\theta_{c2})+p=0, \quad (16)$$

and from the equilibrium condition:

$$\partial\mathcal{H}_{\parallel}/\partial\theta=[-\Delta\chi H_{c2}{}^{2}-2\Delta\chi H_{c2}d^{*}\cos\theta_{c2}+a_{1}^{*}$$
$$+a_{2}^{*}\sin^{2}\theta_{c2}]\cos\theta_{c2}+\Delta\chi H_{c2}d^{*}\sin^{2}\theta_{c2}=0, \quad (17)$$

all of which yield

$$H_{c2}=\{(1/\Delta\chi)[a_{1}^{*}+{}^{1}/_{2}a_{2}^{*}(3\sin^{2}\theta_{c2}-1)+p/\cos^{2}\theta_{c2}]$$
$$+4d^{*}\cos^{2}\theta_{c2}\}^{1/2}-2d^{*}\cos\theta_{c2}. \quad (18)$$

It can be seen that at $p\neq 0$ the transition in question cannot be of second order, since $\cos\theta_{c2}$ cannot vanish. This is a consequence of the fact that the symmetry group of the canted phase is not a subgroup of the more symmetrical spin-flop phase, inasmuch as in the canted phase A the antiferromagnetic vector l lies in a plane passing through the diagonal of the basis square, whereas in the spin-flop phase it passes along a side of this square. If, however, $p=0$ and $d^{*}=0$, the transition in the field H_{c2} can be of second order.

The picture of the phase transitions in the vicinity of the transition into the spin-flop state may also be more complicated: namely, a transition from the canted phase A to the canted phase B, and next from the canted phase B into the spin-flop state. The last transition can at $p\neq 0$ be of either

first or second order. We shall not investigate this situation in detail, and assume that a first-order phase transition takes place directly from the canted phase A into the spin-flop state in CoF_2 in the field H_{c2}.

With further increase of the field ($H > H_{c2}$), a gradual rotation of the sublattices takes place toward the field direction and terminates in the field H_{c3}. The latter can be obtained from Eq. (5) in which we put $m = 1$ and $l = 0$:

$$H_{c3}=1/\chi_\perp=E. \tag{19}$$

In the field H_{c3} a phase transition takes place from the spin-flop into the paramagnetic ("collapsed") state and is of second order. Magnetic saturation sets in then.

B2. Transverse field, H = (H,0,0)

Writing out Eq. (6) fully for this particular case and changing over to the polar coordinates of the vector γ, we obtain

$$\begin{aligned}\mathcal{H}_\perp=&-{}^1/_2\chi_\perp H^2+p\sin^4\theta\sin^2 2\varphi\\&+\chi_\perp Hd\sin\theta\sin\varphi+{}^1/_2\Delta\chi H^2\sin^2\theta\cos^2\varphi\\&-\Delta\chi Hd^*\sin^3\theta\cos^2\varphi\sin\varphi+{}^1/_2a_1^*\sin^2\theta+{}^1/_4a_2\sin^4\theta.\end{aligned} \tag{20}$$

Minimizing this expression with respect to φ and θ we find that four solutions are possible:

$\sin\theta = 0$—antiferromagnetic phase (21a)

$\cos\theta = 0$—weakly ferromagnetic phase (21b)

$\sin\theta = q(H)$,

$\cos 2\varphi = 0$—phase with sublattice rotation around the field (21c)

$\sin\theta = r(H)$, $\cos\varphi = s(H)$—canted phase C, (21d)

where q, r, and s are functions of the field and are determined from the equilibrium conditions.

It is known that in a transverse field $H < H_{c1}$ CoF_2 has a phase with rotation of the sublattices around the field direction, and the canted phase C is not realized at all.[17] In a field $H_{c1} = 125$ kOe a transition takes place into a weakly ferromagnetic state. Generally speaking the transition in this field can be of either first or second order.

The condition that the difference $\Delta\mathcal{H}_\perp$ between the energies of the phase with sublattice rotation around the field and of the weakly ferromagnetic phase be zero yields the following equation for H_{c1} and for the critical angle θ_{c1} in this field:

$$\begin{aligned}\Delta\mathcal{H}_\perp=&(1-\sin\theta_{c\perp})\,[-\Delta\chi H_{c\perp}d+{}^1/_2a_1^*(1+\sin\theta_{c\perp})\\&+{}^1/_4a_2^*(1+\sin\theta_{c\perp})\,(1+\sin^2\theta_{c\perp})]=0.\end{aligned} \tag{22}$$

From the equilibrium condition $\partial\mathcal{H}_\perp/\partial\theta = 0$ we can find the dependence of the angle θ on the field:

$$H=(1/\chi_\perp d)\,(a_1^*\sin\theta+a_2\sin^3\theta). \tag{23}$$

If the transition in question is of second order, then

$$H_{c\perp}(\mathrm{II})=(a_1+a_2)/\chi_\perp d \quad \text{и} \quad \sin\theta_{c\perp}=1. \tag{24}$$

If a first-order phase transition takes place in the field H_{c1} i.e., $\sin\theta_{c1} < 1$, we have for H_{c1} (I)

$$H_{c\perp}(\mathrm{I})=(1+\sin\theta_{c\perp})\,[a_1^*+{}^1/_2a_2(1+\sin^2\theta_{c\perp})]/2\chi_\perp d, \tag{25}$$

with

$$\sin\theta_{c\perp}={}^1/_3\{-1\pm[-(2+6a_1^*/a_2)]^{1/2}\}. \tag{26}$$

Using (26) we can obtain a criterion for the order of the transition in the field H_{c1}: at $a_1^*/a_2 > -3$ the transition in this field is of first order, and in the opposite case, of second. This criterion is similar to the criterion for the order of the transition in a transverse field for hematite.[19] The dependence of the magnetic moment on the field in the phase with sublattice rotation around the field can be obtained from (5) by putting in it $\mathcal{H}\cdot\gamma = 0$:

$$m_\perp=\chi_\perp(H+d\sin\theta), \tag{27}$$

where $\sin\theta$ as a function of H is determined from (23). In the weakly ferromagnetic phase we obtain the dependence of the magnetic moment on the field by minimizing (1) with respect to m_x and l_y at $m_y = m_z = l_x = l_z = 0$:

$$\begin{aligned}\mathcal{H}_{\text{w.f.}}=&{}^1/_2Em^2-Dm(1-m^2)^{1/2}+{}^1/_2A_1(1-m^2)\\&+{}^1/_4A_2(1-m^2)^2-\mathbf{mH},\end{aligned} \tag{28}$$

$$m[E-A_1-A_2(1-m^2)]-D(1-2m^2)/(1-m^2)^{1/2}=H. \tag{29}$$

Here $m = m_x$. It can be seen from (29) that the Dzyaloshinskiĭ interaction makes it impossible to reach a state in which the sublattice magnetizations are parallel and directed along the field.

5. MAGNETIZATION CURVES: COMPARISON OF THEORY AND EXPERIMENT

The phenomenological theory expounded above enables us to describe the properties of cobalt fluoride in magnetic fields directed along and across the crystal tetragonal axis. The exchange- and anisotropic-interaction constants contained in expression (1) for the magnetic energy are obtained from the values of the critical fields

$$H_{c1}=210\text{ kOe},\quad H_{c2}=255\text{ kOe},\quad H_{c\perp}=125\text{ kOe}, \tag{30}$$

from the susceptibilities determined from experimental data at $H = 0$,

$$\chi_\perp^*=2.8\cdot10^{-3},\quad \chi_\parallel^*=4.6\cdot10^{-4} \tag{31}$$

and from the jump of the magnetic moment $\Delta m_\parallel(H) = 0.004$, using Eqs. (14), (18), (25), (15), and (27). The constants are determined here by a numerical self-consistent solutions of the system of equations obtained in this manner.

If it is assumed that a second-order phase transition takes place in the field H_{c1}, calculation yields for transverse field orientation an $m(H)$ curve that does not agree qualitatively with experiment (see Fig. 1) at the following values of the anisotropy constants, of the Dzyaloshinskiĭ interaction, and of the exchange interaction (in kOe):

$$A_1=300,\quad A_2=-85,\quad D=350,\quad F=320,\quad E=700. \tag{32}$$

It should be noted that the magnetic-moment jump calculated in this case from (27) and (29) in a transverse field H_{c1} is

less than 1 G, although the jump of the angle θ from $\theta_{c1}^{calc} = 50°$ to 90° is large, i.e., only the components of the vector **l** experience a jump in the transition, while the vector **m** is practically continuous in the transition field, owing to the relatively large value of the Dzyaloshinskiĭ interaction in CoF_2. It is this which explains the negative result of our attempts to find the discontinuity of the moment in a transverse field (see Sec. 3B above).

The magnetization curve of CoF_2 in a longitudinal field, corresponding to the set of constants (32), is also shown in Fig. 1. The discrepancy between the calculated and experimental curves is apparently due to the fact that the condition (2) used by us is not sufficiently accurately satisfied in the field interval from 150 to 250 kOe. A microscopic calculation[5] of the magnetizations of the CoF_2 sublattices shows that this is indeed so, at least at the end of the region where the antiferromagnetic phase exists (i.e., as shown by comparison with experiment, from 150 kOe to $H_{c1} = 210$ kOe).

6. RESONANCE IN A LONGITUDINAL FIELD

We now make a few remarks concerning the picture of the AFMR in CoF_2. As already noted, a second-order phase transition into the canted phase A takes place in the field H_{c1}. This transition is accompanied by softening of one of the AFMR modes (see Fig. 4), as typical of second-order transitions or of those of first order close to second. It was observed in this case that in the field H_{c1} the AFMR frequency does not vanish exactly, but reaches a minimum value of 58 GHz. This gap in the spin-wave spectrum in the transition region can be due both to the dependence of the resonance frequency on the magnetic field direction and to the magnetoelastic interaction. An estimate shows that at our error in the field orientation relative to the C_4 axis ($\pm 3°$ in the resonance measurements) the "orientation" gap does not exceed 10 GHz. On the other hand, the approximate equality of the gaps observed for the longitudinal and transverse fields[7] is apparently evidence that they are of the same (magnetoelastic) origin in both cases. The value of the gap, as indicated in Ref. 7 corresponds to magnetoelastic constants $\sim 10^9$ erg/cm^3, which is of the same order of magnitude as these constants determined from the piezomagnetic effect[27] and magnetostriction.[28]

Generally speaking, in a field H_{c2} there should also be observed some singularity in the field dependence of the AFMR, as is typical of first-order phase transitions (see, e.g., Ref. 19). In our resonance experiments the field was not oriented accurately enough relative to the C_4 axis to be able to observe such a singularity. It appears that if the singularity does exist, it is small and its observation calls for precision investigation of AFMR at frequencies 100–200 GHz in small frequency steps (with the field oriented relative to the C_4 axis accurate to 5′ or less).

7. CANTED PHASES IN STRONGLY ANISOTROPIC MAGNETS

The magnetic phases observed in CoF_2 in strong magnetic fields should exist also in other strongly anisotropic antiferromagnets with large Dzyaloshinskiĭ interaction, and particularly in FeF_2, which is isomorphous to cobalt fluoride. In Ref. 29 is described an experiment on spectroscopic observation of a transition into the canted phase of FeF_2 in a field ~ 200 kOe directed along the C_4 axis, at $T = 14$ K. In Refs. 30 is reported observation, in the same crystal, of a magnetization jump in a field parallel to C_4 and equal to approximately 400 kOe at $T < 40$ K (Fig. 5). Although this jump was attributed to the authors of Ref. 30 to a transition from the antiferomagnetic to the spin-flop phase, we propose that here, as in CoF_2, that the transition is from the canted to the spin-flop phase. On the other hand a transition from the antiferromagnetic to the canted phase takes place apparently in fields close to 260 kOe at 4.2 K, where we have observed in preliminary experiments (see inset of Fig. 5) a singularity of the magnetic susceptibility. This transition is practically unobservable on the $M(H)$ plot (see Fig. 5), and this may be the reason why the transition in a field $H \sim 400$ kOe was interpreted in Ref. 30 as an ordinary spin-flop transition.

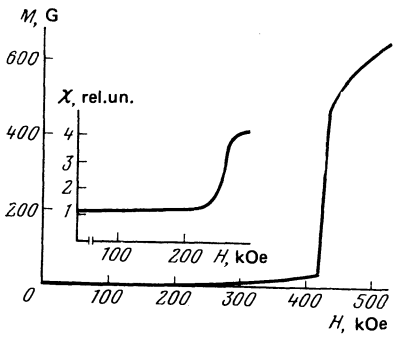

FIG. 5. Magnetization curve of single-crystal FeF_2 at a temperature 4.2 K in a field $\mathbf{H} \sim [001]$.[30b] Inset—our data for $\hat{\chi}(H)$ at $H_{max} = 300$ kOe, the error in $\hat{\chi}$ is ± 0.5 relative units at 150 kOe and ± 1 at 300 kOe.

Magnetization curves similar to those in Fig. 1 were observed in fields up to 50 kOe in cobalt fluorited diluted with zinc, $Co_{0.5}Zn_{0.5}F_2$ (Ref. 31). The model proposed by us for the phenomena in CoF_2 in a longitudinal field can be extended also to include this dilute antiferromagnet.

8. CONCLUSION

Significant singularities of the magnetization by a longitudinal field and of the field dependence of one of the AFMR frequencies (Ref. 8) were observed in antiferromagnetic cobalt fluoride. These data together with the results of magneto-optical measurements[9] allow us to state that we have observed, for the first time ever in the case of antiferromagnets, a transition into the spin-flop state via a canted phase in CoF_2, rather than as a result of the usual spin-flop transition. As expected, the traditional phenomenological approach, in which constancy of the moduli of the magnetizations of the antiferromagnet in a magnetic field is assumed, can not describe the magnetization of so strongly an anisotropic crystal as cobalt fluoride. To calculate the CoF_2 magnetization curves we propose a variant of the aforementioned approach, in which only one of the usual conditions is imposed on the ferro- and antiferromagnetic vectors **m** and **l**, namely $\mathbf{m}^2 + \mathbf{l}^2 = 1$. On the other hand, our approach is not restricted by the orthogonality condition $\mathbf{m} \cdot \mathbf{l} = 0$, in accord with the conclusion that the average spin of the Co^{2+} ion does not

remain constant when the magnetic field is increased, a conclusion obtained by a quantum-mechanical analysis[5] of a four-level model of this ion. The difficulty of analyzing the equations derived in Ref. 5 makes it impossible to obtain a solution corresponding to a low-symmetry noncollinear state. On the other hand, our phenomenological (in the sense indicated above) approach has made it possible to solve this problem and to describe satisfactorily the experimental data. The results of the analysis allow us to suggest the onset of noncollinear magnetic phases in a longitudinal field also in other easy-axis antiferromagnets with large values of the anisotropic interactions.

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[1)] We use this arbitrary term because the calculation employs a result deduced from a quantum-mechanical calculation[5] that the average spin of the Co^{2+} ion does not remain constant when the magnetic field is increased.

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