# Spin-flop phase transition and intermediate state in the quasi-one-dimensional antiferromagnet $CsMnCl_3 \cdot 2H_2O$

V. P. Novikov, V. V. Eremenko, and I. S. Kachur

*Physicotechnical Institute of Low Temperatures, Academy of Sciences, Ukrainian SSR*
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The method of optical spectroscopy is used to investigate the character of the spin-flop phase transition in the quasi-one-dimensional antiferromagnet $CsMnCl_3 \cdot 2H_2O$, as it depends on the angle of inclination of the external magnetic field to the axis of spontaneous magnetization in the flip plane of the magnetic sublattices. It is shown that in a magnetic field oriented along the easy axis, this transition is a transition of first order passing through an intermediate state. A phase diagram is reconstructed for a transition in an inclined magnetic field. Values are found for the critical angle, the instability fields of the original and of the flipped magnetic phases, and the magnetic anisotropy constants—the quantities that determine the character of the transition in this crystal plane.

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## INTRODUCTION

Because of the recent intense study of low-dimension crystalline compounds, the physical properties of the quasi-one-dimensional antiferromagnet $CsMnCl_3 \cdot 2H_2O$ are well known. The magnetic, optical, and high-frequency properties have been investigated. But there are also important gaps. In particular, still unknown, and not yet specially investigated by anyone, is the character of the spin-flop phase transition observed in this crystal when an external magnetic field is oriented along the axis of spontaneous magnetization. It is known[1,2] that, depending on the properties of the magnetic anisotropy, the flipping of the magnetic moments of the sublattices occurs either as a phase transition of first order or by two phase transitions of the second order, located close together. There is no information on just how the transition occurs in $CsMnCl_3 \cdot 2H_2O$ and in what magnetic-field interval, what the instability fields are for the original and for the flipped magnetic phases, whether an intermediate state occurs in the crystal (the possibility of one, in the case of a transition of the first order, follows from general considerations[3,4]). The goal of our work, which was based on a study of the effect of a magnetic field on the optical absorption spectrum of $CsMnCl_3 \cdot 2H_2O$, was to give answers to these questions.

## EXPERIMENTAL METHOD

The possibility of expediency of using a spectral method for solution of the problem posed are clear from the following considerations. First, it is well known[5] that flipping of the magnetic sublattices of antiferromagnets is accompanied by a change of the fine structure of their optical spectra. The frequency shifts then observed in the absorption bands can serve as an indicator of the presence of a phase transition and of the manner in which it occurs. No specification of the fine structure, even, is required; the observed changes in it are what is important. Second, it follows from what has been said that there is a simple and obvious spectroscopic indication of a spatially nonuniform state of the crystal, such as is the intermediate state with a periodic alternation of domains of the original and of the flipped magnetic phases. This is a doublet pseudosplitting of the spectral lines, caused by superposition of the spectra of the two simultaneously present phases. In the range of existence of the intermediate state, with increase of the magnetic field there should occur a smooth replacement of one spectrum by the other because of increase of the volume of the flipped phase at the expense of the original. We note that the first and so far the only such observation in an optical spectrum was made for $MnF_2$ (Ref. 6). It must be mentioned that a similar effect may also be produced by an appreciable nonuniformity of the solenoid field. Therefore for clear separation of the effects, it is necessary that the spread of the values of the magnetic field of the solenoid, caused by its inhomogeneity, be considerably smaller, within the volume of the specimen, than the field interval within which the intermediate state exists.

We used a superconducting solenoid, immersed, together with the specimen, in pumped-on $^4He$. The calculated inhomogeneity of the magnetic field within the specimen was not greater than 0.1%. The temperature of the specimen was determined to be $1.89 \pm 0.005$ K. The specimen was a rectangular prism (with dimensions $5.2 \times 7 \times 4.7$ mm along axes $a$, $b$, and $c$ respectively) cut from a single crystal of $CsMnCl_3 \cdot 2H_2O$, grown by the standard hydrothermal method.[7] The specimen was not of ideal optical quality; in its original state, it had a certain number of inhomogeneities in the form of chains of fine blisters. In the course of the experiments (apparently as a result of temperature effects), there appeared within its thickness small cracks, some of where were located in the cleavage plane $ab$, while the others had no definite form. On the whole, however, the specimen was very far from disintegration, and the relative orientation of its parts did not change. The specimen was mounted in the solenoid in such a way that the magnetic field could be inclined to the axis b in the plane $bc$ at a small angle, measurable with accuracy ~1′. And in conclusion we mention that the frequency variations in the $CsMnCl_3 \cdot 2H_2O$ spectrum during the spin-flop transition were 20 times smaller than those observed in $MnF_2$ (Ref. 6); this required application of a fine-grained photographic

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material and spectral apparatus of high resolution. We used a DFS-13 spectrograph with a 1200 line/mm grating and linear dispersion 2 Å/mm.

## RESULTS OF THE EXPERIMENT, AND DISCUSSION

**1.** The orthorhombic crystal $CsMnCl_3 \cdot 2H_2O$, at $T \leq T_N = 4.89$ K, is a biaxial antiferromagnet, completely ordered in all three dimensions, with the direction of the spontaneous magnetization along the axis b.[8] Its elementary cell in this state is the chemical one doubled along the direction b, with dimensions $a = 9.060$, $b = 7.285$, $c = 11.455$ Å, containing four formula units (Fig. 1a). Thus an elementary cell of anitferromagnetic $CsMnCl_3 \cdot 2H_2O$ contains eight magnetic $Mn^{2+}$ ions, equally distributed between the two sublattices. It has been established experimentally that in a sufficiently strong magnetic field $H \| b$, there occurs a flip of the magnetization direction to the intermediate axis c.[9,10] The hard direction of magnetization is the axis a. The ground states of such a system and the phase transitions in it in a magnetic field directed along the easy axis, and at an angle to it in the plane of the easy and hard magnetizations, have been investigated in detail in theoretical papers.[2,11-13] With the choice of coordinate system shown in Fig. 1a, the results of these papers can be used directly, as we shall do, passing to a presentation (with application to our case) of the appropriate basic theoretical ideas and to a derivation of approximate relations for determination of the quantities of interest to us.

**2.** In consideration of a state of uniform magnetization (the body is of ellipsoidal form), the energy density of a biaxial, two-sublattice antiferromagnet is described phenomenologically as follows:

$$E = \delta \mathbf{M}_1\mathbf{M}_2 + \beta(M_{1x}^2 + M_{2x}^2)/2 + \rho(M_{1y}^2 + M_{2y}^2)/2 + \beta' M_{1x}M_{2x} + \rho' M_{1y}M_{2y} - (\mathbf{M}_1 + \mathbf{M}_2)\mathbf{H}, \quad (1)$$

whence the meanings of the constants are clear: the exchange constant $\delta$ and the magnetic anisotropy constants $\beta, \beta', \rho, \rho'$; or in equivalent form

$$E = 2\delta M_0^2 m^2 + (\beta + \beta')M_0^2 m_x^2 + (\rho + \rho')M_0^2 m_y^2 + (\beta - \beta')M_0^2 l_x^2 + (\rho - \rho')M_0^2 l_y^2 - 2M_0 \mathbf{mH}, \quad (2)$$

where we changed to the standard notation of the ferro- and antiferromagnetism vectors

$$\mathbf{m} = \frac{\mathbf{M}_1 + \mathbf{M}_2}{2M_0} \qquad \mathbf{l} = \frac{\mathbf{M}_1 - \mathbf{M}_2}{2M_0}.$$

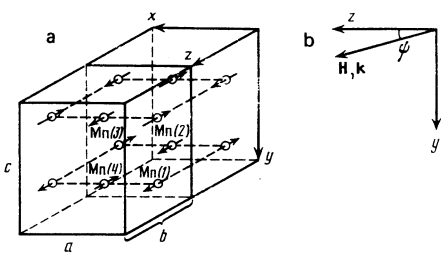


FIG. 1. a) Magnetic structure of antiferromagnetic $CsMnCl_3 \times 2H_2O$. b) Geometry of the experiment in a longitudinal magnetic field. The parallel directions of the external magnetic field H and of the light k are located in the easy plane magnetization.

Here $M_0$ is the magnetization of a sublattice in the ground state; it is supposed that $|\mathbf{M}_1| = |\mathbf{M}_2| = M_0$. The constants $\delta, \beta, \beta', \rho, \rho'$ are dimensionless; the exchange constant is

$$\delta = H_E/M_0 = 1/\chi_\perp, \quad (3)$$

where $H_E$ is the effective exchange field, and where $\chi$ is the magnetic susceptibility. The following relation holds:

$$\delta \gg \beta, \beta', \rho, \rho'. \quad (4)$$

The expressions (1) and (2) formally contain no terms due to the demagnetizing-factor tensor, for allowance for the latter, in the case of a body of ellipsoidal form, does not change the form of (1) and (2) and reduces merely to indeterminacy of the constants:

$$\delta = \delta_0 + 4\pi N_3, \quad \beta = \beta_0 + 4\pi(N_1 - N_3), \quad \beta' = \beta_0' + 4\pi(N_1 - N_3), \quad \rho = \rho_0 + 4\pi(N_2 - N_3), \quad \rho' = \rho_0' + 4\pi(N_2 - N_3), \quad (5)$$

which we shall take into account hereafter. In the expressions (5), $\delta_0, \beta_0, \beta_0', \rho_0, \rho_0'$ are the constants of an infinite crystal, and $N_1, N_2, N_3$ are the demagnetizing factors along axes $x, y, z$ respectively.

Since in $CsMnCl_3 \cdot 2H_2O$ the axis b($z$) is the easy axis, c($y$) is the intermediate, and a($x$) is the hard, the following relation holds:

$$\beta - \beta' > \rho - \rho' > 0. \quad (6)$$

The values of $\beta - \beta'$ and $\rho - \rho'$ can be estimated from literature data, but the values of $\beta, \beta'$, $\rho$, and $\rho'$ separately are unknown. But it is found that the sign and absolute value of the constant $\rho$ exert a decisive influence on the features of the spin-flop phase-transition process when the magnetic field is located in the plane $zy$ of easy magnetization of the crystal (Fig. 1b).

When $\rho > 0$ and the conditions (6) are satisfied, the initial magnetic phase $l_\parallel$ and flipped phase $l_\perp$ are stable, depending on the value of the magnetic field and its angle of inclination $\psi$. Figure 2 shows schematically the regions of stability of these phases with respect to directions of the antiferromagnetism vector 1 in the $zy$ plane, arranged symmetrically with respect to the direction corresponding to a rotation of 1 by angle $\pi/4$. The angle $\Delta\theta$, which characterizes the jump of orientation of the vector l on transition from one phase to the other, depends on the angle of inclination $\psi$ of the magnetic field (Fig. 1b) and varies from a maximum value

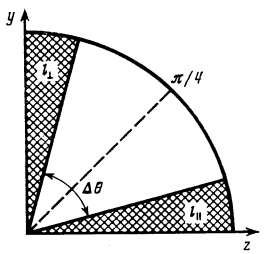


FIG. 2. Regions of stability of the phase $l_\parallel$ and $l_\perp$ with respect to directions of the vector 1 in the plane of easy magnetization, for $0 < \psi < \psi_c$.

$\pi/2$ for the exact orientation $\psi=0$ to zero for an angle of inclination equal to a certain critical angle $\psi_c$. The upper bound $H_1$ of stability of the phase $l_\parallel$ with respect to magnetic field and the lower bound $H_2$ of stability of the phase $l_\perp$, for the exact orientation $\psi=0$, are determined by the expressions

$$H_1=H(1+2\nu)^{1/2}, \quad H_2=H_{tr}(1-2\nu)^{1/2} \tag{7}$$

to the first order in $\nu$, where

$$\nu=\rho/(2\delta+\rho')\ll 1 \tag{8}$$

by virtue of the condition (4).

The quantity $H_{tr}$ that occurs in the expression (7) is the value of the magnetic field at which the energies of phases $l_\parallel$ and $l_\perp$ are equal, and at which there occurs an equilibrium phase transition $(l_\parallel)\rightleftarrows(l_\perp)$ accompanied by a jump of orientation of the vector l and constituting a phase transition of first order. To the principal order in $\nu$, the transition field $H_{tr}$ is independent of the angle $\psi\leqslant\psi_c$ and is determined by the expression

$$H_{tr}=M_0[(2\delta+\rho'-\rho)(\rho-\rho')]^{1/2}. \tag{9}$$

Thus in the $(H,\psi)$ phase diagram shown in Fig. 3, the line of equilibrium phase transition of first order is the straight line $H=H_{tr}$; it terminates at the critical point $K$, which corresponds to the critical angle $\psi_c$. The value of $\psi_c$ is determined by the relation

$$\sin 2\psi_c=2\nu(1-\nu)/[1-2\nu(1-\nu)]\approx 2\nu. \tag{10}$$

At the critical point the values of the instability fields $H_1$ and $H_2$ coincide, and, as was pointed out above, the jump of orientation of the vector l at the phase transition disappears. At angles $\psi\geqslant\psi_c$, the phase transition is via a continuous rotation of the antiferromagnetism vector. We now note that in the case considered, $\rho>0$, the quantity $\nu>0$, and $H_1>H_2$. This means that the regions of stability of phases $l_\parallel$ and $l_\perp$ overlap. Then the region of the phase diagram (Fig. 3) enclosed between the curves of the instability fields $H_1$ and $H_2$ is a region of metastable states. In each point of it not lying on the line $H=H_{tr}$, one of the phases is the ground state, the other a metastable state.

In the case $\rho<0$, the reverse relation $H_2>H_1$ holds. The regions of stability of the phase $l_\parallel$ and $l_\perp$ do not overlap and are separated by a gap $H_2-H_1$. In this case, the phase transition $(l_\parallel)\rightleftarrows(l_\perp)$ occurs by two phase transitions of second order at the boundaries of

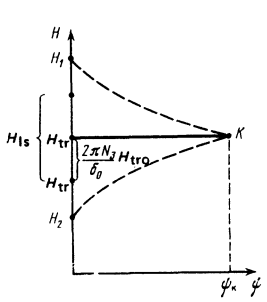


FIG. 3. Phase diagram of the transition of first order in an antiferromagnet in an inclined magnetic field, lying in the plane of flip of the magnetic sublattices.

the stability regions, $H_1$ and $H_2$, and by a smooth rotation of the vector l between them.

Thus the kind of phase transition $(l_\parallel)\rightleftarrows(l_\perp)$ is determined by the sign of the quantity $\rho$. We note now that all the parameters of the phase diagram of the transition of first order, which occurs in the case $\rho>0$, are actually determined by the value of $\rho$. In fact, starting from the definition (8) of $\nu$ and using the smallness of $\nu$ and the relation (4), we have with sufficient accuracy

$$\sin 2\psi_c\approx\rho/\delta, \quad H_1\approx H_{tr}(1+\rho/2\delta), \quad H_2\approx H_{tr}(1-\rho/2\delta), \quad H_1-H_2\approx H_{tr}\rho/\delta, \tag{11}$$

where the values of $H_{tr}$ and $\delta$ for $CsMnCl_3\cdot 2H_2O$ are known from experimental data.

Everything said above is correct in the case of a uniform distribution of magnetization. But it is found that in the case of a transition of the first order in a specimen of finite dimensions, it is necessary to introduce into consideration also a spatially nonuniform distribution.[3,4] The point is that near the spin-flop transition field, when the energies of the magnetic phases are equal, special importance is acquired by the energy term, omitted in (1) and (2), $2\pi(\mathbf{M}_1+\mathbf{M}_2)\hat{N}(\mathbf{M}_1+\mathbf{M}_2)$, which is due to the demagnetizing-factor tensor, because of its sensitivity to destruction of the spatial uniformity of the magnetization, i.e., to splitting of the specimen into domains. Choice of a definite form and orientation of the domains decreases the energy $2\pi(\mathbf{M}_1+\mathbf{M}_2)\hat{N}(\mathbf{M}_1+\mathbf{M}_2)$, but the phase interfaces that then appear give an opposite energy effect. As a result it is found that in a certain field range near $H_{tr}$, the thermodynamically most advantageous state is an intermediate state (IS), in which the specimen is split into domains of the coexisting phases $l_\parallel$ and $l_\perp$. The competition between the opposing factors mentioned above determines all the parameters of the IS as functions of the value of the external magnetic field.[3,4]

In the principal approximation, the region of existence of the IS is determined as follows[4]:

$$H_{tr0}\leqslant H\leqslant H_{tr0}+H_{IS}, \tag{12}$$

where $H_{IS}$ is the magnetic-field interval within which the IS exists, and where $H_{tr0}$ is a quantity determined by the expression (9) for $H_{tr}$, but with constants $\delta_0,\rho_0,\rho_0'$:

$$H_{tr0}=M_0[(2\delta_0+\rho_0'-\rho_0)(\rho_0-\rho_0')]^{1/2}, \tag{13}$$

whence it follows that $H_{tr0}$ has the meaning of transition field in a crystal of infinite dimensions. By using (5), one can easily show that

$$H_{tr}=H_{tr0}(1+2\pi N_3/\delta_0). \tag{14}$$

The interval $H_{IS}$ is determined by the value of the demagnetizing field:

$$H_{tr0}=4\pi N_3\chi_\perp H_{tr0}=4\pi N_3 H_{tr0}/\delta_0, \tag{15}$$

and, in particular, is equal to $4\pi\chi_\perp H_{tr0}$ for a thin plate oriented perpendicular to the field. Comparison of the expressions (12), (14), and (15) shows that the interval $H_{IS}$ is located symmetrically with respect to $H_{tr}$ on the phase diagram (Fig. 3). With increase of the angle $\psi$,

the interval $H_{IS}$, connected with the value of the jump of magnetization during the phase transition, decreases, and it vanishes at the critical value $\psi_c$ of the angle.

In the present work, the intermediate state is of interest to us only because observation of it is, first, a direct indicator of the fact that the spin-flop phase transition is of first order.[1)] Second, observation of the IS offers a possibility of experimentally determining the critical angle $\psi_c$ and thereby the value of $\rho$ and the values of the instability fields $H_1$ and $H_2$, in accordance with the expressions (11). In fact, we emphasize once more that the IS can exist only when a jump $\Delta\theta$ of the orientation of the antiferromagnetism vector (Fig. 2) occurs between phases $l_\parallel$ and $l_\perp$; the jump decreases with increase of the angle $\psi$ and vanishes at the critical point $K$, where $\psi=\psi_c$. As was mentioned in the section on method, the possibility of observation of the IS by a spectral method is based on the frequency shift of the spectra of phases $l_\parallel$ and $l_\perp$, which occurs because of the difference in their directions of the vector l. Hence it is clear that increase of the angle $\psi$, leading to a decrease of the jump of the orientation l, should lead to a gradual decrease of the amount of the pseudosplitting of the spectral lines in the region of existence of the IS and to a collapse of the observed doublet at an angle $\psi$ equal to the critical value.

3. We shall now present numerical values of certain parameters of expressions (1) and (2), which can be obtained for $CsMnCl_3\cdot 2H_2O$ from the available literature data. The magnetic moment at $T=0$ per $Mn^{2+}$ ion in antiferromagnetic $CsMnCl_3\cdot 2H_2O$ is 4.0 $\mu_B$.[14] Since an elementary magnetic cell of the crystal contains four $Mn^{2+}$ ions belonging to each sublattice and has volume $2abc$, where $a$, $b$, and $c$ are the dimensions of the chemical cell given above, the value of the sublattice magnetization is

$$M_0(T=0)=\frac{4\cdot 4\mu_B}{2abc}=98\text{ G}.$$

Using the graphical $M_0$ vs temperature relation given in Ref. 14, we find that at the temperature of our experiment, $M_0(T=1.89\text{ K})=96$ G. We calculate the exchange constant $\delta$ from the relation (3), using the results of measurements of the magnetic susceptibility.[15] Choosing for $\chi_\perp$ the value of the molar susceptibility at the temperature of the experiment, $\chi_a=0.043$ cm$^3$/mol, and using the molecular weight 330.2 g/mol and the density 2.84 g/cm$^3$ (Ref. 7) of $CsMnCl_3\cdot 2H_2O$, we get the dimensionless value $\chi_\perp(T=1.89\text{ K})=37\cdot 10^{-5}$ and the value $\delta(T=1.89\text{ K})=2.7\cdot 10^3$. For these values of $M_0$ and $\delta$, the effective exchange field is $H_E(T=1.89\text{ K})=260$ kOe. In a paper of Anders, Zvyagin, and Petutin,[16] devoted to a study of antiferromagnetic resonance in $CsMnCl_3\cdot 2H_2O$, an expression equivalent to (2) (after subtraction of the second and third terms) was used, and values were obtained for several parameters connecting the fields introduced there for anisotropy with exchange (at $T=1.46$ K). It can be shown that these relations can be written in the following form:

$$[(\rho-\rho')M_0H_E]^{1/2}=16.85\text{ kOe},\quad [(\beta-\beta')M_0H_E]^{1/2}=34.8\text{ kOe},$$

whence we find, using the values of $M_0$ and $H_E$ given above, the values $\rho-\rho'=11$ and $\beta-\beta'=48$.

4. Turning to the discussion of experimental results, we recall that we investigated the case in which the magnetic field is in the plane of easy magnetization of $CsMnCl_3\cdot 2H_2O$ (Fig. 1b). In the optical spectrum of the crystal, the transition chosen was ${}^6A_{1g}({}^6S)\rightarrow{}^4T_2({}^4D)$. It is distinguished by the most highly developed fine structure, of which the longest-wave detail is a very narrow exciton absorption line (26 736.7 cm$^{-1}$ in the absence of a field[17]); this permits use of the line as an indicator of frequency shifts caused by a change of orientation of the magnetization during the phase transition.

Figure 4 illustrates the changes observed in the region of this line with strict parallelism of the magnetic field to the easy axis of the crystal ($\psi=0$) and with gradual change of its value near the spin-flop transition field. The first and last spectra are the spectra of the practically pure phases $l_\parallel$ and $l_\perp$ (the arrows mark the positions of the spectral lines corresponding to these phases), while the intermediate ones give a clear picture of the simultaneous existence of the phases and of the gradual replacement of the spectrum of the original phase by the spectrum of the flipped phase, as should occur when, with increase of the field, there is an increase of the fraction of the material occupied by phase $l_\perp$ in the range of existence of the intermediate state.[4] But such an observation, as was pointed out in the section on method, still does not allow us to connect it unambiguously with the IS. Additional arguments are necessary. In order to make precise the field interval within which the changes described occur, we measured, by a photoelectric method, the variation of the absorption at the frequencies of the spectral lines corresponding to the phases $l_\parallel$ and $l_\perp$ with the value of the magnetic field (Fig. 5). It would be natural to determine the desired interval from the instants of appearance of the (absorption) line of

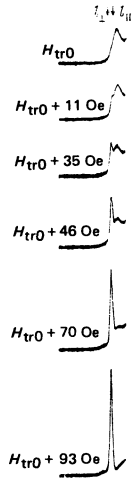


FIG. 4. Pseudosplitting of the exciton line 26736.7 cm$^{-1}$ of the transition ${}^6A_{1g}({}^6S)\rightarrow{}^4T_2({}^4D)$ in antiferromagnetic $CsMnCl_3\cdot 2H_2O$ during the spin-flop transition, caused by the superposition of the spectra of the coexisting phases $l_\parallel$ and $l_\perp$ in the range of existence of an intermediate state; $\psi=0$, $\mathbf{H}\|\mathbf{b}$.

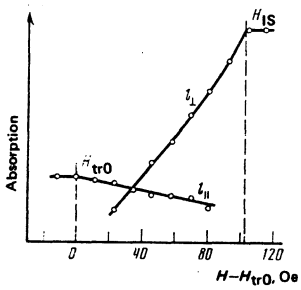


FIG. 5. Variations of the intensities of the absorption lines of phases $l_\parallel$ and $l_\perp$ (Fig. 4) in the range of existence of an intermediate state.

the new phase and of disappearance of that of the original. But in view of the very small observed frequency shift (only 2.5 $cm^{-1}$), measurements of the near-zero absorption of the nucleating or disappearing spectral line are severely disturbed by the influence of the line of the opposite phase. Therefore we determined the region of existence of the intermediate state from the instant of attainment of the maximum absorption at the frequencies of the spectral lines of the two magnetic phases. It is clear that with this measurement method, the influence of a disturbing phase is absent. Having determined this interval, we identify it in accordance with the definition (12). Then $H_{IS}=103$ Oe. As for the transition field $H_{tr0}$, we shall not give an exact value of it. We did not have the possibility of direct measurement of the absolute value of the field with the accuracy necessary for determination of $H_{tr0}$; for calibration of the solenoid, we used the variation of the spin-flop transition field with temperature available in the literature. For the temperature interval 1–4 K, two similar relations are known, determined from measurements of the magnetization[9]

$$H_{sp\,fl}=16.4+0.84\,T \qquad (16)$$

and of the magnetocaloric effect[18]

$$H_{sp\,fl}=16.10+1.02\,T\,, \qquad (17)$$

where $T$ is measured in K and $H_{sp\,fl}$ in kOe. It is easy to notice, however, that even in the range where they were determined, the values of the transition field given by them differ by tens of oersteds. Furthermore, it is not known to which instant of the phase transition observed by us these values should be related. It is reasonable to suppose that the values (16) and (17) of $H_{sp\,fl}$ should be related to the middle of the phase-transition interval, i.e., should be close to $H_{tr}$ (Fig. 3). If the experiments[9,18] were done on specimens of cylindrical form, long in comparison with the transverse dimensions, in which the IS practically does not occur, then $H_{sp\,fl}$ would be $\approx H_{tr0}$, and there would be complete determinacy. But in the experiments mentioned, this condition was not satisfied, and therefore the relations (16) and (17) should give values of $H_{sp\,fl}$ lying somewhere in the interval

$$0\leq H_{sp\,fl}-H_{tr0}\leq(2\pi N_3/\delta_0)_{max}H_{tr0}\,,$$

depending on the shape of the specimens used, concerning which nothing is known. The width of this interval is greatest in the case of a thin plate of appreciable transverse dimensions, oriented perpendicular to the field ($N_3=1$), and in the field range of interest to us (~18 000 Oe) it is 42 Oe. Thus the uncertainty in the position of the quantities (16)–(17) with respect to the field $H_{tr0}$, resulting from disregard in their derivation of the effect of the specimen shape, amounts to tens of oersteds, appreciably exceeding the formal limit of error given [10 Oe for the relation (17)]. We shall hereafter suppose that $H_{tr0}=18\,028$ Oe. This value follows from the relation (17) for experiment temperature $T=1.89$ K, and we shall use it only for estimates of various small field intervals, of interest to us, that are expressed in terms of the absolute value of $H_{tr0}$; its accuracy is quite sufficient for this purpose. In particular, the theoretical value of the field interval of existence of the IS in the case of a thin plate is $H_{IS}=4\pi\chi_\perp H_{tr0}$. Hence we get for $CsMnCl_3\cdot 2H_2O$, on substituting the values of $H_{tr0}$ and $\chi_\perp$ determined above, $H_{IS}^{theor}=84$ Oe. Comparing this value with the experimentally determined (Fig. 5) interval $H_{IS}$, we notice that the latter is broadened because of the inhomogeneity of the magnetic field of the solenoid, which has at the edges of the specimen the value 0.1%, or 18 Oe in the absolute expression in the region of the phase transition. Thus the experimental value is

$$H_{tr}^{expt}=103-18=85\text{ Oe}\,, \qquad (18)$$

which in general agrees excellently with the theoretical prediction, despite the fact that the value of $H_{IS}$ is greatest for a thin plate and that our specimen does not have that form. The experimental value is somewhat high, but this is probably explained by the nonuniformity of the demagnetizing field in a specimen of rectangular form and by a slight structural inhomogeneity of the specimen investigated, as was noted in the section on method. We emphasize that the correspondence of the experimentally determined interval $H_{IS}$ to the demagnetizing field is an important argument in favor of the correctness of our interpretation, which relates it to the intermediate state.

We obtain an additional argument in favor of the existence of an intermediate state in $CsMnCl_3\cdot 2H_2O$ if we turn to the experiments involving variation of the angle $\psi$. Figure 6 shows the spectra obtained by variation of the angle $\psi$ in a constant field in the region of existence of the IS; here is seen most clearly the doublet produced by the coexistence of phases $l_\parallel$ and $l_\perp$ (this field in Fig. 5 corresponds to the point of coincidence of the values of the absorption for the two magnetic phases). In full agreement with what was said at the end of Sec. 2, one clearly observes a gradual decrease of the doublet splitting, reflecting a decrease of the jump in orientation of the vector l with increase of the angle $\psi$. The point of disappearance of the doublet (~15′) determines the boundary of the angular range of existence of the IS, and it should coincide with the critical angle $\psi_c$. At angles $\psi\geq\psi_c$, the phase transition should occur by a continuous rotation of the antiferromagnetism vector; this is also corroborated experimentally by Fig. 7, which demonstrates, in the transition region, the absence of coexisting phases in the

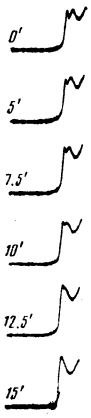


FIG. 6. Change of the value of the doublet pseudosplitting of the exciton line, at $H$ = const, in the range of existence of an intermediate state, reflecting the decrease of the jump of orientation of the antiferromagnetism vector with increase of the angle $\psi$.

crystal and a smooth transformation of a spectrum of the type $l_{\parallel}$ to a spectrum of type $l_{\perp}$ at angle $\psi = 15'$. Further evidence of this is provided by Fig. 8, which shows the frequency variations of the observed spectral lines for the case of exact orientation $\psi = 0$ and for angles 15′ and 60′. The discontinuous character of the frequency variation in the case of exact orientation and the smooth variation of the frequency of the exciton line at angles $\psi = 15'$ and 60′ (we again recall that the change of frequency is caused by change of orientation of the vector l) demonstrate indisputably that in the last two cases the phase transition actually occurs by continuous rotation of the vector l. Thus the experimentally established coincidence of the angular range of existence of the IS with the range of existence of a jump of orientation of the antiferromagnetism vector (fully corresponding to theoretical predictions), together with the arguments presented above regarding the range of field for detection of the IS, prove sufficiently convincingly, in our view, the actual existence of the IS in $CsMnCl_3 \cdot 2H_2O$.

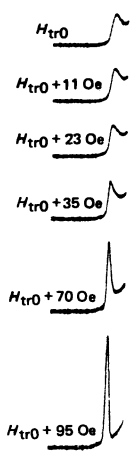


FIG. 7. Continuous transformation of the spectrum of phase $l_{\parallel}$ to the spectrum of phase $l_{\perp}$, corresponding to continuous rotation of the vector 1 in the transcritical range of the angle $\psi$ ($\psi$ = 15′).

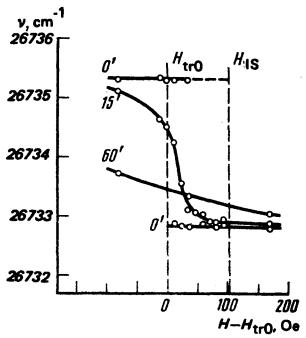


FIG. 8. Changes of frequency of the exciton line, observed in the region of the spin-flop transition with exact orientation of the magnetic field ($\psi$ = 0) and in the transcritical range of angles.

To determine the value of the critical angle $\psi_c$, the variation of the value of the doublet pseudosplitting with the angle $\psi$, observed in Fig. 6, is shown in Fig. 9 in graphical form, whence we have $\psi_c = 14'$. We note that Fig. 9 shows only half the angular dependence, which was determined in the angular interval containing the angle $\psi_c$ and on the other side of the axis b in the easy plane of the crystal. To avoid backlash in the rotation system of the specimen, the whole angular interval was traversed by rotation of the crystal in a single direction. The axis of mirror symmetry obtained in this variation determined the position of exact alignment, corresponding to the angle $\psi = 0$. Alignment simply according to the maximum of the amount of the splitting is inaccurate because of the slight dependence of $\Delta\nu$ on $\psi$ in the region of small angles of inclination.

Knowing the value of $\psi_c$ and using the relations (11) we can now easily obtain the value

$$\rho = \delta \sin 2\psi_c = 2.7 \cdot 10^3 \sin 28' = 22$$

(of course $\rho > 0$) and the width of the region of metastable states for exact orientation of the magnetic field along the easy axis of the crystal,

$$H_1 - H_2 = H_{tr}\rho/\delta = H_{tr} \sin 2\psi_c = 147 \text{ Oe}. \qquad (19)$$

In connection with the last estimate, we note that when we took the crystal through the phase transition in both directions, we were unable to detect any hysteresis. Consequently, all the states through which the crystal passed, including the IS, were in thermodynamic equilibrium.

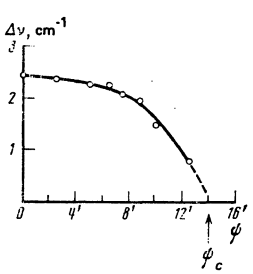


FIG. 9. Determination of the critical angle $\psi_c$ from the angular dependence of the value of the doublet pseudosplitting of the exciton line in the range of existence of an intermediate state.

One notices the fact that in $CsMnCl_3 \cdot 2H_2O$ the width of the region of existence of the intermediate state (18) is of the same order as the width of the region of metastable states (19). This hits one in the eye in a comparison with results of an investigation of $NiWO_4$,[19] also described by a thermodynamic potential of a biaxial antiferromagnet, where the ratio $H_{IS}/(H_1 - H_2)$ is an order of magnitude smaller than in $CsMnCl_3 \cdot 2H_2O$. It is easy to see, by using (11) and (15), that the ratio of interest to us is expressed as follows:

$$H_{tr0}/(H_1 - H_2) = 4\pi N_3/\rho, \qquad (20)$$

and for specimens of the same shape it is determined solely by the value of $\rho$ for the specific antiferromagnet. In fact, using the parameter values given in Ref. 19, $\chi_\perp = 0.25 \cdot 10^{-3}$ and $\psi_c = 1.2°$, we get for $NiWO_4$ the value

$$\rho = \delta \sin 2\psi_c = \chi_\perp^{-1} \sin 2\psi_c = 168,$$

which is about an order of magnitude larger than in $CsMnCl_3 \cdot 2H_2O$; this explains the corresponding decrease of the ratio (20).

In conclusion we note that, knowing the value $\rho = 22$ determined by us experimentally and the value $\rho - \rho' = 11$ found above according to the results of Ref. 16, we can estimate (digressing for simplicity from the temperature dependence of these quantities) also the constant $\rho' = 11$, which is smaller than $\rho$ by only a factor two; this indicates the appreciable nonadditivity of the contributions of the sublattices to the magnetic anisotropy energy of $CsMnCl_3 \cdot 2H_2O$. To complete the determination of all the parameters of the thermodynamic potential (1) it remains only to find the value of $\beta$; but this requires study of the behavior of the crystal under application of a magnetic field in the hard plane of magnetization.

Thus as a result of investigation of the optical absorption spectrum of antiferromagnetic $CsMnCl_3 \cdot 2H_2O$ in a magnetic field, the following principal results have been obtained: 1) it has been established that the spin-flop phase transition in a magnetic field oriented along the easy axis of the crystal is a transition of first order, occurring via an intermediate state; 2) a phase diagram has been reconstructed for this transition in an inclined magnetic field lying in the flip plane of the magnetic sublattices.

[1)] Strictly speaking, in a system with possible ground states $l_\parallel$, $l_\perp$ and IS the spin-flop phase transition occurs by two transitions of first order ($l_\parallel$) $\rightleftarrows$ IS, IS $\rightleftarrows$ ($l_\perp$) and, located between them, the IS.[4]


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