Photoinduced single-ion magnetic anisotropy in antiferromagnetic MnF_2

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(Submitted 1 December 1982)
Zh. Eksp. Teor. Fiz. **84**, 2251–2260 (June 1983)

It is shown experimentally that the absorption spectrum of MnF_2 in magnetic fields exceeding the critical field for spin flop manifests the individuality of the excited states: The splitting of the lines of the transition $^6A_{1g} \rightarrow {}^4T_{1g}(^4G)$ (18419 cm^{-1} and 18436 cm^{-1}) vanishes, but the splitting of the line of the transition $^6A_{1g} \rightarrow {}^4T_{1g}(^4P)$ (31938 cm^{-1}) persists, provided in the latter case that the field **H** is inclined along the [110] direction in the basal plane. The presence of splitting for $H > H_c$ can be described by a Hamiltonian of the photoexcited ion that contains terms corresponding to the magnetic anisotropy in the basal plane and are absent from the spin Hamiltonian for an ion in the ground state. The excited single-ion states are treated as impurity states. Since the two magnetic ions in the opposing sublattices are nonequivalent not only with respect to the orientation of the spins but also with respect to the orientation of the local crystalline field, there arises a hitherto unobserved splitting of the magnetic-dipole absorption lines, i.e., a new type of lifting of the intersublattice degeneracy. The orientation of the spins of the photoexcited ions of the state $^4T_{1g}(^4P)$ is different here from the spin orientation in the ground state. The change in the spin orientation of the ions upon photoexcitation reaches tens of degrees.

PACS numbers: 75.30.Gw, 75.50.Ee, 75.10.Dg, 78.20.Ls

The photoexcitation of magnetic ions leads to changes in their orbital and spin states. If the concentration of magnetic ions in a crystal is considerable, the interaction between them can lead to phase transitions: long-range magnetic order arises[1] or a reorientation of the magnetic sublattices occurs.[2] In crystals containing impurity ions, the polarization of the light also causes macroscopic effects such as photoinduced linear dichroism.[3,4] At a low concentration of photoexcited ions, as is the case in the usual spectral studies, these ions must be considered a noninteracting impurity. It has hitherto been assumed for antiferromagnets (in basic agreement with the available experimental data) that the orientations of the magnetic moments of the photoexcited and unexcited ions coincide. In high-dimensional antiferromagnets with a strong exchange interaction within the sublattice this assumption is completely justified. In the general case, however, the orientations may also be noncoincident even in the absence of an interaction between the photoexcited ions just by virtue of the change in the symmetry of the ion states, and also because of the exchange interaction and magnetic anisotropy. For uniaxial two-sublattice antiferromagnets with magnetic anisotropy of the "easy axis" type, even these reasons can turn out to be insufficient: If the excited state of the magnetic ion has the same type of anisotropy, the spin of this ion is also oriented along the easy axis of the crystal. Only when external influences break the uniaxiality or there is a transformation of the magnetic configuration of the crystal do the differences in the exchange-interaction and anisotropy parameters of the ground and excited states lead to a noncollinearity of the magnetic moments of these states. An external influence of this kind could be a magnetic field, either inclined to the easy axis or in excess of the critical field for a phase transition.

In this paper we show for the case of antiferromagnetic MnF_2 that one in fact does observe a significant change in the orientation of the magnetic moments of the ions in the photoexcited state relative to the those of the ions in the ground state, and that this change in orientation is caused by photoinduced uniaxial magnetic anisotropy in the basal plane.

Manganese fluoride is a two-sublattice antiferromagnet with a magnetic ordering temperature $T_N = 68$ K. It is a crystal of the tetragonal system D_{4h}^{14} and has a magnetic anisotropy of the easy-axis type–the spins of the Mn^{2+} ions are spontaneously oriented in the antiferromagnetic state along the fourfold axis C_4. The effective exchange-interaction field is $H_E = 52.2$ T (Ref. 5). In an external magnetic field $\mathbf{H} \| C_4$, a spin flop occurs when the field reaches $H = H_c = 9.5$ T–the antiferromagnetism vector **l** discontinuously changes its orientation from $\mathbf{l} \| C_4$ to $\mathbf{l} \perp C_4$. The spin flop occurs as a first-order phase transition for the case of a strict orientation $\mathbf{H} \| C^4$ or if the angle ψ by which the orientation of **H** deviates from the tetragonal axis C_4 is not over 30′ (Ref. 6). The energy of anisotropy in the basal plane is small, and, at least for the second-order phase transitions ($\psi > 30'$) one has[5,6] $\mathbf{l}^{\perp} \| \mathbf{H}$, where $\mathbf{l}^{\perp}$ and $\mathbf{H}^{\perp}$ are the projections of the vectors **l** and **H** on the basal plane.

A characteristic of manganese compounds (MnF_2 in particular) is the high symmetry of the ground state of the magnetic ion. This stems from the fact that the completely symmetric ground state of the Mn^{2+} ion $^6A_{1g}(^6S)$—is energetically isolated from the rest: the frequency of the lowest intermultiplet transition $^6A_{1g} \rightarrow {}^4T_{1g}(^4G)$ is of the order of 18000 cm^{-1}. Since the magnetic anisotropy of the ion in the ground state $^6A_{1g}(^6S)$ is determined by the degree to which the excited states are mixed in (i.e., in the second order of perturbation theory), the anisotropy is very small in all compounds of the ion Mn^{2+} without exception, regardless of their crystal structure, and is governed not by the single-ion contribution but by the dipole–dipole interaction. In parti-

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cular, in tetragonal MnF_2, in which the crystalline field of the ligands has a low local symmetry (D_{2h}), the effective field of the uniaxial magnetic anisotropy is $H_a \simeq 0.8$ T (Ref. 5), while the anisotropy in the basal plane is not over 0.1 T (Ref. 6). In the individual photoexcited states, having a lower symmetry than the ground state, the Mn^{2+} ion becomes significantly more sentitive to the crystallographic structure. One expects that for such a photoexcited ion the energy of unixial anisotropy will become appreciable. In this case the role of certain terms in its Hamiltonian can grow markedly, especially in magnetic fields, which bring on the phase transition into an antiferromagnet. In the situation just described, the orientation of the magnetic moments of the photoexcited ions cannot be analogous to the orientation of the ions in the ground state. This is also suggested by the unusual behavior (that was observed in Ref. 7 but not understood at the time) of the splitting of the exciton line in the absorption spectrum of antiferromagnetic MnF_2 in fields exceeding the critical field H_c.

EXPERIMENTAL PROCEDURES

The study of the optical absorption spectrum was done on artificial MnF_2 single crystals grown by S. V. Petrov at the Institute of Physics Problems, Academy of Sciences of the USSR, to whom the author express their sincere gratitude. The samples were cylinders with a diameter of 5 mm and thicknesses from 3 to 6 mm, oriented along the crystallographic axes [001] and [100]. Pulsed magnetic fields ranging up to 25 T were produced in small solenoids cooled by liquid hydrogen and helium. The samples were oriented with respect to the direction of the magnetic field to within ± 1°. The measurements were made at temperatures of 4.2, 14, and 20.4 K. The absorption spectrum was recorded with a DFS-8 spectrograph having a linear dispersion 3 Å/mm.

EXPERIMENTAL RESULTS

In the absorption spectrum of antiferromagnetic MnF_2, we studied the behavior in a magnetic field of the magnetic-dipole lines of the transitions ${}^6A_{1g} \to {}^4T_{1g}({}^4P)$ ($\nu_e = 31938$ cm^{-1}) and ${}^6A_{1g} \to {}^4T_{1g}$ (${}^4G$) ($\nu_e' = 18419$ cm^{-1} and ν_e^* $= 18436$ cm^{-1}), which were identified earlier[7,8] as purely excitonic. The studies were done in magnetic fields inclined to the tetragonal axis C_4 at angles $\psi = 3°$ and 9°. In fields with strengths less than the critical field H_c for the flopping of the magnetic sublattices, we observed the usual doublet line splitting, linear in H (Fig. 1). In fields $H > H_c$ the splitting of the line ν_e of the transition ${}^6A_{1g}$ (${}^6S$) $\to$ ${}^4T_{1g}$ (${}^4P$) turns out to depend on the orientation of the component $\mathbf{H}^\perp$ of the magnetic field in the basal plane: In the case $\mathbf{H}^\perp \| [100]$ the splitting vanishes (Fig. 1b), with a transition region of nearly the same width as than of the phase transition for the given angle ψ. However, this transition region broadens as $\mathbf{H}^\perp$ begins to deviate from the [100] direction. At an angle $\phi \simeq 30°$ between $\mathbf{H}^\perp$ and [100] it has already reached approximately $1.5H_c$, and the field dependence $\nu(H)$ observed in this case is analogous to that given in Ref. 7. For the orientation $\mathbf{H}^\perp \| [110]$ the line remains split all the way to $H = 25$ T. The angle ψ has practically no influence on the magnitude of the line splitting. The character of the periodic dependence of the splitting of the line ν_e on the orientation of $\mathbf{H}^\perp$ for fields exceeding H_c is illustrated in Fig. 2.

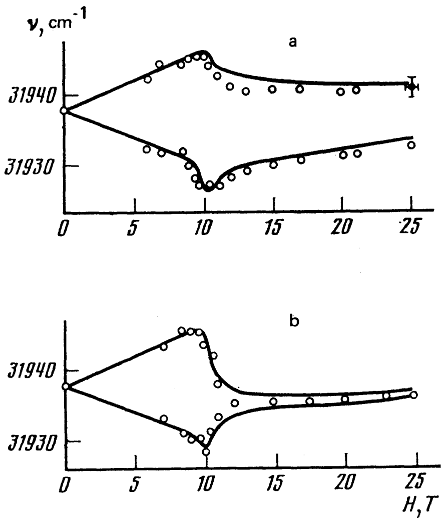

FIG. 1. Dependence of the splitting of the purely excitonic absorption line $\nu_e = 31938$ cm^{-1} on the strengh and orientation of the external magnetic field. The angle between the direction of the field $\mathbf{H}$ and C_4 axis is $\psi = 3°$, $T = 14$ K: a) $\mathbf{H}^\perp \| [110]$, b) $\mathbf{H}^\perp \| [100]$ ($\mathbf{H}^\perp$ is the component of the vector $\mathbf{H}$ in the basal plane). The solid curves are the calculated results.

For the exciton lines ν_e' and ν_e'' of the transition ${}^6A_{1g}$ $\to {}^4T_{1g}$ (${}^4G$) the splitting depends on the magnetic field strength in the same way for all orientations of $\mathbf{H}^\perp$: at $H > H_c$ there is no splitting for either the case $\mathbf{H}^\perp \| [100]$ of for $\mathbf{H}^\perp$ $\| [110]$.

Changing the temperature in the interval 4.2–20 K did not have a significant effect on the dependence of the band frequencies on the magnetic field strength.

DISCUSSION RESULTS

$H < H_c$. The doublet splitting of the exciton bands, linear in the magnetic field strength H, that is seen in this region (Fig. 1), is usual for uniaxial two-sublattice antiferromagnets in the case when the external field $\mathbf{H}$ is directed along the

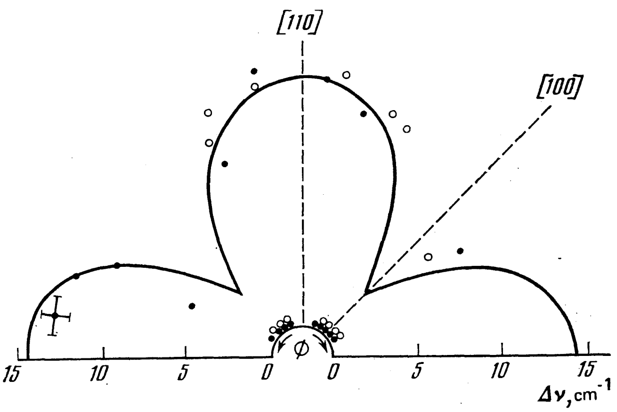

FIG. 2. Anisotropy of the splitting $\Delta\nu$ of the line $\nu_e = 31938$ cm^{-1}: ϕ is the angle between $\mathbf{H}^\perp$ and the twofold axis [100], $H = 12$ T, $T = 14$ K; ●) $\psi = 3°$,○) $\psi = 9°$. The solid curve is the calculated result.

antiferromagnetism vector $\mathbf{l} = (\mathbf{M}_1 - \mathbf{M}_2)/2M_0$, where $\mathbf{M}_1$ and $\mathbf{M}_2$ are the magnetizations of sublattices 1 and 2, and $M_0 = |\mathbf{M}_1| = |\mathbf{M}_2|$. For the absorption lines of MnF_2 this splitting is described in Refs. 7 and 8. The splitting of the exciton lines for $H < H_c$ is a consequence of the lifting of the intersublattice degeneracy on account of the change in the transition energy by an amount $\pm \mu_B H(g^0 S^0 - g^f S^f)$, where μ_B is the Bohr magneton, $S^0 = 5/2$ and $S^f = 3/2$ are the spins of the ground and excited states, g^0 and g^f are the g factors of the ground and excited states; $g^0 = 2$, and the g factor of the excited state is also close to 2; the plus and minus signs correspond to ions of the opposing sublattices with spins oriented along the field and against the field.

$H > H_c$. The periodicity in the magnitude of the splitting of the exciton line ν_e (Fig. 2) indicates that the anisotropy in the basal plane plays a governing role in this effect. This periodicity corresponds to the tetragonal structure of the crystal. The absence of such a behavior for the lines ν_e' and ν_e'' is a clear indication that the effect is due to the properties of the magnetic ion not in the ground state, but in an excited state, for which the anisotropy in the basal plane, as we mentioned earlier, can be significant. Since the energy of anisotropy in the basal plane of the ground state is small, an inclination of $\mathbf{H}$ with respect to the C_4 axis in excess of 30′ is sufficient to orient the vector $\mathbf{l}^{\perp}$ parallel to $\mathbf{H}^{\perp}$. It follows that the role of the inclination of the field $\mathbf{H}$ in the anisotropy of the splitting of the line ν_e reduces to the assigning of the direction of the component $\mathbf{l}^{\perp}$ of the antiferromagnetism vector in the basal plane after the flopping of the magnetic moments of the sublattices. Additional evidence of this is the fact that increasing the angle of inclination ψ of the field $\mathbf{H}$ from 3° to 9° has no appreciable influence on the observed splitting.

To describe quantitatively the splitting of the line ν_e, let us treat the photoexcited ion as a substitutional impurity. The orientation of its spin is determined both by intraionic interactions and by the fields produced by the surrounding ions. Here we shall not take into account the disorienting reaction of the photoexcited ion to the nearest unexcited ions. This approximation is justified in high-dimensional antiferromagnets, since the environment of these nearest neighbors consists of z-1 unexcited ions and only one excited ion (z is the number of neighbors in the first coordination sphere; as a rule, for high-dimensional antiferromagnets this number is of the order of 6-8). The use of this approximation reduces the problem to that of the behavior of a magnetic ion in the molecular field produced by its nearest neighbors.

We write the Hamiltonian of a photoexcited ion in the form

$$\mathscr{H}_\alpha = J^f \sum_{i=1}^{z} (\mathbf{S}^0_{\alpha' i} \mathbf{S}_\alpha{}^f) + J^{f\zeta} \sum_{i=1}^{z} S^{0\zeta}_{\alpha' i} S_\alpha{}^{f\zeta} + B(S_\alpha{}^\zeta)^2$$
$$+(-1)^{\alpha+1}\{E[(S_\alpha{}^{f\xi})^2 - (S_\alpha{}^{f\eta})^2] + 2DS_\alpha{}^{f\xi} S_\alpha{}^{f\eta}\} - \mu_B g^f \mathbf{H} \mathbf{S}_\alpha{}^f. \quad (1)$$

In this expression α and α' number the sublattices ($\alpha, \alpha' = 1,2$; $\alpha \neq \alpha'$, $\mathbf{S}_\alpha^f$ is the spin of the photoexcited ion, $\mathbf{S}_{\alpha' i}{}^0$ is the spin of its nearest unexcited neighbor i of the opposing sublattice (the number z of such neighbors in the case of the rutile crystal structure is eight), ξ, η, and ζ are three mutually perpendicular axes, with ξ corresponding to the crystallographic axis C_4 (the [001] direction) and ξ taken along the [100] direction in the basal plane of the crystal. The first two terms in the summation in (1) correspond to the exchange interaction between the excited ion and the unexcited ions (the isotropic and anisotropic exchange, respectively). The third term describes the single-ion uniaxial anisotropy, and the terms in the curly brackets correspond to the magnetic anisotropy in the basal plane. The plus and minus signs in front of these last terms reflect the fact that the structure of the ligands of the MnF_2 complex which belong to Mn^{2+} ions of opposing sublattices are rotated by 90° with respect to each other; for the sake of argument we let $\alpha = 1$ refer to the magnetic ions with positive spin projections on the direction of the field $\mathbf{H}$, and $\alpha = 2$ to ions with negative spin projections. The last term in the summation in (1) describes the interaction of the photoexcited ion with the external magnetic field $\mathbf{H}$. Antiferromagnetic ordering of the excited ion with respect to its nearest neighbors in the subcritical region ($H < H_c$) corresponds to a positive sign of the sum $J^f + J^{f\zeta}$.

For the calculations which follow it is convenient to transform (1) from Cartesian to spherical coordinates:

$$\mathscr{H}_\alpha = \sin^2\vartheta_\alpha[-b + (-1)^{\alpha+1} r\cos(2\varphi_\alpha - \tau)]$$
$$+ a_\alpha \cos\vartheta_\alpha + p_\alpha \sin\vartheta_\alpha \cos(\phi - \varphi_\alpha), \quad (2)$$

where

$$a_\alpha = (A^f + A^{f\zeta}) z\cos\theta_{\alpha'} - h\cos\psi; \quad p_\alpha = A^f z \sin\theta_{\alpha'} - h\sin\psi,$$
$$r = (e^2 + d^2)^{1/2}, \quad b = B(S^f)^2, \quad d = D(S^f)^2, \quad e = E(S^f)^2,$$
$$A^f = J^f S^0 S^f, \quad A^{f\zeta} = J^{f\zeta} S^0 S^f, \quad h = \mu_B g^f H S^f,$$
$$\tau = \operatorname{arctg}(d/e), \quad S^0 = |S^0|, \quad S^f = |\mathbf{S}^f|, \quad (3)$$

ψ is the angle of deviation of the field $\mathbf{H}$ from the C_4 axis, θ_α and ϑ_α are the angles between the C_4 axis and the spins of the unexcited and excited states, respectively, ϕ and φ_α are the angles between the C_2 axis (the [100] direction) and the spin components in the basal plane of the ground and photoexcited states, respectively. The angle τ is determined by the relationship between the two anisotropy fields in the basal plane: the rhombic anisotropy, of the type $(S^\xi)^2 - (S^\eta)^2$, and the Dzyaloshinskiĭ-Moriya anisotropy, of the type $S^\xi S^\eta$.

To find the angles ϑ_1, ϑ_2, φ_1, and φ_2 one must solve the system of equations

$$\frac{\partial \mathscr{H}_\alpha}{\partial \vartheta_\alpha} = 2\sin\vartheta_\alpha\cos\vartheta_\alpha[-b + (-1)^{\alpha+1} r\cos(2\varphi_\alpha - \tau)]$$
$$- a_\alpha \sin\vartheta_\alpha + p_\alpha \cos\vartheta_\alpha \cos(\phi - \varphi_\alpha) = 0, \quad (4)$$

$$\frac{\partial \mathscr{H}_\alpha}{\partial \varphi_\alpha} = 2(-1)^\alpha r\sin^2\vartheta_\alpha \sin(2\varphi_\alpha - \tau) + p_\alpha \sin\vartheta_\alpha \sin(\phi - \varphi_\alpha) = 0. \quad (5)$$

The angles θ_1 and θ_2 appearing in the expressions for a_α and p_α are found from the formulas of Golovenchits and Sanina[1] which give the angles between the spins of the ground state of the ions and the C_4 axis as functions of the angle of inclination ψ and strength H of the magnetic field.

To simplify the analysis of equations (4) and (5) we set the angle of inclination ψ of the field $\mathbf{H}$ to the C_4 axis equal to zero. For comparison with the experimental curves of the components of the splitting of the line ν_e versus the field strength H, the system of equations (4) and (5) was solved numerically for specific values of the angle ψ. Allowance for $\psi \neq 0$ does not affect the basic results of the analysis. We recall that the role of this deviation reduces to the assigning of an orientation of the component of the antiferromagnetism vector $\mathbf{l}^{\perp}$. Equation (5) has two solutions.

1. $\vartheta_\alpha = \pi n$, with $n =$ integer. This solution is realized for $p_\alpha = 0$ or $\theta_\alpha = \pi n$ i.e., for fields in the subcritical region. Recognizing that $\cos\vartheta_\alpha \cos\theta_{\alpha'} = -1$ for antiferromagnetic ordering of the photoexcited ion with respect to its nearest neighbors on the opposing sublattice, we have

$$\mathscr{H}_\alpha = -(A^f + A^{f\zeta})z + (-1)^\alpha h. \qquad (7)$$

Because the ground-state energy for fields in the subcritical region $H < H_c$ changes by an amount $\mu_B g^0 H S^0$, the energy of transition of an ion to the photoexcited state can be represented with the aid of (3) and (7) in the form

$$\mathscr{E}_\alpha = -(J^f + J^{f\zeta}) S^0 S^f z + (-1)^{\alpha+1} \mu_B H (g^0 S^0 - g^f S^f). \qquad (8)$$

2. $2(-1)^\alpha r \sin\vartheta_\alpha \sin(2\varphi_\alpha - \tau) + p_\alpha \sin(\phi - \varphi_\alpha) = 0. \qquad (9)$

Solution (9) obtains for $H < H_c$. To determine the angles ϑ_α and φ_α in this field region one must solve the system of equations (4) and (9).

It follows from Eq. (9) that for $\phi \neq \pi n/2 + \tau/2$ with $n =$ integer one has $\varphi_\alpha \neq \phi$, i.e., the spin components $\mathbf{S}^{f\perp}$ of the photoexcited states are noncollinear with the spin components of the unexcited states. Of particular interest is the case $\phi = \pi/4 + \tau/2$. Substituting $\varphi_1 = \pi/4 - \gamma_1 + \tau/2$ and $\varphi_2 = \pi/4 + \gamma_2 + \tau/2$ into (4) and (9), where γ_α are the angles between $\mathbf{S}_\alpha^{0\perp}$ and $\mathbf{S}_\alpha^{f\perp}$, we obtain the system of equations

$$2\sin\vartheta_\alpha \cos\vartheta_\alpha(-b - r\sin 2\gamma_\alpha) - a_\alpha \sin\vartheta_\alpha + p_\alpha \cos\vartheta_\alpha \cos\gamma_\alpha = 0, \qquad (10)$$

$$-2r\sin\vartheta_\alpha \cos 2\gamma_\alpha + p_\alpha \sin\gamma_\alpha = 0. \qquad (11)$$

Recognizing that in a field $H > H_c$ one has $\theta_1 = -\theta_2$, i.e., $p_1 = -p_2$, $a_1 = a_2$ we obtain $\vartheta_1 = -\vartheta_2$, $\gamma_1 = \gamma_2$ and

$$\mathscr{E}_\alpha = \sin^2\vartheta_\alpha(-b - r\sin 2\gamma_\alpha) + a_\alpha \cos\vartheta_\alpha + p_\alpha \sin\vartheta_\alpha \cos\gamma_\alpha. \qquad (12)$$

It follows that for $\phi = \pi n/2 + \pi/4 + \tau/2$ the energies of the components are equal—there is no splitting. In this case the moments of the excited states of different sublattices have equivalent orientations with respect to the C_4 axis (Fig. 3a). The component $\mathbf{S}_\alpha^{f\perp}$ of these moments in the basal plane are noncollinear and are rotated with respect to the direction of the antiferromagnetism vector $\mathbf{l}$ by angles γ of equal magnitude and opposite sign (Fig. 3b). One has in order of magnitude

$$\gamma \approx 2r/A^f z = 2S^f(E^2 + D^2)^{1/2}/J^f M z.$$

In the case $\phi = \pi n/2 + \tau/2$, two types of solutions are possible:

$$\varphi_\alpha = \phi = \pi n/2 + \tau/2, \qquad (13)$$

which corresponds to Fig. 3d, and

$$\varphi_\alpha = \frac{\pi n}{2} + \frac{\tau}{2} + \arccos\frac{A^f z \sin\theta_{\alpha'}}{4(-1)^\alpha \sin\vartheta_\alpha}, \qquad (14)$$

which corresponds to Fig. 3e.

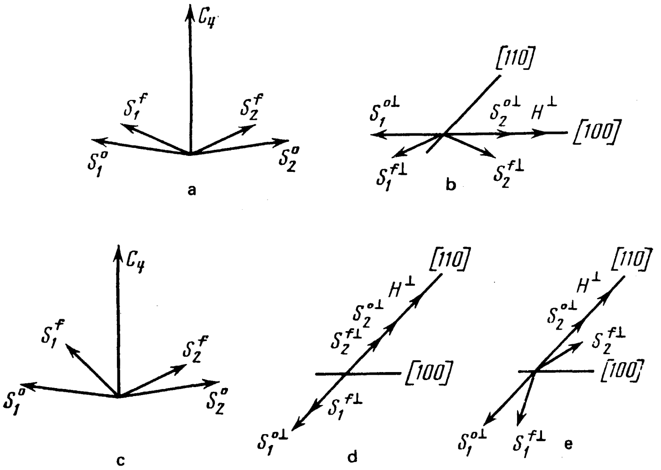

FIG. 3. Diagram of the orientation of the magnetic moments of Mn^{2+} ions in the ground and excited ${}^4T_{1g}$ (${}^4G$) states for $H > H_c$ and for the following parameters of the uniaxial anisotropy in the basal plane: $E = 0, D \neq 0$; *a,b*) $\mathbf{H}^\perp \parallel [100]$; c,d,e) $\mathbf{H}^\perp \parallel [110]$.

Depending on the relationship between the parameters, either solution (13) or solution (14) can be realized. Solution (13) corresponds to the minimum energy if

$$\left| \frac{A^f z \sin\theta_{\alpha'}}{4r\sin\theta_\alpha} \right| > 1; \qquad (15)$$

in the opposite case solution (14) obtains.

Assuming for purposes of estimation that $|\theta_{\alpha'}| \approx |\vartheta_\alpha|$, we find that for $A^f z \geqslant 4r$ the angles φ_α and ϕ are equal. For $A^f z < 4r$ the components of the moments of the photoexcited ions are rotated with respect to those of the unexcited ions by an angle $\gamma \simeq \arccos(A^f z/4(-1)^\alpha)$.

Let us suppose that condition (15) is satisfied and consider the case $\phi = \varphi_\alpha = \tau/2$. In this case Eq. (4) gives

$$2\sin\vartheta_\alpha \cos\vartheta_\alpha[-b + (-1)^{\alpha+1} r] - a_\alpha \sin\vartheta_\alpha + p_\alpha \cos\vartheta_\alpha = 0, \qquad (16)$$

from which one can determine ϑ_α. The energy of the components is given by the expression

$$\mathscr{E}_\alpha = \sin^2\vartheta_\alpha[-b + (-1)^{\alpha+1} r] + a_\alpha \cos\vartheta_\alpha + p_\alpha \sin\vartheta_\alpha. \qquad (17)$$

The maximum contribution to the splitting of the components is given by the term

$$\Delta = r(\sin^2\vartheta_1 + \sin^2\vartheta_2). \qquad (18)$$

The case $\phi = \pi n/2 + \tau/2$, in which maximum splitting of the components of the exciton line takes place, corresponds to a collinear orientation of the spin components $\mathbf{S}_\alpha^{f\perp}$ of the excited states on opposing sublattices (Fig. 3d). At the same time, the moments $\mathbf{S}_1^f$ and $\mathbf{S}_2^f$ have substantially nonequivalent orientations (Fig. 3c).

Thus, the difference in the orientation of the spins of the excited and unexcited ions with respect to the C_4 axis upon flopping of the magnetic sublattices of MnF_2 is primarily due to the difference in the size of the exchange interaction energy in these states. The nonequivalence of the orientations of the spins of just the photoexcited ions on opposing sublattices with respect to C_4, on the other hand, and also the noncollinearity of their components $\mathbf{S}_\alpha^{f\perp}$ with those of the unexcited ions $\mathbf{S}_\alpha^{01}$, are governed by the ratio of the anisotropy in the basal plane in the excited state to the exchange interaction in the same state.

To study the details of the behavior and the orientations of the magnetic moments of the photoexcited Mn^{2+} ions in magnetic fields, we solved Eqs. (4) and (5) numerically. The results of a computer calculation with the actual value of the angle of inclination of the field $\psi = 3°$ are in complete agreement with the results of the qualitative analysis given above. The ratio of the parameters E and D was found in the experiment from the value of the angle $\tau = \arctan(D/E)$ between the [100] axis and the direction of $\mathbf{H}^\perp$ for which we observed the maximum splitting of the line ν_e. The maximum splitting was observed when $\mathbf{H}^\perp \| [110]$, and, consequently, $\tau = 90° \pm 10°$ and $E \simeq 0$. The best agreement with experiment was found for the following values of the parameters: $J^f = 1\ \mathrm{cm}^{-1}$, $D = 3.33\ \mathrm{cm}^{-1}$, $J^{f\xi} = b = 0$. The calculated curves shown in Figs. 1, 2, 4, and 4 were obtained with these parameters. It follows from these calculations that the size of the splitting of the exciton line ν_e in the case of the orientation $\mathbf{H}^\perp \| [110]$ $(H > H_c)$ should fall off monotonically with increasing magnetic field strength. The agreement with experiment, as can be seen in Figs. 1 and 4 (inset) is good. By virtue of a certain nonequivalence of the orientations of the spins of the ions on opposing sublattices with respect to the direction of the field $\mathbf{H}$ (at angles $\psi \neq 0$), a slight Zeeman splitting of the line ν_e in fields $H > H_c$ should be present even in the case $\mathbf{H}^\perp \| [100]$ (Fig. 1b). However, owing to the relatively large ($\sim 4.5\ \mathrm{cm}^{-1}$) half-width of the components of the exciton line, we were unable to determine unequivocally whether such a splitting is present, and only the position of the centroid of the absorption line is plotted in Fig. 1b.

For fields $H \geqslant 1.5 H_c$, where the changes in the orientation of the vector $\mathbf{l}$ due to the magnetic phase transition are practically complete, the spins of the unexcited ions of opposing sublattices $\mathbf{S}_1^0$ and $\mathbf{S}_2^0$ have a practically equivalent orientation with respect to the direction of $\mathbf{H}$ (Fig. 4, solid curves). The orientation of the magnetic moments of the photoexcited ions, on the other hand, differs very substantially from the orientation of the moments in the ground state. The angle between the spins of the photoexcited ions of opposing sublattices $\mathbf{S}_1^f$ and $\mathbf{S}_2^f$ differs from the angle between $\mathbf{S}_1^0$ and $\mathbf{S}_2^0$ by almost a factor of two in a field $H = 20$ T both in the case $\mathbf{H}^\perp \| [100]$ and in the case $\mathbf{H}^\perp \| [110]$ (Fig. 4). For the case $\mathbf{H}^\perp \| [110]$, in which the situation illustrated in Figs. 3c, d is realized, the nonequivalence of the orientations of $\mathbf{S}_1^f$ and $\mathbf{S}_2^f$ relative to the direction of the external magnetic field $\mathbf{H}$ reaches 30–15° for fields of 12–20 T (Fig. 4, dashed curves). In the case $\mathbf{H}^\perp \| [100]$, on the other hand, in which the situation illustrated in Figs. 3a, b is realized, there is nonequivalence of the orientation of the spin components $\mathbf{S}_\alpha^{f1}$ and $\mathbf{S}_\alpha^{01}$ of the excited and unexcited ions, respectively (the angle between them is $\gamma = 20°$ in a field $H = 12\ T$). The maximum value of the angle γ is reached when $\mathbf{H}^\perp$ is rotated with respect to the [100] direction by an angle $\phi = 20°$ and amounts to about 25° in a field of the same value (Fig. 5).

Thus, in all orientations of $\mathbf{H}^\perp$ and throughout the experimentally investigated range of fields $H > H_c$ the effects of the change in orientation of the magnetic moment of the photoexcited ion in the state ${}^4T_{1g}\,({}^4P)$ are significant, amounting to tens of degrees. Allowance for the next coordination sphere, i.e., allowance for the influence of the photoexcited ion on the orientation of the magnetic moments of its nearest neighbors, should apparently lead to no fundamental changes.

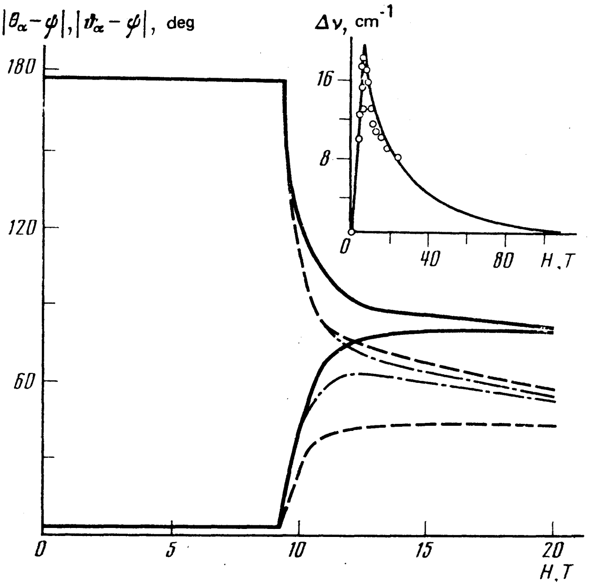

FIG. 4. Calculated dependence on the magnetic field strength of the angles $|\theta_\alpha - \psi|$ and $|\vartheta_\alpha - \psi|$ between the direction of the field $\mathbf{H}$ and the spins $\mathbf{S}_\alpha^0$ and $\mathbf{S}_\alpha^f$ of the ground and excited states, respectively, of the Mn^{2+} ions of the two sublattices of antiferromagnetic MnF_2. The solid curves are $|\theta_\alpha - \psi|$ for arbitrary orientation of the component of the antiferromagnetism vector $\mathbf{l}^\perp \| \mathbf{H}^\perp$ in the basal plane. The dashed curves are $|\vartheta_\alpha - \psi|$ for $\mathbf{l}^\perp \| [110]$, and the dot-and-dash curves are $|\vartheta_\alpha - \psi|$ for $\mathbf{l}^\perp \| [100]$; θ_α and ϑ_α are the angles between the C_4 axis and the vectors $\mathbf{S}_\alpha^0$ and $\mathbf{S}_\alpha^f$, respectively. The inset shows the dependence of the splitting of the line ν_e on the strength of the magnetic field for $\mathbf{H}^\perp \| [110]$. The solid curve is the calculated curve for $\psi = 3°$, an exchange integral in the excited state $J^f = 1\ \mathrm{cm}^{-1}$, and uniaxial and interionic anisotropy parameters $b = J^{f\xi} = 0$, $E = 0$, $D = 3.33\ \mathrm{cm}^{-1}$.

The breakdown of the uniaxiality of MnF_2 in inclined

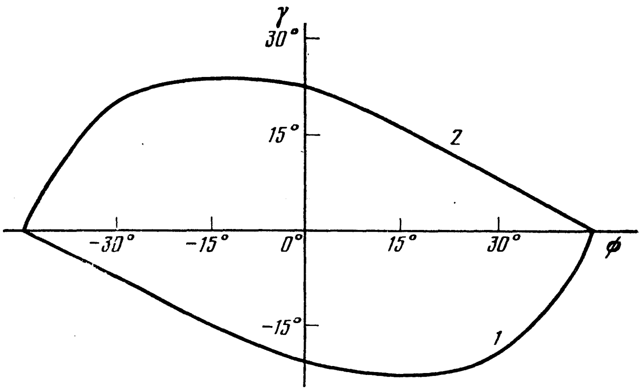

FIG. 5. Calculated deviation of the orientations of the spin component $\mathbf{S}_\alpha^{f1}$ of the photoexcited ion in the basal plane (the angles γ_α from the direction of the spin component $\mathbf{S}_\alpha^{01}$ of the unexcited ion at various orientations of $\mathbf{H}^\perp$ ($\psi = 3°$, $b = J^{f\xi} = E = 0$, $J^f = 1\ \mathrm{cm}^{-1}$, $D = 3.33\ \mathrm{cm}^{-1}$, $H = 12\ T$): Curve 1) γ_1, curve 2) γ_2.

magnetic fields also occurs for fields, in the range $H < H_c$, and so here too there should be a change in the orientation of the magnetic moments of the ions upon their photoexcitation to the ^4P state. However, the methods of optical spectroscopy are incapable of detecting the nonequivalence of the orientations of the spins $\mathbf{S}_1^f$ and $\mathbf{S}_2^f$ of the excited states with respect to the direction of the field **H** in this case—the size of the effect here is governed by the small angle ψ.

As for the orientation of the photoexcited ions in the state $^4T_{1g}(^4G)$, the coalescence of the components of the splitting of the lines ν_e' and ν_e'' for all orientations of $\mathbf{H}^\perp$ in the basal plane in fields $H > H_c$ indicates that the anisotropy in this plane is small for an ion in an excited ^4G state, i.e., $D \simeq E \simeq 0$. A change in the orientation of the spin of the ion upon photoexcitation to the state $^4T_{1g}(^4G)$ can nevertheless occur through a change in the exchange interaction, but the equivalence of the orientations of the magnetic moments of the ions of opposing sublattices with respect to the direction of the field **H** will essentially be preserved, and there will be no splitting of the absorption lines for $H > H_c$.

In summary, we have shown that photoexcitation of the magnetic ions in antiferromagnetic MnF_2 leads to appreciable changes in the parameters characterizing the intraionic and interionic interactions. In the excited state $^4T_{1g}(^4P)$ the Mn^{2+} ion acquires a significant (5 T) single-ion magnetic anisotropy of the type $S_\alpha^{f\xi} S_\alpha^{f\eta}$ in the basal plane, exceeding by at least two orders of magnitude the analogous anisotropy of the ions in the ground state; the exchange interaction parameter decreases by more than a factor of two $H_E^0 = 50$ T, $H_E^f = 20$ T). These changes lead to substantial differences (of up to tens of degrees) in the orientation of the spins of the photoexcited and unexcited states upon the spin flop in antiferromagnetic MnF_2.

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Translated by Steve Torstveit