ESR study of the Tm^{3+} ions in $KTm(MoO_4)_2$

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Electron spin resonance experiments have been performed on single crystals of $KTm(MoO_4)_2$. In the frequency range from 10 to 190 GHz, the magnetic field dependence of absorption spectra of the Tm^{3+} ions is studied at helium temperatures for different crystal orientations. It is shown that this compound has a Ising magnetic structure with an high anisotropy of the spin-spin interactions. Two magnetically inequivalent paramagnetic centers of the Tm^{3+} ions are observed. The local magnetic axes of these centers make an angle of $\pm(7.6\pm0.1)^\circ$ with the c axis in the (ac) plane. The ground state of the Tm^{3+} ions $(^3H_6)$ is a non-Kramers doublet consisting mainly of $M_J=|\pm6\rangle$ with a zero-field splitting $\Delta=2.33\pm0.02$ cm^{-1} and a single g value of 13.99 ± 0.05.

I. INTRODUCTION

The double molybdates and tungstates with the general formula $M\mathrm{Ln}(XO_4)_2$ (M = alkali metal; Ln = lanthanide ion; X = Mo, W) form a wide class of interesting host lattices for rare-earth ions with laser activity. At the same time the spin systems containing the chains of magnetic atoms with integer or half-integer spin with a large orbital contribution to the ground state make these materials very useful as model systems for fundamental studies of low-dimensional magnetism. There is a continuous interest in the experimental checks of the predictions regarding the behavior of a quasi-one-dimensional Heisenberg-Ising magnets with nearest-neighbor interactions. The trivalent thulium Tm^{3+} $(S=1,L=5,J=6)$ is well known as a laser-active rare-earth ion. Recently, the optical properties of $NaLa(MoO_4)_2$ and $KLa(MoO_4)_2$ doped with the Tm^{3+} ions have been measured by spectroscopic means.[1,2] Here, we present the electron spin resonance (ESR) data on the single crystal samples of $KTm(MoO_4)_2$ in order to shed light on the magnetic ground state of the Tm^{3+} ion in this crystal and on the role of the ligand environment in the formation of the magnetic properties of this compound.

Although not studied in detail, the double potassium-thulium molybdate $KTm(MoO_4)_2$ is a typical representative of the crystal family $KLn(MoO_4)_2$ (Ln = Y, Dy, Ho, Er, Tm, Yb, Lu). The polarized IR and Raman spectra of these crystals were reported by Hanuza and Macalik.[3] Until now the magnetoresonance properties of the $KTm(MoO_4)_2$ compound were not investigated. The $KTm(MoO_4)_2$ crystal has the layered crystal structure of $KY(MoO_4)_2$,[4] with orthorhombic symmetry in the space group $Pbcn$ (D_{2h}^{14}) and four formula units per unit cell: $a=5.047$ Å , $b=18.28$ Å , $c=7.892$ Å .[5] The structure consists of infinite chains of octacoordinated TmO_8 polyhedra elongated along the c axis and connected in their edges. As shown by Harris and Furniss,[6] the eightfold coordination with high symmetry of the trivalent lanthanide ion (like a square antiprism with D_{4d} symmetry) could lead to a $|\pm6\rangle$ doublet ground state for the Tm^{3+} ion. This is a unique phenomenon since usually one would expect the ligand field to remove completely the 13-fold degeneracy of the ground $^3H_6$ multiplet, giving a set of 13 singlets for the non-Kramers ion Tm^{3+}. It should be noted that the high symmetry effects surrounding the Tm^{3+} ion can exist even in a crystalline system with lower symmetry—monoclinic, for instance, when the site symmetry of the Tm^{3+} ion has a twofold axis of rotation.[7] In this case the lowest pair of nearly degenerate crystalline Stark levels is separated by a large energy interval from the next higher group of Stark levels. This pair of levels consists of nearly pure $|\pm6\rangle$ states. Thus the "splitted doublet" model may be taken as an excellent approximation to the direction of higher symmetry giving the quasidegeneracy for two singlets and the Tm^{3+} ion with the strong anisotropy in the g tensor as an excellent probe for studying higher symmetry effects.

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Electron spin resonance is known to be a powerful tool in the study of solids, where valuable information about the local environment of a paramagnetic ion and the nature of the ground state of the ions can be obtained from the dependence of the ESR spectrum on applied field direction. Since the optical experiments only observe the splitting of the ground states indirectly, the transition between these two splitted levels can be observed directly by using a high frequency ESR technique.

II. EXPERIMENTAL RESULTS

Single crystals of $KTm(MoO_4)_2$ were obtained by means of a flux growth method.[8] $KTm(MoO_4)_2$ forms layered crystals, which are cleavable in the (ac) plane. The structure consists of anionic layers of $[Tm(MoO_4)_2]^-$ parallel to the (ac) plane separated by K^+ ions. In the (ac) plane the chains of TmO_8 polyhedra are linked through Mo_2O_8 dimers. By analogy with the isomorphous compound $KY(MoO_4)_2$,[4] we will consider that the arrangement of the eight oxygens around a central thulium ion in the TmO_8 polyhedra has C_2 symmetry. Note that the oxygen coordination in the TmO_8 polyhedra is very close to a slightly distorted square antiprism.

The high-frequency properties of single crystal $KTm(MoO_4)_2$ were investigated in the frequency interval 10–190 GHz at $T=4.2$ K. The measurements have been performed on several spectrometers with a resonator cavity of the appropriate frequency region as an active element. In the resonator cavity the sample was placed on a dielectric rotation device with one degree of freedom in the rotation. The characteristic dimension of the single crystals used in our experiments is $3\times3\times0.5$ mm^3. It should be noted that for the optimal performance of the cavities the dimension of the single crystals is chosen different for different frequency regions. A superconducting solenoid with a maximum field of 8 T was used.

The angular dependencies of the ESR absorption spectra of the Tm^{3+} ions are studied in three crystallographic planes of the crystal. The accuracy of the orientation of the applied magnetic field relatively to the crystallographic axes of the $KTm(MoO_4)_2$ crystal was better than 0.5°. The complete frequency-field dependence of the absorption lines has been obtained for the external magnetic field along the c axis.

Since the non-Kramers ion Tm^{3+} $(S=1, L=5, J=6)$ has a large orbital contribution to the ground state, it is very sensitive to the variations in the local electric field leading to an inhomogeneous broadening of the resonance line. In magnetic resonance, one of the main sources of linewidth broadening is also the spin-spin interaction. The variation in magnetic field at different ions arises from the local magnetic field of randomly oriented neighbors. At sufficiently low temperatures, where kT becomes comparable with the level separations, the ions fall into the lowest level and the randomness begins to disappear. Consequently, the optimal conditions for observing ESR spectrum of the rare-earth ions require to use liquid-helium temperatures. Since the ground manifold $J=6$ should be split by the ligand field into $2J+1$ singlet levels with an overall splitting of several hundred wave numbers, no electron paramagnetic resonance spectrum should be expected for frequencies below a few cm^{-1}.

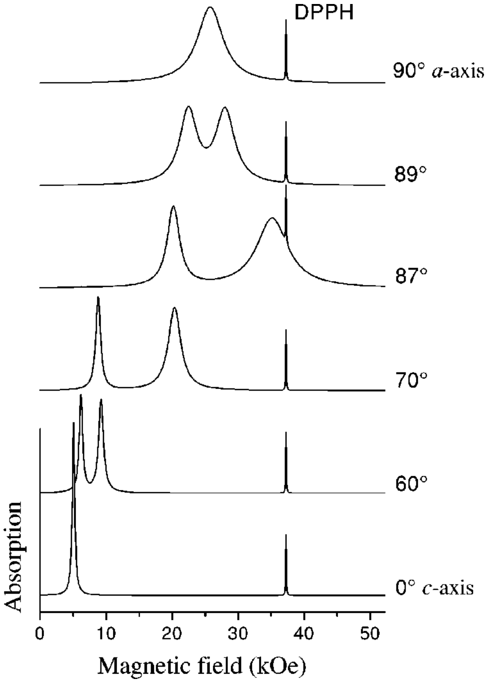

FIG. 1. The ESR spectrum of the Tm^{3+} ions in a single crystal of $KTm(MoO_4)_2$ at 104.3 GHz for different orientations of the external magnetic field in the (ac) plane. The angle $\theta=0°$ corresponds to $H\|c$ axis. The narrow line is a marker of DPPH.

We have not observed any ESR spectrum arising from thulium ions in the frequency region 10–70 GHz at $T=4.2$ K. Above $\nu=70$ GHz the observed electron spin resonance of the Tm^{3+} ions consists of one or two lines with almost Lorentzian line shapes. The occurrence of a single or double resonance structure in the spectra depends on the orientation of the external magnetic field. Figure 1 shows the transformation of the ESR spectra of the Tm^{3+} ions for different orientations of the external magnetic field in the (ac) plane at $\nu=104.3$ GHz. The maximum intensity of the absorption line is found around the c axis.

In Figs. 2(a) and 2(b), the angular dependencies of the resonance fields in $KTm(MoO_4)_2$ are shown, when the external magnetic field is rotated in the crystallographic (ac) and (bc) planes of the crystal, respectively. These measurements have been done by using millimeter waves of $\nu=104.3$ GHz and $\nu=104.76$ GHz at helium temperatures. For the orientation of the applied magnetic field in the (ac) plane, two absorption lines are well resolved. The angular dependencies of these two resonance lines are symmetric with respect to the crystallographic axes. The angular dependence of each of the two lines has a symmetry c' axis, which are turned away from the crystallographic c axis by a small angle. Such behavior in the ESR spectra can be ascribed to the presence of two magnetically nonequivalent paramagnetic Tm^{3+} centers in $KTm(MoO_4)_2$. This is a typical phenomenon for the majority of the crystals in this family.[9] In the (bc) plane, the ESR absorption has a single line at all angles, even for the external field parallel to the b axis. In all planes of field rotation the angular dependencies of the resonance fields $H_{res}(\alpha)$ obey the relation $H_{res}(\alpha)\cos\alpha=\text{const}$, where α is the angle between the applied magnetic field and the symmetry c' axis belonging to the particular magnetic

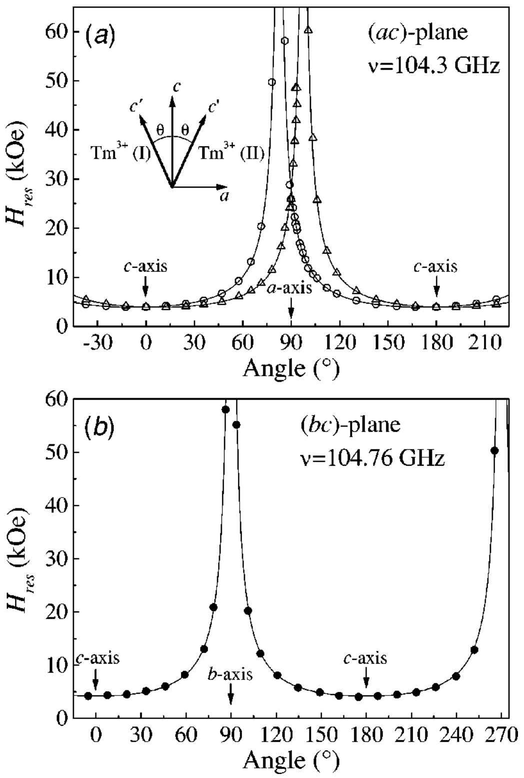

FIG. 2. Positions of the ESR absorption lines as the applied magnetic field is rotated (a) in the (ac) plane at 104.3 GHz and (b) in the (bc) plane at 104.76 GHz. The open circles (○) and the open triangles (△) represent experimental points for two different paramagnetic centers of the Tm^{3+} ion. The local magnetic c' axes of these centers are turned in the (ac) plane with an angle of $\pm(7.6\pm0.1)°$ from the c axis. In the (bc) plane the field positions for these centers are coincident [solid circles (●)]. The solid lines are plotted using the expression $H_{res}(\alpha)\cos\alpha$=const.

center. This situation corresponds to a finite value of $g_{\|}$ and $g_{\perp}=0$, which is characteristic of a non-Kramers doublet.[10] Later on we will try to estimate the maximum possible values for the perpendicular components of the g tensor, which are due to the contribution from the highest energy states and can be extracted from our experiments. By using the functional dependence $H_{res}(\alpha)\cos\alpha$=const, the value of the angle between the c axis and the principal c' axis of the two paramagnetic centers (i.e., the direction of the magnetic moment μ) is found to be $\pm(7.6\pm0.1)°$.

For the field orientations with respect to the crystal, a strong angular dependence of the linewidth $\Delta H_{1/2}$ of the absorption resonance line is found (see Fig. 3). The minimum value of half linewidth at half height for the ESR line of the Tm^{3+} ions $[\Delta H_{1/2}(0°)=500\ \mathrm{G}]$ corresponds to the c' axis of the crystal. In proportion to the deviation from the c' axis to the a' or b' axes the resonance line gradually broadens (see the examples of the ESR spectra in Fig. 1). The significant broadening of the absorption resonance line, especially in the vicinity of the local a' and b' axes of the paramagnetic centers of the Tm^{3+} ion, and the small spectroscopic splitting along these axes (i.e., small values $g_{a'}$ and $g_{b'}$) have not allowed us to determine directly the extreme resonance field positions along these directions. Because the field position of the absorption line at the orientation of the external magnetic field along the a' and b' axes exceeded the accessible magnetic field range, we could only evaluate an upper limit of these g values. For these directions the estimated components of the g tensor do not exceed 0.4. More exact estimations of the g factor values along the a' and b' axes were obtained from the ESR spectra upon the rotation of the external magnetic field in the (ab) plane of the crystal.

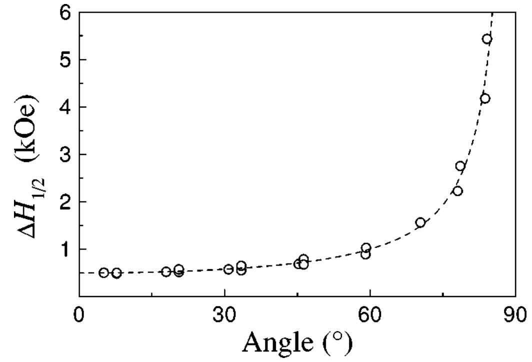

FIG. 3. Dependence of the ESR linewidth $\Delta H_{1/2}$ on the angle between the local magnetic c' axis belonging to one paramagnetic center of the Tm^{3+} ions and the applied magnetic field in the $(a'c')$ and $(b'c')$ planes of field rotation. The dashed line shows the function $\Delta H_{1/2}(\alpha)=\Delta H_{1/2}(0°)/\cos\alpha$ with $\Delta H_{1/2}(0°)=0.5$ kOe.

Figure 4 shows the frequency-field dependence of the ESR spectrum in $KTm(MoO_4)_2$ at the orientation of the external magnetic field H along the c axis of the crystal $(T=4.2\ \mathrm{K})$. The obtained frequency-field dependence of the ESR absorption line has a nonlinear character. The good description for this behavior is a square law $(h\nu)^2=(\Delta)^2+(g_c\mu_B H_z)^2$ with a gap Δ. Below this gap, in the frequency range from Δ down to 10 GHz, the ESR spectrum of the Tm^{3+} ions is absent. The inset in Fig. 4 represents the same experimental data in squared scales (the resonance frequency squared as a function of the resonance field squared) and clearly demonstrates this square law. Extrapolation to zero field gives the zero-field splitting parameter Δ to be 69.9 ± 0.5 GHz $(2.33\pm0.02\ \mathrm{cm}^{-1})$ and from the slope we have obtained the value of the g factor for the c axis of the crystal as $g_c=13.87\pm0.05$.

III. DISCUSSION OF RESULTS

The experimental study of the angular dependence of the ESR spectra of the Tm^{3+} ions in the $KTm(MoO_4)_2$ lattice

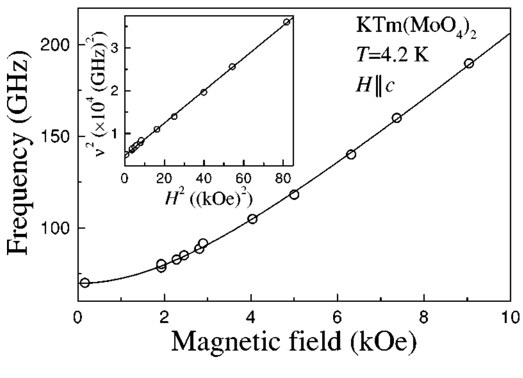

FIG. 4. The frequency-field dependence of the resonance line in $KTm(MoO_4)_2$ at the orientation of the external magnetic field along the c axis. The inset shows the frequency squared as a function of magnetic field squared.

testify that this rare-earth ion can be considered to a good approximation as a typical Ising ion. The high anisotropy of the g tensor ($g_{a'}, g_{b'} \ll g_{c'}$, where a', b', c' are the local magnetic axes of a paramagnetic center) permits to use a Ising Hamiltonian for the description of magnetoresonance properties. In the frame of this model the main contribution to the Hamiltonian has terms containing z components of the operator of the total magnetic moment J (in our convention the z axis coincides to the direction of local c' axis).

A. Hamiltonian for non-Kramers doublet ground state

ESR measurements on the Tm^{3+} ions in the single crystal of $\mathrm{KTm(MoO_4)_2}$ show that the ground state is a closely spaced doublet corresponding to the maximum possible M_J values: $|M_J\rangle = |\pm J\rangle = |\pm 6\rangle$. The occurrence of a doublet state for Tm^{3+}, which is a non-Kramers ion with $4f^{12}$ configuration and ${}^3H_6$ multiplet, is very surprising, because one would expect that the ligand-field interaction of the orthorhombic crystal would completely remove the electronic degeneracy of a non-Kramers ion ground state, producing a set of $2J+1$ singlets. Sometimes some degeneracy may remain, either accidentally or when the ion is at the site of high symmetry, and the ESR is possible in this case.

The ground state of such systems are described by using the conventional non-Kramers doublet spin Hamiltonian for an effective spin $S=1/2$:[10]

$$\mathcal{H} = g_z \mu_B H_z S_z + \Delta_x S_x + \Delta_y S_y . \tag{1}$$

The terms $\Delta_x S_x$ and $\Delta_y S_y$ give rise to a zero-field energy splitting $\Delta = [\Delta_x^2 + \Delta_y^2]^{1/2}$ and also mix the two lowest nondegenerate states $|A\rangle$ and $|B\rangle$, remove the time conjugacy and allow a transition probability between them when the microwave field has a parallel component along the z direction. A term $\Delta_y S_y$ can be easily excluded by a rotation of coordinate system or by a different phase choice of the states. Here we have neglected the hyperfine spin-nuclear interaction $A_z I_z S_z$ for the thulium ion.

The energy levels obtained by diagonalizing Eq. (1) are given by

$$W_{1,2} = \pm 1/2 [\Delta^2 + (g_\parallel \mu_B H_z)^2]^{1/2}, \tag{2}$$

where for the electronic angular momentum J we have defined $g_\parallel^2 = (2g_J)^2 |\langle B|J_z|A\rangle|^2$ (g_J is the Landé factor for the ${}^3H_6$ term and μ_B is the Bohr magneton). Since $g_\perp = 0$, the magnetic dipole transitions can be induced only by a z component of the microwave field.

The resonance condition for a microwave frequency is

$$h\nu = [\Delta^2 + (g_\parallel \mu_B H_z)^2]^{1/2}, \tag{3}$$

where $H_z = H\cos\alpha$ and α is the angle between the z direction and applied magnetic field H. Thus for any deviation of the magnetic field from the z axis (in our case the local magnetic c' axis corresponding to the direction of the magnetic moment) the relative separation between the two lowest Stark levels of the ${}^3H_6$ term will vary as $\cos\alpha$. This dependence has been demonstrated experimentally and is shown in Figs. 2(a) and 2(b).

The states are no longer pure $|A\rangle$ and $|B\rangle$ states but have been mixed by the field to become

$$\begin{aligned} |+\rangle &= (\cos\xi)|A\rangle + (\sin\xi)|B\rangle, \\ |-\rangle &= (\cos\xi)|A\rangle - (\sin\xi)|B\rangle, \end{aligned} \tag{4}$$

where $\tan(2\xi) = g_\parallel \mu_B H_z / \Delta$.

B. The frequency-field dependence at $H \| c$

As can be seen in the inset of Fig. 4, the frequency-field dependence of the ESR absorption line at $H\|c$ can be well described by formula $(h\nu)^2 = \Delta^2 + (g_c \mu_B H_z)^2$ (where $\Delta = h\nu_0$) with the following values of the parameters: $\nu_0 = 69.9 \pm 0.5$ GHz ($2.33 \pm 0.02\ \mathrm{cm}^{-1}$) and $g_c = 13.87 \pm 0.05$. In Fig. 4 and also in the inset of Fig. 4, the curves, which correspond to these parameters, are shown as solid lines. By using the parameters $\theta = 7.6°$ and $g_c \cong g_{c'} \cos\theta$ we have obtained the $g_{c'}$ value of Tm^{3+} ions to be 13.99 ± 0.05.

It is possible to compare the obtained value of $g_{c'}$ with the maximally permissible value for the Tm^{3+} ion. For this estimation we will use $J=6$ for the main multiplet of the Tm^{3+} ion. The main multiplet is characterized by a Landé factor $g_J = 7/6$. The maximum possible magnetic moment of the rare-earth ion is equal to $g_J [J(J+1)]^{1/2} \mu_B \cong 7.56 \mu_B$, which corresponds to $g_{max} = g_J 2J = 14$. The same value of g_{max} can be obtained by using the definition in Eq. (2). The good agreement between the theoretical and the obtained experimental g value allow us to conclude that the ground state of the Tm^{3+} ions consists mainly of $M_J = |\pm 6\rangle$ and that the influence from the next higher grouping of Stark levels is negligible. Our optical experiments[11] have shown that the nearest Stark level of the trivalent thulium is located about $200\ \mathrm{cm}^{-1}$ higher than the ground doublet.

C. Linewidth

The fact that the resonance line shape of the Tm^{3+} ion is not the usual inhomogeneously broadened asymmetric shape of a non-Kramers doublet, but is relatively narrow ($\Delta H_{1/2} = 500$ G at $H\|c'$) with an approximately Lorentzian line shape, indicates that the zero-field splitting of Stark levels has a well fixed value. Thus the nature of the zero-field splitting is not due to the random deviations of the ligand environment of the trivalent thulium.

The observed ESR linewidth in $\mathrm{KTm(MoO_4)_2}$ has been satisfactorily interpreted by the theory of the dipolar broadening of magnetic resonance lines in crystals.[12–14] In order to examine the contribution of the dipole-dipole interaction in the ESR linewidth of $\mathrm{KTm(MoO_4)_2}$, let us consider that all the Tm^{3+} ions are at crystallographically equivalent sites. Because the magnetic system has just one $g_\parallel$ value, the mean square linewidth must be calculated along the principal z axis with this $g_\parallel$ value. For the direction making an angle α with z axis, its value must be multiplied by $(1/\cos\alpha)^2$. For magnetic ions with effective spin $S=1/2$, the dipole contribution coming from the neighboring magnetic moments to the mean square local field is given by

$$\langle H_{loc}^2 \rangle = \frac{1}{3} g_\parallel^2 \mu_B^2 S(S+1) \sum_{j>i} \frac{(3\cos^2\theta_{ij} - 1)^2}{r_{ij}^6}, \tag{5}$$

where r_{ij} is the vector connecting two moments numbered i and j and θ_{ij} is the angle between applied magnetic field H and r_{ij}. $j>i$ indicates that pairs of ions must only be counted once. This expression describes the change in the z component of magnetic field by the z components of the neighboring magnetic moments. The dipolar linewidth of Eq. (5) could be roughly estimated as $\sqrt{\langle H_{loc}^2\rangle}\approx 2000$ G by considering only first nearest-neighbor sites ($r_{ij}\approx 4$ Å). The observed linewidth of order of 500 G is smaller than the estimated one for $\mathrm{KTm(MoO_4)_2}$ and, in addition, the ESR lines are approximately Lorentzian indicating that they are exchange narrowed.

From a classical point of view the mean dipolar field H_{dip}, which adds to the applied field H_z and thus produces a shift $\Delta H_z = -H_{dip}$ in the field required for the resonance at a fixed frequency, can be written as[14]

$$H_{dip}=\langle\mu_z\rangle\sum_{j>i}\frac{(3\cos^2\theta_{ij}-1)}{r_{ij}^3}, \tag{6}$$

where the average moment $\langle\mu_z\rangle$ is given by

$$\langle\mu_z\rangle=\frac{g_J^2\mu_B^2 J(J+1)H_z}{3k_B(T+\theta_W)}. \tag{7}$$

At the helium temperatures the magnetic susceptibility of $\mathrm{KTm(MoO_4)_2}$ has a paramagnetic behavior with the Curie-Weiss temperature $\theta_W\sim 0$ K. For two nearest-neighbor magnetic moments, at $T=4.2$ K and for $H_z=H_{res}\approx 5000$ G ($\nu=104$ GHz), the mean dipolar field H_{dip} is estimated to be ~ 450 G. Thus the dipole-dipole interaction seems to able to explain the observed ESR linewidth in the $\mathrm{KTm(MoO_4)_2}$ single crystals.

D. The estimation of the perpendicular components of the *g* tensor

In order to estimate the upper possible values for the perpendicular components of the g tensor along the local a' and b' axes we have assumed that the two paramagnetic centers are independent and that the Ising-like g tensor has three nonzero components such that $g_{a'}, g_{b'} \ll g_{c'}$. In this case one can do the analysis of each of them separately. Note that the g tensor clearly has a needle-shaped form. Therefore, an essential role is played by the orientation of the local c' axis in the space. This direction corresponds to the maximum value of the g factor.

At the rotation of the external magnetic field in any plane the g tensor produces an ellipse function $g(\alpha)^2=g_{max}^2\cos^2(\alpha)+g_{min}^2\sin^2(\alpha)$, where the value of g_{max} is formed by the projection of $g_{c'}$ component of the g tensor's ellipsoid on the rotation plane. The exact situation, when $g_{max}=g_{a'}$ and $g_{min}=g_{b'}$, is not possible to realize in the experiments, because a small angular deviation always exists due to experimental error. By this reason we do not present here the angular dependence of the resonance fields in the (ab) plane. But by only using simple geometrical relations one can easily obtain the following expressions for g_{max} for a rotation of magnetic field in the three crystallographic planes:

$$(ac)\ \text{plane:}\ g_{max}^2\cong g_{c'}^2(\cos^2\theta+\sin^2\theta\cos^2\varphi),$$

$$(bc)\ \text{plane:}\ g_{max}^2\cong g_{c'}^2(\cos^2\theta+\sin^2\theta\sin^2\varphi), \tag{8}$$

$$(ab)\ \text{plane:}\ g_{max}^2\cong g_{c'}^2(\sin^2\theta),$$

where θ and φ are the azimuthal and the polar angles, respectively. As you can see from Eq. (8), at the rotation of the external magnetic field in the (ac) and (bc) planes g_{max} well coincides to the value of $g_{c'}$ (especially for small angle θ). For the (ab) plane this question remains open, because the projection $g_{c'}\sin\theta$ can be of order of or even more than the values $g_{a'}$ or $g_{b'}$. In the (ab) plane the angular dependence of the ESR spectrum of Tm^{3+} is formed by two factors: the field position of the absorption line is defined both by the components $g_{a'}$ and $g_{b'}$ of the g tensor and in large degree by the projection $g_{c'}\sin\theta$ on this plane.

The best fit for the description of experimental data in the (ab) plane (not presented here) and in the (ac) and (bc) planes [Figs. 2(a) and 2(b), respectively] is obtained for the following parameters of one paramagnetic center of the Tm^{3+} ions: $g_{a'}=0.2\pm0.2$, $g_{b'}=0.2\pm0.2$, $g_{c'}=13.9\pm0.1$, $\theta=(7.6\pm0.1)°$, $\varphi=0°$, where θ is the angle between the crystallographic c axis and the local magnetic c' axis of the paramagnetic center. Note that this result has also a good agreement with the experiment and with the model for the non-Kramers doublet ground state.

IV. CONCLUSIONS

The angular and frequency-field dependence of the ESR spectra of the Tm^{3+} ions in a single crystal of $\mathrm{KTm(MoO_4)_2}$ have been analyzed in the frame of a Ising model with a highly anisotropic spin-spin interaction. It is shown that in the studied system the phenomenological approach based on the Hamiltonian for a non-Kramers doublet ground state seems to be sufficient for the description of the resonance properties of the Tm^{3+} ions in $\mathrm{KTm(MoO_4)_2}$. Two lowest crystalline Stark levels of the $^3H_6$ term form a closely spaced electronic doublet with a zero-field splitting parameter $\Delta=2.33\pm0.02\ \mathrm{cm}^{-1}$ and a single g value 13.99 ± 0.05. This nearly degenerate pair of crystal field levels consists mainly of $M_J=|\pm6\rangle$. The relatively narrow absorption resonance lines arising from the Tm^{3+} ions ($\Delta H_{1/2}=500$ G at $H\|c'$) indicate that the zero-field splitting has a well fixed value. The ESR linewidth in $\mathrm{KTm(MoO_4)_2}$ can satisfactorily be explained by introducing the dipole-dipole interaction. Two nonequivalent paramagnetic centers of the Tm^{3+} ions in $\mathrm{KTm(MoO_4)_2}$ are found. The local magnetic c' axis of these centers are turned in the crystallographic (ac) plane and make up an angle of $\pm(7.6\pm0.1)°$ with the c axis.

It should be emphasized that the resonance behavior of trivalent thulium is very sensitive to the presence a higher symmetry direction in the crystal. Therefore, this ion is an excellent candidate to probe high symmetry effects of ligand environment in solids.

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