# Submillimeter ESR spectroscopy of van Vleck paramagnets in parallel fields

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The hyperfine structure of the magnetic dipole transition between the ground and excited singlet states of a $Ho^{3+}$ ion was resolved in the ESR spectrum of the van Vleck paramagnet $KY_3F_{10}$:Ho using parallel (static and alternating) magnetic fields. © *1995 American Institute of Physics.*

**1.** Investigations of the electron-spin resonance (ESR) spectra of single-crystal rare-earth (RE) paramagnets in the submillimeter wavelength range, which in many cases provide the only real possibility of obtaining information about the Stark structure of the ground-state multiplet of the rare-earth ion, have been performed since the end of the 1970s.[1,2] Molecular lasers or generators with backward-wave tubes are employed as sources of rf radiation (far-infrared region of the spectrum). The laser radiation usually is delivered to the sample along the axis of a superconducting solenoid, which produces a static magnetic field, and the measurements are performed in transverse static (**H**) and alternating ($\mathbf{H}_1$) magnetic fields. The intensities of the lines in the ESR spectra (and correspondingly the possibility of observing them) depend on the effectiveness of the modulation of the excitation spectrum of the paramagnetic ion with small changes of the static magnetic field and on the matrix elements of the magnetic or electric dipole moment operators with respect to the wave functions of the states which are resonantly coupled by the alternating field. At frequencies up to 1600 GHz the ESR spectra have been investigated. These frequencies correspond to the transitions between the Zeeman sublevels of the rare-earth ions in activated and regular paramagnets, which have in the ground state Kramers doublets[3–5] and non-Kramers doublets,[1–3,5–8] and also quasidoublets with small initial splitting.[3,9] Unique information about the spectra of the rare-earth ions was obtained in the measurements of the absorption in magnetic transitions between the Stark sublevels of the ground multiplets of the $Dy^{2+}$ ions (doublet–triplet),[2] $Er^{3+}$ (doublet–doublet),[3,4] and $Ho^{3+}$ (doublet–singlet).[3,8] As a rule, the measurements are performed at liquid-helium temperatures and in strong magnetic fields which suppress the magnetic broadening of the spectral lines. All data on submillimeter ESR spectroscopy published to date pertain to systems which do not contain magnetically nonequivalent rare-earth ions.

**2.** In the present study we measured the ESR spectra of the van Vleck paramagnets and we resolved the hyperfine structure of the magnetic singlet-singlet transitions in a <Ã"weak" magnetic field (under the condition $g_J\mu_B H \ll \Delta$, where $g_J$ is the Landé factor of the ground-state multiplet, $\mu_B$ is the Bohr magneton, and $\Delta$ is the splitting of the singlet states in the crystal field). In contrast to systems with a magnetic ground state, in

  

van Vleck paramagnets the magnetic broadening at low temperatures ($kT \ll \Delta$) is small and there is no need to use a strong field to suppress it. The optical conditions for observing intense ESR signals are determined by the structure of the wave functions of the initial and final states of the transitions. As an example, we shall consider the results of the experimental studies of cubic single crystals of the complex fluorides $KY_3F_{10}$:$Ho^{3+}$ (space group Fm3m). The $Ho^{3+}$ ions replace the $Y^{3+}$ ions ($C_{4v}$ point symmetry group) in three magnetically nonequivalent positions I, II, and III, which differ only by the orientations of the fourfold local symmetry axes along the crystallographic directions [001], [010], and [100], respectively. The structure of the energy spectrum of the ground-state multiplet $^5I_8$ of the $Ho^{3+}$ ions is described by the Hamiltonian $\mathscr{H}=\mathscr{H}_0+g_J\mu_B\mathbf{JH}+A\mathbf{JI}$, where the nuclear Zeeman energy and the energy of the quadrupole moments of the $^{165}$Ho nuclei are ignored, $\mathscr{H}_0=\Sigma_{p,q}B_p^q\alpha_pO_p^q$ is the energy of the ion in the crystal field, $O_p^q$ are Stevens operators, $\alpha_p$ are the reduced matrix elements, **J** is the total electronic angular momentum, operator **I** is the nuclear spin operator ($I=7/2$), and $A=0.812$ GHz is the hyperfine structure constant.[10] Our objective in this study was to determine more accurately the parameters of the crystal field, whose initial values were assumed to be the arithmetic-mean values found previously from the optical data for $KY_3F_{10}$:$Er^{3+}$ and $KY_3F_{10}$:$Dy^{3+}$ crystals:[11,12] $B_2^0=-284$, $B_4^0=-167$, $B_6^0=36$, $B_4^4=425$, $B_6^4=-28.5$ cm$^{-1}$. The nearest-neighbor environment of the rare-earth ion in $KR_3F_{10}$ crystals — eight $F^-$ ions — is a square antiprism (with several different dimensions of the base). A characteristic feature of the crystal field produced by the antiprism is the relatively large axial component. The ground-state doublet $|J_z=\pm4\rangle$ of the multiplet $^5I_8$ in an axial field is split further by the tetragonal component, so that the ground state of the $Ho^{3+}$ ions is a singlet with $A_1$ symmetry with the wave function $|A_1\rangle=\alpha(|8\rangle+|-8\rangle)+\beta(|4\rangle+|-4\rangle)+\gamma|0\rangle$, where $\alpha \ll \beta \approx 1/\sqrt{2}$, and the nearest excited state is a singlet with $A_2$ symmetry with the energy $\Delta=7.4$ cm$^{-1}$ and wave function $|A_2\rangle=\alpha(|8\rangle-|-8\rangle)+\beta(|4\rangle-|-4\rangle)$. The next excited state — the doublet $E$ — has an energy greater than 20 cm$^{-1}$. The magnetic moment associated with the states $A_1$ and $A_2$ has only one nonzero projection onto symmetry axis of the $Ho^{3+}$ ion, equal to $g_J\mu_B\langle A_1|J_z|A_2\rangle \approx 5\mu_B$. Consequently, the optimal conditions for observing magnetic dipole transitions $A_1 \rightarrow A_2$ in the alternating field $\mathbf{H}_1(t)$, whose probabilities are proportional to $|\langle A_1|g_J\mu_B\mathbf{JH}_1(t)|A_2\rangle|^2$, correspond to the collinear magnetic fields. As the intensity of the field **H** increases, the effectiveness of the modulation increases but the transition probabilities decrease. The hyperfine interaction leads to the formation of mixed electronic-nuclear states (in particular, it mixes the electronic singlets and doublets), and an additional hyperfine structure of the Stark sublevels appears even in the absence of an external magnetic field (for example, singlets split into four nuclear doublets with maximum splitting of up to 0.03 cm$^{-1}$, and for an arbitrary orientation of the external field, the probabilities of all $(2I+1)^2=64$ transitions between the hyperfine components of the two electronic states are different from zero. We calculated the absorption spectra in parallel fields in the transitions $A_1 \rightarrow A_2$ of three magnetically nonequivalent centers, using the results of numerical diagonalization of the Hamiltonians $\mathscr{H}$. without applying the perturbation theory methods, in the full basis consisting of 136 electronic-nuclear states of the multiplet $^5I_8$. We assumed that for the holmium ions the possible positions are filled with equal probability and the intensity has a normal distribution with the same width 0.8 GHz in each line. The computational results are illustrated

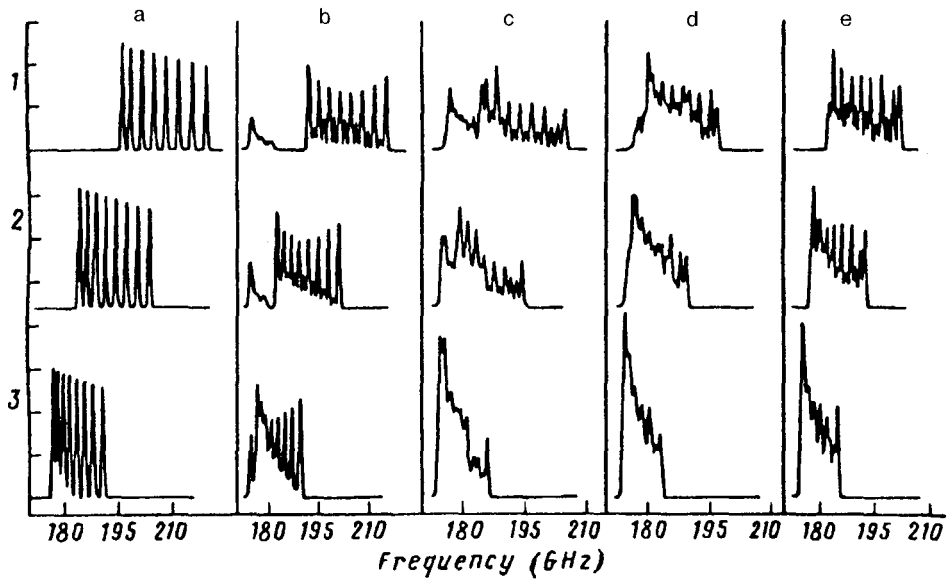


FIG. 1. Computed absorption spectra of a $KY_3F_{10}$:$Ho^{3+}$ crystal in parallel fields plotted as a function of the static magnetic field (*1* — **H**=8 kOe; *2* — **H**=6 kOe; *3* — **H**=4 kOe) and its orientation in the (110) plane. Angle $\varphi$ between **H** and the crystallographic axis [001]: a — 0, b — 20°, c — 40°, d — 60°, e — 90°.

in Fig. 1, which shows the predicted transformations of the absorption spectrum in a rotating magnetic field from the crystallographic $C_4$ axis [001] to the $C_2$ symmetry axis [110] in the (1 -1 0) plane. To make the measured transition frequencies (see below) agree with the computational results, a small correction of the initial parameters of the crystal field was required. The parameters $B_2^0=-276$, $B_4^0=-172$, $B_6^0=42$, $B_4^4=394$, and $B_6^4=-28.5$ $cm^{-1}$, corresponding to the initial splitting $\Delta=5.8$ $cm^{-1}$, were used in the calculation. In a magnetic field $\mathbf{H} \parallel C_4$ only the spectrum of type-I centers with a symmetry axis parallel to the field can be observed. For a small deviation of the field from the symmetry axis, the width of the spectrum (I) and its shift from the frequency of the initial splitting decrease, and a spectrum of type-II and -III centers appears (in the experimental geometry the spectra of these centers are identical) — the leftmost peaks in Figs. 1b and 1c. The eight hyperfine components in Fig. 1a correspond to the transitions with $\Delta I_z=0$. As the angle $\varphi$ between the field **H** and the $C_4$ axis increases, the transitions with $\Delta I_z=\pm 1$, $\pm 2$,... become allowed as a result of the mixing of electronic singlets with doublets. The envelope of the absorption spectrum and of the ESR signals can have a very complex shape. In the simplest cases, the shifted structure of seven lines of the transitions with $\Delta I_z=+1$ or $-1$ (see Fig. 1b), whose intensity increases with the intensity of the static field, is superimposed on the eight main lines. When the angle $\varphi=\cos^{-1}(1/\sqrt{3})$ is reached, the spectra of all centers merge. As the field is further rotated, the spectrum of centers I vanishes, and at $\varphi=90°$ the only spectrum that remains is the spectrum of the centers II and III, which exceeds by a factor of 2 the intensity of the spectrum of I centers at $\varphi=45°$.

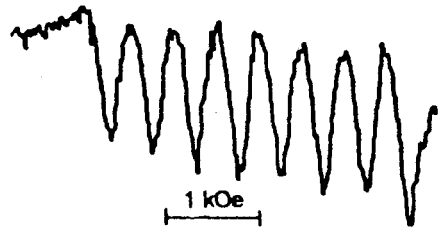


FIG. 2. ESR signal from a $KY_3F_{10}$:$Ho^{3+}$ crystal at 196 GHz with $\mathbf{H}\|\mathbf{H}_1\|C_4$ ($T$=4.2 K).

3. The measurements were performed at a temperature of 4.2 K on a single crystal in the form of a 3×6×10 mm rectangular parallelepiped, containing 0.4 at.% $Ho^{3+}$ ions. We used a wideband ESR spectrometer operating in the frequency range 60–535 GHz.[13] Backward-wave tubes served as sources of the polarized coherent submillimeter radiation. A $n$-InSb single crystal, cooled to 4.2 K, was used as a radiation detector. An open quasioptical channel was used to deliver radiation to the sample. The spectrometer was assembled according to a resonator-free scheme, and the sample was placed in the field of the traveling electromagnetic wave. A magnetic field of up to 1 T was produced with an ordinary electromagnet. The experiments were performed in the Voigt geometry; i.e., the wave vector of the electromagnetic radiation was perpendicular to the direction of the magnetic field **H**. The angle between the directions of the alternating and static magnetic fields could be changed by rotating the polarization plane of the microwave radiation in the quasioptical channel. This rotation was performed with the help of wire polarizers which were placed in the channel. The design of the liquid-helium cryostat was such that it was possible to rotate the sample around an axis parallel to the wave vector of the microwave radiation.

Resonance microwave absorption was observed in the frequency range 178–201 GHz. The sample was rotated around the [110] axis of the crystal lattice. The shape and intensity of the experimental spectra depended strongly on the experimental conditions. The signals obtained in parallel fields were much stronger than the signals obtained in crossed fields. A well-resolved hyperfine structure consisting of eight lines was observed only near orientations of **H** and $\mathbf{H}_1$ along the [001] axis (see Fig. 2). The most intense lines in the spectrum are the outermost lines which correspond to transitions from the states $I_z=\pm 7/2$, consistent with the computational results (Figs. 1b–1e). When the field is inclined away from the symmetry axis, the spectrum of the $Ho^{3+}$ ions becomes much weaker, and the hyperfine structure virtually vanished for angles $\varphi\approx 40°$. According to the curve, shown in Fig. 3, of the resonance fields plotted as a function of the frequency of the generator compared with the computational results obtained with the corrected parameters of the crystal field, the relative error in determining the initial splitting ($\Delta=174$ GHz) does not exceed 0.6%.

It follows from the results obtained by us and from the calculation of the local dipole magnetic fields presented in Ref. 12 that antiferromagnetic ordering (with the formation of magnetic structure with $\Gamma_{3g}$ symmetry) is possible in regular $KHo_3F_{10}$ crystals, but only of a mixed electronic-nuclear type and at temperatures below 0.05 K. In conclusion,

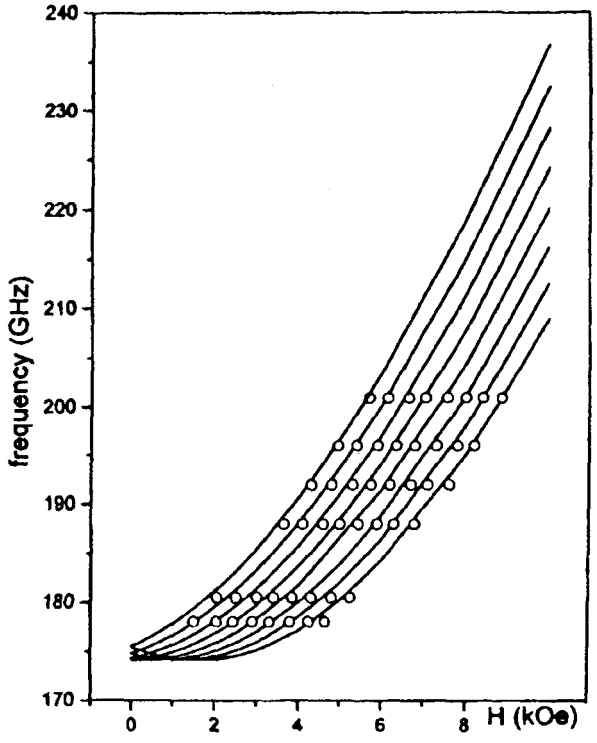


FIG. 3. Computed frequencies of the magnetic dipole transitions in a $KY_3F_{10}:Ho^{3+}$ crystal with $\mathbf{H}\|\mathbf{H}_1\|C_4$. The circles represent the measurements.

we note that the information content of submillimeter wavelength ESR spectra obtained by using laser radiation sources can be substantially increased (in particular, in experimental studies of magnetoelastic spectral effects in van Vleck paramagnets) if the radiation is directed perpendicular to the static magnetic field.

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