NMR, high frequency EPR and magnetization studies of 
YF$_3$:Tm$^{3+}$ and TmF$_3$

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Abstract. Magnetic properties of single crystal and powder samples of thulium fluoride, TmF$_3$ (orthorhombic Pnma space group), and single crystals of YF$_3$ doped with the Tm$^{3+}$ ions are studied by NMR, high-frequency EPR and dc-magnetometry. It is shown that TmF$_3$ is a Van Vleck paramagnet. Zero field splitting between two lowest ground state energy levels (ground $^3$H$_6$ multiplet) of Tm$^{3+}$ ion in TmF$_3$ crystal lattice is found to be ~6.5 cm$^{-1}$. The $^{19}$F nuclear spin-lattice relaxation in TmF$_3$ at liquid helium temperatures is driven by the fluctuating magnetic fields created by Tm$^{3+}$ ions occupying the lowest excited singlet.

1. Introduction

The heavy-rare-earth fluorides, from SmF$_3$ to YbF$_3$, having an orthorhombic $\beta$-YF$_3$ structure with the space group Pnma (62), show a variety of magnetic and optical properties and attract interest for several reasons. The heavy-rare-earth fluorides are model systems for studies of magnetic ordering in rare-earth insulators with competing dipole and exchange interactions. The magnetic ordering was observed in ErF$_3$ ($T_N = 1.05$ K) [1], TbF$_3$ ($T_C = 3.95$ K) [2, 3], HoF$_3$ ($T_C = 0.53$ K) [4], DyF$_3$ ($T_C = 2.55$ K) [5, 6] and GdF$_3$ ($T_C = 1.25$ K) [7]. Crystals of the heavy-rare-earth fluorides may be also suitable as potential solid-state laser materials and scintillators. Optical spectra of RF$_3$ and rare earth doped isostructural YF$_3$:R$^{3+}$ crystals (R = Eu, Tb, Dy, Ho, Er, and Yb) have been measured in Refs. [8-12]. At the present time the PrF$_3$ and other rare-earth fluorides have attracted more and more attention due to synthesis of the hollow fullerene-like nanoparticles RF$_3$ (R = Pr, Nd, Sm) [13,14] which can have widespread potential for practical applications.

Fluoride TmF$_3$ (Tm$^{3+}$ is non-Kramers rare-earth ion, electronic configuration of the partially filled shell $4f^{12}$) has been the subject of quite a few studies in the past. As a result, scanty information exists on magnetic properties of rare-earth ions in both concentrated TmF$_3$ and diluted YF$_3$:Tm$^{3+}$ compounds. The Van Vleck paramagnetism often occurs in systems with non-Kramers rare-earth ions (Pr$^{3+}$, Eu$^{3+}$, Tb$^{3+}$, Ho$^{3+}$ and Tm$^{3+}$ as well) in which the crystalline electric field lifts the degeneracy of the $J$ multiplets, giving rise to splittings which are typically of the order of 10 – 100 cm$^{-1}$ with the ground state being the electronic singlet. Since conventional EPR microwave frequencies correspond to much smaller energies observation of EPR in Van Vleck paramagnets is rare. The other principal method to study the magnetic properties of Van Vleck paramagnets is a enhanced nuclear magnetic resonance (ENMR). However, often the enhanced nuclear magnetic moment of the rare earth ion is so
big that the nuclear dipole-dipole and exchange interactions make ENMR observation difficult, at least by the pulsed NMR techniques. In this report we present magnetic properties of thulium fluoride (TmF$_3$) studied by high-frequency EPR, $^{19}$F NMR methods and dc-magnetometry.

2. Experiment

The TmF$_3$ and YF$_3$: 0.5 at % Tm$^{3+}$ single crystals were grown by the Bridgman method in carbon crucibles in the atmosphere of the high purity argon at a pulling rate of 1 mm/h. High purity the TmF$_3$ and YF$_3$ powders (99.99% grade) were used as starting materials. Additionally, the growth atmosphere was fluorinated by burning the tetra-fluorine-ethylene. The TmF$_3$ single crystals were grown for magnetometry measurements and the YF$_3$: 0.5 at % Tm$^{3+}$ single crystal was grown for measurements by the high-frequency EPR. All single crystals have a needle shape. The samples were oriented in the sample holder using the X-ray diffraction pattern with the accuracy of $3^\circ$. The TmF$_3$ powder for NMR measurements was prepared by grinding of TmF$_3$ single crystals in agate mortar.

Figure 1. High frequency EPR spectra measured for YF$_3$:Tm$^{3+}$ (0.5%) single crystal in the field $B_0 \perp b$ (angular step in ac-plane is $5^\circ$) at frequency 207 GHz.

Figure 2. Measured temperature dependence of the static magnetic susceptibility in TmF$_3$ powder (open symbols). Curie’s Law simulation is given by dashed line.

The dc-SQUID magnetometer MPMS (Quantum Design) was used for measurements of the magnetic susceptibility in the temperature range 1.8 – 300 K at applied magnetic field 0.01 T. High frequency EPR spectra of Tm$^{3+}$ ion in diluted YF$_3$:Tm$^{3+}$ (0.5% Tm) single crystal were taken with high-frequency tunable EPR spectrometer [15] in magnetic fields from 0 to 0.9 T at temperature 4.2 K. In the high frequency EPR measurements radiofrequency magnetic field $B_1$ was applied parallel to static magnetic field $B_0$, i.e. $B_1 \parallel B_0$. For the detection of the $^{19}$F NMR signal a standard NMR pulse spectrometer was used employing spin-echo technique and echo recording in quadrature. The NMR powder spectra of $^{19}$F were taken in TmF$_3$ powder at $T = 4.2$ K and 1.5 K as the magnetic field dependence of the spin echo intensity at a frequency 16.5 MHz. The measurements were performed in magnetic field $B_0$ from 0 to 1.05 T. The $^{19}$F nuclear longitudinal relaxation time $T_1$ was measured by plotting the $^{19}$F nuclear spin-echo intensity as a function of the time between a saturating and $\pi/2$–$\pi$ probing pulses; the nuclear transverse relaxation time $T_2$ was measured by plotting the $^{19}$F spin-echo intensity as a function of the interval time between $\pi/2$ and $\pi$ pulses.
3. Experimental results and discussion

Figure 1 shows high frequency EPR spectra for YF$_3$:Tm$^{3+}$ (0.5%) single crystal in the field $B_0 \perp b$ (angular step in $ac$-plane was $5^\circ$) at frequency 207 GHz and $T = 4.2$ K. The hyperfine structure of the EPR spectra consisting of two resonant lines was observed. This gives evidence, that the lines belong to Tm$^{3+}$ ions ($^{169}$Tm, 100% natural abundance, $I = 1/2$). The angular dependence of the EPR spectra revealed the occurrence of two magnetically non-equivalent sites of Tm$^{3+}$ ions in TmF$_3$ crystal structure. High frequency EPR spectrum in the field directed in the $ab$-plane wasn’t observed because the EPR signals were out of magnetic field range of our magnet.

Dependence of the resonance transitions on the magnetic field implies that the transitions occur between two lowest singlet states of Tm$^{3+}$. The EPR spectra are described by the effective spin Hamiltonian $H = g\mu_B S_z B_0 + \Delta S_x$, where $\Delta$ is the zero-field splitting (actually, the energy gap between two lowest singlets of Tm$^{3+}$), $\mu_B$ is the Bohr magneton, $B_0$ is the component of the external magnetic field along the local $z$-axis. The EPR experiment shows that these two lowest singlets of the $^{3}$H$_6$ ground multiplet of Tm$^{3+}$ ion are separated by the energy gap $\Delta \sim 195$ GHz $\sim 6.5$ cm$^{-1}$. Such structure of electron energy levels is typical for Van-Vleck paramagnets. The magnetic moments corresponding to this quasi-doublet (two singlets) are determined by the $g$-factor $\sim 13.5$ and lie in the $ac$-plane along the directions declined by $\sim 23^\circ$ from the $c$-axis. Defined value of the $g$-factor is close to that of the free Tm$^{3+}$ ion. It is also evidenced that observed EPR signals belong to Tm$^{3+}$ ions.

Some of EPR lines were distorted and split, weak satellite signals were observed. The extra lines can appear due to forbidden electron-nuclear transitions ($\Delta M_I \neq 0$). Wave functions of Tm$^{3+}$ lowest singlets depend on the magnetic field strength, therefore probabilities of transitions are also field dependent. Besides, the strong dispersion of microwave radiation in the needle-shaped crystals occurs near the resonance, this can change the refractive index of the sample and thus change the microwave power reflected to a detector.

Figure 3 shows the NMR powder spectra of $^{19}$F (I = 1/2) for TmF$_3$ powder at $T = 4.2$ K and 1.5 K at a frequency 16.5 MHz. At low temperatures in the external magnetic field all fluorine nuclei are

Temperature dependence of the static magnetic susceptibility in TmF$_3$ powder is shown in Fig.2. One can see that the susceptibility deviates from the Curie law at temperatures below $\sim 15$ K. At temperatures below $\sim 2$ K the susceptibility tends to a constant value implying that only the ground state singlet is populated at $T < 2$ K. Such temperature behavior of dc-susceptibility is typical for Van-Vleck paramagnets.

Figure 3 shows the NMR powder spectra of $^{19}$F (I = 1/2) for TmF$_3$ powder at $T = 4.2$ K and 1.5 K at a frequency 16.5 MHz. At low temperatures in the external magnetic field all fluorine nuclei are
additionally subject to the internal quasi-static magnetic field (dipole and transferred) created by the adjacent Tm$^{3+}$ electronic magnetic moments induced by the external field. This internal field depends on the direction of the external field in respect to the crystal axes. In general four magnetically nonequivalent sites of $^{19}$F are possible in TmF$_3$ structure, so in single crystal one should observe four orientation-dependent $^{19}$F NMR lines. These lines should be broad due to the distribution of the internal magnetic field. In powder sample the $^{19}$F NMR spectrum should also be additionally broadened due to averaging of crystallites orientations in respect to the external magnetic field. This can be observed in the experimental spectrum of Fig.3 extending from about 2 to 10 kG. Such broad spectrum evidences on rather strong local magnetic fields on the $^{19}$F sites due to dipole and transferred super-hyperfine interactions between the Tm$^{3+}$ ions and fluorine nuclei.

The measured value of the transverse relaxation time $T_2$ of $^{19}$F was about 18 $\mu$s at $T = 4.2$ K and $\sim$63 $\mu$s at 1.5 K for all over the spectrum. Figure 4 shows the longitudinal relaxation rate $T_1^{-1}$ of $^{19}$F nuclei in the magnetic field 4.3 kG in the temperature range 1.5 – 4.2 K. The $T_1^{-1}(T)$ behavior is clearly exponential and can be well described by the function $T_1^{-1} \sim \exp(\Delta/T)$ with $\Delta = 9.3(4)$ K = 6.5(3) cm$^{-1}$. Such temperature dependence of the nuclear longitudinal relaxation for ligands with I = 1/2 is typical for Van-Vleck paramagnets [16] and is governed by the fluctuating magnetic field created by the Van-Vleck ion at ligands sites at temperatures when the excited electronic energy levels become populated. The parameter $\Delta$ in this dependence is equal to the splitting between the ground and first excited states of the Van-Vleck ion. Thus, the splitting between two lowest electron states of Tm$^{3+}$ ion in TmF$_3$ obtained from the high frequency EPR is confirmed by $^{19}$F NMR measurements.

Our attempts to observe $^{169}$Tm NMR signal at helium temperatures were not successful, most likely due to extremely short transverse relaxation time of $^{169}$Tm nuclei.

### 4. Conclusion

The results of the present work give unambiguous evidence that TmF$_3$ is a Van Vleck paramagnet. Both $^{19}$F NMR and Tm$^{3+}$ high frequency EPR measurements give the same splitting between the ground state and lowest excited level of Tm$^{3+}$ ion: $\Delta \sim 6.5$ cm$^{-1}$.

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