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Ultrahigh-frequency NMR of Tm^{3+} ions in single crystals of thulium ethylsulfate at high magnetic fields

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Abstract

Resonant transitions predicted earlier between low-lying electron–nuclear sublevels of the Tm^{3+} ground state were observed at frequencies up to 700 MHz in a dielectric Van Vleck paramagnet—thulium ethylsulfate (TmES) single crystal. It is shown that, due to the distortion of the 4f-electron shell of rare-earth ion in an applied magnetic field, the parameters of electron–nuclear interaction become field dependent. Experimental results of second moment of Tm^{3+} enhanced NMR line in TmES are presented. The possible mechanisms of line broadening are considered, particularly as a result of the first excited doublet splitting.

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1. Van Vleck (polarization) paramagnetism is most often observed in crystals containing non-Kramers rare-earth (RE) ions, i.e., RE ions with an even number of electrons in the unfilled 4f shells. The crystal electric field removes degeneracy of the ground multiplet of these ions to generate Stark splitting on the order of 10–100 cm^{-1}. In this case, the ground $^{2S+1}L_J$ electronic state is a singlet or a nonmagnetic doublet, so that all magnetic properties of Van Vleck (VV) paramagnets are caused by the Zeeman effect, which, as a rule, can be calculated using second-order perturbation theory [1,2].

However, in rather strong magnetic fields, conditions for the applicability of the perturbation theory are broken, and a number of new physical effects arises [3]. Among them, field-induced structural phase transitions in the dielectric VV paramagnets $TmPO_4$ [4] and $LiTmF_4$ [5] and the appearance of bound 4f-electron–phonon excitations in thulium ethylsulfate crystals $Tm(C_2H_5SO_4)_2 \cdot 9H_2O$ (TmES) [6] are noteworthy. Strong magnetic fields also give rise to the coupled 4f-electron–nuclear states in dielectric VV paramagnets [3,7].

It should be noted that the transition frequencies between the electron–nuclear sublevels of the singlet ground state in TmES crystals fall, practically, within the EPR X-band, whereas the transition probabilities are induced by the matrix elements of nuclear spin operators. In this

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