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PARAMAGNETIC RELAXATION PROCESSES IN $Al(NO_3)_3 \cdot 9H_2O : Fe^{3+}$ *SINGLE CRYSTALS AT HELIUM TEMPERATURES*

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Spin-lattice relaxation, spin-spin cross relaxation, and a discrete saturation effect were investigated experimentally at liquid helium temperatures in aluminum nitrate single crystals containing paramagnetic iron ion impurities. The dependence of the relaxation processes and of the discrete saturation effect on the concentration of Fe^{3+} ions was investigated in a wide range of concentrations.

CRYSTALS of aluminum nitrate with iron ion impurities were used by Hughes and Richards[1,2] as the working substance of a maser operating in zero magnetic field. This maser was pumped at a frequency of 23.7 GHz and it emitted at a frequency of 9.35 GHz. Hughes and Richards demonstrated that an aluminum nitrate maser was a good frequency standard capable of producing a few hundreds of microwatts and having a fairly high stability.

Since there are no published data on the electron paramagnetic resonance and relaxation in aluminum nitrate, we investigated the EPR spectrum and relaxation processes in a wide range of Fe^{3+} ion concentrations. The measurements were carried out on a superheterodyne spectrometer operating at 9.35 GHz and using transitions corresponding to various values of the magnetic field H, including zero field. The relaxation times were determined by the conventional method of pulse saturation at liquid helium temperatures. The nature of broadening of the EPR lines (uniform or nonuniform) and its relationship with the relaxation processes were determined by investigating also the discrete saturation effect.[3-6] This was done by pulse saturation of a line and a simultaneous magnetic sweep.

Our investigation of the EPR spectrum showed that the $Al(NO_3)_3 \cdot 9H_2O : Fe^{3+}$ lattice had two magnetically nonequivalent positions of the Fe^{3+} ions and the spectrum was described approximately by the Hamiltonian

$$\mathcal{H} = g\beta HS + D[S_z^2 - {}^1/_3 S(S+1)] + E(S_x^2 - S_y^2)$$

with the constants S = 5/2, g = 1.98, D = 3.7 GHz, E = 0.6 GHz. The relaxation and the line profile were investigated in the H ∥ z orientation, where z is the direction of the crystal axis for one of the nonequivalent ions. Our measurements showed that the spin-lattice relaxation times T_1, corresponding to the slow exponential relaxation (in the majority of cases we obtained double exponential curves), depended on the concentration of the Fe^{3+} ions and this dependence was different for different transitions. These results, obtained at a temperature of 1.7°K, are presented in Fig. 1. The same figure includes the concentration dependence of the EPR line width Δ for the M = –5/2 ⟷ –3/2 transition. The dependence Δ(f) for the other transitions was similar to that shown in Fig. 1. The concentration f was deduced from the concentration of the Fe^{3+} ions in the original charge, measured relative to the number of Al^{3+} ions.

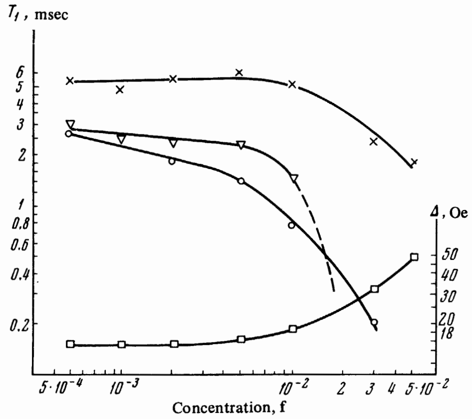

FIG. 1. Dependences of the spin-lattice relaxation time T_1 for different transitions and the dependence of the line width Δ for the M = –5/2 ↔ –3/2 transition on the concentration f of Fe^{3+} ions at 1.7°K. ×) T_1(f), M = ±3/2 ↔ ±1/2, H = 0; ▽) T_1(f), M = 1/2 ↔ –1/2, H = 3400 Oe; ○) T_1(f), M = –5/2 ↔ –3/2, H = 1500 Oe; □) Δ(f), M = –5/2 ↔ –3/2.

Figure 1 shows that the strongest dependence T_1(f) was observed for the M = 1/2 ⟷ –1/2 transition and the weakest dependence was found for the ±1/2 ⟷ ±3/2 transition in zero magnetic field. The efficiency of the spin-spin cross relaxation processes, occurring between the levels corresponding to the fast exponential component at the beginning of relaxation, was found to increase rapidly with increasing concentration, beginning from f = 10^{-2}. The dependences Δ(f) and T_1(f) for different transitions appeared at approximately the same value of f.

A special feature of the relaxation of the M = ±1/2 ⟷ ±3/2 transition was that, even at the highest concentrations (f = 5×10^{-2}) used in our experiments, there was no cross relaxation between the levels and the relaxation curve was of the single-exponential type with a time constant T_1.

In the course of our investigation we detected a strong discrete saturation effect. This effect was observed only for the M = 1/2 ⟷ –1/2 transition at low concentrations. Figure 2 shows an oscillogram of a line for a sample with f = 5×10^{-4}, which was obtained by satura-

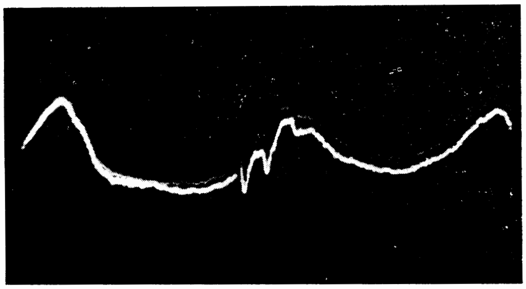

FIG. 2. Oscillogram of a line (M = 1/2 ↔ −1/2 transition, $f = 5 \times 10^{-4}$) in the case of saturation with a short power pulse and a simultaneous 50 Hz magnetic field sweep at 1.7°K.

tion with a short pulse accompanied by a simultaneous magnetic sweep.

It was important to note that "holes" in the spectrum had a complex fine structure which depended on the angle between H and z. We assumed that these "holes" were due to saturation of the superhyperfine structure sublevels (this structure was associated with the interaction of the Fe^{3+} ions with the surrounding paramagnetic nuclei of aluminum and nitrogen and with protons). The fine structure of the "holes" was evidently due to the quadrupole interaction of paramagnetic nuclei with the crystal field. We observed an equidistant shift of the whole system of "holes" which followed the motion of the saturating pulse along the EPR line profile. This effect could be explained by a nonuniform broadening of the line due to a scatter of the directions of the z axis of the crystal field in a sample.

The relaxation curve for the $f = 5 \times 10^{-4}$ concentration was described by a single exponential function and it corresponded to the spin-lattice relaxation of a single spin packet.

When the concentration was increased to $f = 10^{-3}$, the fine structure of the "holes" disappeared. At the same time a fast exponential component appeared in the relaxation curve. This component corresponded evidently to the spin diffusion within the line which made it more difficult to observe the discrete saturation effect. When the concentration of iron was increased still further, the discrete saturation effect disappeared completely and the diffusion processes were completed within the duration of the saturating pulse.

Thus, using the conventional pulse saturation method and the method for the observation of the discrete saturation effect, we established that the spin-relaxation time of Fe^{3+} ions in $Al(NO_3)_3 \cdot 9H_2O$, determined for various transitions, depended considerably on the concentration of Fe^{3+}. Moreover, a large contribution to the relaxation was made also by the concentration-dependent processes of the spin diffusion within the line and by the spin-spin cross relaxation in a multilevel system. The discrete saturation effect, associated with the superhyperfine interaction of the Fe^{3+} ions with paramagnetic nuclei, depended strongly on the concentration and it appeared only at low concentrations of paramagnetic ions when the electron dipole interactions became negligible.

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