Temperature dependence of the dipole-dipole width of the ESR line in a dilute paramagnet in the case of strong spin polarization

I. N. Kurkin and K. P. Chernov
V. I. Ul'yanov-Lenin State University, Kazan

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It is shown experimentally for the first time that in dilute paramagnets the dipole-dipole width of an ESR line increases with decreasing temperature in the case of strong spin polarization.

The dipole-dipole line width of the electron spin resonance, ΔH_{dd}, generally does not depend on the temperature, since the so-called high-temperature approximation $kT > g\beta HS$, in practice, is usually achieved; i.e., the Zeeman splitting of $g\beta HS$ is smaller than the temperature T of the sample and the spin sublevels are populated nearly equally. It is thus clearly of interest to carry out experimental studies of ΔH_{dd} in the low-temperature approximation ($kT < g\beta HS$), i.e., under conditions of high spin polarization p, since ΔH_{dd} can be assumed to change in this case because of the preferential population of the lower spin sublevels.

In concentrated paramagnets the position and shape of the ESR line were studied previously both experimentally and theoretically under the condition $kT < g\beta HS$ (see, e.g., Ref. 1). The width of the ESR line was found to decrease substantially with decreasing temperature, in agreement with the theory which states that in the case of a concentrated paramagnet the line width contains a temperature factor $f(T) = \sqrt{1-p^2}$.

Dilute paramagnets differ fundamentally from concentrated paramagnets because the difference in the local magnetic fields of single paramagnetic ions is determined not only by the spin distribution in the energy levels but also by their random distribution in the lattice sites. It was shown theoretically[2] that this difference accounts for the fact that at $kT < g\beta HS$ a dilute paramagnet (in contrast with a concentrated paramagnet) should, on the contrary, exhibit an increase in ΔH_{dd}, because at $kT < g\beta HS$ the spins

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are parallel to each other and their local fields increase but remain randomly distributed. The case with $S = 1/2$, for which ΔH_{dd} should not change with the temperature or at $kT < g\beta HS$, is an exception. The temperature dependence of dipole-dipole ESR line width has also been recently analyzed theoretically in Refs. 3 and 4. The theory has been tested experimentally in Ref. 5, but only for the case with $S = 1/2$. The case with $S > 1/2$, which is a more general case of greater fundamental importance, has heretofore not been studied experimentally. In this letter we report the results of an experimental study of this case.

As a test sample we chose a $LiYF_4$ single crystal which was activated by Gd^{3+} ions with a spin $S = 7/2$. The large spin and the splitting of the spin sublevels in the absence of a magnetic field, which has the value ~ 1 cm^{-1}, account for the Zeeman splitting of ~ 4.5 cm$^{-1} \equiv 6.5$ K in an easily attainable magnetic field of ~ 7 kG (Ref. 6) and a reasonably high polarization ($p = 0.6$) at an easily attainable temperature $T = 1.6$ K. The Gd^{3+} ions were substituted for the position Y^{3+} in the $LiYF_4$ crystal. The isovalent substitution and approximately the same ionic radius make it possible to introduce a very high concentration of Gd^{3+} ions into $LiYF_4$ crystal. We have studied two $LiYF_4$ crystals with different concentrations of Gd^{3+} ions, 0.08 and 2.0%.

The ESR spectrum was studied at a frequency of ~ 9.4 GHz over a temperature range 1.6–4.2 K with use of a superheterodyne spectrometer. The ESR absorption signal was recorded on a chart recorder and the width of this signal at half-maximum ($\Delta H_{1/2}$) was measured. We obtained the following results.

In the $LiYF_4 + 0.08\%$ Gd^{3+} sample the width of the ESR lines, which does not depend on the temperature, is ~ 15 G and these lines have an approximately Gaussian shape.

In the $LiYF_4 + 2\%$ Gd^{3+} sample the width of the ESR lines is ~ 120 G at 4.2 K and they have an approximately Lorentzian shape. We assume that the width of the ESR lines in this sample is determined primarily by the dipole-dipole interactions of Gd^{3+} ions for the following three reasons: 1) $\Delta H_{1/2}$ increases with increasing density of Gd^{3+} ions, 2) the shape of the line changes from a Gaussian to Lorentzian, and 3) the measured line width is in good agreement with the value calculated from an equation for the dipole-dipole width. According to Ref. 7, $\Delta H_{dd} = 7.6 g\beta n\sqrt{S(S+1)}$, where n is the density of Gd^{3+} ions per cm^3. Since 2% of Gd^{3+} corresponds to 2.8×10^{20} ions/cm^3, a calculation gives us $\Delta H_{dd} \sim 160$ G.

Figure 1 is a plot of the temperature dependence of ΔH_{dd} for the Gd^{3+} ion in the $LiYF_4 + 2\%$ Gd^{3+} sample. We see that ΔH_{dd} increases appreciably with decreasing temperature. Also shown in this figure for comparison are data on ΔH in the $LiYF_4 + 0.08\%$ Gd^{3+} sample for the same transition. We see that in the absence of dipole broadening the line width remains constant as the temperature is varied.

In this letter we have thus shown experimentally that in the case of strong spin polarization (i.e., at $kT < g\beta HS$), the dipole-dipole width of the ESR line (ΔH_{dd}) increases in dilute paramagnets as the temperature is lowered. Such a behavior, which was predicted theoretically by Al'tshuler and Mokeev,[2] differs fundamentally from the concentrated paramagnets in which ΔH_{dd} decreases at $kT < g\beta HS$.

A more detailed information about the dipole-dipole width of ESR lines in dilute

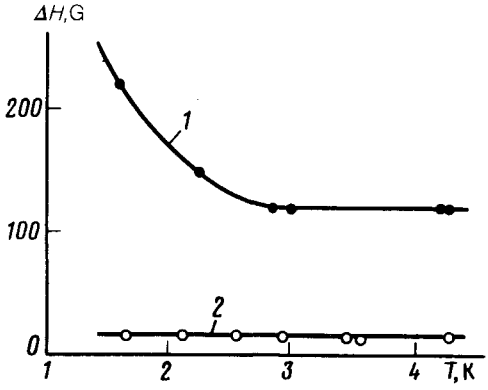

FIG. 1. Temperature dependence of the width of the ESR line of a Gd^{3+} ion in $LiYF_4$ single crystals. $\nu = 9.4$ GHz, $H_0 \perp C$, $H_0 = 6.75$ kG, transition $\langle -7/2| - 5/2\rangle$. 1—2% Gd^{3+}; 2—0.08% Gd^{3+}.

paramagnets in the case of strong spin polarization can be obtained through further experimental studies (the study of ΔH_{dd} in stronger magnetic fields, in different Zeeman transitions, and at different orientations of the external magnetic field) and further theoretical studies (quantitative calculations of experimental data).

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