CONTRIBUTION TO THE THEORY OF SPIN-LATTICE RELAXATION IN CRYSTALS WITH PARAMAGNETIC IMPURITIES

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The effect of inhomogeneous EPR broadening on relaxation of nuclei in crystals with magnetic impurities is discussed. It is shown that the concentration dependence of the relaxation rate agrees with the experimental data.

As is well known,[1,2] the relaxation of nuclei in diamagnets having a small amount of paramagnetic ions is determined by its coupling with the electron spins of the impurity ions, and for sufficiently low temperatures and not very small concentrations of the impurity, the major role is played by the electron spin-spin interaction (the so-called dipole-dipole reservoir (DDR)).

A detailed consideration of the relaxation of nuclei with account of the role of DDR for homogeneous EPR line broadening of the magnetic ions is given in[2,3]. However, the so-called inhomogeneous EPR line broadening is usually observed in the experiment.[4] In this case, the relaxation of nuclei without account of DDR has been considered in[5]. In the present paper it is shown that the presence of DDR can change the picture of nuclear relaxation considerably.

For inhomogeneous broadening, the magnetic field H_i acting on the electron spin, located at the i-th node, is the sum of two fields: $H_i = H_0 + H_i^*$, where H_0 is the applied constant field, H_i^* the local field, which usually satisfies the condition $\sum_i H_i^* = 0$.

In such a situation, the exchange of energies between the different spins is usually difficult, inasmuch as they have different Larmor frequencies. But if the time of the spin-lattice relaxation is sufficiently large, the case is possible in which the exchange of energies among all the different spins manages to occur. As a result of this, the number of parameters characterizing the spin system is decreased, and a quasi-equilibrium state is established for which one can represent the electron spin system, following[6], as the combination of two subsystems: the Zeeman subsystem, with Hamiltonian

$$\mathscr{H}_z = \omega_0 \sum_i S_i^z$$

and the reservoir of local fields (RLF) with energy

$$\mathscr{H}_d = \sum_i \omega_i S_i^z + \mathscr{H}_{SS}, \quad \omega_i = \gamma_S H_i^*,$$

where S_i^α is the electron spin operator (α = x, y, z), $\mathscr{H}_{SS}$ the secular part of the dipole-dipole (d – d) interaction. The basis for this splitting into subsystems is the fact that, first, $\mathscr{H}_z$ commutes with $\mathscr{H}_d$ and second, in the high temperature limit, $\mathscr{H}_z$ and $\mathscr{H}_d$ can be expressed in terms of independent collective variables.

In fact, we consider the Fourier expansion

$$S_i^\alpha = \sum_q e^{iqr_i} S_q^\alpha.$$

It is easy to show that

$$\mathscr{H}_z \sim S_{q=0}^z, \quad \sum_i \omega_i S_i^z \sim S_{q\neq 0}^z, \quad \mathscr{H}_{SS} \sim (S_{q=0}^z)^2, \quad S_{q\neq 0}^\alpha.$$

Thus, at high temperatures, when one can neglect the term $(S_{q=0})^2$ (as also in the case of uniform broadening), $\mathscr{H}_z$ and $\mathscr{H}_d$ depend on the independent collective variables $S_{q=0}^z$ and $S_{q\neq 0}^\alpha$, respectively, and therefore one can be characterized in general by different reciprocal temperatures β_z and β_d. In such a model, the inhomogeneous line behaves at saturation like a homogeneous line with width Δ^* (Δ^{*2} is the second moment of the inhomogeneous line).

If the exchange of energy between spins takes place within the spin-relaxation time in the spin system only inside separate groups, in which the spins possess close Larmor frequencies, then independent holes burning at different frequencies is possible in the inhomogeneous lines and the description of the saturation requires the introduction of many temperatures. In such cases, it is no longer possible to separate the general Zeeman subsystem, inasmuch as it is not possible to express $\mathscr{H}_z$ and the RLF for spins of the separate groups in terms of the independent variables ($\Sigma\omega_i = 0$ and contains $S_{q=0}^z$ in first degree if the summation is carried out over spins of one definite group). Therefore, for the description of the inhomogeneous broadening in this case, it is convenient to use the so-called "spin-packet" model,[4] in which a characteristic temperature corresponds to each packet and a single DDR is also introduced.[5,7]

We proceed to the consideration of the spin-lattice relaxation of nuclei. In the spin-packet model, the picture of relaxation with DDR participation is practically the same as in the homogeneous broadening. In the two-temperature model, the character of the relaxation is different, since the role of DDR here is played by the RLF. Actually, the rate of direct spin-lattice relaxation $1/T_N$ is proportional to $\varphi(\omega)$[2]—the Fourier transform of the correlator

$$\varphi(t) = \mathrm{Sp}(S_i^z S_i^z(t)) \,/\, \mathrm{Sp}(S_i^z)^2,$$

while the term $\sum_i \omega_i S_i^z$ gives the contribution only in the fourth moment of the function $\varphi(\omega)$. Just as in exchange interaction, which narrows down the absorption line of magnetic resonance, this term, for

$$\Delta^{*2} \gg \omega_{SS}^2 = \mathrm{Sp}\mathscr{H}_{SS}^2 / \mathrm{Sp}\left(\sum_i S_i^z\right)^2,$$

also "narrows down" $\varphi(\omega)$.

A simple calculation gives

$$\frac{M_4}{3M_2^2}=\frac{2\Delta^{*2}}{3M_2}+\left(\frac{M_4}{3M_2^2}\right)_0, \quad M_n=\int_{-\infty}^{+\infty}\omega^n\varphi(\omega)\,d\omega. \tag{1}$$

The expression $(M_4/3m_2^2)_0$ is computed in[8] and represents the contribution of uniform broadening in nuclear relaxation. If $M_4/3M_2^2 \gg 1$ (this is possible either for $\Delta^{*2}/\omega_{SS}^2 \gg 1$ or for sufficiently dilute crystals, when $(M_4/3M_2^2)_0 \gg 1$), then $\varphi(\omega)$ can be approximated by a truncated Lorentzian form. The corresponding correlation time τ_S and the cutoff parameter α are determined by the expressions (we assume $(M_4/3M_2^2)_0 \gg 1$)

$$\frac{1}{\tau_S}=\frac{\pi M_2}{2\sqrt{6}}\left(\Delta^{*2}+\frac{\pi^2}{24}M_2^2\tau_{S0}^2\right)^{-1/2}, \tag{2}$$

$$\alpha=\sqrt{6}\left(\Delta^{*2}+\frac{\pi^2}{24}M_2^2\tau_{S0}^2\right)^{1/2}\gg\frac{1}{\tau_S},$$

where the homogeneous width

$$\frac{1}{\tau_{S0}}=\frac{\pi\sqrt{M_2}}{6}\left(\frac{M_4}{3M_2^2}\right)_0^{1/2}$$

is computed in explicit form in[9]. If

$$\Delta^{*2}\gg\frac{\pi^2}{24}M_2^2\tau_{S0}^2, \tag{3}$$

then

$$\frac{1}{\tau_S}=\frac{\pi}{\sqrt{6}}\frac{M_2}{\Delta^*}\ll\frac{1}{\tau_{S0}}. \tag{4}$$

The latter circumstance leads to an increase in the time of establishment of equilibrium between the nuclear Zeeman subsystem (NZS) and the DDR in comparison with the case of homogeneous EPR broadening and the corresponding delay of the spin-lattice relaxation of the nuclei in the absence of "heating" of DDR.

If the DDR heating is important, then the relaxation time of the nuclei T_N is determined by the formula

$$\frac{1}{T_N}=\frac{S(S+1)}{I(I+1)}\frac{f(\Delta^{*2}+\omega_{SS}^2)}{\omega_I^2}\frac{1}{T_{dL}}, \tag{5}$$

where S is the spin of the ion, I the spin of the nucleus, f the impurity concentration, and ω_I the nuclear Zeeman frequency. Inasmuch as $\omega_{SS} \approx 1/\sqrt{f}\,\tau_{S_0}$, the case is possible for which $1/\tau_{S_0} \ll \Delta^* \ll \omega_{SS}$ and inhomogeneous broadening does not affect the spin-lattice relaxation of the nuclei, although it exceeds the homogeneous broadening. Generally speaking, Equation (5) leads to a concentration dependence of T_N that differs from the homogeneous case. Inasmuch as $M_2 \approx \omega_{SS}^2 \sim f$ for randomly distributed impurities, we obtain

$$\frac{1}{T_N}=\begin{cases} f & \text{if } \omega_{SS}^2\ll\Delta^{*2} \\ f^2 & \text{if } \omega_{SS}^2\gg\Delta^{*2}\end{cases} \tag{6}$$

while for homogeneous broadening ($\Delta^* \ll \omega_{SS}$) $1/T_N \propto f^2$ always. In the experiments of the Leiden group[9] for sufficiently small f, the dependence is $1/T_N \propto f$, while for large f, the dependence is $1/T_N \propto f^2$ which is in qualitative agreement with Eq. (6).

Finally, we note that the inequality (3) first, does not depend on f (this is evidently connected with the fact that for small f, both M_2 and M_4 depend linearly on the concentration) and, second, it is stronger than the inequality $\Delta^{*2} \gg \omega_{SS}^2$. For this reason, the case is possible in which one can neglect the contribution of inhomogeneous broadening in the direct relaxation of nuclei, but at the same time, its account is significant under conditions of DDR heating.

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