EFFECT OF MAGNETIC RESONANCE SATURATION ON CROSS RELAXATION

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The theory developed by Provotorov [1-4] is utilized to ascertain the possibility of inhibiting cross relaxation in a spin system. Calculations have shown that in the case of a sufficiently large shift Δ_1 of the frequency of the field saturating the first kind of spins in the direction away from the resonance of spins of the second kind, the spin interaction energy is altered in such a manner that the transfer of high frequency energy to spins of the second kind by means of cross relaxation turns out to be impossible. The spins of the second kind remain in equilibrium with the lattice or even "cool off." Very simple estimates show that the effect should be measurable.

IN the recent papers of Provotorov [1-4] it is shown that in analyzing phenomena in solid-state spin systems one should take into account the possibility of a change in the average energy of interaction between the spins in a number of processes such as, for example, the saturation of magnetic resonance and cross relaxation. Since the interaction energy between the spins interconnects all types of spins and all the transitions in the system, a certain additional mutual interdependence is established between all the processes that occur involving this interaction energy.

The present note is devoted to the naturally arising question—whether it is possible, in particular, to suppress cross relaxation between two given transitions if the frequency of the saturating field is shifted by a definite amount from the resonance frequency. From physical considerations it is clear that such a frequency shift, for example to the left of resonance, should by diminishing the average interaction energy of the spins stimulate cross relaxation involving a transfer of energy from right to left and, conversely, should suppress cross relaxation involving transfer of energy from left to right; a shift of frequency of the saturating field to the right should, evidently, give the opposite results.

Calculations and estimates are particularly simple in the case of the spin system investigated in [2] which consists of two kinds of magnetic moments of nearly equal magnitude; their numbers, their resonance (Larmor) frequencies, and their spin-lattice relaxation times are respectively given by N_1 and N_2, ω_1 and ω_2, and $T_1^{(1)}$ and $T_1^{(2)}$.

We assume that all the conditions for the validity of the system of equations (16) from [2] are satisfied, and we solve it in the stationary case for the quantity β which is proportional to the difference in the populations of the levels of the second kind of spins; the frequency of the high frequency field saturating the first kind of spins is $\omega = \omega_1 + \Delta_1$. We assume that ω_1 and ω_2 are sufficiently large and that therefore cross relaxation is significant only between the first and the second kinds of spins, i.e., when the Zeeman energy changes by an amount $\pm h\Delta_{21}$ (which is compensated by a corresponding change in the average energy of the interaction of the spins); the relaxation time characterizing this process is T_{12}; we neglect the cross relaxation which involves the direct conversion of the Zeeman quanta $h\omega_{1,2}$ into interaction energy.

We quote the expression for $(\beta - \beta_0)/\beta_0$ —the relative change in the difference of populations of levels of the second kind of spins in the case when saturation is obtained at a frequency ω (β_0 refers to equilibrium with the lattice):

$$(\beta - \beta_0)/\beta_0 = (\Delta N_2 - \Delta N_2^0)/\Delta N_2^0 = -\frac{\omega_1 + \Delta_1}{\omega_1 + \Delta_{21}} \times \frac{\Delta_1\Delta_{21} + H_{\mathrm{loc}}^2\left(\gamma_1^2 + \gamma_2^2 N_2/N_1\right) T_1^{(1)}/T_1''}{[\Delta_1^2 + H_{\mathrm{loc}}^2(\gamma_1^2 + \gamma_2^2 N_2/N_1)\, T_1^{(1)}/T_1''](1 + N_2 T_{12}/N_1 T_1^{(2)}) + (\Delta_1 - \Delta_{21})^2 N_2 T_1^{(1)}/N_1 T_1^{(2)}}. \tag{1}$$

Here γ_1, γ_2 are the gyromagnetic ratios for the first and second kinds of spins; H_{loc} is the local magnetic field in the sample; T_1'' is the spin-lattice relaxation time for the average energy of the spin-spin interaction[1-4].

We see that the traditional result of cross relaxation—"heating" of the spins of the second kind (a decrease in the difference of populations of their levels, $\beta < \beta_0$) as a result of the saturation of spins of the first kind—is obtained only in the case when the frequency ω_1 of the saturating field is shifted in the direction towards the resonance frequency ω_2 for the second kind of spins ($\Delta_1\Delta_{21} \geq 0$), or if it is shifted by a small amount in the opposite direction; such "heating" can, naturally, be prevented by a rapid spin-lattice relaxation of the spins undergoing heating ($T_1^{(2)}N_1/N_2 \ll T_{12}, T_1^{(1)}$).

However, if the frequency ω is shifted by a sufficiently large amount from its resonance value ω_1 in the other direction from ω_2, so that the product $\Delta_1\Delta_{21}$ attains its limiting value

$$(\Delta_1\Delta_{21})^{\lim} = -H_{loc}^2(\gamma_1^2 + \gamma_2^2 N_2/N_1)\, T_1^{(1)}/T_1'', \tag{2}$$

then the difference of populations of the second kind of spins remains at its equilibrium value ($\beta = \beta_0$), and this manifests itself as a cessation of cross relaxation. When $\Delta_1\Delta_{21} < 0$ and $|\Delta_1\Delta_{21}| > |(\Delta_1\Delta_{21})^{\lim}|$, the spins of the second kind are "cooled" ($\beta > \beta_0$).

It is essential to note that condition (2) does not require that saturation be reached; it can be obtained directly from the system (16) of [2] and guarantees the "passage through zero" of cross relaxation independently of the level of the power absorbed at the frequency ω.

In order to obtain a more direct interpretation of the above result we can imagine that the spins of the second kind have been removed from the system; the consequences of saturation can be probed, for example, by a weak high-frequency field, thereby achieving double resonance[3,4]. The required formulas can be obtained either from the equations for one kind of spins[1,3,4], or from formulas (1) and (2) with $N_2/N_1 \to 0$. If the saturating field deviates from resonance ω_0 by Δ_1, then the nature of the simultaneous change in the magnetization of the spins (the difference in populations of their levels) and of the average energy of their interaction is such that on the other side from resonance the limit $\omega_0 + \Delta_2^{\lim}$ for the "heating" of the spins is produced:

$$\Delta_1\Delta_2^{\lim} = -H_{loc}^2\gamma^2 T_1/T_1''.$$

When the frequency of the weak field ω is equal to $\omega_0 + \Delta_2^{\lim}$ the probing will not show any deviation from equilibrium with the lattice, while for $|\omega - \omega_0| > |\Delta_2^{\lim}|$ it will show a "cooling" (the absorption signal will turn out to be larger than the equilibrium one). It is true that it may be more difficult to obtain an indication of "cooling" because the transition probability decreases in the skirts of the magnetic resonance line. Perhaps it is just because of this that experimentally so far a shift of the maximum of the nuclear magnetic resonance line has been observed only in the direction opposite to the shift of the saturating field[3-5]. From this point of view a cessation of the transfer of energy by means of cross relaxation to the second kind of spins when the saturating field is detuned appears to be more accessible to observation. It is necessary to guarantee only that the broadening of the line as a result of the interaction of spins should predominate over inhomogeneous broadening (for example, over the consequences of the scatter in the values of the parameters).

We give some estimates. We introduce the notation $\gamma_1^2 + \gamma_2^2 N_2/N_1 = k^2$; $H_{loc} \sim \mu/r^3 \sim \mu n$, where n is the number of spins per cm^3. For electron spins in the case $N_1 \sim N_2$ we have $k^2 \sim 2 \times 10^{13}$. Taking $n \sim 10^{20}\ cm^{-3}$ (which corresponds to $H_{loc} \sim 1$ Oe we obtain

$$|(\Delta_1\Delta_{21})^{\lim}| \sim 2 \cdot 10^{13} T_1^{(1)}/T_1''.$$

The ratio $T_1^{(1)}/T_1''$ in the case of electron paramagnetic resonance remains the least clear. Evidently, a sufficiently large value of $T_1^{(1)}/T_1''$ (which denotes that the average energy of interaction practically retains its equilibrium value) leads to the disappearance of the effects under consideration. In the case of nuclear resonance experiments[6,7] give good confirmation for the value $T_1/T_1'' \sim 2$ which is based on simple considerations with respect to the relaxation of the interaction energy by means of relaxation of individual spins. If the same value for the ratio T_1/T_1'' is also adopted for electron paramagnetic resonance, then we have

$$|(\Delta_1\Delta_{21})^{\lim}| \sim 4 \cdot 10^{13}\ \text{cps}^2.$$

We see that the product $|(\Delta_1\Delta_{21})^{\lim}|$ has turned out to be small, and in usual crystals with the spin density assumed earlier one can suppress cross relaxation between sufficiently close transitions (whose probability is sufficiently great) by means of a very small amount of detuning of the saturating field.[1)]

[1)]In increasing $|\Delta_1|$ we are limited not only by experimental difficulties in obtaining saturation, but also by the conditions required for the validity of Provotorov's procedure, i.e., $H_1 \ll H_{loc}$, where H_1 is the amplitude of the saturating field.

We also estimate the degree of "cooling" of the second kind of spins in the case $|\Delta_1| > |\Delta_1^{\lim}|$. For example, let $|\Delta_{21}| = 4 \times 10^7$ cps. Then under our conditions $|\Delta_1^{\lim}| = 10^6$ cps. We utilize the condition $T_{12} \ll T_1^{(2)} \sim T_1^{(1)}$. Then it follows from (1) that a shift of the saturating field away from resonance within the range between 2×10^6 cps and 5×10^6 cps will lead to a relative "cooling" (an increase in the difference of populations of the levels) of the second kind of spins from 2.5 to 10%.

We note in conclusion that a corresponding detuning of the saturating field could possibly aid in the reestablishment of an inversion in the populations of spin levels in crystals with a high concentration of paramagnetic ions if the inversion has disappeared as a result of cross relaxation.

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