

Statistical theory of the relaxation of a spin-spin reservoir

E. K. Khenner

Perm State Pedagogical Institute

I. G. Shaposhnikov

Perm State University

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The spin-lattice relaxation of the spin-spin interaction reservoir in solids is considered. The rates of the indicated relaxation directly to the lattice and via fast-relaxing centers are computed. In the first case the rate does not depend on the concentration of the paramagnetic centers, and is of the same order of magnitude as the normal spin-lattice relaxation rate; in the second, it increases with the concentration, and can be significantly higher than the normal rate. The concentration in $\text{Cr}^{3+}:\text{Al}_2\text{O}_3$ of the exchange-coupled Cr^{3+} ion pairs, which, as fast-relaxing centers, can guarantee the observed spin-lattice relaxation rates, is estimated.

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1. The concept of spin temperature has turned out to be extremely fruitful in the theory of magnetic resonance. It became clear in the course of its development that, in solids, during a short period of time (much shorter than the spin-lattice relaxation time), quasi-equilibrium is in many cases established not in the entire spin system, but in parts of it: the Zeeman reservoir, the dipole-dipole reservoir, etc. The spin-lattice relaxation (SLR) of the spin-spin interaction reservoir determines many NMR parameters¹ and EPR parameters under saturation conditions,² as well as the mechanisms underlying the spin-lattice relaxation and the dynamical polarization of nuclei.

The existing theory of the SLR of the interaction reservoir is based either on the concept of fluctuating random fields, and essentially employs the single-particle approximation¹ and the correlation times, which are not determined by this theory, or on the method of moments,³ whose application to magnetically dilute systems is not always justified. In the present paper the statistical method is used to construct a theory of the relaxation of a spin-spin reservoir. After the derivation of the general relations, it is concretized to two mechanisms for the spin-lattice interaction: the direct transfer of the energy of the spin system to the lattice and the transfer of the energy to the lattice via fast-relaxing impurities. The results obtained are compared with the experimental data on the rate of the SLR of the spin-spin reservoir of the Cr^{3+} ions in ruby.⁴

2. Let us represent the Hamiltonian of the spin system in a solid in the form

$$H = H_S + H_{SS} + H_{SL} + H_L, \quad (1)$$

where H_S is the single-particle spin Hamiltonian, which describes the interaction of the spins with the constant magnetic and crystal fields, H_{SS} and H_{SL} are the spin-spin and spin-lattice interactions respectively, and H_L is the Hamiltonian of the lattice. If the spin system is brought out of a thermodynamic equilibrium characterized by the reciprocal temperature β_L , then, according to the fundamental hypothesis, there will be established over a short period of time in the single-

particle and secular spin-spin reservoirs quasiequilibria with reciprocal temperatures β_S and β_R . Their subsequent evolution can be described within the framework of the nonequilibrium statistical-operator method.⁵ In the high-temperature—with respect to the magnetic subsystems—approximation, we obtain with the aid of this method the following system of linear equations for β_S and β_R :

$$\begin{aligned} \dot{\beta}_S &= -(\dot{\beta}_S - \dot{\beta}_L)/\tau_{SL} - (\dot{\beta}_R - \dot{\beta}_L)/\tau_{SR}, \\ \dot{\beta}_R &= -(\dot{\beta}_S - \dot{\beta}_L)/\tau_{RS} - (\dot{\beta}_R - \dot{\beta}_L)/\tau_{RL}. \end{aligned} \quad (2)$$

The details of the procedure for deriving the relaxation equations by the indicated method are well known (see, for example, Ref. 6). The relaxation times entering into (2) have the form

$$\frac{1}{\tau_{SL}} = \frac{1}{2\langle H_S^2 \rangle} \int_{-\infty}^{\infty} \langle \{K_S(t)K_S(0)\} \rangle \quad (3)$$

and similarly for τ_{RL} , τ_{SR} , and τ_{RS} ; here

$$K_j(t) = \exp(iH_0 t) [H_{int}, H_j] \exp(-iH_0 t), \quad (4)$$

$$H_0 = H_S + H_R + H_L, \quad H_{int} = H_{SL} + H',$$

H' being the nonsecular part of H_{SS} .

Let us write the relaxation times in the energy representation. Let $\langle a|$ denote the states of the spin system; $\langle \alpha|$, those of the lattice. Denoting the sum of the diagonal matrix elements of a corresponding operator by $\langle \dots \rangle$, and using (4), we obtain

$$\frac{1}{\tau_{SL}} = \sum_{ab} (E_a^{(0)} - E_b^{(0)})^2 W_{ab} / 2 \sum_c E_c^{(0)2}, \quad (5a)$$

$$\frac{1}{\tau_{SR}} = \sum_{ab} (E_a^{(0)} - E_b^{(0)}) (\Delta E_a - \Delta E_b) W_{ab} / 2 \sum_c E_c^{(0)2}, \quad (5b)$$

$$\frac{1}{\tau_{RS}} = \frac{1}{\tau_{SR}} \sum_a E_a^{(0)2} / \sum_b \Delta E_b^2, \quad (5c)$$

$$\frac{1}{\tau_{RL}} = \sum_{ab} (\Delta E_a - \Delta E_b)^2 W_{ab} / 2 \sum_c \Delta E_c^2. \quad (5d)$$

Here the $E_a^{(0)}$ are the eigenvalues of H_S ; the ΔE_a , their shifts under the influence of H_R ; W_{ab} is the probability for transition, induced by the interaction H_{int} , from the state $\langle a|$ into the state $\langle b|$:

$$W_{ab} = \frac{2\pi}{\hbar} \left[\sum_{\alpha\beta} \exp(-\beta_L E_a) \langle \alpha\alpha | H_{in} | b\beta \rangle \right. \\ \left. \times \langle b\beta | H_{in} | \alpha\alpha \rangle \delta(E_a - E_b + E_a - E_b) \right] / \sum_{\alpha} \exp(-\beta_L E_a). \quad (6)$$

The formulas (5) are similar to the well-known Gorter formula, which gives the rate of relaxation of a spin system with a single spin temperature [(5a) goes over into the Gorter formula when $E^{(0)}$ is replaced by E]. The essentially many-particle character of such system as a spin-spin reservoir does not allow us to use the formula (5d) directly to compute the relaxation rate of the system.

3. The statistical method is based on the assumption that the many-particle-interaction-induced energy shifts with respect to the spin-pair-interaction-induced shifts are additive. Let us fix some spin j , and let $P(r_{jk})$ be the probability that the k -th site is occupied by a spin. Considering the interaction of the given spin with all the rest, and taking the indicated assumption into account, we obtain from (5d) the expression

$$\frac{1}{\tau_{RL}} = \sum_k P(r_{jk}) \sum_{cd} (\Delta E_c^{jk} - \Delta E_d^{jk})^2 W_{cd}^{jk} / 2 \sum_i P(r_{ji}) \sum_c (\Delta E_c^{ji})^2, \quad (7)$$

where c , d , and e number the states of the pair spectrum. Similarly, we can write down the expressions for τ_{SR}^{-1} and τ_{RS}^{-1} ; τ_{SL}^{-1} can be computed in the single-particle approximation if necessary.

It is well known¹ that, in a strong field, the rate of mixing of the single-particle and spin-spin reservoirs is so low that this process can be neglected in comparison with the spin-lattice relaxation. In other words, in a strong field, β_S and β_R relax independently in accordance with the equations (2) at the rates τ_{SL}^{-1} and τ_{RL}^{-1} respectively.

4. Let us consider the SLR of a spin-spin reservoir, assuming that the relaxation occurs through the individual uncorrelated spin "flips" with direct transfer of energy to the lattice. This process can be described with the aid of a dynamic spin Hamiltonian that, in the approximation linear in the strains, gives

$$W_{cd}^{jk} = \frac{8\pi^3}{\hbar\rho v^5} \Phi_{cd}^{jk} v^3 \frac{\exp(\hbar v \beta_L)}{\exp(\hbar v \beta_L) - 1}, \quad (8)$$

where ρ is the density, $v = 1/3(v_l + v_t)$ is the mean velocity of sound (v_l and v_t are the longitudinal and transverse velocities), ν is the transition frequency

$$\Phi_{cd}^{jk} = \frac{1}{3}(3\alpha_l^2 + 2\alpha_t^2) \Phi_{cd}^{(1)} + \frac{1}{15}(2\alpha_l^5 + 3\alpha_t^5) \Phi_{cd}^{(2)} + \frac{1}{15}(\alpha_l^5 - \alpha_t^5) \Phi_{cd}^{(3)}, \\ \alpha_l = \frac{\nu}{v_l}, \quad \alpha_t = \frac{\nu}{v_t}, \quad \Phi_{cd}^{(1)} = \sum_j | \langle c | A_{Tj}^{jk} | d \rangle |^2, \quad (9) \\ \Phi_{cd}^{(2)} = \sum_{10} | \langle c | A_{10}^{jk} | d \rangle |^2 \quad \Phi_{cd}^{(3)} = \sum_{10} \langle d | A_{Tj}^{jk} | c \rangle \langle c | A_{00}^{jk} | d \rangle.$$

The expression for the $A_{\gamma 0}^{jk}$ has the form

$$A_{\gamma 0}^{jk} = \frac{1}{2} \sum_{\alpha\beta} G_{\alpha\beta\gamma 0} (S_\alpha^j S_\beta^k + S_\beta^j S_\alpha^k + S_\alpha^k S_\beta^j + S_\beta^k S_\alpha^j), \quad (10)$$

where $G_{\alpha\beta\gamma 0}$ is the dynamical spin-phonon coupling tensor.

Let us carry out a detailed calculation of the relaxation of the dipole-dipole reservoir for Cr^{3+} ions in ruby

in zero field. In this case

$$H_s = \sum_j D \left[(S_j^z)^2 - \frac{1}{3} S(S+1) \right] \quad (11)$$

($S = 3/2$), and the single-particle spectrum consists of two doubly degenerate levels with energies $\pm D$ ($D < 0$). The secular part of the dipole-dipole interaction from the Hamiltonian (10), which is quadratic in the spin, has been derived by Abragam and Kambe⁸ for $S = 3/2$. In first order perturbation theory the indicated part almost completely lifts the degeneracy of the 16 states of a spin pair. The spin-phonon coupling tensor contains, when allowance is made for the local symmetry at the sites where the Cr^{3+} ions are localized, 10 independent elements⁹; in the Voigt notation

$$G_{11} = 4.57 \pm 0.03; \quad G_{12} = -1.94 \pm 0.3; \quad G_{33} = 6.40 \pm 0.13; \\ G_{44} = 1.97 \pm 0.13; \quad G_{45} = -0.43 \pm 0.13; \quad G_{46} = -0.63 \pm 0.30; \\ G_{25} = \pm 1.50 \pm 0.2; \quad G_{52} = \pm 1.43 \pm 0.03; \quad G_{16} = G_{43} = 0$$

(in cm^{-1} ; the signs \pm in G_{25} and G_{52} correspond to the two magnetically nonequivalent positions of the Cr^{3+} ions). The indicated values together with

$$v_l = (10.81 \pm 0.03) \cdot 10^3, \quad v_t = (6.35 \pm 0.03) \cdot 10^3 \text{ cm/sec}, \\ \rho = 3.99 \text{ g/cm}^3, \quad |2D| = 0.38 \text{ cm}^{-1}$$

allowed us to obtain a good agreement between the computed and the experimentally obtained values for the rate of the normal spin-lattice relaxation of Cr^{3+} ions in ruby in zero field.

To find τ_{RL}^{-1} from the formula (7), we need to carry out the fairly tedious calculation of the probabilities (8) of the transitions in the spin-pair spectrum, using the formulas (10) and (11). After the substitution of these probabilities into (7) and the computation of the sums over the states, it becomes necessary to compute the lattice sums over the Cr^{3+} -ion localization sites. In the present single-particle mechanism of spin-lattice interaction, τ_{RL}^{-1} does not depend on the spin concentration. The lattice sums were evaluated both with allowance for the lattice structure and in the isotropic model (for the data on the structure, see Ref. 10). Allowance was also made for the fact that the ions coupled by strong exchange interactions ($\geq |D|$), and located within a sphere of radius smaller than some distance r_0 (r_0 is the exchange range) do not make a contribution to the dipole-dipole reservoir. The results can be represented in the form

$$\tau_{RL}^{-1} = \gamma_{RL} \exp(2|D|\beta_L) / [\exp(2|D|\beta_L) - 1], \quad (12)$$

where in the isotropic model $\gamma_{RL} = 0.46 \pm 0.10 \text{ sec}^{-1}$ irrespective of the value of r_0 , while when the structure is taken into account $\gamma_{RL} = 0.38 \pm 0.10 \text{ sec}^{-1}$ for $r_0 = 5 \text{ \AA}$, $\gamma_{RL} = 0.39 \pm 0.10 \text{ sec}^{-1}$ for $r_0 = 8 \text{ \AA}$, and $\gamma_{RL} = 0.40 \pm 0.10 \text{ sec}^{-1}$ for $r_0 = 12 \text{ \AA}$. The exchange zone can, in principle, be nonspherical, but, as simple model calculations show, this circumstance does not significantly change the value of τ_{RL}^{-1} . It can be seen from these results that τ_{RL} depends very weakly on the exchange-interaction range.

Of interest in applications is the ratio of the "normal" spin-lattice relaxation time τ_{SL} to the time τ_{RL} : $\xi = \tau_{SL} / \tau_{RL}$. The time τ_{SL} has been computed with the same parameter values by Bates *et al.*¹¹, and the re-

sults have been experimentally confirmed. If we represent τ_{SL} in a form similar to (12) with γ_{RL} replaced by γ_{SL} , then $\gamma_{SL} = 0.54 \pm 0.14 \text{ sec}^{-1}$ at low Cr^{3+} concentrations, at which τ_{SL} does not depend on the concentration. Using the above-presented results, we obtain $\xi = 0.7-0.9$. The considerable scatter of the experimental points on the plot of the dependence $\tau_{RL}^{-1}(C)$ (Ref. 4) makes a quantitative comparison difficult, but the qualitatively indicated ξ values are not at variance with the experimental data.

5. The role of fast-relaxing centers (FC) in the SLR process is quite great in both NMR¹² and EPR. Atsarkin *et al.*⁴ have observed a strong concentration dependence of τ_{RL} even in that region of Cr^{3+} concentrations in which the normal relaxation time τ_{SL} is already concentration independent.

A general analysis of the SLR of paramagnetic impurities interacting with FC¹³ reveals two limiting cases for the nature of the concentration dependence of τ_{SL}^{-1} :

$$\frac{1}{\tau_{SL}} \sim \begin{cases} n, & \tau^{FC} \ll \tau_{tr} \\ n/C, & \tau^{FC} \gg \tau_{tr} \end{cases} \quad (13a)$$

$$(13b)$$

where C and n are the concentrations of the paramagnetic impurities and the fast-relaxing center, τ^{FC} is the relaxation time of the FC, and τ_{tr} is the characteristic time of the energy transfer from a paramagnetic impurity to a FC. In EPR there can act as FC other kinds of impurity ions having shorter relaxation times than the ions of the observed system, as well as clusters (groups of closely spaced ions) of the base system, in which these ions are coupled by strong spin-spin interactions. The thermal modulation of the latter gives rise to an effective mechanism for the SLR of clusters.¹⁴ In the overwhelming majority of cases τ_{SL}^{-1} increases with increasing C , which has been repeatedly associated with the dominating role of the exchange-coupled clusters in the relaxation process. Since the number of exchange-coupled pairs at low concentrations increases in proportion to C^2 ; the number of exchanged-coupled triads, in proportion to C^3 ; etc., the experimentally observed dependence $\tau_{SL}^{-1} \sim C$ is impossible in the case (13a), but can be due to exchange-coupled pairs in the case (13b); the dependence $\tau_{SL}^{-1} \sim C^2$ is associated with pairs in the case (13a) and with triads in the case (13b). For $\text{Cr}^{3+}:\text{Al}_2\text{O}_3$ the dependence

$$\tau_{SL}^{-1} = \alpha + \beta C^2$$

has been repeatedly observed at low temperatures, and the experimental data for τ_{RL}^{-1} (Ref. 4) are also quite well approximated by a similar dependence.

Let us carry out the calculation of the transition probabilities within the framework of the stochastic perturbation theory in terms of the dipole-dipole interaction of the spins of the system in question and the FC.¹² Let us first consider one dipole-coupled pair of spins j and k , whose interaction with the FC is described by the Hamiltonian

$$H_{int} = \sum_{m=j,k} \frac{(g\beta)(g\beta)_\alpha}{r_m^3} \sum_{\tau_0} A_{\tau_0}^{(m)} S_{\tau_0}^{(m)} S_{\delta}^{FC} \quad (14)$$

$A_{\gamma\delta}(\theta, \varphi)$ contains the angular dependence of the interaction energy ($\gamma, \delta = z, +, -$). Using (14) and the integral representation of the δ function, we transform (6) into the form

$$W_{cd}^{jk} = \sum_{m,n=j,k} \frac{(g\beta)^2 (g\beta)_\alpha^2}{\hbar^2 r_m^3 r_n^3} \sum_{\tau_1\tau'} \langle c | S_{\tau_1}^{(m)} | d \rangle \langle d | S_{\tau'}^{(n)} | c \rangle \sum_{\delta\delta'} A_{\tau_0}^{(m)} A_{\tau_0'}^{(n)} \times 2 \text{Re} \int_0^\infty \langle S_{\delta}^{FC}(t) S_{\delta'}^{FC} \rangle \exp(i\omega_{cd}t) \exp(-\beta_L \Delta) / \sum_p \exp(-\beta_L E_p), \quad (15)$$

where $\omega_{cd} = (E_c - E_d)/\hbar$ and Δ is the energy, relative to the ground state of the FC, of that active multiplet of the FC which is coupled by the dipole-dipole interaction to the dipole pair.

Let us describe the relaxation of the FC phenomenologically with the aid of the longitudinal and transverse relaxation times T_1 and T_2 , assuming that the FC has one resonance frequency ω_α , and that the correlation functions $\langle S_{\delta}^{FC}(t) S_{\delta'}^{FC} \rangle$ can be represented in the form

$$\langle S_{\pm}^{FC}(t) S_{\pm}^{FC} \rangle = 1/2 S^{FC} (S^{FC} + 1) \exp(-t/T_1), \quad (16)$$

$$\langle S_{\pm}^{FC}(t) S_{\mp}^{FC} \rangle = 1/2 S^{FC} (S^{FC} + 1) \exp(-t/T_2).$$

Using (16), we obtain

$$W_{cd}^{jk} = \sum_{m,n=j,k} \frac{(g\beta)^2 (g\beta)_\alpha^2}{\hbar^2 r_m^3 r_n^3} \sum_{\tau_1\tau'} \langle c | S_{\tau_1}^{(m)} | d \rangle \langle d | S_{\tau'}^{(n)} | c \rangle \times \left\{ 2 \exp(-\beta_L \Delta) / \sum_p \exp(-\beta_L E_p) \right\} \left\{ A_{\tau_1\tau'}^{(m)} A_{\tau_1\tau'}^{(n)} \frac{T_1}{1 + \omega_{cd}^2 T_1^2} + A_{\tau_1\tau'}^{(m)} A_{\tau_1\tau'}^{(n)} \frac{T_2}{1 + (\omega_{cd} + \omega_\alpha)^2 T_2^2} + A_{\tau_1\tau'}^{(m)} A_{\tau_1\tau'}^{(n)} \frac{T_2}{1 + (\omega_{cd} - \omega_\alpha)^2 T_2^2} \right\}. \quad (17)$$

A similar approach has been used to describe both the relaxation of nuclei via paramagnetic impurities¹² and the relaxation of a system of magnetic ions via FC.¹⁵

The probabilities (17) for the transitions between the states of a spin pair turn out to be nonzero not only for the intermultiplet transitions, but also for the intramultiplet ones, i.e., for the transitions with frequencies of the order of the frequency ω_L of the local field. Such transitions make a negligibly small contribution to τ_{RL}^{-1} in the situation considered above in Sec. 4, since the transition probability (8) is proportional to ν^2 (when $h\nu \ll kT$) and the density of states in the phonon spectrum near the resonance frequency is much higher than the density near $\omega \sim \omega_L$. But the form of those spectral densities of the correlation functions which are connected with the relaxation via FC is such that the transitions with frequencies of the order of ω_L can make the dominant contribution to τ_{RL}^{-1} .

Let us give the result of the calculation of τ_{RL}^{-1} for the dipole-dipole interaction reservoir of Cr^{3+} ions in ruby in zero field. Let us assume that there are several kinds of FC with resonance frequencies ω_α , relaxation times $T_{1\alpha}$, $T_{2\alpha}$, and partial concentrations n_α . In the isotropic approximation, after finding the matrix elements entering into (17) and averaging over the equiprobable FC and Cr^{3+} -ion distributions, we obtain

$$\frac{1}{\tau_{RL}} = \frac{(g\beta)^2}{\hbar^2 r_0^3} \sum_{\alpha} \left\{ \frac{1}{3} S_{\alpha}^{FC} (S_{\alpha}^{FC} + 1) (g\beta)_\alpha^2 n_\alpha \times \left[\exp(-\beta_L \Delta_\alpha) / \sum_p \exp(-\beta_L E_p^{(\alpha)}) \right] \right\} \quad (18)$$

$$\times \left[\frac{10T_{2\alpha}}{1+(\omega_0+\omega_\alpha)^2 T_{2\alpha}^2} + \frac{1.7T_{2\alpha}}{1+(\omega_0-\omega_\alpha)^2 T_{2\alpha}^2} + \frac{5.2T_{1\alpha}}{1+\omega_0^2 T_{1\alpha}^2} + \frac{9.4T_{2\alpha}}{1+\omega_\alpha^2 T_{2\alpha}^2} + f(T_{1\alpha}) \right],$$

where $\omega_0 = 2D$. The first three terms in the second square brackets are due to those transitions in the pair spectra whose frequencies are of the order of ω_0 ; the remaining terms, to those transitions with frequencies of the order of ω_L .

In deriving (18) we assumed that $\omega_L \ll \omega_\alpha$. The last term appeared as a result of the averaging of the quantity containing

$$T_{1\alpha} \omega_{cd}^2 / (1 + \omega_{cd}^2 T_{1\alpha}^2),$$

(where ω_{cd} is the frequency of the local field produced by the spin c at the point of localization of the spin d) over the spatial disposition of the ions. If the rate of the longitudinal relaxation of the FC is so high that the condition $\omega_{cd} T_{1\alpha} \ll 1$ is fulfilled for all the spin pairs, then

$$f(T_{1\alpha}) \approx 4.6T_{1\alpha},$$

and if there are dipole pairs that are so close that for them $\omega_{cd} T_{1\alpha} > 1$, then

$$f(T_{1\alpha}) \approx 1.1hr_0^3/g^2\beta^2$$

and does not depend on $T_{1\alpha}$.

For the purpose of comparison, let us also give the result of the computation of τ_{SL}^{-1} in the same approximation:

$$\frac{1}{\tau_{SL}} = \frac{(g\beta)^2}{\hbar^2 r_0^3} \sum_{\alpha} \left\{ \frac{1}{3} S_{\alpha}^{FC} (S_{\alpha}^{FC} + 1) (g\beta)_{\alpha}^2 n_{\alpha} \times \left[\exp(-\beta_L \Delta_{\alpha}) / \sum_p \exp(-\beta_L E_p^{(\alpha)}) \right] \times \left[\frac{29T_{2\alpha}}{1+(\omega_0+\omega_\alpha)^2 T_{2\alpha}^2} + \frac{5.4T_{2\alpha}}{1+(\omega_0-\omega_\alpha)^2 T_{2\alpha}^2} + \frac{14T_{1\alpha}}{1+\omega_0^2 T_{1\alpha}^2} \right] \right\}. \quad (19)$$

It follows from a comparison of (18) and (19) that, if we neglect in τ_{RL}^{-1} the contribution due to the transitions with frequency equal to that of the local field, then, irrespective of the nature of the FC and the character of the cross relaxation (i.e., irrespective of whether it is a resonance relaxation or a nonresonance one), we shall always have $\tau_{SL}^{-1} > \tau_{RL}^{-1}$ ($\xi \approx 1/3$). In the case of a very fast longitudinal relaxation (i.e., for $\omega_0^2 T_{1\alpha}^2 \ll 1$), τ_{SL}^{-1} is largely determined by that relaxation; for $\omega_0^2 T_{1\alpha}^2 \gg 1$ and a nonresonance cross relaxation, the contribution of the transverse relaxation to τ_{SL}^{-1} becomes important when $\omega_0^2 T_{2\alpha}^2 \gg 1$; for a resonance cross relaxation, when $\omega_0 T_{2\alpha} > (\omega_0 T_{1\alpha})^{-1}$. The possibility that the condition $\tau_{RL}^{-1} > \tau_{SL}^{-1}$ will be fulfilled is due to the last term in (18), i.e., to the longitudinal relaxation of the fast-relaxing centers, which induces in the spectrum of the base system transitions with $\omega \sim \omega_L$.

6. Let us turn to the analysis of the data on the relaxation of the spin-spin reservoir of Cr^{3+} ions in ruby.⁴ The observed concentration dependence of τ_{RL}^{-1} allows us to assume that exchange-coupled Cr^{3+} -ion clusters play the role of FC. It is known that exchange-coupled Cr^{3+} -ion pairs with isotropic-exchange-interaction strength J form, when $|J| \gg |D|$, FC the mechanism

for whose relaxation is determined by the thermal modulation of $J(r)$. The relaxation of pairs with $J \approx 0.5 \text{ cm}^{-1}$ has been experimentally observed,¹⁶ and at $T = 4.2 \text{ K}$ the corresponding $T_{1\alpha} \approx 10^{-3} \text{ sec}$. Exchange triads should relax even faster¹⁷ (for comparable values of J). The observed values of τ_{RL}^{-1} (Ref. 4) and τ_{SL}^{-1} (Ref. 11), in contrast to the indicated cluster-relaxation rates, indicate that in the present case (13a) is realized. It is precisely in this case that the correlation theory of perturbations, i.e., the expressions (18) and (19), can be applied. Then, as pointed out above, the dependences τ_{RL}^{-1} , $\tau_{SL}^{-1} \sim C^2$ are associated with exchange-coupled pairs (the spectrum is shown in Fig. 1).

The modulation of the isotropic exchange interaction leads to the occurrence in the exchange-pair spectrum of transitions with $\Delta S = 2$ and probability^{14,16}

$$p_{ij} = \frac{1}{6\pi\hbar^4} \frac{J^2}{\rho\nu^3} \frac{E_{ij}^3}{1 - \exp(-\beta_L E_{ij})} \left(\frac{D}{J}\right)^2 \left(\frac{dJ}{dr}\right)^2, \quad (20)$$

where E_{ij} is the difference between the energies of the corresponding states. For pairs with spacing $r \approx 5 \text{ \AA}$, we have $J \approx 0.5 \text{ cm}^{-1}$ and $|dJ/dr| \approx 13 \text{ cm}^{-1} \text{ \AA}$, and the value $T_1 = (p_{3-1} + p_{1-3})^{-1} \approx 2 \text{ msec}$ obtained from (20) is in good agreement with the experimental value.¹⁶ Pairs with $r = 5 \text{ \AA}$ are fairly distant neighbors; near neighbors have the following r (in \AA) and J (in cm^{-1}) values^{16,18}:

$$r_1 = 2.733; \quad r_2 = 2.809; \quad r_3 = 3.185; \quad r_4 = 3.504; \\ J_1 = 240; \quad J_2 = 84; \quad J_3 = 11.6; \quad J_4 = -7.$$

Let us, setting E_{ij} in (20) equal to $5J$ (the transition $S = 1 - S = 3$), and making the approximation $dJ/dr \approx \Delta J/\Delta r$, estimate the probabilities for the downward transitions: in the range 1.7–4.2 K they practically do not depend on temperature, and have the values (in sec^{-1}):

$$p_{31}^{(1)} \approx 2 \cdot 10^6, \quad p_{31}^{(2)} \approx 2 \cdot 10^6, \\ p_{31}^{(3)} \approx 5 \cdot 10^5, \quad p_{31}^{(4)} \approx 5 \cdot 10^4$$

(in the last case the spectrum is inverted with respect to the spectrum shown in Fig. 1). The probabilities for the inverse transitions are $\exp(-5|J|\beta_L)$ times lower. Thus, close pairs relax significantly faster than distant

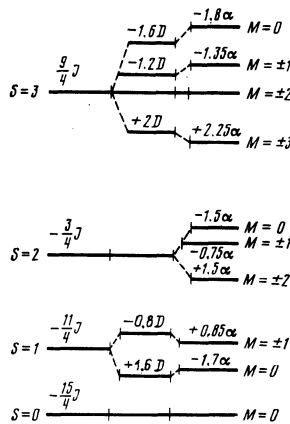


FIG. 1. Spectrum of an exchange-coupled pair with allowance for the crystal field and the dipole-dipole interaction [$\alpha = g^2\beta^2 r^{-3} \times (1 - 3 \cos^2 \theta)$, $|J| \gg |D|$; the antisymmetric exchange in first-order perturbation theory does not cause a level shift].

ones, but their contribution to the relaxation rates of interest to us is proportional to the populations of the corresponding levels. Let us note one important circumstance in this connection. The total exchange interaction includes, besides the dominant isotropic part, both an anisotropic and an antisymmetric part, which are, in order of magnitude, equal respectively to $(\lambda/\delta)^2 J$ and $(\lambda/\delta)J$, where λ is the spin-orbit coupling constant and δ is the orbital-level spacing.¹⁹ For $\text{Cr}^{3+}:\text{Al}_2\text{O}_3$, $(\lambda/\delta) \approx 3 \times 10^{-3}$, and if the anisotropic part of the exchange is negligibly small even in comparison with the dipole-dipole interactions, the antisymmetric part for close pairs is large enough for its modulation to provide an effective mechanism for the relaxation. This interaction induces transitions with $\Delta S = \pm 1$ in the exchange-pair spectrum even in the zeroth order in the crystal field. The transition probabilities differ from (20) in that they contain $(\lambda/\delta)^2$ in place of the factor $(D/J)^2$. For close exchange pairs, setting $E_{ij} = J(J > 0)$ or $E_{ij} = 3J(J < 0)$, we obtain (in sec^{-1})

$$p_{i\alpha}^{(1)} = 2 \cdot 40^6, \quad p_{i\alpha}^{(2)} = 2 \cdot 40^6, \quad p_{i\alpha}^{(3)} = 2 \cdot 40^2, \quad p_{i\alpha}^{(4)} = 1 \cdot 40^2.$$

At low temperatures, the populations of the states are such that the considered mechanism for close pairs makes a significantly greater contribution to the relaxation of a system of isolated ions, i.e., ions not contained in clusters, than to the relaxation process due to the modulation of the isotropic part of the exchange interaction.

Let us estimate the value of τ_{SL}^{-1} as given by the formula (19). The contribution made to it by the close exchange pairs as a result of the modulation of the antisymmetric exchange interaction is greatest for pairs with $r = 3.185 \text{ \AA}$; but when the number of such pairs is roughly equal to the pairs with $r \approx 5 \text{ \AA}$, the contribution of the latter pairs that stems from the modulation of the isotropic exchange interaction is two orders of magnitude higher at $T = 4.2 \text{ K}$ and four orders of magnitude higher at $T = 1.7 \text{ K}$. The number of isolated Cr^{3+} -ion pairs with distance r between them is, when their distribution over the lattice is an equiprobable one, equal to

$$n = \frac{1}{2} n_0 k C^2 (1 - C)^{2m},$$

where $n_0 = 4.9 \times 10^{22} \text{ cm}^{-3}$ is the number density for the cation sites, k is the number of such sites over a distance r from a given site, and m is the number of them in a sphere of radius r . For $C = 0.07\%$ the number of nearest pairs in this case is $n = 1.2 \times 10^{16} \text{ pairs/cm}^3$, and the number of pairs with $r = 5 \text{ \AA}$ is $10^{17} \text{ pairs/cm}^3$. Setting in (19)

$$T_{2\alpha} = T_{1\alpha}, \quad |\omega_{\alpha \pm} \omega_{\alpha}| \approx |D|, \quad r_0 = 8 \text{ \AA},$$

we find that the experimentally observed value of the concentration dependent part of τ_{SL}^{-1} (which is of the order of 1 sec^{-1} for $C = 0.07\%$) may be due to the set of exchange pairs with inter-ion distances of $4-8 \text{ \AA}$ if the number of them is 5-10 times higher than what it would be if the distribution of the Cr^{3+} ions over the cation sites were an equiprobable one. The inference of an elevated degree of clustering of the Cr^{3+} ions in this

system gave earlier²⁰ an insight into the concentration dependence of the EPR line width as well.

The greatest contribution in the formula (18) for τ_{RL}^{-1} is made by the last term. This contribution is due to the $\Delta S = \pm 1$ transitions of the close exchange pairs, and is greatest for pairs with $r = 3.185 \text{ \AA}$ and $J = 11.6 \text{ cm}^{-1}$ (the contribution of closer pairs is several orders of magnitude smaller because of the strong exchange and correspondingly low populations, while the contribution of the pairs with $r = 3.504 \text{ \AA}$ is smaller because of the increase in the multiplet spacing as a result of the inverted character of the spectrum). For $n_0 \approx 10^{18}$ and $C = 0.037\%$ this corresponds with the experimentally observed value $\tau_{RL}^{-1} \approx 10 \text{ sec}^{-1}$ and, to a considerable degree, the observed temperature dependence

$$\tau_{RL}^{-1} \sim \exp(-\beta_n \Delta)$$

with $\Delta = 12.8 \text{ cm}^{-1}$ (Ref. 4). Thus, the experimental results are not contradicted by the interference that the process involving the transfer of the spin-spin interaction energy to the lattice largely via the above-indicated exchange-coupled pairs is dominant in the relaxation of the spin-spin reservoir of Cr^{3+} ions at sufficiently high ion concentrations and low temperatures.¹⁾

7. Thus, the statistical theory of the relaxation of a spin-spin reservoir enables us to understand the qualitative characteristics of this process, and to some extent leads to a quantitative agreement with the experimental data. The main conclusions consist in the following. The rate of relaxation of a spin-spin reservoir in the presence of fast-relaxing impurities can be significantly higher than the normal SLR rate as a result of transitions in the spin spectrum with frequencies equal to the local-field frequencies. A comparison of the indicated relaxation rates, their concentration and temperature dependences allows us in some cases to judge the character of the mutual spatial disposition (i.e., the short-range order) in a system of magnetic ions. In the $0.02-0.07\%$ range of Cr^{3+} -ion concentrations in ruby exchange-coupled pairs can be an effective link in the relaxation under conditions of a somewhat elevated degree of short-range order in a system of the indicated ions. An important role is played in the relaxation of exchange-coupled pairs by the modulation of the antisymmetric part of the exchange interaction.

Measurements of the rates of relaxation of spin-spin reservoirs in crystals with equal magnetic-ion concentrations, but grown by different methods (which apparently has an appreciable effect on the degree of short-range order in the system of impurity ions²¹) could become an important source of additional information.

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¹⁾ A deviation of the temperature dependence from the above-indicated law is observed at higher temperatures.²² This may be due to an increase in the concentration of the Cr^{3+} ions, which are also fast-relaxing centers.

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