Spin-lattice relaxation of an electron spin-spin reservoir in paramagnetic crystals

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A method was developed for determining the spin-spin relaxation time τ_{SSL} of an electron spin-spin reservoir in paramagnetic systems with spin $S = 3/2$ in zero external magnetic field. Relaxation was observed during return to equilibrium of a low-frequency magnetic susceptibility signal previously amplified by slightly off-resonance ESR saturation of the $\pm 1/2 \to \pm 3/2$ transition. The method was used to determine the relaxation time τ_{SSL} of ruby crystals in the range of temperatures T_0 from 1.7 to 20 °K and chromium concentrations c from 0.018 to 0.08%. It was found that τ_{SSL} was much shorter than the usual electron spin-lattice relaxation time τ_{SL} and that the ratio τ_{SSL}/τ_{SL} decreased on increase in T_0 or in c. The experimental results were interpreted on the basis of a theory developed allowing for relaxation of a spin-spin reservoir via the Stark subsystem of Cr^{3+} and via additional fast-relaxing impurities in the form of Cr^{2+} ions and Cr^{3+} exchange clusters. The enhanced susceptibility was used to determine the local field in ruby. It was found that the main contribution to this field was made by the magnetic dipole interactions of the Cr^{3+} ions.

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1. FORMULATION OF THE PROBLEM AND DESIGN OF EXPERIMENTS

Electron spin–lattice relaxation in paramagnetic crystals has been investigated intensively for decades.[1] However, such investigations have been mainly concerned with relaxation of just the Zeeman energy of paramagnetic centers in an external magnetic field H_0(and also of the Stark energy in an internal crystal electric field), whereas hardly any information has been acquired about the coupling between the lattice and the energy subsystem of electron spin–spin interactions. This coupling is very important because the subsystem in question forms a quasiequilibrium electron spin–spin reservoir (ESSR) in solids and this reservoir has its own temperature T_{SS}, which frequently plays a decisive role in the dynamics of magnetic resonance phenomena. The ESSR–lattice relaxation time τ_{SSL} largely determines such important effects as lowering of T_{SS} and dynamic polarization of nuclei under the influence of continuous microwave pumping.[2-4]

These effects can be calculated if we know the ratio $a=\tau_{SL}/\tau_{SSL}$, where τ_{SL} is the "usual" (Zeeman) spin–lattice relaxation time. The actual value of a is usually unknown, so that one has to use very simple theoretical estimates postulating that $a=2-3$ (see, for example, Ref. 4). However, these theoretical predictions apply to a very much idealized situation: the spin–spin interactions are assumed to be of purely dipole type, no allowance is made for the effects of the crystal field, accidental impurities are ignored, etc. It is not surprising that in those few cases when the relaxation time τ_{SSL} can be measured, the result differs considerably from that expected theoretically.[5-7] There is a striking contrast between this unhappy situation and the state of the corresponding problem in nuclear magnetic resonance: measurement of the dipole–lattice relaxation time (which is the analog of τ_{SSL} in the case of nuclear spin systems) has been for some time a standard technique in NMR spectroscopy and it is used widely in investigations of solids.[8]

Reliable and sufficiently accurate measurements of the relaxation time τ_{SSL} can be made if the investigated object and the experimental method satisfy a number of requirements. First of all, we have to be able to set an initial deviation of an ESSR from its equilibrium with the lattice. Secondly, means must be provided for controlling the evolution of T_{SS} in the course of the spin–lattice relaxation. Thirdly, the influence of the Zeeman subsystem of nuclear spins of the matrix must be eliminated, because this subsystem is strongly coupled to an ESSR and complicates the relaxation behavior (see, for example, Ref. 7). Finally, it is highly desirable to ensure that measurements are made on the simplest possible (preferably two-level) Zeeman (or Stark) spin system so as to minimize ambiguity of interpretation and facilitate the theoretical analysis.

All these conditions can be satisfied in the case of paramagnetic centers with spin $S=3/2$ in zero field ($H_0=0$). In a crystal field of moderately high symmetry the energy spectrum of such centers consists of two degenerate Kramers doublets $\pm 1/2$ and $\pm 3/2$ separated by an initial Stark splitting $h\nu_0$ (Ref. 1). In view of the degeneracy of the doublets, spin–spin relaxation gives rise to a considerable magnetic susceptibility $\chi(\Omega)$ in the frequency interval $1/\tau_{SL} \ll \Omega \leq \nu_L$, where ν_L is the local spin–spin field (expressed in frequency units). The corresponding dispersion $\chi'(\Omega)$ and absorption $\chi''(\Omega)$ signals can be regarded, if desired, as an ESR in local fields due to transitions within the Kramers doublets split by the spin–spin interactions, in other words, due to transitions in the ESSR spectrum. Clearly, the amplitudes of these signals should be proportional to $1/T_{SS}=\beta_{SS}$ and can be regarded as a measure of this quantity.

Modulation saturation, i.e., heating of an ESSR by a strong alternating field of frequency Ω, can be used to make T_{SS} different from the lattice temperature T_0 (Refs. 7 and 9). However, it much more convenient not to heat but to cool the spin–spin subsystem because this increases $|\chi(\Omega)|$ and, consequently, increases the sen-

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sitivity and precision of the measurements.

Cooling of an ESR is in this case produced by saturating an ESR line corresponding to a transition between doublets and detuned by a small amount Δ relative to the central frequency ν_0. In accordance with the Provotorov theory[10, 12] this increases $|\beta_{SS}|$ by a factor of about $\nu_0/2\nu_L$, the quantity $|\chi(\Omega)|$ increases by approximately the same factor (this is known as the enhanced susceptibility effect[11, 12]). Observation of the return of $\chi(\Omega)$ to its equilibrium value after the end of microwave pumping allows us to determine directly and very accurately the relaxation time τ_{SSL}. Clearly, if $H_0=0$, the Zeeman energy of the lattice nuclei vanishes and cannot influence the results of the measurements.

Our investigation was carried out on ruby crystals (representing corundum Al_{203} doped with Cr^{3+} ions) which has long been used as a touchstone for checking new ideas and methods on magnetic resonance. The spin of the Cr^{3+} ions is $S=3/2$ and the frequency of the initial splitting is $\nu_0=11.46$ GHz (Ref. 1). An important advantage of ruby is the very extensive experimental information available on the usual spin–lattice relaxation, including that in a field of $H_0=0$ (Refs. 13–15). This information is needed to determine the parameter a and to compare the temperature and concentration dependences of τ_{SL} and τ_{SSL}.

For all its advantages the use of ruby has one shortcoming which may affect the planned experiments. The ^{27}Al nuclei in the crystal lattice of corundum have spin $I=5/2$ and an electric quadrupole moment. This causes splitting of the energy levels in $H_0=0$ into three doublets separated by 358 and 716 kHz (Ref. 16). At low temperatures the quadrupole subsystem of ^{27}Al is strongly coupled to the ESSR (like the nuclear Zeeman subsystem in strong fields H_0) and this results in an apparent increase in the "weight" of the ESSR and in an increase in the experimentally determined ESSR spin-lattice relaxation time to

$$\tilde{\tau}_{SSL}=\frac{C_{IQ}+C_{SS}}{C_{SS}}\tau_{SSL}, \tag{1}$$

where C_{IQ} and C_{SS} are the specific heats of the nuclear quadrupole subsystem and ESSR, respectively.[17, 7]

Elementary estimates indicate that when the chromium concentration is $C\gtrsim 0.1\%$, the inequality $C_{IQ}\ll C_{SS}$ is obeyed, so that the influence of nuclear spins can be ignored. However, if $c<0.1\%$, there is no such certainty and one has to carry out control experiments to determine independently C_{SS} and/or τ_{SSL}. Anticipating the conclusions reached later, we shall note that the distorting influence of the ^{27}Al nuclei was observed in our experiments only in the sample with the lowest concentration of these nuclei ($c\approx 0.02\%$) and even then it was not very important.

We shall therefore proceed as follows: in a brief description of the experimental method (Sec. 2a) we shall give the main results on the temperature and concentration dependences of τ_{SSL} (Sec. 2b) and only then we shall introduce corrections which allow for the ^{27}Al subsystem (Sec. 2c). We shall also determine the value of ν_L. Next, in Sec. 3, we shall give the results of a theoretical calculation of the ratio τ_{SL}/τ_{SSL} for $H_0=0$ making various assumptions of the nature of the spin–spin interactions predominating in ruby. These calculations also yield expressions for the second moment of an acoustic paramagnetic resonance line in $H_0=0$, which are given in the Appendix. Finally, the theory is compared with the experimental results in Sec. 4.

2. EXPERIMENTS

a. Experimental method

Our investigation was carried out in the temperature range 1.7–20°K on samples with chromium concentrations of 0.018–0.08 at.%. All eleven samples were prepared by the Verneuil method.

Ruby samples of about 0.5 cm^3 volume were placed together with an rf coil used to measure $\chi(\Omega)$, inside a short-circuited waveguide subjected to periodic microwave pulses of frequency ν in the vicinity of $\nu_0=11.46$ GHz. The magnetic susceptibility $\chi(\Omega)$ was determined at frequencies $\Omega\sim 0.5$–2 MHz with a Q-meter circuit. We recorded the dispersion signal χ', which in all cases was considerably greater than the value of χ''. Consequently, the frequency Ω was in this case less than the spin–spin relaxation rate, i.e., the susceptibility was close to the adiabatic value.

Typical oscillograms are shown in Fig. 1. We can see that immediately after the application of a microwave pulse the χ' signal reached its maximum and then gradually dropped to a steady-state value; the sign of the susceptibility was opposite to the sign of $\Delta=\nu-\nu_0$. This was in full agreement with the evolution of β_{SS} predicted by Provotorov[10] and Rodak.[18] Regrettably this simple and striking experiment had not been carried out some ten years ago when the very existence of an ESSR was still in need of experimental proof.

In the case of sufficiently long pulses $t_p>\tau_{SL}$ the process of relaxation of the χ' signal after the end of a pump pulse always obeyed a single exponential function with the relaxation time τ_{SSL}. This time was determined with an error of 10–20%. Modulation saturation of the ESSR was avoided by making all the measurements in the absence of magnetic modulation, i.e., under *dc* conditions.

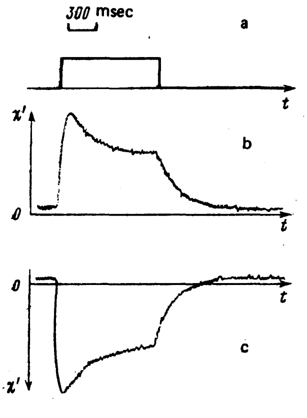

FIG. 1. Dependence of the amplitude of the dispersion signal χ' on time t in the case of pulsed microwave pumping; a) microwave pulse; b) $\Delta<0$; c) $\Delta>0$.

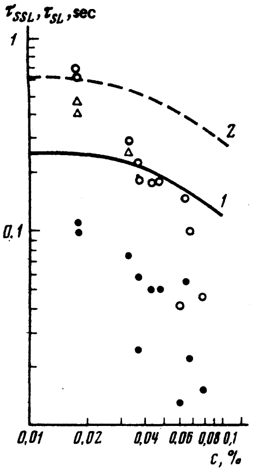

FIG. 2. Dependences of the relaxation times τ_{SSL} (points, experimental values) and τ_{SL} (curves taken from Refs. 13-15) on the concentration of Cr^{3+}. The black symbols refer to curve *1* and represent the experimental results obtained at 4.2°K; the open symbols referred to curve *2* and were obtained at 1.7°K. Triangles are the values of τ_{SSL} corrected in accordance with Eq. (1).

b. Concentration and temperature dependences of τ_{SSL}

The results of the measurements of the relaxation time τ_{SSL} and $T_0 = 1.7$ and 4.2 °K are plotted in Fig. 2. For comparison, this figure includes the published[13-15] data on the spin-lattice relaxation time τ_{SL} measured in $H_0 = 0$ for the $\pm 1/2 \to \pm 3/2$ transition.

It is worth noting the following characteristic features of the results obtained.

1. The time τ_{SSL} decreased as $c^{-1}-c^{-2}$ when the chromium concentration was increased. This began at lower values of c and was steeper than the concentration dependence of τ_{SL}.

2. The values of the parameter a varied from 1–2 at the lowest concentrations at 1.7 °K to 5–10 the highest concentrations c at the lattice temperature T_0.

3. There was a considerable scatter of the results from one sample to another and this scatter increased significantly when T_0 and c increased.

4. The temperature dependence of τ_{SSL} was stronger than $1/T_0$: an increase in temperature by a factor of 2.5 reduced the time τ_{SSL} by a factor of 3.5–6.5.

A more detailed investigation of the temperature dependence was made on two samples with Cr^{3+} concentrations of 0.018 and 0.037% for which the deviation from the $1/T_0$ law (Fig. 2) was strongest. The results are shown in Fig. 3. We can see that the dependence $\tau_{SSL}(1/T_0)$ was clearly nonlinear although it approached linearity at both ends of the investigated temperature range 1.7–20 °K.

c. Allowance for the ^{27}Al nuclear subsystem and determination of the local field

A study of the samples with the lowest Cr^{3+} concentrations (0.018 and 0.030%) revealed that reduction in the duration of the saturation pulses produced an initially faster relaxation. For $c = 0.018\%$ and $T_0 = 1.7$ °K, the time constant at this stage was about 40 msec and the relative amplitude for pulses of $t_p \lesssim 30$ msec duration reached a limiting value of about 0.5.

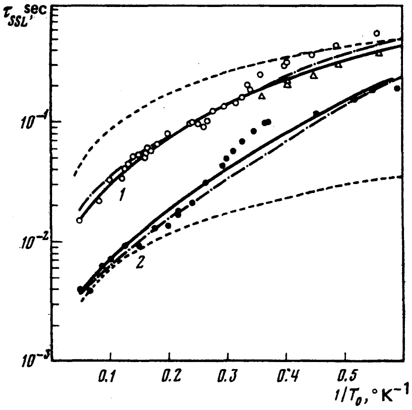

FIG. 3. Temperature dependences of the relaxation time τ_{SSL}: 1) $c = 0.018\%$; 2) $c = 0.037\%$. The points are the experimental values; the chain curve represents calculations based on Eq. (9); the continuous curves are calculated using the method of Ref. 28; the dashed curves give the dependence $\tau_{SSL} \propto 1/T_0$. The triangles are the values of τ_{SSL} corrected in accordance with Eq. (1).

This was typical of transient processes involving the nuclear spin subsystem.[7,17] Thus, the dangers outlined in Sec. 1 were confirmed; at low values of c the process of relaxation of the ESSR was distorted by the influence of the ^{27}Al quadrupole subsystem and the measured values of τ_{SSL} required correction.

The results obtained indicated that thermal mixing of the ESSR with the nuclear subsystem was completed in a time of $\tau_{SSI} \gtrsim 40$ msec. Consequently, the value of β_{SS} reached during a sufficiently short microwave pulse ($t_p \ll \tau_{SSI}$) was independent of the coupling between the ESSR and the nuclei and if the ESR saturation was sufficiently strong, it could be calculated from the familiar formula[18,2]

$$E_{\mathrm{sh}} \equiv (T_0/T_{SS})_{\mathrm{sh}} = 1 - \frac{\nu\Delta}{\nu_L^2 + \Delta^2} \tag{2}$$

(the index "sh" shows that the above expression applies in the case of short pulses).

On the other hand, in the case of strong continuous saturation of the ESR reached in a time $t_p \gg \tau_{SL}$, τ_{SSL}, the nuclear system without its own relaxation channel to the lattice should not affect the results and we should have[18,2]:

$$E_{\mathrm{c}} \equiv (T_0/T_{SS})_{\mathrm{c}} = 1 - \frac{\nu\Delta}{a\nu_L^2 + \Delta^2} \tag{3}$$

(the index "c" denotes continuous saturation).

We can thus see that measurements of E_{sh} and E_{c} and the substitution in Eqs. (2) and (3) can be used to determine the true values of a and ν_L. It is most convenient to use the relationship

$$a \approx (E_{\mathrm{sh}} - 1)/(E_{\mathrm{c}} - 1), \tag{4}$$

which is valid if $\Delta^2 \ll \nu_L^2$ [see Eqs. (2) and (3)]. It should

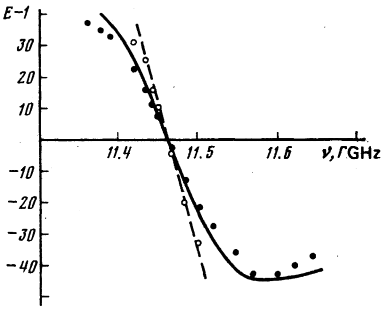

FIG. 4. Dependence of the enhancement of the susceptibility E on the microwave pump frequency ν. The open circles correspond to short microwave pulses (E_p); the black dots represent continuous pumping (E_c). The continuous curve is calculated on the basis of Eq. (3).

be noted that in the range of such small detunings it is easiest to achieve strong saturation of the ESR and the dependences of $E_{sh}-1$ and E_c-1 on Δ should be linear.

The experimental results for $c=0.018$ and $T_0=1.7\,^{\circ}\mathrm{K}$ are plotted in Fig. 4. We can see that in the case of small detunings the values of $E_{sh}-1$ and E_c-1 are indeed proportional to Δ, and—moreover—in accordance with Eq. (4), we have $a=1.7\pm 0.2$. A comparison of this value with the ratio $\tau_{SL}/\tau_{SSL}=1.0$ obtained for the same sample from Fig. 2 and application of Eq. (1) give

$$C_{IQ}/C_{SS}=0.7\pm 0.2. \tag{5}$$

We shall now allow for the fact that

$$C_{IQ}/C_{SS}=\mathrm{Sp}\,\hat{\mathscr{H}}_{IQ}^{2}/\mathrm{Sp}(\hat{\mathscr{H}}_{SS}^{0})^{2},$$

where $\hat{\mathscr{H}}_{IQ}$ and $\hat{\mathscr{H}}_{SS}^{0}$ are the Hamiltonians of the nuclear quadrupole subsystem and of the ESSR. Assuming a specific form of $\hat{\mathscr{H}}_{IQ}$ for the ^{27}Al nuclei in ruby[16] and allowing for the fact that if $S=3/2$ and $H_0=0$ we can use[9]

$$(2\pi\nu_L)^2\equiv\omega_L^2=4\mathrm{Sp}(\mathscr{H}_{SS}^{0})^2/(\mathrm{Sp}\,1\cdot N\hbar^2),$$

where N is the number of the spins S per unit volume and Sp 1 is the trace of a unit matrix, we find that the value of C_{IQ}/C_{SS} in Eq. (5) corresponds to $\nu_L=100\pm 20$ MHz. This frequency together with the above value of a were used to calculate E_c from Eq. (3). It is clear from Fig. 4 that the results of such a calculation were is satisfactory agreement with the experiments up to very large values of detuning, when strong saturation of an ESR was no longer attainable.

Similar experiments carried out on a sample with $c=0.03\%$ yield C_{IQ}/C_{SS}. Thus, it was found that $C_{SS}\propto c^2$, typical of the case when an inhomogeneous broadening of an ESR line makes no significant contribution to C_{SS}. Extrapolation of this dependence to higher concentrations led us to the conclusion that in the range $c>0.03\%$ we could ignore the influence of nuclei.

A correction was required in accordance with Eq. (1) in the case of three samples with the lowest concentrations. The values of τ_{SSL} corrected in this way are identified by triangles in Figs. 2 and 3.

3. THEORY

A special property of the process of spin–lattice relaxation of an ESSR is that its spectrum lies at relatively low frequencies (of the order of ν_L). The spectral density of phonons is then so low that direct relaxation of the ESSR as a result of one-phonon processes can be ignored. The exchange of energy between the ESSR and the lattice occurs only in the case of participation of hihg-frequency Zeeman or Stark subsystem. In particular, creation of a phonon of frequency $\nu_{ph}=\nu_0+\Delta_{ph}$ is accompanied by acquisition of an energy $h\nu_0$ from the high-frequency subsystem and of an energy $h\Delta_{ph}$ from the ESSR, exactly as in the case of the interaction between the spin system and a quantum of a microwave field of frequency $\nu=\nu_0+\Delta$. Therefore, naturally the equations describing the spin–lattice relaxation of the whole spin system are similar to the equations of Provotorov although they look somewhat more complex because of the finite lattice temperature and the need to integrate over the frequencies of all the phonons within the resonance line profile.[19,20,4]

We can show that if the frequency dependence of the rate of relaxation within a line profile is ignored,1) then both subsystems (high-frequency and ESSR) reach an equilibrium with the lattice independently of one another at rates characterized by the relaxation times τ_{SL} and τ_{SSL} and the ratio of these relaxation times is

$$a=M_2/\omega_L^2, \tag{6}$$

where M_2 is the second moment of a spin–phonon interaction line (for example that observed in an acoustic paramagnetic resonance).[19,20]

The difference between M_2 and the second moment M_2^{ESR} of an ESR line is frequently ignored. Then, at high values of H_0 it follows directly from Eq. (6) that $a=3$ for a pure Zeeman high-frequency subsystem and magnetic dipole–dipole interactions.[19,4] Clearly, this result was inapplicable to our case so that we had to calculate a the values of M_2 and ω_L^2 for $H_0=0$ making various assumptions on the spin–spin interaction mechanisms.

The calculation was carried out using standard procedures and allowing for the fact that the secular part of the spin–spin interactions $\hat{\mathscr{H}}_{SS}^{0}$ in $H_0=0$ contains only those matrix elements which retain the Stark energy with a characteristic frequency ν_0 (Refs. 22 and 23). The degeneracy of the Kramers doublets makes it necessary to allow also for the spin–phonon transitions accompanied by a change in the magnetic quantum number $\Delta m=\pm 1$ and ± 2 (Ref. 20). If the second moments corresponding to these transitions are denoted by $M_2^{(1)}$ and $M_2^{(2)}$, Eq. (6) can be replaced with

$$a=W_1a_1+W_2a_2,$$

where $a_i=M_2^{(i)}/\omega_L^2$ and W_i is the relative probability of the spin–phonon transitions characterized by $\Delta m=\pm i$ (it is assumed that $W_1+W_2=1$). It is known that in the case of ruby in zero field we have $W_2/W_1=2.07$ (Ref. 15), so that

$$a=0.326a_1+0.674a_2.$$

Our calculations were carried out for three types of the spin–spin interaction: magnetic dipole–dipole, isotropic exchange, and electric quadrupole–quadrupole (a possible role of the latter in ruby was pointed out by

TABLE I. Calculated parameters of ESSR for different types of spin–spin interactions.

Type of interaction	ω_L^2	a_1	a_2	a (for ruby)
Magnetic dipole–dipole	$8.48\hbar^2\gamma^4 c\sum_j r_{ij}^{-6}$	0,75	1,25	1,09
Exchange	$\frac{21}{4}c\sum_j A_{ij}^2$	1/2	9/7	1,03
Quadrupole–quadrupole (isotropic q tensor, $q_{20}=q_{21}=q_{22}=q$	$285q^4\hbar^{-2}c\sum_j r_{ij}^{-10}$	0.94	1.15	1.08
Same, for $q_{21}=q_{22}=0$	$50.5q_{20}^4\hbar^{-2}c\sum_j r_{ij}^{-10}$	2	2	2
Inhomogeneous broadening	M_2^{ESR}	1	1	1

Peskovatskii[24]). Complete formulas for ω_L, $M_2^{(1)}$, and $M_2^{(2)}$ are given in the Appendix; they may be useful in an analysis of the profile of an acoustic spin resonance line (both electron and nuclear quadrupole) in $H_0 = 0$.

Simplified expressions obtained by averaging the lattice sums in Eqs. (A.1)–(A.6) over the angles are collected in Table I. This table includes also the results for the case when the main contribution to an ESSR is made by a "reservoir of local fields" formed by cross relaxation inside an inhomogeneously broadened ESR line.[25,2] The following notation is used in Table I and in the Appendix: r_{ij}, θ_{ij}, and φ_{ij} are the polar coordinates of the j-th spin relative to the i-th spin (the z axis is specified by the crystal field); γ is the gyromagnetic ratio, q_{2m} are the components of the tensor of the quadrupole moment of the Cr^{3+} ions in the ground state; A_{ij} is the constant of the exchange interaction between the spins i and j. Summation in Table I is carried out over all the lattice sites and all the frequencies quoted are angular.

It is clear from Table I that, with the exception of the unlikely case of quadrupole interactions with a strongly anisotropic q tensor, all the mechanism under discussion give almost the same result2) for ruby: $a = 1.0$–1.1.

We shall now consider a different mechanism of spin-lattice relaxation of an ESSR. We shall assume that, in addition to the main impurity (with a spin S), there are also other paramagnetic centers (with a spin S_1) and the number of the latter is $N_1 \ll N$, whereas the spin-relaxation time of these centers is $\tau_1 \ll \tau_{SL}, \tau_{SSL}$. Fluctuating local fields created by the spins S_1 during their spin–lattice relaxation stimulate transitions in the ESSR spectrum and create a new ESSR–lattice coupling channel. The effectiveness of this mechanism is particularly high for $H_0 = 0$ and in this case the operator $\mathscr{H}_{SS}^0$ does not commute with $\mathbf{S}_z$, so that transitions with a change in the total magnetic quantum number by ±1 are possible (corresponding to a "resonance" inside the $\pm 1/2$ doublet).

There is as yet no self-consistent theory of this mechanism so that we shall confine ourselves to qualitative estimates on the basis of an analogy with nuclear spin–lattice relaxation induced by a paramagnetic impurity[26,27] (the same mechanism in the case of electron spin systems is known as nonresonant cross relaxation, described, for example, in Ref. 28). We must bear in mind that paramagnetic centers with a large initial splitting of the levels ΔE may have a fairly short time τ_1. In particular, we can expect that at helium temperatures $\Delta E \gtrsim kT_0$ and therefore, we cannot use the formulas deduced in the high-temperature approximation.

Employing this analogy and Ref. 29, we obtain the following expression for the relaxation time of an ESSR in the case of rapidly relaxing impurities:

$$\tau_{SSL}' \propto \frac{N\nu_L^2\tau_1}{N_1}\mathrm{ch}^2\left(\frac{\Delta E}{2kT_0}\right) \tag{7}$$

(we are assuming here fast spin diffusion of the main impurity with the spin S). If the time τ_1 is due to one-phonon processes, i.e., if it is proportional[1] to $\tanh(\Delta E/2kT_0)$, we find from Eq. (7) that

$$\tau_{SSL}' \propto \frac{N\nu_L^2}{N_1}\mathrm{sh}\left(\frac{\Delta E}{kT_0}\right). \tag{8}$$

Naturally, Eq. (8) should be treated with caution: in fact, the relaxation time τ_{SSL}' should depend on the actual structure of the energy spectrum of the S_1 spins, composition of their wave functions, details of spin diffusion, etc. Nevertheless, a deviation from the law $\tau_{SSL} \propto 1/T_0$ can be regarded as a reliable distinguishing feature of the influence of a rapidly relaxing impurity.

4. DISCUSSION OF RESULTS

A comparison of the experimental values of τ_{SL}/τ_{SSL} (Sec. 2) with the parameter a in Table I shows that the experimental results cannot be explained simply by the relaxation of an ESSR via its "own" Stark subsystem of the Cr^{3+} ions. Consequently, rapidly relaxing accidental impurities must play an important role.

This is supported also by the strongly nonlinear nature of the dependence $\tau_{SSL}(1/T_0)$ shown in Fig. 3.

On the other hand, it is clear that cooling and reduction in T_0 should reduce gradually a, which approaches more and more closely its theoretical value of unity. Consequently, we shall try to represent the experimental values of τ_{SSL}^{-1} in the form of a sum:

$$\tau_{SSL}^{-1} = \tau_{SL}^{-1} + (\tau_{SSL}')^{-1},$$

where the first term corresponds to the process of ESSR relaxation via the Stark subsystem of Cr^{3+} (it is assumed that $a = 1$) and the second term describes the influence of an unknown impurity.

Using Eq. (8) and the temperature dependence of τ_{SL} for ruby,[13-15] we obtain

$$\tau_{SSL}^{-1} = AT_0 + B\,\mathrm{csch}\,(\Delta E/kT_0), \tag{9}$$

where $A = 1.0$ and $1.15\ \mathrm{sec}^{-1}\cdot{}^\circ\mathrm{K}^{-1}$ applies to $c = 0.018$ and 0.037%, respectively[13-15]; B is an adjustable coefficient independent of T_0.

The results of a calculation carried out using Eq. (9) and assuming that $\Delta E/k = 8.0\,^\circ\mathrm{K}$, $B(0.018\%) = 19\ \mathrm{sec}^{-1}$, and $B(0.037\%) = 115\ \mathrm{sec}^{-1}$ are represented by the chain curve in Fig. 3. We can see that there is a generally good agreement with the experimental results although in some cases the experimental points deviate considerably from the theoretical curve.3)

A comparison of our value of ΔE with the published data[30] shows that the rapidly relaxing impurities can be the Cr^{2+} ions for which the separation between the lower levels is close to the value of ΔE. It is known that the Cr^{2+} ions present in ruby in concentrations of the order of $10^{-3}\%$ reduce considerably the relaxation time τ_{SL}, particularly in the field $H_0=0$ (Refs. 28 and 31). The mechanism of this influence is still the same cross relaxation whose theoretical analysis has been carried out in Ref. 28 allowing for the whole multilevel spectrum of Cr^{2+}.

The results of application of this calculation to our case are also included in Fig. 3 (continuous curves). We can see that the agreement with the experiment is retained and is even slightly improved compared with the simplified formula (9).

We recall that relaxation of the Cr^{3+} Stark subsystem with a frequency ν_0 was investigated in Ref. 28 and in our experiments we studied the relaxation of an ESSR of frequency ν_L. We can see from Fig. 3 that the influence of stray impurities is amplified by a factor of $(\nu_0/\nu_L)^2$. Thus, the reduction in τ_{SSL} in our experiments may occur already at the Cr^{2+} concentrations of the order of $10^{-6}\%$, which are difficult to detect by any other method.

Our assumption that the ruby crystals are contaminated by Cr^{2+} ions can explain also the observed strong scatter of the values of τ_{SSL} from one sample to another (Fig. 2), which can naturally be attributed to different concentrations of the accidental impurity. It is more difficult to account for the reason in the unavoidable reduction in τ_{SSL} on increase in the Cr^{3+} concentration (Fig. 2); a similar behavior has been reported also for the τ_{SL} time in Refs. 28 and 32, where rapidly relaxing paramagnetic centers have been introduced in a controlled manner. However, we have been unable to alter τ_{SSL} by illumination of a sample with ultraviolet light for many hours, known to convert Cr^{2+} into Cr^{3+} (Refs. 28 and 31).[4] Consequently, it is desirable to consider other possible reasons for the reduction in τ_{SSL} observed in our experiments.

One of these alternative hypothesis is the identification of the unknown impurity with exchange pairs (or triplets) of Cr^{3+} ions known to have fairly high values of ΔE and $1/\tau_1$ (Refs. 33 and 34). In the case of a random distribution of the impurities the number of pairs is proportional to c^2 and the number of triplets to c^3 so that we can now easily explain the concentration-induced reduction in τ_{SSL}. A possible reason for the strong scatter of the results might be a deviation from the random distribution of the Cr^{3+} ions, i.e., an excess number of clusters in those samples for which τ_{SSL} is short. We checked this hypothesis by selecting samples with similar values of c but very different values of τ_{SSL}, and we determined the intensity of the luminescence due to two types of exchange pairs (N_1 and N_2 lines, see Ref. 25). There was no correlation between the concentrations of these pairs and the reduction in τ_{SSL}, which was evidently not in agreement with the proposed interpretation, although one could not exclude a possible role of other types of cluster.

We shall now consider the nature of the dominant spin–spin interactions in ruby on the basis of the value $\nu_L=100$ MHz obtained in Sec. 2 for $c=0.018\%$. This value is considerably greater than the half-width of the ESR line (amounting to 40 MHz—Ref. 24). Thus, an inhomogeneously broadened ESR line of Gaussian profile observed in the usual way is only the "tip of the iceberg," whereas the main contribution to C_{SS} is made by the invisible extended wings of the line due to the spin-spin interactions. However, it is known that these wings are not wide enough for detuning of the order of ν_0, because otherwise it would have been impossible to cool an ESSR by microwave pumping (such a situation may occur at higher values of c—see Ref. 24).

We shall now compare the above value of ν_L with the theoretical results of Sec. 3. We shall bear in mind that if $r_{ij} \leq 5.5$ Å the Cr^{3+} ions from exchange pairs with the coupling energy of the order of 1 cm^{-1} or higher.[33] Such interactions clearly do not form part of the quasicontinuous spectrum of an ESSR and, therefore, we can drop the corresponding terms of the lattice sums in Table I and for $r_{ij} > 5.5$ Å we can replace summation with integration. Consequently, in the case of dipole interactions and for $c=0.018\%$ we obtain $\nu_L=70$ MHz, which is 1.5 times less than the experimental value. In our opinion this discrepancy is not so large as to raise doubts about the dominant role of the magnetic dipole interactions, although some contribution to $\mathscr{H}^0_{SS}$ must be made also by the exchange interaction and inhomogeneous width. It should be stressed that the experiments involving cooling of an ESSR[2,7] provide possibly the only reliable way of measuring ν_L (and, consequently, M_2^{ESR}) whereas the traditional method for the determination of these quantities from the ESR line width almost always underestimates the results.

The final interpretation of our and future results on spin–lattice relaxation of an ESSR will require development of a suitable theory, which is still in the initial stages. We hope that our investigation will draw attention of theoreticians to this pressing need.

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APPENDIX

We shall give below the results of a calculation of ω_L^2, $M_2^{(1)}$, and $M_2^{(2)}$ for two types of spin–spin interaction in a system with $S=3/2$ in $H_0=0$ (for an axially symmetric spin Hamiltonian):

Magnetic dipole–dipole interaction

This case is described by

$$\omega_L{}^2=\frac{\hbar^2\gamma^4}{32N}\sum_{i\neq j}{}' r_{ij}{}^{-6}(117x+720y+153z), \tag{A.1}$$

$$M_2{}^{(1)}=\frac{\hbar^2\gamma^4}{32N}\sum_{i\neq j}{}' r_{ij}{}^{-6}(69x+504y+153z), \tag{A.2}$$

$$M_2{}^{(2)}=\frac{\hbar^2\gamma^4}{32N}\sum_{i\neq j}{}' r_{ij}{}^{-6}(165x+936y+153z). \tag{A.3}$$

Here, $x=(1-3\cos^2\theta_{ij})^2$, $y=\sin^2\theta_{ij}\cos^2\theta_{ij}$, $z=\sin^4\theta_{ij}$. The prime of the summation sign denotes that this operation should be carried out over all the sites occupied by impurity centers. Equations (A.2) and (A.3) differ from those obtained in Ref. 23 by the absence of the terms proportional to $\cos 2\varphi_{ij}$ and $\cos 4\varphi_{ij}$; these terms disappear in the presence of the crystal axis C_3.

Electric quadrupole–quadrupole interaction[36,24]

In this case we have

$$\omega_L^2=\frac{256\pi^3}{225\hbar^2N}\sum_{i>j}{}' r_{ij}^{-10}(aq_{20}^4+bq_{21}^4+cq_{22}^4+dq_{21}^2q_{22}^2), \qquad \text{(A.4)}$$

$$M_2^{(1)}=\frac{256\pi^3}{225\hbar^2N}\sum_{i>j}{}' r_{ij}^{-10}(2aq_{20}^4+bq_{21}^4+cq_{22}^4+dq_{21}^2q_{22}^2-8fq_{20}^2q_{21}^2), \qquad \text{(A.5)}$$

$$M_2^{(2)}=\frac{256\pi^3}{225\hbar^2N}\sum_{i>j}{}' r_{ij}^{-10}(2aq_{20}^4+bq_{21}^4+cq_{22}^4+dq_{21}^2q_{22}^2-fq_{20}^2q_{21}^2). \qquad \text{(A.6)}$$

Here, $a=36Y_{4,0}^2$, $b=16(10Y_{4,-2}Y_{4,-2}+Y_{4,0}^2)$, and $c=70Y_{4,2}Y_{4,-2}+Y_{4,0}^2$, $d=-10(7Y_{4,3}Y_{4,-3}+Y_{4,-1})$, and $f=6Y_{4,0}^2$, where $Y_{4,m}$ are spherical harmonics which are functions of the angles θ_j and φ_{ij}.

1) Possible consequences of this dependence are considered in Refs. 19 and 21.

2) This conclusion does not apply to crystals with a different relationship between a_1 and a_2 (see the relevant columns in Table I).

3) The presence of such a region in the interval 2.5–4.2°K for a sample with $c=0.037\%$ resulted in an overestimate of the value of E in our preliminary experiments.[12]

4) It is possible that the reaction $\mathrm{Cr}^{2+}\rightarrow\mathrm{Cr}^{3+}$ does not occur at such very low concentrations of Cr^{2+}.

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