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PARAMAGNETIC RELAXATION IN $K_3(Fe, Co)(CN)_6$ *AT TEMPERATURES FROM 0.1 TO 4.2°K*

A. M. PROKHOROV and V. B. FEDOROV

P. N. Lebedev Physics Institute, Academy of Sciences, U.S.S.R.

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The temperature dependence of the paramagnetic spin-lattice relaxation time of the Fe^{3+} ion in the $K_3Co(CN)_6$ lattice in the range $T = 0.08-4.2°K$ was measured by continuous saturation of the electron paramagnetic resonance absorption line at 42 Mcs. The temperature dependence of the relaxation time was studied for ferric-ion concentrations of 0.1%, 0.21%, and 0.46% in a constant magnetic field directed along the c axis of the crystal and also for three orientations of the constant magnetic field relative to the crystal ($H_0 \parallel a, b, c$) for a concentration of 0.21%. Unlike the experiments carried out by various authors at frequencies of 10^4 Mcs, the present results contradict the Van Vleck–Kronig theory of paramagnetic relaxation. In this connection, the role of exchange-coupled ions ("ion pairs," not important at high frequencies) in the transfer of excitation energy from Fe^{3+} ions to the thermal motion of the lattice is discussed. A mechanism for the relaxation process is proposed which is based on the energy spectrum of ion pairs in iron cyanide and on certain assumptions; the mechanism is capable of qualitatively explaining the experimental data. A theory of single-phonon spin-lattice interaction of ion pairs is developed for the case of strong (compared to the Zeeman energy) exchange coupling of the iron ions. The theoretical calculations confirm the assumptions that were made in order to interpret the experimental facts and also yield, from the experimental point of view, satisfactory absolute values of the non-radiative transitions of the ion pairs. The comparison of theory and experimental data indicates that ion pairs play a principal role in the transfer of energy from the ferric ions to the lattice at low temperatures and low frequencies.

IN the last few years, investigations of paramagnetic relaxation have become essential in connection with various applications of paramagnetic crystals. Of particular practical and theoretical interest is the study of paramagnetic relaxation at low temperatures.

The spin-lattice relaxation time in monocrystals of potassium cobalticyanide $K_3CO(CN)_6$ containing admixtures of trivalent iron Fe^{3+} has been investigated in a number of papers.[1-4] The experiments were carried out by saturation of the EPR (electron paramagnetic resonance) line with centimeter waves ($\lambda \approx 3$ to 10 cm). The results thus obtained were in satisfactory agreement with the Van Vleck–Kronig theory.[3,4] Since this theory does not take into account spin-spin interactions of the paramagnetic ions but in essence considers the transfer of the excitation energy of an isolated paramagnetic ion to the thermal motion of the crystal lattice, the probability of a non-radiative transition in the theory is derived to be independent of the concentration. Our experiments, which were conducted at the low frequency $\nu = 42$ Mcs ($\lambda = 714$ cm) disclosed a strong concentration dependence of the relaxation time; for example, at temperature $T = 1°K$ the relaxation time of samples with a ferric-ion concentration $f_1 = 2.1 \times 10^{-3}$ and $f_2 = 4.6 \times 10^{-3}$ (with respect to the number of diamagnetic cobalt ions) differs by a factor of about 60. The absolute value of the relaxation time in our experiments (e.g., at $T = 1°K$ and $f_1 = 2.1 \times 10^{-3}$, $\tau \approx 0.02$ sec) differs strongly from the value $\tau \sim 3 \times 10^8$ sec at $T = 1°K$ obtained by converting the experimental data on the saturation of the EPR line of the ferrycyanide at the frequency $\nu \approx 10^4$ Mcs[3] to the frequency $\nu \approx 50$ Mcs (according to theory[3,4] $1/\tau \sim \nu^4$). Thus, our experiments cannot be understood in the framework of the usual Van Vleck–Kronig theory.

In this paper it is shown that the observed peculiarities of the paramagnetic relaxation in ferricyanide in experiments at low frequencies are associated with weak exchange interactions in the system of paramagnetic ferric ions, which interactions are unimportant in experiments in high magnetic fields and high frequencies.

1. EXPERIMENTAL RESULTS

The EPR spectrum of $K_3(Fe, Co)(CN)_6$ consists of a single absorption line and is described by a spin Hamiltonian with an effective spin $s = 1/2$[5]:

$$\mathscr{H} = \beta (H_x g_{xx} \hat{s}_x + H_y g_{yy} \hat{s}_y + H_z g_{zz} \hat{s}_z), \qquad (1)$$

where β is the Bohr magneton, $g_{xx} = 2.35$, $g_{yy} = 2.10$, and $g_{zz} = 0.91$ are the principal values of the spectroscopic splitting g tensor, H_x, H_y, and H_z are the components of the dc magnetic field on the x, y, and z axes, and $\hat{s}_x$, $\hat{s}_y$, and $\hat{s}_z$ are spin operators. The orientation of the x, y, z and the x′, y′, z′ axes for the two unequivalent positions of the iron ions in a unit cell of the crystal relative to the orthorhombic axes a, b, c[5] is shown in Fig. 1. If the dc magnetic field is directed along one of the crystal axes a, b, or c, the spectra of the unequivalent ions coincide exactly. The corresponding g factors are $g_{aa} = 2.29$, $g_{bb} = 2.16$, $g_{cc} = 0.91$.

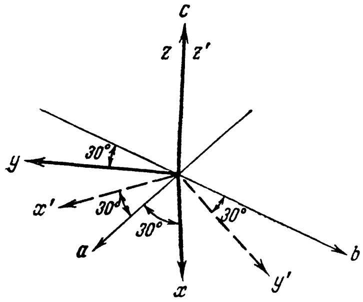

FIG. 1. Orientation of the octahedron of six CN^- groups for the two unequivalent iron ions in a unit cell relative to the a, b, c axes. Because of the deformation of the octahedron, the c axis is its two-fold symmetry axis; y and y′ are four-fold symmetry axes.[5]

In our experiments we measured by the saturation method the temperature dependence of the spin-lattice relaxation time in the interval 0.08 to 4.20°K, at a frequency of 42 Mcs. In the case with the external magnetic field parallel to the crystal c axis ($H_0 \parallel c$), we investigated samples with iron-ion concentrations $f = 10^{-3}$, 2.1×10^{-3}, 4.6×10^{-3} (as determined by chemical analysis) and of weights 0.31, 0.6 to 0.45, and 0.15 g, respectively. For the concentration f = 0.21%, the temperature behavior of the relaxation time was taken for three orientations of the crystal relative to the constant magnetic field, corresponding to the cases $H_0 \parallel a, b, c$. The curves obtained for the samples with f = 0.21 and 0.46% are presented in Fig. 2. Far fewer data on spin-lattice relaxation were obtained from the sample with $f = 10^{-3}$ because of limited spectrometer sensitivity and the very low rate of the relaxation process. It was found that for $H_0 \parallel c$ the spin-lattice relaxation time $\tau = (2-6) \times 10^{-3}$ sec at T = 4.2°K, $\tau = (0.7 \pm 0.3)$ sec at T = 2.25°K, and $\tau = (1.8 \pm 0.8)$ sec at T = 1.5°K. At lower temperatures the absorption line was not observed because of strong saturation even with the minimum of rf power in the sample coil.

The spin-lattice relaxation time τ was calculated from the relation

$$\frac{1}{\tau} = \left(\frac{\varkappa}{1-\varkappa}\right) \frac{k\gamma H_1^2}{\Delta H}, \qquad (2)$$

where $\gamma = 2\pi g\beta/h$ is the gyromagnetic ratio, $k = 0.62 \pm 0.12$ (k = 0.74 for a Gaussian line and 0.50 for a Lorentzian line), $H_1^2 = 5 \times 10^{-4} U_0^2$ is the squared amplitude of the alternating magnetic field of frequency 42 Mcs, measured in the experiment from the amplitude of the rf voltage U_0 on the sample coil, ΔH and κ are the experimentally measured line width and saturation factor.

The experiment was performed in the following way. During pumping on the liquid helium in the temperature interval 4.2 to 1.5°K, and then during warming of the pre-cooled sample in the interval 0.08 to 1.50°K, the temperature dependence of the amplitude and width of the absorption line was measured at various values of U_0 (see Fig. 2). The spectrometer circuit provided for an absolute measurement of the intensity of absorption by means of comparing the EPR signal with a calibrating signal from a variable active resistance connected parallel to the sample coil.

The intensity of absorption, referred to the calibrating signal, did not depend on the rf magnetic field in the absence of saturation. The calibrating signal was also used to control the linearity of the spectrometer. The absorption line was observed on an oscilloscope simultaneously with the calibrating signal and photographed. In order to observe the EPR signal on the oscilloscope the dc magnetic field was modulated sinusoidally at a frequency of 0.5 cps and amplitude 25 to 35 Oe. It was found that over the entire temperature interval the line width of the investigated samples did not depend on temperature and the amplitude of the applied rf field within the limits of error (see the table, where the measured values of ΔH are given in Oersteds). Hence, at all temperatures the saturation factor was determined as the ratio $\kappa = I/I_0$, where I and I_0 are the peak amplitudes of the EPR line referred to the magnitude of the

Orientation	Concentration	
	$2.1\cdot10^{-3}$	$4.6\cdot10^{-3}$
$H_0 \parallel a$	9.5 ± 1.0	—
$H_0 \parallel b$	$10.8\pm1,6$	—
$H_0 \parallel c$	$14,5\pm1,3$	$18\pm1,3$

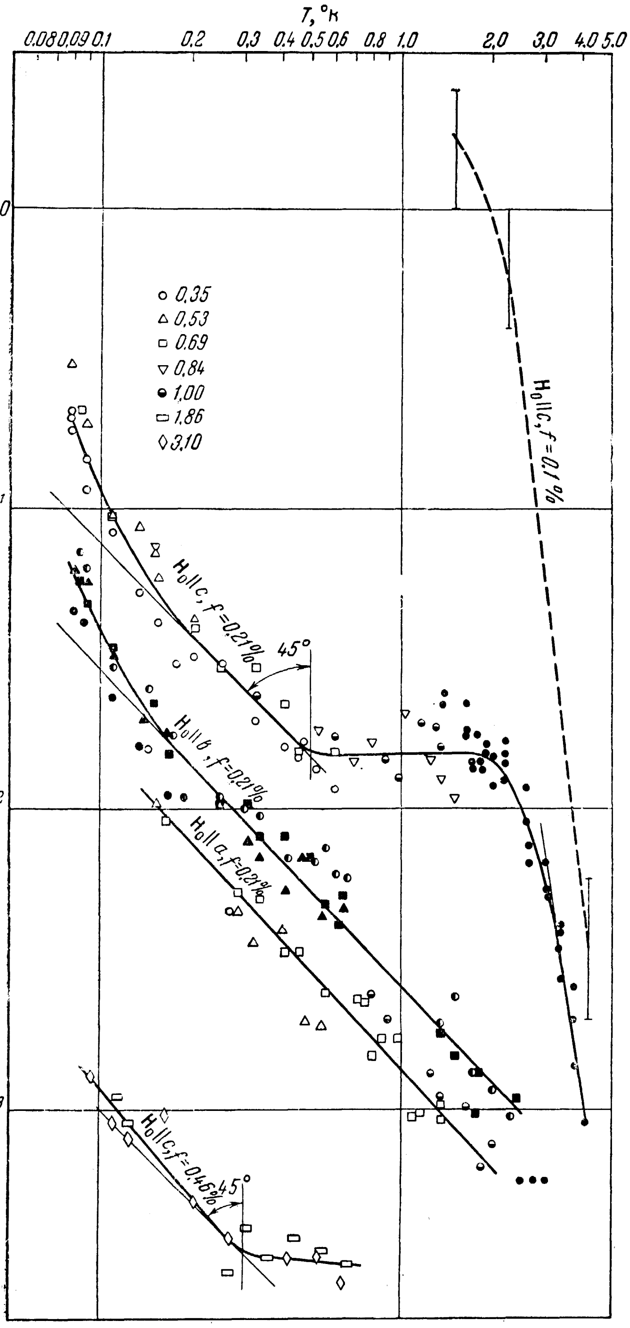

FIG. 2. The temperature dependence of the relaxation transition probability of Fe^{3+} ions in ferricyanide. The concentration of the ions and the orientation of the external magnetic field relative to the crystal axes are shown next to the curves. The different symbols give the points for different amplitudes of the rf voltage U_0 on the sample coil ($H_1^2 = 5 \times 10^{-4}\ U_0^2$).

calibrating signal: I—in the presence of a saturating rf magnetic field H_1, I_0—with a small value of the rf magnetic field that does not change (within the limits of experimental error) the magnitude of I_0, i.e., in the absence of saturation. However, in our experiments, noticeable saturation was always observed in the region of lowest temperatures even with the smallest possible voltage on the coil, $U_0 \sim 0.3$ V. In this temperature region the magnitude of I_0 was determined by extrapolation of the values of I_0 at high temperatures, where reduction of the rf voltage permitted elimination of the saturation effect, according to the T^{-1} law. The values of τ obtained in this way from Eq. (2) for different values of H_1 at each temperature agreed well with each other.

The relative accuracy of our measurements is characterized by the scatter of the points on the curves of Fig. 2. We have estimated the systematic error to be $\Delta\tau/\tau \lesssim \pm 0.6$. The accuracy of the temperature measurement was better than 10%.

The crystal to be investigated was placed in the coil during preparation of the apparatus for the experiment such that the angle between one of its axes and the dc magnetic field H_0 did not exceed ± 5°. In the experiment the direction of the dc field was perpendicular to the direction of the rf field and could be changed by an arbitrary angle in the ac or bc plane. No special efforts to measure the g factors were made. However, the ratio of the resonance fields in the cases $H_0 \parallel c$ and $H_0 \parallel a$ or b was ~ 2 in all the runs, which agrees with the data in [5].

We omit here any detailed description of the spectrometer we used for observation of EPR absorption at temperatures below 1°K. This description was given earlier.[6,7] Some time earlier, experiments were also published on EPR at very low temperatures in the centimeter-wave region.[8]

To conclude this section we summarize the results of the experiments performed. In Fig. 2 two temperature regions can be distinguished. In the region of relatively high temperature, T = 4.2—2.0°K, we have experimental data for concentrations f = 0.21 and 0.10% in the case $H_0 \parallel c$. For f = 0.21% the relaxation time $\tau(4.2°\text{K}) \approx 10^{-3}$ sec does not differ much from the value $\tau(4.2°\text{K}) \approx 5 \times 10^{-4}$ sec obtained in the experiments at $\sim 10^4$ Mcs. In the temperature interval 4.2 to 2.25°K for the concentration 0.1% we have the dependence $1/\tau \sim T^9$, for f = 0.21% the analogous relation in the interval 4.2—3.4°K has the form $1/\tau \sim T^7$. The strong temperature dependence of the relaxation time in this region indicates that the transfer of energy from the spins to the lattice proceeds principally via the mechanism of Raman scattering of the phonons by the paramagnetic ions (two-phonon processes). The aforementioned difference in the non-radiative transition probability for $f = 0.1$ and 0.21% close to $T = 4.2°K$ and the data of experiments at $\lambda \sim 3$ cm point to the presence (along with the usual spin-phonon interaction via spin-orbit coupling in the Van Vleck–Kronig theory) of an interaction of the spins with the thermal vibrations of the lattice according to the Waller mechanism via spin-spin interactions that depend on the concentration of paramagnetic ions (the nature of these is discussed below).

From our point of view, the most interesting as well as the most detailed experimental data pertain to the temperature region $T < 2°K$. First, we note for the case $\mathbf{H}_0 \parallel c$ the constancy of the relaxation time for $T < 2°K$, which only in the region of lowest temperatures turns to a linear dependence $1/\tau \sim T$ (see Fig. 2). Second, an approximately two-fold increase in the concentration of paramagnetic ions does not change, apparently, the form of the curve $1/\tau(T°K)$ in the case $\mathbf{H}_0 \parallel c$, but very strongly, up to a hundred-fold, increases the probability of a non-radiative transition. From the data for $f = 0.1\%$ and $\mathbf{H}_0 \parallel c$ at $T \approx 2°K$ it follows (if it is assumed that $1/\tau$ cannot increase on cooling) that in the region $T < 2°K$ for this concentration $1/\tau$ is also reduced in comparison to $f = 0.21\%$ not less than 100-fold. And, finally, a change in orientation relative to the external magnetic field of the investigated crystal with ferric-ion concentration of 0.21% completely changes the character of the dependence of $1/\tau$ on temperature. In the cases $\mathbf{H}_0 \parallel a$ and $\mathbf{H}_0 \parallel b$ one sees a nearly linear temperature behavior of the relaxation time. The latter fact obviously indicates that the relaxation mechanisms in the cases $\mathbf{H}_0 \parallel c$ and $\mathbf{H}_0 \parallel a$ are different.

We note that even at the lowest temperatures no effect of heating the lattice was observed at the frequencies of single-phonon relaxation processes, since within the limits of experimental error the results obtained from Eq. (2) do not depend on the amplitude of the rf field.

2. THE HYPOTHETICAL SPIN-LATTICE RELAXATION MECHANISM

We shall discuss the possibility of an effect on spin-lattice relaxation due to exchange interactions of paramagnetic ions.

In magnetically dilute crystals the energy of the exchange interaction differs from zero only for a relatively small number of pairs of ions n_i located at adjacent or nearby crystal lattice points. For a small concentration of paramagnetic ions ($f \ll 1$),

$$n_i = \frac{N}{2} f z_i. \tag{3}$$

Here N is the total number of paramagnetic ions in the crystal, and z_i is the number of possible locations in the lattice of one of the ions of the pair with respect to the other for which the energy spectrum of the pair of ions is identical. Such pairs are labeled by the index i. We can speak of an exchange spin system described by the Hamiltonian

$$\hat{\mathcal{H}} = \tfrac{1}{2} N f \sum_i z_i \hat{\mathcal{H}}_i^{ex},$$

where $\hat{\mathcal{H}}_i^{ex}$ is the Hamiltonian of one pair of the i-th kind. If the ion pairs have a short relaxation time, then even at small concentrations they can play an important role in the transfer of energy from isolated paramagnetic ions to the lattice. Van Vleck[9] was the first to call attention to this possibility. Two mechanisms of spin-lattice relaxation involving ion pairs were treated theoretically in [10-12].

The first mechanism is similar to that proposed by Bloembergen and Wang.[13] It leads to a relaxation time for the paramagnetic ions:

$$\tau = \tau_1(1 + A_1\tau_2 / A_2\tau_1). \tag{4}$$

Here τ_1 is the temperature independent characteristic time of establishment of equilibrium between the two spin subsystems: the Zeeman, with Hamiltonian (1), and the exchange system; τ_2 is a time that characterizes the rate of non-radiative transitions from the exchange system to the lattice; $A_1 \sim N(h\nu_Z)^2$ and $A_2 \sim n(h\nu_{ex})^2$ are temperature-independent constants in the expressions for the energy of the Zeeman and exchange subsystems, respectively, $E = \text{const} - A/kT$. The transfer of excitation from the spins in the magnetic field to the pairs proceeds via cross-relaxation. Therefore, this mechanism is possible if there are in the spectrum of an ion pair frequencies that are so close to the Zeeman frequency that the difference $(h\nu_{ex} - h\nu_Z)$ is not very much greater than the energy of the dipolar spin-spin interaction of the ion pair with isolated ions. Cross-relaxation processes of higher order are also possible in case some frequency in the spectrum of the ion pair is a multiple of the Zeeman transition frequency.[10]

The second mechanism for spin-lattice relaxation is free from this limitation on the ratio of the Zeeman and exchange frequencies. It consists in the simultaneous quantum transition of an isolated spin with emission of a photon $h\nu_z$, of an ion pair with emission or absorption of a quantum $h\nu_{ex}$, and the creation or absorption of a phonon with energy $(h\nu_{ex} \pm h\nu_z)$. The possible large values of the ratio $h\nu_{ex}/h\nu_z \gg 1$ strongly shorten the relaxation time. In order of magnitude[10]

$$\frac{1}{\tau} \sim \frac{1}{\tau_2}\left(\frac{\mu_1\mu_2/r^3{}_0}{h\nu_z}\right)^2 \approx \frac{1}{\tau_2}\left(\frac{g^2\beta^2/r^3{}_0}{h\nu_z}\right)^2. \qquad (5)$$

The simultaneity of the process is due to the dipolar interaction between the magnetic moments of an isolated ion μ_1 and an ion pair μ_2.

The hypothesis proposed to explain the experimental data is that the first spin-lattice relaxation mechanism operates when $\mathbf{H}_0 \parallel c$ for the concentrations f = 0.21% and 0.46%, and the second operates in the cases $\mathbf{H}_0 \parallel a$ and $\mathbf{H}_0 \parallel b$ for the iron-ion concentration f = 0.21%.

The linear behavior with temperature of the quantity $1/\tau$ for the orientations $\mathbf{H}_0 \parallel a$ and $\mathbf{H}_0 \parallel b$ is due, then, to the relation $1/\tau \sim T$ arising from the single-phonon resonant transfer of energy from the exchange pairs to the lattice at low temperatures. Because of the dependence $1/\tau \sim g^4$ when $h\nu_z = \text{const}$, this mechanism is very much less effective in the case $\mathbf{H}_0 \parallel c$, since $g_{cc} \approx 1$, and $g_{aa} = 2.29$, $g_{bb} = 2.16$. Conversion of the experimental data (see Fig. 2) for the case $\mathbf{H}_0 \parallel a$ to the g factor for the orientation $\mathbf{H}_0 \parallel c$ by using Eq. (5) leads to values of $1/\tau$ that are approximately five times less than the experimentally observed values for $\mathbf{H}_0 \parallel c$.

In the orientation $\mathbf{H}_0 \parallel c$ the horizontal portion of the $1/\tau$ vs. T curve corresponds to the case

$$A_1\tau_2 / A_2\tau_1 < 1 \text{ and } \tau \approx \tau_1. \qquad (4a)$$

The lower-temperature interval, where the relaxation time increases approximately linearly with temperature, belongs to the case

$$A_1\tau_2 / A_2\tau_1 > 1 \text{ and } \tau \approx A_1\tau_2 / A_2. \qquad (4b)$$

As before, a linear dependence of τ_2^{-1} on temperature indicates that a transfer of energy from the exchange system to the lattice, resonant at frequency ν_{ex} (single-phonon process), takes place.

The proposed hypothesis permits a qualitative explanation of the strong concentration dependence of the relaxation time in the orientation $\mathbf{H}_0 \parallel c$. Since at low concentrations of paramagnetic ions cross relaxation between Zeeman and exchange transitions with significantly different frequencies is made difficult, it can happen that at low temperatures the thermal contact of the exchange system with the lattice is established by means of single-phonon processes not at all possible frequencies of the spectrum of the exchange system, but only at certain ones. Here it is important that there is no cross relaxation inside the exchange system, since the ion pairs interact weakly with each other. Considering the frequency dependence $1/\tau_2 \sim \nu_{ex}^2$ (see Sec. 4), we have for $1/\tau$, on the basis of Eq. (4b),

$$1/\tau \sim f(\nu^4{}_{ex}/\nu^2{}_z)\,kT. \qquad (4b')$$

To explain the experimental data we now propose that for the crystal with f = 0.46%, the transfer of energy to the lattice goes in a fundamental quantum with energy $h\nu''_{ex}$ that is larger than $h\nu'_{ex}$ for the concentration f = 0.21%. The ratio $h\nu''_{ex}/h\nu'_{ex} = 2.2$ explains, by Eq. (4b′), the shortening of the time τ by ~ 50 times. Experimentally, the relaxation times for these concentrations at T = 0.2°K differ by ~ 80 times.

In order that the indicated dependence on concentration in the transfer of excitation from the ion pairs to the lattice be possible, an abrupt shortening of the cross-relaxation time τ_1 between the Zeeman transition and an exchange transition with frequency ν''_{ex} compared to the cross-relaxation time between the Zeeman transition and an exchange transition with the lower frequency ν'_{ex} is required when the concentration goes from 0.21% to 0.46%. Experimentally, this shortening of the time τ_1 (see Fig. 2) corresponds to ~ 50. Cross-relaxation processes of high order can give such a strong concentration dependence.[10] The relatively large absolute value of $1/\tau_1$ in this case is attained only when the frequency of the exchange subsystem is a multiple of the Zeeman frequency. A contribution to the degree of the dependence of τ_1 on concentration can also be furnished by spin diffusion, which evidently is responsible for the transfer of excitation to the immediate surroundings of the ion pair and takes priority over a cross-relaxation transition with transfer of excitation energy from an isolated ion to an ion pair.

If the sample is cooled so much that $kT < J$, where J is the separation between the energy levels of the ion pair that participate in the relaxation transitions and the ground state, then the number of pairs, and consequently also the probability of a relaxation transition, falls exponentially as the temperature is lowered, in accordance with Eq. (4b):

$$1/\tau \sim kT \exp(-J/kT). \qquad (4b'')$$

This effect explains the faster-than-linear growth of $1/\tau$ on cooling for the case $\mathbf{H}_0 \parallel c$.

Thus, the hypothesis considered here qualitatively encompasses the experimental facts for $T < 2°K$. In order to prove the hypothesis, it is necessary to determine the energy spectrum of the exchange system in ferricyanide, then calculate theoretically the probabilities of relaxation transitions $1/\tau_1$ and $1/\tau_2$ and compare them with experiment. This problem is partially solved in the succeeding sections of this paper.

3. ENERGY SPECTRUM OF ION PAIRS IN FERRICYANIDE

The exchange interactions of ferric ions in cyanides have been studied in [14,15,5]. In the first of these, the static magnetic susceptibility of $K_3Fe(CN)_6$ was measured in the interval 1.0 to 20°K. In the second work, a direct observation was made of the EPR spectrum of ion pairs in $K_3(Fe, Co)(CN)_6$ at an iron concentration of about 5%. The lattice parameters of both crystals are practically the same.[16] The experiments were interpreted in terms of the Hamiltonian

$$\hat{\mathscr{H}}_{12} = J\hat{s}_1\hat{s}_2 + \hat{s}_1\Gamma\hat{s}_2 - \beta H_0 g(\hat{s}_1 + \hat{s}_2). \tag{6}$$

The first term corresponds to an isotropic exchange interaction of the ions with $s_1 = s_2 = 1/2$, the second to a symmetrical anisotropic exchange interaction. The following results were obtained: $J = 0.29\ \text{cm}^{-1}$, the principal axes of the tensor Γ coincide with the crystal axes a, b, c, and $\Gamma_a = -0.043\ \text{cm}^{-1}$, $\Gamma_b = -0.021\ \text{cm}^{-1}$, $\Gamma_c = +0.064\ \text{cm}^{-1}$, $\Gamma_a + \Gamma_b + \Gamma_c = 0$. These numbers correspond to the nearest-neighbor positions of the iron ions in the crystal lattice. It was shown that the maximum number z_1 of neighbors to which a given ion can be coupled by the exchange interaction of the indicated magnitude is 2. This circumstance and also the structure of the crystal lattice apparently show [16] that the ion pairs with the maximum exchange interaction are formed from ferric ions that are arranged along the a axis of the unit cell. Along the two other lattice directions the tetrahedral $[Fe(CN)_6]^{3-}$ complexes are separated by potassium K^+ ions; the ionic character of the coupling between these ions and the cyanide complexes obviously precludes the possibility of electronic exchange between the ferric ions in these directions. The maximum exchange interaction also cannot be attributed to ions in the two unequivalent sites in one unit cell of the crystal since in this case $z_1 = 4$. Ohtsuka [15] also observed other, unexplained absorption lines evidently belonging to pairs of nearest unequivalent ions or to pairs of more widely separated iron ions.

We shall consider the experimental data in terms of a spin Hamiltonian more general than Eq. (6):

$$\begin{aligned}
&\hat{\mathscr{H}}^S = \hat{\mathscr{H}}^J + \hat{\mathscr{H}}^D + \hat{\mathscr{H}}^\Gamma + \hat{\mathscr{H}}^Z,\\
&\hat{\mathscr{H}}^J = \frac{J}{2}\left[S(S+1) - \frac{3}{2}\right],\\
&\hat{\mathscr{H}}^D = \mathbf{D}\,[\hat{\mathrm{s}}_1\hat{\mathrm{s}}_2],\\
&\hat{\mathscr{H}}^\Gamma = \frac{1}{2}(\Gamma_a\hat{S}_a{}^2 + \Gamma_b\hat{S}_b{}^2 + \Gamma_c\hat{S}_c{}^2),\\
&\hat{\mathscr{H}}^Z = -\beta\mathbf{H}_0 g\mathrm{S}.
\end{aligned} \tag{7}$$

The difference from Eq. (6) consists in the addition of an antisymmetric anisotropic exchange coupling $\hat{\mathcal{H}}^D$, which was suggested in the work of Dzyaloshinskiĭ [17] and calculated quantum mechanically by Moriya.[18] The total spin of the pair $\mathbf{S} = \mathbf{s}_1 + \mathbf{s}_2$ ($S = 0, 1$) is introduced in Eq. (7).

We shall find the eigenvalues and eigenfunctions of the Hamiltonian (7) by the perturbation method, taking $\hat{\mathcal{H}}^J \gg \hat{\mathcal{H}}^D + \hat{\mathcal{H}}^\Gamma + \hat{\mathcal{H}}^Z$. In the zeroth approximation of the theory there are two energy levels: a lower level $E_0 = -3J/4$, corresponding to the spin value $S = 0$, and a triply degenerate higher level $E_1 = J/4$, with $S = 1$. The eigenfunctions of the zeroth approximation are symbolized by $|S, M\rangle$, where M is the projection of the vector $\mathbf{S}$ on the axis of quantization. A property of the perturbation theory being applied here is the equality $\langle 1, M'|\mathcal{H}^D|1, M\rangle = 0$ for any $M, M = 0, \pm 1$, and since, generally speaking, $\hat{\mathcal{H}}^D > \hat{\mathcal{H}}^\Gamma, \hat{\mathcal{H}}^Z$,[18] it is necessary in the perturbation theory simultaneously to take into account terms quadratic in $\hat{\mathcal{H}}^D$ and linear relative to $\hat{\mathcal{H}}^\Gamma, \hat{\mathcal{H}}^Z$.[19] In subsequent calculations we have taken everywhere, for simplicity,

$$D_c = D, \qquad D_a = D_b = 0. \tag{8}$$

Some justification for this is Moriya's theory,[18] according to which $D_c \sim |2 - g_{cc}|$ is greater than $D_a \sim |2 - g_{aa}|$, since $g_{cc} = 0.91$ and $g_{aa} = 2.29$. One might think, therefore, that calculating with $D_a, D_b \neq 0$ would not significantly alter the energy spectrum of the ion pair. The splitting of the triplet E_1 under the action of the perturbation in (7) for the cases $\mathbf{H}_0 \parallel c$ and $\mathbf{H}_0 \parallel a$, which correspond to the conditions of the experiment, is given to terms in second order by the formulas [19]

$\mathbf{H}_0 \parallel a$,

$$\begin{aligned}
&\varepsilon_{\mathrm{I,\,III}} = \left(\frac{\Gamma_a}{4} + \frac{D^2}{8J}\right) \mp \left[\delta^2 + \left[\frac{\Gamma_c - \Gamma_b}{4} - \frac{D^2}{8J}\right]^2\right]^{1/2},\\
&\varepsilon_{\mathrm{II}} = -\frac{\Gamma_a}{2}, \qquad \delta = \beta g_{aa} H_0;
\end{aligned} \tag{9'}$$

$$H_0 \| c, \qquad \varepsilon_{\mathrm{I,III}} = \Gamma_c/4 \mp [\delta^2 + (\Gamma_b - \Gamma_a)^2/16]^{1/2},$$

$$\varepsilon_{\mathrm{II}} = -\frac{\Gamma_c}{2} + \frac{D^2}{4J}, \qquad \delta = \beta g_{cc} H_0. \qquad (9'')$$

The values of the energies ϵ_{I}, ϵ_{II}, ϵ_{III} are reckoned from $E_1 = J/4$. The corresponding eigenfunctions of the states with $S = 1$ to terms of first order are written in the form

$$|K\rangle = \sum_M C_{KM}\left[\,|1, M\rangle + \frac{1}{J}\langle 0, 0\,|\mathscr{H}^D|\,1, M\rangle\,|\,0, 0\rangle\right]$$

$$(K = \mathrm{I, II, III}). \qquad (10)$$

The coefficients C_{KM} are given by the following relations for the zero order functions (the direction of the dc magnetic field is chosen as the axis of quantization):

$$|\mathrm{I}\rangle = N|1{,}1\rangle + M|1,\ 1\rangle, \qquad |\mathrm{II}\rangle = 1{,}0\rangle,$$
$$|\,\mathrm{III}\rangle = -M\,|\,1{,}1\rangle + N\,|+1, -1\rangle. \qquad (11)$$

With the assumptions $\Gamma_c > \Gamma_b > \Gamma_a$[15] and $(\Gamma_c - \Gamma_b)/4 > D^2/8J$ for $H_0 \parallel a$

$$M = \left[1 + \left(\frac{\Gamma_c - \Gamma_b}{4} - \frac{D^2}{8J}\right)^2 \times \left(-\delta + \sqrt{\delta^2 + \left(\frac{\Gamma_c - \Gamma_b}{4} - \frac{D^2}{8J}\right)^2}\right)^{-2}\right]^{-1/2},$$

$$N = \left[1 + \left(-\delta + \sqrt{\delta^2 + \left(\frac{\Gamma_c - \Gamma_b}{4} - \frac{D^2}{8J}\right)^2}\right)^2 \times \left(\frac{\Gamma_c - \Gamma_b}{4} - \frac{D^2}{8J}\right)^{-2}\right]^{-1/2}, \qquad (12')$$

and for $H_0 \parallel c$

$$M = \left[1 + \frac{1}{16}(\Gamma_b - \Gamma_a)^2 \times \left(-\delta + \sqrt{\delta^2 + \frac{1}{16}(\Gamma_b - \Gamma_a)^2}\right)^{-2}\right]^{-1/2},$$

$$N = \left[1 + \left(-\delta + \sqrt{\delta^2 + \left(\frac{\Gamma_a - \Gamma_b}{4}\right)^2}\right)^2 \times 16\,(\Gamma_b - \Gamma_a)^{-2}\right]^{-1/2}. \qquad (12'')$$

Note that when $\delta = 0$, $N = M = (2)^{-1/2}$, and when $\delta \rightarrow \infty$, $M \rightarrow 0$, $N \rightarrow 1$.

The energy levels of an ion pair corresponding to spin $S = 1$ for the two orientations of the dc magnetic field relative to the crystal are shown in Fig. 3.

Everywhere below we shall consider the non-radiative transitions as involving only these levels. It follows from experiment that the triplet-singlet transitions do not contribute to the measured spin-lattice relaxation of the ferric ions. The observed linear temperature dependence of the rate of the single-phonon process down to 0.1°K (Fig. 2) means [see Eqs. (4) and (5)] that the non-radiative transitions in the pair spectrum occur at frequencies that satisfy the condition $kT \gg h\nu_{\mathrm{ex}} \approx 0.1-0.03$°K, which are significantly less than the frequencies of the transitions between the states $S = 1$ and $S = 0$ for the ion pairs considered below. The insignificant role played by the non-radiative singlet-triplet transitions for the first relaxation mechanism (Sec. 2) is due to the large (~ 10—100 times) difference between the frequencies of the Zeeman and exchange transitions, and for the second mechanism apparently to the small magnitude of the constant D in the Hamiltonian (7).

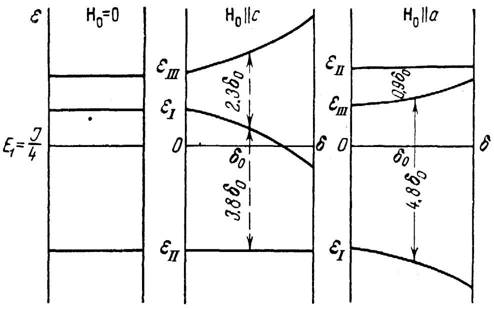

FIG. 3. The energy levels of an ion pair with $S = 1$ as a function of the magnitude of the Zeeman splitting of an isolated ion δ. The arrows show the transitions that play the fundamental role in the transfer of energy from isolated ions to the lattice. In our experiments $\delta = 0.002$°K.

The non-radiative transitions between the triplet levels of the ion pairs with the strongest exchange interaction $J = 0.42$°K, $\Gamma_a = -0.06$°K, $\Gamma_b = -0.03$°K, $\Gamma_c = 0.09$°K, $D \lesssim 0.14$°K, also turn out to be ineffective as an explanation for the experimental data. The upper limit given here on the magnitude of D evidently does not contradict the data.[15] From the point of view of the mechanism proposed in Sec. 2, such pairs do satisfy experiment for the following reasons. First, the Zeeman splitting of the levels of an isolated ion $\delta_0 = 0.002$°K is much less than the minimum splitting of the levels of a pair for $H_0 = 0$, which equals 0.015°K. Therefore, in order to transfer energy from the Zeeman system to the exchange system, a cross-relaxation process is required that is at least of the 7th or 8th order, which is difficult to reconcile with the relatively short absolute value of τ_1 observed in the experiment. Second, for $H_0 \parallel c$ and $kT \sim J = 0.42$°K, the exponential growth of the relaxation time expected on the basis of Eq. (4b″) is still not observed. In the case $H_0 \parallel a$ for $kT \sim J = 0.42$°K, a rapid increase in τ on account of the decrease in population of the levels with spin $S = 1$ is likewise not observed.

We shall consider ion pairs with a much weaker exchange coupling, e.g., pairs of ions separated from one another along the a axis by a distance equal to twice the lattice constant. The value of $J \approx 0.06°K$ for such pairs according to Eq. (4b″) is not inconsistent with the experimental curve $\tau(T)$ for f = 0.21% in the orientation $H_0 \parallel c$ for the lowest temperatures. It is true that in view of the significant scatter of the points in Fig. 2, this value must be considered a rough one. Since the constants D and Γ are proportional to J,[18] we shall assume for pairs of this type that they are also ~ 7 times less than those for the ion pairs with maximum exchange coupling. The spectrum of such a pair for the constant value of the Zeeman splitting in our experiment, $\delta_0 = 0.002°K$, depends strongly (see Fig. 3) on the direction of the dc field relative to the crystal. The approximate values of the spacings between the levels are shown in Fig. 3.

The level scheme in Fig. 3 permits a detailed examination of the spin-lattice relaxation mechanism considered in Sec. 2, by indicating the transition frequencies in the spectrum of the exchange system at which the transfer of energy from the ion pairs to the lattice occurs. Thus in the case $H_0 \parallel c$ and f = 0.21% a single-phonon process of energy transfer can occur at the lowest frequency of the exchange system—the frequency of the transition $\epsilon_{III} - \epsilon_I = 2.3\delta_0$, and for f = 0.46% at the frequency $\epsilon_I - \epsilon_{II} = 3.8\delta_0$ as well (first relaxation mechanism, Eq. (4)). In case $H_0 \parallel a$, f = 0.21%, the second relaxation mechanism (see Eq. (5)) is realized in the transition with the highest frequency $\epsilon_{III} - \epsilon_I = 4.8\delta_0$ or $\epsilon_{II} - \epsilon_I = 5.7\delta_0$.

Final confirmation requires additional comparison with experiment. One needs to be convinced from the curves of Fig. 2 and Eqs. (4) and (5) that the second relaxation mechanism in the case $H_0 \parallel c$ is less effective than the first, and, inversely, that in the case $H_0 \parallel a$ and f = 0.21%, the first mechanism cannot compete with the second. At T = 0.2°K the probability of a non-radiative transition for f = 0.21% (Fig. 2) when $H_0 \parallel a$ is five times greater than when $H_0 \parallel c$. Since the maximum splittings of the triplet in the cases $H_0 \parallel c$ and $H_0 \parallel a$ are approximately the same, then in accordance with Eq. (5) the second mechanism gives in the case $H_0 \parallel c$ a relaxation transition probability less than in the case $H_0 \parallel a$ by a factor of $(g_{aa}/g_{cc})^4 \sim 25$. That is, at T = 0.2°K and $H_0 \parallel c$, the second mechanism is at most one-fifth as effective as the first. On the other hand, the first relaxation mechanism in the case $H_0 \parallel a$ can operate at the frequency $\epsilon_{II} - \epsilon_{III} = 0.9\delta_0$. The corresponding probability of a non-radiative transition, however, is according to Eq. (4b′) less than for the orientation $H_0 \parallel c$, meaning that it is insignificant compared to the rate of energy transfer given by the second mechanism in the orientation $H_0 \parallel a$.

Thus, the energy spectrum of the exchange system in ferricyanide qualitatively satisfies the spin-lattice relaxation mechanism proposed in Sec. 2.

The possibility of some departure from the simple scheme presented here for the relaxation process on the basis of the Hamiltonian (7) should be kept in mind. Such a possibility is associated with a more complex spectrum for the exchange system than is considered here and is indicated by the presence of unexplained absorption lines from ion pairs in Ohtsuka's experiment.[15]

4. SINGLE-PHONON SPIN-LATTICE INTERACTION OF EXCHANGE-COUPLED FERRIC IONS

Let us estimate the probabilities of non-radiative transitions for an ion pair. We shall consider only a single-phonon spin-lattice relaxation, which gives a linear temperature dependence of the relaxation probability and predominates at low temperatures. The lattice vibrations act on the spin in two ways: a) via the position-dependent spin-spin interaction between the ions of a pair (Waller mechanism) and b) via spin-orbit coupling (Van Vleck–Kronig mechanism).

Consider first the Waller mechanism. If we assume the proportionality $D, \Gamma \sim J$,[18] and also $J \sim \exp(-\xi R_0)$, where R_0 is the separation between the ions in a pair, then the operator for the single-phonon spin-lattice interaction $\hat{V}$ is written in the form

$$\hat{V} = (\hat{\mathscr{H}}^J + \hat{\mathscr{H}}^D + \hat{\mathscr{H}}^\Gamma)\,\xi\delta\hat{R}_0 = \hat{\tilde{V}}\xi(\delta\hat{R}_0). \qquad (13)$$

Expanding the relative shift of the ions in the pair $\delta\hat{R}_0$ in the normal vibrations of the lattice and using the well-known relations,[20] we obtain in the approximation $h\nu_{ex} \ll kT$ that the probability of a non-radiative transition in the ion-pair spectrum is

$$1/\tau_2 \approx (96\,\pi^3\nu^2_{ex}kT\,/\,h^2c^5\rho)\;(\xi R_0)^2|\langle K'|\hat{\tilde{V}}|K\rangle|^2, \qquad (14)$$

where ν_{ex} is the frequency of the one-phonon process, c is the speed of sound, and ρ is the macroscopic density of the crystal. The matrix element, according to Eq. (10), is

$$\langle K'|\hat{\tilde{V}}|K\rangle = \sum_{M',M} C^*_{K'M'}C_{KM}\,[\langle 1, M'|\hat{\mathscr{H}}^\Gamma|1, M\rangle + \frac{2}{J}\langle 1, M'|\hat{\mathscr{H}}^D|0, 0\rangle\langle 0, 0|\hat{\mathscr{H}}^D|1, M\rangle]. \qquad (15)$$

With the assumption of Eq. (8), Eqs. (11) and (12) give a single non-zero matrix element:

$$\mathbf{H}_0 \| a, \qquad \langle \mathrm{I} | \hat{\tilde{V}} | \mathrm{III} \rangle = -(N^2 - M^2)\left(\frac{\Gamma_c - \Gamma_b}{4} - \frac{D^2}{4J}\right),$$

$$\mathbf{H}_0 \| c, \qquad \langle \mathrm{I} | \hat{\tilde{V}} | \mathrm{III} \rangle = -(N^2 - M^2)\frac{\Gamma_b - \Gamma_a}{4} \tag{16}$$

(equal to zero for $\delta = 0$, since $N = M$). The prohibition against other transitions can be lifted if it is assumed that $D_a, D_b \neq 0$. In this case the order of magnitude of (16) should not change. Calculations from Eqs. (14)–(16) for $\mathbf{H}_0 \parallel c$ at $T = 0.1°\mathrm{K}$, $\nu_{ex} = 2.3\delta_0 = 10^8$ cps, $c = 10^5$ cm/sec, $\rho = 1.85$ g/cm^3, $R_0 = 1.4 \times 10^{-7}$ cm, $\xi = 2.5 \times 10^7$, $\delta_0 = 0.002°\mathrm{K}$ give the result $1/\tau_2 \sim 1.5 \times 10^{-7}$ sec^{-1}.

Such a small probability sharply contradicts experiment.

We now estimate the order of magnitude of the probability of a one-phonon relaxation transition in the spectrum of an ion pair for the Van Vleck–Kronig spin-lattice interaction. The statement of the problem is similar to the case of an isolated ion considered in [20]. The operators of the single-particle electron-phonon interaction $\hat{V}_1$ and $\hat{V}_2$ appear (for single-phonon relaxation) as terms in the expansion of the energy of the ions of the pair in the crystal field and are linear in the normal displacements of the nearest neighbor ions. The operator for the electron-phonon interaction of the ion pair $\hat{V} = \hat{V}_1 + \hat{V}_2$ does not depend on the spin variables. Hence, for the considered spin-lattice relaxation between the spin levels A and A′ of the ground orbital state of the pair there are important admixtures of excited states of the ions of the pair in the crystal field arising from the spin-orbit interaction.

Since in the experiments at low frequencies the exchange interaction of the ions in the pair is stronger than the interaction of the ions with the external dc magnetic field, the ion pair in theory [20] must be considered as a particle with spin $S = 1$. For the case $S = 1$ the matrix element of the electron-phonon operator for the transition between the spin levels of the ground orbital state of the pair is, according to Eq. (42) of Mattuck and Strandberg,[20] of the order

$$\langle A' | V | A \rangle \sim (4\lambda^2 / \Delta^2) V_1, \tag{17}$$

where λ is the spin-orbit interaction constant, Δ is the energy difference between the ground and first excited states of the ion pair in the crystal field.

This magnitude for the matrix element for the ion pair is considerably greater than the corresponding matrix element for an isolated ferric ion with spin $s = 1/2$, which is of the order

$$\langle A' | V_1 | A \rangle \sim [\lambda (g\beta H) / \Delta^2] V_1.$$

Here $g\beta H$ is the Zeeman splitting of the energy levels of an isolated ion. The factor $\lambda/g\rho H$, as shown below, is sufficiently large to explain the experimental data.

With the aid of Eq. (17) and the formulas of the theory of the spin-lattice relaxation of an isolated ferric ion,[20] we can express the relaxation time of an ion pair τ_2 in terms of the relaxation time τ^* of an isolated ion:

$$\frac{1}{\tau_2} \approx \frac{1}{\tau^*} 16 \frac{\nu_{ex}^2 \lambda^2}{\nu_z^*}.$$

At a Zeeman frequency $\nu_z^* = 8.7 \times 10^9$ cps it was found experimentally[3] that for an isolated ferric ion there is a single-phonon spin-lattice interaction of the Van Vleck–Kronig type with $(1/\tau^*) = 5.4T$. Consequently in the case $\mathbf{H}_0 \parallel a$, where $\nu_{ex} = 4.8\delta_0 = 2 \times 10^8$ cps and with $\lambda = 280$ cm^{-1},[3] we obtain $1/\tau_2 = 4 \times 10^4 T$, which gives $1/\tau_2 = 4 \times 10^3$ sec^{-1} at $T = 0.1°\mathrm{K}$. In the case $\mathbf{H}_0 \parallel c$, $\nu_{ex} = 2.3\delta_0$, and therefore $1/\tau_2 = 10^3$ sec^{-1} at $T = 0.1°\mathrm{K}$. The measured relaxation time of isolated ions in the latter case, according to Eq. (4), is connected with τ_2 by the relation ($f = 2.1 \times 10^{-3}$, $\nu_{ex} = 2.3\nu_z$)

$$\frac{1}{\tau} = \frac{1}{\tau_2} f \left(\frac{\nu_{ex}}{\nu_z}\right)^2 = 11 \ (\mathrm{sec}^{-1}).$$

This result agrees with the experimental value under these conditions, $1/\tau = 8$ sec^{-1} (see Fig. 2). From Eq. (5) it is also seen that in the case $\mathbf{H}_0 \parallel a$ and $T = 0.1°\mathrm{K}$ the value of $1/\tau_2 = 4 \times 10^3$ sec^{-1} does not contradict the experimental value under these conditions $1/\tau = 60$–70 sec^{-1}.

Thus, calculation of the electron-phonon interaction of the ion pair by the Van Vleck–Kronig mechanism allows one theoretically to obtain values for the relaxation transition probabilities that satisfactorily agree with experiment. This agreement confirms the important role played in our experiments by exchange-coupled ferric ions in the transfer of energy from isolated ions to the thermal motion of the lattice.

CONCLUSION

The theoretical part of this work did not touch upon the calculation of the cross-relaxation time τ_1 in Eq. (4). To solve this problem accurate knowledge is required of the spectrum and line widths of the absorption lines corresponding to the considered transitions in the ion-pair spectrum. Hence in the framework of the present communication this work is incomplete. Nevertheless, the comparison given here of the experimental data with theory clearly favors the mechanism proposed in Sec. 2 for paramagnetic relaxation in ferricyanide at low temperatures.

We remark that in a number of papers the effect of exchange interaction on spin-lattice relaxation in ruby has been investigated. A temperature-independent spin-lattice relaxation was observed in ruby by Zverev.[21] The spectrum and relaxation of exchange-coupled pairs of chromium ions in ruby was studied by Statz et al.[22] and by Gill.[23] The theory of the effect on the relaxation of isolated chromium ions in ruby of an exchange interaction between the ions that is weak compared to the Zeeman interaction has been developed by Al'tshuler.[24] From our point of view, however, ruby, which has a more complex energy spectrum, is a less convenient object than ferricyanide for the study of the mechanism of paramagnetic relaxation involving exchange-coupled paramagnetic ions.

The authors thank K. K. Svidzinskiĭ for discussions and important comments on the theoretical part of the work and B. V. Ershov for his great help in carrying out the measurements and preparing the experimental material.

A preliminary account of this work was presented at the Third Quantum Electronics Conference in Paris in February, 1963. Before sending the paper to press the authors learned of measurements of spin-lattice relaxation in ferricyanide at frequencies of 8500 Mcs and 1800 Mcs at helium temperatures.[25]

Note added in proof (May 4, 1964): Just recently V. A. Atsarkin (Institute of Radiotechnology and Electronics, Academy of Sciences, USSR) has investigated the low-temperature paramagnetic spin-lattice relaxation of the Cr^{3+} ion in magnesium tungstate $MgWO_4$ at chromium concentrations of about 10^{-3} at a frequency of about 10^4 Mcs. In these experiments, just as in those of Zverev[21] and in ours, a temperature-independent spin-lattice relaxation of the paramagnetic ions was found. An analysis of the temperature and concentration dependences of the experimental data on the rate of the relaxation process discloses the important role of exchange-coupled ions in the transfer of excitation energy from the spins to the lattice, just as in the case of the ferricyanide $K_3(Fe, Co)(CN)_6$ that we studied.

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Errata

Vol. 15, no. 6, 1063-1064 (N. G. Basov and A. N. Oraevskiĭ)

Formulas (8), (9), (10), (16), and (17) should read

$$P_\omega(t_0) = \frac{1}{\tau} \int_{t_0}^{t_0+\tau} P(t', t_0) e^{i\omega t'} dt'. \tag{8}$$

$$Z_\omega E_\omega = \alpha_\omega E_\omega + 4\pi\omega^2 \beta_\omega \int_0^\infty \rho_{21}{}^{(0)} e^{i(\omega-\omega_{21})t_0} dt_0, \tag{9}$$

$$\alpha_\omega = 8\pi\omega^2 \frac{i}{\hbar} \frac{|\mu_{12}|^2 N}{\tau} [\rho_{22}{}^{(0)} - \rho_{11}{}^{(0)}] \frac{e^{i(\omega-\omega_{21})\tau} - i(\omega-\omega_{21})\tau - 1}{(\omega-\omega_{21})^2},$$

$$\beta_\omega = 2\mu_{12} \frac{N}{\tau} [e^{i(\omega-\omega_{21})\tau} - 1]/i(\omega-\omega_{21}). \tag{10}$$

$$\rho_{12} = \tilde{\rho}_{12}{}^0 e^{i(\omega_1-\omega_{21})(t_1+\tau_1)} e^{i\omega_{21}t}, \tag{16}$$

$$R_\omega = \langle \tilde{\rho}_{21}{}^0 e^{i(\omega_1-\omega_{21})T} \beta_\omega \rangle, \tag{17}$$

These errors do not affect the main conclusions of the article. The authors thank G. L. Suchkin for pointing out these misprints.

Vol. 19 no. 3 p. 581 (K. Huang and F. E. Low)

In Eq. (21) and the second equation in footnote 2, the comma between x and Φ_θ should be omitted. Thus Eq. (21) should read

$$K(x, \theta, g) = F_\theta(A), \text{ where } A \equiv x\Phi_\theta(g).$$

The second equation in footnote 2 should read

$$K(x, \theta, g, f) = \alpha_\theta(g, f)\, F_\theta(A, B),$$

where

$$A \equiv x\Phi_\theta(g, f), \quad B \equiv \beta_\theta(g, f).$$

Vol. 19, no. 6, p. 1313 (A. M. Prokhorov and V. V. Fedorov)

Right hand column, second formula from top, replace v_z^* in denominator by v_z^{*4}.

Vol. 20, no. 1, p. 122 (Poluektov, Presnyakov, and Sobel'man)

An error was made in the approximate calculation of the integral (AI.1) in Appendix I. The points z_n in the vicinity of which the derivative of the argument of the exponential vanishes must be sought prior to approximating the radical in the integrand of (AI.1). As a result, γ in (AI.2) is replaced by 2γ, the parameter $\pi\omega/\gamma v$, in (18), (AI.3), (AI.4), (AI.5), and (AI.6) is replaced by $\pi\omega/2\gamma v$, and ω in (20) and (AII.7) is replaced by $\omega/2$. Elimination of this error improves the agreement between the experimental and theoretical curves in the region of the maximum. The authors thank E. E. Nikitin for noting this error.