ON THE MECHANISM OF PARAMAGNETIC SPIN-LATTICE RELAXATION AT LOW TEMPERATURES

V. A. ATSARKIN

Institute of Radio and Electronics, Academy of Sciences, U.S.S.R.

Submitted to JETP editor February 21, 1965

J. Exptl. Theoret. Phys. (U.S.S.R.) **49**, 148-158 (July, 1965)

The spin-lattice relaxation of the chromium ion was studied experimentally in a number of paramagnetic crystals (aluminum acetylacetonate, zinc tungstate, potassium cobalticyanide) as a function of temperature and concentration of the paramagnetic impurity. The experimental results are interpreted on the basis of the two stage relaxation model; ion pairs are considered to be the mediator between the chromium ions and the crystal lattice. Theoretical estimates of the spin-lattice relaxation probability of exchange pairs and the probability for cross relaxation between the pairs and single ions are made. The estimates are in good agreement with the experiments if it is assumed that the main role in the spin-lattice relaxation process is played by exchange pairs with a relatively small interaction ($J \sim 10^{-2}$ cm^{-1}).

1. INTRODUCTION

AT the present time the nature of spin-lattice relaxation in paramagnetic crystals is not completely clear. The Kronig—Van Vleck theory,[1,2] which does not take the interaction between paramagnetic ions into account, agrees with experiment only for very dilute paramagnetic substances. In order to explain the dependence of the spin-lattice relaxation time T_1 on the concentration of the paramagnetic impurity, Van Vleck[3] put forth a hypothesis about the possible role in the relaxation process of paramagnetic ions which, as a consequence of random dilution, happen to be close to each other and coupled by a strong exchange interaction. Such "exchange pairs" can have short spin-lattice relaxation times (confirmed by experiments on ruby[4]), and can affect the T_1 of isolated ions by means of cross relaxation.[5]

In a study of the temperature dependence of T_1 in ruby Zverev[6] found a region in which T_1 was independent of temperature (we shall hereafter call such regions "plateaus"). Just such a plateau was observed by Prokhorov and Fedorov in potassium ferricyanide,[7] and by the author and Popov in magnesium and zinc tungstates containing chromium as an impurity.[8] In order to explain their results, all of these authors assumed that over a certain interval of temperature it was not really the spin-lattice relaxation time of the paramagnetic ions that was being experimentally measured, but the cross-relaxation time between these ions and certain other centers that were

well-coupled to the crystal lattice. The whole relaxation process therefore occurs in two stages: initially the energy of the spin system is transferred by cross relaxation to these other centers, and then it is transferred from them to the crystal lattice.

The solution of the rate equations describing this process gives the following expression for the exponential coefficient for the restoration of the paramagnetic absorption signal after the end of a saturating pulse[9]:

$$W = w_1 + w_{12}N[1 + w_{12}n/(w_2 - w_1)]^{-1}. \qquad (1)$$

Here n is the number of the principal paramagnetic ions; w_1 is their rate of spin-lattice relaxation; N and w_2 is the number of auxiliary centers and the rate of their spin-lattice relaxation; w_{12} is the probability of cross relaxation between the two types of particles. In the derivation of Eq. (1) it was assumed that $N \ll n$ and $w_2 > w_1$.

If the rate of the whole relaxation process is limited by cross relaxation, i.e.,

$$w_{12}n \ll w_2 - w_1, \qquad (2)$$

then from (1) we have

$$W = w_1 + w_{12}N. \qquad (3)$$

In this case the extra spin-lattice relaxation rate $w_{12}N$ does not depend on the temperature of the lattice, which corresponds to the aforementioned temperature plateau. Under the condition

$$w_{12}n \gg w_2 - w_1 \qquad (4)$$

106

the rate of the relaxation process is limited by the transfer of energy from the auxiliary centers to the crystal lattice. Then it follows from (1) that

$$W = w_1 + Nn^{-1}(w_2 - w_1). \qquad (5)$$

The transition from (2), (3) to (4), (5) should take place when the temperature is lowered (because of the decrease in w_2) and when the concentration is increased (increase in n). This has been observed experimentally by a number of authors,[6-8] and they assumed that the auxiliary centers that speed up the spin-lattice relaxation are exchange pairs of ions. In order to verify this assumption it is necessary to investigate thoroughly the concentration dependence of the relaxation times both over the plateau regions and outside of them. It is also of interest to study the spin-lattice relaxation in crystals with a large lattice constant, in which strong exchange interaction between the paramagnetic ions does not exist. Finally, it is necessary to calculate theoretically the relaxation rate of the exchange pairs and to consider the conditions under which cross relaxation between isolated ions and exchange pairs is possible. In this paper these problems are investigated for some specific cases.

2. EXPERIMENTAL RESULTS AND DISCUSSION

A. Spin-lattice relaxation of trivalent chromium in aluminum acetylacetonate.—The EPR spectrum of the Cr^{3+} ion, substituting for aluminum in the acetylacetonate $Al(CH_3COCHCOCH_3)_3$, was investi-

gated by Singer[10] and is described by a spin Hamiltonian of rhombic symmetry with the parameters g = 1.983, $|D| = 0.592 \ cm^{-1}$, and E = 0.052 cm^{-1}. At room temperature there are two magnetically non-equivalent complexes, differing only in the directions of their principal axes. At 4.2°K however, we observed six non-equivalent complexes, which is evidently due to the lowering of the lattice symmetry upon cooling.

Since the closest separation between the aluminum ions in the acetylacetonate is about 7.5 Å (see [11]), the exchange interaction between the chromium ions cannot be large compared with $|D|$ (in ruby, for example, this interaction is about 0.5 cm^{-1} for an inter-ionic spacing of about 6 Å [12]). In view of this, the hypothesis about the effect of exchange pairs with a large interaction on the spin-lattice relaxation[4] is inapplicable in this case.

All the spin-lattice measurements described in this paper were carried out by the pulse-saturation method at X-band frequencies (the apparatus was described in [8]). In order to separate the concentration-dependent spin relaxation from the Kronig-Van Vleck type, the results of the measurements were treated in the following way.

If w = $1/T_1$ is the total spin-lattice relaxation probability and $w_0 = 1/T_1^0$ is the relaxation probability for a small chromium concentration, independent of the concentration C, then the quantity

$$w' = w - w_0 \qquad (6)$$
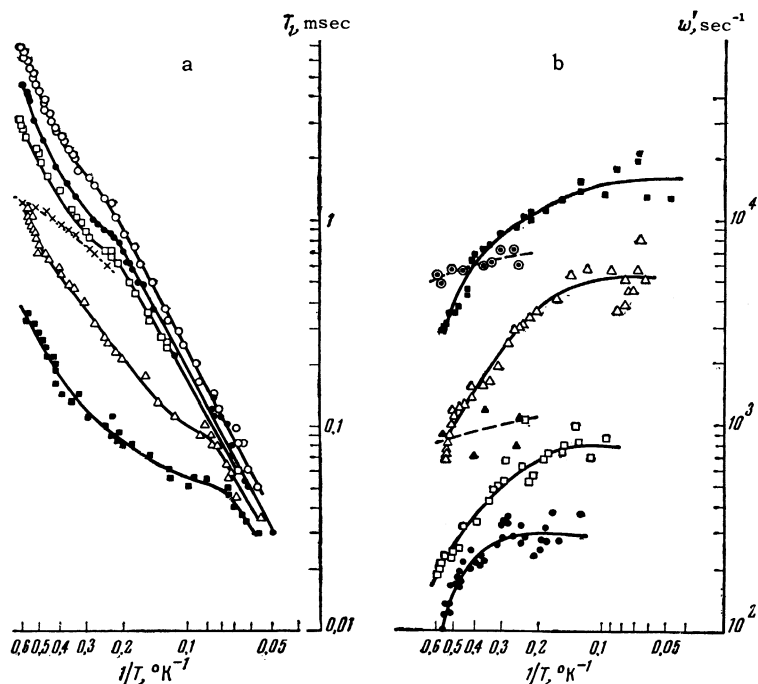
is that part of the relaxation probability that de-

FIG. 1. Temperature dependence of: a — spin-lattice relaxation time T_1, b — probability w' for $Al(CH_3COCHCOCH_3)_3$, Cr^{3+}: + — C = 0.3%, ▲ — C = 1%, ⊙ — C = 1.65%, and for $ZnWO_4$,Cr^{3+}: o — C = 0.02%, ● — C = 0.18%, □ — C = 0.27%, △ — C = 0.46%, ■ — C = 0.57%.

pends on C and is the subject of the present investigation. In the two-stage relaxation mechanism the quantity w' corresponds to the second term in (1).

Figure 1 shows the results of the measurements of T_1 of the transition $-\frac{1}{2} \longleftrightarrow +\frac{1}{2}$ for $H \parallel z$ for one of the magnetic complexes of chromium in the acetylacetonate. The relaxation time measured at chromium concentrations $C \leq 0.3$ atomic percent (Fig. 1a) is independent of C; these data were used to determine w_0. In Fig. 1b is shown the temperature behavior of the probability w' for $C = 1\%$ and $C = 1.65\%$. It is seen that for $C = 1.65\%$ the quantity $w' \approx 0.6 \times 10^3$ sec^{-1} depends very slightly on temperature, i.e., a temperature plateau is observed, similar to the one described in [6-8].

For $C = 1\%$ the measurement errors did not permit an accurate determination of w'; nevertheless, it is clear that in every case, $w' \leq 0.12 \times 10^3$ sec^{-1}, and thus there is a strong concentration dependence of w' ($w' \propto C^3 - C^4$).

Therefore a two-stage relaxation process also takes place in the acetylacetonate. The number of auxiliary centers that speed up this process depends strongly on concentration, as would be the case also if these centers are exchange pairs or groups of chromium ions; in this case, as has already been mentioned, they can only be pairs with a relatively weak interaction.

B. The concentration dependence of the probability w' in the plateau regions.—A thorough investigation of this dependence was carried out on zinc tungstate containing chromium as an impurity; the range of temperatures and concentrations was considerably wider than that used in [8]. The principal measurements were carried out for the transition $-\frac{1}{2} \longleftrightarrow +\frac{1}{2}$ for $H \parallel a$, i.e., at an angle of about 4° with the magnetic z axis. The measured time T_1 did not vary with a change in this angle of $15-20°$; consequently, the harmonic cross-relaxation between the transitions $-\frac{1}{2} \longleftrightarrow +\frac{1}{2}$ and $-\frac{3}{2} \longleftrightarrow +\frac{3}{2}$ observed by Manenkov and Prokhorov in ruby[13] did not affect the results.
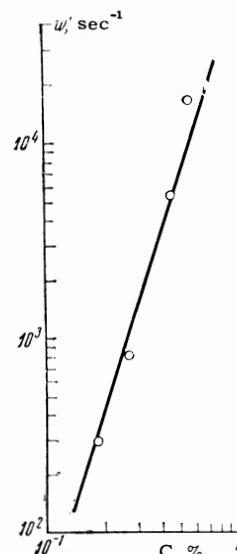

FIG. 2. Dependence of the quantity w' in the plateau regions on the concentration of chromium in $ZnWO_4$.

The dependence of T_1 and w' on temperature for various concentrations of chromium is shown in Figs. 1a and 1b; in the latter, plateau regions are clearly visible. Figure 2 shows the dependence of w' on the plateau on the chromium concentration; the solid line corresponds to the law $w' \propto C^3$.

The table gives all the presently available data on w' over regions of the temperature plateau. It is seen from the table that the presence of plateaus in the temperature behavior of w' is not accidental, but is rather a rule that holds for the entire series of substances. The table also gives an ample amount of information about the dependence of w' on C; in all cases we have $w' \propto C^3$. Since w' corresponds to the term $w_{12}N$ of Eq. (3), we can speak about the corresponding concentration dependence of the number of auxiliary centers responsible for speeding up the relaxation.

There are many fewer data on the Fe^{3+} ion in the table; however an extremely strong concentration dependence of w' is obvious (not less than a fifth power law). The possible reasons for such a

Data on the plateaus in the temperature dependence of w'

Substance	C, %	Wavelength, cm	Dependence of w' on C	Reference
Al_2O_3, Cr^{3+}	0.28	3	No data	[6]
$K_3Co(CN)_6$, Fe^{3+}	$\begin{cases} 1.7 \\ 0.21;\ 0.46 \end{cases}$	3,5; 17 750	$w' \propto C^6$ $w' \propto C^5$	[9] * [7]
$MgWO_4$, Cr^{3+}	0.12; 0.23	3	$w' \propto C^3$	[8]
$ZnWO_4$, Cr^{3+}	0.1—0.56	3	$w' \propto C^3$	[8], present paper
$Al(CH_3COCHCOCH_3)_3$, Cr^{3+}	1; 1.65	3	$w' \propto C^3 - C^4$	present paper

*We found the plateau by analyzing the table of results given in the paper by Rannstad and Wagner.[9]

strong concentration dependence will be discussed in Sec. 4.

C. Spin-lattice relaxation of Cr^{3+} in crystals of $K_3Co(CN)_6$.—The EPR spectrum of Cr^{3+} in crystals of $K_3Co(CN)_6$ was studied by Baker, Bleaney, and Bowers[14] and is described by a spin Hamiltonian of rhombic symmetry with the parameters $S = {}^3/_2$, $D = 0.0831$ cm^{-1}, $E = 0.0108$ cm^{-1}, $g_Z = 1.993$, $g_X = g_Y = 1.991$, and there are two non-equivalent magnetic complexes, differing by the directions of the x and z axes. Up until the present, investigations of the spin-lattice relaxation in this substance[15,16] have been carried out with such orientations of the external magnetic field **H** that the spectra from both magnetic complexes were superposed. We measured the relaxation time T_1 as a function of the superposition or non-superposition of the EPR lines belonging to the different magnetic complexes.

We investigated samples of $K_3Co(CN)_6$ having chromium concentrations of 0.05, 0.3, and 0.9%. The time T_1 was measured for the transition ${}^3/_2 \longleftrightarrow {}^1/_2$ (quantum numbers in the high-field approximation), with the field **H** located in the crystallographic ab plane. In this plane are found the magnetic axes of the two complexes x_1, x_2 and z_1, z_2, and the superposition of both spectra occurs when **H** ∥ a and **H** ∥ b.

Figure 3 shows the dependence of T_1 on the orientation of the magnetic field **H** at temperatures 4.2 and 1.75° K for different chromium concentrations. It is seen that at the concentrations 0.3 and 0.9% the relaxation time in the immediate vicinity of the direction a depends on the separation between the lines belonging to the two unequivalent complexes; this may be due to the cross relaxation between them. However, for a greater separation of the lines T_1 becomes constant, but remains shorter than in the case when the complexes are superposed (**H** ∥ a). At the same time, for $C = 0.05\%$ (when T_1 is independent of concentration) this reduction in the relaxation time does not take place.

This result, unexpected at first sight, can also be explained on the basis of the two-stage relaxation model proposed above. Actually, when there is good coupling between the chromium ions and the auxiliary paramagnetic centers (the exchange pairs) that accelerate the relaxation, the relations (4) and (5) are in effect. If it is assumed that the number of auxiliary centers N that interact with the chromium ions does not vary much when the angle θ between the field **H** and the a axis is changed, then when the two spectra are superposed the second term of the sum in (5) should be de-
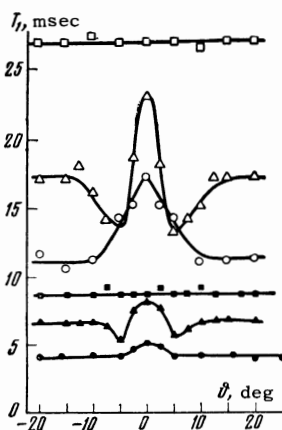

FIG. 3   FIG. 4

FIG. 3. Dependence of the spin-lattice relaxation time of chromium in $K_3Co(CN)_6$ on the direction of the magnetic field relative to the a axis: □,■ – C = 0.05%, ▲,△ – C = 0.3%, ●,○ – C = 0.9%. The open signs correspond to T = 1.75°K, the solid ones to 4.2°K.
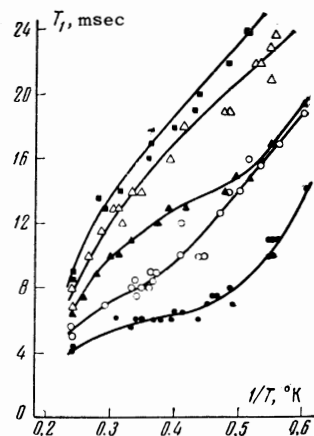
FIG. 4. The temperature dependence of the spin-lattice relaxation time of chromium in $K_3Co(CN)_6$ under conditions of superposition and non-superposition of the spectra belonging to the unequivalent magnetic complexes: ■ – C = 0.05%, △ – C = 0.3%, ○ – C = 0.9%. The open triangles and circles correspond to coincidence of the spectra ($\theta = 0$), the solid ones to non-coincidence ($\theta = 17°$).

creased, since the number of chromium ions participating in the process n is doubled. In Fig. 4, which gives the temperature behavior of T_1 for different concentrations and for angles $\theta = 0$ and $\theta = 17°$, it is seen that effect of increasing T_1 when the spectra are superposed is enhanced as the temperature is lowered. The curve in Fig. 4 corresponding to $C = 0.9\%$ and $\theta = 17°$ has a region of weak dependence on temperature (a plateau), whereas at $\theta = 0$ the plateau is not observed. This feature can also be explained on the basis of condition (2), if it is considered that at $\theta = 0$ the number n is doubled, and the inequality (2), which is necessary for the existence of the plateau, can cease to be fulfilled.

It should be realized that, in contrast to the substances considered above with a large zero-field splitting of the energy levels (tungstate, acetylacetonate), where the spin-lattice relaxation is accomplished via widely-spaced energy levels, [8,17] in the cyanide the exponent of the relaxation exponential is a complicated combination of six relaxation transition probabilities w_{ij} among the four chromium energy levels. In view of this it is impossible in this case to treat the results according to the method specified by Eq. (6). In addition, the different dependence of the quantities w_{ij} on concentration can lead to complication of the curve of restoration of the EPR signal after saturation,

and this is in fact observed at C = 0.9%. Already in this case the relaxation curve is not described by a single exponential (which was noted by Castle, Chester, and Wagner[16]). The results shown in Figs. 3 and 4 for C = 0.9% correspond to an asymptotic time constant measured on the "tail" of the restoration curve.

We remark that the shortening of T_1 when the chromium concentration is increased (for a given angle θ) indicates that there is no superheating of the phonons.[18,19]

3. THEORETICAL EVALUATION OF THE SPIN-LATTICE RELAXATION OF EXCHANGE PAIRS

We shall consider a pair of Cr^{3+} ions, coupled by an isotropic exchange interaction of the form $J\hat{S}_1\hat{S}_2$, where J is the exchange integral, $\hat{S}_1$ and $\hat{S}_2$ are the spin operators of each of the ions that make up the pair. We assume that $J = J_0 \exp(-\xi r)$, where r is the spacing between the ions in the pair, and J_0 and ξ are constants. We shall determine the rate of spin-lattice relaxation of this pair under the influence of the lattice vibrations, which modulate the exchange interaction between the ions (the variation of the Waller mechanism considered by Al'tshuler[20]).

Using the procedure suggested by Mattuck and Strandberg,[21] we obtain an expression for the spin-lattice relaxation probability:

$$w_{ik} = \frac{96\pi^3 v^2 kT \xi^2 r^2 J^2}{h^2 v^5 \rho} |a_{ik}|^2, \qquad (7)$$

where ν is the transition frequency, v is the speed of sound, ρ is the density of the crystal, and a_{ik} is the matrix element of the transition between states i and k of the pair under the influence of the operator $\hat{S}_1\hat{S}_2$. Equation (7) is analogous to the relation given by Al'tshuler.[20] However, in[21] it is assumed that all the ions in the crystal are exchange coupled, which also leads to acceleration of the spin-lattice relaxation; but here it is presumed that only an insignificant portion of the ions consist of exchange pairs, and the relaxation of the remaining particles proceeds in two stages. Such a treatment is dictated by the experimental data (see Sec. 2).

To calculate the a_{ik} we used the eigenvalues and eigenfunctions given by Mash and Rodak[22] for a pair of chromium ions coupled by an isotropic exchange interaction and situated in an axial crystalline field and in an external field H parallel to the magnetic z axis. The result of the calculation gives unwieldy expressions for the four non-zero matrix elements, which we do not give

here for lack of space. For the case $J \gg D$ (D is the spin Hamiltonian parameter)

$$a_{9,10} = a_{11,12} = 2\sqrt{6}D/5J, \quad a_{13,14} = 6D/5J, \quad a_{15,16} = 2D/J,$$

and for the case $J \ll D$

$$a_{9,10} = a_{11,12} = \sqrt{6}, \quad a_{13,14} = a_{15,16} = {}^3/_2$$

(the levels are numbered to correspond to the work of Mash and Rodak[22]). The frequencies of the corresponding transitions are determined from the expressions

$$\nu_{9,10} = \nu_{11,12} = 2h^{-1}[(D - {}^1/_2 J)^2 + 6J^2]^{1/2},$$
$$\nu_{13,14} = 2h^{-1}[{}^9/_4 J^2 + (2D - 2J)^2]^{1/2},$$
$$\nu_{15,16} = 2h^{-1}[(2D)^2 + {}^9/_4 J^2]^{1/2}. \qquad (8)$$

We shall now find the minimum value of J for which the quantity w_{ik} calculated from Eq. (7) would correspond to the experimental data for the Cr^{3+} ion in $ZnWO_4$ (Fig. 1). For T = 4.2° K, ρ = 5.7, v ≈ 10^5 cm/sec, 2D/h = 50 Gcs,[18] ξ = 1.6 × 10^8 cm^{-1}, J/h = 2.5 × 10^8 cps, r = 8 × 10^{-8} cm, we find from Eq. (7) that w_{ik} ≈ 10^4 sec^{-1}. The magnitudes of r and ξ were here chosen on the basis of the paper by Statz et al.[12] where, in particular, the dependence of the exchange integral in ruby on distance is shown.

In that region of temperatures and concentrations where the relaxation "bottleneck" is the transfer of energy from the exchange pairs to the lattice, the experimental magnitude of w' corresponds to the expression Nw_{ik}/n (Eq. (5)). The concentration C_2 of the exchange pairs, for which J/h ≈ 2.5 × 10^8 cps, equals

$$C_2 = {}^1/_2 ZC^2, \qquad (9)$$

where Z is the number of lattice sites in the coordination sphere of radius r in the center of which the chromium ion is located. For the tungstate lattice[23] the number Z = 20 in a spherical layer of thickness 1 Å with a mean radius of 8 Å, and for C = 3 × 10^{-3} we obtain Nw_{ik}/n ≈ 3 × 10^2 sec^{-1}, which agrees well with experiment.

If the spacing r between the ions is increased, the integral J will decrease exponentially, and w_{ik} rapidly diminishes, in spite of the increase in Z (Z ∝ r^2), to values that do not correspond to experiment. Hence the ratio J/h ≈ 2.5 × 10^8 cps is, under the assumptions made, the minimum value of the isotropic exchange interaction that is sufficient to provide a mechanism for the relaxation of the chromium ion in $ZnWO_4$ via exchange pairs. Pairs of ions for which r < 8 Å and J/h > 2.5 × 10^8 cps can in principle be even more effective. It will be shown below, however, that

pairs with a large value of J cannot always play a role in the relaxation process because of weak coupling to the isolated ions.

The calculation presented is valid for a crystalline field of axial symmetry. The inclusion of terms in the spin Hamiltonian corresponding to a small admixture of rhombic symmetry (the parameter E) in the tungstates, acetylacetonate, and cyanide, lead to the appearance of several new nonzero matrix elements a_{ik}. However, if the ratio E/D is small, these matrix elements turn out to be much smaller than unity, and the corresponding spin-lattice relaxation probabilities can be neglected.

4. CROSS-RELAXATION BETWEEN SINGLE IONS AND EXCHANGE PAIRS

The transfer of energy from single ions to the exchange pairs can take place by cross relaxation.[5] In order that this process be effective, it is necessary that any of the transitions in the spectrum of the single ion should be close in frequency to one of the exchange-pair transitions indicated in (8). The fulfillment of this condition depends on the relation between the splitting of the energy levels of the single ion in zero magnetic field, equal to ~ 2D, and the quantity $h\nu_0$, where ν_0 is the frequency at which measurements are made.

We shall consider first the case $2D \gg h\nu_0$, corresponding to the spectra of Cr^{3+} in the tungstates and the acetylacetonate. For **H** ∥ z and E ≪ D the frequencies of the transitions of a single chromium ion are given by the expressions

$$\nu(-^1/_2 \leftrightarrow +^1/_2) = h^{-1}g\beta H, \quad \nu(-^3/_2 \leftrightarrow +^3/_2) = 3h^{-1}g\beta H,$$

$$\nu(\pm^3/_2 \leftrightarrow \pm^1/_2) = h^{-1}(2D \pm g\beta H),$$

$$\nu(\pm^3/_2 \leftrightarrow \mp^1/_2) = h^{-1}(2D \pm 2g\beta H). \quad (10)$$

From a comparison of (8) and (10) it is seen that for $2D \gg g\beta H$ we can expect approximate coincidence only for frequencies $\nu_{9,10} = \nu_{11,12}$ on the one hand and $\nu(+^3/_2 \leftrightarrow \pm^1/_2)$ on the other. However such a coincidence is possible only for a completely specified value of the exchange integral J. Thus, for example, for 2D/h = 50 Gcs and ν_0 = 10 Gcs, the condition $\nu(+^3/_2 \leftrightarrow +^1/_2) \approx \nu_{9,10}$ is fulfilled for J/h = 10 Gcs, and the condition $\nu(+^3/_2 \leftrightarrow -^1/_2) \approx \nu_{9\ 10}$ for J/h = 12 Gcs. And if in the given crystal there are no exchange pairs with these values of J, then the necessary closeness of frequencies for the accomplishment of cross relaxation will not exist. We also note that in the acetylacetonate, where the closest distance

between ions is 7.5 Å, the existence of exchange pairs for which J/h ≈ 10 Gcs is rather doubtful.

Therefore, direct spin-spin coupling between single ions and exchange pairs at frequencies corresponding to rapidly relaxing transitions of the latter is not very likely in substances with a large zero-field splitting.

Nonetheless, in such crystals rapid relaxation of exchange pairs can influence the spin-lattice relaxation of the single ions. Consider the case J ≪ gβH ≪ 2D. Figure 5 shows a diagram of the energy levels of an exchange pair corresponding to this condition; alongside of it for comparison are shown the levels of a single chromium ion. The wavy arrows in Fig. 5 indicate transitions with fast relaxation to which correspond the frequencies $\nu_{9,10} = \nu_{11,12} \approx 2D/h$ and $\nu_{13,14} \approx \nu_{15,16} \approx 4D/h$. Cross relaxation at these frequencies is possible if there is included in the process, in addition to the exchange pair and the single chromium ion being observed (ion No. 1), still another single ion (ion No. 2). The process can go in this way, for example: First there is a transition $+^1/_2 \leftrightarrow -^1/_2$ in ion No. 1 (Fig. 5b) with a simultaneous transition 12 → 14 in the pair spectrum (Fig. 5a), where $\nu(+^1/_2 \leftrightarrow -^1/_2) \approx \nu_{12,14}$, and then ion No. 2 makes a transition from level $-^3/_2$ to level $-^1/_2$, with a simultaneous pair transition from state 14 to level 11. In this $\nu(-^3/_2 \leftrightarrow -^1/_2) \approx \nu_{11,14}$. Both times the difference in the frequencies of the transitions participating in the cross relaxation is of the order $\nu_\alpha - \nu_\beta \approx J/h$ (see [22]). As a result of this process, ion No. 1, which is being observed at frequency ν_0, undergoes a relaxation transition to a lower energy level, and the exchange pair makes a transition from level 12
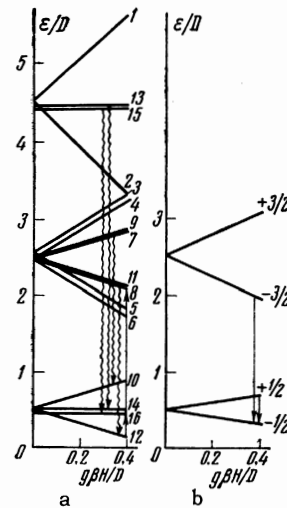

FIG. 5. Energy levels of an exchange pair of chromium ions for the case J ≪ 2D (a) and of a single ion (b).

to level 11, whereupon it rapidly gives up the energy to the crystal lattice at the frequency $\nu_{11,12}$. One can easily discern several other variants of processes of this kind, in which the exchange pair and ions No. 1 and No. 2 participate.

If it is assumed that cross relaxation occurs mainly via the dipole-dipole interaction of the exchange pair with its nearest-neighbor single ions, which are distributed in some spherical layer of thickness Δr with mean radius r (the radius of effective interaction), then the cross-relaxation probability w_{cr}, which corresponds in our case to the quantity Nw_{12} introduced in (1), is determined by the formula[24]

$$w_{cr} \approx \frac{(2\pi)^{3/2}}{2.145} Z' C_2' \langle \Delta\nu_{\alpha\beta}^2 \rangle^{1/2} \exp\left[-\frac{(\nu_\alpha - \nu_\beta)^2}{2\langle \Delta\nu_{\alpha\beta}^2 \rangle} \right]. \quad (11)$$

Here $\langle \Delta\nu_{\alpha\beta}^2 \rangle$ is the total second moment of the shape function corresponding to the cross-relaxation process, Z' is the number of sites in the effective interaction layer, and C_2' is the concentration of exchange pairs participating in the cross relaxation process considered above, i.e., only those pairs that have an additional ion (ion No. 2) near them. The number C_2' is proportional to the cube of the concentration of the paramagnetic impurity, which explains the experimentally observed dependence $w' \propto C^3$ (see the table). We note that for ions with spin $s = \frac{1}{2}$ (e.g., Fe^{3+} in the cyanide), the spectrum of which consists only of a single transition, a cross relaxation process similar to the one described above occurs only with the participation in the interaction of a still greater number of particles. In this case one has to expect a still stronger dependence of w' on concentration, which is indeed observed experimentally (table).

For further estimates, it is reasonable to take $r = 10$ Å, since evidently exchange forces stronger than the dipole-dipole interaction act between ions that are still closer together than that. Consequently, such ions have to be considered as components of exchange pairs. For this value of r, we find that the quantity $\langle \Delta\nu_{\alpha\beta}^2 \rangle^{1/2} \approx 10^8$ cps (see [24]), and on the basis of the calculation carried out in the preceding section, we take the difference $\nu_\alpha - \nu_\beta \approx J/h$ equal to 2.5×10^8 cps. For zinc tungstate the value of Z' is about 50 for $\Delta r = 2$ Å, and for $C = 3 \times 10^{-3}$ we find from (11) that $w_{cr} \approx 10^3$ sec^{-1}, which agrees well with the experimental quantity w' in the plateau regions.

The transfer of energy from the single ions to the exchange pairs is facilitated if $2D \sim h\nu_0$. In fact, in this case, for $J \ll 2D$, the transition frequencies of the exchange pair (8) that are well-coupled to the lattice are close to the transition frequencies of the single ion, and besides the cross relaxation process we have discussed involving the exchange pair and two single ions, a direct cross relaxation process is also possible. Apparently this is the situation for the chromium ion in the hexacyanide. We remark that in this substance (and generally in crystals with a small zero-field splitting), pairs with the stronger exchange interaction $J \sim 2D$ can also be effective (see Eqs. (8) and (10)), if such pairs exist in the crystal.

5. CONCLUSIONS

Thus the experimental data on the spin-lattice relaxation of an entire series of paramagnetic crystals and the theoretical estimates thereof furnish evidence that in a certain interval of concentrations and temperatures the relaxation process goes in two stages, and the mediator between the paramagnetic impurity and the crystal lattice can be pairs of exchange-coupled ions. For substances with large zero-field splitting, the principal role is evidently played by weakly-coupled pairs ($J \sim 10^{-2}$ cm^{-1}) whose spectrum allows a cross relaxation interaction with single ions. We note that the spectrum of such pairs essentially lies in the far wings of the principal absorption lines; from this viewpoint one may say that the line gives up its energy to the lattice via its own wings.

The calculation of the interaction between the exchange pairs and the crystal lattice on the one hand, and the single ions on the other, gives good agreement with experiment both in the numerical estimates and in the determination of the form of the concentration dependence of the relaxation rate. It should be kept in mind, of course, that these numerical estimates are very approximate and give only order-of-magnitude results.

In conclusion, we note that in ruby, in contrast to the other crystals considered, the temperature plateau was observed only for $C = 0.28\%$,[6] whereas T_1 is already concentration dependent in this substance at $C \approx 0.05\%$.[25] It is extremely probable that at $C < 0.28\%$ the spin-lattice relaxation in ruby is controlled by another mechanism, for example phonon scattering by structural defects (in particular, by the impurity ions), as suggested by Kochelaev.[26] Because of the low spin-lattice relaxation rate, this mechanism can turn out to be more effective in ruby with a low concentration of chromium than in the other paramagnetic crystals.

The author thanks M. E. Zhabotinskiĭ, A. V.

[1] R. de L. Kronig, Physica **6**, 33 (1939).

[2] J. H. Van Vleck, Phys. Rev. **57**, 426 (1940).

[3] J. H. Van Vleck, Quantum Electronics, Columbia Univ. Press, N. Y., 1960, p. 392.

[4] J. C. Gill, Proc. Phys. Soc. (London) **79**, 58 (1962).

[5] Bloembergen, Shapiro, Pershan, and Artman, Phys. Rev. **114**, 445 (1959).

[6] G. M. Zverev, JETP **40**, 1667 (1961), Soviet Phys. JETP **13**, 1175 (1961).

[7] A. M. Prokhorov and V. B. Federov, JETP **46**, 1937 (1964), Soviet Phys. JETP **19**, 1305 (1964).

[8] V. A. Atsarkin and V. I. Popov, JETP **47**, 865 (1964), Soviet Phys. JETP **20**, 578 (1965).

[9] A. Rannestad and P. E. Wagner, Phys. Rev. **131**, 1953 (1963).

[10] L. S. Singer, J. Chem. Phys. **23**, 379 (1955).

[11] L. M. Shkol'nikova and E. A. Shugam, Kristallografiya **5**, 32 (1960), Soviet Phys. Crystallography **5**, 24 (1960).

[12] Statz, Rimai, Weber, and de Mars, J. Appl. Phys. **32**, 218S (1961).

[13] A. A. Manenkov and A. M. Prokhorov, JETP **42**, 75 (1962), Soviet Phys. JETP **15**, 54 (1962).

[14] Baker, Bleaney, and Bowers, Proc. Phys. Soc. (London) **B69**, 1205 (1956).

[15] G. V. Marr and P. Swarup, Can. J. Phys. **38**, 495 (1960).

[16] Castle, Chester, and Wagner, Phys. Rev. **119**, 953 (1960).

[17] Emel'yanova, Karlov, Manenkov, Milyaev, Prokhorov, Smirnov, and Shirkov, JETP **44**, 868 (1963), Soviet Phys. JETP **17**, 591 (1963).

[18] Giordmaine, Alsop, Nash, and Townes, Phys. Rev. **109**, 302 (1958).

[19] M. W. P. Strandberg, Phys. Rev. **110**, 65 (1958).

[20] S. A. Al'tshuler, JETP **43**, 2318 (1962), Soviet Phys. JETP **16**, 1637 (1962).

[21] R. D. Mattuck and M. W. P. Strandberg, Phys. Rev. **119**, 1204 (1960).

[22] I. D. Mash and M. I. Rodak, FTT **7**, 717 (1965), Soviet Phys. Solid State **7**, 576 (1965).

[23] B. F. Ormont, Struktury neorganicheskikh veshchestv (Structures of Inorganic Substances), Gostekhizdat, 1950.

[24] M. Hirono, J. Radio Res. Lab (Tokyo) **8**, 1 (1961).

[25] A. A. Manenkov and A. M. Prokhorov, JETP **38**, 729 (1960), Soviet Phys. JETP **11**, 527 (1960).

[26] B. I. Kochelaev, DAN SSSR **131**, 1053 (1960), Soviet Phys. Doklady **5**, 349 (1960).

Translated by L. M. Matarrese
21