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ON THE THEORY OF LONGITUDINAL RELAXATION OF PARAMAGNETIC SALT SOLUTIONS

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Paramagnetic longitudinal (spin-lattice) relaxation in solutions of salts of the iron group and rare earth elements is considered theoretically. The calculations are based on the assumption that, like ionic crystals, liquid solutions contain paramagnetic complexes. The normal vibrations of these complexes are perturbed by the Brownian motion of the surrounding particles; as a result, the electric field acting on the paramagnetic ions is changed and relaxation transitions are induced between different stationary states. It is shown that, when the interval between the two lower Stark sublevels of the ion is $\delta \sim 2kT$, two longitudinal relaxation times exist; one is due to transitions between various Stark (orbital) levels without spin flip, and the other is due to transitions within a Stark level with change of the spin direction. The paramagnetic resonance line width is due to transitions of the first type. The predictions of the theory are in good agreement with the experimental data referring on copper, chromium, and manganese salt solutions.

1. INTRODUCTION

THE current theories of longitudinal (spin-lattice) relaxation in liquid solutions of paramagnetic salts are in contradiction with many experimental facts. At the base of the theory of Bloembergen, Purcell, and Pound,[1] which finds wide application in the region of nuclear magnetic resonance, lies the assumption that the exchange of energies between the spin system and Brownian motion takes place through the fluctuations of the magnetic dipole-dipole interaction of the particles, brought about by this Brownian motion. In its application to solutions of paramagnetic salts, this theory gives values for the longitudinal relaxation times which are comparable to those observed by experiment only for very high concentrations of the magnetic particles.

McConnell[2] and McGarvey[3] have proposed another relaxation mechanism. They consider the paramagnetic ion, together with the solvate shell surrounding it, as a "micro-crystallite" which can rotate under the action of Brownian motion. The energy of the paramagnetic ion in the external magnetic field H, the Stark splitting of the spin levels in the crystalline field, and the hyperfine structure will depend on the direction of H relative to the axes of the crystallite. Therefore, rotations of the crystallite produces an exchange of energy between the paramagnetic ion and Brownian motion. The theoretical conclusions of McConnell and McGarvey confirm the experimental investigations of the paramagnetic-resonance line width in absorption, which unfortunately has been carried out only at a single frequency of the radiofrequency field and at one temperature. The many-sided experimental investigation of paramagnetic resonance in liquid solutions of salts, carried out by Kozyrev[4] at different temperatures and over a wide frequency range, has revealed that, in the majority of cases, the experimental dependence of the longitudinal relaxation time on temperature and direction of the applied magnetic field is completely at variance with the predictions of the theory.[2,3] Evidently, none of the different mechanisms which can guarantee spin-lattice interaction could be considered important in current theories. We shall show that the principal mechanism corresponding to paramagnetic relaxation in liquids of paramagnetic solutions is the following.

In solid paramagnetic ionic crystals, the paramagnetic particle m and with the adjacent diamagnetic particles X usually form a paramagnetic complex, for example, MX_6 (M is a metallic ion, X is a molecule of water or other diamagnetic particle), the internal interaction of which must be considered first in the explanation of magnetic properties of the material. In solutions, the presence of a solvate shell allows us to make a similar assumption. We can assume that, at least in the course of time larger than the correlation time of the spin-lattice interaction, the paramagnetic ion and the neighboring molecules of the solvent form a stable complex whose vibrations can be characterized by a set of normal coordinates Q_i. The Brownian motion of the molecule of the liquid excites vibrations of the paramagnetic complex, and the latter changes the electric field in which the paramagnetic particle finds itself. This change is shown in the spin-orbit interactions of the electrons of the paramagnetic ion, and consequently can bring about a re-orientation of its magnetic moment.

2. METHOD OF COMPUTATION

The Hamiltonian that takes into account both the internal interaction of the paramagnetic ion M and the effect on it of the surrounding diamagnetic particles X of the complex is of the form

$$\hat{\mathscr{H}} = \hat{\mathscr{H}}_0 + \hat{\mathscr{H}}'(t), \tag{1}$$

where the main part $\hat{\mathscr{H}}_0$ contains the coordinates and the spin variables of the electrons of the ion M, while the perturbation $\mathscr{H}'$ depends also on the normal coordinates Q_i of the complex, which are random functions of the time t. Let E_l and E_k be a pair of energy levels of the unperturbed system $\hat{\mathscr{H}}_0$. We shall be interested in transitions of E_l and E_k under the action of the perturbation $\hat{\mathscr{H}}'$, the probability of which is obviously proportional to the square of the modulus of the matrix element $\mathscr{H}'_{lk}(t)$. Since $\mathscr{H}'_{lk}$ depends on Q_i, we shall apply the method of correlations. If we introduce the correlation function $K_{lk}(\tau) = \overline{\mathscr{H}'_{lk}(t)\,\mathscr{H}'_{lk}(t+\tau)}$ in the usual way, then the average transition probability per second between the levels E_l and E_k will be equal to

$$A_{lk} = \hbar^{-2} J(\omega_{lk}), \tag{2}$$

where $\omega_{lk} = (E_l - E_k)/\hbar$ while $J(\omega_{lk})$ is the Fourier component of the correlation function, equal to

$$J(\omega_{lk}) = \int\limits_{-\infty}^{\infty} K_{lk}(\tau) \exp(i\omega_{lk}\tau)\, d\tau. \tag{3}$$

If it is assumed that the dependence of the correlation function on τ is determined by a Markoff law:

$$K_{lk}(\tau) = K(0) \exp(-|\tau|/\tau_c), \tag{4}$$

then the transition probability takes the form

$$A_{lk} = \hbar^{-2}\,\overline{|\mathscr{H}'_{lk}|^2}. \tag{5}$$

The meaning of the correlation time τ_c will be explained below.

In what follows, we shall assume for definiteness that the paramagnetic complex contains six diamagnetic particles X, distributed at the vertices of an octahedron. The spin-lattice interactions that arise through the normal vibrations of the octahedral complex were considered by Van Vleck,[5] who found that

$$\hat{\mathscr{H}}' = \sum_{i=2}^{6} V^{(i)} Q_i, \tag{6}$$

where

$$V^{(2)} = -18C(x^2 - y^2), \quad V^{(3)} = -18C(r^2 - 3z^2)/\sqrt{3},$$
$$V^{(4)} = 24Cxy, \quad V^{(5)} = 24Cxz, \quad V^{(6)} = 24Cyz, \quad C = e'\mu/R^5. \tag{7}$$

here $\mathbf{r}(x, y, z)$ is the radius vector drawn from the nucleus to the electron of the unfilled shell M; R is the equilibrium distance between the particles M and X, e′ is the charge of the ion M, and μ is the dipole moment of the molecule X. In the expressions derived for the coefficients $V^{(i)}$, terms proportional to $(r/R)^4$ and $(r/R)^6$ are omitted.

Thus, if we substitute

$$\mathscr{H}'_{lk}(t) = \sum_i V_{lk}^{(i)} Q_i(t) \tag{8}$$

in formula (5) and consider the orthogonality of the normal coordinates, we obtain

$$A_{lk} = (\overline{Q^2}/\hbar^2) \sum_i |V_{lk}^{(i)}|^2\, 2\tau_c / (1 + \omega_{lk}^2 \tau_c^2). \tag{9}$$

For all normal vibrations, we have introduced a certain average quantity $\overline{Q_i^2} = \overline{Q^2}$.

It is known from optical[6] that the eigenfrequencies of the normal vibrations of the octahedral complexes of ions of the transition group lie within the range 4×10^{13} to 16×10^{13} sec^{-1} (200 to 800 cm^{-1}). The quantum mechanical mean square of the amplitude of the oscillator is equal to

$$\overline{Q^2} = (\hbar/2m\omega_0) \coth(\hbar\omega_0/2kT). \tag{10}$$

For all normal coordinates Q_i of the complex, we have introduced a certain average frequency ω_0 and mass m (close to the mass of the complex).

The correlation time τ_c of the oscillators Q_i, brought about by the action of the dissipative forces, is naturally determined as the reciprocal value of the damping coefficient γ which can be compared with the width of the satellite lines in the Raman spectra of paramagnetic ions: $\gamma \sim 10$ cm^{-1} and $\tau_c \approx 1/\gamma \sim 10^{-12}$ sec. From experimental data (see reference 8) on the temperature dependence of the line width of the vibrational structure of optical spectra of the ions in crystals, it follows that the width increase upon heating is proportional to $\sqrt{T}$. We can reach this conclusion also by starting from theoretical considerations.[8,9] Thus the temperature dependence of the transition probability (9) will be given by the formula

$$A_{lk} \sim T^{-1/2} \coth(\hbar\omega_0 / 2kT) \tag{11}$$

for $\tau_c^2 \omega_{lk}^2 \ll 1$, and

$$A_{lk} \sim T^{1/2} \coth(\hbar\omega_0 / 2kT) \tag{12}$$

for $\tau_c^2 \omega_{lk}^2 \gg 1$.

Finally, we shall establish a simple connection which exists between the probabilities of relaxation transitions in liquid solutions and the probabilities of single phonon processes in crystals. For crystals, the transition probability is computed from the formula (see reference 10):

$$A_{lk}^{(k)} = 2\pi\hbar^{-2}\rho_{\omega_{lk}} \overline{|\mathscr{H}'_{lk}|^2}, \tag{13}$$

where $\rho_\omega = 3V\omega^2/2\pi v^3$ is the spectral density of vibrations of the lattice of frequency ω, v is the average sound velocity, V is the volume of the crystal. If we denote the mass of the crystal by M_0, and the temperature by T_0, then the mean square of the matrix element of the energy of spin-lattice coupling will have the form:

$$\overline{|\mathscr{H}'_{lk}|^2} = \sum_i |V_{lk}^{(i)}|^2 \frac{\hbar}{2M_0\omega_{lk}} \frac{2R^2\omega_{lk}^2}{15\,v^2} \frac{\exp(\hbar\omega_{lk}/kT_0)}{\exp(h\omega_{lk}/kT_0) - 1}\,. \tag{14}$$

Assuming $\hbar\omega_{lk} = g\beta H \ll kT_0$, we obtain

$$A_{lk}^{(k)} = (1/5\,\pi\hbar^2) \sum_i |V_{lk}^{(i)}|^2 (R^2\omega_{lk}^2/\rho v^5)\, kT_0, \tag{15}$$

where ρ is the density of the crystal. Comparing (15) and (9), we readily obtain

$$A_{lk} = \frac{5\pi\rho v^5}{\omega_{lk}^2 (kT_0)} \frac{\overline{Q^2}}{R^2} \frac{2\tau_c}{1 + \omega_{lk}^2\tau_c^2} A_{lk}^{(k)}. \tag{16}$$

Taking for the constants the values $\rho = 2$ gm/cm^3, $v = 2 \times 10^5$ cm/sec, $T = 300°K$, $T_0 = 1°K$, $\overline{Q^2}/R^2 = 10^{-4}$, $\omega_{lk} = 10^{10}$ cps, and $\tau_c = 10^{-12}$ sec we obtain

$$A_{lk} = 10^8 A_{lk}^{(k)}. \tag{17}$$

Thus, in measurements in crystals at low temperatures, the relaxation time in liquid solutions can be estimated from the spin-lattice relaxation time. In many salts of elements of the iron group, the relaxation time at helium temperatures is of the order of 10^{-2} to 10^{-1} sec. Therefore, for longitudinal relaxation times in liquid solutions of these salts at room temperature, we obtain $T_1 \sim 10^{-9}$ sec, which is of the same order as quantities obtained experimentally.

Let us turn our attention to a detailed consideration of the most typical paramagnetic salts. We shall consider, successively, solutions containing ions of elements of the iron group, ions of rare earth elements and, as a separate class, ions found in S-states.

3. IONS OF ELEMENTS OF THE IRON GROUP; CASE OF $S = \frac{1}{2}$

Among the ions of elements of the iron group we must single out those for which the spin $S = \frac{1}{2}$ because in this case, according to Kramers' theorem,[11] Stark splitting of the spin energy levels is absent. We shall first consider doubly ionized copper atoms (ground state ^2D). Six molecules of water form a distorted octahedron around the copper ion, creating a strong electric field of cubic symmetry and a weak tetragonal field. We can characterize the system of orbital energy levels of Cu^{+2} (Fig. 1), which are formed in these electric fields, by the following wave functions:[12]

$$\psi_a = (\psi_2 + \psi_{-2})/\sqrt{2}, \quad \psi_b = \psi_0, \quad \psi_c = (\psi_2 - \psi_{-2})/\sqrt{2},$$
$$\psi_d = (\psi_1 + \psi_{-1})/\sqrt{2}, \quad \psi_e = (\psi_1 - \psi_{-1})/\sqrt{2}. \tag{18}$$

The double spin degeneracy of each of the simple orbital levels is removed in the magnetic field; the magnetic sublevels can be characterized by the quantum numbers $M = \pm\frac{1}{2}$. The width $\Delta\nu$ of the resonance line $(a;\ M = -\frac{1}{2} \rightarrow \frac{1}{2})$ is equal to the sum of the transition probabilities from each of the sublevels $(a;\ M = \pm\frac{1}{2})$ to all the remaining. Since the transition probabilities from the lower levels to the upper are proportional to the corresponding Boltzmann factors, we obviously cannot consider transitions to the levels c, d and e. Of the remaining transitions; the only important ones are those completed between different orbital levels without a change in the spin direction. The matrix elements of the perturbation $\mathcal{H}'$ for these transitions are equal to

$$\mathscr{H}'_{a,-1/2;\,b,-1/2} = \mathscr{H}'_{a,1/2;\,b,1/2} = \mathscr{H}'_{ab}$$
$$= 16\sqrt{3}\, e'\mu\bar{r}^2 Q_4 / 7R^5, \tag{19}$$

while for a transition between the magnetic sublevels of the lower orbital state, a matrix element differing from zero appears only in the third approximation, and is equal to

$$\mathscr{H}'_{a,-1/2;\,a,+1/2} \approx \lambda g\beta H \Delta^{-2} \mathscr{H}'_{ab}. \tag{20}$$

Here λ is the spin-orbit coupling constant. Finally, with the help of (19) and (9), we get the following expression for the half-width of the resonance line:

$$\Delta\nu = 6\left(\frac{16\, e'\mu\bar{r}^2}{7R^5}\right)^2 \frac{\overline{Q^2}}{\hbar^2} \frac{2\tau_c}{1 + \tau_c\omega_{ab}^2} \exp(-\delta/2kT). \tag{21}$$

This equation gives a good account of all the experimental facts established by Kozyrev[13] for several copper salts. It follows from (21) that the width of the paramagnetic resonance line $\Delta\nu$ ought not to depend upon the direction of the magnetic field H. Actually, experiments carried out at different frequencies of the oscillating magnetic field (which differ over a range of one hundred) have not revealed any notable change in the width $\Delta\nu$. If the relaxation were determined by a McConnell mechanism,[2] then the width ought to change by $\sim 10^4$ times. We note that the mechanism assumed by us also would give such a strong dependence on the field H if the relaxation transitions with change of spin orientation played the dominant role, as is evident from (20).

It has been established from experiments on aqueous solutions of $Cu(NO_3)_2$ that, heating from $\sim 300°$ to $400°K$ increases the width by a factor of 1.8.[14] In crystals, the interval $\delta = \hbar\omega_{ab} \sim 1000$ cm^{-1}. It is natural to assume that in aqueous solutions, too, the value of δ has this same order of magnitude. In this case, $\omega_{ab}^2\tau_c^2 \gg 1$, and therefore the temperature dependence of the width will be given by the formula

$$\Delta\nu \sim \sqrt{T}\coth(\hbar\omega_0 / 2kT)\exp(-\delta / 2kT). \qquad (22)$$

We assume the frequency ω_0 to be $500\ cm^{-1}$, Hence, to explain the increased width observed in the heating from $\sim 300°$ to $400°K$, it is necessary to set $\delta \approx 750\ cm^{-1}$. A certain decrease in the value of δ in the transition from the crystal to the liquid solution is possibly connected with the fact that the distortion of the regular octahedral form of the paramagnetic complex in the solutions is connected only with the effect of Yang and Teller.

To estimate the order of magnitude of the quantity $\Delta\nu$, we transform (21) into

$$\Delta\nu = 12\left(\frac{16}{7}\frac{e'\mu}{R^2\delta}\frac{\overline{r^2}}{R^2}\right)^2\frac{\overline{Q^2}}{R^2}\frac{\exp(-\delta / 2kT)}{\tau_c}. \qquad (23)$$

We assume the dimensionless quantity in the parentheses to be equal to unity. It is uncertain whether an estimate obtained by direct calculation is more accurate, because the substitution of the paramagnetic complex for a point charge and six dipoles in the calculation of the energy of spin-lattice interaction is obtained only in very rough approximation. If we assume that $\overline{Q^2}/R^2 \sim 10^{-4}$, we obtain $\Delta\nu \sim 10^9$ cps, which agrees well with the experimental value.

Measurement of paramagnetic resonance in different copper-salt solutions permits us to establish an interesting fact:[4] the closer the g-factor is to the pure spin value, the greater will be the width of the absorption line. In first approximation,[15] $g = 2 - 4\lambda/\Delta$. The increase in the width $\Delta\nu$ with decrease in the ratio $|\lambda/\Delta|$ follows directly from (21). A decrease in $|\lambda/\Delta|$ can be a consequence only of the preservation of the equilibrium distance R between the Cu^{++} ion and the water molecules; in this case, the energy interval δ is probably preserved, too.

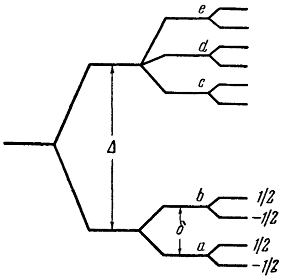

FIG. 1. Successive splitting of the ground energy level of Cu^{+2} under the action of a strong cubic field, a weak tetragonal field, and a magnetic field.

Hitherto we could recognize "spin-lattice" interactions in paramagnetic solutions only from experimental data on the width of the paramagnetic resonance line. However, we shall employ an entirely different method of investigation — measurement of the paramagnetic absorption in parallel fields in which we can determine the longitudinal (spin-lattice) relaxation time T_1. In the case of copper salts (since the interval between two lowest orbital levels is comparatively small) there is a large difference between the values of $\Delta\nu$ and $1/T_1$. In the computation of T_1 for Cu^{++}, we make use of the equation:[16]

$$1 / T_1 = \alpha / C, \qquad (24)$$

where α is the coefficient of thermal conductivity between the spin system and the lattice, while C is the specific heat of the spin system. With sufficient accuracy we can regard as possible relaxation transitions only those between the levels a and b (Fig. 1) which takes place without a change in spin. Let the lattice temperature be equal to T and let $T_s = T + \Theta$ be the temperature of the spin system. The excess of the number transitions per second from level b to level a over the inverse transitions will be equal to

$$\Delta N = N_b A_{ba} - N_a A_{ab} = N_a A_{ab} \qquad (25)$$
$$\times[\exp(-\delta / k(T+\Theta) + \delta / kT) - 1] = N_a A_{ab}\delta\Theta / kT^2.$$

Here N_a and N_b are the numbers of particles in levels a and b, respectively. The coefficient α (the energy given up by the lattice per second if $\Theta = 1°$) will be equal to

$$\alpha = N_a A_{ab}\delta^2 / kT^2. \qquad (26)$$

For calculation of the specific heat C, we make use of the equation (see reference 17):

$$C = \overline{(\Delta E)^2} / kT^2. \qquad (27)$$

Here $\overline{(\Delta E)^2}$ is the mean-square energy fluctuation, which can easily be calculated by taking into account the population of levels a and b. As a result we obtain

$$\overline{(\Delta E)^2} = N_a \delta^2 (e^{-\delta / kT} - e^{-2\delta / kT}). \tag{28}$$

If we take into consideration that $\Delta\nu = 2A_{ab}$, we easily obtain with the aid of (24), (26), (27), and (23)

$$\frac{1}{T_1} = 6\left(\frac{16}{7}\frac{e'\mu}{R^2\delta}\frac{\overline{r^2}}{R^2}\right)^2 \frac{\overline{Q^2}}{R^2\tau_c}\frac{\exp(\delta / 2kT)}{(1 - e^{-\delta / kT})} \cdot$$
$$\approx \frac{\Delta\nu}{2}\frac{e^{\delta / kT}}{(1 - e^{-\delta / kt})} \cdot \tag{29}$$

It is interesting to note that, in contrast to the width $\Delta\nu$, the quantity $1/T_1$ decreases with increasing temperature. This unusual temperature dependence of the relaxation time is explained by the fact that in our case the specific heat of the spin system will increase upon heating more rapidly than the probability of relaxation transitions.

It should be kept in mind that the nonequilibrium distribution of particles between the levels a, $-\frac{1}{2}$ and a, $\frac{1}{2}$ (or the levels b, $-\frac{1}{2}$ and b, $\frac{1}{2}$) cannot be cancelled out with the help of the relaxation transitions a, $-\frac{1}{2} \to$ b, $-\frac{1}{2}$ and a, $\frac{1}{2} \to$ b, $\frac{1}{2}$. Therefore, there will be another relaxation time T_1' in addition to the time T_1. The value of T_1' can be estimated, according to (9), (19), and (20), by the formula:

$$\frac{1}{T_1'} \approx 6\frac{\overline{Q^2}}{\hbar^2 R^2}\left(\frac{\lambda g\beta H}{\Delta^2}\right)^2\left(\frac{16}{7}\frac{e'\mu}{R^2}\frac{\overline{r^2}}{R^2}\right)^2 2\tau_c. \tag{30}$$

At $H \sim 10^4$ Oe and room temperature, we have $1/T_1' \sim 10^8\ \text{sec}^{-1}$.

There is also a third way of measuring quantities which depend on the probabilities of relaxation transition. According to reference 18, the changes in the magnetic field of paramagnetic ions in a solution, which take place during relaxation processes, determine the value of the longitudinal relaxation time of the nuclei of the solvent. Changes of the magnetic field in the transitions a, $\frac{1}{2} \to$ b, $\frac{1}{2}$ and a, $-\frac{1}{2} \to$ b, $-\frac{1}{2}$ take place only as a result of the small difference in the values of the g-factors of the levels a and b. Therefore, special consideration is required for the solution of the problem as to whether these transitions or the transitions in the change in the spin direction play the dominant role in processes of nuclear relaxation.

In addition to the Cu^{++} ion, the case $S = \frac{1}{2}$ also applies to the triply-charged titanium ion and the quadruply-charged vanadium ion. (solutions of vanadium require special consideration because the linear molecule V — 0 and the ion V^{+4} have completely different systems of energy levels. The orders of the orbital levels will be reversed in these ions. The width of the resonance line will be determined by relaxation transitions between the levels e → d and e → c (the e level is now the ground level). It was shown in reference 10 that

$$\mathscr{H}'_{ed} = -\frac{12\sqrt{3}}{7}C\left(\sqrt{2}\,Q_3 - \frac{2}{3}Q_6\right),$$
$$\mathscr{H}'_{ec} = \frac{12\sqrt{3}}{7}C\left(\sqrt{2}\,Q_2 + \frac{2}{3}Q_5\right). \tag{31}$$

Thence, with the help of (9) we obtain an equation similar to (21), namely:

$$\Delta\nu = \frac{528\,\overline{Q^2}}{\hbar^2}\left(\frac{e'\mu\overline{r^2}}{R^5}\right)^2\left[\frac{2\tau_c e^{-\delta_{ed}/kT}}{1 + \tau_c^2\,\omega_{ed}^2} + \frac{2\tau_c e^{-\delta_{ec}/kT}}{1 + \tau_c^2\,\omega_{ec}^2}\right]. \tag{32}$$

In solutions containing the ions Ti^{+3} and V^{+4}, the resonance lines will be 1 to 2 orders of magnitude wider than for Cu^{+2} for the following reasons: (1) the intervals δ_{ed} and δ_{ec} here are less than the interval δ for Cu^{+2}; (2) the splitting in a cubic field, and consequently the effective charge e′, is larger here than for Cu^{+2}; (3) two orbital levels are located close to the ground level.

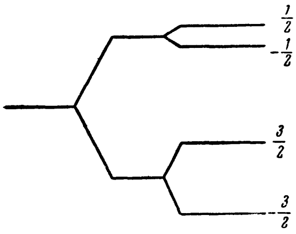

FIG. 2. Splitting of the spin quadruplet of the Cr^{+3} ion, which is located in the ground orbital energy level in electric and magnetic fields.

4. IONS OF THE IRON GROUP; THE CASE $S > \frac{1}{2}$

Let us first consider the Cr^{+3} ion. The ground term of the free ion Cr^{+3} in a cubic field created by the six particles X is so split that the lowest orbital level is simple. The "crystalline" field splits the spin-quadruplet into two doublets, (Fig. 2) the interval between which is equal to $\sim 0.1\ \text{cm}^{-1}$. We shall assume that the magnetic field is directed along the axis of symmetry of the weak trigonal electric field. It is easy to establish that a change in the direction of H relative to the axes of symmetry of the paramagnetic complex has little effect on the relaxation mechanism that we have considered. We shall enumerate the spin levels by the value of the paramagnetic quantum number M. The matrix element of the perturbation $\mathscr{H}'$ which connects the spin levels M and M′, differs from zero only in the third approximation, and has the form:[10]

$$\mathscr{H}'_{M,M'} = \{\varepsilon_1[\sqrt{3}(\hat{S}_y^2 - \hat{S}_x^2)Q_2 + (3\hat{S}_z^2 - {}^{15}/_4)Q_3] + \varepsilon_2[(\hat{S}_x\hat{S}_y + \hat{S}_y\hat{S}_x)Q_4 + (\hat{S}_z\hat{S}_x + \hat{S}_x\hat{S}_z)Q_5 + (\hat{S}_z\hat{S}_y + \hat{S}_y\hat{S}_z)Q_6)]\}_{M,M'}, \tag{33}$$

where

$$\varepsilon_1 = 54\sqrt{3}\frac{\lambda^2}{\Delta^2}\left(\frac{e'\mu}{R^3}\right)\frac{\overline{r^4}}{R^4},$$

$$\varepsilon_2 = \frac{12{,}324}{175}\frac{\lambda^2}{\Delta^2}\left(\frac{e'\mu}{R^3}\right)\left(\frac{\overline{r^2}}{R^2} - \frac{55}{36}\frac{\overline{r^4}}{R^4}\right).$$

Here $\hat{S}$ is the spin operator; $M, M' = \pm{}^1/_2, \pm{}^3/_2$. Substituting (33) in (9), we obtain for relaxations transitions:

$$A_{M,M+1} = 4\hbar^{-2}\varepsilon_2^2\overline{Q^2}\tau_c(S_xS_z + S_zS_x)^2_{M,M+1},$$
$$A_{M,M+2} = 2\hbar^{-2}(\varepsilon_2^2 + 3\varepsilon_1^2)\overline{Q^2}\tau_c(S_x^2 - S_y^2)^2_{M,M+2}. \tag{34}$$

Here we have assumed that $\tau_c\omega_{M,M'} \ll 1$. Calculation of the longitudinal relaxation time is carried out by using the expression:[16]

$$\frac{1}{T_1} = (2S+1)\sum_{l>k} A_{lk}(E_l - E_k)^2 \Big/ \sum_{l>k}(E_l - E_k)^2, \tag{35}$$

which is valid if $E_l - E_k \ll kT$ for all values of l and k. We shall carry out calculations for two limiting cases of strong and weak magnetic fields. If the field H is strong and the spin levels are equidistant, then

$$\frac{1}{T_1} = (96\,\overline{Q^2}/20\,\hbar^2)(3\varepsilon_1^2 + 2\varepsilon_2^2)\tau_c. \tag{36}$$

If $H = 0$, then

$$1/T_1 = (36\,\overline{Q^2}/\hbar^2)(\varepsilon_1^2 + \varepsilon_2^2)\tau_c. \tag{37}$$

Taking $\lambda/\Delta \sim 0.01$, and assigning to the remaining constants in (36) and (37) the values assumed in the previous section, we obtain $1/T_1 \sim 10^9 - 10^{10}$ sec^{-1}. The line width observed[14] in measurements of paramagnetic resonance in solutions containing Cr^{+3} has the same order of magnitude and falls off slowly with increasing temperature. Equations (36) and (37) predict a temperature dependence for the width of the form

$$1/T_1 \sim T^{-1/2}\coth(\hbar\omega_0/2kT). \tag{11'}$$

It is well known from chemical and optical investigations that complexes of the Cr^{+3} ion in solutions are very stable. The stability of the complex characterizes the value of the binding energy in the complex, and consequently the frequency of the normal vibrations of the complex, which in this case[6] reaches ~800 cm^{-1}. It then follows that in the temperature range 300° – 400°K the change in the line width should be given by the relation $1/T_1 \sim T^{1/2}$, which explains the results of experiments sufficiently accurately.

For all ions for which the lowest orbital level in the octahedral field is a singlet, we obtain Eqs. (36) and (37). The ions Ni^{+2} and V^{+2} belong to this group. For the remaining ions of the iron group, with the exception of Mn^{+2} and Fe^{+3} considered below, we can assume that the width of the resonant line will, as for Cu^{+2}, be determined by relaxation transitions between different orbital levels.

5. IONS IN S -STATES

Crystals of the ions Mn^{+2}, Fe^{+3}, Gd^{+3}, Eu^{+4}, and Cm^{+3} make up a special place among the paramagnets. These ions are in S states, as a consequence of which the electric field of the crystal (acting by means of the very distance perturbation terms of the ion) bring about a very small (less than 1 cm^{-1}) splitting of the ground energy level. For this same reason, the spin-lattice relaxation time in crystals containing these ions is comparatively long. The behavior of liquid solutions containing ions in the S states is quite similar. We shall carry out a calculation of the longitudinal relaxation for the Mn^{+2} ion, (ground state ^6S). As in the calculations for the relaxation times in crystals,[19] we shall calculate the matrix elements by the method equivalent operators; we shall estimate the factor α arising here from the value of the fine structure of the spin levels. The matrix elements of $\mathcal{H}'$ that differ from 0 are:

$$\mathscr{H}'_{M,M+1} = (12\,e'\mu\alpha\overline{r^2}/R^4) \times (S_xS_z + S_zS_x)_{M,M+1}(Q_5 + iQ_6)/R. \tag{38}$$

$$\mathscr{H}'_{M,M+2} = (12\,e'\mu\alpha\overline{r^2}/R^4) \times (S_x^2 - S_y^2)_{M,M+2}(3Q_2 + iQ_4)/R. \tag{39}$$

The value of $e'\mu\alpha\overline{r^2}/R^4$ has the order of magnitude of the Stark splitting of the ground state. In view of this fact, we replace it by the fine-structure constant which for Mn^{+2}, in particular, is equal to $D = 0.025$ cm^{-1}.[20] We can then represent the transition probabilities in the following from:

$$A_{M,M+1} = \frac{36\cdot16\,D^2\overline{Q^2}}{\hbar^2R^2}\tau_c(S_xS_z + S_zS_x)^2_{M,M+1}, \tag{40}$$

$$A_{M,M+2} = \frac{36\cdot80\,D^2\overline{Q^2}}{\hbar^2R^2}\tau_c(S_x^2 - S_y^2)_{M,M+2}. \tag{41}$$

We compute the relaxation time with the help of (35). For strong magnetic fields,

$$\frac{1}{T_1} = \frac{274\cdot64\cdot36}{105}\frac{D^2\overline{Q^2}}{\hbar^2R^2}\tau_c. \tag{42}$$

If $H = 0$, however, then

$$\frac{1}{T_1} = \frac{36\cdot 16\cdot 157}{7}\frac{D^2}{\hbar^2}\frac{\overline{Q^2}}{R^2}\tau_c. \tag{43}$$

A numerical estimate yields $T_1 \sim 10^{-7}$ sec.

Experiments[14] show that the line width in solutions of Mn^{+2} at first decreases upon heating and then, beginning at temperatures $T_0 \sim 350°K$, increases. Equation (11) explains such a change if it is assumed that $\hbar\omega_0 \approx kT_0 \approx 250\ cm^{-1}$.

6. IONS OF THE RARE EARTH ELEMENTS

Judging from the vibrational structure of the optical absorption lines of the rare earth ions, the solvate complexes formed in solutions of salts of rare earth elements are as stable as those in solutions of salts of the iron group. In the case of aqueous solutions, we can assume that the metallic ion is surrounded by six water molecules located at the vertices of an octahedron, and that the fundamental component of the electric field has a cubic symmetry while the weak component is rhombic. Of those ions with an odd number of electrons, we consider Ce^{+3} (ground state $^2F_{5/2}$). The diagram of the successive splitting of the levels of $^2F_{5/2}$ in cubic, rhombic, and magnetic fields is drawn in Fig. 3; the magnetic sublevels are characterized by the following wave functions:[20]

$$\psi_a = (\sqrt{5}\Phi_{-5/2} + \Phi_{3/2})/\sqrt{6}, \quad \psi_b = (\sqrt{5}\Phi_{5/2} + \Phi_{-3/2})/\sqrt{6},$$
$$\psi_c = \Phi_{1/2}, \quad \psi_d = \Phi_{-1/2}, \tag{44}$$
$$\psi_f = (\Phi_{-5/2} - \sqrt{5}\Phi_{3/2})/\sqrt{6}, \quad \psi_g = (\Phi_{5/2} - \sqrt{5}\Phi_{-3/2})/\sqrt{6}.$$

The width of the resonance line due to transitions between the sublevels of the lowest Kramers' doublet is

$$\Delta\nu_{fg} = A_{fg} + \sum_i A_{fi} + \sum_i A_{gi}; \quad i = a, b, c, d. \tag{45}$$

The greatest matrix element of the perturbation $\mathcal{H}'_{fg}$ arises in the second approximation upon consideration of the non-diagonal matrix elements of the Zeeman energy of the ion:

$$\mathscr{H}_z = {}^6/_7\,\beta(\mathscr{H}\mathbf{J}), \quad \mathscr{H}_z(f, a)$$
$$= -\mathscr{H}_z(b, g) = -(4\sqrt{5}/7)\beta H.$$

The matrix elements of $\mathcal{H}'$, which connect the different Stark sublevels, differ from zero in the first approximation. Some of these are:[21]

$$\mathscr{H}'(f, b) = -\mathscr{H}'(a, g) = -\left(\sqrt{5}\frac{e'\mu}{R^5}\right)\overline{r^2}(Q_5 + iQ_6). \tag{46}$$

Now we can compute the matrix element

$$\mathscr{H}'_{fg} = \mathscr{H}_z(f, a)\mathscr{H}'(a, g)/(-\Delta)$$
$$+ \mathscr{H}'(f, b)\mathscr{H}_z(b, g)/(-\Delta) \tag{47}$$
$$= ({}^{40}/_7)(\beta H/\Delta)(e'\mu\overline{r^2}/R^5)(Q_5 + iQ_6).$$

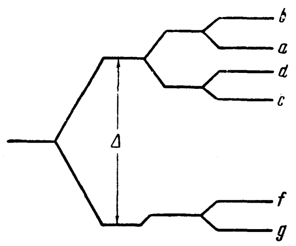

FIG. 3. Successive splitting of the ground energy level of the Ce^{+3} ion under the action of a strong cubic field, a weak rhombic field, and a magnetic field.

In addition to those in (46), matrix elements of the following transitions also differ from zero: f → a, f → c, f → d, g → b, g → c; in magnitude, these are close to (46). Therefore, in the calculation of transition probabilities to the upper Stark level we multiply the matrix element of (46) by $\sqrt{8}$. After calculation of the transition probabilities in accord with Eqs. (9), (46), and (47), we obtain

$$A_{fg} = \frac{800}{49\hbar^2}\left(\frac{\beta\mathscr{H}}{\Delta}\right)^2\left(\frac{e'\mu\overline{r^2}}{R^5}\right)^2\overline{Q^2}\frac{2\tau_c}{1+\tau_c^2\omega_{fg}^2}; \tag{48}$$

$$\sum_i A_{fi} \approx \frac{180}{\hbar^2}\left(\frac{e'\mu\overline{r^2}}{R^5}\right)^2\overline{Q^2}\frac{2\tau_c}{1+\tau_c^2\omega_{fi}^2}\exp(-\hbar\omega_{fi}/2kT). \tag{49}$$

Here $\hbar\omega_{fi}$ is the mean interval between Stark sublevels and has a value of $\sim 100\ cm^{-1}$. Comparison of (48) and (49) shows that transitions to the higher Stark levels make the chief contribution to the line width. This conclusion obviously applies to all ions in which the lower Stark level is a Kramers' doublet and the energy interval up to the next sublevel is $\hbar\omega_{fi} \sim kT$, i.e., in all rare earth ions with an odd number of electrons. An estimate of the width $\Delta\nu_{fg}$ will be most accurate if we equate (49) and (21). For Ce^{+3}, the resonance line is one or two orders of magnitude wider than for Cu^{+2}, owing to the smaller value of the intervals between the lower Stark sublevels and the large number of the sublevels.

In the case of ions with an even number of electrons, the Stark sublevels preserve a non-Kramers degeneracy. Therefore, the matrix elements of the perturbations between the Zeeman sublevels are different from zero in first approximation and have the order of (46). Moreover, there are the same effective relaxation transitions between different Stark levels for ions with a different number of electrons. Thus, if the number of electrons is even, the width of resonance lines ought to be larger (all the conditions being equal) than for ions with an odd number of electrons.

CONCLUSION

Let us consider briefly the effects shown by the hyperfine interactions on the intensity of relaxation transitions. The simplest spin-Hamiltonian, for an ion whose nucleus has a spin I not equal to zero, is of the form:

$$\hat{\mathscr{H}}_S = 2\beta H S_z + (g-2)\beta H S_z + A\mathbf{SI}. \tag{50}$$

The vibrations of particles surrounding a paramagnetic ion lead to a change in the quantities $(g-2)$ and A. If the changes are comparable, the hyperfine interactions can markedly change the probability of relaxation transitions. It is easy to represent the width of the individual hyperfine components of the resonance line as

$$\Delta\nu_{I_z} = (p + qI_z)^2. \tag{51}$$

Here p^2 is the width at $I = 0$, and detailed calculations are required for each ion separately in the determination of the constant q.

Finally, we note that Eq. (16), which connects the probabilities of relaxation transitions in liquid solutions and in crystals, is not always valid. In liquids, if the interval δ between the lowest Stark sublevels does not exceed approximately $5kT$, the width of resonance line is determined by relaxation transitions between the sublevels. In crystals, if the quantity δ/k is greater than the Debye temperature, relaxation transitions between different Stark sublevels are scarcely probable. Equation (16) can be used to establish differences in the origin of relaxations in crystals and in the liquid solutions.

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