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ON THE THEORY OF QUADRUPOLE RELAXATION OF NUCLEAR SPINS IN LIQUIDS

K. A. VALIEV

Physico-Technical Institute, Kazan' Branch, Academy of Sciences, U.S.S.R.

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Quadrupole relaxation of nuclear spins of diamagnetic atoms in liquids is treated theoretically. The calculations are made on the assumption that the thermal motion of the liquid particles is a free translational diffusion. This assumption is valid for metal and salt melts and for weakly solvated ions in electrolyte solutions. It is found that $T_2^{-1} \sim \eta/T$ (η is the viscosity of the liquid) which is in good agreement with the measurements of T_2^{-1} for the nuclear spin of I^{127} in aqueous solutions of NaI and KI salts.

1. INTRODUCTION

ONE of the reasons for the lack of a complete theory of liquids and of liquid solutions is our poor knowledge of the potential of interaction between the particles of a liquid, particularly at small distances. Therefore, it is difficult to obtain unambiguous results on structure and on the motion of particles in a liquid from a comparison of the physical properties of the liquid with a theory which utilizes an approximate interaction potential.

However, if we study liquids by the method of magnetic resonance, the potential of the interaction between the magnetic moments of the particles can be determined quite accurately. Therefore, in a comparison between theory and experiment the only unknowns are the data on the structure of the liquid and the constants which characterize the motion of its particles (the diffusion coefficient or the correlation time). Investigations carried out during the last few years by the method of magnetic resonance have demonstrated the great promise of this method, particularly for the investigation of the structure of a liquid and of the nature of motion of its particles. In the first place a study was made of homogeneous diamagnetic liquids (water). It was shown that the magnetic resonance line in water is narrowed as a result of the influence of thermal motion: the thermal motion averages out the magnetic fields with which the magnetic particles act on one another, and this leads to line narrowing.[1] Considerable progress was made in the study by the nuclear magnetic resonance method of internally hindered rotations of molecules in solid molecular substances. Later studies were extended to solutions of diamagnetic and paramagnetic salts in various solvents. It turned out that the shape and the width of the magnetic-resonance line due to paramagnetic ions dissolved in a dilute solution depend primarily on the structure of the complex formed by the ion and the molecules of the solvent, and on the nature of motion of the particles of this complex.[2,3] The same situation was also observed in solutions of some diamagnetic ions whose nuclei possess large quadrupole moments.[4] It became clear from this work that the dissolved ions can play the role of probes which are very convenient for the study of the nature of thermal motion and of structure in electrolyte solutions. It is obvious that this conclusion also applies fully to liquid melts of metals (alloys) and of salts.

However, the number of experimental investigations of solutions of electrolytes and ionic liquids (metal and salt melts) carried out by the magnetic resonance method is so far comparatively small. The reason for this lies partly in the lack of a theory which would enable one to interpret the experimental results unambiguously. Such a theory must, by starting with a specific model of the liquid, predict the line shape and its behavior as a function of the temperature, the external field etc. First attempts of this kind were the investigations of McConnell[5] and McGarvey.[6] They based their work on a model which assumes the existence in a solution of a paramagnetic salt of a stable solvated complex, and they investigated the contribution to the width of the electron resonance line made by the random rotation of the complex. They considered the complex to be a rigid microcrystal. Comparison with experiment showed that such a mechanism for the broadening of the resonance line turns out to be the principal one only in rare cases. In a joint paper by Al'tshuler and the present author[6] it is shown that in solutions of paramagnetic electrolytes the principal mechanism of line broadening is the interaction of the electron spin of the ion with the internal thermal vibrations of the solvated complex ion.[3] A theory based on a similar line-broadening mechanism turned out to be justified also in the case of nuclear magnetic resonance lines of diamagnetic ions whose nuclei possess an electric quadrupole moment, under the condition that the ions form stable solvated complexes in water.[4]

In this paper we investigate the theory of the width of nuclear magnetic-resonance lines in liquids in which the atoms under investigation have a quadrupole moment and do not form stable complexes with other particles of the liquid. This assumption is applicable, for example, to the quadrupole relaxation of nuclear spins of halogen ions in aqueous solutions of electrolytes, since, as is well known from physical-chemistry studies, the halogen ions do not form stable associations (complexes) with the molecules of the solvent. With certain limitations, a molecule of water may be represented by a point charge; the choice of the value of the effective charge of the molecule will affect the value of the calculated line width, leaving unaltered the physically important dependence of the line width on the temperature and on the nature of the thermal motion of the particles. A similar situation also exists in the case of alloys of metals and ionic salts, and in these cases the charge (ionic) model of the liquid is quite accurate. On the basis of the foregoing we assume that the thermal motion of the particles of the liquid represents free translational diffusion. This assumption will be justified best of all in the case of liquids at temperatures considerably above their melting point. Near the melting point microcrystals can exist in the melt; the quadrupole relaxation of nuclear spins in these microcrystals will evidently be determined by random rotation or by internal vibrations. These mechanisms are similar to those studied by us in reference 4.

We now elucidate the essence of the relaxation mechanism under consideration at present.

We single out of the bulk of the liquid one ion whose nucleus has an electric quadrupole moment. The other particles, regarded as point charges and occupying, generally speaking, random positions with respect to the singled-out ion, will give rise at its nucleus to a resultant inhomogeneous field **E**. Due to diffusion the relative position of the particles will change; this will lead to random variations of the electric field **E** with time. By acting on the quadrupole moment of the nucleus the field **E** can affect its spin. Random shifts of the energy sublevels of the nuclear spin will result from this interaction, and this will give rise to secular broadening of the resonance line and to broadening due to relaxation transitions between the sublevels.

2. THE METHOD OF CALCULATION

The Hamiltonian for a system of spins of nuclei possessing quadrupole moments has the following form in a strong magnetic field

$$\hat{H} = -\gamma\beta_N \mathbf{H}_0 \sum_i \mathbf{I}_i + \hat{H}'. \tag{1}$$

The energy of the internal interactions H' is a small perturbation compared to the Zeeman energy of the spins; in our problem it represents the energy of the nuclear quadrupole moments in the electric fields due to the surrounding particles.

If we neglect the thermal motion of the particles of the system, then the broadening of the resonance line caused by the perturbation H' can be calculated in the following manner. The (secular) part of H' diagonal with respect to the spin of the particle under consideration will result in a displacement of the spin levels of this particle. For a system containing a large number of particles such displacements will form a continuum giving a line of a certain width $\Delta\omega$ which can be evaluated by means of the formulas:[1]

$$\langle \Delta\omega^2 \rangle = T_2^{-2} = \hbar^{-2} \langle | H'_{mm} |^2 \rangle. \tag{2}$$

The averaging indicated by the angular brackets is taken over the space and the spin variables.

We now must take into account the effect on the line width of the thermal motion of the particles. In our problem the thermal motion of the particles represents a translational diffusion. Since diffusion is a random process the matrix element H'_{mm} which depends on the spatial coordinates of the particles of the system will be a random function of the time. The square of the matrix element H'_{mm} can be represented in the form of the Fourier integral

$$\langle | H'_{mm}(t) |^2 \rangle = \int_{-\infty}^{+\infty} J_{mm}(\omega)\, d\omega, \tag{3}$$

where $J_{mm}(\omega)$ is a function describing the frequency spectrum of the perturbation. According to the theory of random processes, the spectral function $J_{mm}(\omega)$ is determined by the correlation function $g_{mm}(\tau)$:

$$J_{mm}(\omega) = \Omega_{mm}^2 \int_{-\infty}^{+\infty} e^{-i\omega\tau} g(\tau)\, d\tau, \qquad \Omega_{mm}^2 = \langle | H'_{mm} |^2 \rangle; \tag{4}$$

$$g_{mm}(\tau) = \Omega_{mm}^{-2} \langle H'_{mm}(t+\tau)\, H'^{*}_{mm}(t) \rangle. \tag{5}$$

We shall evaluate the quantity T_2^{-1}, which characterizes the secular line broadening, by means of the formula[1]

$$T_2^{-1} = \hbar^{-2} J_{mm}(0), \tag{6}$$

which is sufficiently accurate when rapid motion occurs in the system.

The exponential function $\exp(-\tau/\tau_C)$ is often adopted for the correlation function $g_{mm}(\tau)$. However, in those cases when the distribution density $U(q_0, q)$ of the spatial coordinates q of the system is known, the function $g(\tau)$ can be calculated directly. Our case is just of this kind. H'_{mm} depends on the radius vector $\mathbf{R}_A$ $(R_A, \theta_A, \varphi_A)$ from the center of mass of the nucleus under consideration to the charge e_A. The distance $\mathbf{R}_A$ varies as a result of the process of diffusion, and therefore the distribution $U(\mathbf{R}_A)$ is a solution of the free translational diffusion equation[7]

$$U(R_A, \tau;\ R_A^0,\ 0) = \frac{1}{(2\pi)^3} \int_0^\infty e^{-2k_1^2 D\tau} \sum g_l(kR_A)\, g_l^*(kR_A^0)$$

$$\times\ Y_l^m(\theta, \varphi)\, Y_l^{m*}(\theta_0, \varphi_0)\, k^2 dk, \tag{7}$$

$$g_l(x) = (2\pi)^{3/2} i^l J_{l+1/2}(x) / \sqrt{x}, \tag{8}$$

$D = kT/6\pi\eta a$ is the diffusion constant, a is the ionic radius.

The function U is equal to the probability density of finding the charge e_A at the instant of time τ within the volume dv, at a distance $\mathbf{R}_A$ from the nucleus under consideration if at zero time it was at a distance $\mathbf{R}_A^0$ from the nucleus within the element of volume dv_0. In (7) the solution of the diffusion equation is written in the form of an expansion in terms of spherical harmonics, which is convenient for the subsequent averaging.

In place of (5) we now have

$$g_{mm}(\tau) = \Omega_{mm}^{-2} \int H'_{mm}(q)\, H'^{*}_{mm}(q_0)\, U(q,\ q_0)\, dq\, dq_0. \tag{9}$$

The matrix elements nondiagonal with respect to spin $H'_{mm'}$; $|m - m'| \neq 0$ give rise to an additional non-secular line broadening due to the decrease in the lifetime of the spin in a given state due to relaxation transitions between different states. The probability of these transitions is determined by the formula[1]

$$w_{mm'} = \hbar^{-2} J_{mm'}(\omega) = \frac{\Omega_{mm}^2}{\hbar^2} \int_{-\infty}^{+\infty} \exp(-i\omega_{mm'}\tau)\, g(\tau)\, d\tau, \tag{10}$$

and the corresponding relaxation time by the formula[8]

$$T_1^{-1} = (2I + 1) \sum_{l>k} w_{lk} (E_l - E_k)^2 / \sum_{l>k} (E_l - E_k)^2. \tag{11}$$

3. THE ENERGY OF THE QUADRUPOLE MOMENT OF A NUCLEUS IN THE FIELD OF A POINT CHARGE

The energy of the quadrupole moment of a nucleus in an inhomogeneous electric field produced by external charges can be represented in the form of the scalar product of the electric quadrupole moment tensor for the nucleus D_{ik} and the electric field gradient tensor at the nucleus[9]

$$H' = \sum_{i,k} \tfrac{1}{6} D_{ik} (\nabla \mathbf{E})^{ik}, \qquad (\nabla \mathbf{E})^{ik} = \partial^2 \varphi / \partial x_i \partial x_k. \tag{12}$$

In the representation in which I^2 and I_z are diagonal the five independent components of the tensor D_{ik} are quadratic functions of the components of the nuclear spin

$$D_0 = \tfrac{1}{2} C (3I_z^2 - I(I+1)), \qquad D_{\pm 1} = \tfrac{3}{2} C \{I_z I_\pm\},$$

$$D_{\pm 2} = 3C I_\pm^2, \qquad I_\pm = I_x \mp i I_y,$$

$$\{I_i I_j\} = I_i I_j + I_j I_i, \qquad C = eQ / I(2I - 1). \tag{13}$$

We choose the origin of the laboratory system xyz at the center of mass of the nucleus under consideration, and we direct the z axis along the external magnetic field. We denote by $\mathbf{R}_A$ $(R_A, \theta_A, \varphi_A)$ the radius vector of the charge e_A. In spherical polar coordinates, the components of the tensor $(\nabla \mathbf{E})^{ik}$ can be written in the form

$$(\nabla \mathbf{E})^0 = 3\sqrt{\frac{16\pi}{5}} \sum e_A R_A^{-3} Y_2^0(\varphi_A,\ \theta_A),$$

$$(\nabla \mathbf{E})^{\pm 1} = \sqrt{\frac{24\pi}{5}} \sum e_A R_A^{-3} Y_2^{\pm 1}(\theta_A, \varphi_A),$$

$$(\nabla \mathbf{E})^{\pm 2} = \sqrt{\frac{6\pi}{5}} \sum e_A R_A^{-3} Y_2^{\pm 2}(\theta_A, \varphi_A). \tag{14}$$

We can easily evaluate the non-zero matrix elements of the operator for the quadrupole energy of the nucleus (12)

$$H'_{mm} = \sqrt{\frac{\pi}{5}} C (1 + \gamma)(3m^2 - I(I+1)) \sum e_A R_A^{-3} Y_2^0$$

$$= A_{mm} \sum_A e_A R_A^{-3} Y_2^0, \tag{15}$$

$$H'_{m,\,m\pm 1} = \sqrt{\frac{\pi}{10}} C (1 + \gamma) \{I_z I_\mp\}_m^{m\pm 1} \sum e_A R_A^{-3} Y_2^{\pm 1}$$

$$= A_{m,\,m\pm 1} \sum e_A R_A^{-3} Y_2^{\pm 1}, \tag{16}$$

$$H'_{m,\,m\pm 2} = \sqrt{\frac{\pi}{10}} C (1 + \gamma) (I_\pm^2)_m^{m\pm 2} \sum e_A R_A^{--3} Y_2^{\pm 2}$$

$$= A_{m,\,m\pm 2} \sum e_A R_A^{-3} Y_2^{\pm 2}. \tag{17}$$

The factors $1 + \gamma$ have been introduced into (15) and (16) to take into account the effect called antishielding, which consists of an enhancement of the fields produced at the nucleus by charges external to the ion containing the given nucleus as a result of the deformation of the electron shells of the ion. The numerical values of $|\gamma|$ have been calculated theoretically for most ions having a nuclear quadrupole moment.[10]

4. THE CORRELATION FUNCTION

We now evaluate the correlation function for the matrix elements (15) — (17). The coordinate part of the matrix elements (15) — (17) coincides with the coordinate part of the matrix elements of the energy operator for spin-spin interaction. The correlation function for the latter defined by (5) and (9) has been evaluated by Skrotskiĭ and Kokin.[7] They obtained the following result:

$$g_{mm'}(p) = g(p) = \frac{6}{\pi}\int_0^\infty e^{-px^2}\left(\frac{\sin x}{x} - \cos x\right)^2 x^{-2}dx, \tag{18}$$

where $p = \tau/\tau_c$, $\tau_c = 2a^2/D$; however, they did not carry out the further evaluation of the integral.

The integral (18) can be evaluated by differentiating it with respect to the parameter p:

$$g'_p(p) = -\frac{6}{\pi}\int_0^\infty e^{-px^2}\left(\frac{\sin x}{x} - \cos x\right)^2 dx. \tag{19}$$

The resulting integral can be easily evaluated by means of breaking it up into parts:

$$g'_p(p) = -\frac{3}{\sqrt{\pi}}\left[p^{1/2}(e^{-1/p} - 1) + \frac{1}{2}p^{-1/2}(e^{-1/p} + 1)\right]. \tag{20}$$

The correlation function (18) can now be rewritten

$$g(p) = -\frac{3}{2\sqrt{\pi}}\int_0^p [2p^{1/2}(e^{-1/p} - 1) + p^{-1/2}(e^{-1/p} + 1)]\,dp + \text{const}, \tag{21}$$

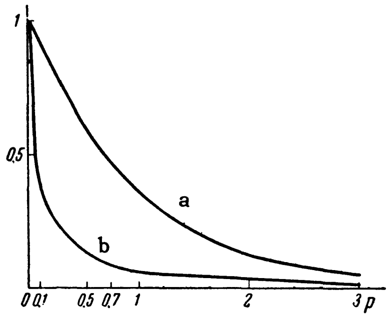
the integration constant is determined from the condition $g(\infty) = 0$.

On carrying out the integration required in (21) we obtain the final form of the correlation function for the matrix elements (15) — (17):

$$g(p) = \frac{3}{\sqrt{\pi}}\left[\frac{\sqrt{\pi}}{3}\Phi(p^{-1/2}) + \frac{1}{3}p^{1/2}e^{-1/p} - p^{1/2} + \frac{2}{3}p^{3/2}(1 - e^{-1/p})\right]; \tag{22}$$

it is normalized to the values $g(0) = 1$ and $g(\infty) = 0$; $\Phi(x)$ is the error function.

It is appropriate to make a few remarks on the form of the function g(p). As can be seen from (22) and from the figure, the function g(p) differs appreciably from exp(−p). Yet the exponential function is often chosen for the correlation function for quite different random processes perturbed by different motions. Such a choice is dictated both by a desire for simplicity of calculation, and also apparently by the widespread opinion that the exponential form of the correlation function necessarily follows from the Markov character of the process. We see that although the diffusion process is a Markov process, the correlation function obtained by us does not have an exponential form. There is no doubt that the simplification of the correlation function to exponential form introduces a definite error into the results as has been specifically established, in particular, by Skrotskiĭ and Kokin.[7]



a – graph of the function exp(−p), b – graph of the function (22).

5. THE RELAXATION TIMES T_2 AND T_1

We evaluate the normalized spectral densities of the matrix elements in accordance with (2), (10), and (22). The correlation function can now be conveniently written in the form

$$g(p) = \frac{3}{2\sqrt{\pi}}\int_p^\infty [2x^{1/2}(1 - e^{-1/x}) - x^{-1/2}(1 + e^{-1/x})]\,dx; \tag{23}$$

and with this definition the constant of integration will be equal to zero. We denote the normalized spectral density by

$$j(\omega) = \int_{-\infty}^{+\infty} e^{-i\omega\tau}g(\tau)\,d\tau = \frac{3\tau_c}{\pi^{1/2}}\int_0^\infty \cos\alpha p\,dp\int_p^\infty [2x^{1/2}(1 - e^{-1/x}) - x^{-1/2}(1 + e^{-1/x})]\,dx, \tag{24}$$

where

$$\alpha = \omega\tau_c, \qquad \omega = \lambda\omega_0, \qquad \lambda = |m - m'|,$$

ω_0 is the nuclear spin precession frequency. The integral (24) can be evaluated by changing the order of integration:

$$j(\omega) = \frac{3\tau_c}{\pi^{1/2}}\int_0^\infty [2x^{1/2}(1 - e^{-1/x}) - x^{-1/2}(1 + e^{-1/x})]\,dx\int_0^x \cos\alpha p\,dp$$
$$= 3\tau_c\,[(z^{-3} - 2z^{-5}) + e^{-z}\cos z\,(z^{-3} + 4z^{-4} + 2z^{-5}) + e^{-z}\sin z\,(z^{-3} - 2z^{-5})], \tag{25}$$

where

$$z = (2\alpha)^{1/2} = (2\lambda\omega_0\tau_c)^{1/2}.$$

Expansions of the function (25) in the limiting cases $z \ll 1$ (rapid motion) and $z \gg 1$ (slow motion) are given in reference 7.

$$j(\lambda\omega_0) = \frac{2\tau_c}{5}\left(1 - 5\sqrt{2\lambda\omega_0\tau_c}\,/\,12\right) \qquad \text{for } z \ll 1,$$

$$j(\lambda\omega_0) = \frac{2\tau_c}{5}\left[\delta_{\lambda 0} + \frac{15}{2}(1-\delta_{\lambda 0})(2\lambda\omega_0\tau_c)^{-3/2}\right] \qquad \text{for } z \gg 1. \tag{26}$$

We can easily obtain the averaged squares of the matrix elements

$$\Omega^2_{mm'} = \langle |H'_{mm'}(0)|^2\rangle = |A_{mm'}|^2 (N/V)(e_A^2/24a^3), \tag{27}$$

since

$$\sum_A \langle R_A^{-6} |Y_2^\lambda|^2\rangle = N/(24a^3V).$$

In a liquid the condition $z \ll 1$ is practically always fulfilled. In this case we obtain for the relaxation time T_2

$$T_2^{-1} = \frac{2\pi}{75\hbar^2}[ee_AQ(1+\gamma)]^2\left[\frac{3m^2 - I(I+1)}{I(2I-1)}\right]^2 \frac{N}{V}\frac{\tau_c}{(2a)^3}. \tag{28}$$

The factor contining the spins is equal to 1 and 0.56 for spins $^3/_2$ and $^5/_2$ respectively.

Under the condition $z \ll 1$ the probabilities of relaxation transitions are equal to:

$$I = {}^3/_2 \qquad w(^3/_2, {}^1/_2) = w(-{}^1/_2, -{}^3/_2) = 12U,$$

$$w(^3/_2, -{}^1/_2) = w(^1/_2, -{}^3/_2) = 12U, \tag{29}$$

$$I = {}^5/_2 \qquad w(^5/_2, {}^3/_2) = w(-{}^3/_2, -{}^5/_2) = 80U,$$

$$w(^3/_2, {}^1/_2) = w(-{}^1/_2, -{}^3/_2) = 32U,$$

$$w(^5/_2, {}^1/_2) = w(-{}^1/_2, -{}^5/_2) = 40U,$$

$$w(^3/_2, -{}^1/_2) = w(^1/_2, -{}^3/_2) = 72U, \tag{30}$$

$$U = 2\pi(1/150\hbar^2)(ee_AQ(1+\gamma)/I(2I-1))^2 N\tau_c/V(2a)^3. \tag{31}$$

By utilizing formula (11) and the probabilities (29) and (30), we find that the relaxation time T_1 for spins $^3/_2$ and $^5/_2$ is, respectively,

$$T_1^{-1} = \frac{8\pi}{225}\hbar^{-2}(ee_AQ(1+\gamma))^2(N/V)\tau_c/8a^3,$$

$$T_1^{-1} = \frac{16\pi}{1875}\hbar^{-2}(ee_AQ(1+\gamma))^2(N/V)\tau_c/8a^3. \tag{32}$$

6. AQUEOUS SOLUTIONS OF ELECTROLYTES

We have investigated the quadrupole relaxation of nuclear spins in diamagnetic solutions of electrolytes in reference 4, where we used as our basis the assumption that around ions in solution stable hydrated (solvated) complexes are formed consisting of molecules of the solvent, or of molecules of the solvent together with ions of the electrolyte dissociated in the solution. For aqueous complexes of Al^{3+} and Ga^{3+} ions, which form stable hydrated complexes in solution, we obtain good agreement between the calculated and the measured values of the width of resonance lines. For I^-, Br^-, Na^+ ions the measured line widths do not agree with those calculated on the assumption of the existence of a stable complex. This is apparently associated with the fact that the lifetimes of the hydrated complexes of the I^-, Br^-, Na^+ ions are shorter than the relaxation times T_1 (or T_2) calculated by us for these ions, while the complexes of the Al^{3+} and Ga^{3+} ions live longer than the lattice relaxation times of their nuclear spins (10^{-4} sec). It is natural to assume that the I^-, Br^-, Na^+ ions do not form stable complexes at all in aqueous solution (this also follows from investigations in physical chemistry), and that the relative motion of the molecules of the solvent and of the ions of the dissociated electrolyte represents free translational diffusion. Then in order to determine the line widths and the spin-lattice relaxation times for the I^-, Br^-, Na^+ ions (and for other non-solvated ions) we can utilize formulas (28) and (32).

Let us calculate T_2^{-1} for I^- ions in aqueous solution. The antishielding coefficient $1+\gamma$ for the I^- ion is equal to[10] 179.85, the nuclear constants for the I^{127} isotope are: spin equal to $^5/_2$, and quadrupole moment $Q = 0.7$ b. Instead of 2a one should now naturally take the sum of the radii of the I^- ion and of the water molecule $2a = r_{I^-} + r_{H_2O} = 2.16 + 1.45 = 3.61$ A. Moreover, the diffusion coefficient for water at 23° C is equal to[11] 2×10^{-5}, so that $\tau_c = 2a^2/D = 3 \times 10^{-11}$ sec. The number of particles per unit volume is equal to $N/V = 3 \times 10^{22}$. We shall determine the effective charge of the water molecules later by means of comparison with experiment. On substituting the above values of the constants into (28) we obtain

$$T_2^{-1} = 6.9 \cdot 10^5 (e_A/e)^2. \tag{33}$$

Itoh and Yamagata[12] have investigated the variation of T_2^{-1} for the nuclear spins of the I^- ions in aqueous solution. They found that the dependence of T_2^{-1} on the temperature has a close resemblance to the temperature dependence of the ratio η/T for any given solution. Formula (28) predicts just such a dependence

$$\tau_c = (12a^3\pi/k)\eta/T, \qquad T_2^{-1} \sim \tau_c \sim \eta/T. \tag{34}$$

Further, the isothermals of the quantity T_2^{-1} must be proportional to the viscosity of the solution:

$$T_2^{-1} \sim \eta. \tag{35}$$

Itoh and Yamagata[12] have studied the dependence of T_2^{-1} on the concentration of the solution, and this dependence has turned out to be considerable in a solution of NaI and not very great in solutions of

KI. At first glance formula (28) does not show any dependence on the concentration of the solution. However, the viscosity of the liquid depends on the concentration of the solution: the experimentally observed dependence of T_2^{-1} on the concentration agrees closely with the dependence of the viscosity on the concentration in accordance with (35).

We now turn to formula (33) and determine the effective charge of the water molecule. On substituting the value of $T_2^{-1} = 7 \times 10^3 \text{ sec}^{-1}$ obtained[12] for 23° C and extrapolated to infinite dilution we get

$$e_A = 0{,}1\, e. \qquad (36)$$

As may be seen, the effective charge of the water molecule obtained from the study of quadrupole relaxation in non-associated solutions is even somewhat smaller than the usually adopted values $\sim 0.5\,e$.

An exact calculation of T_2^{-1} taking into account the dipole nature of the water molecules and their rotational motion will be given by us elsewhere.

In concluding this section we note the following. In the presence of a stable solvated (hydrated) ionic shell the relaxation of nuclear spin proceeds by means of the interaction of the quadrupole moment of the nucleus with the normal vibrations of the complex; in this case the temperature dependence of the width of the resonance line is determined by the equation[3,4]

$$T_2^{-1} \sim T^{-1/2} \coth\,(\hbar\omega_0 / 2kT), \qquad (37)$$

where ω_0 is the frequency of the characteristic vibrations of the complex which amounts to $(4 \text{ to } 16) \times 10^{13} \text{ sec}^{-1}$. Relation (37) was verified by the study of the widths of electron resonance lines for a whole series of paramagnetic ions which form stable complexes in solution;[3] so far there have been no experiments on the study of the temperature dependence of the widths of nuclear magnetic resonance lines of diamagnetic ions solvated in solution. On the other hand, if an ion does not form a stable solvated complex, and the motion of the neighboring particles consists of free diffusion, then relation (34) must be satisfied. A comparison of (34) and (37) shows that a study of the temperature dependence of T_2^{-1} can yield a completely unambiguous determination of the occurrence of complex formation in solution.

7. MELTS OF METALS

In metallic crystals having a cubic structure the energy of the nuclear quadrupole moment is equal to zero, and the principal role in the spin relaxation of the nuclei is played by their interaction with the conduction electrons and among themselves: the spin-lattice relaxation (the relaxation time T_1) is determined by the interaction with the conduction electrons, while the line width (the relaxation time T_2) is determined by the magnetic interaction of the nuclei among themselves.[13,14] A result of this is the inequality $T_1 \neq T_2$. As a crystal is heated various lattice defects are produced: the cubic structure of the lattice is destroyed, and this results in the appearance of quadrupole broadening of magnetic resonance lines which has been experimentally established for Al^{27} nuclei in metallic aluminum.[14] If the structure of the crystal has symmetry lower than cubic (for example, in gallium), then quadrupole effects occur even in a perfect lattice without any defects.[15]

Thus, from experiments on magnetic resonance in metals it follows that the quadrupole energy of nuclei is due primarily to the electric fields produced by ionic cores in the metal lattice; the electric fields at the nuclei due to the conduction electrons have symmetry close to spherical, which is characteristic of S-state electrons, and as a result of their high symmetry cannot produce quadrupole splitting of the nuclear spin energy levels. Apparently, basically the same situation also exists in a metallic melt. But since in a melt the instantaneous configurations of the ion positions which vary with time do not have any symmetry, the fields produced at the nuclei are, generally speaking, different from zero, and give rise to relaxation effects, whose magnitude may be computed from formulas (28) and (32).

A calculation which we have made for Li and Na yielded values of T_1 and T_2 greater than the experimentally observed ones.[13] The Li^6, Li^7, and Na^{23} nuclei have small quadrupole moments and, therefore, the quadrupole effects are small. Al^{27} has a somewhat larger quadrupole moment. The relaxation time calculated with the aid of (28) is $T_2(Al^{27}) = 3 \times 10^{-2}$ sec, which also exceeds the experimentally found value[14] $T_2 = T_1 = 2.1 \times 10^{-3}$ sec by a factor of ~ 15. (For the evaluation of $T_2(Al^{27})$ the following values of the constants were adopted: $e_A = e$, i.e., it was assumed that the Al ions in the melt are singly charged; the metallic radius of the Al atom $a = 1.4$ A, $I = 5/2$, $Q = 0.156$ b, $N/V = 10^{23}$, $D = 2 \times 10^{-5}$ and $\tau_c = 2a^2/D = 10^{-11}$ sec, $1 + \gamma = 3.59$. The value of $1 + \gamma$ which we have utilized was calculated[10] for the Al^{3+} ion: for a singly charged ion the value of $1 + \gamma$ will probably be greater, since the antishielding effect is associated with the deformability of the electron shell of the atom.)

Our results show that in lithium, sodium, and aluminum melts the quadrupole relaxation of nuclear spins plays a subordinate role; other mechanisms predominate. However, in an aluminum melt, so far as we can judge from our calculations, the rate of quadrupole relaxation of nuclei differs from the rate of relaxation due to the dominant mechanism by a factor of ~ 10. We can expect that in the case of metals having a quadrupole moment of ~ 1 b, quadrupole relaxation will give a contribution comparable to the contribution of the mechanisms predominant in Li, Na, Al, and will possibly become dominant. It should be noted that the antishielding effects, on which the rate of quadrupole relaxation depends in a large measure, are quite insignificant for the Li^+, Na^+, and Al^+ ions. For ions which are isoelectronic with the inert gases the antishielding coefficient $|\gamma|$ increases as the number of the electrons in the ion increases: for the series of ions Na^+, K^+, Rb^+, Cs^+ the values of γ are equal to 4.53, 12.84, 49.3, and 110 respectively.[10] This shows that quadrupole effects will be large for heavy atoms. For example, metallic indium is convenient for carrying out experiments: it has a relatively low melting point and a large quadrupole moment (for the isotope In^{115} $I = 9/2$ and $Q = 1.16$ b). We can assume that the antishielding effects will also be large for the In ion; according to Rhoderick's estimates[16] made on the basis of an experiment in a mixed single crystal of InSb, $\gamma(\mathrm{In}) \approx 1000$.

8. MELTS OF IONIC SALTS

Formulas (28) and (32) which we have obtained may be found applicable to interpreting widths of resonance lines and the spin-lattice relaxation time of nuclear spins in melts of salts, for example, of the NaCl type. The new feature which has to be taken into account in discussing melts of salts as compared to melts of metals and solutions of electrolytes consists of the difference in the sign of the charges of the ions composing the melt. This means that ions of different sign can appear near the ion under consideration as a result of the process of diffusion; this circumstance will in some way affect the relaxation times T_1 and T_2, and this, generally speaking, can be taken into account by introducing a certain factor into the right hand side of (28) and (32). The functional dependence of T_1 and T_2 on the temperature and on the viscosity expressed by (34) and (35) will remain valid.

We now estimate the order of magnitude of the factors in (28) and (32). X-ray investigations show the existence in liquids of a sharply pronounced short-range order with atomic configurations corresponding to close packing.[17] On the basis of this we can assume that atoms which are the nearest neighbors of the ion under consideration have a configuration corresponding to one of the close packed configurations, for example, octahedral. If we assume that all the atoms of this octahedron have charges of the same magnitude and of the same sign, then the field gradient ∇E at the center of the octahedron will be due only to the displacements of the atoms from their equilibrium positions in the octahedron, the magnitude of the components will be given by $\nabla E \sim e_A a^{-4} Q_i$, where a is the equilibrium distance between the atoms, Q_i are linear combinations of the displacements of the atoms from their equilibrium positions in the octahedron, $a \approx 3$ A; the magnitude of Q_i can be estimated[17] from the width of the first maximum of the radial distribution function of the particles in the liquid: $Q_i \approx 0.5$ A.

On the other hand, let us assume that in the process of diffusion either ions with charges of different sign or vacancies have appeared in the neighborhood of the ion under consideration. Then, as a simple calculation shows, the components of the tensor ∇E differ from zero even in the case of the correct atomic configuration; the magnitude of the components is given by $\nabla E \sim e_A a^{-3}$. It is clear that the ratio of the gradients in the second and in the first case is equal to $a/Q_i \sim 6$, while the ratio of the magnitudes of T_2^{-1} amounts to ~ 36. Consequently, in a salt melt, if we admit the possibility of formation of coordination spheres for the ions consisting of particles of charges of different sign, the magnitude of T_2^{-1} increases by a factor of 10 to 100 and attains a value of ~ 10^5 $\sec^{-1}$ (~ 100 oe). Such an estimate of the width agrees with the result of Flynk and Seymour:[18] in a melt of bismuth iodide these authors were unable to observe the nuclear resonance of Bi^{209} ($I = 9/2$, $Q = 0.4$ b), even though their spectroscope permitted them to observe lines of width up to 40 oe.

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