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POLARIZATION OF NUCLEAR MOMENTS AND NUCLEAR-RESONANCE LINE WIDTHS IN CRYSTALS OF CU^{++} ION SALTS

Sh. Sh. BASHKIROV and K. A. VALIEV

Kazan' State Pedagogical Institute

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The probabilities of nuclear relaxation transitions in Cu^{++} ion salts are computed. The magnitude of nuclear polarization appearing on saturation of electron and nuclear resonance transitions is calculated. The effect of electron and nuclear relaxation on the broadening of nuclear resonance lines in paramagnetic atoms is considered.

1. INTRODUCTION

It has been shown by many investigators[1,2] that by saturating the electron magnetic resonance it is possible to obtain polarization of nuclear magnetic moments amounting to several percent at comparatively high temperatures of 1 to 4°K. Later experiments were carried out on the polarization of nuclei by means of saturating "forbidden" electronic transitions, which arise in the second approximation if the constant and the variable magnetic fields are parallel to each other.[3] Feher[4] obtained polarized nuclei by exciting magnetic dipole transitions between energy sublevels of electronic and nuclear spins of paramagnetic atoms.

The success of the above experiments on nuclear polarization depends largely on spin-lattice relaxation processes. Such processes are characterized by the probabilities of electronic transitions $A_{M,M-1}$ (M is the magnetic quantum number of the electron spin of the atom), which occur without a change in the quantum number of nuclear spin, and by the probabilities $a_{m,m-1}$ of nuclear-relaxation transitions. The latter transitions may be accompanied by a change in the orientation of electronic spin from M to M+1. Calculations of nuclear polarization, taking into account both electronic and nuclear relaxation transitions, have been carried out by Abragam[2] for the case of a simple atom with $S = \frac{1}{2}$, $I = \frac{1}{2}$ in liquid solutions.

In this paper we calculate the transition probabilities $A_{M,M-1}$ and $a_{m,m-1}$ for doubly-charged copper ions in hydrated crystals. The relations obtained for the probabilities are then used to calculate the polarization of nuclei of Cu^{64} [$I = 1$, $|\mu| = 0.40\,\mu_N$ (reference 5)]. It should be noted that the calculations of $a_{m,m-1}$ carried out by the authors[6,7] for a number of rare earth ions and for ions of the iron group can be used to calculate nuclear polarization in salts of these ions.

2. PROBABILITIES OF NUCLEAR RELAXATION TRANSITIONS

Relaxation transitions between hyperfine energy sublevels of the ion are due to the modulation of the hyperfine splittings of the ion by thermal vibrations of the lattice. The lattice vibrations affect directly only the orbital splittings of the ion, but through spin-orbit interactions of the form $\lambda \mathbf{L}\cdot\mathbf{S}$ this leads to a modulation of the intervals between the levels of the electron spin. Changes in the spacing between energy levels of nuclear spin arise, in turn, through the hyperfine magnetic interaction of the ion of the form $AJ_zS_z + B(I_xS_x + I_yS_y)$. Thus, the perturbation that gives rise to relaxation transitions between the hyperfine sublevels of the ion has the form:

$$\mathscr{H} = \mathscr{H}_{OL} + \lambda(\mathbf{L}\cdot\mathbf{S}) + AI_zS_z + B(I_xS_x + I_yS_y) \quad (1)$$

For the operator $\mathscr{H}_{OL}$, which connects the normal coordinates of the lattice oscillators q with the orbital angular momentum (electron coordinates) of the magnetic ion, we use Kronig's expression[8]

$$\begin{gathered}\mathscr{H}_{OL} = 8e\mu a^{-5}q\varphi\,[(3z^2 - r^2)f_1 + 2(x^2 - y^2)f_2 \\ - 2xyf_{xy} - 2xzf_{xz} - 2yzf_{yz}], \\ f_1 = (u_z\lambda_z - {}^2/_3\,\lambda_x u_x - {}^2/_3\,u_y\lambda_y), \\ f_2 = (u_x\lambda_x - u_y\lambda_y), \quad f_{ij} = (u_i\lambda_j + u_j\lambda_i).\end{gathered} \quad (2)$$

Here λ, u are unit vectors in the direction of polarization and the direction of propagation of the Debye waves, r (x, y, z) is the distance between the nucleus and the magnetic electron, e is the electronic charge, μ is the effective electric dipole moment of the neutral molecule closest to the

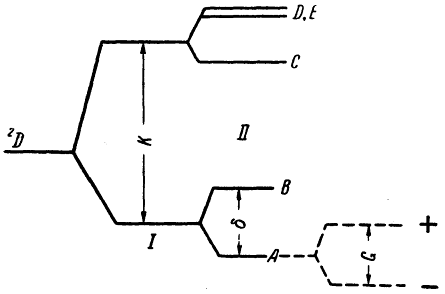

FIG. 1. Diagram of the successive splitting of the ground level of the Cu^{++} ion in an electric field of cubic (I) and tetragonal (II) symmetry. Dotted lines show the splitting of the lower Kramers doublet in an external magnetic field.

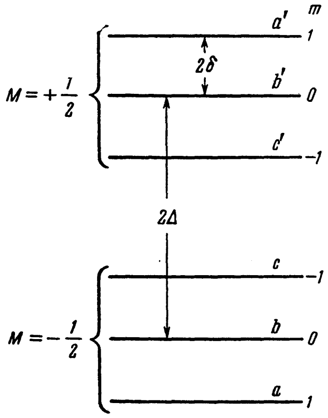

FIG. 2. Diagram of hyperfine splitting of the lower Kramers doublet of the Cu^{++} ion (isotope 64 with spin I = 1).

ion, $\varphi = 2\pi a\nu/c$, c and ν are the velocity and the frequency of the Debye wave, and a is the lattice constant.

In hydrated salts the system of orbital levels of the Cu^{++} ion (^{2}D ground state) can be characterized by the following wave functions[9] (Fig. 1):

$$\Phi_A = (\psi_2 + \psi_{-2})/\sqrt{2}, \quad \Phi_B = \psi_0, \quad \Phi_C = i(\psi_2 - \psi_{-2})/\sqrt{2},$$
$$\Phi_D = i(\psi_1 + \psi_{-1})/\sqrt{2}, \quad \Phi_E = (\psi_1 - \psi_{-1})/\sqrt{2}. \tag{3}$$

The splittings K and δ due to the cubic and tetragonal components of the crystalline field are equal respectively[10] to 12,300 and 1,400 cm^{-1}. Figure 2 shows the hyperfine splittings of the lower Kramers doublet of the ion in a strong magnetic field directed along the axis of symmetry of the crystalline field (G ≫ A, B). The wave functions of these levels have the form

$$\Psi_{M,m} = \varphi_{M,m} + \frac{B}{G} f_{M,m}\varphi_{M-1,m+1} - \frac{B}{G} f_{M+1,m-1}\varphi_{M+1,m-1}, \tag{4}$$
$$f_{M,m} = {}^1\!/_2\,[(S+M)(S-M+1)(I+m+1)(I-m)]^{1/2},$$
$$G = g\,\beta H_0.$$

The matrix elements of the perturbation (1) may be easily calculated using the functions (3) and (4). The matrix elements of (2) calculated by the method of equivalent operators are given by Bashkirov.[11]

The perturbation (1) can cause relaxation transitions in which one or two (or more) lattice phonons can take part. At temperatures down to ~ 1°K the probability of single-phonon processes will be small compared to the probabilities of two-phonon processes. The latter can be calculated by means of the following formula:[12]

$$a_{m,m-1} = 4\pi^2 h^{-2} \times \int_0^{k\Theta/h} H(\pm {}^1\!/_2, m, n, n'; \pm {}^1\!/_2, m-1, n-1, n'+1)|^2_{\text{av}}\,\rho_\nu \rho_{\nu'}\,d\nu, \tag{5}$$

where n and n′ are quantum numbers of the oscillators q and q′, ρ_ν is the density of lattice oscillators of frequency ν, and Θ is the Debye temperature. The matrix element appearing in (5) differs from zero in the fourth order and is equal to:

$$\mathscr{H}(\pm {}^1\!/_2, m; \pm {}^1\!/_2, m-1) = p f_{{}^1\!/_2, m-1}\mathscr{H}'(+{}^1\!/_2, n, n'; -{}^1\!/_2, n-1, n'+1) \tag{6}$$

$$\mathscr{H}' = \frac{3\cdot 32^2\lambda h\nu}{\delta^2 K}\left(\frac{e\mu\varphi\overline{r^2}}{a^5}\right)(f_2' f_{xz} + i f_2' f_{yz} - f_2 f_{xz}' - i f_2 f_{yz}')\, q(n, n-1)\, q'(n', n'+1). \tag{6a}$$

The quantity f′ refers to oscillator q′; p = B/G.

It is important to note that the matrix element of the transition between nuclear sublevels is proportional to the matrix element of the transition between electronic sublevels which occurs without a change in the quantum number m. The averaging of (6a) in accordance with formula (5) gives the electronic transition probability A $(\frac{1}{2}, -\frac{1}{2})$. This allows us to express the probabilities of nuclear relaxation transitions in terms of the probabilities of the electronic transitions:

$$a(\pm {}^1\!/_2, m; \pm {}^1\!/_2, m-1) = p^2 f^2_{{}^1\!/_2, m-1} A({}^1\!/_2, -{}^1\!/_2) = \lambda_1 A. \tag{7}$$

In addition to the relaxation transitions considered above, there are other possible nuclear-relaxation transitions, which involve the simultaneous reorientation of the electronic and nuclear spins. Calculations yield the following relation for the probabilities of such transitions:

$$a({}^1\!/_2, m; -{}^1\!/_2, m+1) = 2p^2 f^2_{{}^1\!/_2, m} A = 2\lambda_1 A. \tag{8}$$

The above results can also be presented in the following form (I = 1):

Transition	$\pm {}^1\!/_2\, m; \mp {}^1\!/_2\, m$	$M, 1; M, 0$	$M, 0; M, -1$	${}^1\!/_2, 0; -{}^1\!/_2, 1$	${}^1\!/_2, -1; -{}^1\!/_2, 0$
a_{ij}/A	1	λ_1	λ_1	$2\lambda_1$	$2\lambda_1$

3. POLARIZATION OF Cu^{64} NUCLEI IN PARAMAGNETIC SALTS

We have calculated the polarization of Cu^{64} nuclei in the cases listed above. This is the first time that polarization is calculated by the method of saturating electronic transitions that are forbidden in the first approximation. According to Jeffries,[3] allowance for nuclear-relaxation transitions can decrease the polarization obtained from simple considerations (without detailed account of nuclear transitions) by a factor of ~ 2. According to our calculations, a noticeable decrease in the polarization due to nuclear transitions is possible only at low intensities of the external field ($G \sim A, B$). The method of nuclear polarization by means of simultaneous saturation of electronic and nuclear resonance discussed below (in subsection B) is of some interest. Feher[4] excited these transitions not simultaneously, but one after the other. This makes possible nuclear polarization only in crystals with a very long electron relaxation time, when the nonequilibrium populations of levels that result from excitation of the (electronic) resonance can be preserved until the instant of excitation of the other (nuclear) resonance. In salts of paramagnetic ions of the iron group, the electronic relaxation times are of the order of $\sim 10^{-3}$ sec at $T = 4°K$ and the method described by Feher[4] cannot be used. The electronic and the nuclear resonances must therefore be excited simultaneously. The results of the calculations are discussed below.

(A) We first consider the case when two electronic resonance transitions are saturated by a radio frequency field: $a \rightarrow a'$, $b \rightarrow b'$. We denote by $a, b \ldots c'$ the relative level populations and set up the system of equations for the populations in the nonequilibrium state which has been established:[13]

$$\frac{dx_i}{dt} = {\sum_j}' (x_j W_{ji} - x_i W_{ij}) = 0, \quad x_i = a, b, \ldots, c',$$
$$W_{aa'} = a_{aa'} + V_{aa'}, \quad W_{bb'} = a_{bb'} + V_{bb'}, \quad W_{ij} = a_{ij}. \tag{9}$$

Here $V_{aa'}$ and $V_{bb'}$ are the probabilities of magnetic dipole transitions produced by the variable external field.* The probabilities of the direct and the inverse transitions are connected by the following relations:[13]

$$a_{ij} \exp(-\varepsilon_i / kT) = a_{ji} \exp(-\varepsilon_j / kT), \quad V_{aa'} = V_{a'a}. \tag{10}$$

The nonzero probabilities a_{ij} have been calculated earlier. The system (9) must be solved subject to the conditions of saturation and normalization: $a = a'$; $b = b'$; $a + b + \ldots + c' = 1$.

The constants in Eq. (9) are of the following order of magnitude: $\Delta = 0.1$, $\delta = 10^{-3}$, and $\lambda_1 = 10^{-4}$ at $T = 4°K$ and $H_0 = 3{,}000$ Oe; $\Delta = 0.4$ and $\delta = 2 \times 10^{-3}$ at $T = 1°K$. It is seen that at these temperatures we can expand the exponentials and retain only one term of the expansion. The resultant solution of (9) is of the form:

$$a = a' = b(1 + \Delta), \quad c = b(1 + \Delta/2),$$
$$c' = b(1 - 3\Delta/2), \quad b = b'. \tag{11}$$

In expressions (11) we have omitted terms proportional to λ_1, δ, and their products. For the field intensity used in the experiments ($\sim 10^{-4}$ Oe), the contribution of these terms to the polarization will be small.*

We have also considered the case of saturation of a single electronic transition: $a \rightarrow a'$. The solution which we have obtained is of the form:

$$a = a' = b(1 - \Delta/2), \quad b' = b(1 - 2\Delta),$$
$$c' = b(1 - 2\Delta), \quad c = b. \tag{12}$$

(B) We give the solution of equations (9) for the case of simultaneous saturation of electronic and nuclear transitions, $a \rightarrow a'$; $b' \rightarrow a'$:

$$a = a' = b' = b(1 - 2\Delta),$$
$$c' = b(1 - 2\Delta), \quad c = b. \tag{13}$$

We now compare the results given by (11) to (13). It is convenient to describe the resultant polarization by the ratio $(a + a')/(b + b')$. This ratio is given in the three cases by $1 + \Delta$, $1 + \Delta/2$, $1 - \Delta$ respectively. Polarization due to saturating two electronic transitions or to simultaneous saturation of electronic and nuclear transitions is twice the polarization due to saturating a single electronic transition. It is evident that it is difficult to realize simultaneous saturation of two electronic transitions. It is easier to realize saturation of a nuclear and an electronic transition, and this would give rise to the same degree of nuclear polarization.

(C) We now give the calculated polarization of Cu^{64} nuclei by saturation of "forbidden" transitions. From the form of the wave functions given

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*It is assumed that equilibrium in the spin system is established through the interaction of the spins with the lattice; this is the case in magnetically-diluted crystals.

*It is worth noting that the probabilities of nuclear transitions characterize the duration of the transition processes from the time of switching on the rf resonance field until the time that a stationary population of levels becomes established.

by (4) it follows that the transitions will be $a \rightarrow b'$ and $b \rightarrow c'$. We consider the case when the transition $a \rightarrow b'$ is saturated. The level populations and the polarization which are established in this case are given by:

$$b' = c' = a, \ a' = a(1 - 2\Delta),$$
$$c = a(1 + 2\Delta), \ b = a(1 + 2\Delta). \qquad (14)$$

This corresponds to the appearance of nuclear polarization along directions of nuclear spin with projections $m = 0, -1$.

(D) We now discuss briefly the question of the saturation of nuclear resonance transitions. Let us ascertain which relaxation transitions, nuclear or electronic, determine whether a splitting of nuclear resonance is possible. To do this we must find the population of levels in the presence of the resonance field and we must determine the saturation parameter:[13]

$$S(\mathcal{H}_1) = (a - b)/(a_0 - b_0) = (1 + V/W)^{-1}, \qquad (15)$$

where a, b are the populations of the levels between which resonance takes place (the subscript zero refers to the population of the level in the absence of the resonance field $\mathcal{H}_1$): V is the probability of resonance transitions to which the field $\mathcal{H}_1$ gives rise; W is the probability of all the relaxation transitions $b \rightarrow a$. In addition to the direct relaxation transition $b \rightarrow a$ with the probability $a(0; 1)$, two other transitions via intermediate levels are possible: $b \rightarrow b' \rightarrow a$ and $b \rightarrow b' \rightarrow a' \rightarrow a$. The efficiency of these latter processes is evidently determined by the least probable of the transitions involved, i.e., by the probabilities of nuclear transitions $b' \rightarrow a$ and $b' \rightarrow a'$. It follows from this that $W \approx a_{ba} + a_{b'a} + a_{b'a'}$. Our exact calculation of W leads to the same result.

Thus, saturation of nuclear resonance in the case of paramagnetic atoms depends only on the probabilities of nuclear relaxation transitions. We also note that the degree of saturation of nuclear resonance depends strongly on the intensity of the constant field due to the quadratic decrease of the probabilities W as the field decreases.

4. WIDTH OF MAGNETIC RESONANCE LINES OF NUCLEI OF PARAMAGNETIC ATOMS

Valiev[6,7] and Bashkirov[7] have studied theoretically the possibility of experimental investigation of paramagnetic crystals by means of observing magnetic resonance of nuclei of paramagnetic atoms. It was found that the energy absorbed in nuclear resonance in the case of paramagnetic atoms is considerably larger than the energy absorbed by the resonance of nuclei of diamagnetic atoms. The possibility of directly observing the effect depends, in addition to the amount of energy absorbed, also to a large extent on the line width. Valiev[6] has given an approximate estimate of the width of the lines in question by means of the relation: $\Delta\nu_{m-1,m} = 1/a_{m,m-1}$ where $a_{m,m-1}$ is the probability of a relaxation transition between the hyperfine sublevels of the ion. However, this relation will be valid only at very low temperatures. Let us consider the example of the Cu^{++} ion.

The width of the resonance line arising as a result of transitions between a certain pair of hyperfine sublevels, for example a and b, is equal to the sum of the widths of these sublevels: $\Delta\nu_{a,b} = \gamma_a + \gamma_b$. The level width, in turn, is equal to the sum of the probabilities of all the relaxation transitions originating from that level; in our case $\gamma_a = A_{aa'} + a_{ab} + a_{ab'}$; $\gamma_b = A_{bb'} + a_{ba} + a_{bc} + a_{bc'}$. As we have shown above the ratio a_{ij}/A is of the order 10^{-4} for an external field intensity ~ 5,000 Oe and at relatively high temperatures. From this it follows that the line width of nuclear resonance is mainly determined by the probabilities of electronic relaxation transitions. Nuclear relaxation transitions will determine line widths only at very low temperatures, as can be seen from the following. Electronic transitions originating in the level $M = -\frac{1}{2}$ are accompanied by absorption of energy of lattice vibrations; therefore at low temperatures (when single-phonon processes predominate) the probability $A(-\frac{1}{2}, \frac{1}{2})$ is proportional to the average number of phonons of the lattice oscillator with the electronic resonance frequency $\nu_e : A \sim \bar{n}_{\nu_e} = [\exp(h\nu_e/kT) - 1]^{-1}$. On the other hand, the probabilities a_{ij} are proportional to $\bar{n}_{\nu_N} + 1$ or $\bar{n}_{\nu_N}$ (depending on whether the lattice phonon is absorbed or emitted in the transition $i \rightarrow j$; ν_N is the frequency of nuclear resonance). It can be easily seen that in the temperature region $h\nu_N/k \ll T \ll h\nu_e/k$, $\bar{n}_{\nu_e} \ll 1$ and the number of electronic transitions is sharply decreased, while $\bar{n}_{\nu_N} \gg 1$ and the number of nuclear transitions is still relatively large. Under these conditions the ratio a_{ij}/A may be greater than unity. Nevertheless, right down to temperatures ~ 1°K, the main contribution to the line width of nuclear resonance is made by electronic transitions.

At liquid-helium temperatures the probabilities $A \sim 10^3 \text{ sec}^{-1}$ for most paramagnetic ions of the iron group, which corresponds to a line width of $\sim 10^3$ cps. Such lines may be observed by quadrupole-resonance techniques or by modulating the constant magnetic field. Spectroscopes employing field modulation are capable of detecting nuclear resonance lines 10 Oe wide.[14] To observe nuclear resonance in the case of magnetic atoms, the probabilities of electronic relaxation transitions of these atoms, expressed in oersteds (by means of the relation $hA = \gamma\beta_N\Delta H$), must therefore be of the order of 10 Oe. This is the case when $A \sim 10^4\ \text{sec}^{-1}$. The probabilities A in the case of salts of ions which are in the S state (Mn^{++}, Gd^{+++}) turn out to be of the order of $10^4\ \text{sec}^{-1}$ already at liquid hydrogen temperatures.[15] Under these conditions it is possible to observe the effect directly.

It should be noted that an important condition for observing this effect is the proper choice of resonance frequency, since it is practically impossible to attain resonance by varying the magnetic field, owing to the weak dependence of the resonance frequency on the field (it is determined by the constants A, B of the magnetic coupling between the electronic and the nuclear spins of the ion).

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