ly sealed at 10^{-6} Torr. The material was then melted by resistance heating of the tantalum. The final sample was coarsely grained polycrystalline material with some single-crystal pieces as large as 0.1 cm^3. Resistivity measurements have been performed by Andres and Bucher (unpublished) on samples obtained from this batch and also on samples supplied by Vogt. They find that TmSb exhibits metallic behavior with a resistance ratio of about 18 and a residual resistivity of 1.4 $\mu\Omega$ cm at 1 °K.

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[20] Only the second- and third-nearest neighbors are of any quantitative importance at all. They may be easily included in Eq. (2) by changing Z(Sb) to

$$Z(\mathrm{Sb}) \rightarrow Z(\mathrm{Sb}) - [(2\sqrt{2}-1)/32]Z(\mathrm{Pr}) \text{ for } A_4\,\langle r^4\rangle,$$

$$Z(\mathrm{Sb}) \rightarrow Z(\mathrm{Sb}) - [(13\sqrt{2}-1)/128]Z(\mathrm{Pr}) \text{ for } A_6\,\langle r^6\rangle.$$

Since $Z(\mathrm{Pr}) \simeq -Z(\mathrm{Sb})$ this means that in the absence of shielding the second- and third-nearest neighbors increase the point-charge estimate of $A_4\,\langle r^4\rangle$ by ~5.7% and $A_6\,\langle r^6\rangle$ by ~14%.

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PHYSICAL REVIEW B VOLUME 4, NUMBER 3 1 AUGUST 1971

Nuclear Relaxation via a Two-Phonon Process in a Paramagnetic System*

B. Gregory and G. Seidel
Department of Physics, Brown University, Providence, Rhode Island 02912

(Received 5 March 1971)

The magnetic relaxation of the Co^{59} nucleus within the Co^{2+} ion in paramagnetic $Co(NH_4)_2(SO_4)_2 \cdot 6H_2O$ has been studied experimentally under the condition of nearly complete electron-spin alignment achieved at low temperatures (1 °K) and high magnetic fields (60 kG). An exponential variation of the nuclear relaxation time with temperature is found and ascribed to a two-phonon (Orbach) relaxation process operating through the intermediary of the upper levels of the electron-spin Kramers doublet. Calculations, in the spin-Hamiltonian framework, of the dependence of the relaxation time upon both temperature and magnetic field are presented which show this model to be in good agreement with experimental results. The relaxation time is of the form $T_1^{-1} = AH^7 e^{-g\mu_B H/kT}$. A theoretical relationship between the Orbach NMR relaxation time and the direct process ESR relaxation time is derived and compared with the available data.

I. INTRODUCTION

The nuclear magnetic resonance of Co^{59} in cobalt ammonium sulfate, $Co(NH_4)_2(SO_4)_2 \cdot 6H_2O$, has been discussed in some detail by Choh and Seidel.[1] They showed that it is possible to observe the NMR of the Co^{59} nucleus within the magnetic Co^{2+} ion by performing the resonance measurements at low temperatures and high magnetic fields such that the electronic moments are almost completely aligned by the Zeeman interaction with the external field. The purpose of that study was primarily to investigate the magnetic interaction between the nuclear moment and the electronic orbital moment induced by the external field.

In the course of pursuing the earlier measurements it was noted that the saturation characteristics of the NMR absorption lines were extremely sensitive to temperature. It is the purpose of this paper to describe the experimental results of a study of the relaxation behavior of the Co^{59} nucleus within the Co^{2+} ion and to present a theoretical explanation for the observed behavior.

II. SPIN HAMILTONIAN

The magnetic properties of the Co^{2+} ion in cobalt ammonium sulfate have been extensively studied by electron-spin resonance[2] as well as by NMR. The electronic ground-state Kramers doublet including interaction with the Co^{59} nucleus ($I = \frac{7}{2}$) can be described by the spin Hamiltonian as

$$\mathcal{H} = \mu_B \vec{\mathrm{H}} \cdot \overleftrightarrow{\mathrm{g}} \cdot \vec{\mathrm{S}} + \vec{\mathrm{I}} \cdot \overleftrightarrow{\mathrm{A}} \cdot \vec{\mathrm{S}} - \gamma \mu_N \vec{\mathrm{H}} \cdot (\overleftrightarrow{\mathrm{T}} + \overleftrightarrow{\sigma}) \cdot \vec{\mathrm{I}} + \mathcal{H}_Q , \tag{1}$$

where the terms, written in order of descending magnitude, are the electronic Zeeman, hyperfine, nuclear Zeeman, induced-moment-nuclear, and quadrupole interactions. For tetragonal symmetry with the magnetic field at an angle θ with respect to the tetragonal axis, the Hamiltonian becomes

$$\mathcal{H} = g\mu_B H S_z + K I_z S_z + \left[\left(\frac{AB}{K}\right) I_x S_x + B I_y S_y\right] + \frac{B^2 - A^2}{K} \frac{g_\parallel g_\perp}{g^2} \sin\theta \cos\theta\, I_z S_x$$
$$- [A g_\parallel (1 + \sigma_\parallel) \cos^2\theta + B g_\perp (1 + \sigma_\perp) \sin^2\theta\,] (\gamma \mu_B / Kg) H I_z$$
$$- [A g_\parallel (1 + \sigma_\perp) - B g_\perp (1 + \sigma_\parallel)] (\gamma \mu_N / Kg) \sin\theta \cos\theta\, H I_x + \mathcal{H}_{Q'} \,, \qquad (2)$$

where

$$\mathcal{H}_{Q'} = Q' \left[\left(\frac{A g_\parallel \cos\theta}{Kg}\right)^2 I_z^2 - 2\, \frac{AB g_\parallel g_\perp \cos\theta \sin\theta}{K^2 g^2} I_x I_z + \left(\frac{B g_\perp \sin\theta}{Kg}\right)^2 I_x^2 \right] . \qquad (3)$$

The z axis is taken parallel to the applied field, while the x axis is perpendicular to the z axis in the plane formed by the tetragonal axis and the direction of the field. The quantities g and K have the usual definitions

$$g^2 = g_\parallel^2 \cos^2\theta + g_\perp^2 \sin^2\theta \,,$$
$$K^2 g^2 = A^2 g_\parallel^2 \cos^2\theta + B^2 g_\perp^2 \sin^2\theta \,. \qquad (4)$$

Keeping only terms in I_z^2 in $\mathcal{H}_{Q'}$, the eigenstates of the Hamiltonian, derived using perturbation theory, are

$$E(M, m) = M g \mu_B H + m(MK - GH) + \frac{m(FH)^2}{2(MK - GH)} - \frac{m B^2}{4 g \mu_B H} \frac{A}{K} + \frac{M}{4 g \mu_B H} \times \left(2m^2 J^2 + \frac{B^2(A^2 + K^2)}{K^2} [I(I+1) - m^2]\right) + m^2 Q' \left(\frac{A g_\parallel \cos\theta}{Kg}\right)^2 , \qquad (5)$$

where

$$F = [A g_\parallel (1 + \sigma_\perp) - B g_\perp (1 + \sigma_\parallel)] (\gamma \mu_N / Kg) \sin\theta \cos\theta \,,$$
$$G = [A g_\parallel (1 + \sigma_\parallel) \cos^2\theta + B g_\perp (1 + \sigma_\perp) \sin^2\theta\,] (\gamma \mu_N / Kg) , \qquad (6)$$
$$J = [(B^2 - A^2)/K\,] (g_\parallel g_\perp / g^2) \sin\theta \cos\theta \,.$$

The experimentally determined values, of the various parameters are

$g_\parallel = 6.48 \pm 0.5$, $g_\perp = 3.12 \pm 0.08$,

$A = (2.52 \pm 0.02) \times 10^{-2}\ \text{cm}^{-1}$,

$B = (2.0 \pm 0.1) \times 10^{-3}\ \text{cm}^{-1}$,

$\sigma_\parallel = 0.38 \pm 0.02$, $\sigma_\perp = 0.18 \pm 0.05$,

$Q' = -(2.5 \pm 0.5) \times 10^{-5}\ \text{cm}^{-1}$.

The magnitudes of these spin-Hamiltonian parameters agree reasonably well with crystal-field calculations.

III. EXPERIMENT

The nuclear-resonance transitions, $\Delta M = 0$, $\Delta m = \pm 1$, the ion remaining in the electronic ground state $M = -\frac{1}{2}$, occur in the frequency range 100–500 MHz depending upon the magnitude and direction of the magnetic field. Magnetic fields between 40 and 80 kG were employed in this work. The nuclear absorption, in general, consists of seven well-resolved lines, the splitting arising from both the hyperfine and quadrupole interactions.

The apparatus used to perform the present NMR measurements was a standard superheterodyne reflection spectrometer previously described.[1] The spin-lattice relaxation time of the nuclear-spin system was determined by observing the recovery of the absorption following saturation. A large rf field was applied to saturate a transition between a particular pair of levels $| -\frac{1}{2}, m\rangle$ and $| -\frac{1}{2}, m+1\rangle$ ($M = -\frac{1}{2}$), and the recovery of the absorption was observed by recording the absorption signal during resaturation at successively later times. Although the signal-to-noise ratio prevented accurate determination of the recovery behavior, the results were always consistent with an exponential dependence on the time, notwithstanding the multilevel nature of the system.

Measurements were made at a fixed angle of the magnetic field with respect to the crystalline axes, specifically, $\theta = 40^\circ$. The relaxation time was then measured as a function of temperature and magnetic field (frequency). No essential difference was noted in the relaxation behavior of the several different transitions studied. The data given here are for the most intense line: the central transition $| -\frac{1}{2}, -\frac{1}{2}\rangle \leftrightarrow | -\frac{1}{2}, +\frac{1}{2}\rangle$.

The variation of the nuclear-spin-lattice relaxation time T_{1n} with both temperature and field is summarized in Fig. 1 where the quantity $H^7 T_{1n}$ is plotted against H/T. All the experimental data can be represented by the relation

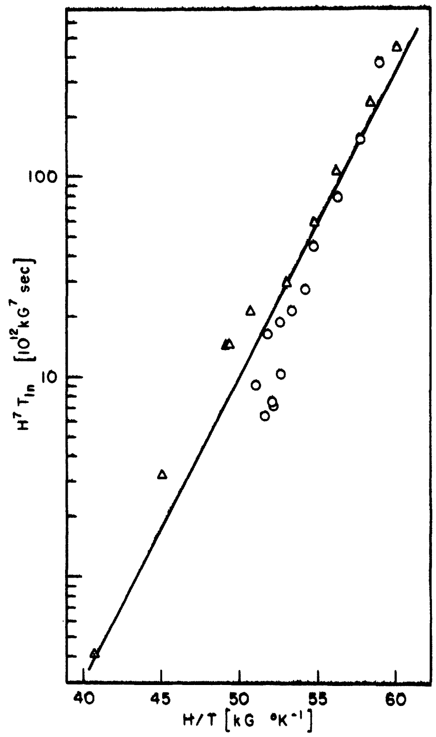

FIG. 1. Dependence of the observed nuclear spin-lattice relaxation time, T_{1n} on field and temperature, plotted so as to give a linear dependence on H/T. The points in circles were taken at a constant applied field of 58.847 kG. The points in triangles were taken at an approximately constant temperature of 1.01 °K. The solid line is a graph of $1/T_{1n}=AH^7 e^{-g\mu_B H/kT}$, where $A=5.2\times10^{-27}$ G^{-7} sec^{-1} and $g=5.31$, the value expected from the known spin-Hamiltonian parameters and sample orientation.

$$1/T_{1n}=AH^7 e^{-g\mu_B H/kT}\,, \tag{7}$$

where

$$A=5.2\times10^{-27}(\mathrm{G}^{-7}\,\mathrm{sec}^{-1})\,.$$

Note that the slope of the curve in Fig. 1 yields, to the accuracy of the measurements, the factor $g\mu_B/k$.

IV. DISCUSSION

The nucleus of the Co^{2+} ion is coupled with the lattice by a variety of mechanisms, by far the strongest of which is the combined influence of the hyperfine field and the orbit-lattice interaction yielding a nuclear-phonon coupling via the intermediary of the electronic orbitals. Various nuclear-lattice couplings, mechanisms important in other contexts, such as the quadrupole interaction with crystalline electric field gradients or the dipolar interaction with the magnetic moments on neighboring lattice sites, are many orders of magnitude too small to account for the observed relaxation time.

The electronic spin-lattice coupling can induce transitions among the nuclear states by virtue of the off-diagonal elements in the Hamiltonian [Eq. (2)]. These terms produce appreciable admixtures of the basis states in the $|M, m\rangle$ representation so that the eigenfunctions cannot be completely characterized by a choice of M and m. Consider the unperturbed state $|-\frac{1}{2}, m\rangle$. To first order in perturbation theory, this state becomes, under the influence of the off-diagonal elements,

$$|a\rangle=|-\tfrac{1}{2}, m\rangle+\alpha_+(-m)\,|+\tfrac{1}{2}, m-1\rangle+\alpha_-(m)\,|+\tfrac{1}{2}, m+1\rangle+\beta(m)\,|+\tfrac{1}{2}, m\rangle$$
$$+\gamma_+(-m)\,|-\tfrac{1}{2}, m-1\rangle-\gamma_+(m)\,|-\tfrac{1}{2}, m+1\rangle\,. \tag{8}$$

Similarly,

$$|b\rangle=|-\tfrac{1}{2}, m+1\rangle+\alpha_+(-m-1)\,|+\tfrac{1}{2}, m\rangle+\alpha_-(m+1)\,|+\tfrac{1}{2}, m+2\rangle+\beta(m+1)\,|+\tfrac{1}{2}, m+1\rangle$$
$$+\gamma_+(-m-1)\,|-\tfrac{1}{2}, m\rangle-\gamma_+(m+1)\,|-\tfrac{1}{2}, m+2\rangle\,. \tag{9}$$

Using the notation of Eq. (6), the coefficients are

$$\alpha_\pm(m)=-[(I+m+1)(I-m)]^{1/2}\tfrac{1}{4}[(AB/K)\pm B]/g\mu_B H\,,$$
$$\beta(m)=-Jm/2g\mu_B H\,, \tag{10}$$
$$\gamma_\pm(m)=[(I+m+1)(I-m)]^{1/2}\,\frac{FH}{2}\,\frac{1}{\frac{1}{2}K\pm GH}\,.$$

The effect of $\mathcal{H}_{Q'}$ has been neglected.

A. Direct Process

Because of the admixture α, due solely to the hyperfine interaction, the orbit-lattice coupling can induce transitions directly between states $|a\rangle$ and $|b\rangle$ with the emission or absorption of a single phonon. Following Orbach,[3] the direct-process relaxation time is

$$\left.\frac{1}{T_{1n}}\right|_{\mathrm{direct}}=3\left(\frac{\delta_{ab}}{\hbar}\right)^3\frac{1}{2\pi\rho v^5\hbar}$$
$$\times\coth\frac{\delta_{ab}}{2kT}\,\Big|\langle a|\sum_{n,m}V_n^m|b\rangle\Big|^2\,, \tag{11}$$

where

$$\delta_{ab} = \tfrac{1}{2}K + GH$$

is the energy separation of the levels, ρ is the density of the crystal, v the velocity of sound, and $\langle a \mid \sum_{n,m} V_n^m \mid b\rangle$ is the matrix element of the orbit-lattice interaction associated with the strain components ϵ_{nm}. (Since no further use of the structure of the orbit-lattice interaction will be made, the expansion $\sum_{n,m} V_n^m$ will be denoted below simply by V_{01}.) The matrix element is, in turn,

$$\langle a \mid V_{01} \mid b\rangle = \alpha_-(m)\langle M=+\tfrac{1}{2} \mid V_{01} \mid M=-\tfrac{1}{2}\rangle + \alpha_+(-m-1)\langle M=-\tfrac{1}{2} \mid V_{01} \mid M=+\tfrac{1}{2}\rangle, \quad (12)$$

so that the relaxation time is

$$\left.\frac{1}{T_{1n}}\right|_{\text{direct}} = 3\left(\frac{\delta_{ab}}{\hbar}\right)^3 \frac{1}{2\pi\rho v^5\hbar} \times \left[(I+m+1)(I-m)\left(\frac{AB}{2g\mu_B HK}\right)^2\right] \times |\langle M=-\tfrac{1}{2} \mid V_{01} \mid M=+\tfrac{1}{2}\rangle|^2 \coth(\delta_{ab}/2kT)\,. \quad (13)$$

The crystalline field has zero matrix elements between the pair of states of the Kramers doublet except insofar as there exists an interaction, in particular the Zeeman interaction, that lifts the time-conjugate nature of the states. If the field dependence of the matrix element is indicated explicitly, such as

$$|\langle M=-\tfrac{1}{2} \mid V_{01} \mid M=+\tfrac{1}{2}\rangle|^2 = \mathcal{G}^2 H^2\,,$$

Eq. (13) becomes

$$\left.\frac{1}{T_{1n}}\right|_{\text{direct}} = 3\left(\frac{\frac{1}{2}K+GH}{\hbar}\right)^3 \frac{1}{2\pi\rho v^5\hbar}(I+m+1)(I-m) \times \left(\frac{AB}{2g\mu_B HK}\right)^2 \mathcal{G}^2 H^2 \coth\left(\frac{\frac{1}{2}K+GH}{2kT}\right). \quad (14)$$

Thus for $\frac{1}{2}K > GH$ and $\frac{1}{2}K \gg kT$ the direct-process relaxation time is independent of H and inversely proportional to T.

Also, the nuclear relaxation time can be compared to the electronic spin-lattice relaxation time, since the latter is

$$\left.\frac{1}{T_{1n}}\right|_{\text{direct}} = 3\left(\frac{g\mu_B H}{\hbar}\right)^3 \frac{1}{2\pi\rho v^5\hbar} \coth\left(\frac{g\mu_B H}{2kT}\right) \times |\langle M=-\tfrac{1}{2} \mid V_{01} \mid M=+\tfrac{1}{2}\rangle|^2\,. \quad (15)$$

Thus

$$\left.\frac{1}{T_{1n}}\right|_{\text{direct}} = \left.\frac{1}{T_{1e}}\right|_{\text{direct}} (I+m+1)(I-m)\left(\frac{AB}{2g\mu_B HK}\right)^2 \times \left(\frac{\frac{1}{2}K+GH}{g\mu_B H}\right)^3 \frac{\coth[(\frac{1}{2}K+GH)/2kT]}{\coth(g\mu_B H/2kT)}\,. \quad (16)$$

For $\theta = 40°$, $H = 50\,\text{kG}$, $T = 1\,°\text{K}$, this results for the central transition in

$$T_{1n}|_{\text{direct}} = 0.77\times 10^{15}\, T_{1e}|_{\text{direct}}\,.$$

The direct-process nuclear spin-lattice relaxation is much longer than the electronic relaxation time for several reasons: (i) The admixture of the wave functions is small; (ii) the density of the phonon states is smaller at the nuclear-energy separation; and (iii) the matrix element of the strain operator is less for the longer-wavelength phonons. It is clear both from the magnitude and functional dependence of T_{1n} upon H and T that the direct, single-phonon process is not responsible for the observed rates.

B. Two-Phonon Processes

Two-phonon processes, in which the nucleus makes a transition from state $\mid a\rangle$ to $\mid b\rangle$ by virtue of the time-dependent perturbation acting through the intermediary of an excited state, are of primary importance because of the existence of the low-lying states $\mid +\frac{1}{2}, m\rangle$ and $\mid +\frac{1}{2}, m+1\rangle$. The structure of these states is, in the same notation as for the states $\mid a\rangle$ and $\mid b\rangle$,

$$\begin{aligned} \mid c\rangle &= \mid +\tfrac{1}{2}, m\rangle - \alpha_-(-m) \mid -\tfrac{1}{2}, m-1\rangle - \alpha_+(m) \mid -\tfrac{1}{2}, m+1\rangle \\ &\quad - \beta(m) \mid -\tfrac{1}{2}, m\rangle - \gamma_-(-m) \mid +\tfrac{1}{2}, m-1\rangle + \gamma_-(m) \mid +\tfrac{1}{2}, m+1\rangle, \\ \mid d\rangle &= \mid +\tfrac{1}{2}, m+1\rangle - \alpha_-(-m-1) \mid -\tfrac{1}{2}, m\rangle - \alpha_+(m+1) \mid -\tfrac{1}{2}, m+2\rangle \\ &\quad - \beta(m+1) \mid -\tfrac{1}{2}, m+1\rangle - \gamma_-(-m-1) \mid +\tfrac{1}{2}, m\rangle + \gamma_-(m+1) \mid +\tfrac{1}{2}, m+2\rangle. \end{aligned} \quad (17)$$

Note that the coefficients γ are two to three orders of magnitude larger than either α or β under the conditions of the experiment. The energy denominator in the γ's is approximately $\frac{1}{2}K \sim 0.01\ \text{cm}^{-1}$, whereas in α and β it is $g\mu_B H \sim 13\ \text{cm}^{-1}$. The coefficient γ is not involved in direct processes between the nuclear levels because it is associated with basis states of the same value of M as the unperturbed state, and hence does not contribute to the matrix element of the time-dependent orbit-lattice interaction which only connects states of different M. Conversely, in the two-phonon processes, admixture of states with different electronic quantum number is no longer required, since the unperturbed states between which the orbit-lattice interaction acts have different values of M. In this case, the admixtures associated with the γ's are required to make transition between levels differing in nuclear quantum number. Indeed, it is precisely these admixtures which give rise to the "forbidden" transitions observed in the ESR spectrum[2] ($\Delta M = \pm 1$, $\Delta m = \pm 1$).

Two types of two-phonon processes need to be considered: Raman processes and resonance, or Orbach, processes. Although the Raman process employs the full spectrum of phonons, its influence on the observed relaxation rate is negligible. The main contributions of the state $|\, c\rangle$ and $|\, d\rangle$ to the Raman relaxation rate cancel if the small difference in energies of the states is neglected. The matrix-element products involved in the Raman process are

$$\langle b \,|\, V_{01} \,|\, c\rangle\langle c \,|\, V_{01} \,|\, a\rangle = \{-\gamma_-(-m-1) - \gamma_+(m)\} ,$$

$$\langle b \,|\, V_{01} \,|\, d\rangle\langle d \,|\, V_{01} \,|\, a\rangle = \{\gamma_-(m) + \gamma_+(-m-1)\} . \tag{18}$$

However,

$$\gamma_{\mp}(m) = \gamma_{\mp}(-m-1) ,$$

and in the coherent summation over these products in the Raman process,

$$\langle b \,|\, V_{\text{eff}} \,|\, a\rangle \approx \sum_{t=c,d} \frac{\langle b \,|\, V_{01} \,|\, t\rangle\langle t \,|\, V_{01} \,|\, a\rangle}{g\mu_B H} = 0 .$$

Certainly higher-order terms in γ and terms including α and β will lead to Raman relaxation processes, but such mechanisms will not be considered here. The Orbach-type processes, in which the ion makes a real transition to an intermediate state $|\, c\rangle$ or $|\, d\rangle$ in going from $|\, a\rangle$ to $|\, b\rangle$, do not suffer from the cancellation and, partly for that reason, are many orders of magnitude larger.

The Orbach relaxation time is given by the expression

$$\left.\frac{1}{T_{1n}}\right|_{\text{Orbach}} = \frac{3}{2\pi\rho v^5 \hbar}\left(\frac{g\mu_B H}{\hbar}\right)^3 (e^{g\mu_B H/kT} - 1)^{-1} \times \sum_{t=c,d} \frac{|\langle b \,|\, V_{01} \,|\, t\rangle\langle t \,|\, V_{01} \,|\, a\rangle|^2}{|\langle b \,|\, V_{01} \,|\, t\rangle|^2 + |\langle t \,|\, V_{01} \,|\, a\rangle|^2} . \tag{19}$$

Under the conditions $\gamma \ll 1$ and $g\mu_B H \gg kT$ and using Eq. (18), the Orbach relaxation time becomes

$$\left.\frac{1}{T_{1n}}\right|_{\text{Orbach}} = \frac{6}{2\pi\rho v^5 \hbar}\left(\frac{g\mu_B H}{\hbar}\right)^3 e^{-g\mu_B H/kT} \times \{\gamma_-(m) + \gamma_+(-m-1)\}^2 \,|\, \langle M = +\tfrac{1}{2} \,|\, V_{01} \,|\, M = -\tfrac{1}{2}\rangle \,|^2 . \tag{20}$$

If $\frac{1}{2}K \gg GH$, then $\gamma_+(m) \cong \gamma_-(m)$. With the aid of Eqs. (10) and (14), we have

$$\left.\frac{1}{T_{1n}}\right|_{\text{Orbach}} = \frac{12(I+m)(I+m+1)}{\pi\rho v^5 \hbar}\left(\frac{g\mu_B}{\hbar}\right)^3 \left(\frac{F\mathcal{G}}{K}\right)^2 \times H^7 e^{-g\mu_B H/kT} . \tag{21}$$

This relaxation rate has precisely the dependence upon temperature and field, $H^7 e^{-g\mu_B H/kT}$, observed in the experimental results summarized by Eq. (7).

At the temperature, magnetic field, and sample orientation of the experiment, the Orbach relaxation rate strongly dominates the direct process. The matrix element of the time-dependent orbit-lattice interaction is larger by the ratio γ/α of the coefficients in the admixtures, and, since the Orbach process utilizes higher-frequency phonons, the phonon density of states and the strain associated with the phonons are higher. These effects more than compensate for the fact that, at the temperature at which these experiments were carried out, the Bose-Einstein occupation number of the high-frequency phonons ($\hbar\omega \sim g\mu_B H$) involved in the Orbach process is much lower than that of the low-frequency phonons ($\hbar\omega \sim \frac{1}{2}K + GH$) involved in the direct process. At 1 °K, 50 kG, and $\theta = 40°$, the Orbach-process relaxation time is calculated to be shorter than the direct-process relaxation time by a factor of 2.5×10^{-6}. As the temperature is lowered, the exponentially decreasing population of the higher-frequency phonons will eventually bring about the dominance of the direct process. The temperature at which the two rates are equal, under otherwise identical conditions, is $T = 0.58$ °K.

Although a first-principles calculation of the magnitude of the relaxation time T_{1n} is well beyond the scope of this paper, there is a rigorous relationship between the magnitude of the direct electronic relaxation time T_{1e} (direct), for transitions between states $|a\rangle$ or $|b\rangle$ and $|c\rangle$ or $|d\rangle$, and T_{1n} following from the model for the Orbach relaxation process.

Since the matrix elements of the orbit-lattice interaction involved in both processes are the same, the Orbach nuclear relaxation time can be expressed in terms of the direct electronic relaxation time at the same field and temperature [Eq. (15)]:

$$\frac{1}{T_{1n}}\bigg|_{\text{Orbach}} = \frac{1}{T_{1e}}\bigg|_{\text{direct}} 2(I-m)(I+m+1)\left(\frac{FH}{\frac{1}{2}K}\right)^2 \times (e^{g\mu_B H/kT}+1)^{-1} . \qquad (22)$$

The comparison between relaxation times can be made with equal rigor if the experiments are performed at different temperatures and fields, though of course the expression for the ratio is not so simple.

Experimental data for T_{1e} are not available in Co^{2+} $(\text{NH}_4)_2(\text{SO}_4)_2\cdot 6\text{H}_2\text{O}$, but data from similar systems give order-of-magnitude agreement with this result. For example, using the data from this experiment, it is expected that the ESR relaxation rate at X-band frequencies of Co^{2+} in $\text{Co}(\text{NH}_4)_2(\text{SO}_4)_2\cdot 6\text{H}_2\text{O}$ would be

$$\frac{1}{T_1}\bigg|_{\text{ESR}} = 11T \text{ sec}^{-1} .$$

The only data on electron-spin relaxation in the literature for Co^{2+} with a similar ground state appear to be those of Atsarkin *et al.*,[4] who observed that for Co^{2+} in MgWo_4 at X-band frequencies

$$\frac{1}{T_1}\bigg|_{\text{ESR}} = 220T \text{ sec}^{-1} .$$

The comparison would seem to be satisfactory in view of the large differences between the two systems.

V. CONCLUSIONS

This paper describes a mechanism whereby the time-dependent orbit-lattice interaction, in combination with the hyperfine interaction, can couple the phonon thermal reservoir to nuclear-spin excitations among the hyperfine levels of a particular paramagnetic ion: Co^{2+} in $\text{Co}(\text{NH}_4)_2(\text{SO}_4)_2\cdot 6\text{H}_2\text{O}$. While many of the features of this description apply quite generally to paramagnetic systems at low temperatures and high fields ($g\mu_B H \gg kT$), it is important to realize that the anisotropy of the g and hyperfine tensors is essential to the two-phonon mechanism discussed above. The anisotropy is reflected in the strong angular dependence of the two-phonon relaxation time. In contrast, the direct-process single-phonon relaxation, treated theoretically in Sec. IV A, does not depend on anisotropy.

The two-phonon process of nuclear relaxation described here is similar in many respects to the mechanism for proton relaxation found by Jeffries and co-workers[5] in lanthanum magnesium nitrate doped with paramagnetic impurities. In that case, the protons of the waters of hydration are weakly coupled to the paramagnetic ions via the dipolar interaction and are relaxed by electron spin flips. As in the case of $\text{Co}(\text{NH}_4)_2(\text{SO}_4)_2\cdot 6\text{H}_2\text{O}$, the relaxation rate depends exponentially on $g\mu_B H/kT$ at low temperatures.

A process somewhat analogous to the one described here is reviewed by Jaccarino[6] for the case of nuclear relaxation in antiferromagnets at temperatures such that $kT \ll E_{\text{gap}}$, where E_{gap} is the energy of the $k=0$ spin wave. In that case, processes involving two spin waves dominate the relaxation. A nuclear spin flip is accompanied by the simultaneous absorption and emission of spin waves differing in energy by the nuclear spin-flip energy. Since, at these temperatures the population of thermal spin waves in the spin-wave band decreases exponentially with temperature, the dependence of the relaxation time is dominated by the factor $e^{-E_{\text{gap}}/kT}$.

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*Work supported in part by the National Science Foundation and the Advanced Researach Projects Agency.

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