SOVIET PHYSICS JETP VOLUME 19, NUMBER 1 JULY, 1964

THE TEMPERATURE DEPENDENCE OF THE OVERHAUSER EFFECT IN DILUTE AQUEOUS MANGANESE ION SOLUTIONS IN LOW MAGNETIC FIELDS

V. E. KUL'BEDA

Submitted to JETP editor July 15, 1963

J. Exptl. Theoret. Phys. (U.S.S.R.) **46**, 106-109 (January, 1964)

The temperature dependence of the Overhauser effect in aqueous solutions of $MnCl_2$ (concentrations 0.001—0.015 M) is investigated. A temperature is found at which the contributions of the dipole-dipole and exchange interactions cancel each other and the effect disappears. The dependence of the cancellation temperature on the strength of the dc magnetic field is calculated.

THE theory of magnetic relaxation of hydrogen nuclei in aqueous solutions of the paramagnetic ion Mn^{++} that has been developed in recent years [1-4] is based on the assumption of two mechanisms for proton magnetic relaxation in these solutions: dipole-dipole and exchange interactions between the magnetic moments of the hydrogen nuclei and of the paramagnetic ions. The existence of exchange interaction in these systems was confirmed by Codrington and Bloembergen,[5] who observed a positive Overhauser effect in aqueous solutions of $MnCl_2$ in magnetic fields of 10 to 20 Oe at 25°C by saturating the transitions $\Delta F = 0$, $\Delta m_F = \pm 1$ of the paramagnetic resonance of the Mn^{++} ion. They also noted that the effect is enhanced when the temperature of the sample is raised. The results of an investigation of the dependence of the relaxation times T_1 and T_2 of the protons on temperature [2] is in good agreement with the predictions of the theory. However, the large number of phenomenological constants in the theory makes it desirable to search for new ways to measure them.

We undertook the investigation of the temperature dependence of the Overhauser effect because the observation of this effect permits a direct determination to be made of the relative contributions of both mechanisms to the relaxation of the magnetic moments of the protons and gives a new method for measuring the constants that appear in the theory of relaxation.

The Mn^{++} ion in a magnetic field has a developed structure of energy levels consisting of 36 components that are separated into six groups corresponding to different F. In weak fields, however, the Lande factor $g_F \approx 1$ for transitions of the type $\Delta F = 0$, $\Delta m_F = \pm 1$ is independent of the number F.[6] In this case the paramagnetic resonance spectrum of the ions consists of a single line, the position of which is given by the relation

$$\omega_S = g_F \beta_S H_0 = \tfrac{1}{2} \gamma_S H_0, \qquad (1)$$

where γ_S is the gyromagnetic ratio for a free electron, H_0 is the dc magnetic field. To describe the saturation of the resonance we can make use of the concept of spin temperature:

$$T_S = T\left(1 + \tfrac{1}{4}\gamma_S^2 H_{1s}^2 \tau_s^2\right), \qquad (2)$$

where T is the temperature of the sample, H_{1S} is the amplitude of the saturating high-frequency field, and τ_S is the relaxation time of the electron spins ($T_{1S} = T_{2S} = \tau_S$).

Assuming that the relaxation of the protons proceeds only as a result of their interactions with the paramagnetic ions, and using the method developed by Solomon,[7] we can obtain the following formula for the Overhauser effect in aqueous solutions of Mn^{++} in weak magnetic fields:

$$\frac{\langle I_z\rangle - I_0}{I_0} = \frac{1}{2}\left(1 - \frac{T}{T_S}\right)\left|\frac{\gamma_S}{\gamma_I}\right| \frac{\tau_e/(1+\omega_S^2\tau_e^2) - \alpha\tau_c}{\tau_e/(1+\omega_S^2\tau_e^2) + 2\alpha\tau_c}, \qquad (3)$$

where $\langle I_z \rangle$ is the dynamic polarization of the protons, I_0 is the equilibrium polarization, τ_e and τ_c the correlation times respectively for the exchange and dipole-dipole interactions, and γ_I is the gyromagnetic ratio of the protons.

The parameter α is defined as the relative intensity of the dipole-dipole and exchange interactions:

$$\alpha = \frac{1}{4}\frac{\hbar^2\gamma_S^2\gamma_I^2}{\langle r_{ij}^6\rangle\,(\hbar^{-2}\langle A_{IS}^2\rangle)}, \qquad (4)$$

where r_{ij} is the distance between the paramagnetic ion under consideration and a hydrogen nucleus; $\langle A_{IS} \rangle$ is the intensity of the exchange interaction.

To calculate the correlation time τ_e it is necessary to take into account both the lifetime τ_s of the electron spins in a given state and the lifetime τ_h of the considered hydrogen atom in the hydrated complex formed by the Mn^{++} ion. Because of the independence of both quantities we can write

$$\tau_e^{-1} = \tau_s^{-1} + \tau_h^{-1}. \qquad (5)$$

(In the derivation of Eq. (3) it was assumed that $\omega_S \tau_c \ll 1$, $\omega_I \tau_c \ll 1$, and $\omega_I \ll \omega_S$. Since $\tau_c \sim 10^{-11}$ sec these conditions are met at low intensities of the field H_0.)

The temperature dependence of the Overhauser effect is determined in principle by the temperature dependence of the correlation times entering into Eq. (3)[2-4,8]:

$$\tau_c = \tau_{c0} \exp (V_c/RT), \qquad (6)$$

$$\tau_h = \tau_{h0} \exp (V_h/RT), \quad \tau_s = \tau_{s0} \exp (-V_v/RT), \qquad (7)$$

and the spin temperature T_S defined according to Eq. (2). (Here R is the Rydberg constant, and V_c, V_h, and V_v are the energies of activation of the corresponding processes.)

As can be seen from Eq. (3), it is possible for a temperature to exist at which the contributions of the dipole-dipole and exchange interactions counteract each other and the Overhauser effect disappears. We have observed this phenomenon experimentally.

For recording nuclear resonance we constructed a radiospectrometer working on the principle of the measurement of the Q of a passive circuit. The block diagram of this apparatus is shown in Fig. 1. The coil of the short-wave circuit was wound directly on the glass ampoule containing the sample and placed coaxially within the coil of the nuclear circuit. The short-wave transmitter delivered about 75 W at 108 Mc.

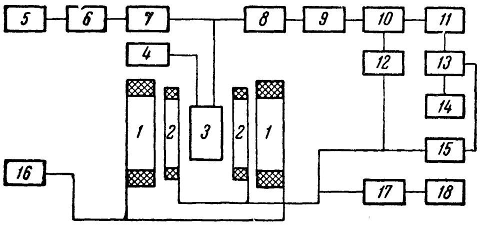

FIG. 1. Block diagram of the measuring apparatus: 1—Helmholtz coil for producing the dc magnetic field, 2—Helmholtz coil for the modulation field, 3—Overhauser effect transducer, 4—short-wave transmitter, 5—high-frequency generator at 250–350 kcs, 6—attenuator, 7,8—LC blocking filters, tuned to the transmitter frequency, 9—high-frequency amplifier, 10—low-frequency detector and amplifier, 11—selective 78 cps amplifier, 12—oscillograph, 13—lock-in amplifier, 14—EPP-09 recorder, 15—78 cps reference generator, 16—power supply for coil 1, 17—buffering filter, 18—sawtooth generator.

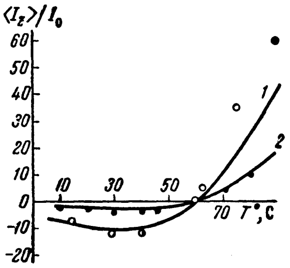

FIG. 2. Dependence of the polarization of protons on temperature in an Overhauser effect in an aqueous solution of $MnCl_2$. Concentration 0.005 M, H_0 = 73 Oe, ν_s = 108 Mc, ν_1 = 310 kc. Solid curves constructed from Eq. (3) for V_h = 8.4 kcal/mole, V_c = 5.5 kcal/mole, V_v = 2.5 kcal/mole, $\tau_c (300° K) = 3 \times 10^{-11}$ sec, $\tau_{h0} \doteq 2.2 \times 10^{-14}$ sec.[2-4,8] Curve 1—H_{1s} = 8 Oe; 2—H_{1s} = 4 Oe.

The samples were aqueous solutions of $MnCl_2$ with concentrations of 0.001 to 0.015 M. The experiments were carried out in fields of 60 to 80 Oe, in which $\omega_S \tau_e \sim 1$, and in the temperature region 8—90°C. Air cooling was used to retard the heating of the sample by the high short-wave power. A natural scanning of the heating process was thus obtained while the NMR signals were recorded on the recorder 14 and the magnetic field H_0 was linearly scanned periodically by means of the sawtooth generator 18.

The results of the measurements show (Fig. 2) that the dipole-dipole relaxation mechanism for the protons predominates up to about 60°C in a dc field of about 70 Oe, this is shown by the negative dynamic polarization of the protons upon saturation of the electron paramagnetic resonance. Above 60°C, the exchange interaction mechanism becomes predominant, and the dynamic polarization is positive. As calculations show, the increase in the relative contribution of the exchange interaction to the proton relaxation is mainly a result of the decrease in the lifetime τ_h of the

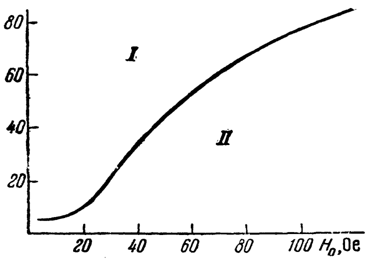

FIG. 3. Dependence of the compensation temperature on the dc magnetic field for a concentration of 0.005 M. I—region of positive polarization, II—region of negative polarization.

hydrogen atoms in the hydrated complex of the ion as the temperature is increased. The temperature at which the sign of the polarization reverses is 60 ± 3°C in a field of 70 Oe and does not depend, within the limits of experimental error, on the concentration of the solution when this is varied from 0.001 to 0.015 M. The parameter α calculated for a concentration of 0.005 M equals approximately 48.

Figure 3 shows the theoretical dependence of the temperature T_0, at which the sign of the polarization changes, on the dc magnetic field for a concentration of 0.005 M, as calculated from Eq. (3).

In conclusion the author would like to thank S. M. Rubinskiĭ and M. P. Zel'dovich for helpful advice and discussions of the results.

---

[1] N. Bloembergen, J. Chem. Phys. **27**, 572 (1957).

[2] Bernheim, Brown, Gutowsky, and Woessner, J. Chem. Phys. **30**, 950 (1959).

[3] A. A. Kokin, JETP **36**, 508 (1959), Soviet Phys. JETP **9**, 353 (1959).

[4] N. Bloembergen and L. O. Morgan, J. Chem. Phys. **34**, 842 (1961).

[5] R. S. Codrington and N. Bloembergen, J. Chem. Phys. **29**, 600 (1958).

[6] B. M. Kozyrev, Izv. AN SSSR, ser. fiz. **16**, 533 (1952).

[7] I. Solomon, Phys. Rev. **99**, 559 (1955).

[8] A. W. Nolle and L. O. Morgan, J. Chem. Phys. **36**, 378 (1962).

Translated by L. M. Matarrese
14