

# Temperature dependence of the NMR shift and line width in Van Vleck paramagnets

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The temperature dependences of the NMR shift and line width for thulium ethylsulphate in an external magnetic field parallel to a crystal axis are studied theoretically and experimentally. The model of random variation of the resonance frequency as a result of relaxation transitions between three electronic states may be applied to this system. The theory is in good agreement with experiment in the limit of small correlation times  $\tau$ . At low temperatures (corresponding to those used in the experiments) the probability per unit time for transitions from excited electronic states to the ground state plays the part of  $\tau^{-1}$ . The smallness of the correlation time justifies a phenomenological approach in which the resonance-frequency shift is proportional to the static paramagnetic susceptibility of the crystal.

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## INTRODUCTION

The magnetic resonance of the nuclei of paramagnetic ions having a singlet electronic ground state occupies an intermediate position as regards resonance frequencies, widths, and intensities of the absorption lines, between the usual NMR and EPR effects.<sup>1</sup> The unfilled electron shell of the ion is strongly polarized by an applied magnetic field because of the presence of close-lying excited states. A "hyperfine" magnetic field proportional to the external field arises at the nucleus and shifts the resonance toward the higher frequencies. The NMR shift is described by a symmetric second-rank tensor  $\alpha_{ij}$ , whose principal axes coincide with those of the electric field in the crystal and whose eigenvalues, in crystals that do not have cubic symmetry, may differ by factors of tens or hundreds. At low temperatures, when only the (singlet) ground state of the paramagnetic ion is populated, the components of this tensor are constant and their magnitudes are determined only by the mixing of the wave functions of the  $4f$  electrons in the applied magnetic field. As the temperature rises, the electron shell of the ion spends more and more of its time in excited states; then the nucleus briefly feels the action of other hyperfine fields produced by the thermally excited electrons, and in place of a single nuclear-spin precession frequency there appears a spectrum of them. The NMR signal from the paramagnetic ions must obviously be considerably different under these conditions. This type of temperature dependence of the NMR signal was first observed by Jones,<sup>2</sup> who investigated intermetallic compounds of praseodymium and thulium. This effect was later detected in dielectric compounds of thulium,<sup>3,4</sup> praseodymium,<sup>5</sup> and holmium.<sup>6</sup> A common approach, based on intuitive considerations, to the interpretation of the temperature dependence of the NMR shift was used in all these papers: the shift of the resonance was assumed to be proportional to the static paramagnetic susceptibility of the crystal, i.e., the time average of the hyperfine magnetic field at the nucleus was replaced by the statistical average. This simple approach, which implies rapid relaxation transitions between the energy levels of the paramagnetic ion, yields

good results in a number of cases, but it obviously needs a more rigorous foundation. In this paper we present an experimental and theoretical study of the temperature dependences of the NMR line shift and width in a system having three electronic energy levels and set more accurate limits to the applicability of the simple assumption that the NMR line shift is proportional to the electron paramagnetic susceptibility.

## THEORY

Our analyses of the NMR line shape is based on the assumption of random variation of the resonance frequency. In this model the line shape is given by the formula<sup>7</sup>

$$I(\omega) = \text{Re}(W \cdot A^{-1} \cdot 1), \quad (1)$$

in which  $W = (W_1, W_2, \dots)$  is a row vector whose  $m$ -th component  $W_m$  is the probability that the system has the frequency  $\omega_m$ ,  $1$  is a column vector whose components are all unity, and the matrix  $A^{-1}$  is the inverse of the matrix

$$A_{mn} = i(\omega_m - \omega) \delta_{mn} + \pi_{mn},$$

where  $\pi_{mn}$  is the probability per unit time that the system will undergo a transition from the state with frequency  $\omega_m$  to the state with frequency  $\omega_n$ , and  $-\pi_{nn} \equiv \tau_n^{-1}$  is the probability for a transition from the  $n$ -th state. The transition probabilities must satisfy the conditions

$$\sum_n \pi_{mn} = 0, \quad W_m \pi_{mn} = W_n \pi_{nm}. \quad (2)$$

In our problem the quantities  $W_m$  are the Boltzmann factors for the corresponding electronic states; if we assign the subscript 1 to the singlet ground state we have  $W_1 \gg W_2, W_3, \dots$  at the low temperatures of interest to us. If there are only two electronic states, the correlation time<sup>8</sup> is given by

$$\tau_c = (\pi_{12} + \pi_{21})^{-1}, \quad (3)$$

i.e., it is determined by the highest transition rate, and the function (1) assumes the comparatively simple form

$$I(\omega) = \frac{W_1 W_2 (\omega_2 - \omega_1)^2 (\pi_{11} + \pi_{22})}{(\omega_1 - \omega)^2 (\omega_2 - \omega)^2 + [\pi_{11} (\omega_2 - \omega) + \pi_{22} (\omega_1 - \omega)]^2}. \quad (4)$$

It is not difficult to show that when  $W_1 \gg W_2$ , the function (4) always has its maximum close to the point  $\omega = \omega_1$ , regardless of the relation between the quantities  $\Delta\omega_2 = \omega_2 - \omega_1$  and  $\tau_c^{-1}$ . Actually, the denominator in (4) can be written in the form

$$(\omega_1 - \omega)^4 + 2\Delta\omega_2 (\omega_1 - \omega)^2 + (\Delta\omega_2^2 + \tau_c^{-2}) [(\omega_1 - \omega + \Omega)^2 + \Gamma^2], \quad (5)$$

where

$$\Omega = \frac{\Delta\omega_2 \pi_{11} (\pi_{11} + \pi_{22})}{\Delta\omega_2^2 + (\pi_{11} + \pi_{22})^2}, \quad \Gamma = \frac{|\pi_{11}| \Delta\omega_2^2}{\Delta\omega_2^2 + (\pi_{11} + \pi_{22})^2}. \quad (6)$$

In the vicinity of the fundamental frequency, i.e., when  $|\omega_1 - \omega| \leq \Gamma + |\Omega|$ , the ratio of the first two terms in (5) to the last one does not exceed

$$[(\Gamma + |\Omega|)^4 + 2\Delta\omega_2 (\Gamma + |\Omega|)^2 + (\Delta\omega_2^2 + \tau_c^{-2})]^{-1} \Gamma^{-2} \tau_c^2.$$

On substituting the values of  $\Gamma$  and  $\Omega$  from (6) into this expression and taking account of the relation  $\pi_{11}/\pi_{22} = W_2/W_1$ , which follows from (2), we find that the above expression is equal to

$$\left(\frac{W_2}{W_1}\right)^2 \frac{(1 + \Delta\omega_2 \tau_c)^4}{(1 + \Delta\omega_2^2 \tau_c^2)^3} + \frac{2W_2 (1 + \Delta\omega_2 \tau_c)^3}{W_1 (1 + \Delta\omega_2^2 \tau_c^2)^2} \quad (7)$$

which is much smaller than unity for any values of  $\Delta\omega_2 \tau_c$ . On neglecting the first two terms in (5) we obtain the following Lorentz function for the line shape:

$$I(\omega) \approx \frac{W_1 W_2 \Delta\omega_2^2 \tau_c}{1 + \Delta\omega_2^2 \tau_c^2} \frac{1}{(\omega_1 - \omega + \Omega)^2 + \Gamma^2}. \quad (8)$$

We note that the shift  $\Omega$  of the resonance frequency turns out to be proportional to the line width  $\Gamma$ :

$$\Omega = \Gamma / \Delta\omega_2 \tau_c. \quad (9)$$

In the case of three electronic energy levels we can also obtain a simple expression like (8) if we assume that the probabilities for transitions between excited states are low, i.e., that

$$\pi_{23}, \pi_{32} \approx 0, \quad (10)$$

so that

$$-\pi_{22} = \pi_{21}, \quad -\pi_{33} = \pi_{31}. \quad (11)$$

Again using estimates analogous to (7), we obtain an expression for the line shape,

$$I(\omega) \approx W_1 \Gamma / [(\omega_1 - \omega + \Omega)^2 + \Gamma^2], \quad (12)$$

in which

$$\Omega = \frac{\pi_{12} \pi_{21} \Delta\omega_2}{\Delta\omega_2^2 + \pi_{21}^2} + \frac{\pi_{13} \pi_{31} \Delta\omega_3}{\Delta\omega_3^2 + \pi_{31}^2}, \quad (13)$$

$$\Gamma = \frac{\pi_{12} \Delta\omega_2^2}{\Delta\omega_2^2 + \pi_{21}^2} + \frac{\pi_{13} \Delta\omega_3^2}{\Delta\omega_3^2 + \pi_{31}^2}, \quad \Delta\omega_2 = \omega_2 - \omega_1, \quad \Delta\omega_3 = \omega_3 - \omega_1.$$

Within the limitations of the approximations employed, expression (12) agrees precisely with (8), while the shift and width (13) of the resonance line are natural generalizations of (6). On comparing (6) and (13), it becomes clear what the formulas for  $\Omega$  and  $\Gamma$  for a multilevel system would look like.

Returning to the problem of the temperature dependence of the NMR frequency, we note that a simple proportionality between the line shift  $\Omega$  and the paramagnetic susceptibility follows from (13) provided the con-

dition

$$\pi_{m1} \gg |\Delta\omega_m| \quad (14)$$

holds and the electronic energy levels are well enough resolved (their separations should be greater than their hyperfine splittings and widths). Actually, under these conditions it follows from (13) and (2) that

$$\omega_{\text{res}} = \omega_1 + \Delta\omega_2 \frac{\pi_{12}}{\pi_{21}} + \Delta\omega_3 \frac{\pi_{13}}{\pi_{31}} \approx W_1 \omega_1 + W_2 \omega_2 + W_3 \omega_3, \quad (15)$$

i.e., the resonance frequency is the weighted sum of the resonance frequencies of all the electronic states, the weights being the Boltzmann factors for the corresponding states. Condition (14) evidently requires comparatively high transition rates only for transitions from excited electronic levels.

## EXPERIMENTAL RESULTS AND DISCUSSION

As an example, let us consider the temperature dependence of the NMR shift and line width for  $^{169}\text{Tm}$  in the thulium ethylsulphate (TmES) crystal, which is an ideal "touchstone" to test the formulas presented above. The inherent electric field in the TmES crystal has hexagonal symmetry ( $C_{3h}$ ), and the low-lying energy levels of the  $\text{Tm}^{3+}$  ion ( $4f^{12}$ ,  $^3H_6$ ) are a singlet  $|g\rangle$  and a doublet  $|d\rangle$  separated by  $\Delta = 32 \text{ cm}^{-1}$ . These three states of the  $4f$  electron shell alone determine the temperature trend of the thulium NMR frequency and line width; the remaining electron levels lie much higher ( $> 100 \text{ cm}^{-1}$ ), and their contribution to the effects under consideration may be neglected.

The splitting of the nuclear energy levels of thulium (spin  $I = 1/2$ ) in an external magnetic field is described by the axially symmetric spin Hamiltonian

$$\mathcal{H}_I = -\gamma_I \hbar (1 + \alpha_{\parallel}) H_x I_x - \gamma_I \hbar (1 + \alpha_{\perp}) (H_x I_x + H_y I_y). \quad (16)$$

Here  $\gamma_I / 2\pi = -352 \text{ Hz/Oe}$  is the gyromagnetic ratio of "free"  $^{169}\text{Tm}$  nuclei. At liquid helium temperatures the components of the paramagnetic NMR shift reach the values

$$\alpha_{\parallel}^{(0)} = 0.364(2), \quad \alpha_{\perp}^{(0)} = 73.2(3), \quad (17)$$

while the NMR line width, measured at 4 MHz as the interval between the extrema of the derivative of the absorption, amounts to 50 Oe (24 kHz) in a field  $H$  parallel to the  $c$  axis of the crystal, and to 4.8 Oe (125 kHz) in a field  $H$  perpendicular to  $c$ . The magnetic resonance of thulium nuclei in a field  $H \perp c$  can be observed at temperatures clear up to 16 °K, whereas in a field  $H \parallel c$  the NMR line broadens sharply as the specimen is heated and cannot be observed at temperatures above 7 °K.

The paramagnetic shift and width of the NMR line for the case  $H \parallel c$  are shown as functions of temperature in Figs. 1 and 2. In these experiments a cylindrical TmES specimen ~5 mm in diameter and altitude was mounted with a heater in the cryostat vacuum chamber containing  $^4\text{He}$  and the temperature was measured with a calibrated carbon thermistor fastened to the specimen with cement and vacuum grease. The most important experimental results were as follows: 1) the NMR line

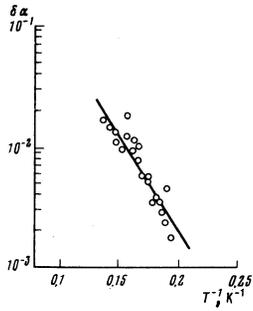


FIG. 1. The component  $\alpha_{\parallel}$  of the paramagnetic NMR shift of  $^{169}\text{Tm}$  in TmES vs the reciprocal temperature.

shift increased sharply with rising temperature:

$$\delta\alpha_{\parallel} = (100/T) \exp(-\Delta/kT) \quad (18)$$

( $\Delta$  is the energy of the excited doublet  $|d\rangle$ ); and 2) the increment of the line width also exhibited an exponential temperature dependence:

$$\delta\nu_{\parallel} (\text{Hz}) = 1.3 \cdot 10^6 \exp(-\Delta/kT). \quad (19)$$

The electronic-nuclear energy-level scheme is shown in Fig. 3; the symbols  $d$  and  $d' = \Theta d$  denote the states of the electronic doublet ( $\Theta$  is the time reversal operator), and the indices  $\pm$  correspond to the nuclear states. Substituting the relaxation-transition probabilities

$$\pi_{d\pm} \approx \pi_{d'\pm} = \tau^{-1}, \quad \pi_{gd\pm} = \tau^{-1} e^{-\Delta/kT}, \quad \pi_{gd\pm} = \tau^{-1} e^{-(\Delta+\delta)/kT}, \quad (20)$$

into formula (13) and assuming that  $\delta \ll kT \ll \Delta$ , we find

$$\Omega = \frac{\Delta\omega}{1+\Delta\omega^2\tau^2} \frac{\delta}{kT} e^{-\Delta/kT}, \quad (21)$$

and

$$\Gamma = \frac{2\Delta\omega^2\tau}{1+\Delta\omega^2\tau^2} e^{-\Delta/kT}. \quad (22)$$

In the case of fast relaxation when

$$\tau\Delta\omega \ll 1 \quad (23)$$

formula (21) also gives a temperature shift

$$\delta\alpha_{\parallel} = \frac{\Omega}{\gamma_I H} = \frac{2A_J g_J \mu_B |\langle d|J_z|d\rangle|^2}{\gamma_I H} \frac{1}{kT} e^{-\Delta/kT}, \quad (24)$$

that is proportional to the increment of the ionic paramagnetic susceptibility

$$\delta\chi_{\parallel} = 2g_J^2 \mu_B^2 |\langle d|J_z|d\rangle|^2 \frac{1}{kT} e^{-\Delta/kT}. \quad (25)$$

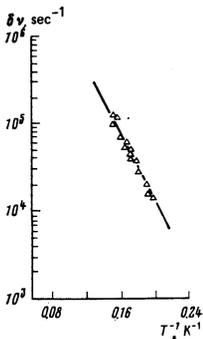


FIG. 2. The increment  $\delta\nu_{\parallel}$  of the NMR line width of  $^{169}\text{Tm}$  in TmES vs the reciprocal temperature.

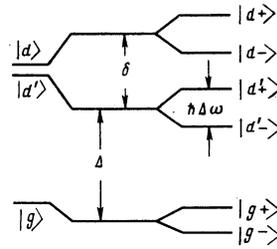


FIG. 3. Low-lying electronic-nuclear energy levels of the  $^{169}\text{Tm}^{3+}$  ion in a magnetic field parallel to the  $c$  axis of the crystal;  $\delta = 2g_J \mu_B H |\langle d|J_z|d\rangle|$  is the Zeeman splitting of the electronic doublet, and  $\hbar\Delta\omega = A_J |\langle d|J_z|d\rangle|$  is the hyperfine structure ( $\Delta\omega = \Delta\omega_d = -\Delta\omega_d$ ).

On substituting the numerical values  $g_J = 1.1638$  of the Landé factor<sup>9</sup> and  $A_J/h = -393.5$  MHz for the hyperfine interaction constant<sup>10</sup> for the free ion and expressing the matrix element  $|\langle d|J_z|d\rangle| = g_J/2g_J$  in terms of the known value<sup>11</sup>  $g_{\parallel} = 1.14$  in the LaES: Tm<sup>3+</sup> crystal, we obtain the increment of the shift:

$$\delta\alpha_{\parallel} = (42/T) e^{-\Delta/kT}. \quad (26)$$

That the calculated value (26) is close to the experimental value (18) shows that the condition for fast relaxation is satisfied in this case.

The experimentally measured increment of the line width (for a Lorentz line shape) is connected with Eq. (22) by the simple relation  $\delta\nu \cdot \pi\sqrt{3} = \Gamma$ , from which it follows at once that

$$\delta\nu_{\parallel} = \frac{4}{\sqrt{3}} \left( \frac{A_J}{h} \right) |\langle d|J_z|d\rangle| e^{-\Delta/kT} \frac{\tau\Delta\omega}{1+\tau^2\Delta\omega^2}. \quad (27)$$

Equation (27) agrees with the experimental value (19) provided  $\tau\Delta\omega$  has one of the two values 0.32 and 3, of which the smaller is not inconsistent with condition (23). Thus, the results of measuring the temperature dependence of the shift and width of the NMR line in a magnetic field parallel to the  $c$  axis of the crystal makes it possible to estimate the transition probability from the excited state to the ground state in the  $4f$  electron shell of the ion:

$$\tau^{-1} \gg \Delta\omega \sim 10^6 \text{ sec}^{-1}. \quad (28)$$

This value lies within the limits  $(10^3-10^5)\Delta^3$  (the energy  $\Delta$  is in Kelvins) established in experiments on the spin-lattice relaxation of rare earth ions in magnetically dilute ionic crystals,<sup>10,12</sup> and we may therefore assume the electron-vibrational interaction to be responsible for the relaxation transitions between energy levels of the Tm<sup>3+</sup> ion. Moreover, since we are dealing with a magnetically concentrated crystal we should not overlook the magnetic dipole interaction of the Tm<sup>3+</sup> ions. This interaction (terms of the type  $J_j \cdot J_{j'}$ ) can ensure rapid transfer of electronic excitation ( $\Delta = 32 \text{ cm}^{-1}$ ) from ion to ion—a process analogous to the well-known spin diffusion. A simple estimate of the rate of such relaxation in the TmES crystal (in which the ions are  $\sim 7 \text{ \AA}$  apart) yields the value

$$\tau_{\text{dip}}^{-1} \sim \hbar^{-1} |\mathcal{H}_{\text{dip}} - \text{dip}| \sim 10^6 \text{ sec}^{-1} \quad (29)$$

which is of the same order as the value (28) found above.

One can already see from the above example what sort of difficulties will be encountered in applying the general theory of random frequency change to the NMR problem of Van Vleck paramagnets. In fact, when the ion is excited to the doublet electronic state there arise not two resonant frequencies, but four of them, and the two "extra" frequencies  $\pm \delta$  contribute, in principle, to the shift of the fundamental frequency. Transitions of the type  $|d_+\rangle - |d'_-\rangle$  are not purely nuclear transitions: they also change the electronic states. In our example  $\delta \gg \tau^{-1}$  (this corresponds precisely to good resolution of the electronic states), and the additional contribution noted above can be neglected. In a field  $H \perp c$ , however, the electronic doublet is not split, and all the frequencies that arise when the hyperfine splitting is taken into account turn out to be comparable. Actually, we encounter a situation that should be described as a change in the number of resonant frequencies as a result of random transitions of the system. We can evidently avoid further complications as well as a rather cumbersome theoretical apparatus if we take account of the previously mentioned fact that the correlation time of the electronic subsystem is short. In any case, the shift of the nuclear resonance frequency will then be determined by the statistical average value of the hyperfine magnetic field. The corresponding line-width calculations and a discussion of the connection with the spin-lattice relaxation will be presented elsewhere.

## CONCLUSION

In this paper we have discussed the nuclear magnetic resonance of paramagnetic ions having an even number of electrons and well resolved singlet electronic states (Stark and Zeeman splittings) within the framework of the model of random variation of the resonance frequency. The frequency shift is due to random transitions between electronic states. The model is applied here to the Van Vleck paramagnet  $TmES$  in a magnetic field  $H \parallel c$ . The theory yielded values of the tempera-

ture-dependent NMR frequency shift and line width that agree well with experiment in the limit of small correlation times  $\tau$  (i.e., for  $\tau\Delta\omega \ll 1$ , where  $\Delta\omega$  corresponds to the hyperfine splittings). At low temperatures (corresponding to those used in the experiments) the probability per unit time for transitions from excited electronic states to the ground state plays the part of  $\tau^{-1}$ . The dipole-dipole and electronic-vibrational interactions ensure that this transition probability will be high enough. The smallness of the correlation time provides a basis for a phenomenological approach in which the resonant-frequency shift is proportional to the static paramagnetic susceptibility of the crystal.

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