Mössbauer Effect Studies of Nuclear Hyperfine Structure in Tm^{169} in Fe_2Tm†

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The nuclear hyperfine structure of the 8.4-keV transition in Tm^{169} in Fe_2Tm has been studied as a function of temperature from 4 to 400°K using the Mössbauer effect. The main source of the nuclear hyperfine interaction is the Tm $4f$ electron shell which is polarized through the exchange interaction with the iron atoms, which are themselves ferromagnetically coupled. A theoretical analysis based on the assumption that the thulium ion ground-state energy levels are determined only by this exchange interaction is successful in explaining the observed temperature variation of the magnetic and electric nuclear interactions. The magnetic hyperfine interaction in the nuclear ground state is $1.05\pm0.05\times10^{-5}$ eV at 4°K. The nuclear quadrupole moment of the 8.4-keV state has been estimated to be -1.3 b, the ratio μ_e/μ_g of the nuclear magnetic moments is -2.17 ± 0.10, the magnetic moment of the Tm ion in Tm metal at 4°K is $6.4\pm0.3\ \mu_B$, and the value $\langle r^{-3}\rangle$ for the $4f$ electrons has been measured as 12.5 ± 0.7 au. These results are compared with the theoretical values and other experimental results.

I. INTRODUCTION

THE Mössbauer effect is a useful technique for studying rare-earth (RE) nuclear hyperfine structure in which the interaction of the nucleus with the $4f$ electrons is dominant. The results of such studies can provide valuable information about nuclear moments in the highly deformed nuclei and the electronic structure of RE ions in crystals. In most of the experiments reported to date, however, lack of precise knowledge of the ground-state nuclear moment and/or the electronic wave functions has prevented absolute determinations of nuclear moments and internal fields.

The nucleus Tm^{169} is an exception to this, since the nuclear ground-state magnetic moment has been accurately measured[1] by an atomic-beam technique which requires no wave function correction. In addition, measurements can be made in the intermetallic compound Fe_2Tm, in which the RE electronic wave functions can be approximated without relatively unreliable crystal-field calculations. The combination of these circumstances makes it possible to evaluate the results of Mössbauer effect hyperfine-structure measurements in a relatively simple and exact way and tie together a number of other experiments in nuclear and solid-state physics.

The Mössbauer effect in Tm^{169} has been studied previously,[2–4] and both electric and magnetic hyperfine interactions have been observed and analyzed.

II. EXPERIMENTAL EQUIPMENT

The measurements described were made using techniques that are standard for Mössbauer spectroscopy. Natural erbium metal was irradiated with neutrons, producing Er^{169}. The erbium was then evaporated in ultrahigh vacuum to produce a thin layer of erbium metal. At room temperature, the Tm^{169} nuclei produced by the beta decay of the Er^{169} emit an unsplit 8.4-keV gamma ray with a recoil-free fraction of about 90%.[5] The source was moved with constant acceleration by a loudspeaker drive which has been described.[6] The absorbers, containing about 10 mg/cm² Tm, were made by sedimenting Fe_2Tm powder onto a beryllium disc. The gamma rays were detected by an argon proportional counter. The counter output pulses were amplified and then selected by a single channel analyzer; data were stored in 200 channels of a 400-channel analyzer used in the multiscaler mode. The velocity drive was calibrated against splittings measured with constant velocity drives in Fe^{57} and other Tm^{169} compounds; the absolute accuracy is expected to be within 5%.[7]

III. THEORY

The theory of nuclear hyperfine interactions in rare-earth ions in solids has been extensively studied.[8–10] The splitting of the nuclear energy levels can be conveniently written in the form

$$E=E_M+E_Q=\mu H_{\rm int}m_I/I + eQV_{zz}[3m_I^2-I(I+1)]/[4I(2I-1)], \quad (1)$$

where μ is the nuclear magnetic moment, $H_{\rm int}$ is the magnetic field at the nucleus, Q is the spectroscopic nuclear quadrupole moment, V_{zz} is the electric field gradient at the nucleus (assumed axially symmetric and along the direction of $H_{\rm int}$), and I and m_I are the nuclear

† A preliminary report of this work was presented at the Third International Conference on the Mössbauer Effect [Rev. Mod. Phys. **36**, 393 (1964)].

[1] G. J. Ritter, Phys. Rev. **128**, 2238 (1962).

[2] M. Kalvius, P. Kienle, H. Eicher, W. Wiedemann and C. Schüler, Z. Physik **172**, 231 (1963).

[3] *Proceedings of the Second International Conference on the Mössbauer Effect*, edited by D. M. J. Compton and A. H. Schoen, (John Wiley & Sons, Inc., New York, 1962), p. 172 ff. and p. 185 ff.; and R. L. Cohen, Bull. Am. Phys. Soc. **8**, 43 (1963).

[4] S. Hüfner, M. Kalvius, P. Kienle, W. Wiedemann, and H. Eicher, Z. Physik **175**, 416 (1963).

[5] The measured absorption is relatively weak because the 8.4-keV gamma ray is diluted by an intense L x-ray complex.

[6] R. L. Cohen, P. G. McMullin, and G. K. Wertheim, Rev. Sci. Instr. **34**, 671 (1963).

[7] The value obtained for the over-all splitting in Tm metal at 4°K, 106 cm/sec, is in good agreement with the value 107 cm/sec obtained by Kalvius *et al.* (Ref. 2).

[8] H. Eicher, Z. Physik **169**, 178 (1962).

[9] B. Bleaney (to be published).

[10] J. Kondo, J. Phys. Soc. Japan **16**, 1690 (1961).

spin and spin projection quantum numbers. The perturbations expressed in Eq. (1) split the nuclear levels as shown in Fig. 1; in either absorption or emission the 8.42-keV transition is, in general, split into six lines. The magnetic and electric terms in the hyperfine interaction will be considered separately. The sources of H_{int} are:

(1) The partly filled $4f$ electron shell.
(2) Polarization of the conduction electrons.
(3) Polarization of the filled electron shells through interactions with the spin of the $4f$ electrons.
(4) Fields from nearby magnetic ions and externally applied fields.

The first source listed above provides an internal field of approximately 7×10^6 Oe, which will be shown to be large in comparison with the other effects: Terms (2) and (3) each can be estimated to be on the order of 60 kOe or less from results[11] in spin-only Eu ions[12]; and (4) is on the order of 20 kOe or less.

The electric-field gradients at the nucleus come from the following sources:

(1) The partly filled $4f$ electron shell.
(2) The field gradient from the surrounding ions, enhanced by the Sternheimer effect.[13,14]
(3) Shielding by the closed shell electrons of the field gradient from the $4f$ electrons; an "internal" Sternheimer effect.

Only terms (1) and (3) are expected to make a significant contribution to the internal field gradient. Term (2) is expected to be identically zero because of the high symmetry ($\bar{4}3m$) of the surrounding of the Tm ion. [It has been measured to be less than 5% of (1) in Al_2Tm, which is isostructural with Fe_2Tm.]

These arguments show that it is satisfactory to consider the internal fields as resulting entirely from the $4f$ electrons, plus shielding terms. The first electronic state above the $^3H_6$ ground state is at about 6000 cm^{-1}, so that only the lowest J state need be considered. It is convenient to use Kondo's[10] formulation of the Hamiltonian of Abragam and Pryce[15] to write the internal fields as

$$H_{\text{int}}=2\mu_B\zeta\langle r^{-3}\rangle_{\text{eff}}\langle J_z\rangle\,, \tag{2a}$$

$$V_{zz}=e\beta\langle r^{-3}\rangle_{\text{eff}}\langle 3J_z^2-J(J+1)\rangle(1-R)\,, \tag{2b}$$

where $\zeta=7/9$ and $\beta=-1/99$ are parameters for the $^3H_6$ state and the expectation values are taken over the $4f$ electronic wave function. The use of the same

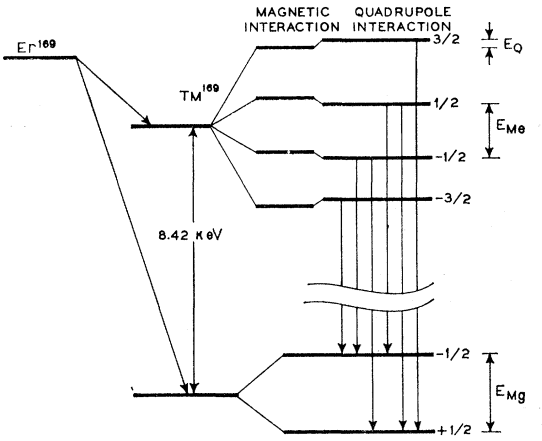

FIG. 1. Hyperfine structure in the ground and first excited states of Tm^{169}.

$\langle r^{-3}\rangle_{\text{eff}}$ for the magnetic and electric interactions is not rigorously valid because of various undetermined shielding corrections which will be discussed later, but in the absence of accurate estimates of these differences, we will assume that the same value can be used. The factor (1-R) represents the difference between magnetic and electric shielding due to closed-shell distortions.

It is at this point in the analysis that the advantages resulting from the use of Fe_2Tm as an absorber become apparent. In Fe_2Tm, the crystal field perturbations on the Tm ion, on the order of 100°K, are relatively weak when compared with the exchange interaction, which is 660°K. Thus, to a first approximation, the Tm ion-level splitting is determined by the exchange interaction, and the $^3H_6$ level is split into $2J+1=13$ equally spaced substates with J_z a good quantum number. In this respect, the system is a much simpler one to analyze than those occurring in other magnetic compounds such as TmIG and Tm metal where the crystal field mixes terms of different J_z. The energies of the magnetic substates are given by $-\langle\mathbf{S}\cdot\mathbf{K}\rangle$, with $\mathbf{S}$ the spin of the substate and $\mathbf{K}$ the molecular field parameter.[16] From the results of magnetization studies in other Fe_2R compounds and the isostructural Al_2R compounds, it can be shown that the iron sublattice, which is strongly ferromagnetic, is the main source of the exchange interaction. The relative populations of these magnetic substates will be given by $\exp(+\langle\mathbf{S}\cdot\mathbf{K}\rangle/T)$. Since the spin-lattice relaxation time is much shorter than the nuclear lifetime, it is appropriate to consider the internal fields as an average over those of the individual substates.[3,17] Equations (2a) and (2b) can then be written

$$H_{\text{int}}=2\mu_B\zeta\langle r^{-3}\rangle_{\text{eff}}J\theta_M\,, \tag{3a}$$

[11] P. H. Barrett and D. A. Shirley, Phys. Rev. **131**, 132 (1963).
[12] Term (2) is expected to be extremely small, since Knight-shift measurements in isostructural $LaAl_2$ indicate extremely low conduction-electron density at the nucleus (private communication V. Jaccarino); see also discussion in Sec. VII of this paper.
[13] H. M. Foley, R. M. Sternheimer, and D. Tycko, Phys. Rev. **93**, 734 (1954) and R. M. Sternheimer, *ibid.* **105**, 158 (1957).
[14] A. J. Freeman and R. E. Watson, Phys. Rev. **132**, 706 (1963).
[15] A. Abragam and M. H. L. Pryce, Proc. Roy. Soc. (London) **A205**, 135 (1951).
[16] B. Bleaney and L. R. Walker have pointed out that the usual way of writing this as $\langle\mathbf{J}\cdot\mathbf{K}\rangle$ is physically wrong but leads to the same result, since $\langle\mathbf{S}\cdot\mathbf{K}\rangle\propto\langle\mathbf{J}\cdot\mathbf{K}\rangle$ if L-S coupling holds.
[17] A. J. F. Boyle and H. E. Hall, Rept. Progr. Phys. **25**, 441 (1962).

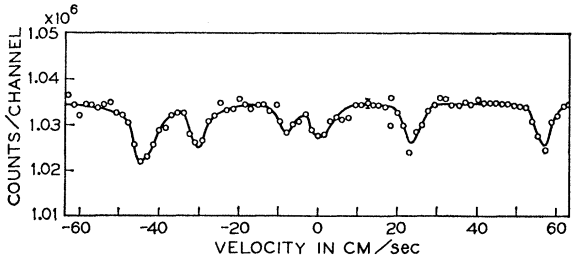

FIG. 2. Observed resonance absorption pattern in Tm^{169} in Fe_2Tm at 78°K: Source is erbium metal at 300°K; size of peaks corresponds approximately to 3:2:1:1:2:3-intensity ratio expected for $\frac{3}{2} \rightarrow \frac{1}{2}$ M1 transition.

with

$$J\theta_M = \frac{\sum_{J_z} J_z \exp(\langle \mathbf{S}\cdot\mathbf{K}\rangle/T)}{\sum_{J_z} \exp(\langle \mathbf{S}\cdot\mathbf{K}\rangle/T)},$$

and

$$V_{zz} = e\beta\langle r^{-3}\rangle_{\text{eff}}(1-R)[3J^2 - J(J+1)]\theta_Q, \quad \text{(3b)}$$

with

$$[3J^2 - J(J+1)]\theta_Q = \frac{\sum_{J_z}[3J_z^2 - J(J+1)]\exp(\langle \mathbf{S}\cdot\mathbf{K}\rangle/T)}{\sum_{J_z} \exp(\langle \mathbf{S}\cdot\mathbf{K}\rangle/T)},$$

where the θ's give the temperature dependence of the internal fields. At very low temperatures, only the lowest substate is populated (this is confirmed by bulk magnetization measurements,[18] which show the rare-earth sublattice magnetization to be almost exactly the gJ value), and both θ's approach unity. As the temperature is raised, the other substates become populated, reducing the internal fields and therefore the hyperfine splitting. The value of $\mathbf{K}$ in the above formulas is not absolutely constant, since it is proportional to the iron sublattice magnetization, which decreases with increasing temperature. This variation has been measured by G. K. Wertheim,[19] using the Mössbauer effect to observe the hyperfine splitting in Fe^{57} in the Fe_2Tm; the results have been incorporated in the calculations of the θ's. If the nuclear ground-state magnetic splitting, E_{M_g} is measured at a temperature for which $\theta_M \sim 1$, using Eq. (1) and Eq. (3a), and the measured value of the nuclear ground-state magnetic moment, we can find H_{int} and $\langle r^{-3}\rangle_{\text{eff}}$. These determinations are independent of wave-function calculations. The relation to calculated values is discussed below.

Using the above derived value of $\langle r^{-3}\rangle_{\text{eff}}$ and E_Q measured at a temperature for which $\theta_Q \sim 1$, the quantity $(1-R)Q$ can be obtained from Eqs. (1) and (3b). This result is also discussed later.

[18] E. A. Nesbitt, H. J. Williams, J. H. Wernick, and R. C. Sherwood as quoted in Ref. (19); W. E. Wallace and E. A. Skrabek, in Proceedings of the Third Rare Earth Conference, April 1963, Clearwater, Florida (unpublished).

[19] G. K. Wertheim and J. H. Wernick, Phys. Rev. **125**, 1937 (1962), and private communication.

IV. RESULTS

A typical resonance-absorption pattern is shown in Fig. 2. With absorber temperatures of 300°K or less, the line positions, from which the hyperfine-interaction parameters were determined, were clearly defined and internally consistent. Above 300°K, due to the broadening of the resonance-absorption lines and the relatively small hyperfine interaction it was possible to determine only the over-all splitting. A summary of the data from runs at various temperatures is given in Table I.

TABLE I. Results of hyperfine structure measurements in Tm^{169} in Fe_2Tm.

Temp.	Over-all splitting, cm/sec[a]	Internal field[b] (10^6 Oe)	$E_Q(10^{-7}\text{eV})$	μ_e/μ_g[c]
4°K	116	7.2	22	
20°K	117	7.3	22	−2.14
78°K	100	6.2	13	−2.20
195°K	62	3.9	4	−2.16
295°K	42	2.6	1	−2.11
365°K	34	2.1		
400°K	29	1.8		

[a] This quantity corresponds to $3E_{M_e} + E_{M_g}$.

[b] These values differ slightly from those to be expected from Kalvius *et al.*,[2] who used Lindenberger's [K. H. Lindenberger, Z. Physik **141**, 476 (1955)] earlier value of μ_g.

[c] The value −2.17 given in the text is a weighted average of these results.

The results are plotted as a function of temperature in Fig. 3. The solid lines A and B are plots of Eqs. (3a) and (3b), respectively, with parameter $\langle \mathbf{S}\cdot\mathbf{K}\rangle = 330$°K (for $S=1$ and saturation iron-sublattice magnetization). The shape of the curves is quite sensitive to the value of $\langle \mathbf{S}\cdot\mathbf{K}\rangle$, and the fact that both curves fit the observed data so well with just the one adjustable parameter gives considerable confidence that the theory considered

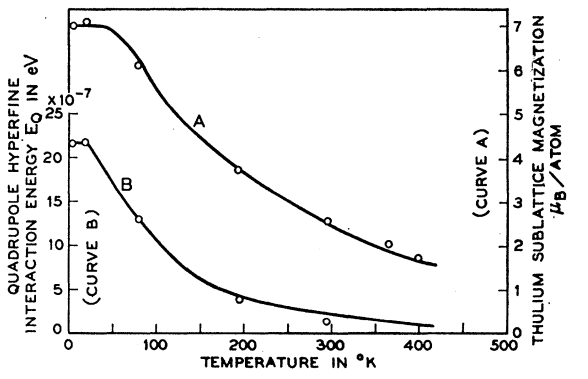

FIG. 3. Magnetic and electric nuclear hyperfine interactions in Tm^{169} in Fe_2Tm as a function of temperature. A: Magnetic interaction; B: Quadrupole interaction; circles: experimental points; solid line: theoretical result discussed in text. In most cases, the relative experimental errors are about the size of the points themselves.

here is adequate to describe the electronic structure of the Tm ion in Fe_2Tm.

V. NUCLEAR MOMENTS

From the relative separation of the six lines of the resonance-absorption pattern, μ_e/μ_g, the ratio of the excited-state to ground-state nuclear moments, can be readily obtained. The best value for this ratio obtained in the present experiments is -2.17 ± 0.10, in fair agreement with the value -2.33 ± 0.03 obtained by Kalvius *et al.*[2,20] Using $\mu_g=-0.229$, μ_e is 0.50 nm. This experimental result is in fair agreement with the moments calculated from the Nilsson model (with $\delta=0.28$, $\mu_e=0.29$ nm) and the rotational model (with g_K, g_R and b_0 derived from μ_g and the B values quoted in[21] $\mu_e=0.34$ nm).

As stated previously, the quantity $(1-R)Q$ can be derived from the measured value of $\langle r^{-3}\rangle_{\text{eff}}$ and quadrupole splitting; the value obtained is -1.08 ± 0.08 b. The stated error includes the uncertainties in determining E_Q and $\langle r^{-3}\rangle$. Using the rotational model with $\delta=0.28$, the value of Q calculated is -1.4 b. The internal-shielding factor has not been studied as carefully as the ordinary Sternheimer factor, and estimates are still crude. A recent publication of Barnes *et al.*[22] gives an estimate of approximately 0.12 for R, but this estimate is subject to an uncertainty of as much as ±0.15 since it was derived using calculated values for both Q and $\langle r^{-3}\rangle$. In any case, it would be specious to use this value of R to correct the present results to obtain the actual Q (which could then be compared with the theoretical value) since the value of R was obtained essentially by taking the ratio between a value $(1-R)Q$ [measured in Tm ethyl sulphate (TmES)] and the theoretical moment. From a very early publication by Sternheimer,[23] Barnes *et al.* have derived $R=0.16$, but this value is subject to considerable uncertainty because of the relatively simple model used and the fact that angular and radial shielding contributions may be relatively large and of opposite sign, tending to cancel [see Ref. (14)]. If this estimate is used, we get $Q=-1.3$ b, in excellent agreement with the theoretical estimates.

The quadrupole coupling constant has also been measured recently in TmES by Hüfner *et al.*[4] They obtain a value of -1.1 b for $Q(1-R)$, in very good agreement with the present value. This agreement is probably somewhat fortuitous, since Hüfner *et al.* used a value of $\langle r^{-3}\rangle=11.2$ au, different from the present work, and also did not consider another shielding factor discussed in Ref. 22.

[20] P. Kienle (private communication) indicates that a preliminary recalculation of this result brings the value to -2.27, which is then in agreement with the present result. The stated error in the present result comes mostly from uncertainty in the measured line positions.

[21] E. M. Bernstein and J. De Boer, Nucl. Phys. **18**, 40 (1960).

[22] R. G. Barnes, E. Kankeleit, R. L. Mössbauer, and J. M. Poindexter, Phys. Rev. Letters **11**, 253 (1963).

[23] R. M. Sternheimer, Phys. Rev. **84**, 244 (1951).

VI. THE SIZE OF $\langle r^{-3}\rangle$

There are numerous calculations of $\langle r^{-3}\rangle$ for $4f$ electrons in RE ions.[24] Before these results can be compared with the value of $\langle r^{-3}\rangle_{\text{eff}}=12.5\pm0.7$[25] au obtained from Eq. (3a) of the present paper, it must be realized that there may be some magnetic shielding factors to consider; these may make the $\langle r^{-3}\rangle_{\text{eff}}$ noticeably different from the true Coulombic $\langle r^{-3}\rangle$. Since these factors are not available, in this paper we have chosen the $\langle r^{-3}\rangle_{\text{eff}}$ determined from the magnetic interaction as the "true" value, and calculated from that. The value of $\langle r^{-3}\rangle_{\text{eff}}$ obtained in the present work, 12.5 au, lies between the Coulombic values 12.9 and 11.2 au calculated by Freeman and Watson[24] and Lindgren[26], respectively. The value obtained in this work is consistent with that obtained by Ritter[1] for the free Tm atom with the $^2F_{7/2}$ configuration, and disagrees slightly with the results of Doyle and Marrus[27] on the $^3H_6$ Er^{169} atom.

VII. MOMENT OF THE Tm ION IN Tm METAL

Under the assumptions of L-S coupling and negligible polarization effects, the internal magnetic field should be proportional to $\langle J_z\rangle$ and therefore to the moment of the Tm ion. We can then easily determine the ratio of the ion moments in Fe_2Tm and Tm metal by comparing the total hyperfine splitting in the two substances; this ratio is 1.09 ± 0.02 (extrap. to 0°K). If we assume the gJ value of 7 μ_B for the Tm ion in Fe_2Tm, the moment of the ion in Tm metal is 6.4 μ_B; this is in agreement with the neutron diffraction result of 6.8 ± 0.4 μ_B.[28] We arbitrarily assign a 5% error to the Tm metal ion moment to allow for crystal field and polarization effects.

This difference between the free-ion moment and that in Tm metal can be explained on the basis of admixture of various J_z states by the crystal field, and Kalvius *et al.*[2] have considered this effect in their analysis of results in Tm metal. A comparison of results in Tm metal and Fe_2Tm also provides further confirmation of the argument presented earlier that the internal field comes almost entirely from the $4f$ electrons. If the difference between H_{int} in Tm metal and Fe_2Tm involved primarily core or conduction-electron polarization, the $4f$ configuration should be essentially unchanged, and therefore the quadrupole splitting in the two materials should be the same. However, the quadrupole splitting in Fe_2Tm is about 10% larger than that observed[2] in Tm metal, leading us to the conclusion

[24] A. J. Freeman and R. E. Watson, Phys. Rev. **127**, 2058 (1962).

[25] The stated error includes possible drive errors as well as polarization corrections previously discussed.

[26] I. Lindgren, Nucl. Phys. **32**, 151 (1962).

[27] W. M. Doyle and R. Marrus, Phys. Rev. **131**, 1586 (1963).

[28] W. C. Koehler, J. W. Cable, E. O. Wollan, and M. K. Wilkinson, Phys. Rev. **126**, 1672 (1962).

that the configuration of the $4f$ electrons is different in the two materials.

VIII. SUMMARY

Using the Mössbauer effect, the hyperfine structure of Tm^{169} in Fe_2Tm has been studied as a function of temperature. The results have been adequately explained by a relatively simple treatment of the Tm-ion energy levels and straightforward evaluation of the hyperfine interaction. Using the measured value of Tm^{169} nuclear ground-state moment, various nuclear and electronic quantities have been derived and found in general to be in satisfactory agreement with previous results.

ACKNOWLEDGMENTS

The author would like to thank R. E. Watson for many enlightening discussions of the values of $\langle r^{-3} \rangle$ values and shielding corrections discussed in the text, and J. H. Wernick for preparing the Fe_2Tm used in this experiment. V. Jaccarino, L. R. Walker, and G. K. Wertheim have provided useful discussion and comments.

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Theory of Spin Resonance and Relaxation

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A quantum-statistical-mechanical theory of spin resonance and relaxation is presented, which avoids the assumptions of earlier theories, is capable of extension to other than the lowest Born approximation for the strength of the relaxation mechanism, and is applicable over a broader range of physical situations. From the Liouville equation for the combined system of spin+bath, the theory yields a non-Markoffian equation for the time development of the statistical density operator for the spin system alone. Detailed consideration is given to the response of the spin system linear in the driving field, and an equation for the steady-state spin density operator is deduced. A simple application exemplifies the new features of the theory and it is shown that it describes the phenomenon of "motional" narrowing. The response to an arbitrary external field is studied with particular reference to the problem of approach to thermal equilibrium and the phenomenon of spin resonance saturation. The latter is considered in some detail for a system of independent spins, for which an equation for the steady-state magnetization is derived and discussed.

1. INTRODUCTION

EQUATIONS of motion for the macroscopic magnetization of a sample under the combined action of external magnetic fields and a "heat bath" have been very useful in the study of magnetic resonance and relaxation. Bloch's[1] equations and later modifications[2,3] were the first ones to be suggested on phenomenological grounds, where the main assumption was made that the effects of the bath can be described by means of two constants, the so-called relaxation times, to be determined from experiment. Microscopic theories of the relaxation of the spin system were presented soon afterwards, beginning with the well-known work of Bloembergen, Purcell, and Pound,[4] where the bath was approximated to be an external fluctuating field. This latter semiclassical approximation was eliminated and a quantum-mechanical treatment of the problem was presented in the pioneering work of Wangsness and Bloch[5] and Bloch.[6,7] Redfield,[8] Fano,[9] and other authors[10–12] have subsequently given similar theories. In all these theories, the bath was considered as a quantum-mechanical system, that remained in thermodynamic equilibrium, while its exchange of energy with the spin system was taken into account. These theories have provided a derivation of the phenomenological equations while they pointed out the limits of their validity, and have given a microscopic determination of the relaxation times. They have also yielded much more general equations[7,8,10,11] of motion for the statistical-mechanical density operator of the spin system, which determines all its observable properties.

In the theories mentioned above, some assumptions were made, which were clearly stated in the works of Bloch,[5–7] Fano[9] and Abragam.[2] In particular, the sta-

* Operated with support from the U. S. Air Force.

[1] F. Bloch, Phys. Rev. **70**, 460 (1946).

[2] For this and other topics in this paper see A. Abragam, *The Principles of Nuclear Magnetism* (Clarendon Press, Oxford, 1961).

[3] C. P. Slichter, *Principles of Magnetic Resonance* (Harper and Row Publishers, New York, 1963).

[4] N. Bloembergen, E. M. Purcell, and R. V. Pound, Phys. Rev. **73**, 679 (1948).

[5] R. K. Wangsness and F. Bloch, Phys. Rev. **89**, 728 (1953).

[6] F. Bloch, Phys. Rev. **102**, 104 (1956).

[7] F. Bloch, Phys. Rev. **105**, 1206 (1957).

[8] A. G. Redfield, IBM J. Res. Develop. **1**, 19 (1957).

[9] U. Fano, Phys. Rev. **96**, 869 (1954).

[10] K. Tomita, Progr. Theoret. Phys. (Kyoto) **19**, 541 (1958).

[11] P. Hubbard, Rev. Mod. Phys. **33**, 249 (1961).

[12] V. M. Fain, Zh. Eksperim. i Teor. Fiz. **42**, 1075 (1962) [English transl.: Soviet Phys.—JETP **15**, 743 (1962)].