*Present address: 11 Camelot Drive, Bloomfield, Conn.

[1] K. Mitchell, Proc. Roy. Soc. (London) A146, 442 (1934); A153, 513 (1935).

[2] R. E. B. Makinson, Proc. Roy. Soc. (London) A162, 367 (1937); Phys. Rev. 75, 1908 (1949).

[3] M. J. Buckingham, Phys. Rev. 80, 704 (1950).

[4] I. Adawi, Phys. Rev. 134, A788 (1964); 134, A1649 (1964).

[5] J. Elster and H. Geitel, Ann. Phys. (Leipzig) 52, 433 (1894); 55, 684 (1895); 61, 445 (1897).

[6] H. Ives, Astrophys. J. 60, 209 (1924); 60, 231 (1924); Phys. Rev. 38, 45 (1931).

[7] H. Y. Fan, Phys. Rev. 68, 43 (1945).

[8] H. Thomas, Z. Physik 147, 395 (1957).

[9] H. Mayer and H. Thomas, Z. Physik 147, 419 (1957).

[10] S. Methfessel, Z. Physik 147, 442 (1957).

[11] A. Meesen, J. Phys. Radium 22, 135 (1961); 22, 308 (1961); Phys. Status Solidi 26, 125 (1968).

[12] L. Apker, E. Taft, and J. Dickey, Phys. Rev. 74, 1462 (1948).

[13] D. Redfield, Phys. Rev. 124, 1809 (1961).

[14] J. J. Scheer, Philips Res. Rept. 15, 584 (1960).

[15] W. E. Spicer, J. Appl. Phys. 31, 2077 (1960); RCA Rev. 19, 555 (1958).

[16] G. W. Gobeli and F. G. Allen, Phys. Rev. 127, 141 (1962); 127, 150 (1962).

[17] F. G. Allen and G. W. Gobeli, J. Appl. Phys. 35, 597 (1964).

[18] R. M. Broudy, Phys. Rev. B 1, 3430 (1970).

[19] For recent references on semiconductors, see, also, T. E. Fischer, Surface Sci. 13, 30 (1969).

[20] C. N. Berglund and W. E. Spicer, Phys. Rev. 136, A1030 (1964); 136, A1044 (1964).

[21] For recent references on metals, see, also, D. H. Seib and W. E. Spicer, Phys. Rev. B 2, 1676 (1970); 2, 1694 (1970).

[22] M. Brauer, Phys. Status Solidi 14, 413 (1966).

[23] G. Frischmuth-Hoffman, P. Görlich, H. Hora, W. Heimann, and H. Marseille, Z. Naturforsch. 15a, 648 (1960).

[24] D. W. Juenker, J. P. Waldron, and R. J. Jaccodine, J. Opt. Soc. Am. 54, 216 (1964).

[25] A preliminary account has appeared elsewhere (unpublished).

[26] W. L. Schaich and N. W. Ashcroft, Solid State Commun. 8, 1959 (1970).

[27] L. I. Schiff and L. H. Thomas, Phys. Rev. 47, 860 (1935).

[28] G. D. Mahan and G. Obermaier, Phys. Rev. 183, 834 (1969).

[29] G. W. Gobeli and F. G. Allen, Phys. Rev. 144, A558 (1966).

[30] G. W. Gobeli, F. G. Allen, and E. O. Kane, Phys. Rev. Letters 12, 94 (1964).

[31] B. S. Gourary (private communication).

[32] H. Puff, Phys. Status Solidi 1, 636 (1961); 1, 704 (1961); 4, 125 (1964); 4, 365 (1964); 4, 569 (1964).

[33] For a recent derivation and reference to previous work, see J. G. Collins, Appl. Sci. Res. B7, 1 (1957).

[34] E. A. Stern, in *Proceedings of the Fourth International Materials Symposium*, edited by G. A. Somorjai (Wiley, New York, 1969).

[35] E. A. Stern, Phys. Rev. 162, 565 (1967).

[36] J. A. Stratton, *Electromagnetic Theory* (McGraw-Hill, New York, 1941), Chap. 9.

[37] R. C. Eden, Ph.D. thesis (Stanford University, 1967) (unpublished).

[38] H. R. Philip and E. A. Taft, Phys. Rev. 120, 37 (1960).

PHYSICAL REVIEW B VOLUME 3, NUMBER 11 1 JUNE 1971

Electron Paramagnetic Resonance of Coupled Spin Systems: $Gd_xZr_{1-x}Zn_2$

D. Davidov,* G. Dublon, and D. Shaltiel†
Department of Physics, Hebrew University, Jerusalem, Israel

(Received 25 August 1970)

The electron paramagnetic resonance (EPR) of the coupled spin system $Gd_xZr_{1-x}Zn_2$ was measured as a function of the temperature T and the Gd concentration x. By varying x and T we were able to vary the relaxation parameters in a systematic way and obtain appreciable variation of both the EPR g shift and linewidth. We succeeded in correlating the variation of the relaxation parameters with the modified Hasegawa model. This is the first time that such a correlation has been obtained in a nonbottlenecked system.

The dynamic and static behavior of conduction electrons and paramagnetic ions coupled by exchange interactions is a subject of considerable interest. Hasegawa[1] was the first to suggest that these coupled spin systems may be described by phenomenological Bloch-type equations. The solutions of Hasegawa's equations give the transverse susceptibility as well as the electron paramagnetic resonance (EPR) g shift and linewidth of both the paramagnetic ions and conduction electrons. These solutions also indicate the existence of the well-known "bottleneck" effect[2] and dynamic effects.[3] In the past few years these problems have been studied extensively both theoretically[4] and experimentally.[5] There exists experimental studies that confirm Hasegawa's theory.[2,5,6] Most of these studies are concerned with the CuMn system and in the extreme bottleneck regime. $LaNi_5$[7] is somewhat exceptional in that the variation of the g shift arises from dynamic effects. However, as yet there are no experimental studies (except for bottlenecked systems) in which the variation of both the EPR g shift and linewidth were observed and are in agreement with theory. The purpose of this paper is to report EPR measurements in the system $\mathrm{Gd}_x\mathrm{Zr}_{1-x}\mathrm{Zn}_2$ ($x = 0.06$, 0.05, 0.03). We shall show that the appreciable variations of both g shift and linewidth in $\mathrm{Gd}_x\mathrm{Zr}_{1-x}\mathrm{Zn}_2$ are explained by modified Hasegawa equations.

ZrZn_2 is a "very weak" itinerant ferromagnet.[8] It is believed that the understanding of its magnetic properties may contribute greatly to the understanding of magnetism in metals. This has motivated the extensive theoretical[8,9] and experimental[10,11] work done on this compound during the last few years. Various authors[10,12] report slightly different values of T_C in the neighborhood of 20 °K. Above T_C, the susceptibility of ZrZn_2 obeys a Curie-Weiss law with[13,14]

$$\chi_e = 0.22/(T - \Theta)\ \text{emu/mole}, \qquad (1)$$

where Θ is the paramagnetic Curie temperature. Previous conduction-electron EPR measurements on ZrZn_2[15] have indicated that the linewidth in the paramagnetic region ($T > T_C$) increases appreciably with temperature. The temperature dependence of the linewidth in the paramagnetic region yields a relaxation rate of the itinerant electrons to the lattice due to spin-orbit coupling given by[15]

$$\delta_{eL} = 10^9\,(T - \Theta)\ .$$

Recent susceptibility measurements of $\mathrm{Gd}_x\mathrm{Zr}_{1-x}\mathrm{Zn}_2$ ($x < 0.05$) indicate that substituting Gd for Zr in ZrZn_2 lowers the Curie temperature.[16] According to those measurements, the exchange-interaction parameter between the Gd ions and the conduction electrons λ was too small to be determined. We shall show, however, that λ and other parameters of profound importance in the system $\mathrm{Gd}_x\mathrm{Zr}_{1-x}\mathrm{Zn}_2$ can be estimated from EPR measurements.

We have measured the EPR of powdered samples of $\mathrm{Gd}_x\mathrm{Zr}_{1-x}\mathrm{Zn}_2$ ($x = 0.03$, 0.04, 0.05, 0.06, 0.1) as function of temperature ($2 \leq T \leq 150$ °K) at the 1-cm wavelength. The samples were prepared by sintering and were examined by x rays. The g shift and linewidth of $\mathrm{Gd}_{0.06}\mathrm{Zr}_{0.94}\mathrm{Zn}_2$ and $\mathrm{Gd}_{0.03}\mathrm{Zr}_{0.97}\mathrm{Zn}_2$ are shown in Figs. 1 and 2. Similar behavior has been obtained for the other compounds. In addition we have measured the susceptibility of $\mathrm{Gd}_{0.06}\mathrm{Zr}_{0.94}\mathrm{Zn}_2$. A plot of[8] M^2 vs H/M yields $T_C = 20$ °K for this sample, while extrapolating $1/\chi = 0$ gives $\Theta = 23$ °K. The experimental results may be summarized as follows.

(a) The linewidth varies appreciably with temperature and has a maximum at 40 °K approximately. Above 40 °K it decreases sharply up to $T = 60$ °K and then increases moderately at the rate of approximately 3 G per degree at higher temperatures (Fig. 1).

(b) Although the g shift is always negative, it varies with temperature. It has maximum at 30 °K, a shallow minimum at 50 °K and decreases asymp-

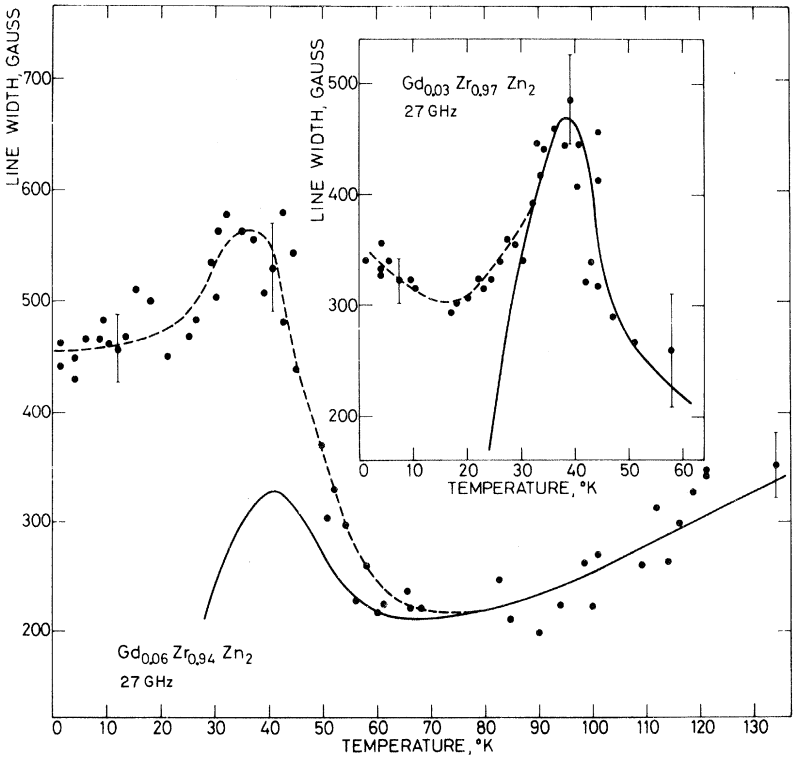

FIG. 1. Linewidth of $\mathrm{Gd}_{0.06}\mathrm{Zr}_{0.94}\mathrm{Zn}_2$ and $\mathrm{Gd}_{0.03}\mathrm{Zr}_{0.97}\mathrm{Zn}_2$ as a function of temperature. The solid curves represent the calculated linewidth (in the paramagnetic region) according to Eq. (2). The difference between the theoretical and the experimental linewidth is attributed to residual Gd linewidth and demagnetization effects as outlined in Ref. 19.

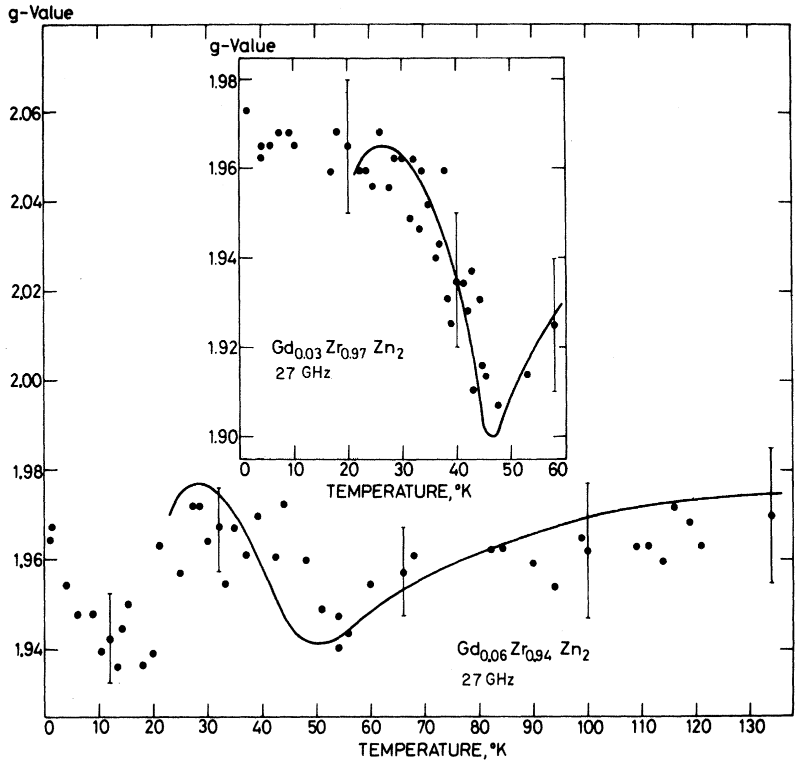

FIG. 2. g value of $Gd_{0.06}Zr_{0.94}Zn_2$ and $Gd_{0.03}Zr_{0.97}Zn_2$ as a function of temperature. The solid curves represent the calculated g value (in the paramagnetic region) according to Eq. (2).

totically at higher temperatures (Fig. 2).

In order to explain our experimental results, we have solved the equation of motion of a two-spin systems, proposed by Giovanini[17]:

$$\frac{d\vec{M}_i}{dt}=\gamma_i[\vec{M}_i\times(H+\lambda\vec{M}_e)]-\delta_{ie}[\vec{M}_i-\chi_i(\vec{H}+\lambda\vec{M}_e)]+\delta_{ei}[\vec{M}_e-\chi_e(H+\lambda\vec{M}_i)]\,,$$
$$\frac{d\vec{M}_e}{dt}=\gamma_e[\vec{M}_e\times(\vec{H}+\vec{M}_i)]-(\delta_{eL}+\delta_{ei})[\vec{M}_e-\chi_e(\vec{H}+\lambda\vec{M}_i)]+\delta_{ie}[\vec{M}_i-\chi_i(H+\lambda\vec{M}_e)]\,, \qquad (2)$$

where χ_i and χ_e are the spin susceptibilities of the Gd ions and the conduction electrons, respectively, δ_{ie} is the relaxation rate of the Gd ion to the conduction electrons, δ_{ei} is the relaxation rate of the conduction electrons to the Gd ions, and $\vec{H}+\lambda\vec{M}_e$ and $\vec{H}+\lambda\vec{M}_i$ are effective fields on the Gd ions and the conduction electrons, respectively. $\chi_e(\vec{H}+\lambda\vec{M}_e)$ and $\chi_i(\vec{H}+\lambda\vec{M}_e)$ represent, therefore, the equilibrium electronic and ionic magnetization, respectively.

Following Cottet *et al.*,[3] we have calculated the transverse susceptibility $\chi^+(\omega)$ from Eq. (2). The poles of $\chi^+(\omega)$ which correspond to the two resonance modes are given by

$$\omega_\pm=+\tfrac{1}{2}(\omega_e+\omega_i)\pm\tfrac{1}{2}\left[(\omega_e-\omega_i)^2+4\eta_{12}\eta_{21}\right]^{1/2}\,,$$

where

$$\begin{aligned}\omega_e&=-\gamma_e(H^z+\lambda M_i^z)+i(\delta_{eL}+\delta_{ei})+i\delta_{ie}\lambda\chi_i\,,\\ \omega_i&=-\gamma_i(H^z+\lambda M_e^z)+i\delta_{ie}+i\delta_{ei}\lambda\chi_e\,,\\ \eta_{12}&=-\gamma_e\lambda M_e^z+i(\delta_{eL}+\delta_{ei})\lambda\chi_e+i\delta_{ie}\,,\\ \eta_{21}&=-\gamma_i\lambda M_i^z+i\delta_{ie}\lambda\chi_i+i\delta_{ei}\,.\end{aligned} \qquad (3)$$

For λ = 0 these modes are the ionic and the electronic resonances. The interaction parameter mixes the two modes. The real part of $\omega_\pm$, $\mathrm{Re}(\omega_\pm)$, gives the line position while the imaginary part $\mathrm{Im}(\omega_\pm)$ is the linewidth.[3] Computation of $\mathrm{Re}(\omega_\pm)$ and $\mathrm{Im}(\omega_\pm)$ requires the knowledge of the quantities appearing in Eq. (3) and the advantage of using $ZrZn_2$ system for this study is the abundance of measured information available. Therefore rather than fitting the parameters in Eq. (3) to the results, we may estimate them independent of the functional behavior of the observed g shift and linewidth and thus test the Hasegawa model in a critical manner. The parameters are determined as follows: χ_e, the spin susceptibility of pure $ZrZn_2$, and its temperature dependence are given by Eq. (1). χ_i, the spin susceptibility of the Gd ions for the concentration C, is given by the Curie-Weiss law

$$\chi_i=\frac{N\mu_B^2g^2S(S+1)}{3k(T-\Theta_{\mathrm{Gd}})}=\frac{7.6C}{T-\Theta_{\mathrm{Gd}}}\ \text{emu/mole}\,,$$

where Θ_{Gd} is an unknown parameter. In estimating δ_{ie}, δ_{ei}, and λ we assume that there is no bottleneck in $Gd_xZr_{1-x}Zn_2$.[18] To obtain δ_{ie} we note that previous EPR measurements of pure $ZrZn_2$ have failed to detect any signal above 60 °K. This behavior is probably due to the appreciable broadening of the resonance line and the decrease of its intensity at high temperatures. We believe therefore, that the observed EPR resonance of $Gd_{0.06}Zr_{0.94}Zn_2$ at high temperatures ($T > 60$ °K) is mainly due to the Gd ions, while at low temperatures, the resonance is due to both the ions and the conduction electrons. The linewidth of $Gd_{0.06}Zr_{0.94}Zn_2$ in the high-temperature range ($T > 70$ °K), increases almost linearly with temperature. Its magnitude is approximately $\Delta H_k = 3T$ G.[18] We attribute this broadening to the Gd relaxation to the conduction electrons according to the Korringa mechanism. Using the relation $\delta_{ie} = g\mu_B \Delta H_k/\hbar$, we estimate the relaxation rate of the Gd ions to the conduction electrons to be $\delta_{ie} = 5.10^7 T$ sec^{-1}. The quantity δ_{ei} is given according to the detailed balance condition as[7] $\delta_{ei} = (\chi_i/\chi_e)\delta_{ie}$. The value of λ can be found by the following procedure: The real part of ω yields a g shift at high temperature which is given by $\Delta g = g\lambda\chi_e$. Since χ_e is known and the experimental Δg at these temperatures is approximately -0.03 (see Fig. 2), we obtain for λ the value $\lambda = -8 \pm 1$. The value of γ_i is 1.759×10^7 ($g = 2$) while that of γ_e is 1.724×10^7 which corresponds to $g = 1.95$ of pure $ZrZn_2$.[11] The only unknown parameter is Θ_{Gd}. It was found that the computed results are not very sensitive to this parameter in the range of $0 < \Theta_{Gd} < 20$ °K. Substituting all the other parameters in Eq. (4), we have computed the value of $\mathrm{Re}(\omega_-)$ and $\mathrm{Im}(\omega_-)$ numerically. (The g shift and the linewidth are related to this physical quantity as was explained before.[3]) The solid curves in Figs. 1 and 2 represent the calculated g value and linewidth according to this method for $\Theta_{Gd} = 10$ °K for $x = 0.06$ and $\Theta_{Gd} = 5$ °K for $x = 0.03$. It is clearly seen that the calculated g value yields a maximum at 30 °K and a minimum at 50 °K while the calculated linewidth yields a maximum at 40 °K and a shallow minimum at 60 °K, both in agreement with the experimental results[19] (Figs. 1 and 2).

It was found that the calculated values of Δg and ΔH are very sensitive to any variation of δ_{eL} and δ_{ei} (which determine the bottleneck effect). As was stressed previously the value of δ_{eL} was deduced from the linewidth behavior of pure $ZrZn_2$. We assume here that substitution of Gd instead of Zr in $ZrZn_2$ does not change δ_{eL} appreciably. This assumption was confirmed by our previous EPR measurements in which we introduced various impurities (Ti, Hf) into $ZrZn_2$.[20]

Using the relation $\lambda = J_{Gd}/g_e g_{Gd} \mu_B^2 N_0$ we have found $J_{Gd} = -10^{-3}$ eV. The small value of the exchange interaction J_{Gd} is consistent with susceptibility measurements,[16] and can be understood as the sum of the positive Heisenberg exchange interaction and the negative covalent mixing.[3]

In conclusion, we have demonstrated for the first time that Hasegawa's theory completely describes (in a nonbottlenecked system) the temperature dependence of both the EPR g shift and the linewidth. Various parameters which could not be estimated by other techniques were deduced and information was added to the understanding of the itinerant ferromagnet $ZrZn_2$ in the paramagnetic region.

The authors are indebted to E. Valach for preliminary experiments; S. Alexander, N. Kaplan, and M. Weger for stimulating discussions; A. Gabai for help in sample preparation; R. Kohen Arazi for x-ray measurements; and A. Grill for susceptibility measurements.

---

*Present address: Physics Department, University of California Los Angeles, Los Angeles, Calif. 90024.

†On leave from Hebrew University, Jerusalem, Israel.

[1] R. Hasegawa, Progr. Theoret. Phys. (Kyoto) 21, 483 (1959).

[2] A. C. Gossard, A. J. Heeger, and J. H. Wernick, J. Appl. Phys. 38, 1251 (1967).

[3] H. Cottet, P. Donze, J. Dupraz, B. Giovannini, and M. Peter, Z. Angew. Phys. 24, 249 (1968).

[4] H. J. Spencer and R. Orbach, Phys. Rev. 179, 683 (1969); R. Orbach and H. J. Spencer, *ibid.* 179, 690 (1969).

[5] S. Shultz, M. R. Shanaberber, and P. M. Platzman, Phys. Rev. Letters 19, 749 (1967).

[6] A. C. Gossard, T. Y. Kometany, and J. H. Wernick, J. Appl. Phys. 39, 849 (1968).

[7] D. Davidov and D. Shaltiel, Phys. Rev. Letters 21, 1752 (1968).

[8] E. P. Wohlfarth, J. Appl. Phys. 39, 1061 (1968).

[9] M. Mathon, Proc. Roy. Soc. (London) A306, 319 (1968).

[10] S. Ogawa and N. Sakamoto, J. Phys. Soc. Japan 22, 1214 (1967).

[11] E. Vallach, A. Gabai, and D. Shaltiel, Phys. Letters 30A, 341 (1969).

[12] B. T. Matthias and R. M. Bozorth, Phys. Rev. 109, 604 (1958).

[13] S. Ogawa and N. Sakamoto, Phys. Letters 23, 199 (1966).

[14] G. S. Knapp, J. Appl. Phys. 41, 1073 (1970).

[15] W. M. Walsh, Jr., *et al.*, J. Appl. Phys. 41, 1081 (1970).

[16] M. Asanuma and T. Yamadaya, J. Appl. Phys. 39, 1244 (1968).

[17] B. Giovannini, Phys. Letters 26A, 80 (1967).

[18] As was stressed before, a criterion for the existence of "bottleneck effect," is the decrease of the slope of linewidth versus temperature with the increase of Gd concentration. Our EPR measurement of $Gd_{0.1}Zr_{0.9}Zn_2$ indicates that above 170 °K, the linewidth increases with increasing temperature at a rate of 4 G/deg approximately. Therefore no bottleneck effect exists in the sys-

tem $Gd_xZr_{1-x}Zn_2$. More than that, our calculations indicate that the observed maximum in ΔH and minimum in Δg are not explained by the existence of a bottleneck effect.

[19] Our experimental results indicate that the total linewidth in $Gd_xZr_{1-x}Zn_2$ increases with the increase of Gd concentration (at low temperatures). This behavior is probably due to Gd-Gd interaction as well as to demagnetization effects. We therefore attribute the differences between the theoretical and experimental results for the sample $Gd_{0.06}Zr_{0.94}Zn_2$ to this effect.

[20] D. Shaltiel, D. Davidov, G. Dublon, A. Gabai, and A. Grill, International Conference on Magnetism, Grenoble, 1970 (unpublished).

PHYSICAL REVIEW B VOLUME 3, NUMBER 11 1 JUNE 1971

Transverse-Magnetization Recovery in the Rotating Frame*

Won-Kyu Rhim† and Horst Kessemeier
Department of Physics, University of North Carolina, Chapel Hill, North Carolina 27514

(Received 12 March 1970; revised manuscript received 12 February 1971)

The transverse relaxation of F^{19} nuclei in Teflon in the rotating frame at exact resonance has been studied by using rf fields large compared to the local field in this solid. Various pulse sequences are explored which serve to trace out the decay of the magnetization in the rotating frame and, further, to recover the magnetization lost under the action of secular dipolar terms and of the inhomogeneity of the rf magnetic field. It is found theoretically, and partially confirmed experimentally, that the rotary free-induction decay can be refocussed even after the spin system has presumably attained a steady state in the rotating frame, contrary to the assumption of the spin-temperature approximation.

I. INTRODUCTION

A nuclear resonance signal in the presence of a strong rf magnetic field at right angles to the dc magnetic field cannot be observed directly. Instead, the height of the free-induction decay (FID) following an rf pulse of length τ has to be recorded and related to the magnetization existing at time τ. Two procedures are available which permit the tracing out of the FID in the tilted rotating frame by recording the FID in the laboratory frame.

(i) An rf pulse of variable length τ is followed by a 90° sampling pulse at time t_d later with t_d satisfying the condition $T_2 \ll t_d \ll T_1$. If a laboratory system of coordinates is chosen with its z axis along the direction of the dc field and its x axis along the rf field, then this pulse sequence represents a measure of the z component of magnetization $M_z(\tau)$. In this fashion, Goldburg and Lee[1] have measured the rotary FID in a single crystal of CaF_2 and found that at exact resonance the decay envelope of $M_z(\tau)$ approximately coincides with the laboratory FID with its time scale expanded by a factor of 2.

(ii) Similarly, one should suppose, the component of magnetization in the x, y plane, say, $M_y(\tau)$, can be determined directly by reading the height of the FID following the rf pulse of length τ. Barnaal and Lowe[2] have measured as a function of τ the variation in the positions of the zero points of the FID in single crystals of CaF_2 and gypsum. For pulse lengths of up to 20 μsec, they demonstrated the expected line narrowing by a factor of 2 at exact resonance with considerable accuracy.

We have simultaneously measured both components of magnetization of the F^{19} resonance in Teflon at exact resonance for longer pulse widths and found that the rotary-decay envelopes differ both in width and shape, contrary to the expectation of a precessing and dephasing magnetization in the tilted rotating frame. The purpose of the present investigation is therefore twofold, namely, (i) to present a calculation accounting for this discrepancy, and (ii) to lock or recover the magnetization by means of various pulse sequences which existed at the time of shutoff of the rf pulse.

An important implication of the calculation is that the isolated spin system does not attain a state of internal equilibrium in the presence of a strong rf field contrary to the assumption of the spin-temperature approximation. The magnetization which has dephased under the action of the secular dipolar coupling may, under certain conditions, be recovered independently of the length of the rf pulse.

A theoretical analysis of these phenomena is presented in Sec. II. The experimental results are reported and discussed in Sec. III, and Sec. IV contains a summary of this investigation.

II. THEORETICAL CONSIDERATIONS

Consider a sample containing N identical nuclei having spin $\vec{I}$ and gyromagnetic ratio γ. The sample is exposed to a dc magnetic field $\vec{H}_0$ pointing along the z axis of a laboratory system of coordinates