

$J$  is the exchange integral. For this system, neither the internal energy, as a function of the distribution  $\rho_f = \langle n_f \rangle$ , is given by

$$E\{\rho_f\} = E_0 + \sum_f (-\mu H + J(0))\rho_f - \frac{1}{2} \sum_f \sum_{g \neq f} J_{fg} \rho_f \rho_g, \quad (9.3)$$

nor the entropy by

$$S\{\rho_f\}/k_B = -\sum_f [\rho_f \ln \rho_f + (1-\rho_f) \ln(1-\rho_f)], \quad (9.4)$$

nor the logarithm of the partition function,  $\ln Z$ , by

$$-\beta E\{\rho_f\} + S\{\rho_f\}/k_B. \quad (9.5)$$

However, we have an approximation to the Ising system called "Husimi-Temperley" model<sup>10</sup> where the energy is given by Eq. (9.1) with

$$J_{fg} = J/N, \quad (9.6)$$

which is independent of the distance between  $f$  and  $g$  and where  $N$  is the total number of lattice sites in the system. In this case, the energy, the entropy and the

<sup>10</sup> K. Husimi, *Proceedings of the International Conference on Theoretical Physics, Kyoto and Tokyo, September 1953*; (Science Council of Japan, Tokyo, 1954); H. N. V. Temperley, *Proc. Phys. Soc. (London) A67*, 233 (1954).

logarithm of the partition function are given by Eqs. (9.3), (9.4), and (9.5), respectively, and the average occupation number is given by the variation principle:

$$\delta[\ln Z \text{ given by Eq. (9.5)}]/\delta\rho_f = 0, \quad (9.7)$$

or

$$\rho_f = \{\exp\beta[-\mu H + J(0) - \sum_g J_{fg}\rho_g] + 1\}^{-1}, \quad (9.8)$$

where

$$-\mu H + J(0) - \sum_g J_{fg}\rho_g = \delta E\{\rho_f\}/\delta\rho_f. \quad (9.9)$$

This case is quite similar to the cases investigated in this article: because of  $J_{fg} = O(N^{-1})$ , the contribution from the complex diagrams in the virial expansion formula is of  $O(1)$  and is negligible.<sup>11</sup>

It is concluded from the above investigation that the Bose and Fermi distribution functions for the quasi-particles are entirely due to the assumption that  $\epsilon(\mathbf{k}_1, \dots, \mathbf{k}_n)$  for  $n \geq 2$  is of  $O(V^{-n+1})$ . This condition is more general and has a wider applicability than the one given by Landau.

<sup>11</sup> The authors are indebted to Dr. S. Katsura for pointing out this fact to them. A similar discussion for the contributions from the attractive part of the potential for the Kac-Uhlenbeck-Hemmer model of classical fluid has been given by Katsura: M. Kac, G. E. Uhlenbeck, and P. C. Hemmer, *J. Phys. Math.* **4**, 216 (1963); and S. Katsura, *Advan. Phys.* **12**, 391 (1963).

## Zeeman Spin-Spin Relaxation in Platinum Metal†

R. E. WALSTEDT

*University of California, Berkeley, California*

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Pulsed dispersion measurements with high radio-frequency fields are reported here for the Pt<sup>195</sup> nuclear-spin system in platinum metal. Under the conditions used, these data provide a measure of the Zeeman spin-spin relaxation rate (i.e., the saturation rate) in the rotating reference frame. The results have been analyzed using a thermodynamic approach similar to that given by Provotorov and based on Redfield's hypothesis of a spin temperature in the rotating frame. Data have been obtained with pulses both long and short compared with the spin-lattice relaxation time  $T_1$ . Good agreement between experiment and theory is found using Zeeman spin-spin relaxation times calculated by means of time-dependent perturbation theory. These calculations are essentially an extension of Provotorov's saturation theory to high radio-frequency fields. For this purpose, the saturation process is considered to be generated by nonsecular dipolar coupling terms in the rotating frame rather than the traditional approach of using the radio-frequency field as the relevant perturbation. Such an approach is closely analogous to the Zeeman spin-spin relaxation theory for spin systems in static fields given by Hartmann and Anderson. These results serve to corroborate other measurements of the pseudodipolar interaction and predominant Ruderman-Kittel exchange coupling in platinum. A reinterpretation of earlier measurements of  $T_1$  versus  $H_0$ , which deviate from the well-tested theories of Redfield and of Hebel and Slichter, is suggested. This reinterpretation would require an anomalously long Zeeman spin-spin relaxation time for platinum in small dc fields, i.e., nonsecular pseudodipolar coupling terms differing considerably in magnitude from the secular part. Experiments are suggested to test this hypothesis.

### I. INTRODUCTION

THE importance of the nuclear spin-spin interactions in solids as reservoirs for energy and entropy was first pointed out by Redfield,<sup>1</sup> who showed

that in the limit of weak spin-lattice interactions a precessing nuclear magnetization in the presence of a radio-frequency (rf) field  $H_1$  could decay only by exchanging energy with the spin-spin interaction "reservoir." The spin-temperature experiments of Abragam and Proctor<sup>2</sup>

† Work supported by the National Science Foundation and the Office of Naval Research.

<sup>1</sup> A. G. Redfield, *Phys. Rev.* **98**, 1787 (1955).

<sup>2</sup> A. Abragam and W. G. Proctor, *Phys. Rev.* **102**, 1441 (1958).

clarified this idea considerably by showing that energy and entropy can be transferred reversibly between the magnetic-field (Zeeman) interaction and the spin-spin interactions at low dc fields. In particular, it was shown that in isentropically demagnetizing a nuclear-spin system, appreciable entropy transfer to the spin-spin interactions takes place for external fields  $H_0$  less than a suitably defined "local field"  $H_L$ .  $H_L^2$  is, loosely speaking, the mean-square value of the nuclear spin-spin interaction field.

More recently, Slichter and Holton<sup>3</sup> have performed similar experiments on a nuclear-spin system viewed from a reference frame rotating in synchronism with an intense applied radio-frequency field  $H_1$ , using Redfield's hypothesis<sup>1</sup> of the existence of a spin temperature in such a rotating coordinate system. In close analogy with the work of Abragam and Proctor, it was shown that one can perform a reversible isentropic demagnetization of a nuclear spin system in the "rotating frame," causing an exchange of energy and entropy between the rotating magnetic field and the spin-spin interaction reservoir. It was correspondingly found that appreciable entropy transfer to the local interactions takes place only for "effective" magnetic fields in the rotating frame less than a local field  $H_L'$  closely related to  $H_L$ .

Redfield's rotating-frame spin-temperature hypothesis has been extensively tested at this point, notably by Goldburg,<sup>4</sup> who obtained experimental results in good agreement with calculated values of  $H_L'$  under the specified condition of "extreme saturation." A whole host of other investigators have also successfully used this hypothesis and the consequent application of thermodynamics to the rotating frame to explain a variety of experimental results.<sup>5-12</sup> In addition, the concept of spin temperature in the laboratory frame<sup>2</sup> has been usefully applied to experiments<sup>13-15</sup> which determine the variation of the nuclear spin-lattice relaxation time  $T_1$  with dc field  $H_0$  for values of  $H_0 \sim H_L$ , an effect which requires "thermal contact" or energy exchange between the magnetic field and the spin-spin energy reservoirs. We shall not dwell upon the details of these various experiments, but merely note that the ideas of nuclear spin temperature in the rotating and laboratory frames and the thermodynamics of spin systems are at this point firmly established.

Our primary concern here is with the mechanism, essential to the experiments mentioned above, whereby the transfer of energy between the Zeeman term and the spin-spin interaction term of the nuclear-spin Hamiltonian takes place. In particular we present here the results of an experimental investigation of this mechanism for the case of Pt<sup>196</sup> nuclear spins in platinum metal. We first examine briefly the work of previous researchers on this and related problems.

It has long been realized that Zeeman spin-spin relaxation takes place through the influence of nonsecular ( $\Delta m \neq 0$ ) terms of the nuclear dipolar coupling. Caspers<sup>16</sup> has given an extensive treatment of this problem for electronic spin systems. For the dc-field ("laboratory frame") case Hartmann and Anderson<sup>17</sup> have used density-matrix perturbation methods to calculate a Zeeman spin-spin relaxation time, finding reasonable agreement with experiment. For the rf field ("rotating frame") case, dipolar coupling terms have also been used to calculate cross-relaxation rates, e.g., the work of Schumacher,<sup>6</sup> Hartmann and Hahn,<sup>8</sup> and Slichter and Lurie.<sup>11</sup>

Of greatest pertinence to the present work is the rotating frame Zeeman spin-spin relaxation rate calculated by Provotorov.<sup>18</sup> In this analysis the rf magnetic field  $H_1$  is used as the perturbation which couples the Zeeman and spin-spin energy terms in close correspondence with the saturation theory of Bloembergen, Purcell, and Pound.<sup>19</sup> For this purpose  $H_1$  is required to be small compared with the nmr linewidth in gauss. Rough agreement with Provotorov's relaxation theory has been found by Goldburg<sup>5</sup> for the case of Na<sup>23</sup> spins in NaCl. It would be perfectly natural to use this theory to explain the present data but for the fact that the approximations break down because of the large rf fields used here. Hence a slightly different approach is dictated, wherein the *nonsecular dipolar coupling terms in the rotating frame* (rather than  $H_1$ ) are used as the perturbation operator which generates the Zeeman spin-spin relaxation process. This is closely analogous to the procedure adopted by Hartmann and Anderson<sup>17</sup> for the laboratory frame case. Again, the calculations are carried out using the density-matrix formalism, assuming the process is describable by means of a single relaxation time. The success of this method for studying rotating-frame relaxation processes in platinum depends in part on the peculiar circumstance of a predominant Ruderman-Kittel<sup>20</sup> exchange interaction coupling the nuclear spins of this metal.<sup>21,22</sup> Nevertheless, this ap-

<sup>3</sup> C. P. Slichter and W. C. Holton, Phys. Rev. **122**, 1701 (1961).

<sup>4</sup> W. I. Goldburg, Phys. Rev. **122**, 831 (1961).

<sup>5</sup> W. I. Goldburg, Phys. Rev. **128**, 1554 (1962).

<sup>6</sup> R. T. Schumacher, Phys. Rev. **112**, 837 (1958).

<sup>7</sup> I. Solomon and J. Ezrahy, Phys. Rev. **127**, 78 (1962).

<sup>8</sup> S. R. Hartmann and E. L. Hahn, Phys. Rev. **128**, 2042 (1962).

<sup>9</sup> A. G. Anderson and S. R. Hartmann, Phys. Rev. **128**, 2023 (1962).

<sup>10</sup> M. Goldman and A. Landesman, Phys. Rev. **132**, 610 (1963).

<sup>11</sup> C. P. Slichter and F. M. Lurie, Phys. Rev. **133**, A1108 (1964).

<sup>12</sup> J. Jeener, H. Eisendrath, and R. Van Steenwinkel, Phys. Rev. **133**, A478 (1964).

<sup>13</sup> A. G. Redfield, IBM J. Res. Develop. **1**, 19 (1957).

<sup>14</sup> A. G. Anderson and A. G. Redfield, Phys. Rev. **116**, 583 (1959).

<sup>15</sup> L. C. Hebel and C. P. Slichter, Phys. Rev. **113**, 1504 (1959).

<sup>16</sup> W. J. Caspers, Physica **26**, 778 (1960).

<sup>17</sup> S. R. Hartmann and A. G. Anderson, in *Magnetic and Electric Resonance and Relaxation*, edited by J. Smidt (Interscience Publishers, Inc., New York, 1963), p. 157.

<sup>18</sup> B. N. Provotorov, Zh. Eksperim. i Teor. Fiz. **41**, 1582 (1961) [English transl.: Soviet Phys.—JETP **14**, 1126 (1962)].

<sup>19</sup> N. Bloembergen, E. M. Purcell, and R. V. Pound, Phys. Rev. **73**, 679 (1948).

<sup>20</sup> M. A. Ruderman and C. Kittel, Phys. Rev. **96**, 99 (1954).

<sup>21</sup> R. E. Walstedt, M. W. Dowley, E. L. Hahn, and C. Froidevaux, Phys. Rev. Letters **8**, 406 (1962).

<sup>22</sup> C. Froidevaux and M. Weger, Phys. Rev. Letters **12**, 123 (1964).

proach to Zeeman spin-spin relaxation in the presence of large rf fields should be applicable to a variety of other systems as long as the approximation of a single relaxation time is useful. Interestingly, this type of calculation gives results in good agreement with Provotorov's theory under conditions where they are comparable.

Platinum presents a favorable case for the investigation of rotating-frame relaxation processes, since only one nuclear species ( $\text{Pt}^{195}$ ) is present; also, the spin quantum number  $I = \frac{1}{2}$  precludes complications from quadrupole effects and simplifies some of the trace calculations involved in the theory. In addition, earlier work<sup>21</sup> has shown that the platinum spin system possesses certain interesting properties. In particular, this work has indicated the presence of a certain amount of pseudodipolar<sup>23</sup> broadening as well as the predominant exchange coupling mentioned above. The net result of all the spin-spin interactions present is an exchange-narrowed resonance line, having a linewidth less than one would calculate on the basis of classical dipolar interactions alone. The magnitude of the various spin-spin interactions present was first deduced from two pieces of data: (1) The value of the local field  $H_L$  obtained from measurements of  $T_1$  versus  $H_0$  as interpreted using the theories of Redfield<sup>13</sup> and of Hebel and Slichter<sup>15</sup>; (2) the lifetime  $T_2$  of the exponential free precession decay function as interpreted using the exchange-narrowing theory of Anderson and Weiss.<sup>24</sup> This analysis is redone here (see Appendix C) using the direct measurement of the nearest-neighbor exchange coupling constant  $J$  given by Froidevaux and Weger,<sup>22</sup> again concluding that the pseudodipolar broadening gives rise to a second moment  $\langle \Delta\omega^2 \rangle$  for the platinum nmr line about six times greater than a calculated value based on classical dipolar interactions. The strength of the Zeeman spin-spin relaxation process investigated here depends critically on the magnitude of the various spin-spin couplings. Thus the present work serves the additional purpose of corroborating the above analysis of the magnitudes of these couplings.

The experiments reported here are of the "pulsed dispersion" type reported by Goldburg.<sup>4,5</sup> The basic procedure is to apply a pulse of rotating magnetic field of amplitude  $H_1$  and duration  $t_w$  at some frequency  $\omega$  near the nuclear-precession frequency  $\omega_0 = \gamma H_0$ , where  $\gamma$  is the nuclear-gyromagnetic ratio and  $H_0$  is the dc magnetic field. This is followed by a  $\pi/2$  pulse to measure the surviving  $z$  component of nuclear magnetization  $M_z(\omega, t_w)$ . With a proper adjustment of the parameters the curve of  $M_z(\omega, t_w)$  plotted as a function of  $\omega$  (i.e., of  $\Delta H = H_0 - \omega/\gamma$ ) provides a measurement of the Zeeman spin-spin relaxation time. It is of interest to study the dispersion curves so obtained in two limiting cases: (a) for  $t_w \ll T_1$ , so that the nuclear spins

remain isolated from the lattice during the measurement, and (b) for  $t_w \gg T_1$  so that spin-lattice equilibrium is achieved during the rf pulse. The detailed shape and width of the curves expected for these two cases are derived in the next section from a set of thermodynamic equations which describe the relaxation processes taking place during the pulse. These equations are obtained by a method similar to the work of Schumacher.<sup>6</sup> The experimental data are then fitted with the curves so derived using Zeeman spin-spin relaxation times calculated as outlined in Sec. IV. The details of the latter calculations are presented in Appendix A. Reasonable agreement is found between theoretical curves so constructed and the experimental data.<sup>25</sup> Because of the strong spin-lattice relaxation process in platinum metal,<sup>21,26</sup> it was necessary to undertake these experiments at helium temperatures or below. At these temperatures eddy-current heating effects in the metallic specimens were found to be troublesome. In the present experiments such heating was important in the  $T_1$  equilibrium dispersion measurements [type (b) above] and obscured the meaning of the data to some degree. The results are nevertheless consistent with the calculations presented.

We also note that the value of the nearest-neighbor exchange coupling constant  $J$  measured directly by Froidevaux and Weger<sup>22</sup> is rather larger than that obtained earlier from  $T_1$  versus  $H_0$  measurements performed on platinum.<sup>21</sup> In addition, the experimental plots of  $T_1$  versus  $H_0$  deviated somewhat from the predicted theoretical curves.<sup>13,15</sup> No further data are available at present to resolve this discrepancy. However, a possible reinterpretation of the earlier data is considered in Sec. III-C incorporating the effects of Zeeman spin-spin relaxation. For this reinterpretation to be valid, one would require the nonsecular ( $\Delta m = \pm 1, \pm 2$ ) terms of the pseudodipolar interaction to differ considerably in magnitude from those terms which contribute to the high-field second moment  $\langle \Delta\omega^2 \rangle$  and in fact to cancel to some degree the corresponding terms from the classical dipolar interaction. This seems unlikely, yet is not unfeasible, since, as pointed out by Abragam,<sup>27</sup> there is no clear relationship between the sizes of the secular and nonsecular terms of this interaction in metals with complicated band structures. Furthermore, the radial dependence of such indirect spin-spin interactions is known to be oscillatory,<sup>23</sup> suggesting a possible cancellation with similar interactions of a different origin. Further experiments which could throw light on this matter are suggested in Sec. V.

## II. THERMODYNAMIC EQUATIONS

We begin by obtaining a set of differential equations which govern the processes of energy transfer taking

<sup>23</sup> N. Bloembergen and T. J. Rowland, Phys. Rev. **97**, 1679 (1955).

<sup>24</sup> P. W. Anderson and P. R. Weiss, Rev. Mod. Phys. **25**, 271 (1953).

<sup>25</sup> A brief account of some of the results presented here is given by R. E. Walstedt and E. Geissler, Phys. Letters **13**, 24 (1964).

<sup>26</sup> J. Butterworth, Phys. Rev. Letters **6**, 423 (1962.)

<sup>27</sup> A. Abragam, *Nuclear Magnetism* (Oxford University Press, New York, 1961), Chap. V.

place between the nuclear Zeeman, spin-spin, and lattice reservoirs of a specimen containing a single species of nuclear spin. The derivation given here is based (a) on a simple time-independent transition-rate picture of the relaxation processes involved, and (b) on a spin-temperature description of the states of the nuclear Zeeman and spin-spin reservoirs. Justification for this type of approach in the case of platinum metal will be discussed in Sec. IV where a density-matrix calculation of the Zeeman spin-spin relaxation time is outlined. The set of equations given here will be relevant to relaxation processes in both the laboratory and rotating reference frames, the transition between these two cases being made by simply changing certain of the parameters involved. For the rotating frame case, assumption (b) above is valid only for rf fields well above the saturation level defined by  $\gamma^2 H_1^2 T_1 T_2 = 1$ . Detailed solutions of these equations will then be used in Sec. III-A and III-B to interpret the dispersion measurements reported here. These equations will also be used in Sec. III-C to discuss the influence of the Zeeman spin-spin relaxation process on the measurement of spin-lattice relaxation times in platinum at low fields.

In the derivation to follow we visualize the relaxation processes taking place by means of the reservoir diagram in Fig. 1. Such processes are represented in the figure by linkages labeled with the appropriate relaxation time. The nuclear Zeeman and spin-spin energy reservoirs are identified with the corresponding spin-Hamiltonian terms  $\mathcal{H}_Z$  and  $\mathcal{H}_{SS}$ . In the laboratory frame one has  $\mathcal{H}_Z = -\hbar\omega_0 \sum_i I_{zi}$ , where  $\omega_0 = \gamma H_0$ ,  $H_0$  being the applied dc field (no rf field is present).  $\mathcal{H}_{SS}$  is taken to be the total spin-spin interaction consisting of classical dipolar, pseudodipolar, and indirect-exchange terms. For the rotating-frame case the Zeeman and spin-spin reservoirs are identified with appropriate terms from the transformed spin Hamiltonian as viewed from a reference frame rotating at the frequency  $\omega$  of the applied rf field  $H_1$  and having an axis of quantization (the  $z'$  axis) tilted at an angle  $\theta$  to the  $z$  axis as shown in Fig. 2. This quantization axis is arranged to coincide with the rotating-frame "effective field"  $\mathbf{H}_e = H_1 \hat{j} + \Delta H \hat{k}$ , where  $\Delta H = H_0 - \omega/\gamma$ , and  $\hat{j}$  and  $\hat{k}$  are unit vectors along the  $y$  and  $z$  axes in the rotating frame, respectively. In this reference frame, then, we identify  $\mathcal{H}_z \equiv -\hbar\omega_e \sum_i I_{z'i}$ , where  $\omega_e = \gamma |\mathbf{H}_e| = \gamma (\Delta H^2 + H_1^2)^{1/2}$ .  $\mathcal{H}_{SS}$  is taken to be the secular ( $\Delta m = 0$ ) portion of the total spin-spin interaction Hamiltonian, since in large dc fields the nonsecular ( $\Delta m \neq 0$ ) are out of thermal contact with the

FIG. 1. Energy-reservoir diagram for a nuclear-spin system showing energy-transfer processes as links labeled with the appropriate relaxation time.

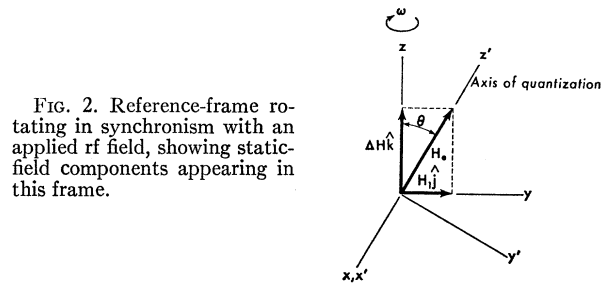
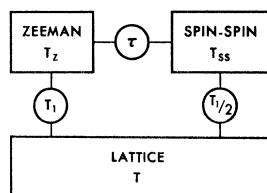


FIG. 2. Reference-frame rotating in synchronism with an applied rf field, showing static-field components appearing in this frame.

rest of the spin Hamiltonian and may be neglected.<sup>28</sup> It is easy to show that the total rotating-frame nuclear-spin energy  $\langle \mathcal{H}_z \rangle + \langle \mathcal{H}_{SS} \rangle$  as identified above is conserved<sup>18</sup> for times short compared with  $T_1$ , in accord with the reservoir diagram representation in Fig. 1.

The states of the Zeeman and spin-spin reservoirs are assumed to be well-described by spin temperatures  $T_Z$  and  $T_{SS}$ , respectively, i.e., the coupling between them and with the lattice is assumed to be weak. One might object at this point to the assumption that the two Hamiltonian terms  $\mathcal{H}_Z$  and  $\mathcal{H}_{SS}$  constructed from the same spin operators  $\mathbf{I}_i$  constitute independent energy reservoirs. Philippot<sup>29</sup> has examined this question in some detail and has shown that, whereas two operators are truly independent only if they occupy different manifolds in Hilbert space, the Zeeman and spin-spin Hamiltonian terms are very nearly independent in the high-temperature approximation,  $\hbar\omega_0/kT \ll 1$ . Here this approximation is valid throughout.

Using the assumptions of independent reservoirs and weak coupling, one may then proceed to construct a set of rate equations for energy transfer in the same way as was done by Schumacher<sup>6</sup> for the closely analogous case of cross relaxation between different nuclear species. As the latter derivation is easily adapted to the present problem, we shall not reproduce the details here. Instead, a simpler course is chosen which leads to the same result. We begin with a phenomenological relaxation equation for the rate of change of the nuclear magnetization  $M$  due to thermal contact with the spin-spin reservoir, namely,

$$dM(T_Z)/dt = -\tau^{-1}[M(T_Z) - M(T_{SS})], \quad (1)$$

where  $M(T_Z)$  is the instantaneous magnetization corresponding to a Zeeman temperature  $T_Z$ , and  $M(T_{SS})$  is the "equilibrium" magnetization toward which the Zeeman reservoir is instantaneously relaxing. We define  $\tau$  to be the Zeeman spin-spin relaxation time (see Fig. 1). A kinematic equation of the form of Eq. (1) will hold for weak thermal contact with any reservoir having a definable temperature, provided the Zeeman reservoir is able to maintain an internal Boltzmann distribution. It is important to note that  $T_Z$  and  $T_{SS}$  in Eq. (1) are both functions of time.

In order to use the conservation of nuclear spin

<sup>28</sup>For a particularly lucid discussion of this point, see Ref. 3.

<sup>29</sup>J. Philippot, Phys. Rev. **133**, A471 (1964).

energy  $\langle \mathcal{H}_Z \rangle + \langle \mathcal{H}_{SS} \rangle$ , it is convenient to express Eq. (1) in terms of the Zeeman energy  $E_Z(T_Z) = \langle \mathcal{H}_Z \rangle = -M(T_Z)H$ , where  $H$  is the steady field, taken to be  $H_0$  for the laboratory frame case and  $H_e$  for the rotating frame case. Equation (1) then becomes

$$dE_Z(T_Z)/dt = -\tau^{-1}[E_Z(T_Z) - E_Z(T_{SS})]. \quad (2)$$

Denoting the spin-spin energy  $\langle \mathcal{H}_{SS} \rangle$  as  $E_{SS}(T_{SS})$  we have by conservation of energy ( $E_Z + E_{SS}$ )

$$dE_{SS}(T_{SS})/dt = -\tau^{-1}[E_Z(T_{SS}) - E_Z(T_Z)]. \quad (3)$$

The time derivatives in Eqs. (2) and (3) refer only to the Zeeman spin-spin relaxation process; we must also add terms to the right-hand side of these equations to represent the spin-lattice relaxation processes. Before doing this, however, let us simplify the form of Eqs. (2) and (3) by expressing  $E_Z$  and  $E_{SS}$  explicitly in terms of  $T_Z$  and  $T_{SS}$ . This is accomplished by means of the well-known density-matrix relation  $E_{Z,SS} = \text{Tr}(\rho \mathcal{H}_{Z,SS})$ . We use for  $\rho$  the density matrix corresponding to thermal equilibrium within the Zeeman and spin-spin reservoirs

$$\rho = \left[ \exp\left(-\frac{\hbar \mathcal{H}_Z}{kT_Z} - \frac{\hbar \mathcal{H}_{SS}}{kT_{SS}}\right) \right] \times \left\{ \text{Tr} \left[ \exp\left(-\frac{\hbar \mathcal{H}_Z}{kT_Z} - \frac{\hbar \mathcal{H}_{SS}}{kT_{SS}}\right) \right] \right\}^{-1}.$$

In the standard high-temperature approximation this expression becomes

$$\rho \cong -[\hbar/k \text{Tr}(1)] \left[ \frac{\mathcal{H}_Z}{T_Z} + \frac{\mathcal{H}_{SS}}{T_{SS}} \right],$$

whereupon the energy expressions sought are

$$E_Z(T_Z) = -[\hbar \text{Tr}(\mu_z^2)/k \text{Tr}(1)](H^2/T_Z)$$

and

$$E_{SS}(T_{SS}) = -[\hbar \text{Tr}(\mu_z^2)/k \text{Tr}(1)](H_{\text{loc}}^2/T_{SS}).$$

The relation  $\mathcal{H}_Z = -H\mu_z$  has been used where  $\mu_z = \gamma \hbar \sum_i \mathbf{I}_{zi}$  is the magnetic moment operator, and the local field  $H_{\text{loc}}$  is defined by the usual relation  $H_{\text{loc}}^2 \text{Tr} \mu_z^2 = \hbar^2 \text{Tr} \mathcal{H}_{SS}^2$ . In accord with our earlier notation  $H_{\text{loc}}$  is taken equal to  $H_L$  for the laboratory frame case and  $H_L'$  for the rotating frame case. Substituting the expressions for  $E_Z$  and  $E_{SS}$  above, then, Eqs. (2) and (3) become

$$(\partial/\partial t)(T_Z^{-1})|_{\tau} = -\tau^{-1}(T_Z^{-1} - T_{SS}^{-1}), \quad (4)$$

$$(\partial/\partial t)(T_{SS}^{-1})|_{\tau} = -[(H^2)/(H_{\text{loc}}^2)]\tau^{-1}(T_{SS}^{-1} - T_Z^{-1}), \quad (5)$$

where the partial derivatives give the variation due to the Zeeman spin-spin relaxation process only.

To complete the derivation we now add to Eqs. (4) and (5) phenomenological terms corresponding to the spin-lattice relaxation links shown in Fig. 1. The form

of these terms is well known,<sup>1</sup> and so we simply state the results

$$(\partial/\partial t)(T_Z^{-1})|_{T_1} = -T_1^{-1}[T_Z^{-1} - T_Z^{-1}(\text{eq.})], \quad (6)$$

$$(\partial/\partial t)(T_{SS}^{-1})|_{T_1} = -2T_1^{-1}[T_{SS}^{-1} - T_{SS}^{-1}(\text{eq.})]. \quad (7)$$

The partial derivatives here give the variation of  $T_Z$  and  $T_{SS}$  due to spin-lattice relaxation alone.  $T_Z(\text{eq.})$  and  $T_{SS}(\text{eq.})$  correspond to spin-lattice equilibrium for the Zeeman and spin-spin energy reservoirs. For the laboratory frame case these temperatures are simply equal to the lattice temperature  $T$ . In the rotating frame, however, these temperatures are not what one would naively think and must be obtained by careful analysis. Redfield<sup>1</sup> has shown by physical arguments that  $T_Z(\text{eq.}) = TH_e/H_0 \cos \theta$  and  $T_{SS}(\text{eq.}) = \infty$ . Abragam<sup>30</sup> has used more rigorous methods to justify these expressions. It is worthwhile to remark that these expressions are correct in the neglect of terms of the order of  $T$ , a procedure that is certainly valid for the present experiments. In writing Eqs. (6) and (7) it is assumed that the spin-lattice relaxation processes of the Zeeman and spin-spin reservoirs are independent. Such an assumption will be valid if the relaxation of neighboring spins in the lattice is uncorrelated. The uncorrelated nature of the spin-lattice interactions in platinum is reflected by the experimental factor of two between the high- and low-field spin-lattice relaxation times for this metal<sup>21</sup> as interpreted by the theories of Redfield<sup>13</sup> and Hebel and Slichter.<sup>15</sup> This same factor of two appears in the spin-lattice relaxation rate in Eq. (7).

Equations (4)–(7) may now be combined according to the relation  $d/dt(T_{Z,SS}^{-1}) = \partial/\partial t|_{\tau}(T_{Z,SS}^{-1}) + \partial/\partial t|_{T_1} \times (T_{Z,SS}^{-1})$ , giving for the completed set of equations corresponding to the reservoir diagram in Fig. 1

$$(d/dt)(T_Z^{-1}) = -\tau^{-1}(T_Z^{-1} - T_{SS}^{-1}) - T_1^{-1}[T_Z^{-1} - T_Z^{-1}(\text{eq.})] \quad (8)$$

$$(d/dt)(T_{SS}^{-1}) = -\left(\frac{H^2}{H_{\text{loc}}^2}\tau^{-1}\right)(T_{SS}^{-1} - T_Z^{-1}) - 2T_1^{-1}[T_{SS}^{-1} - T_{SS}^{-1}(\text{eq.})]. \quad (9)$$

These equations are of the same form as those obtained by Schumacher<sup>6</sup> for cross relaxation and the rotating-frame equations given by Provotorov.<sup>18</sup> They hold only for the case of extreme saturation, i.e., for  $\gamma^2 H_1^2 T_1 T_2 \gg 1$ . Further, they depend on the assumption that the spin-lattice and Zeeman spin-spin relaxation processes are independent in addition to the assumptions stated above. This assumption is thought to be admissible as long as  $T_1$  is long compared with the correlation time  $\tau_c \sim J^{-1}$  of the dipolar local fields, where  $J$  is the nearest-neighbor exchange coupling constant. In applying these equations to the laboratory and rotating reference

<sup>30</sup> Reference 27, Chap. XII.

frames we distinguish the Zeeman spin-spin relaxation times for these cases as  $\tau_L$  and  $\tau_e$ , respectively. The appropriate parameters for Eqs. (8) and (9) are summed up in Table I. The closed parallel between the thermodynamics of these reference frames is reflected by the similarity of Eqs. (8) and (9) as particularized for either case using Table I.

### III. EXPERIMENTS

Equations (8) and (9) of the previous section are now used to analyze the results of pulsed dispersion measurements performed on platinum metal. The pulse sequence used is shown in Fig. 3 and is the same as that employed by Goldburg<sup>4,5</sup> to do similar measurements on diamagnetic crystals. The first pulse has an amplitude  $H_1$ , a circular frequency  $\omega$  in the vicinity of  $\omega_0$ , and a duration  $t_w$ . The rise and fall times of this pulse must be short compared with  $(\gamma H_e)^{-1}$  in order to ensure nonadiabatic field-switching in the rotating frame. The second pulse produces a free-precession signal proportional to the surviving  $z$  component of magnetization  $M_z(t_w, \Delta H)$ ; this signal amplitude is measured and plotted as a function of  $\Delta H = H_0 - \omega/\gamma$ .

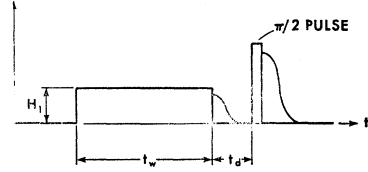
TABLE I. Approach parameters for Eqs. (8) and (9).

Parameter	$\tau$	$H$	$H_{100}$	$T_Z(\text{eq.})$	$T_{SS}(\text{eq.})$
Laboratory frame	$\tau_L$	$H_0$	$H_L$	$T$	$T$
Rotating frame	$\tau_e$	$H_e$	$H_L'$	$TH_e/H_0 \cos\theta$	$\infty$

The processes which take place during the pulse sequence can be visualized by means of the rotating frame diagram in Fig. 4. At the instant that  $H_1$  is applied, the steady field  $\mathbf{H}_e$  is established in the rotating frame. The component of the initial magnetization  $M_0 \hat{k}$  which is perpendicular to  $\mathbf{H}_e$  (not shown) precesses about  $\mathbf{H}_e$  and is assumed to decay in a time short compared with  $t_w$ . This assumption is examined in detail in Appendix B and is found to be valid under the conditions used in these experiments.  $\mathbf{M}_e$ , the nuclear magnetization vector parallel to  $\mathbf{H}_e$ , relaxes during the pulse by exchanging energy with the spin-spin and lattice reservoirs. The magnitude of this vector has an initial value  $M_e(0) = M_0 \cos\theta$  and reaches a final value  $M_e(t_w, \Delta H)$  at time  $t_w$ . When  $H_1$  is turned off abruptly, the  $z$  component of  $\mathbf{M}_e$ ,  $M_z(t_w, \Delta H)$ , is preserved for times short compared with  $T_1$  and is measured by the ensuing  $\pi/2$  pulse. Note also that the  $y$  component of  $\mathbf{M}_e$  produces a free-precession signal at the end of the dispersion first pulse, as indicated in Fig. 3. For experimental reasons this signal was ignored.

Under the proper conditions the experimental plot of  $M_z(t_w, \Delta H)$  versus  $\Delta H$  provides a measure of the Zeeman spin-spin relaxation time  $\tau_e$ . The shape and width of the dispersion curve obtained depend on  $H_1$ , which must be well into the saturation region as

FIG. 3. Pulse sequence used to perform the dispersion measurements.



mentioned in Sec. II, and on the pulse duration  $t_w$ . Experiments have been done for the two limiting cases (A)  $t_w \ll T_1$ , where the nuclear spins remain essentially isolated from the lattice during the pulse sequence and (B)  $t_w \gg T_1$ , where spin-lattice equilibrium is attained during time  $t_w$ . Expressions for  $M_z(t_w, \Delta H)$  are easily obtained from Eqs. (8) and (9) for these two limiting cases and are given in conjunction with the data presentation below.

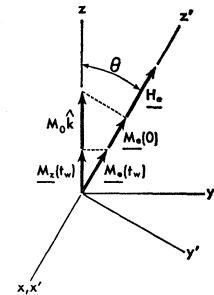
(A) For the case  $t_w \ll T_1$  experimental data was obtained with a precession field  $H_0$  of roughly 400 G using a specimen of powdered, high-purity platinum cooled to a temperature  $T \cong 0.1^\circ\text{K}$  by means of thermal contact with a demagnetized chrome-alum salt pill.<sup>31</sup> Dispersion pulses having an amplitude  $H_1 = 0.34 \pm 20\%$  G and a duration  $t_w = 6$  msec were used. At this temperature platinum has a  $T_1$  value of 300 msec,<sup>32</sup> so that the approximation  $t_w \ll T_1$  was well satisfied. Furthermore, the saturation factor  $S = \gamma^2 H_1^2 T_1 T_2$  under these conditions is roughly  $10^4$ , ensuring the validity of the rotating frame spin temperature approach to the data analysis.

In using Eqs. (8) and (9) for this case, then, we may ignore the spin-lattice relaxation terms. The variable  $T_{SS}$  is easily eliminated from the resulting pair of equations, giving for the motion of  $T_Z$

$$\begin{aligned} (d/dt)(T_Z^{-1}) = & -\tau_e^{-1} \left( 1 + \frac{H_e^2}{H_L'^2} \right) T_Z^{-1} \\ & + \tau_e^{-1} \left( \frac{H_e^2}{H_L'^2} \right) T_Z^{-1}(0), \quad (10) \end{aligned}$$

where  $T_Z(0) = TH_e/H_0 \cos\theta$  is the initial rotating-frame Zeeman temperature corresponding to the magnetiza-

FIG. 4. Rotating-frame diagram showing the nuclear magnetization in various stages of the relaxation process during a dispersion measurement.



<sup>31</sup> For details of the cooling techniques see R. E. Walstedt, E. L. Hahn, C. Froidevaux, and E. Geissler, Proc. Roy. Soc. (London) (to be published).

<sup>32</sup> This constitutes a revision of the data given in Ref. 21. For details see the article given in Ref. 31.

tion  $M_e(0)$ . The solution of Eq. (10) for  $t=t_w$  is

$$T_z^{-1}(t_w) = T_z^{-1}(0)(1 + H_e^2/H_L'^2)^{-1} \times [\exp(-t_w/\tau_r) + H_e^2/H_L'^2], \quad (11)$$

using  $\tau_r = \tau_e(1 + H_e^2/H_L'^2)^{-1}$  for the actual relaxation time which is modified by the relative heat capacity of the reservoirs. From this we calculate  $M_z(t_w, \Delta H) = M_e(t_w, \Delta H) \cos\theta$  using Curie's law

$$M_e(t_w, \Delta H) = CH_e T_z^{-1}(t_w),$$

where  $C$  is the nuclear Curie constant. This gives

$$M_z(t_w, \Delta H) = M_0(\Delta H^2/H_e^2)(H_e^2 + H_L'^2)^{-1} \times [H_L'^2 \exp(-t_w/\tau_r) + H_e^2]. \quad (12)$$

In Eq. (12) the relations  $\cos\theta = \Delta H/H_e$  and  $M_0 = CH_e T^{-1}$  have been used. This equation is the theoretical dispersion curve expression to be compared with the data. It is instructive to examine this expression in the limits  $t_w \ll \tau_r$  and  $t_w \gg \tau_r$ . For  $t_w \ll \tau_r$ , one obtains  $M_z(t_w, \Delta H) \cong M_0(\Delta H^2/H_e^2)$ , showing that no energy is lost to the spin-spin reservoir in this limit. The dispersion curve has a width  $H_1$  and merely reflects the loss of magnetization from being projected onto  $\mathbf{H}_e$  and back onto the  $z$  axis by the pulse. For  $t_w \gg \tau_r$ , one has  $M_z(t_w, \Delta H) \cong M_z(\text{eq.}) = M_0 \Delta H^2 (H_e^2 + H_L'^2)^{-1}$ , which is the value corresponding to thermal equilibrium within the nuclear spin system. This was derived by Abragam (Ref. 27, p. 549) and used by Goldburg<sup>5</sup> to interpret his results on NaCl and CaF<sub>2</sub>. Under the latter condition the width of the dispersion curve is  $(H_1^2 + H_L'^2)^{1/2}$  and provides a measure of  $H_L'$  if  $H_1$  is known. In the present experiments it was not feasible to measure  $H_L'$  in this way because of eddy-current heating and short  $T_1$  values. Hence we shall use the value  $H_L' = 5.6$  G obtained from the measurements of Froidevaux and Weger<sup>22</sup> (as explained in Sec. IV) in the calculations to follow.

Experimental values of  $M_z(t_w, \Delta H)/M_0$  versus  $\Delta H$  are plotted in Fig. 5 for the conditions stated above. A

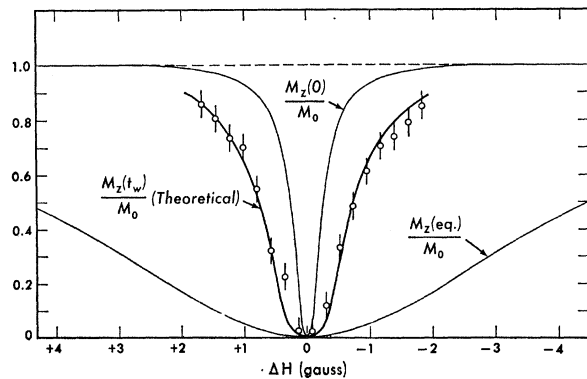


FIG. 5. Experimental data and theoretical curves for platinum dispersion measurements done with pulses of duration short compared with  $T_1$ .

theoretical curve based on Eq. (12) is also plotted using the expression for  $\tau_e$  obtained from density matrix calculations in Appendix A. For these data it is sufficient to use the asymptotic value of  $\tau_e$  in the limit  $H_e \ll H_L'$  which is

$$\tau_e = \tau_0 H_e^2 / H_1^2, \quad \tau_0 = 1.1 \text{ msec}. \quad (13)$$

For the theoretical curve the value  $H_1 = 0.3$  G giving the best fit to the data was used. This value lies well within the experimental accuracy of the  $H_1$  measurements. Theory and experiment are seen to be in good agreement. Also plotted in Fig. 5 are curves for  $M_z(0)/M_0$  and for  $M_z(\text{eq.})/M_0$ . The experimental curve lies below the former curve and above the latter one, showing the effect of Zeeman spin-spin relaxation. These data reflect values of  $\tau_e$  ranging from 1 msec near the center of the line to 30 msec for the largest values of  $\Delta H$  used here. The accuracy of this test of the calculated expression for  $\tau_e$  [Eq. (13)] is limited by the rather imprecise knowledge of  $H_1$ . The form of  $\tau_e$  given in this equation is well tested by the experiment, whereas the calculated value of  $\tau_0$  is only confirmed to within 40% or so.

One might attempt to account for the data in Fig. 5 using Provotorov's theory<sup>18</sup> of the approach to equilibrium in the rotating frame. This theory is valid for  $H_1 \ll (\gamma T_2)^{-1} = 0.16$  G for platinum, a condition which is obviously violated here. It is further assumed that during the relaxation process the magnetization remains parallel to the  $z$  axis (rather than along  $\mathbf{H}_e$ , as is supposed here). Further details of this theory are given in the next section. As applied to the present problem, it yields an expression similar to Eq. (12). As one may expect under the present conditions, this expression does not give as good a fit to the data as does Eq. (12). It is interesting, however, to compare Provotorov's expression for the relaxation time  $\tau_z$  of the  $z$  component of magnetization with  $\tau_e$  in the limit  $\Delta H \gg H_1$  where the  $z$  axis and  $\mathbf{H}_e$  coincide. In this limit the expression for  $\tau_z$  in the case of platinum, given in Appendix A [Eq. (A23)], is

$$\tau_z = T_2(\Delta H^2/H_1^2), \quad T_2 = 1.1 \text{ msec}, \quad (14)$$

which is remarkably close to Eq. (13).

One might also note that the Bloch equations<sup>33</sup> yield a relaxation time for  $M_e$  of the same form as Eq. (13). It must be pointed out, however, that such a relaxation time does not arise out of an energy transfer process as do  $\tau_e$  and  $\tau_z$  above, but merely out of a projection of the transverse  $T_2$  process onto a different axis. This theory includes, of course, no effects due to the spin-spin energy reservoir and therefore no parameter of the nature of  $H_L'$ .

(B) Next we turn to the platinum dispersion measurements done with pulses such that  $t_w \gg T_1$ , the pulse sequence being the same as in Fig. 3. These measurements were made with a precession field  $H_0$  of 1900 G

<sup>33</sup> F. Bloch, Phys. Rev. **70**, 460 (1946).

using a powdered specimen of high-purity platinum immersed in a bath of liquid helium at 4.2°K. Dispersion pulses of amplitude  $H_1 = 0.45 \pm 10\%$  G and a duration  $t_w = 14$  msec were used. Since  $T_1$  at this temperature is roughly 7 msec, the condition  $t_w \gg T_1$  would not have been well satisfied had there not been eddy-current heating during the pulse causing the specimen temperature to rise and  $T_1$  to shorten according to the relation  $T_1 = 30T^{-1}$  msec.<sup>21,26</sup> The effect of this temperature drift on the results is discussed in detail below. Under these conditions the saturation factor was calculated to have a minimum value of 17, i.e., well into the range of validity of the rotating-frame spin-temperature hypothesis.

The measurements we report are similar to the work of Goldberg<sup>4</sup> on NaCl and CaF<sub>2</sub>, except that Goldberg's implicit condition  $\tau_e \ll T_1$  no longer holds here. From Part A above we expect  $\tau_e$  to have values of several milliseconds, which is just the order of magnitude of  $T_1$ . As we shall see, this leads to rather different dispersion linewidths from those obtained by Goldberg.

To find the theoretical dispersion function, we assume the state of the system at the end of the pulse of width  $t_w$  to be characterized by the conditions  $d/dt(T_Z) = d/dt(T_{SS}) = 0$ . Hence the steady-state values of  $T_Z$  and  $T_{SS}$  are determined by the equations

$$\tau_e^{-1}(T_Z^{-1} - T_{SS}^{-1}) + T_1^{-1}(T_Z^{-1} - H_0 \cos\theta / TH_e) = 0, \quad (15a)$$

$$\tau_e^{-1}H_e^2/H_L'^2(T_{SS}^{-1} - T_Z^{-1}) + 2T_1^{-1}T_{SS}^{-1} = 0. \quad (15b)$$

Solving these for  $T_Z^{-1}$  one finds

$$T_Z^{-1}(\text{st.}) = H_0 \cos\theta (H_e^2/H_L'^2 + 2\tau_e/T_1) T^{-1} \times [H_e^2/H_L'^2 + 2(1 + \tau_e/T_1)]^{-1}, \quad (16)$$

where (st.) refers to the steady-state value. As in Part A of this section we use  $T_Z^{-1}$  to find the final  $z$  component of magnetization according to the formula  $M_Z(t_w, \Delta H) = CH_e \cos\theta T_Z^{-1}(\text{st.})$ . This quantity, written as a function of  $\Delta H$ , is the desired dispersion expression. We obtain this function in the limit  $H_e^2 \ll H_L'^2$ , so that  $\tau_e$  may be written as in Eq. (13). As we shall see, this limiting value will be appropriate for the experimental data. Under these conditions we find

$$M_z(t_w, \Delta H) = \frac{M_0 \Delta H^2}{\Delta H^2 + H_1^2 + 2H_L'^2/(1 + \Delta)}, \quad (17)$$

where  $\Delta = 2\tau_0 H_L'^2 / T_1 H_1^2$ . Note first that in this approximation the dispersion curve retains its inverted Lorentzian form. This is a direct consequence of the functional dependence of  $\tau_e$  on  $H_e$ . Further, it is seen that the effect of long  $\tau_e$ 's is to reduce the dispersion linewidth. In the limit  $\Delta \ll 1$ , i.e.,  $\tau_0 \ll T_1 H_1^2 / 2H_L'^2$ , Eq. (17) reduces to the formula given by Redfield.<sup>1</sup> In the present case where  $\tau_e \sim T_1$ ,  $H_1 \ll H_L'$ , we have  $\Delta \gg 1$ . In

this limit Eq. (17) becomes

$$M_z(t_w, \Delta H) = \frac{M_0 \Delta H^2}{\Delta H^2 + H_1^2 (1 + T_1/\tau_0)}. \quad (18)$$

We see that the linewidth  $H_w = H_1(1 + T_1/\tau_0)^{1/2}$  has ceased to depend on  $H_L'$ . Instead,  $H_w$  provides a measure of  $\tau_0$  when  $T_1$  and  $H_1$  are known. We shall now use Eq. (18) to interpret the present data on platinum.

The "T<sub>1</sub>-equilibrium" dispersion data for platinum are presented in Fig. 6 for the conditions stated above. In interpreting this data there are two experimental complications that need to be taken account of, namely, inhomogeneous broadening of the nmr line and the temperature drift mentioned above. Inhomogeneous broadening gave rise to the non-zero value for  $M_z(t_w, 0)$  which the data in Fig. 6 displays. This broadening arose, not from the inhomogeneity of the applied magnetic field, but from demagnetizing fields in and around the specimen particles. As shown by Drain,<sup>34</sup> such effects can cause appreciable broadening of nmr lines for highly paramagnetic metals like platinum. Drain's results for platinum predict for the present conditions an inhomogeneous linewidth  $H_I$  of the order of 0.1 G, as is observed.

The inhomogeneity was taken account of by folding the expression for  $M_z(t_w, \Delta H)$  with a hypothetical Lorentzian distribution of Larmor frequencies according to the equation

$$D(\Delta H) = \int_{-\infty}^{\infty} dh G(h) M_z(t_w, \Delta H - h) / M_0, \quad (19)$$

where  $D(\Delta H)$  is the expected dispersion function,  $G(h) = H_I \pi^{-1} (h^2 + H_I^2)^{-1}$ , and  $M_z(t_w, \Delta H - h)$  is taken from Eq. (18). Evaluating the integral in Eq. (19),

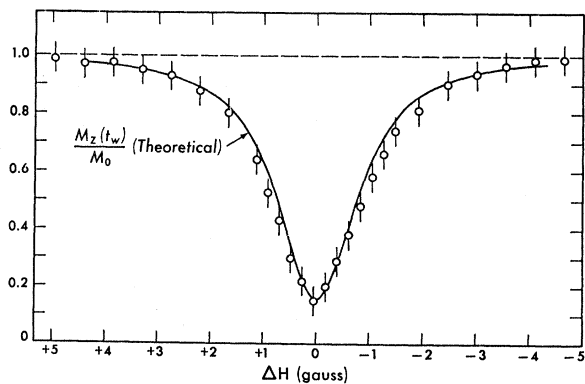


FIG. 6. Experimental data and theoretical curve plotted using Eq. (20) for platinum dispersion measurements done with pulses of duration long compared with  $T_1$ .

<sup>34</sup> L. E. Drain, Proc. Phys. Soc. (London) **80**, 1380 (1962).



we get

$$D(\Delta H) = 1 - \frac{H_w(H_I + H_w)[\Delta H^2 + (H_I - H_w)^2]}{(H_w^2 - H_I^2)^2 + \Delta H^2[\Delta H^2 + 2H_w^2 + 2H_I^2]}. \quad (20)$$

Equation (20) reduces to Eq. (18) in the limit  $H_I \rightarrow 0$ . The Lorentzian form for  $G(h)$  was chosen for mathematical convenience, the real distribution probably being much more nearly Gaussian. By using fields  $H_I$  such that  $H_w \gg H_I$  the detailed shape of  $G(h)$  was caused to be relatively unimportant.

The temperature drift due to eddy-current heating was sufficient to cause the specimen temperature to increase by a factor of 3 during the 14-msec pulses used. This effect could have been reduced by using smaller values of  $H_I$ ; this, however, would have led to a breakdown of the inequality  $H_w \gg H_I$  used in dealing with the inhomogeneous broadening. In taking account of this effect there are two main difficulties encountered, (a) temperature inhomogeneities giving rise to a distribution of equilibrium magnetization values  $M_{e0} = CH_0 \cos\theta T^{-1}$  and a distribution of  $T_1$ 's and dispersion linewidths according to Eq. (18); and (b) nonequilibrium conditions during the dispersion pulse as a result of the temperature drift. Apart from these problems the effect was reproducible and easily calibrated. In interpreting the data in Fig. 6 we shall simply assume that the final distribution of lattice temperatures is narrow, i.e., that the behavior of the specimen at time  $t_w$  is reasonably well represented by a suitable average temperature. At the outset we shall also assume that  $T_1$  is short enough to establish the  $T_1$ -equilibrium conditions represented by Eq. (20). [Note added in proof. This assumption is valid under the condition  $T_1 T^{-1} (dT/dt) \ll 1$ . For the present experiment the quantity in this inequality is of the order of 0.1.] A correction to this picture which alters the observed linewidth is discussed below.

Accordingly, Eq. (20) was used to plot the theoretical curve shown in Fig. 6 in the following way. From Eq. (20) one obtains  $D(0) = H_I / (H_w + H_I)$ ; this quantity is experimentally equal to 0.15, yielding the relation  $H_w = 5.66H_I$ . This relation is used to eliminate  $H_I$  from the equation. The value of  $H_w$  is then calculated from the measured value  $H_I = 0.45$  G, the theoretical value  $\tau_0 = 1.2$  msec, and the calculated value  $T_1 = 2.05$  msec from the measured temperature at the end of the 14-msec pulse (see below). Using the expression for  $H_w$  given with Eq. (18), one finds with these values  $H_w^2 = 0.55$  G<sup>2</sup>. The theoretical curve in Fig. 6 was plotted with this value of  $H_w^2$ , introducing small corrections in the wings of the line for deviations from  $\tau_e$  as given by Eq. (13) [see Eq. (A19) in Appendix A]. The agreement between the experimental and theoretical curves is seen to be quite good, the experimental curve being, however, slightly broader for small values of  $\Delta H$  than the theory predicts.

The slight broadening effect observed may be partially accounted for by deviations from instantaneous equilibrium within the spin system caused by temperature drift during the long rf pulse. This temperature variation was measured by applying the rf pulse at a frequency well away from the dispersion line. The reduction of  $M_z(t_w)$  with  $t_w$  under such conditions is due solely to the increase in  $T$  (rather than Zeeman spin-spin relaxation). The ability of  $M_z$  to follow this increase may be estimated by means of the spin-lattice relaxation equation  $\dot{M}_z = -T_1^{-1}(M_z - M_0)$ . Using  $T_1 = KT^{-1}$  and  $M_0 = CH_0 T^{-1}$ , this equation becomes

$$\dot{M}_z + K^{-1} T M_z = K^{-1} C H_0. \quad (21)$$

Considering  $\dot{M}_z$  to be a small quantity and approximating  $\dot{T} = \alpha = \text{constant}$ , Eq. (21) may easily be iterated to give

$$M_z(t) = M_0(t) [1 + (\alpha K / T^2) + 3(\alpha K / T^2)^2 + \dots], \quad (22)$$

where  $M_0(t) = CH_0 / T(t)$ . Using the experimental values  $\alpha = 6 \times 10^2$  °K/sec and  $K = 3 \times 10^{-2}$  sec °K, one finds a 15% correction  $[M_z(t) - M_0(t)] / M_0(t)$  at  $T = 12.5$  °K. Such a correction would not alter the dispersion line shape if it were a constant percentage for all values of  $\Delta H$ . It is easy to show from Eqs. (8) and (9), however, that for  $H_e \ll H_L'$  there are two exponential rates involved in the approach to equilibrium in the rotating frame, namely  $2T_1^{-1}$  and  $\tau_e^{-1} + T_1^{-1}$ . Since these rates are faster than the off-resonance rate  $T_1^{-1}$ , the "lag" in  $M_z$  from temperature drift is less under on-resonance conditions, giving rise to an artificial line broadening. All things considered, the data are very well accounted for by the theory.

Because of the many complications of this particular experiment, the precise quantitative interpretation of the data is subject to certain doubts. What is important, however, is that the dispersion narrowing for  $\tau_e \sim T_1$  predicted by Eq. (19) is observed and is consistent with the calculated expression for  $\tau_e$ . It is interesting to examine the predictions of the Bloch theory for this experiment. The dispersion function analogous to Eq. (20) is

$$M_z(\Delta H) / M_0 = \frac{\Delta H^2 + (\gamma^2 T_2^2)^{-1}}{\Delta H^2 + (\gamma^2 T_2^2)^{-1} + H_I^2 T_1 / T^2}. \quad (23)$$

This gives very nearly the inverted Lorentzian line shape of Eq. (20) in the limit of extreme saturation, with a predicted linewidth  $H_w^2 = 0.38$  G<sup>2</sup> as opposed to the theoretical value  $H_w^2 = 0.55$  G<sup>2</sup> using Eqs. (20) and (13). The experimental result certainly favors the present theory, though further work is necessary to give a definitive confirmation of this approach.

(C) Lastly we consider a possible reinterpretation of the earlier  $T_1$  versus  $H_0$  data including the effects of Zeeman spin-spin relaxation. This data is plotted in Fig. 7 along with a theoretical function given by

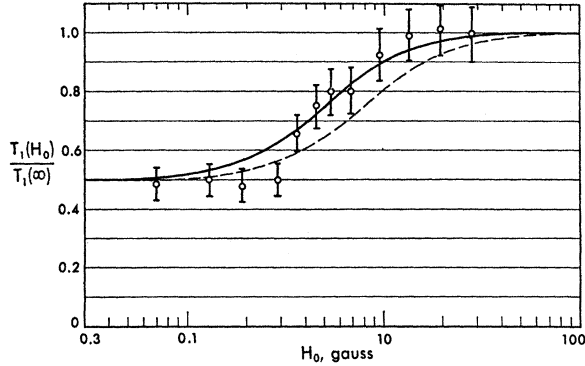


FIG. 7. Plot of  $T_1$  versus  $H_0$  data for platinum obtained earlier, showing the discrepancy with a theoretical curve (dashed line) based on a value for  $H_L$  calculated from the exchange constant  $J$  measured by Froidevaux and Weger.

Redfield<sup>13</sup>

$$T_1(H_0) = T_1(\infty)(H_0^2 + H_L^2)/(H_0^2 + 2H_L^2). \quad (24)$$

For  $H_L$  we have used the value of  $H_L'$  stated in Part A of this section, thus neglecting the small contribution to  $H_L$  from nonsecular terms of  $\mathcal{H}_{SS}$ . The neglect of the latter contribution, which is unknown because of the pseudodipolar term in  $\mathcal{H}_{SS}$ , does not alter the essence of the result. We see that there is a considerable discrepancy between the experimental and theoretical curves. Assuming the theoretical curve to be correct, it is seen that this discrepancy would be accounted for if the laboratory frame Zeeman spin-spin relaxation time  $\tau_L$  were long ( $\tau_L > T_1$ ) for  $H_0 \geq 10$  G, making a transition to shorter values  $\tau_L \ll T_1(\infty)$  for  $H_0 \leq 3$  G. In other words, for  $H_0 > 10$  G the Zeeman and spin-spin reservoirs are in poor thermal contact and the magnetization relaxes only by direct interaction with the lattice; whereas, as  $H_0$  is lowered below 10 G these reservoirs come into good thermal contact, and the system relaxes at the rate  $2T_1(\infty)^{-1}$  corresponding to  $H_0 \ll H_L$ . According to the expression for  $\tau_L$  given in Eq. (A25) of Appendix A, the qualitative behavior of  $\tau_L$  fits the above interpretation in that it makes a rapid transition from the  $H_0 = 0$  value to much longer values at  $H_0 \sim H_L$ .

These qualitative conclusions about the behavior of measured  $T_1$  values may be confirmed with detailed solutions to Eqs. (8) and (9) for the laboratory frame case. In the absence of further data we shall not state these solutions in detail, but merely comment on them qualitatively. These solutions show that  $T_z^{-1}$  relaxes with the rates  $T_1(\infty)^{-1}$  for  $\tau_L \gg T_1(\infty)$  and  $T_1(\infty)^{-1} \times (H_0^2 + 2H_L^2)(H_0^2 + H_L^2)^{-1}$  for  $\tau_L \ll T_1(\infty)$  as expected from physical arguments. In the intermediate case  $\tau_L \sim T_1(\infty)$  there are two exponential terms in the relaxation function, so that the rate one measures depends on how the measurement is made. Non-exponential behavior was not observed in this region,  $3 \text{ G} \leq H_0 \leq 10 \text{ G}$ , though it may have been masked by the scatter of the data.

At this point we must ask how large the nonsecular dipolar terms  $\mathcal{H}_{dd}^{(\pm 1, \pm 2)}$  need to be in order to account for the  $T_1$  versus  $H_0$  data in the fashion outlined above, i.e., in order to make  $\tau_L \sim T_1(\infty) = 0.3$  sec at  $H_0 = 10$  G. Calculating  $\tau_L$  with Eq. (A25), one finds that the total nonsecular dipolar terms (pseudodipolar plus classical dipolar) must be *smaller* by a factor of 5 than the corresponding classical dipolar terms. This is a rather startling result and seems unlikely in view of the large contribution of the pseudodipolar terms to the high-field second moment.<sup>35</sup> However, the destructive interference of classical dipolar and pseudodipolar terms necessary to explain this is not unfeasible, since the pseudodipolar interaction was found to have an oscillatory radial dependence in the simple case for which it has been calculated.<sup>23</sup> Further experimentation is required to resolve these questions; some experiments which would accomplish this are suggested in Sec. V.

#### IV. CALCULATION OF ZEEMAN SPIN-SPIN RELAXATION TIMES

The density matrix equations of motion for the Pt<sup>195</sup> spin system in platinum metal are used here to calculate the Zeeman spin-spin relaxation times  $\tau_e$  and  $\tau_L$  introduced in Sec. II. The detailed calculations are carried out in Appendix A using the well-known time-dependent perturbation method<sup>36</sup> as applied to this problem by Provotorov.<sup>18</sup> These calculations are essentially an extension of Provotorov's work to the case of high rf fields. For this purpose a somewhat different approach to the problem is used, which is felt to be in keeping with Redfield's original conception of the rotating frame spin temperature. As we develop this approach, particular attention is paid to the approximations involved in the perturbation method.

We begin by discussing the nuclear-spin Hamiltonian for platinum in the absence of time-dependent magnetic fields. This is given by  $\mathcal{H} = \mathcal{H}_Z + \mathcal{H}_{SS}$ , where  $\mathcal{H}_Z = -\omega_0 I_z$  ( $I_z = \sum_i I_{zi}$ ) is the Zeeman term and  $\mathcal{H}_{SS}$  is the total spin-spin interaction.  $\mathcal{H}_{SS}$  consists of a predominant Ruderman-Kittel indirect exchange term

$$\mathcal{H}_{ex} = \sum_{i>j} J_{ij} \mathbf{I}_i \cdot \mathbf{I}_j$$

and a dipolar-type term  $\mathcal{H}_{dd}$  made up of both classical dipolar<sup>37</sup> and pseudodipolar<sup>23</sup> contributions. All Hamiltonian operators are expressed in units of radians/second. It is important for this discussion to divide  $\mathcal{H}_{dd}$  into its various components which change the magnetic quantum number of the spin system by either zero, one, or two units. Thus

$$\mathcal{H}_{dd} = \sum_{\Delta m = -2}^2 \mathcal{H}_{dd}^{(\Delta m)}. \quad (25)$$

<sup>35</sup> See Appendix C for an evaluation of the pseudodipolar contribution to the platinum high-field second moment.

<sup>36</sup> Reference 27, Chap. VIII.

<sup>37</sup> J. H. Van Vleck, Phys. Rev. 74, 1168 (1948).

$\mathcal{H}_{dd}^{(0)}$  is the secular part of  $\mathcal{H}_{dd}$  which, like  $\mathcal{H}_{ex}$ , commutes with  $\mathcal{H}_z$ . The other terms of  $\mathcal{H}_{dd}$  do not commute with  $\mathcal{H}_z$  and, as we shall see, give rise to the dc field Zeeman spin-spin relaxation process.

Because of the pseudodipolar contribution to  $\mathcal{H}_{dd}$ , neither the magnitude nor the radial dependence of the dipolar coupling coefficients is known. Furthermore, as pointed out by Abragam,<sup>27</sup> the relative magnitude of the various  $\Delta m$  components of the pseudodipolar interaction is not known in general. Thus, for example, the magnitude of  $\mathcal{H}_{dd}^{(0)}$  implies nothing about the terms  $\mathcal{H}_{dd}^{(\Delta m)}$ ,  $\Delta m \neq 0$ .

One may estimate the magnitude of the secular portion of the pseudodipolar interaction from its contribution to the high-field second moment  $\langle \Delta\omega^2 \rangle$ . The latter quantity is found experimentally to be larger by a factor of roughly 6 than can be accounted for by the classical dipolar interactions alone. Assuming, then, that the coefficients in  $\mathcal{H}_{dd}^{(0)}$  have the same radial dependence as their classical counterparts, one would estimate that the pseudodipolar coupling coefficient is either 1.5 or  $-3.5$  times the classical one. The calculations using  $\mathcal{H}_{dd}^{(0)}$  are carried out here with a total dipolar interaction operator given by  $2.5\mathcal{H}_{dd}^{(0)}$  (classical). This procedure is justified only by the success of the results.

At present there is virtually nothing known about the size of the terms  $\mathcal{H}_{dd}^{(\Delta m)}$ ,  $\Delta m \neq 0$ . The discussion in Sec. III-C may give a hint as to their magnitude, but a conclusive analysis can come only from further experimentation.

In the calculations to follow, it is assumed that  $\mathcal{H}_{dd}$  is a small perturbation on the total spin-spin interaction operator  $\mathcal{H}_{dd} + \mathcal{H}_{ex}$ . To justify this approximation we shall content ourselves with a comparison of  $\mathcal{H}_{dd}^{(0)}$  and  $\mathcal{H}_{ex}$ . The relative magnitudes of these terms can be estimated from their respective contributions to the local field  $H_L'$  defined by  $H_L'^2 = \text{Tr}(\mathcal{H}_{ex}^2 + \mathcal{H}_{dd}^{(0)2}) / \gamma^2 \text{Tr}I_z^2$ . We evaluate  $\text{Tr}\mathcal{H}_{ex}^2$  using the nearest-neighbor exchange coupling constant measured by Froidevaux and Weger,<sup>22</sup>  $J = 4.14$  kc/sec, assuming all other  $J_{ij}$ 's to be zero.  $\text{Tr}\mathcal{H}_{dd}^{(0)2}$  is obtained from the measured second moment  $\langle \Delta\omega^2 \rangle$  by means of the relation  $\text{Tr}\mathcal{H}_{dd}^{(0)2} = \text{Tr}I_z^2 \langle \Delta\omega^2 \rangle / 3$ . Combining these, one finds

$$H_L'^2 = [(0.013)_{dd} + (0.987)_{ex}] \times 31.2 \text{ G}^2. \quad (26)$$

It is apparent from this comparison that  $\mathcal{H}_{dd}^{(0)}$  may indeed be considered a small perturbation. We shall assume in calculating  $\tau_L$  that the same holds true for the other terms of  $\mathcal{H}_{dd}$ .

Lumping the nonsecular terms of  $\mathcal{H}_{dd}$  into the perturbation operator  $\mathcal{H}_p = \sum_{\Delta m \neq 0} H_{dd}^{(\Delta m)}$  and expressing the secular spin-spin terms as  $\mathcal{H}_{SS}^{(0)} = \mathcal{H}_{ex} + \mathcal{H}_{dd}^{(0)}$ , one may write the equation of motion for the laboratory frame nuclear spin density matrix  $\rho$  as

$$i(d/dt)\rho = [(\mathcal{H}_Z + \mathcal{H}_p + \mathcal{H}_{SS}^{(0)}), \rho]. \quad (27)$$

This is the equation used by Hartmann and Anderson<sup>17</sup> to calculate  $\tau_L$ , where  $\mathcal{H}_p$  is considered to be a perturbation which couples energy between the Zeeman reservoir ( $\mathcal{H}_Z$ ) and the spin-spin reservoir ( $\mathcal{H}_{SS}^{(0)}$ ). This approach has also been used successfully by Hartmann<sup>38</sup> to calculate the Zeeman spin-spin relaxation time for solid He<sup>3</sup>.

The validity of the perturbation approximation for  $\mathcal{H}_p$  is closely connected with the spin-temperature assumption used in describing the states of the energy reservoirs  $\mathcal{H}_Z$  and  $\mathcal{H}_{SS}^{(0)}$ . If  $\mathcal{H}_p$  is truly a small perturbation, then  $\tau_L$  will be long compared with the correlation time  $\tau_c \sim (\gamma H_L')^{-1}$  of the dipolar interaction fields.  $\tau_c$  is also, however, the time constant for the approach to thermal equilibrium within the reservoirs  $\mathcal{H}_S$  and  $\mathcal{H}_{SS}^{(0)}$ , so that the relation  $\tau_c \ll \tau_L$  is required in order to use the spin-temperature representation for these reservoirs. The Zeeman spin-spin relaxation process for a system having  $\tau_c \sim \tau_L$  has been investigated by Strombotne and Hahn<sup>39</sup> and found to be oscillatory. For such a case the description of this relaxation process by means of a single relaxation time is no longer useful. For platinum  $\tau_c$  is of the order of  $25 \mu\text{sec}$ , which is an order of magnitude shorter than any of the relaxation times calculated. This justification of the perturbation approximation is equivalent to Eq. (26).

Next we develop the analog of Eq. (27) above for the rotating frame case. This is done by adding an rf-field Hamiltonian term

$$\mathcal{H}_{rf} = -2\gamma H_1 \cos\omega t \sum_i I_{yi}$$

to the equation of motion above and transforming  $\rho$  according to

$$\rho = \exp(i\omega t I_z) \rho_r \exp(-i\omega t I_z). \quad (28)$$

Using  $\omega_1 = \gamma H_1$  and  $\Delta\omega = \omega_0 - \omega$ , the transformed equation of motion for  $\rho_r$  is

$$i\dot{\rho}_r = [(-\Delta\omega I_z - \omega_1 I_y + \mathcal{H}_{SS}^{(0)}), \rho_r]. \quad (29)$$

This is the equation upon which Provotorov<sup>18</sup> based his calculation of the time constant for the approach to equilibrium in the rotating frame. This calculation proceeds by considering the rf-field term  $-\omega_1 I_y$  to be a perturbation operator which couples energy between the other two terms. This procedure leads to a simple and useful result, relating the Zeeman spin-spin relaxation time (which we shall call  $\tau_z$ ) to the measured absorption line-shape function  $g(\omega)$ . The calculation, which was originally carried out for the case of purely dipolar interactions, is easily modified to include the effects of exchange coupling. Under these conditions the perturbation approximation for the rf coupling field is valid in the limit  $H_1 \ll (\gamma T_2)^{-1}$ . For platinum  $(\gamma T_2)^{-1}$

<sup>38</sup> S. R. Hartmann, Phys. Rev. **133**, A17 (1964).

<sup>39</sup> R. L. Strombotne and E. L. Hahn, Phys. Rev. **133**, A1616 (1964).

=0.16 G, so that the above condition is violated for both of the experiments reported in Sec. III.

We now show that Provotorov's calculation can be extended to high rf fields by transforming the equation of motion into a reference frame where the axis of quantization is along the effective field  $\mathbf{H}_e$  as discussed in Sec. II (see Fig. 2). This is accomplished by the transformation

$$\rho_r = \exp(i\theta I_x) \rho_e \exp(-i\theta I_x), \quad (30)$$

where  $\theta = \tan^{-1}(\omega_1/\Delta\omega)$ . The equation of motion for  $\rho_e$  is

$$i\dot{\rho}_e = [(-\omega_e I_z + \mathcal{H}_{pe} + \mathcal{H}_{SS}^{(0)}), \rho_e], \quad (31)$$

where  $\omega_e = \gamma H_e$ , and  $\mathcal{H}_{pe}$  and  $\mathcal{H}_{SS}^{(0)}$  are the secular and nonsecular parts, respectively, of the transformed spin-spin interaction operator  $\exp(-i\theta I_x) \mathcal{H}_{SS}^{(0)} \exp(+i\theta I_x)$ . This equation was first derived in Schrödinger form by Redfield.<sup>1</sup> Since  $\mathcal{H}_{ex}$  is unaltered by the rotational transformations leading to Eq. (31), the rotating frame perturbing operator  $\mathcal{H}_{pe}$  consists of dipolar terms of the order of  $\mathcal{H}_{dd}^{(0)}$  or smaller. It follows that the dominant term in both  $\mathcal{H}_{SS}^{(0)}$  and  $\mathcal{H}_{SS}^{(0)}$  is  $\mathcal{H}_{ex}$ . In close analogy, then, with Eq. (27) we may consider  $\mathcal{H}_{pe}$  to be a small perturbation which couples between the rotating-frame Zeeman ( $-\omega_e I_z$ ) and spin-spin ( $\mathcal{H}_{SS}^{(0)}$ ) reservoirs.

The difference between Eqs. (31) and (29) as applied to the approach to equilibrium in the rotating frame is that in the latter case one is calculating the motion of  $M_e$ , the component of nuclear magnetization parallel to  $\mathbf{H}_e$ , rather than  $M_z$ . Further, Eq. (31) shows that one may consider the nonsecular dipolar terms as the perturbation operator rather than the rf field. The neglect of components of  $\mathbf{M}$  perpendicular to  $\mathbf{H}_e$  in the present experiments is discussed in detail in Appendix B. It is interesting that the relaxation times  $\tau_e$  and  $\tau_z$  calculated for platinum using these two rather different approaches become essentially identical in the limit  $\Delta\omega \gg \omega_1$  [see Eqs. (13) and (14) above].

The perturbation formalism developed by Provotorov<sup>18</sup> is applied to Eq. (31) in Appendix A and is shown to lead to an equation of the form of Eq. (3) in Sec. II, the time constant being identified, of course, as  $\tau_e$ . The perturbation approximation for  $\mathcal{H}_{pe}$  is valid in the case of platinum for arbitrary values of  $H_1$ . The present experiments test this result only for values  $H_1 \ll H_L'$ . The derived expression for  $\tau_e$  is converted to  $\tau_L$  in Appendix A by a simple change of perturbation operators. The result is equivalent to that given by Hartmann and Anderson.

## V. CONCLUSIONS AND DISCUSSION

The rotating-frame Zeeman spin-spin relaxation process in platinum metal has been found to be consistent with the thermodynamic view of this problem implied by the existence of a nuclear spin temperature in the rotating frame. The thermodynamic approach first developed by Provotorov<sup>18</sup> regards the nmr satura-

tion process in solids as an exchange of energy between the rotating-frame Zeeman and spin-spin reservoirs generated by the perturbing rf field. The associated relaxation calculations are limited to rf-field values smaller than the nmr linewidth. These relaxation time calculations have been extended to higher rf fields by considering the rf magnetic field as part of the Zeeman reservoir and by using nonsecular terms of the rotating frame dipolar Hamiltonian as the perturbation operators. In the latter approach, then, the rf field is seen as giving rise to nonsecular dipolar terms which couple the Zeeman and spin-spin reservoirs, rather than in the traditional role of causing energy absorption directly. This procedure is closely analogous to the calculation of dc-field Zeeman spin-spin relaxation times by Hartmann and Anderson<sup>17</sup> and the calculation of the Zeeman-exchange relaxation process in solid He<sup>3</sup> by Hartmann<sup>18</sup> as part of the spin-lattice relaxation rate. Relaxation times  $\tau_e$  calculated in this fashion have been found to be in good agreement with both steady-state and transient experiments; such relaxation times were found also to reduce essentially to the result given by Provotorov (as adapted to the case of platinum metal) under conditions where these calculations can be compared.

The above approach to the phenomenon of nmr saturation in high rf fields is particularly useful in the case of platinum metal, because the dipolar coupling terms are truly a small perturbation owing to the presence of a predominant nuclear spin exchange interaction. It is interesting to look beyond this special case for possible applications of these ideas, e.g., to the case of purely dipolar interactions between abundant nuclear species. For such a system we must require the nonsecular dipolar terms in the rotating frame to be small compared with the total spin-spin reservoir. This in effect requires that  $\theta \ll \pi/2$ , where  $\theta$  is the angle between the rotating frame effective field  $\mathbf{H}_e$  and the external field  $\mathbf{H}_0$ . Under these conditions the calculation of  $\tau_e$  outlined in Sec. IV applies to nuclear spin systems having an arbitrary configuration of spin-spin interactions (in the absence of quadrupole effects). This approach needs, of course, to be confirmed experimentally.

It is further observed that the strong dispersion narrowing effect predicted and measured for platinum in the case of  $\tau_0$  (or  $T_2$ )  $\sim T_1$  does not apply to the case of arbitrary spin-spin coupling. We recall that this effect depends on the satisfaction of two conditions, (1) extreme saturation, i.e.,  $\gamma^2 H_1^2 T_2 T_1 \gg 1$ , and (2) the condition  $\Delta \gg 1$ , where

$$\Delta = 2\tau_0 H_L'^2 / H_1^2 T_1.$$

If we estimate  $\tau_0 \sim T_2$ , then the latter condition may be written

$$2\gamma^2 T_2^2 H_L'^2 / (\gamma^2 H_1^2 T_2 T_1) \gg 1. \quad (32)$$

If  $(\gamma T_2)^{-1} \sim H_L'$ , as is true for many systems, then the numerator in this relationship is of the order of unity. The denominator is the saturation parameter, which

must be large. Such systems are thus limited to  $\Delta \ll 1$ , i.e., to only slight narrowing according to Eq. (17). Appreciable dispersion narrowing with this mechanism should occur for spin systems where  $(\gamma T_2)^{-1} \ll H_L'$ . This condition is presumably satisfied by a weak or rare spin system immersed in a matrix of large, abundant nuclear moments. The abundant spins give rise to a value of  $H_L'$  which will in general be larger than the linewidth of the weak resonance. Dispersion narrowing effects in such systems are subject to further investigation.

Good agreement with experiment has been found for platinum by basing the calculations of  $\tau_e$  on a secular dipolar coupling term given by  $\mathcal{H}_{dd}^{(0)} = 2.5\mathcal{H}_{dd}^{(0)}$  (classical). The success of this procedure holds no implications about the form of the pseudodipolar contribution to  $\mathcal{H}_{dd}^{(0)}$ , since the essential relationship used here is  $\langle \Delta\omega^2 \rangle = 3 \text{Tr}(\mathcal{H}_{dd}^{(0)2}) / \text{Tr}I_z^2$ . This relation is independent of the radial dependence of the coupling coefficients in  $\mathcal{H}_{dd}^{(0)}$ . The agreement found with this approach merely shows the consistency of the Anderson-Weiss model used to obtain a value for  $\langle \Delta\omega^2 \rangle$  (see Appendix C) and the formalism used to calculate  $\tau_e$ .

In reviewing the  $T_1$  versus  $H_0$  data for platinum published earlier, it is suggested above (Sec. III-C) that a distortion of these data may have arisen from anomalously weak Zeeman-exchange coupling for platinum in small dc fields. In the absence of further data this suggestion is purely conjectural. Aside from further measurements of  $T_1$  versus  $H_0$  there are two experiments which could shed light on this matter. First, one could perform nonadiabatic field switching to fields  $H_0$  of the order of  $H_L$  for times short compared with  $T_1$  and measure  $\tau_L$  directly. Alternately, and perhaps more difficult, one could measure  $T_2$  at fields of the order of  $H_L$  in order to observe the low-field increase in the second moment due to the nonsecular components of  $\mathcal{H}_{dd}$ . For dipolar interactions of the classical form one expects  $\langle \Delta\omega^2 \rangle$  to increase at low fields by a factor of 10/3. If these nonsecular components are anomalously small (as is implied by long values for  $\tau_L$ ) one should observe a much smaller increase in  $\langle \Delta\omega^2 \rangle$ . These experiments could be done at 1°K, i.e., the special cooling methods used to measure  $T_1$  versus  $H_0$  would be unnecessary.

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#### APPENDIX A

Expressions for  $\tau_e$  and  $\tau_L$  are evaluated for the case of Pt<sup>195</sup> in platinum metal, using the formalism given by Provotorov.<sup>18</sup> This formalism is equivalent to that used by Hartmann<sup>38</sup> to interpret Zeeman-exchange relaxation effects in solid He<sup>3</sup>. We use the former scheme in order to make a direct comparison with Provotorov's results.

We begin with the equation of motion [Eq. (31)] for the density matrix in the rotating frame, bearing in mind that the same reasoning may be carried through with the laboratory frame Eq. (27). We identify from Eq. (31) above the perturbation operator analogous to Provotorov's<sup>18</sup> Eq. (10) as<sup>40</sup>

$$V(t) = \exp[-i(\omega_e I_z - \mathcal{H}_{SS}^{(0)})t] \mathcal{H}_{pe} \times \exp[+i(\omega_e I_z - \mathcal{H}_{SS}^{(0)})t], \quad (\text{A1})$$

where

$$\mathcal{H}_{pe} = \sum_{i>j} B_{ij}' [(\sin\theta \cos\theta/2)(I_i^+ I_{jz} + I_{iz} I_j^+) + (I_i^- I_{jz} + I_{iz} I_j^-) + (\sin^2\theta/4)(I_i^+ I_j^+ + I_i^- I_j^-)] \quad (\text{A2})$$

and  $B_{ij}' = \frac{3}{2}\alpha\gamma^2\hbar r_{ij}^{-3}(3\cos^2\theta_{ij} - 1)$ .  $\mathcal{H}_{pe}$  is the same as given by Redfield,<sup>1</sup> except that a factor  $\alpha$  has been introduced into  $B_{ij}$  (hence  $B_{ij}'$ ) to account for the secular part of the pseudodipolar interaction, which is assumed for these purposes to have the same radial dependence as the classical one.  $|\alpha|$  is found in Appendix C to equal 2.5. We distinguish the various terms  $\mathcal{H}_{pe}^{(\pm 1)}$ ,  $\mathcal{H}_{pe}^{(\pm 2)}$  in an obvious way from Eq. (A2). The calculation then proceeds from Provotorov's perturbation expansion for  $\rho_1(t)$ , which is the portion of the rotating frame density matrix  $\rho_e'$  that is diagonal in the representation generated by the Hamiltonian  $\mathcal{H}_{e0} = -\omega_e I_z + \mathcal{H}_{SS}^{(0)}$ , where  $\rho_e'$  satisfies the equation  $i\dot{\rho}_e' = [V(t), \rho_e']$ . Provotorov's Eq. (17) gives for  $\rho_1(t)$

$$\rho_1(t + \Delta t) - \rho_1(t) = \int_t^{t+\Delta t} dt'' \int_0^{t''} dt' \times \hat{P}[V(t''); \rho_1(t')], \quad (\text{A3})$$

where  $\hat{P}$  is a projection operator giving the diagonal portion of operators which follow [e.g.,  $\rho_1(t) = \hat{P}\rho_e'(t)$ ].  $\Delta t$  in Eq. (3) is limited by the requirement  $\tau_e \sim (\gamma H_L')^{-1} \ll \Delta t \ll \tau_e$ , where  $\tau_e$  is the relaxation time to be calculated. Following Provotorov, we define the spectral densities of the operators

$$\mathcal{H}_{pe}^{(\Delta m)}(t) = \exp(i\mathcal{H}_{SS}^{(0)}t) \mathcal{H}_{pe}^{(\Delta m)} \exp(-i\mathcal{H}_{SS}^{(0)}t)$$

as

$$\mathcal{H}_{pe}^{(\Delta m)}(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt \mathcal{H}_{pe}^{(\Delta m)}(t) e^{-i\omega t}, \quad \Delta m = \pm 1, \pm 2. \quad (\text{A4})$$

The calculation proceeds by substituting the  $V$ 's into Eq. (A3) in terms of the spectral densities given by Eq. (A4). The remaining steps of the calculation follow Provotorov's treatment closely and are not repeated here. Using the limits on  $\Delta t$  given above, one finds for

<sup>40</sup> This entire calculation is carried out in the primed coordinate system in Fig. 2. For convenience all primes are omitted from spin operators here.

the result analogous to Provotorov's Eq. (22)

$$\dot{\rho}_1(t) = -2\pi\hat{P}'\{[\mathfrak{J}\mathcal{C}_{pe}^{(1)}(\omega_e); \mathfrak{J}\mathcal{C}_{pe}^{(-1)}(-\omega_e), \rho_1(t)] \\ + [\mathfrak{J}\mathcal{C}_{pe}^{(2)}(2\omega_e); \mathfrak{J}\mathcal{C}_{pe}^{(-2)}(-2\omega_e), \rho_1(t)]\}, \quad (\text{A5})$$

where  $\hat{P}'$  eliminates singular functions of the form of  $\delta(\omega)|_{\omega=0}$  as well as performing the function of  $\hat{P}$ . Equation (A5) is the central result of the calculation, which will now be used to derive the rotating frame version of Eq. (4) in Sec. II. In analogy with Provotorov's result, Eq. (A5) may easily be shown to imply conservation of energy  $\langle -\omega_e I_z + \mathfrak{J}\mathcal{C}_{SS}^{(00)} \rangle$  in the rotating frame.

To derive Eq. (4) we use Eq. (A5) to evaluate

$$(\dot{d}/dt)\langle M_e \rangle = \gamma \hbar \text{Tr}[I_z \dot{\rho}_1(t)], \quad (\text{A6})$$

making use of the thermal equilibrium density matrix stated in Sec. II. Evaluating both sides of Eq. (A6) we find

$$(\partial/\partial t)T_Z^{-1}|_{\tau} = -(1/\tau_e)(T_Z^{-1} - T_{SS}^{-1}), \quad (\text{A7})$$

where

$$(1/\tau_e) = (2\pi/\text{Tr}I_z^2) \\ \times \{ \text{Tr}[\hat{P}'I_z[\mathfrak{J}\mathcal{C}_{pe}^{(1)}(\omega_e); \mathfrak{J}\mathcal{C}_{pe}^{(-1)}(-\omega_e), I_z]] \\ + \text{Tr}[\hat{P}'I_z[\mathfrak{J}\mathcal{C}_{pe}^{(2)}(2\omega_e); \mathfrak{J}\mathcal{C}_{pe}^{(-2)}(-2\omega_e), I_z]] \}. \quad (\text{A8})$$

Appealing to the definition of  $\mathfrak{J}\mathcal{C}_{pe}^{(\Delta m)}(\omega)$  [Eq. (A4)] we may simplify the numerators of the right-hand side of Eq. (A8) to give

$$\frac{1}{\tau_e} = \sum_{\Delta m=1,2} (\Delta m)^2 \text{Tr} \int_{-\infty}^{\infty} dt e^{i\Delta m \omega_e t} \\ \times \mathfrak{J}\mathcal{C}_{pe}^{(\Delta m)}[\exp(i\mathfrak{J}\mathcal{C}_{SS}^{(00)}t)] \\ \times \mathfrak{J}\mathcal{C}_{pe}^{(-\Delta m)}[\exp(-i\mathfrak{J}\mathcal{C}_{SS}^{(00)}t)] / \text{Tr}I_z^2. \quad (\text{A9})$$

In order to evaluate Eq. (A9) further, we introduce

$$-\frac{1}{2} \text{Tr}\{[\mathfrak{J}\mathcal{C}_{ex}, \mathfrak{J}\mathcal{C}_{pe}^{(1)}][\mathfrak{J}\mathcal{C}_{ex}, \mathfrak{J}\mathcal{C}_{pe}^{(-1)}]\} = (\sin^2\theta \cos^2\theta/128)2^N \{ \sum_{ijk \neq} [J_{ij}^2(B_{ik}' - B_{jk}')^2 \\ - J_{ij}J_{jk}(B_{ik}' - B_{jk}')(B_{ik}' - B_{ij}') - \sum_{ij \neq j} J_{ij}^2 B_{ij}'^2] \}, \quad (\text{A13})$$

$$-\frac{1}{2} \text{Tr}\{[\mathfrak{J}\mathcal{C}_{ex}, \mathfrak{J}\mathcal{C}_{pe}^{(2)}][\mathfrak{J}\mathcal{C}_{ex}, \mathfrak{J}\mathcal{C}_{pe}^{(-2)}]\} = (\sin^4\theta/512)2^N \sum_{ijk \neq} [J_{ij}^2(B_{ik}' - B_{jk}')^2 + J_{ij}J_{jk}(B_{ik}' - B_{jk}')(B_{ik}' - B_{ij}')], \quad (\text{A14})$$

$$\text{Tr}[\mathfrak{J}\mathcal{C}_{pe}^{(1)}\mathfrak{J}\mathcal{C}_{pe}^{(-1)}] = [\sin^2\theta \cos^2\theta/32]2^N \sum_{ij \neq j} B_{ij}'^2, \quad (\text{A15})$$

$$\text{Tr}[\mathfrak{J}\mathcal{C}_{pe}^{(2)}\mathfrak{J}\mathcal{C}_{pe}^{(-2)}] = (\sin^4\theta/128)2^N \sum_{ij \neq j} B_{ij}'^2, \quad (\text{A16})$$

The isotropic averages of the lattice sums in Eq. (A13) to (A16) have been evaluated for the platinum fcc lattice in the approximation that  $J_{ij} = J = \text{constant}$  for nearest neighbors, zero otherwise. Substituting the resulting expressions into Eq. (A11) and inserting numerical values for the parameters involved it is found that

$$\tau_e^{-1}(1) = \tau_e^{-1}(2) = 1.45J. \quad (\text{A17})$$

the assumption of a Gaussian distribution of local fields. This approximation is roughly equivalent to the Gaussian model used by Anderson and Weiss<sup>24</sup> in their statistical theory of exchange narrowing. Such an approach to Eq. (A9) is necessitated by the lack of more detailed information about the frequency distributions involved. The Gaussian distribution assumption is expressed by the equation

$$\text{Tr}\{\mathfrak{J}\mathcal{C}_{pe}^{(\Delta m)}[\exp(i\mathfrak{J}\mathcal{C}_{SS}^{(00)}t)]\mathfrak{J}\mathcal{C}_{pe}^{(-\Delta m)}[\exp(-i\mathfrak{J}\mathcal{C}_{SS}^{(00)}t)]\} \\ \cong \text{Tr}[\mathfrak{J}\mathcal{C}_{pe}^{(\Delta m)}\mathfrak{J}\mathcal{C}_{pe}^{(-\Delta m)}]e^{-t^2/\tau_e^2(\Delta m)}. \quad (\text{A10})$$

$\tau_e(\Delta m)$  is evaluated by expanding both sides of Eq. (A10) to second order in  $t$  and equating coefficients of  $t^2$ . This gives

$$[1/\tau_e^2(\Delta m)] \\ = -\frac{1}{2} \text{Tr}\{[\mathfrak{J}\mathcal{C}_{SS}^{(00)}, \mathfrak{J}\mathcal{C}_{pe}^{(\Delta m)}][\mathfrak{J}\mathcal{C}_{SS}^{(00)}, \mathfrak{J}\mathcal{C}_{pe}^{(-\Delta m)}]\} / \\ \text{Tr}[\mathfrak{J}\mathcal{C}_{pe}^{(\Delta m)}\mathfrak{J}\mathcal{C}_{pe}^{(-\Delta m)}]. \quad (\text{A11})$$

Using Eq. (A10), Eq. (A9) may now be evaluated to give

$$\tau_e^{-1} = (\pi^{1/2}/\text{Tr}I_z^2) \sum_{\Delta m=1,2} [(\Delta m)^2 \tau_e(\Delta m) \\ \times \text{Tr}(\mathfrak{J}\mathcal{C}_{pe}^{(\Delta m)}\mathfrak{J}\mathcal{C}_{pe}^{(-\Delta m)})e^{[-\Delta m^2 \tau_e^2(\Delta m) \omega_e^2/4}]] \quad (\text{A12})$$

for the final result.

In order to get a numerical value for  $\tau_e$  we first evaluate  $\tau_e(1)$  and  $\tau_e(2)$  from the definition Eq. (A11). These calculations are done in the limit of large exchange, namely by letting  $\mathfrak{J}\mathcal{C}_{SS}^{(00)} \cong \mathfrak{J}\mathcal{C}_{ex}$  and ignoring the effects of the smaller dipolar terms in  $\mathfrak{J}\mathcal{C}_{SS}^{(00)}$ .

On this assumption, then, the numerators and denominators of Eq. (A11) for  $\Delta m=1, 2$  are found, on evaluating traces and specializing to  $I = \frac{1}{2}$ , to be

Using the value for  $J$  stated in Sec. I, we find

$$\tau_e = 26 \mu\text{sec}, \quad (\text{A18})$$

where the indices 1 and 2 have been dropped because of the equality expressed in Eq. (A17). This equality is good to one part in  $10^8$  in the large exchange approximation.

With the evaluated expressions in Eqs. (A15) and

(A16), we find from Eq. (A12)

$$\tau_e^{-1} = 8.93 \times 10^2 \frac{H_1^2}{H_e^2} \left[ \frac{\Delta H^2}{H_e^2} e^{-5.8 \times 10^{-2} H_e^2} + \frac{H_1^2}{H_e^2} e^{-2.31 \times 10^{-2} H_e^2} \right] \text{sec}^{-1}. \quad (\text{A19})$$

For  $H_e \ll H_L'$  the bracketed expression in Eq. (A19) is very nearly one, hence we may say

$$\tau_e \cong \tau_0 H_e^2 / H_1^2, \quad H_e \ll H_L', \quad (\text{A20})$$

where  $\tau_0 = 1.1$  msec.

Let us compare the result for  $\tau_e$  [Eq. (A20)] with Provotorov's results for the analogous relaxation time  $\tau_z$ . From Provotorov's Eq. (35), analogous to Eq. (A7) above, one may identify

$$\tau_z^{-1} = (\gamma H_1)^2 \pi g(\Delta\omega), \quad (\text{A21})$$

where  $g(\Delta\omega)$  is the normalized nmr absorption lineshape function. The platinum nmr lineshape is known to be Lorentzian for  $\Delta\omega < \gamma H_L'$  because of the exponential free-induction decay functions observed for this metal.<sup>21</sup> We therefore take  $g(\Delta\omega) = T_2 \pi^{-1} (1 + \Delta\omega^2 T_2^2)^{-1}$ , whereupon Eq. (A21) becomes

$$\tau_z^{-1} \cong \gamma^2 H_1^2 T_2 / (1 + \Delta\omega^2 T_2^2). \quad (\text{A22})$$

Under conditions where  $\tau_e$  and  $\tau_z$  are comparable (see Appendix B), i.e., for  $\Delta H \gg H_1$ ,  $(T_2 \gamma)^{-1}$ , one has

$$T_2 \cong T_2 \Delta H^2 / H_1^2, \quad (\text{A23})$$

where  $T_2 = 1.1$  msec.<sup>41</sup> This is remarkably close to the result in Eq. (A20).

There is an interesting similarity between  $\tau_z$  given by Eq. (A21) and  $\tau_e$  given by Eq. (A9). From the latter equation we may interpret  $\tau_e^{-1}$  as being a measure of the spectral densities of the autocorrelation functions of the operators  $\mathcal{H}_{pe}^{(\pm 1)}$  and  $\mathcal{H}_{pe}^{(\pm 2)}$  at frequencies  $\omega_e$  and  $2\omega_e$ , respectively. Correspondingly, it is well known that  $g(\Delta\omega)$  and therefore  $\tau_z^{-1}$  is a measure of the spectral density of the autocorrelation function of the operator  $I_x$  at frequency  $\Delta\omega$ . The spectral density functions for  $\mathcal{H}_{pe}^{(\pm 1)}$  and  $\mathcal{H}_{pe}^{(\pm 2)}$  are not individually measurable in a direct way as is  $g(\Delta\omega)$ , hence it is necessary to make some approximation for their shape in order to use the present theory. Nevertheless, the autocorrelation function spectral densities for  $\mathcal{H}_{pe}^{(\pm 1, \pm 2)}$  provide an equally valid, though less familiar, characterization of the spin system as  $g(\Delta\omega)$ .

Finally, the above results are used to obtain an expression for  $\tau_L$  by introducing the appropriate changes in parameters. We may take the result Eq. (A12) over directly by replacing  $\mathcal{H}_{pe}^{(\Delta m)}$  with the laboratory frame nonsecular components of the dipolar

interaction  $\mathcal{H}_{dd}^{(\Delta m)}$ . We must also redefine  $\tau_c(\Delta m)$  as

$$[\tau_c'(\Delta m)]^{-2} = -\frac{1}{2} \text{Tr} \{ [\mathcal{H}_{SS}^{(0)}, \mathcal{H}_{dd}^{(\Delta m)}] [\mathcal{H}_{SS}^{(0)}, \mathcal{H}_{dd}^{(-\Delta m)}] \} / \text{Tr} [\mathcal{H}_{dd}^{(\Delta m)} \mathcal{H}_{dd}^{(-\Delta m)}]. \quad (\text{A24})$$

One has, then, for  $\tau_L$

$$\tau_L^{-1} = \frac{\pi^{1/2}}{\text{Tr} I_z^2} \sum_{\Delta m=1,2} [\Delta m^2 \tau_c'(\Delta m) \times \text{Tr} (\mathcal{H}_{dd}^{(\Delta m)} \mathcal{H}_{dd}^{(-\Delta m)}) e^{-\Delta m^2 \tau_c'(\Delta m) \omega_e^2 / 4}]. \quad (\text{A25})$$

For rough calculations it is probably a reasonable assumption that  $\tau_c'(1) \cong \tau_c'(2) \cong \tau_e$  given in Eq. (A17). Nothing is known of the strength or spatial dependence of the terms  $\mathcal{H}_{dd}^{(\Delta m)}$  because of the strong pseudodipolar coupling. A tentative estimate of the size of these terms from  $T_1$  versus  $H_0$  data is given in Sec. III-C.

## APPENDIX B

The use of relaxation times  $\tau_e$  and  $\tau_z$  (introduced in Secs. II and III) for interpreting Zeeman spin-spin relaxation processes in the rotating frame is discussed here. It is shown that, in the case of predominant exchange,  $\tau_z$  is only appropriate for rf fields  $H_1 < (\gamma T_2)^{-1}$ , whereas  $\tau_e$  applies to the case  $H_1 > (\gamma T_2)^{-1}$ , i.e., to the present data on platinum.

It has been noted above that  $\tau_e$  and  $\tau_z$  describe the relaxation of magnetization components parallel to  $\mathbf{H}_e$  and  $\mathbf{H}_0$ , respectively. For  $\Delta H \gg H_1$ ,  $\mathbf{H}_e$ , and  $\mathbf{H}_0$  are nearly parallel, and the identities of  $\tau_e$  and  $\tau_z$  merge. For  $\Delta H \sim H_1$ , however, one must choose between these relaxation times according to which axis the magnetization lies parallel to during the bulk of the relaxation process.

Equation (31) has been used to study the relaxation of the longitudinal  $z'$  component (see Fig. 4) of magnetization  $M_e$  in the rotating frame. We now apply this equation to a qualitative study of the relaxation processes of the transverse, nonenergy-bearing  $x'$  and  $y'$  components. Let us characterize these processes with relaxation times  $\tau_{x'}$  and  $\tau_{y'}$ . Because these components have no energy in the rotating frame, they decay to zero in the course of the relaxation process for all values of  $\Delta H$  (if  $\gamma^2 H_1^2 T_1 T_2 \gg 1$ ).

We begin by transforming Eq. (31) into a reference frame rotating about the  $z'$  axis at a frequency  $\omega_e$ . This is accomplished with

$$\rho_e = e^{(i\omega_e I_{z'} t)} \rho_e'' e^{(-i\omega_e I_{z'} t)}, \quad (\text{B1})$$

giving

$$i\dot{\rho}_e'' = [e^{(-i\omega_e I_{z'} t)} e^{(i\theta I_x)} \mathcal{H}_{dd}^{(0)} e^{(-i\theta I_x)} e^{(i\omega_e I_{z'} t)} + \mathcal{H}_{ex}], \rho_e'', \quad (\text{B2})$$

where  $\mathcal{H}_{SS}^{(0)} = \mathcal{H}_{dd}^{(0)} + \mathcal{H}_{ex}$  has been substituted,  $\mathcal{H}_{ex}$  being unaffected by the transformations. In interpreting Eq. (B2) with regard to transverse relaxation processes, it is noted that only the first term, which we shall call

<sup>41</sup> This is a measured value of  $T_2$ , obtained by the  $(\pi/2) - \pi$  pulse-spin-echo method. It is considered to be more accurate than the value  $T_2 = 1.05$  msec originally reported (Ref. 21).

$\mathcal{H}_{\text{broad}}(t)$ , gives rise to a direct decay process for  $M_{x'}$  or  $M_{y'}$ , since  $\mathcal{H}_{\text{ex}}$  commutes with these magnetization operators. The strength of the decay processes depends on the noncommuting part of this first term. The effect of  $\mathcal{H}_{\text{ex}}$  is to impose a spin-flip modulation on the broadening terms, weakening the decay processes in exchange-narrowing fashion.

Using  $\mathcal{H}_{\text{ad}}^{(0)} = \sum_{i>j} B_{ij}' [I_{zi} I_{zj} - \frac{1}{3} \mathbf{I}_i \cdot \mathbf{I}_j]$  we expand the first term in Eq. (B2). Here the second term in  $\mathcal{H}_{\text{ad}}^{(0)}$  is unaffected by the indicated transformations and is ignored. Thus

$$\begin{aligned} \mathcal{H}_{\text{broad}}(t) &= \sum_{i>j} B_{ij}' [I_{x'i} \cos \theta - (I_{y'i} \cos \omega_e t - I_{x'i} \sin \omega_e t) \sin \theta] \\ &\quad \times [I_{x'j} \cos \theta - (I_{y'j} \cos \omega_e t - I_{x'j} \sin \omega_e t) \sin \theta]. \quad (\text{B3}) \end{aligned}$$

First one observes that for  $\theta \sim 0, \pi$  the broadening terms for  $M_{x'}$ ,  $M_{y'}$  are large, giving  $\tau_{x'} \cong \tau_{y'} \cong T_2$ . The critical region, however is  $\theta \sim \pi/2$ . For  $\theta = \pi/2$  we may rewrite Eq. (B3) as

$$\begin{aligned} \mathcal{H}_{\text{broad}}(t) &= \sum_{i>j} B_{ij}' [\frac{1}{2} (I_{x'i} I_{x'j} + I_{y'i} I_{y'j}) \\ &\quad + \frac{1}{2} \cos 2\omega_1 t (I_{y'i} I_{y'j} - I_{x'i} I_{x'j}) \\ &\quad + \frac{1}{2} \sin 2\omega_1 t (I_{x'i} I_{y'j} + I_{x'j} I_{y'i})]. \quad (\text{B4}) \end{aligned}$$

We distinguish three ranges of rf field values, (a)  $H_1 < (\gamma T_2)^{-1}$ , (b)  $(\gamma T_2)^{-1} < H_1 < \frac{1}{2} H_L'$ , and (c)  $H_1 > H_L'/2$ . (a) For very small  $H_1$ , we see that  $\mathcal{H}_{\text{broad}}$  commutes with  $I_{y'}$  except for terms  $\propto \omega_1 t$ . This is the region of validity of Provotorov's calculation of  $\tau_z = \tau_{y'}$  for which one expects  $\tau_{y'}^{-1} = \omega_1^2 T_2 < T_2^{-1}$ . In this region  $\tau_{y'} > \tau_e$ , so that the magnetization remains parallel to the  $z$  axis (i.e.,  $y'$  axis) during the relaxation process and  $\tau_e$  does not apply. (b) As  $H_1$  is increased,  $\tau_{y'}$  eventually shortens to  $\tau_{y'} \sim T_2$ . All terms in Eq. (B4) become operative, the  $(\cos, \sin) 2\omega_1 t$  time dependence being rapidly interrupted by the spin-flip modulation imposed on  $\mathcal{H}_{\text{broad}}$  by  $\mathcal{H}_{\text{ex}}$ . This is the region of the present data on platinum. Since  $\tau_{x'}, \tau_{y'} \cong T_2 = 1.1$  msec for all values of  $\Delta H$ , one expects  $M_{x'}$  and  $M_{y'}$  to have no influence on the dispersion measurements done with pulses of duration  $t_w = 6$  msec which were reported in Sec. III-A. (c) When  $2\omega_1 > J$ , the last two terms in Eq. (B4) average to zero, giving  $\tau_{x'} = \tau_{y'} \cong 4T_2$ . This region involves very large rf fields ( $H_1 > 3$  G) and was not touched upon in the present experiments.

For the present work, then, the condition  $t_w \gg \tau_{x'}, \tau_{y'}$  is always valid. Hence the components of magnetization perpendicular to  $\mathbf{H}_e$  in the rotating frame are thought to have no effect on the experimental results. By contrast, for  $H_1 < (\gamma T_2)^{-1}$  the component of magnetization parallel to  $\mathbf{H}_0$  has the longest relaxation time. Correspondingly, this is the relaxation time which one would measure in a "pulsed" dispersion experiment of the

present type. The rotating frame relaxation measurements of Goldberg<sup>5</sup> on NaCl were carried out under the latter condition.

### APPENDIX C

Lastly, the second moment of the exchange-narrowed platinum nmr line is evaluated from experimental values of  $T_2$  and the nearest-neighbor exchange coupling constant  $J$ . The central equation to be used is taken from the exchange-narrowing theory of Anderson and Weiss, namely

$$T_2^{-1} = \langle \Delta\omega^2 \rangle \tau_e'' \quad (\text{C1})$$

for extreme narrowing. Here  $T_2^{-1}$  is the observed decay rate of the free precession signal,  $\langle \Delta\omega^2 \rangle$  is the second moment arising from classical and pseudodipolar interactions, and  $\tau_e'' \sim J^{-1}$  is the correlation time of the dipolar local fields.  $\tau_e''$  is evaluated by equating the fourth moment expression from the Anderson-Weiss model to that given by Van Vleck. In the limit of large exchange this gives for  $I = \frac{1}{2}$ ,

$$\begin{aligned} \frac{\pi \langle \Delta\omega^2 \rangle}{2 \tau_e''^2} &= \frac{1}{8} N^{-1} \sum_{jkl \neq} [J_{jk}^2 (B_{jl}' - B_{kl}')^2 \\ &\quad + J_{jk} J_{kl} (B_{jl}' - B_{jk}') (B_{jl}' - B_{kl}')], \quad (\text{C2}) \end{aligned}$$

where  $N$  is the spin density and the summation is taken over all combinations of  $j, k$ , and  $l$  such that no two are alike. The right-hand side of Eq. (C2) has been evaluated for the fcc platinum lattice under the following conditions. (a)  $B_{jl}'$  has the same radial dependence as the classical dipolar coupling coefficient. (b)  $J_{jk}$  is constant ( $J$ ) for nearest neighbors, zero otherwise. (c) An average is taken over all field directions. Under these conditions, Eq. (C2) reduces to

$$\frac{\pi \langle \Delta\omega^2 \rangle}{2 \tau_e''^2} = 6.2 \times 10^2 J^2 \alpha^2 \gamma^4 \hbar^2 f^2 a^{-6}, \quad (\text{C3})$$

where  $\alpha$  is defined by  $B_{jl}' = \alpha B_{jl}$  (classical dipolar),  $f$  is the isotopic abundance of Pt<sup>195</sup>, and  $a$  is the lattice constant for platinum metal. Substituting the well-known expression for  $\langle \Delta\omega^2 \rangle$  one finds

$$1/\tau_e'' = 1.63J. \quad (\text{C4})$$

This is rather close to the value of  $\tau_e$  obtained in Appendix A for the  $\tau_e$  process, as one may expect. It is notable that within the framework of the above calculation,  $\tau_e''$  is independent of the size of  $B_{jl}'$  (as in Appendix A). Using the extrapolated value of  $J$  from the work of Froidevaux and Weger (see Sec. II) one finds  $\tau_e'' = 24$   $\mu\text{sec}$ . This, combined with  $T_2 = 1.1 \times 10^{-3}$  sec, gives from Eq. (C1)

$$\langle \Delta\omega^2 \rangle = 3.9 \times 10^7 \text{ (rad/sec)}^2, \quad (\text{C5})$$

which is about six times greater than the classical value  $\langle \Delta\omega^2 \rangle_{\text{cl}} = 6.35 \times 10^6 \text{ (rad/sec)}^2$ . Thus, in the approximation that  $B_{jl}'$  has the classical form, one has  $|\alpha| = 2.5$ .