High-Temperature Spin Dynamics of GdP via Transient Nuclear Magnetic Resonance*

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(Received 14 July 1971)

The magnetic field dependence of the longitudinal nuclear-spin relaxation time for ^{31}P nuclei in paramagnetic GdP is shown to yield the Fourier transform of the sum of two electronic-spin correlation functions. This represents a new experimental technique for the study of paramagnetic spin dynamics. A reasonable fit to a theoretical spectrum is achieved, and the resulting exchange strength agrees with that deduced from the Curie-Weiss temperature.

The purpose of this Letter is to demonstrate that the high-temperature magnetic field dependence of the longitudinal and transverse nuclear-spin relaxation times T_1 and T_2, respectively, can provide direct information about electronic-spin dynamics in paramagnets. Most importantly, it will be shown that under proper conditions the field dependence of T_1^{-1} corresponds to the spectral density function of a sum of two spin correlation functions. Such detailed information has previously been available only from inelastic neutron scattering.[1] The specific example treated here is GdP,[2] for which ^{31}P NMR data were obtained at room temperature.

The rare-earth phosphides have the NaCl structure and are metallic.[3] Gadolinium phosphide differs from the other compounds of this series in that the Gd^{3+} $4f$ shell is half filled, with $J=S=\frac{1}{2}$ and $L=0$. Crystal-field effects should therefore be negligible and the Gd-Gd exchange interaction is expected to be isotropic. The system orders antiferromagnetically at 15°K,[4] and has a Curie-Weiss temperature of -22.4 ± 1.2°K.[5] A molecular-field treatment of these numbers yields a next-nearest-neighbor exchange interaction which is about 4 times larger than the nearest-neighbor exchange.[6]

The nuclear-spin relaxation times T_1 and T_2 are given by[7]

$$T_1^{-1}=\tfrac{1}{2}\gamma_n^2\int_{-\infty}^{+\infty}\langle h_+(t)h_-(0)\rangle\exp(-i\omega_n t)\,dt, \tag{1}$$

$$T_2^{-1}=\tfrac{1}{2}T_1^{-1}+\tfrac{1}{2}\gamma_n^2\int_{-\infty}^{+\infty}\langle h_z(t)h_z(0)\rangle\,dt, \tag{2}$$

where $\vec{h}(t)$ is the local-field operator, $\hat{z}$ is the applied-field direction, and the brackets represent an ensemble average. In the present case

$$\vec{h}(t)=(\gamma_P\hbar)^{-1}\textstyle\sum_i A_{P,i}\vec{S}_i(t), \tag{3}$$

where $A_{P,i}$ is the Gd-P transferred hyperfine coupling constant, assumed for the moment to be isotropic, and $\vec{S}_i$ is the gadolinium electronic spin operator. The nuclear precession frequency ω_n in Eq. (1) is completely negligible in comparison to the reciprocal lifetime of the electronic correlation function and may be set equal to zero (i.e., NMR, in effect, probes the zero-frequency fluctuation amplitude). It will be assumed that the transferred hyperfine interaction is nearest neighbor only, and that the exchange interaction is next nearest neighbor only. The latter assumption is made because of the molecular-field result[6] discussed above. Then the fcc lattice of magnetic gadolinium ions may be regarded as four interpenetrating simple-cubic lattices, each of which has zero coupling to the other three. A given phosphorus nucleus is hyperfine coupled to two nearest gadolinium neighbors in three of the four simple cubic arrays, a total of six hyperfine couplings. Applying these conditions to Eq. (3) and substituting into Eq. (1) yields

$$T_1^{-1}=3(A/\hbar)^2\int_{-\infty}^{+\infty}[\langle S_{1+}(t)S_{1-}(0)\rangle+\langle S_{1+}(t)S_{2-}(0)\rangle]\,dt. \tag{4}$$

Here A is the hyperfine coupling constant, and sites 1 and 2 are nearest neighbors on the same simple-cubic magnetic lattice.

It can be shown readily that if the Zeeman and exchange terms in the spin Hamiltonian commute, a condition satisfied for isotropic exchange, then in the high-temperature limit $\langle S_{iz}(t)S_{jz}(0)\rangle$ is independent of field and

$$\langle S_{i+}(t)S_{j-}(0)\rangle=2\langle S_{iz}(t)S_{jz}(0)\rangle\exp(i\omega_0 t). \tag{5}$$

Here $\omega_0 \equiv g\mu_B H/\hbar$, where H is the applied magnetic field. Substituting into Eq. (4) yields

$$T_1^{-1} = 6(A/\hbar)^2 \int_{-\infty}^{+\infty} [\langle S_{1z}(t)S_{1z}(0)\rangle + \langle S_{1z}(t)S_{2z}(0)\rangle] \exp(i\omega_0 t)dt. \quad (6)$$

Similarly, one obtains from Eq. (2)

$$T_2^{-1} = \tfrac{1}{2}T_1^{-1} + 3(A/\hbar)^2 \int_{-\infty}^{+\infty} [\langle S_{1z}(t)S_{1z}(0)\rangle + \langle S_{1z}(t)S_{2z}(0)\rangle]dt. \quad (7)$$

Thus, from Eq. (6), the field dependence of T_1^{-1} yields the Fourier transform of the sum of the autocorrelation function and a pair-correlation function. In zero field, T_1^{-1} equals T_2^{-1}. In the high-field limit, T_1^{-1} becomes vanishingly small while T_2^{-1} approaches one half its low-field value. Physically, these effects may be regarded as due to a Zeeman shift of the transverse spin-fluctuation spectrum to higher frequencies, while the longitudinal fluctuation spectrum is unaffected by the field. The shift produces no distortion in the spectral shape if the Zeeman and exchange Hamiltonians commute.

The present measurements were made on a powdered sample which was previously used in the NMR work of Jones.[5] Magnetic fields to 120 kOe were achieved with a General Electric Nb_3Sn superconducting solenoid, and the sample was maintained at room temperature by means of a separate Dewar. A coherent pulsed-NMR system with $H_1 \approx 80$ Oe was used. Measurements of T_2 employed the usual 90°-180° pulse sequence to produce a spin echo, while T_1 was determined by the stimulated-echo method.[8] The signal-to-noise ratio was small because T_1 and T_2 were comparable to or shorter than the recovery time of the detection system (typically about 8 μsec), which meant that the signal could only be observed after several decay times. Also, the inhomogeneous broadening of the ^{31}P resonance due to demagnetization effects[5] greatly exceeded H_1 at the higher field strengths, so that only a fraction of the nuclei were excited by a given rf pulse. A signal-to-noise enhancement of about 100 was achieved in a two-stage signal-averaging process. As the applied field was swept back and forth through resonance, the echo amplitude was monitored with a PAR model CW-1 boxcar integrator. Successive sweeps were accumulated in a Fabri-Tek model 1062 digital signal averager.

Before applying Eqs. (6) and (7) to the experimental data, it is important to consider what effects a violation of the assumption of isotropic hyperfine coupling would have. Anisotropy would be most evident in T_1^{-1} at high fields because it would introduce field-independent terms of the type which appear in Eq. (7). The only difference would be the replacement of the factor $(A/\hbar)^2$ by an appropriate coupling parameter. If it is assumed that the only anisotropy is due to the classical dipolar field of the gadolinium ion at the phosphorus nucleus, then the anisotropic coupling parameters can be calculated. Furthermore, using the previously stated assumption that the nondipolar transferred hyperfine interaction is nearest neighbor only, the isotropic coupling constant can be deduced from the resonance-shift data of Jones.[5] The ratio of the high-field limits of T_1^{-1} and T_2^{-1} can thus be calculated and, after taking a powder average with respect to the direction of the applied field, a comparison with experiment can be made. The predicted ratio[9] $T_1^{-1}/T_2^{-1} = 0.070$ compares with the experimental value of 0.066 ± 0.007. This comparison is sensitive to both of the above assumptions concerning the transferred hyperfine coupling, and the good agreement tends to support the assumptions.

Figure 1 shows the observed field dependence of T_1^{-1} for GdP. The experimental powder data have been adjusted for the dipolar-produced hyperfine-coupling anisotropy so that they corre-

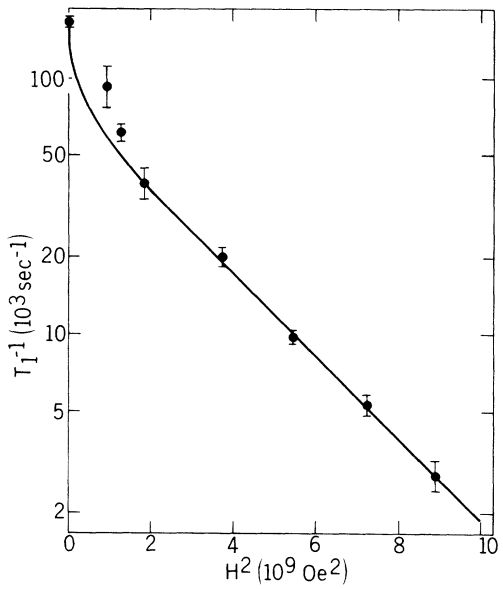

FIG. 1. Field dependence of T_1^{-1} for ^{31}P nuclei in GdP at room temperature. The data have been adjusted to correspond to a ⟨100⟩ orientation of the applied field. The solid line represents a fit to a theoretical spectrum, as described in the text.

spond to a ⟨100⟩ orientation of the applied field. This removes the field-independent contribution. Data were not obtained below about 30 kOe because the very rapid recovery of the nuclear magnetization made the signal-to-noise ratio impracticably small in this range, as discussed above. The point at zero field was obtained by multiplying the high-field limit of T_2^{-1} by a factor of 2. The justification of this is apparent from Eqs. (6) and (7).

The problem of calculating the autocorrelation and pair-correlation functions for a simple-cubic antiferromagnet with nearest-neighbor Heisenberg exchange has been studied by a number of authors.[10] However, an exact result over the entire time axis has not been produced. A relatively simple technique suggested by Gulley *et al.*[11] will be employed here. It consists of using an exact expansion in powers of t up to t^4 for times less than $1/\omega_{ex}$, applying a diffusion equation at times greater than about $2/\omega_{ex}$, and interpolating in the intermediate region. Here the exchange frequency ω_{ex} is defined by

$$\omega_{ex}^2 = \tfrac{2}{3}S(S+1)\frac{1}{\hbar^2}\sum_{j\neq 1} J_{1j}^2, \tag{8}$$

where J is twice the exchange integral. Fourier transformation with respect to time then yields the solid curve in Fig. 1, where the normalization has been chosen to produce coincidence with the zero-field point and ω_{ex} has been adjusted to fit the data above 1.5×10^9 Oe^2. Agreement is excellent except for two of the lower field points, where the origin of the discrepancy is not known. It is worth noting from the figure that the high-frequency tails of both the theoretical and the experimental spectra appear Gaussian. Furthermore, in the theoretical case, the reciprocal of the coefficient of $\frac{1}{2}(\gamma_e H)^2$ in this Gaussian is found to be equal to the coefficient of $\frac{1}{2}t^2$ in the short-time expansion.

The value of ω_{ex} obtained from the above fit is $(7.0\pm0.2)\times10^{11}$ sec^{-1}. This may be compared with the value $(7.4\pm0.4)\times10^{11}$ sec^{-1} deduced from the Curie-Weiss temperature of Jones,[5] again assuming next–nearest-neighbor exchange coupling only. Since the Curie-Weiss temperature depends on a linear sum over the exchange interactions while the nuclear relaxation involves primarily a sum of squares,[11] the good agreement tends to confirm that the coupling is primarily next-nearest neighbor.

If the transferred hyperfine interaction is known, then the area under a plot of T_1^{-1} vs H is uniquely determined. This may be seen by integrating Eq. (6) with respect to ω_0 and noting that $\langle S_{iz}(0)S_{jz}(0)\rangle = \delta_{ij}S(S+1)/3$ in the high-temperature limit, which yields

$$\int_0^\infty T_1^{-1}\,d\omega_0 = 2\pi(A/\hbar)^2 S(S+1). \tag{9}$$

Unfortunately, the low-field data of Fig. 1 do not permit an unambiguous determination of the experimental area. However, the area under the theoretical curve is smaller than predicted by a factor of about 0.59. This might be taken as evidence that the rise of the experimental data above the theoretical curve at fields below 1.5×10^9 Oe^2 is real. Indeed, a reasonable curve drawn through the data with $d(T_1^{-1})/dH = 0$ at the origin encloses an area of about 0.80 the predicted value. Since the spectral shape at low frequencies depends sensitively on the long-time behavior of the correlation functions, these considerations suggest that the accepted form of diffusive behavior[10] cannot account for the data. However, because of the uncertainty in the exchange and transferred hyperfine interactions and because of the limited low-field data, no definite conclusion can be drawn at this time.

In conclusion, it has been shown that the field dependences of T_1 and T_2 in a paramagnet at high temperature yield detailed information about the autocorrelation and pair-correlation functions. This information differs from that obtained by inelastic neutron scattering in that, while the present technique is sensitive to spin fluctuations localized in space, the neutron cross section is proportional to the spatial Fourier transform of the two-spin correlation function.[1] In the specific case studied, namely gadolinium phosphide, excellent agreement with a theoretical calculation was achieved for the high-frequency tail of the fluctuation spectrum. However, although experimental difficulties prevented a clear definition of the low-frequency behavior, evidence of a disagreement with theory in this region was found. It would therefore seem very desirable to apply the present method to a system in which the low-frequency range is experimentally accessible and in which the hyperfine and exchange interactions are well known. If only the low-frequency behavior were of concern, then the exchange interaction could be much larger, resulting in longer relaxation times. Also, the requirement of isotropy in the transferred hyperfine interaction would be much less stringent.

It is a pleasure to acknowledge helpful conversations with Dr. R. R. Bartkowski, Dr. E. D.

Jones, Dr. P. M. Richards, and Dr. B. G. Silbernagel.

*Work supported by the U. S. Atomic Energy Commission.

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[6]E. D. Jones and B. Morosin, Phys. Rev. 160, 451 (1967); note that the value of the Curie-Weiss temperature has been revised in Ref. 5 to −22.4°K. The exchange ratio of 4 given in the text comes from using the latter value in the molecular-field analysis.

[7]See, for example, C. P. Slichter, *Principles of Magnetic Resonance* (Harper & Row, New York, 1963), Chap. 5.

[8]E. L. Hahn, Phys. Rev. 80, 580 (1950).

[9]In the high-field limit, T_1^{-1} is anisotropic with respect to field direction, so that taking a powder average leads to a nonexponential recovery of the total nuclear magnetization. The value used here corresponds to the initial slope of the recovery, and therefore is the average value of the relaxation rate.

[10]See, for example, J. E. Gulley, D. Hone, D. J. Scalapino, and B. G. Silbernagel, Phys. Rev. B 1, 1020 (1970), and references therein.

[11]Gulley, Hone, Scalapino, and Silbernagel, Ref. 10.

Parametric Excitation in the Ionosphere

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(Received 19 July 1971)

Parametric excitation of ion waves is invoked to explain the efficient interaction between electromagnetic waves and the ionosphere.

We wish to report the parametric excitation of ion waves in the ionosphere by irradiation with an electromagnetic wave at the characteristic electron frequency for the desired height. When an electromagnetic wave ($\omega_0, k_0 \approx 0$) is incident upon the ionosphere it can stimulate the emission of an ion mode of ω_i and k_i if an electron mode of ω_e and k_e is emitted such that $\omega_0 = \omega_e + \omega_i$ and $\vec{k}_0 = \vec{k}_e + \vec{k}_i$. In the ionosphere where the gradient is gentle, the ion wave facilitates the coupling between the long-wavelength electromagnetic wave and the electrostatic electron wave of much shorter wavelength. The excited ion wave ω_i can be either a purely growing mode[1] ($\mathrm{Re}\omega_i = 0$, $k_i \neq 0$, the nonoscillatory parametric instability) or a propagating ion acoustic mode[2] ($\omega_i = \alpha k_i v_{i\,\mathrm{th}}$, the oscillatory parametric decay instability). For $T_e \approx T_i$ these two processes have approximately the same thresholds and can occur simultaneously. A consequence of this parametric coupling is that electrostatic electron waves are excited *at* and *below* the electromagnetic frequency ω_0 as dictated by the frequency-matching condition. Indeed, the intercoupling between electron and ion modes establishes a complementarity between the behaviors of these two sets of modes of vastly different frequencies and properties.

Since the intercoupling between ω_0 and ω_i enhances ω_e (and the same holds for the interaction between ω_0 and ω_e) the parametric coupling process possesses a built-in feedback enhancement; such enhancement indeed has been demonstrated for low-frequency ion waves in which one drift wave externally driven decays into two lower-frequency drift waves.[3]

The efficiency of the parametric coupling between an electromagnetic pump near ω_p, the plasma frequency, and an ion acoustic wave has been theoretically predicted to have a minimum excitation power at $T_e \cong T_i$ given by[2]

$$P_0 = c\frac{E_0^2}{8\pi} = c8n_e kT_e \frac{\gamma_e}{\omega_p}\frac{\gamma_i}{\omega_i}, \qquad (1)$$

where γ_i, γ_e are the damping of the ion wave and the electron plasma wave, respectively, n_e is the electron density, and $\omega_i = k_i[(kT_e + kT_i/M_i]^{1/2}$ is ion acoustic wave frequency. We note that the parametric threshold depends on both the electron and ion damping. The threshold power can be considerably reduced if $\gamma_e \ll \omega_p$.

We wish to present preliminary data from ex-