[2] A. A. Galkin and A. P. Koroliuk, Zh. Eksperim. i Teor. Fiz. 34, 1025 (1958) [Soviet Phys. JETP 7, 708 (1958)].

[3] G. A. Alers and P. A. Fleury, Phys. Rev. 129, 2425 (1963).

[4] G. A. Alers, in *Physical Acoustics*, edited by W. P. Mason (Academic, New York, 1966), Vol. IV A.

[5] Y. Shapira and L. J. Neuringer, Phys. Rev. Letters 15, 724 (1965).

[6] D. J. Meredith, R. H. Watts-Tobin, and E. R. Dobbs, J. Acoust. Soc. Am. 45, 1393 (1969).

[7] Y. Shapira, in *Physical Acoustics*, edited by W. P. Mason (Academic, New York, 1968), Vol. V, gives an excellent review of this subject.

[8] E. H. Gregory and H. E. Bömmel, Phys. Rev. Letters 15, 404 (1965).

[9] R. E. Smith and D. I. Bolef, Phys. Rev. Letters 22, 183 (1969).

[10] J. Buttet, E. H. Gregory, and P. K. Baily, Phys. Rev. Letters 23, 1030 (1969).

[11] J. Buttet and P. K. Baily, Phys. Rev. Letters 24, 1220 (1970).

[12] P. K. Baily and H. E. Bömmel, Bull. Am. Phys. Soc. 15, 603 (1970).

[13] W. D. Smith, J. G. Miller, D. I. Bolef, and R. K. Sundfors, J. Appl. Phys. 40, 4967 (1969).

[14] S. Rodriguez, Phys. Letters 2, 271 (1962).

[15] M. J. Harrison, Phys. Rev. Letters 9, 299 (1962).

[16] S. Rodriguez, Phys. Rev. 130, 1778 (1963).

[17] J. J. Quinn and S. C. Ying, Phys. Letters 23, 61 (1966).

[18] J. J. Quinn, J. Phys. Chem. Solids 31, 1701 (1970).

[19] J. J. Quinn (private communication).

[20] M. H. Cohen, M. J. Harrison, and W. H. Harrison, Phys. Rev. 117, 937 (1960).

[21] W. D. Smith, Ph.D. dissertation, Washington University, St. Louis, Mo., 1970 (unpublished).

[22] E. H. Gregory, Bull. Am. Phys. Soc. 14, 401 (1969).

[23] W. D. Smith, J. G. Miller, R. K. Sundfors, and D. E. Bolef, J. Appl. Phys. (to be published).

[24] J. Buttet and E. H. Gregory (private communication).

[25] C. P. Slichter, *Principles of Magnetic Resonance* (Harper and Row, New York, 1963), p. 31.

[26] See, for example, R. Truell, C. Elbaum, and B. B. Chick, *Ultrasonic Methods in Solid State Physics* (Academic, New York, 1969).

[27] R. G. Leisure and D. I. Bolef, Rev. Sci. Instr. 39, 199 (1968).

[28] R. L. Melcher, D. I. Bolef, and J. B. Merry, Rev. Sci. Instr. 39, 1613 (1968).

[29] D. I. Bolef, in *Physical Acoustics*, edited by W. P. Mason (Academic, New York, 1966), Vol. IV A.

PHYSICAL REVIEW B VOLUME 3, NUMBER 5 1 MARCH 1971

Nuclear Resonance Study of Solid n-D$_2$[†]

J. H. Constable and J. R. Gaines
Department of Physics, The Ohio State University, Columbus, Ohio 43210

(Received 19 October 1970)

Pulsed nuclear-magnetic-resonance (NMR) experiments on solid n-D$_2$ samples have been performed over the temperature range 5–0.15 K. The spin-lattice relaxation time and second moments were measured as a function of temperature. No departures from Curie-law behavior were observed down to 0.15 K. Solid-echo techniques were used at several temperatures to demonstrate the contribution to the free-induction decay due to the $J=1$ molecules.

INTRODUCTION

A previous nuclear-magnetic-resonance (NMR) study[1] of the dependence of the longitudinal relaxation time T_1 upon the concentration of $J=1$ molecules in solid D$_2$ has shown that the magnetic properties of D$_2$ are analogous to those of HD doped with o-H$_2$ molecules.[2] In both systems, the sample consists of a mixture of molecules in the rotational states $J=0$ (o-D$_2$ or HD) and $J=1$ (p-D$_2$ or o-H$_2$). The nuclear spins of the $J=1$ molecules relax in a relatively short time to the energy reservoir provided by the rotational degrees of freedom,[3] which in turn is strongly coupled to the phonon modes in the solid. Since the spacings between the nuclear Zeeman energy levels in a large magnetic field are approximately equal for both $J=1$ and $J=0$ molecules, cross relaxation between the two-spin systems provides the mechanism by which the spin temperature of the $J=0$ molecules can relax to the lattice temperature. The direct coupling of the nuclear spins on the $J=0$ molecules to the lattice is very weak and can be neglected.[4] It is entirely possible, depending upon the relative concentration, that most of the observed NMR signal is due to $J=0$ molecules that have no direct relaxation mechanism to the lattice, and that the resonance of of the $J=1$ molecules is essentially unobservable except for its effect on the over-all relaxation behavior.

For n-D$_2$, two-thirds of the molecules have an even value of the rotational quantum number J ($J=0$ at low temperature) which must be associated with an even value of the total nuclear spin I ($I=2$ or $I=0$) according to the restrictions imposed on the total wave function by the Pauli principle. For the other third of the molecules, para-D$_2$, J is odd ($J=1$ at low temperatures) and the nuclear spin is

$I=1$. The relative signal amplitudes in n-D_2 from o-D_2 and p-D_2 are in the ratio 5 to 1, respectively. Thus, at time $t=0$ for the free-induction decay (FID) in a pulsed NMR experiment, the ratio of the signal amplitudes should be 5 to 1; however, if the two groups of nuclear spins have different transverse relaxation times T_2, then the composition of the total signal for $t>0$ can be quite different from 5 to 1. The NMR signal can be dephased by both inter- and intramolecular interactions. The $J=0$ molecules have zero expectation value for the intramolecular interactions so they are dephased only by intermolecular interactions. The $J=1$ molecules have essentially the same intermolecular interactions and, in addition, a nonvanishing intramolecular interaction so that their transverse relaxation time can be appreciably shorter than that for $J=0$ molecules. In a pulse experiment, the maximum ratio of p-D_2 signal to o-D_2 signal ($t=0$) occurs where the signal-to-noise ratio is also maximum, whereas in a steady-state experiment the optimum experimental ratio of signal to noise coincides with the region of minimum p-D_2 signal.

Preliminary reports of steady-state NMR experiments on solid D_2[5] point out that the second moment M_2 of the resonance line does not display the very rapid temperature variation expected by analogy to the similar experiments in H_2.[6] Because of the small temperature variation of M_2, Harris[7] has postulated that the $J=1$ molecules do not resonate and that the small observed temperature variation of M_2 is explained by a mechanism similar to the one postulated by Smith, White, and Gaines[8] to account for anomalous relaxation behavior below T_λ in alloys high in $J=1$ concentration, namely, the deformation of the o-D_2 ground state $J=0$. This deformation arises from the alignment of the $J=1$ molecules due to their mutual quadrupole interaction and results in a wave function containing higher spherical harmonics (namely, $J=2$) with a relative amplitude proportional to Γ/B, where Γ is the quadrupole-quadrupole coupling constant and B is the rotational constant characteristic of the separation of the $J=0$ and $J=2$ rotational levels.

We have performed similar NMR experiments on n-D_2 down to somewhat lower temperatures but have used transient rather than steady-state techniques for observation. We observed signals that had nearly separable contributions from the $I=1$ and $I=2$ spin systems and measured M_2 as a function of temperature. Measurements of the longitudinal relaxation time at temperatures below 1 K may give further evidence for the postulated deformation of the $J=0$ ground state.

EXPERIMENTAL DETAILS

The gas used for the experiment was n-D_2 originally, but the sample was held at temperatures below 4.2 K for so many hours (100 h) that the final concentration was estimated to be $x_p=0.29$ from the rate equation given by Grenier and White.[9] No orientational effects on either the spin-lattice relaxation or the shape of the signal were observed, so the sample was in all likelihood polycrystalline. A liquid-helium mixture ($^3He+{}^4He$) was used to make thermal contact between the solid D_2 sample and the mixing chamber of a continuous ^3He-^4He dilution refrigerator. A sintered copper heat exchanger connected mechanically to the mixing chamber provided the thermal link between the exchange liquid-helium mixture and the mixing chamber. The thermometry in this experiment was based on the temperature variation of the resistance of Speer No. 220 carbon resistors calibrated by means of NMR thermometry on platinum powder. The heat of conversion from p-D_2 to o-D_2 coupled with the boundary resistance between solid D_2 and the liquid-helium mixture combined to limit the ultimate temperature of the sample to approximately 0.1 K. Measurements of the thermal boundary resistance and details of the apparatus will be published elsewhere.

The NMR experiments were performed at 3.0 MHz using an incoherent transmitter receiver combination. The transmitter power was sufficient to produce a 90° pulse in 9 μsec. The blocking time of the amplifier was approximately 50 μsec, which necessitated the usage of a solid-echo technique[10] for some of the observations. The signals were photographed from oscilloscope traces. The data were read from the photographs and corrected for the nonlinearity of the amplifier.

THEORY

On very general grounds one can write the normalized free-induction decay as

$$S(t)=\frac{\mathrm{Tr}\,\rho(t)I_x}{\mathrm{Tr}\,\rho(0)I_x}, \tag{1}$$

where the density matrix $\rho(t)$ is the solution to the equation

$$i\hbar\frac{\partial}{\partial t}\rho(t)=[H',\rho], \tag{2}$$

where H' is the spin Hamiltonian in the rotating references frame, and

$$I_x=\sum_{j=1}^{N}(I_x)_j\ . \tag{3}$$

If H' is independent of time, then

$$\rho(t)=\exp\left(-\frac{1}{\hbar}H't\right)\rho(0)\exp\left(\frac{1}{\hbar}H't\right),$$

whereas if H' is a function of time, then

$$\rho(t)=\exp\left(-\frac{1}{\hbar}\int_0^t H'(t')\,dt'\right)\rho(0)$$

$$\times \exp\left(\frac{1}{\hbar}\int_0^t H'(t')\,dt'\right).$$

Alternatively, we can write

$$\rho(t) = \exp\left(-\frac{1}{\hbar}\bar{H}'t\right)\rho(0)\exp\left(\frac{1}{\hbar}\bar{H}'t\right),$$

where $\bar{H} \equiv (1/t)\int_0^t H'(t')\,dt'$. We will be able to find solutions to Eq. (1) for two extreme cases; namely, where H' is independent of time (long-correlation time limit) and second, where the transitions that change H' are so rapid that $\bar{H}'$ is independent of time (short-correlation time limit) and can be calculated from the thermodynamic average value. Assuming then that H' or $\bar{H}'$ (whichever is appropriate) is independent of time, we can note that for the power-series representation

$$S(t) = \int d\omega e^{i\omega t} g(\omega) = 1 + \left.\frac{dS}{dt}\right|_{t=0} t + \left.\frac{d^2S}{dt^2}\right|_{t=0} \frac{t^2}{2} + \cdots$$

$$= 1 - M_2 t^2/2 + M_4 t^4/4! + \cdots, \tag{4}$$

where $M_{2n} = \int d\omega g(\omega)\omega^{2n} / \int d\omega g(\omega)$ with $g(\omega)$ being the symmetric line-shape function for NMR absorption. By calculating the indicated derivatives of $S(t)$ in Eq. (1) with respect to time and comparing with Eq. (4), we can obtain expressions for the moments of the distribution $g(\omega)$. For instance,

$$M_2 = \left.\frac{d^2S}{dt^2}\right|_{t=0} = -\frac{\mathrm{Tr}\rho(0)[H',[H',I_x]]}{\mathrm{Tr}\rho(0)I_x}. \tag{5}$$

Since $\rho(0) = \rho_I(0)\rho_J(0)$ with $\rho_I(0) = e^{\beta\gamma\hbar H_0 I_x}$ following a 90° pulse, we have

$$M_2 = -\frac{\mathrm{Tr}\rho_J(0)[H',I_x]^2}{\mathrm{Tr}\rho_J(0)I_x^2}, \tag{6}$$

where we have used the usual high-temperature approximation for the Zeeman density matrix $\rho_I(0)$.

If we include both the intramolecular and intermolecular interactions in H' and retain only the secular contributions, neglecting the spin-rotation interaction,[11] one has

$$H' = \frac{d}{4}\sum_i (3\cos^2\Theta_i - 1)(3J_{\xi i}^2 - 2)(3I_{zi}^2 - 2)$$

$$+ \sum_{i>j} \frac{\gamma_i\gamma_i}{r_{ij}^3}(1 - 3\cos^2\theta_{ij})\left(I_{zi}I_{zj} - \frac{(I_i^+I_j^- + I_i^-I_j^+)}{4}\right), \tag{7}$$

where Θ_i is the angle between the bond axis of the ith molecule and the symmetry axis of the crystal, θ_{ij} is the angle the intermolecular vector $\vec{r}_{ij}$ of molecules i and j makes with the z axis, and J_ξ is the projection of the rotational angular momentum on the symmetry axis. I_{zi} is the total nuclear spin projection on the magnetic field direction for the ith molecule. After calculating the commutator, forming the square, and taking the trace, all cross-product terms between the intra- and intermolecular interaction vanish, and one is left with

$$M_2 = M_2^{\mathrm{intra}} + M_2^{\mathrm{inter}}, \tag{8}$$

where expressions for M_2^{inter} are given in Abragam[12] and specialized for H_2 and D_2 by Harris. Expressions for M_2^{intra} are also given by Harris for the high-temperature limiting cases. Numerically for n-D_2 one obtains $M_2^{\mathrm{inter}} = 5.11 \times 10^6$ (rad/sec)^2 independent of the temperature. The calculation of M_2^{intra} is elementary and in the short-correlation time limit, where the fluctuations in H' are rapid compared to the inverse of the width of the nuclear resonance line, one obtains

$$M_2^{\mathrm{intra}} = \left(\frac{3d}{4}\right)^2 (3\cos^2\Theta - 1)^2 \left(\frac{\mathrm{Tr}\rho_J(0)(3J_\xi^2 - 2)}{\mathrm{Tr}\rho_J(0)}\right)^2, \tag{9}$$

where Θ is the angle between the z axis and the symmetry axis. If this is not the appropriate case and one must use H' instead of $\bar{H}'$ in the calculation, then

$$M_2^{\mathrm{intra}} = \left(\frac{3d}{4}\right)^2 (3\cos^2\Theta - 1)^2 \left(\frac{\mathrm{Tr}\rho_J(0)(3J_\xi^2 - 2)^2}{\mathrm{Tr}\rho_J(0)}\right). \tag{10}$$

Taking for $(3\cos^2\Theta - 1)^2$ the powder average value of $\frac{4}{5}$, we tabulate below values of M_2^{intra} appropriate to certain choices of $\rho_J(0)$.

A. Molecular Field Approximation

Suppose the concentration of $J = 1$ molecules is so high that each p-D_2 molecule sees an effective field resulting from the electric quadrupole-quadrupole (EQQ) interaction with several of its neighbors. This effective field could be crudely characterized by a Hamiltonian

$$H_E = \tfrac{1}{3}A(3J_\xi^2 - 2), \tag{11}$$

where the parameter A merely measures the spacing in energy units between $J_z = 0$ and $J_z = \pm 1$. The value for A should be dependent on the concentration of $J = 1$ molecules and be unrelated to the crystal-field interaction measured for vanishingly small $J = 1$ concentrations by others.[13] For this case the calculation is particularly simple and gives

$$\frac{\mathrm{Tr}\rho_J(0)(3J_\xi^2 - 2)}{\mathrm{Tr}\rho_J(0)} = \frac{2e^{-\beta A/3} - 2e^{2\beta A/3}}{2e^{-\beta A/3} + e^{2\beta A/3}}.$$

The extreme limits for M_2^{intra} in the short-correlation time limit are then

$$M_2^{\mathrm{intra}} = 9d^2/5 \quad \text{for } J_\xi = 0 \text{ the ground state}$$

$$= 9d^2/20 \quad \text{for } J_\xi = \pm 1 \text{ the ground state}, \tag{12}$$

for $|\beta A| \gg 1$, and $M_2^{\mathrm{intra}} \cong (d\beta A)^2/5$ for $|\beta A| \ll 1$. The low-temperature limit for M_2 in the long-correlation time approximation is identical to the result obtained in the short-correlation time limit. The high-temperature limit is different but is unrealistic as the long-correlation times and high temperatures are incompatible. Numerically we find that $9d^2/20 = 1.12\times 10^{10}$ (rad/sec)^2 a number more than three orders of magnitude greater than the rigid-lattice value.

B. Nearest-Neighbor EQQ Interaction

If we assume that each $J=1$ molecule has only one nearest neighbor that is also in the state $J=1$, we can obtain for M_2^{intra} in the short-correlation time limit

$$M_2^{\text{intra}} = \left(\frac{3d}{4}\right) \frac{4}{5}\left(\frac{e^{-6\beta\Gamma} - 2e^{-\beta\Gamma} + e^{4\beta\Gamma}}{e^{-6\beta\Gamma} + 2e^{-\beta\Gamma} + 4 + 2e^{4\beta\Gamma}}\right)^2$$

$$= 9d^2/80 \qquad \text{for } \beta\Gamma \gg 1$$

$$\cong 125 d^2\beta^4 I^4/3 \quad \text{for } \beta\Gamma \ll 1 \,. \qquad (13)$$

In the long-correlation time limit the low-temperature limit differs from the above result and gives

$$M_2^{\text{intra}} = 9d^2/8 \,.$$

C. Cooperative Transition

In the cooperative transition, called the λ transition in the solid hydrogens, one has $\langle 3J_\zeta^2 - 2\rangle = -2$, so that the expected result for M_2^{intra} in the short-correlation time limit is $9d^2/5$.

It is of interest to note that in either approximation used for the high-temperature behavior, the effective field or the pair spectrum, the intramolecular contribution to the second moment becomes comparable to the intermolecular contribution when $\beta A \sim 3\times 10^{-2}$ or $\beta\Gamma \sim 3.6\times 10^{-2}$. Since $\Gamma \approx 1$ K, then $T \approx 30$ K. At temperatures of 4.2 K and below, the high-temperature approximation should be inadequate and the second moment should be dominated by the intramolecular contribution arising from the $J=1$ molecules. Since the o-D_2 molecules are in the $J = 0$ state, the expectation value of the intramolecular interaction vanishes and the second moment should be due only to the intermolecular dipolar interaction. Thus, the transverse decay of the p-D_2 molecules should be much more strongly damped than that of the o-D_2 molecules.

EXPERIMENTAL DATA

A. Longitudinal Relaxation

Experimental values of the longitudinal relaxation time T_1 were obtained by using a 90°-τ-90° pulse sequence to measure the signal amplitude $S(t)$, τ seconds after the initial 90° pulse has saturated the resonance. Denoting the thermal equilibrium value of the signal by $S(0)$, one plots $\ln[S(0) - S(\tau)]$ versus τ in order to obtain T_1 from the slope. All our plots were linear giving values of T_1 accurate to ±5%. Data from two experiments on the same gas sample are shown in Fig. 1. The sample was held at 4.2 K or below for the entire time between the two experiments (≈ 100 h) so that para-ortho conversion in the solid changed the initial $J=1$ concentration from 33.3 to about 29%. The final $J=1$ concentration was estimated to be 29% from the decrease in signal amplitude with time assuming only the $J=0$ molecules contribute to the observed signal. This estimation of the concentration is in good agreement with the value obtained from the theoretical conversion rate calculated by Motizuki.[14]

B. Second Moments

Signal amplitudes read from the photographs and corrected for amplifier nonlinearities were plotted versus t^2 on both semilog paper and Cartesian paper in order to determine the second moment M_2. For times shorter than the time it takes the signal to fall to $1/e$ of its initial value but longer than 50 μsec (the amplifier blocking time), the free-induction decay can be well represented by a Gaussian curve. The departure from a Gaussian shape was dependent upon the temperature. At temperatures above the temperature where the maximum in T_1 occurs, the signal is more damped at long times than a Gaussian curve would be. However, the signal is less damped than a Gaussian curve for temperatures below the temperature where the maximum in T_1 occurs. Experimental values of M_2 as a function of temperature are shown in Fig. 2. The second moments obtained in this manner should be in reasonable agreement with those obtained by steady-state techniques in the presence of a finite signal-to-noise ratio. No bandwidth distortion corrections[15] have been applied to our data, so the numer-

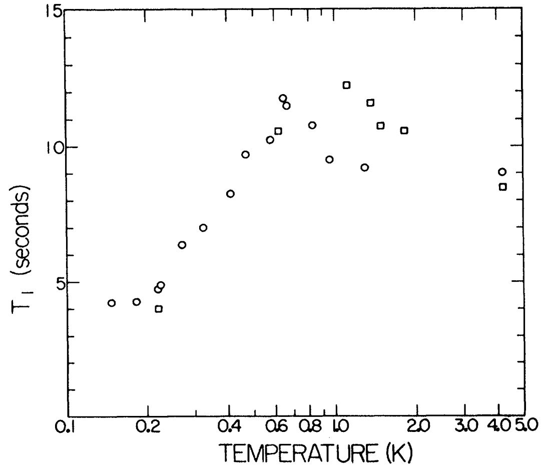

FIG. 1. Spin-lattice relaxation time versus temperature in solid D_2 measured at 3 MHz. The squares are points taken within 24 h after the n-D_2 gas was condensed. The circles are points taken after the p-D_2 concentration had converted to 29%.

ical values cannot be taken any more seriously than ± 15%.

C. Solid Echoes

We used echo-pulse sequences at several selected temperatures because of the experimental difficulty originating from the finite blocking time of the amplifier and the possibility of the existence of two signals with very different relaxation times (both transverse and longitudinal). The sequence used was 90° pulse followed about half a millisecond by a second 90° pulse. The results of three such sequences are shown in Fig. 3.

The echo appears to be composed of two signals having very different transverse relaxation times. The signal having the relatively short relaxation time is apparently lost in the amplifier recovery time when the free-induction decay is observed. It is interesting to note that in Fig. 3(c) for $T = 0.23$ K, the ratio of the two signal heights is roughly 5 to 1, the expected ratio of o-D_2 signal to p-D_2 signal for n-D_2. The spread in Larmor frequencies for the signal with the short relaxation time is so great that the 90° pulse that produces saturation for the spins with long transverse relaxation time does not saturate this resonance [see Fig. 3(b)].

D. Curie-Law Behavior

Extrapolation of the observed FID using a Gaussian fit to time $t = 0$ yields the relative magnetization of the sample. According to the Curie law, the sample temperature is inversely proportional to the net magnetization and hence the signal amplitude. The measurements of the signal amplitude were made by comparing the induced NMR signal to one produced by a reference oscillator (HP 606A).

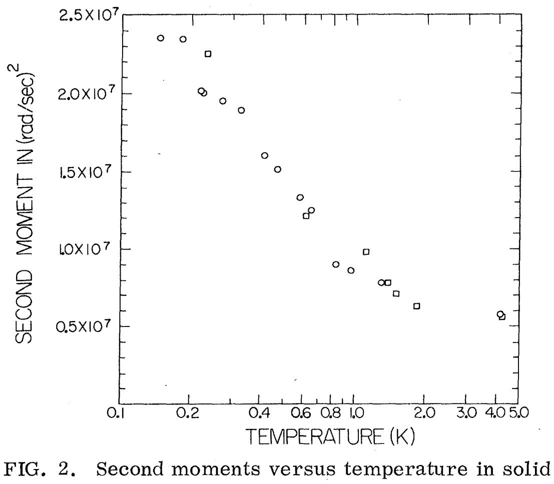

FIG. 2. Second moments versus temperature in solid D_2 measured at 3 MHz. The squares are points taken within 24 h after the n-D_2 gas was condensed. The circles are points taken after the p-D_2 concentration had converted to 29%.

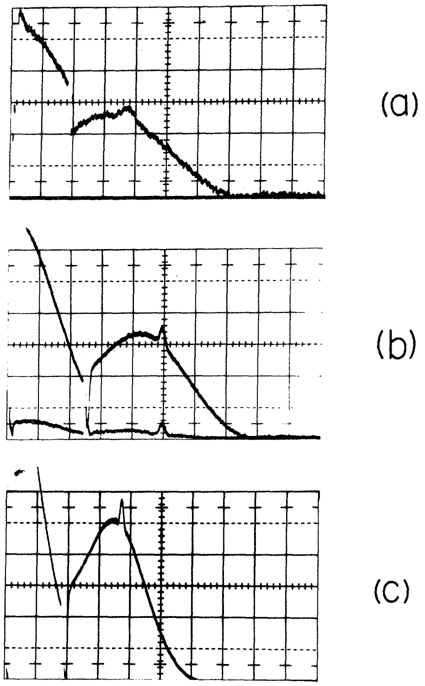

FIG. 3. Oscilloscope traces taken at 200 μsec/cm showing solid echoes in D_2. (a) Echo at 3.2 K formed by a 90°-0.4 msec-90° pulse sequence. (b) Echo at 0.7 K formed by a 90°-0.5 msec-90° pulse sequence, which was repeated 1 sec later. (c) Echo at 0.23 K formed by a 90°-0.4 msec-90° pulse sequence.

A Speer 220-Ω carbon resistor calibrated by means of NMR measurements on Pt powder was used to measure the sample temperature. The results are given in Fig. 4.

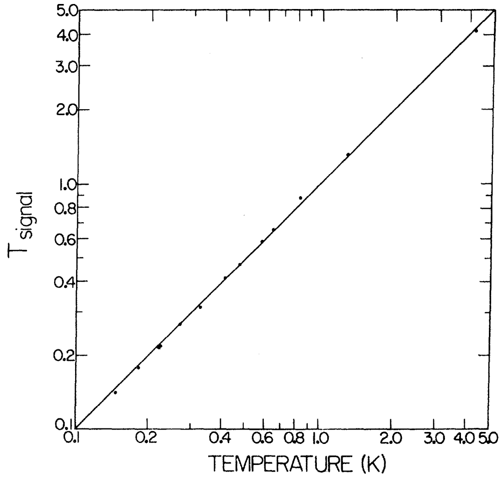

FIG. 4. Temperature, as measured by a resistance thermometer, is plotted against T_{signal} which is inversely proportional to the signal amplitude. The proportionality constant was obtained from the best fit to the Curie-law line drawn. The points correspond to the circles in Figs. 1 and 2.

DISCUSSION

The value of the second moment at 4.2 K obtained from the free-induction decay (using a Gaussian fit for short times) is approximately equal to the calculated rigid-lattice intermolecular contribution. Below 4.2 K the second moment M_2 increases with decreasing temperature reflecting the temperature-dependent intramolecular contribution. The data shown in Fig. 2 seem to support the suggestion of Harris (based on preliminary data of Meyer and coworkers[5]) that the $J=1$ molecules do not contribute to the observed signal both because the experimental value of M_2 is orders of magnitude smaller than expected [Eqs. (12) and (13)] and because the temperature dependence near 4 K is much too small. Harris[7] has predicted that even if the $J=1$ molecules make no contribution to the observed signal the observed value of M_2^{intra} will be temperature dependent as a result of the deformation of the $J=0$ ground state of ortho-D_2 molecules due to orientational order of the $J=1$ molecules. Although we observe approximately a factor of 5 increase in M_2 between 4 and 0.1 K, a detailed comparison with theory is not possible at this time since the expressions developed by Harris are valid only in the limit $\beta\Gamma \ll 1$.

The probable contribution of the $J=1$ molecules to the signal can be seen on the solid echos shown in Fig. 3. The transverse decay is so rapid that it is not surprising that this signal would be lost in the amplifier recovery time in a pulse experiment and lost in the noise in a steady-state experiment. By expanding the oscilloscope trace by a factor of 5, we succeeded in obtaining a value of M_2 for the $J=1$ molecules. At $T=0.23$ K we obtain $M_2 = 1.2 \pm 2 \times 10^{10}$ (rad/sec)^2. This value of M_2 is characteristic of the $J_z = \pm 1$ ground state for $J=1$ molecules in the effective-field approximation [Eq. (12)]. At temperatures near 4.2 K, a departure from a Gaussian shape is apparent near the origin presumably due to the signal from the $J=1$ molecules. No detailed temperature dependence for the $J=1$ second moment can be given since it is not possible to resolve the two signals clearly at higher temperatures (see Fig. 3).

The variation of the signal amplitude with temperature as is shown in Fig. 4 provides evidence that the Curie law is obeyed down to our lowest temperatures. Relative Curie constants proportional to the net magnetization were obtained by fitting straight lines to the experimental points in Fig. 4. The Curie constants so obtained can be used to estimate the para-D_2–ortho-D_2 conversion rate. If we assume that only the $J=0$ molecules contribute to the observed signal, integrate the rate equations given by Grenier and White,[9] and use the relative Curie constants and elapsed time from our data, we obtain a change in concentration which agrees closely with the theoretical predictions of Motizuki.[14] This change is, however, higher than the change observed experimentally by Grenier and White. If we assume that all the molecules contribute to the observed signal, the disagreement with the results of Grenier and White becomes more pronounced.

The variation of T_1 with temperature, coupled with Harris's speculation, seems particularly interesting. The position of the peak near 1 K apparently shifts with $J=1$ concentration since a shift due to hysteresis would be in the opposite direction. The sharp decrease in T_1 below the peak seems difficult to explain based on the conventional model of the relaxation processes in D_2 where the $J=1$ molecules must relax the $J=0$ ones. If the wave function for the $J=0$ molecules now contains (below the peak) an appreciable $J=2$ admixture, then it is possible for the ortho-D_2 molecules to have their own intrinsic relaxation mechanism as the intramolecular interaction is no longer zero on the average. Preliminary evidence for this effect was given by Smith, White, and Gaines[8] earlier. The order of magnitude seems very surprising if this is in fact the explanation.

ACKNOWLEDGMENTS

We would like to express our gratitude to Dr. Walter Hardy (North American Rockwell Science Center) for collaboration on the initial solid-echo experiments on D_2 while at Saclay and our appreciation to Sang Wang who assisted in some of the experimental work at Ohio State University. In addition, we would like to thank Professor A. B. Harris (University of Pennsylvania) and Professor Horst Meyer (Duke University) for communicating results of their work to us prior to publication.

[†] Work supported in part by a grant from the Air Force Office of Scientific Research, Grant No. AFOSR 1273-67.

[1] M. J. Smith, Ph. D. dissertation, The Ohio State University, 1967 (unpublished).

[2] Walter N. Hardy and J. R. Gaines, Phys. Rev. Letters 17, 1278 (1966).

[3] T. Moriya and K. Motizuki, Progr. Theoret. Phys. (Kyoto) 18, 183 (1957).

[4] I. Waller, Z. Physik 79, 370 (1932).

[5] B. Maraviglia, F. Weinhaus, H. Meyer, and R. L. Mills, Solid State Commun. 8, 815 (1970).

[6] L. I. Amstutz, H. Meyer, S. M. Myers, and D. C. Rorer, Phys. Rev. 181, 589 (1969).

[7] A. B. Harris, Phys. Rev. B 2, 3495 (1970).

[8] M. J. Smith, David White, and J. R. Gaines, J. Chem. Phys. 49, 3317 (1968).

[9] George Grenier and David White, J. Chem. Phys. 40, 3015 (1964).

[10] D. S. Metzger and J. R. Gaines, Phys. Rev. 147, 644 (1966).

[11] J. H. Constable and J. R. Gaines (unpublished).

[12] A. Abragam, *Principles of Nuclear Magnetism* (Clarendon, Oxford, 1962), Chap. 4.

[13] Walter N. Hardy and J. R. Gaines, Phys. Rev. Letters 19, 1417 (1967).

[14] K. Motizuki, J. Phys. Soc. Japan 12, 163 (1957).

[15] D. E. Barnaal and I. J. Lowe, Rev. Sci. Instr. 37, 428 (1966).

PHYSICAL REVIEW B VOLUME 3, NUMBER 5 1 MARCH 1971

Enhancement of the Korringa Constant in Alkali Metals by Electron-Electron Interactions

Robert W. Shaw, Jr. and William W. Warren, Jr.
Bell Telephone Laboratories, Murray Hill, New Jersey 07974

(Received 4 September 1970)

The theory of Moriya is extended to include electron-electron interaction potentials with a strong momentum dependence. This extension is based on recent theoretical studies of the electron-gas response. It is shown that the observed enhancement of the Korringa relation in alkali metals can be attributed almost entirely to electron-electron interactions described by an effective interaction potential derived from the pair-correlation function for a low-density electron gas.

I. INTRODUCTION

In the alkali metals, the s-contact hyperfine interaction is the dominant mechanism coupling nuclear spins with the conduction electrons. Consequently, one might expect that the Knight shift K and the spin-lattice relaxation time T_1 would satisfy the well-known Korringa relation[1]

$$K^2 T_1 T = S = (\gamma_e/\gamma_n)^2(\hbar/4\pi k_B) , \qquad (1.1)$$

where γ_e and γ_n are the electronic and nuclear gyromagnetic ratios, respectively. However, experimental values of K^2T_1T are typically 60% higher than predicted by (1.1). Since (1.1) was derived in the independent-particle approximation, this discrepancy has traditionally been attributed to electron-electron interactions.[2,3] The experimental and theoretical situation has been reviewed in a recent paper by Narath and Weaver,[4] and these authors concluded that the data could not be adequately explained by Moriya's theory, in which electron-electron interactions are assumed to have zero range.

Narath and Weaver[4] have given a rather complete discussion of various possible explanations for the remaining discrepancy between theory and experiment. Of these explanations, perhaps the most appealing (and the only one we consider explicitly in this paper) is that a zero-range interaction potential is not realistic, and should be replaced by an effective interaction obtained from detailed theoretical studies of electron-gas response. Actually, Narath and Weaver[4] did consider this possibility briefly. They introduced an effective potential (in momentum space) of the form suggested by Hubbard[5] (a screened Coulomb potential in real space) and found for Na a screening parameter of about $2k_F$. However, they concluded that the result had only qualitative significance, primarily because they felt that approximations made in deriving an expression for the enhancement factor limited the result to potentials with constant Fourier transforms (that is, with no momentum dependence). We have concluded, on the basis of recent studies of electron-gas response,[6] that constraints on the effective interaction potential are less restrictive than suggested by Narath and Weaver.[4]

There exist in the recent literature[6] various expressions for the effective exchange-correlation potentials which are thought to be reasonable approximations at metallic densities. We demonstrate in this paper that when these results are used in Moriya's theory of Korringa enhancement, essentially all of the experimentally observed enhancement can be attributed to electron-electron interactions. This conclusion is based on the observation that Stoner enhancement factors determined by equating theoretical and experimental Korringa enhancement are found to predict correctly the observed enhancement of the susceptibility in sodium and lithium.

II. THEORY AND CALCULATIONS

Since the relevant theory has been clearly reviewed by Narath and Weaver,[4] we will confine the present discussion to a summary of the results pertinent to our calculations. We will, however, consider in some detail the validity of two essential approximations involved in obtaining the results we have used, introducing in this context results