INFLUENCE OF EXCHANGE INTERACTION ON PARAMAGNETIC RELAXATION TIMES*

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Previous investigations have shown that the spin-lattice relaxation time T_1 is equal to the inverse line width[1] T_2 and is independent of temperature in the range 77°K to room temperature in a crystalline free radical with a highly exchange-narrowed line.[2] We have found departures from this behavior in T_1 for several free radicals between 1.5°K and room temperature using the saturation technique.

The measurements were made at 10 kMc/sec and 24 kMc/sec with a conventional magic tee microwave bridge. The solid free radicals used were α, α-diphenyl β-picryl hydrazyl (DPPH), α, γ-bisdiphenylene β-phenyl allyl (BDPA), Wurster's blue perchlorate, and some solid solutions of DPPH in polystyrene. In all of these free radicals the exchange interaction between neighboring spins narrows the resonance line[3] in accordance with the approximate expression[4,5] $\Delta\omega \approx \omega_p^2/\omega_E$, where $\Delta\omega$ is the observed line width, ω_p is the dipolar frequency, and ω_E is the exchange frequency. From our observed line widths and calculations of the dipole width based on Van Vleck's second moment expression,[3] we estimate the exchange frequency to lie between 10 and 40 kMc/sec. In addition, we have investigated solid solutions of DPPH in polystyrene, where the exchange frequency varied from effectively zero to about 10 kMc/sec. DPPH samples recrystallized from different solvents were found to have different line widths as reported by Lothe and Eia.[6] This is because the solvent molecules influence the free radical

spacing and thus the exchange interaction.

We have found that in DPPH, BDPA, and Wurster's blue the spin-lattice relaxation time T_1 is approximately equal to the spin-spin relaxation time T_2 at 77°K and room temperature. In those substances with higher exchange frequency as indicated by the narrower lines, T_1 is more nearly equal to T_2 and temperature independent. Table I shows these line widths and relaxation times.

The solid solutions were made by dissolving DPPH and polystyrene in chloroform and letting the chloroform evaporate. In the most concentrated solution T_1 was found to be equal to T_2 and temperature independent. As the concentration is reduced, T_1 becomes longer than T_2 and also shows a temperature dependence. When the concentration is reduced sufficiently, the exchange interaction diminishes and the hyperfine structure characteristic of DPPH appears. Upon further dilution the line width and shape remain the same, but T_1 continues to increase. Finally, T_1 becomes independent of concentration. Figure 1 is a plot of the above-described result.

These results can be interpreted using the three-reservoir model of Bloembergen and Wang,[2] which was discussed further by Van Vleck.[7] Figure 2 depicts schematically the thermodynamic reservoirs and the relaxation times. Since the exchange Hamiltonian $H_E = -\sum_{ij} J_{ij} \vec{S}_i \cdot \vec{S}_j$ commutes with the Zeeman Hamiltonian $H_Z = \sum_i g\beta H_z S_{zi}$, we can ascribe two temperatures to the spin system, θ_Z relating to the Zeeman system and θ_E

Table I. Line widths and relaxation times for free radicals at room temperature and 77°K.

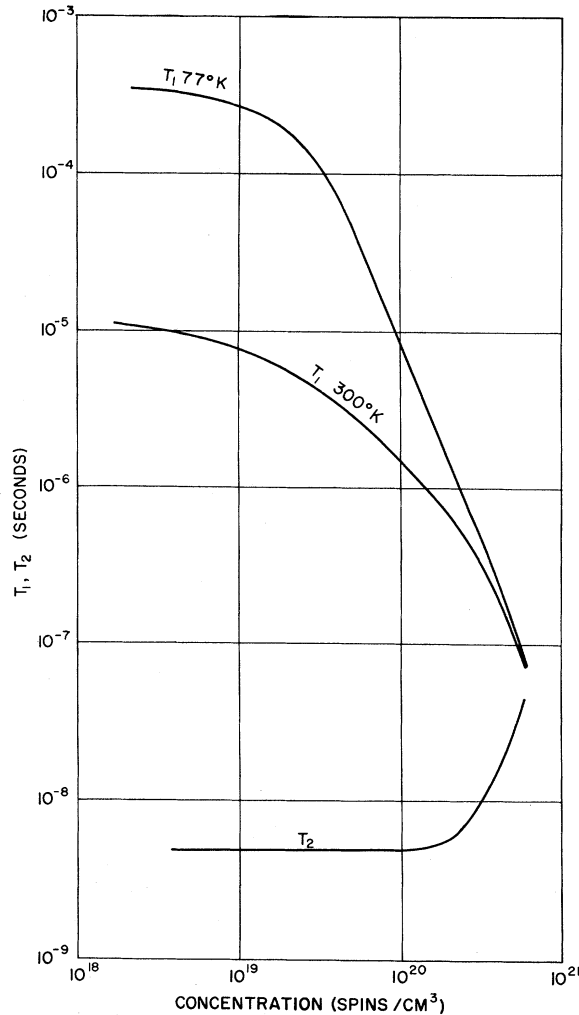|	BDPA	DPPH No. 1 (chloroform)	DPPH No. 2 (benzene)	Wurster's blue
Line width (gauss between points of maximum slope)	0.6	0.8	2.8	2.9
T_2 (sec)	1.0×10^{-7}	8×10^{-8}	2.4×10^{-8}	2.3×10^{-8}
T_1 (sec)	1.1×10^{-7}	8×10^{-8}	5×10^{-8}	6×10^{-8}

FIG. 1. Relaxation times of solid solutions of DPPH in polystyrene as a function of concentration. T_1 values are probably within a factor of two of the true value at low concentrations and 20% at the high concentrations. Ultimately both T_1 and T_2 would increase if higher concentrations were obtainable.

relating to the exchange energy. Both θ_Z and θ_E can be different from the lattice temperature θ_L. Energy transfer between the exchange system and the Zeeman system takes place because the exchange interaction randomly modulates the dipolar interaction. This may be illustrated by the similar random modulation of the dipolar interaction in liquids and the resultant motional narrowing, where the nonadiabatic part of the line width is approximately the relaxation time for energy exchange between the Zeeman system and the lattice.[5] Analogously, the nonadiabatic width for the exchange-narrowed resonance
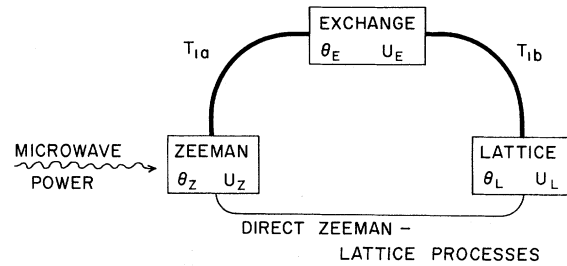

FIG. 2. Schematic diagram of the three-reservoir model of Bloembergen and Wang. The temperature θ and internal energy U of each reservoir is denoted by an appropriate subscript. The diagram also identifies the pairs of reservoirs coupled by the various relaxation times.

should represent the $1/T_1$ coupling the Zeeman and exchange systems. The Gaussian correlation spectrum usually employed, together with Eq. (36) of reference 5, gives an approximate form[8]

$$1/T_{1a} \approx (1/T_2)\ \exp(-\omega_Z{}^2/\omega_E{}^2). \qquad (1)$$

Since this relaxation process does not involve the lattice phonons, it is independent of lattice temperature θ_L. The exchange-lattice relaxation time T_{1b} is due to the modulation of the exchange energy by the lattice vibrations and therefore should be strongly temperature dependent. The direct relaxation between the Zeeman system and the lattice is negligible.[7] In the region $k\theta_Z > 2\beta H$ and $k\theta_E > J$, the specific heats vary[9] as θ^{-2} and thus the Zeeman and exchange energies are $U_Z = -K_Z/\theta_Z$ and $U_E = -K_E/\theta_E$. If one defines T_1 as the inverse decay rate of internal energy, the following equations describe steady-state energy flow from left to right in Fig. 2 (ignoring direct processes):

$$\frac{dU_Z}{dt} = 0 = -\gamma^2 H_1{}^2 T_2 U_Z(\theta_Z) - \frac{1}{T_{1a}}[U_Z(\theta_Z) - U_Z(\theta_E)], \qquad (2)$$

$$\frac{1}{T_{1a}}[U_Z(\theta_Z) - U_Z(\theta_E)] = \frac{1}{T_{1b}}[U_E(\theta_E) - U_E(\theta_L)]. \qquad (3)$$

The observed ratio of Zeeman and lattice temperatures is interpreted as the saturation factor:

$$\theta_Z/\theta_L = 1 + \gamma^2 H_1{}^2 T_2 (T_1)_{eff}. \qquad (4)$$

Equations (2), (3), and (4) yield

$$\theta_E/\theta_L = \frac{1 + \gamma^2 H_1{}^2 T_2 (T_1)_{eff}}{1 + \gamma^2 H_1{}^2 T_2 T_{1a}}, \qquad (5)$$

where

$$(T_1)_{\text{eff}} = T_{1a} + (K_Z/K_E)T_{1b}. \qquad (6)$$

Since the Zeeman and exchange energies are about the same order of magnitude, $K_Z/K_E \approx 1$ and therefore $(T_1)_{\text{eff}} \approx T_{1a} + T_{1b}$. In those samples with appreciable ω_E the observed $(T_1)_{\text{eff}}$ is temperature independent and equal to T_2. We conclude that $T_{1b} \ll T_{1a}$. In the solid solution samples of medium dilution, $(T_1)_{\text{eff}}$ is longer than T_2 in accord with Eq. (1), but only slightly temperature dependent, indicating that T_{1b} is still not long enough to be observed. With increasing dilution, exchange plays a smaller part in producing relaxation of the Zeeman system and finally the direct Zeeman-lattice relaxation is observed.

In the liquid helium temperature range we find a broadening of the lines in samples with a large exchange interaction. This is similar to the behavior observed in known antiferromagnetic substances as the Curie point is approached.[10] At room temperature the correlation frequency of the exchange system is approximately the exchange frequency $J/\hbar$. However, it may be that as the Curie point is approached the onset of local ordering reduces the correlation frequency. As the microwave power is increased, we observe a pronounced narrowing of the resonance line as well as a saturation of the total intensity. This effect is more pronounced in samples with higher exchange interaction. Effective spin-lattice relaxation times calculated from the saturation of total intensity (derivative peak×width^2) lie in the range of 10^{-6} sec and are temperature dependent. We believe that these relaxation times are determined by T_{1b}. This increase in relaxation time is too great to be explained by Eq. (1), even when the reduction of the correlation frequency is taken into account. Since T_{1a} is still about 5×10^{-8} sec, the temperature of the exchange system becomes greater than the lattice

temperature upon saturation, in accord with Eq. (5). It is as if the increased exchange temperature destroys the local order thus raising the correlation frequency and narrowing the line.

In the samples with the highest exchange (DPPH-1, BDPA) we have observed a variation in line shape with power at temperatures below 2°K. In BDPA there is an increase in crystalline anisotropy below 2°K, since the observed line width of a polycrystalline sample is greater than that of a single crystal. In these cases the temperature may be below the Curie point. Specific heat measurements are in progress to determine the Curie temperatures in these materials.

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