

## Rotational Polarization of Molecular Groups in Solids

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When nuclear spin relaxation in solids is due to rapid random rotational motion of molecular groups, magnetic relaxation parameters are dynamically coupled to populations of molecular rotational states. Relaxation of magnetization induces population differences between clockwise and anticlockwise rotational states (rotational polarization), resulting in nonexponential magnetic relaxation. At low temperature a nonequilibrium population difference between rotational states may be generated by a temperature change, and subsequent relaxation induces magnetic dipolar polarization.

In most solids nuclear spin diffusion is responsible for establishing Boltzmann distributions among the levels of the nuclear spin system, permitting a description in terms of two independent parameters, the nuclear Zeeman and dipolar spin temperatures.<sup>1</sup> In liquids this process is absent because the rapid random motions render ineffective the flip-flop terms of the internuclear dipole-dipole interactions. Molecular groups in solids, executing rapid random rotation about symmetry axes, represent an interesting intermediate case because some spin-diffusion transitions are rendered ineffective by this motion, a situation described as symmetry-restricted spin diffusion.<sup>2,3</sup> As a result new parameters must be introduced to describe population differences between nuclear spin species, where each species corresponds to an irreducible representation of the group of permutations of the nuclei arising from the motion.

The consequences may be illustrated by the example of a solid containing rotating methyl groups. If the nuclear dipole-dipole interactions were absent, nuclear spin and space coordinates would be uncoupled and a nuclear spin function for the protons of a particular methyl group could be factored out of an eigenfunction for the whole crystal. Without the dipole-dipole interactions the Hamiltonian is invariant under the separate operations of cyclic permutation of space or spin coordinates of the three protons, so that each member of the product function can be classified according to the irreducible representations  $A$ ,  $E^a$ ,  $E^b$  of the permutation group. The Pauli principle requires<sup>4</sup> that products be of the form  $A \times A$  or  $E^a \times E^b$  or  $E^b \times E^a$ . Thus a single label serves to

identify the symmetry properties of the three species. The random rotation of the methyl group affects these functions only by introducing a random phase modulation of the  $E$  functions.<sup>5</sup> The nuclear dipole-dipole interactions cause conversion between symmetry species by spin diffusion in a time of the order of the spin-spin relaxation time  $T_2$  when there is no motion. The effect of motion is to slow down the conversion rate by causing dipole-dipole matrix elements to fluctuate randomly.

As has already been pointed out,<sup>2</sup> under the condition of strong motional narrowing the flip-flop transition probabilities which do not involve a change in symmetry are of the order of the intermolecular dipolar field  $b$ , while those which involve symmetry conversion are of order  $b^2\tau_c$ , where  $\tau_c$  is the correlation time for the random rotation. As a result, symmetry-restricted spin diffusion can maintain Zeeman and dipolar spin temperatures during magnetic relaxation, but cannot change rapidly the populations of the three symmetry species, which may therefore evolve on a time scale comparable with the spin-lattice relaxation time. Hence the population differences between these species must be introduced. The departure of these differences from the equilibrium values is referred to as rotational polarization. The dynamical equations for rotational polarization are coupled to the magnetization parameters, accounting for nonexponential magnetization recovery at high temperatures<sup>6</sup> and thermally induced dipolar polarization at low temperatures.<sup>7</sup>

We consider a system of  $N$  levels, the  $i$ th level having Zeeman energy  $-\hbar\omega_0 m_i$ , where  $m_i$  is a

magnetic quantum number and  $\omega_0$  is the nuclear Larmor frequency. The usual spin-temperature assumption would be to write the populations of the Zeeman levels as

$$p_i = N^{-1} \exp(\beta_Z m_i) \approx N^{-1} (1 + \beta_Z m_i),$$

with  $\beta_Z = \hbar\omega_0/k\Theta_Z$  where  $\Theta_Z$  is the nuclear Zeeman spin temperature. To take account of symmetry-restricted spin diffusion we introduce  $\mu_i = 0, 1, -1$ , for  $A, E^a, E^b$  species, respectively, and write

$$p_i = N^{-1} [1 + \beta_Z m_i + \beta_d (\mu_i^2 - 1) (m_i^2 - \frac{5}{4}) + \beta_r \mu_i + \beta_t (1 - 2\mu_i^2)]. \quad (1)$$

In (1)  $\beta_d = \hbar\omega_d/k\Theta_d$ , where  $-\hbar\omega_d(\mu_i^2 - 1)(m_i^2 - \frac{5}{4})$  gives the shifts of the energy levels due to the intramethyl-group dipole-dipole interaction<sup>8</sup> and  $\Theta_d$  is the dipolar temperature;  $\beta_r$  is a measure of the difference between populations of  $E^a$  and  $E^b$  species and  $\beta_t$  of the difference between  $E$  and  $A$  populations. Since the  $A$  species is a nuclear spin quartet and the  $E$  species are doublets, the equilibrium values of both  $\beta_r$  and  $\beta_t$  are zero (except at low temperature when tunneling rotation of the methyl groups is important). Since sums over the eight levels of products like  $m_i \mu_i, m_i(1 - 2\mu_i^2)$  are zero, one finds from (1)

$$\begin{aligned} \beta_Z &= N \sum_i m_i p_i / \sum_i m_i^2, \\ \beta_d &= N \frac{\sum_i (\mu_i^2 - 1) (m_i^2 - \frac{5}{4}) p_i}{\sum_i (\mu_i^2 - 1)^2 (m_i^2 - \frac{5}{4})^2}, \\ \beta_r &= N \sum_i \mu_i p_i / \sum_i \mu_i^2, \\ \beta_t &= N \sum_i (1 - 2\mu_i^2) p_i / \sum_i (1 - 2\mu_i^2)^2. \end{aligned} \quad (2)$$

With the introduction of transition probabilities  $W_{ij}$

$$dp_i/dt = \sum_j W_{ij} [p_j - p_i - N^{-1} \beta_L (m_j - m_i)], \quad (3)$$

where  $\beta_L = \hbar\omega_0/k\Theta_L$  and  $\Theta_L$  is the lattice temperature. Combining (2) and (3) and eliminating  $p_i$  through (1) yields differential equations for the  $\beta$ 's. The equations for  $\beta_Z$  and  $\beta_r$  are coupled, but because

$$W(m_i \mu_i, m_j \mu_j) = W(-m_i - \mu_i, -m_j - \mu_j) \quad (4)$$

the coupling terms connecting  $\beta_Z$  or  $\beta_r$  with  $\beta_t$  or  $\beta_d$  vanish. The coupling between  $\beta_d$  and  $\beta_t$  may explain Haupt's experiment<sup>7</sup> where a sudden change in temperature at low temperature causes  $\beta_t$  to depart from its new equilibrium value. As a result of the coupling a change in  $\beta_d$  is induced and so a transient dipolar polarization is observed.

For  $\beta_Z$  and  $\beta_r$  the pair of coupled equations can be written

$$\begin{aligned} d\alpha_Z/dt &= -A_Z \alpha_Z - B \alpha_r, \\ d\alpha_r/dt &= -B \alpha_Z - A_r \alpha_r, \end{aligned} \quad (5)$$

with

$$\begin{aligned} \alpha_Z &= (\sum_i m_i^2)^{1/2} (\beta_Z - \beta_L), \quad \alpha_r = (\sum_i \mu_i^2)^{1/2} \beta_r; \\ A_Z &= \sum_{i>j} W_{ij} (m_i - m_j)^2 / \sum_i m_i^2, \\ A_r &= \sum_{i>j} W_{ij} (\mu_i - \mu_j)^2 / \sum_i \mu_i^2, \\ B &= \frac{\sum_{i>j} W_{ij} (\mu_i - \mu_j) (m_i - m_j)}{(\sum_i m_i^2 \sum_i \mu_i^2)^{1/2}}. \end{aligned} \quad (6)$$

The symbol  $i > j$  means that each term occurs only once in the summations. Equations (4) are decoupled by a simple rotation in the  $\alpha_r, \alpha_Z$  plane through an angle  $\theta$  where  $\tan 2\theta = 2B/(A_r - A_Z)$ . The combinations  $\alpha_Z \cos \theta - \alpha_r \sin \theta$  and  $\alpha_Z \sin \theta + \alpha_r \cos \theta$  relax exponentially with different relaxation times.

As a simple example we consider a solid containing an array of methyl groups oriented with their axes parallel to the external magnetic field. The energy levels are sketched in Fig. 1 which also shows the nonzero transition probabilities  $W$  due to the intra-methyl-group dipole-dipole interaction which are expected to dominate the relaxation which are expected to dominate the relaxation. Taking only these transitions into account gives  $A_Z = 4W/3, A_r = W/2$ , and  $B = -(\frac{2}{3})^{1/2}W$ . Since  $A_Z A_r = B^2$ , one of the relaxation rates is zero and the other is  $A_Z + A_r$ . The lower part of the diagram in Fig. 1 shows the kind of relaxation behavior expected. Equilibrium is represented by the origin  $\alpha_Z = \alpha_r = 0$ . The relaxation trajec-

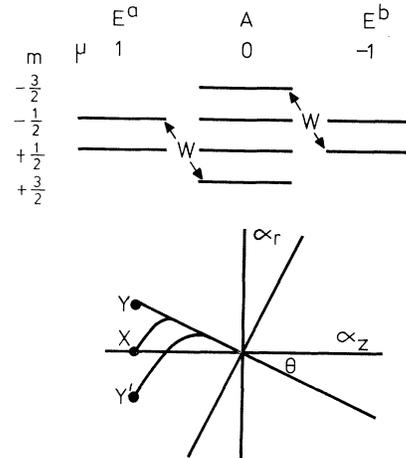


FIG. 1. Energy levels of methyl group and relaxation trajectories in  $\alpha_Z \alpha_r$  plane.

tory on the diagram depends on the mode of preparation.<sup>3</sup> A single short saturating pulse prepares the system at  $X$  on the diagram ( $\beta_z = \alpha_r = 0$ ). The subsequent relaxation is at a rate  $A_z + A_r$ , parallel to one of the principal axes of relaxation, and at a much slower rate ( $\sim 0$ ) parallel to the other. Magnetic relaxation measurements observe the projection of this trajectory on the  $\alpha_z$  axis and this has the form of a sum of two exponential decay terms as is indeed observed experimentally.<sup>6</sup>

Other ways of preparing the system give different results. A long saturating pulse prepares the system at  $Y$  and relaxation occurs at the slow rate. A sudden rotation of the crystal through  $180^\circ$  about an axis perpendicular to the external field has the effect of switching the identities of  $E^a$  and  $E^b$  states and therefore of inverting the rotational polarization. Thus a system prepared at  $Y$  can be transferred to  $Y'$  when most of the re-

laxation would occur at the more rapid rate.

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## Determination of the Optical Properties and Absolute Concentrations of Electron-Hole Drops in Germanium

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We report measurements of the scattering and absorption of  $3.39\text{-}\mu\text{m}$  light by electron-hole drops in Ge. An unexpected Fabry-Perot effect in our samples allows us to measure not only the drop size but also their absolute concentration and the optical indices of refraction of the electron-hole condensate.

The existence of a dense liquid phase of a non-equilibrium electron-hole gas in a cold intrinsic semiconductor was predicted by Keldysh<sup>1</sup> and has been verified, at least in Ge and Si, by several different experiments. Analysis of the shape and separation of certain bands of recombination luminescence<sup>2</sup> has supported the hypothesis that in Ge the liquid phase is a two-component plasma with pair density  $\sim 2 \times 10^{17} \text{ cm}^{-3}$  and binding energy per pair  $\sim 1.8 \text{ meV}$ . These conclusions are consistent with theoretical predictions of a stable liquid-plasma phase.<sup>3</sup>

Measurements of photocurrent noise<sup>4</sup> and infrared light scattering<sup>5</sup> in germanium have established that the liquid phase condenses as droplets with sizes in the  $1\text{-}10\text{-}\mu\text{m}$  range. Luminescence-decay and dimensional-resonance experiments<sup>6</sup> suggesting droplet sizes on the order of hundreds of micrometers are, in our opinion,

less direct, and subject to reinterpretation; though it is conceivable that these large drops are produced in some crystals under excitation conditions different from ours.

In our attempts to reproduce the light-scattering measurements of Pokrovskii and Svistunova,<sup>5</sup> we have discovered, to our surprise and delight, that we have been able to make use of a variable Fabry-Perot effect in our crystals to measure not only the droplet size but also the concentration of droplets and their infrared properties (the complex index of refraction of the liquid phase). Previous analyses of scattered and absorbed light have had to rely on assumed and derived values for the optical indices of the liquid.

Our experimental setup is similar to that reported by Pokrovskii and Svistunova.<sup>5</sup> A rectangular germanium crystal ( $n$  type,  $\rho \geq 45 \Omega \text{ cm}$ ) is immersed in superfluid helium at  $\sim 1.8 \text{ K}$ .