

## THE STABILITY OF SPIN-POLARIZED NITROGEN CRYSTALS

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The magnetic dipole interaction in a spin-polarized nitrogen crystal limits the lifetime of the crystal to much less than 1 s.

In two recent papers Ferrante and Stwalley [1,2] have calculated some of the properties of a hypothetical crystal composed of spin-polarized nitrogen atoms. A somewhat analogous system, spin-polarized atomic hydrogen gas, is known to undergo very rapid recombination [3] due to three-body collisions [4] at densities in excess of  $10^{18}$  atoms/cm<sup>3</sup>. In this note we point out that spin-polarized nitrogen crystals will rapidly decompose into N<sub>2</sub> gas for similar reasons.

A nitrogen atom in its ground state has no orbital angular momentum (it is an S state) and it has spin 3/2 in accordance with Hund's rules for a half-filled p shell. Two ground-state nitrogen atoms can interact with each other along four potential curves of symmetry <sup>1</sup>Σ, <sup>3</sup>Σ, <sup>5</sup>Σ, and <sup>7</sup>Σ. The nature of these potential curves, as estimated by Ferrante and Stwalley, is shown in fig. 1. To lowest order, the total spin of a pair of nitrogen atoms is a good quantum number so one could imagine forming a crystal of spin-polarized nitrogen atoms with each pair of atoms interacting on the weakly attractive <sup>7</sup>Σ curve. Ferrante and Stwalley have shown that the properties of such a crystal should resemble those of the van der Waals crystal formed from neon atoms.

The stability of a crystal of spin-polarized nitrogen atoms requires that there be no transitions from the <sup>7</sup>Σ potential of fig. 1 to the lower-spin potentials and especially to the strongly attractive potentials <sup>3</sup>Σ and <sup>1</sup>Σ which lead to tightly bound N<sub>2</sub> molecules. However, spin-destroying relaxation mechanisms are well known from extensive work on paramagnetic resonance [5-7]. Experiments show that the relaxation

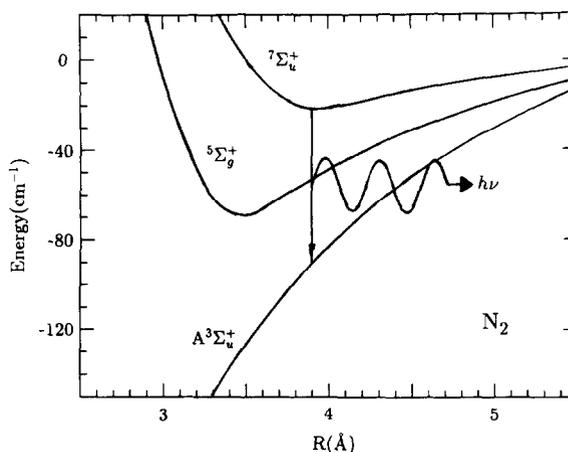


Fig. 1. The magnetic dipole-dipole interaction between a pair of spin-polarized N atoms in a crystal can cause the pair to make a transition from the <sup>7</sup>Σ pair potential to the attractive <sup>3</sup>Σ pair potential with the emission of a phonon of energy  $h\nu$  to the crystal lattice. Details of the vibrational structure of the N<sub>2</sub> molecule are not shown.

rates increase with the concentration of paramagnetic species. The relaxation times seldom exceed 1 ms, and they are often considerably shorter, especially in crystals with high number densities of paramagnetic species. Many physical mechanisms are known to contribute to the spin relaxation. Some of the most important interactions are phonon-induced modulation of the electrostatic crystalline field or of the magnetic dipole-dipole coupling between neighboring paramagnetic species. The same relaxation mechanisms must operate in a crystal of spin-polarized nitrogen atoms. We will not attempt to examine

all of the possible relaxation mechanisms but we will show that one of the simplest, the magnetic dipole-dipole interaction, is already big enough to limit the lifetime of a crystal of spin-polarized nitrogen to much less than 1 s. The magnetic dipole-dipole interaction was first considered by Waller [8] to account for spin relaxation in paramagnetic crystals, but it can cause tightly bound N<sub>2</sub> molecules to form in a spin-polarized nitrogen crystal at a much faster rate than the rate of ordinary paramagnetic relaxation because phonons near the peak of the Debye spectrum are emitted rather than the low-frequency phonons which carry off the energy of a spin flip in a magnetic field.

The magnetic-dipole interaction between two N atoms of spins  $S_1$  and  $S_2$  is

$$H = \frac{(g_S \mu_B)^2}{r^5} [r^2 S_1 \cdot S_2 - 3 S_1 \cdot r r \cdot S_2]. \quad (1)$$

Here  $\mu_B$  is the Bohr magneton,  $g_S \approx 2$  is the  $g$ -value of the  $^4S_{3/2}$  state of the N atom, and  $r$  is the internuclear separation. We denote the spin part of the wavefunction of a pair of N atoms by

$$|SM\rangle = |^{2S+1}\Sigma; SM\rangle,$$

where  $M$  is the projection of the total spin

$$S = S_1 + S_2 \quad (2)$$

along the spin polarization axis of the crystal. The interaction (1) can couple states  $|SM\rangle$  and  $|S'M'\rangle$  with  $|S-S'| = 0$  or 2. In particular, we readily find that the coupling of a polarized pair of N atoms on the  $^7\Sigma$  curve to the same pair on the attractive  $^3\Sigma$  curve of fig. 1 is

$$\langle 11|H|33\rangle = \frac{18}{10^{1/2}} \frac{\mu_B^2}{r^3} \sin^2 \vartheta e^{2i\varphi}, \quad (3)$$

where  $\vartheta$  and  $\varphi$  are the polar angles of the internuclear separation vector  $r$ . To estimate the spin decay rate due to (3) we follow the method outlined by Pake [5].

According to Fermi's golden rule, the pair of N atoms will emit phonons of momentum  $\hbar k$  into the crystal lattice at a rate

$$R = (2\pi/\hbar) |V_{fi}|^2 \rho(E), \quad (4)$$

where the matrix element is

$$V_{fi} = \langle k|\delta q|0\rangle \cdot \nabla \langle 11|H|33\rangle. \quad (5)$$

Here the relative displacement  $\delta q$  of the two nitrogen atoms with respect to each other is related to the total displacement  $q$  of N atoms by

$$\delta q = (i\mathbf{k} \cdot \mathbf{r}) q. \quad (6)$$

The wave vector  $k$  is related to the wavelength  $\lambda$  by  $k = 2\pi/\lambda$ . For simplicity, a phonon wavelength which is long compared to the internuclear separation  $r$  was assumed in (6). For a phonon of polarization  $e$  we have

$$q = \frac{e}{2\pi} \left( \frac{\hbar}{2\rho V\nu} \right)^{1/2} (a + a^\dagger), \quad (7)$$

where  $\rho$  is the mass density of the crystal,  $V$  is the volume,  $\nu$  is the phonon frequency and  $a$  and  $a^\dagger$  are annihilation and creation operators for phonons. Substituting (7), (6), and (3) into (5) we find that the transition matrix element is

$$V_{fi} \approx i \frac{kr}{2\pi} \left( \frac{\hbar}{2\rho V\nu} \right)^{1/2} \frac{54}{10^{1/2}} \frac{\mu_B^2}{r^4}, \quad (8)$$

where we have set all functions of  $\vartheta$  and  $\varphi$  equal to unity and we have considered only radial components of the gradient in (5).

The density of states in the Debye approximation is

$$\rho(E) \approx \frac{12\pi V\nu^2}{\hbar\nu^3}, \quad (9)$$

where  $\nu$  is an average velocity of longitudinal and transverse phonons. Substituting (9) and (8) into (4) we find a decay rate of

$$R \approx 3.45 \times 10^4 \left( \frac{\mu_B^2}{r^3} \right)^2 \frac{\nu^3}{\hbar\rho\nu^5}. \quad (10)$$

The numerical factor ( $1.7486\pi^2$ ) differs from the factor ( $108\pi^2$ ) in Pake's analogous equation (6-37) because our matrix element (3) involves a change in the azimuthal quantum number  $M$  by two units. Neither numerical factor should be considered very precise because of the crude approximations used in the derivations. Using the work of Ferrante and Stwalley [1,2] we estimate the following values for the other parameters in (10):  $r = 3.9 \times 10^{-8}$  cm,  $\nu = 1.3 \times 10^5$  cm/s,  $\rho = 0.39$  g/cm<sup>3</sup>,  $\nu = 2 \times 10^{12}$  s<sup>-1</sup>. Substituting

these values into (10) we find

$$R \approx 3.8 \times 10^7 \text{ s}^{-1}. \quad (11)$$

Note that the estimate (11) remains valid at the largest attainable magnetic fields and at absolute zero of temperature, since we assumed spontaneous emission of phonons at the septet-triplet splitting energy. A more elaborate calculation of the decay rate could be made by using a more detailed phonon spectrum, distinguishing between longitudinal and transverse phonons and accounting for branching to various vibrational states of  $\text{N}_2$  molecules on the  $^3\Sigma$  potential curve. However, the rough estimate of the rate (10) is so large that spin-polarized nitrogen crystals will probably be too short-lived for practical investigation. A dilute solution of spin-polarized nitrogen atoms in a diamagnetic matrix-like solid hydrogen would be much more stable than the neat crystal discussed above, both because of steric hindrances to recombination and because of the rapid decrease of the dipole-dipole interaction (1) with the separation of the nitrogen atoms.

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