Inference of High Atom Densities in Solid Tritium from Nuclear Magnetic Resonance Measurements

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At fixed temperature the ortho concentration in solid T_2, as monitored by NMR, is found to decay exponentially in time with a time constant that has a minimum at 11.4 K. At 11.4 K the ortho-to-para conversion in T_2 is 200 times larger than in H_2. This enhanced conversion rate is attributed to diffusing atoms created by the tritium β decay. A hopping model is used to infer the atom number density and hopping frequency as functions of the temperature.

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When room-temperature equilibrium gases of H_2, D_2, or T_2 are condensed to form solids, the fraction of molecules in the rotational level $J=1$ in the molecular solid (the ortho state of H_2 or T_2) can be approximately 75%. The decay of this metastable population to the thermal-equilibrium value is an interesting solid-state physics problem in its own right. In this Letter, we report measurements of a larger, temperature-dependent ortho-to-para rate in solid T_2, a result that may have important practical consequences. However, the real significance of this paper lies in the interpretation that the enhanced rate of conversion is due to the existence of a gas of T atoms in the solid and the inference of the density and mobility of this gas as functions of the temperature.

Two sets of experiments have shown that it is possible to produce and store large numbers of atoms in molecular solids. One of the most illuminating experiments was performed by Leach and Fitzsimmons[1] on molecular H_2 irradiated by 200-keV pulses from an electron gun. The electron pulses produced H atoms, easily identified in the ESR spectra by their characteristic hyperfine splitting of 509 G. At sample temperatures between 8.1 and 6.5 K, the time decay of the ESR intensity after the electron beam was switched off yielded the atom recombination coefficient, $\alpha(T)$:

$$\alpha(T)=\alpha_0\exp(-E_A/kT), \tag{1}$$

where $\alpha_0=4.1\times10^{-8}\ \mathrm{cm}^3\cdot\mathrm{s}^{-1}$ and $E_A/k=195\pm10$ K. This result suggests that H_2, in the presence of a *constant* electron flux, would acquire an equilibrium number of atoms that would increase exponentially with decreasing temperature.

A second important result was obtained by Sharnoff and Pound,[2] who made ESR measurements on D_2 containing about 1% T_2. Radioactive decay of the T_2 produced D (and T) atoms. At 4.2 K, the atom density was measured to be 10^{18} atoms/cm^3. Extension of this work to lower temperatures by Webeler[3] and the interpretations by Rosen[4] and Zeleznik[5] indicated that atom densities large enough to become unstable could be produced.

Previous work by our group[6] on the temperature dependence of the ortho-to -para conversion in solid T_2 was interpreted in terms of a large atom population since an exponentially increasing density *could* result from our constant atom production in T_2. Our previous work suffered because a poor choice of sample design (both geometry and choice of materials) led to a large temperature uncertainty. Using an improved design, we have extended the earlier measurements and have obtained some striking new results from our NMR experiments.

One additional motivation for the present study was the possibility of the use of molecular DT, with both species of nuclear spins polarized, as a target for laser fusion. If dynamic polarization is to be used to obtain high nuclear-spin polarizations in molecular DT, it is essential to have long nuclear-spin–lattice relaxation times for both D and T nuclei. As these times depend on the concentrations of o-T_2 and p-D_2 in the sample,[7] the time dependence of these concentrations must be known.

We determined the o-T_2 concentrations *in situ* from NMR signal-height measurements with a constant-voltage signal being used for gain calibration. Since "fresh" samples are used for each *constant-temperature run,* the initial o-T_2 concentration is 0.75. Mass-spectrographic analysis is used on the gas samples before and after each run to determine the HT and DT impurity concentrations that contribute to the NMR signal. Thus the (calibrated) voltage associated with the initial signal is used to determine the concentration at all later times.

Our previous finding that, at fixed temperature, the ortho concentration decayed exponentially in time is found to be rigorously correct over the entire range (15 to 6.4 K) of these experiments. This indicates that the conversion is *not* intrinsic conversion but is catalyzed.

Earlier we found that the conversion rate increased as we decreased the temperature. Our new data show that *there is a peak in the conversion rate.* Additionally, the strength of the NMR signal at long times, after subtraction of the contributions from HT and DT impurities, is larger than that expected from the Boltzmann distribution applied to the $J=1$ and $J=0$ rotational levels, indicating that atom recombination is "pumping" the upper level. Therefore, we must take into account the atom dynamics when writing the "gain-loss" equations for the ortho and para populations.

The radiation from the tritium β decay produces atoms at a constant rate, K. The atoms can then form molecules with a recombination coefficient $\alpha(T)$. The rate of atom production does depend on the number of tritium molecules but should be independent of temperature and time (on the time scale of our experiments). If m is the number of atoms, then

$$dm/dt = K - \alpha(T)m^2, \tag{2}$$

where the recombination is assumed to be quadratic[1] in m. If the atom population is in equilibrium, the steady-state number of atoms present in the sample, m_a, is given by $m_a = [K\alpha(T)]^{1/2}$. The radiation destroys molecules of both types with probability per unit time, γ. From atom recombination, o-T_2 should be formed at a rate 3 times larger than the rate to form p-T_2, with use of the high-temperature equilibrium ratios. These two effects, incorporated into the rate equations for the numbers of ortho (N_1) and para (N_0) molecules, yield

$$dN_1/dt = W_{01}N_0 - W_{10}N_1 - \gamma N_1 + \tfrac{3}{8}\alpha(T)m_a^2, \tag{3}$$

$$dN_0/dt = W_{10}N_1 - W_{01}N_0 - \gamma N_0 + \tfrac{1}{8}\alpha(T)m_a^2; \tag{4}$$

since the number of molecules ($N_T = N_1 + N_0$) is constant in time we obtain $2\gamma N_T = \alpha(T)m_a^2 = K$ so that only one new parameter (γ) is needed in the rate equations. The quantities W_{10} and W_{01} are the transition probabilities per unit time between the $J=1$ and $J=0$ levels. In the steady state, $dN_1/dt = 0$, and we obtain for the *steady-state* concentration of the $J=1$ level $x_e = (W_{01} + \frac{3}{4}\gamma/(W_{01} + W_{10} + \frac{3}{4}\gamma)$. Without the radiation, we would have $x_e = x_B$ so that $x_B = W_{01}/(W_{01} + W_{10})$. If W_{10} and W_{01} are the independent of N_1, the solution to Eq. (3) is

$$x_1(t) - x_e = \{x_1(0) - x_e\}\exp(-t/\tau), \tag{5}$$

where τ is $\tau^{-1} = W_{01} + W_{10} + \gamma$. If we take the "known" quantities to be the *measured* ortho-para exponential decay time τ, the *measured* equilibrium concentration of $J=1$ molecules x_e, and the *calculated* concentration of $J=1$ molecules expected from the Boltzmann distribution, x_B, we can extract from the data the three "unknowns," W_{10}, W_{01}, and the parameter γ, related to the production rate of atoms in the solid.

The values for W_{10} obtained from this analysis are shown in Fig. 1 along with the measured quantity x_e and the calculated values of x_B. A clear peak is seen at 11.4 K where the fitted straight lines give a rate of $R_m = 8 \times 10^{-4}$ s^{-1}, 200 times larger than the temperature-independent intrinsic conversion rate in solid H_2. The value of $\gamma = 3.4 \times 10^{-6}$ s^{-1}, obtained here, is 3 times higher than expected from gas-phase data indicating a more efficient atom production in the solid.

A peak in the rate *cannot* be explained by an ever increasing number of atoms as *fixed* converting centers, but can be explained if the atoms are in motion. A time-dependent magnetic field gradient is necessary for ortho-para conversion.[8] On the assumption that the conversion process is catalyzed by the atoms present in the solid, there are two different types of motion that will give the required gradient.[9] In the first type, the time dependence of the Hamiltonian is supplied by the phonons with atomic hopping from site to site enhancing the overall conversion rate (the "hopping model"). In the second type of motion, the time-dependent magnetic field gradient comes from the translational motion of the elec-

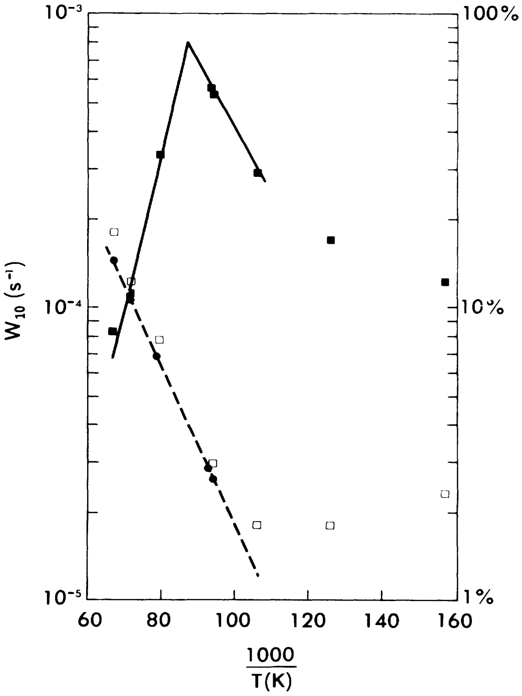

FIG. 1. The transition probability per unit time from the $J=1$ to the $J=0$ state, W_{10}, as deduced from τ, the equilibrium concentration x_e, and the concentration obtained from the Boltzmann distribution x_B, plotted (filled squares) as a function of the inverse temperature, $1000/T$. A peak is evident near 11.4 K. The fitted lines indicate a peak rate of 8×10^{-4} s^{-1}. The equilibrium concentration (x_e) is plotted (open squares) as a function of the inverse temperature along with the Boltzmann value (shown by filled circles and the dashed line).

tron spins themselves (the "ballistic model") with no phonons involved. In the first process, the hopping could just as well be molecular hopping with the electron spins fixed in space. To test this possibility, we measured the molecular self-diffusion coefficient in solid T_2 by NMR techniques. We conclude that the molecules are more localized than the atoms over the temperature range of our experiments.

For the hopping model, the conversion rate R in the low-concentration limit, can be written as

$$R = cz\Omega_0\Gamma/(z\Omega_0+\Gamma). \qquad (6)$$

In this expression, c denotes the concentration of unpaired electron spins (atoms), Γ is the rate for an electron spin to hop to a neighboring site, z is the number of neighboring sites, and Ω_0 is the conversion rate for a single molecule adjacent to an electron spin. The *calculated* value of the product $z\Omega_0=\Omega$, based on the assumption that the atoms are in the large interstitial positions between hops to nearby interstitial positions, is $\Omega = 14.1$ s^{-1} when $z=6$.

Since the recombination coefficient α also depends on the atom hopping frequency Γ, the equilibrium number of atoms and hence the atom concentration will depend on Γ. If we take $c \propto \Gamma^{-1/2}$, $\Gamma=\Omega$ at the peak where the maximum rate is $R_m = c\Omega/2$. If we can use our previous results for m_a, we can express c in terms of γ and α and ultimately[10] as a function of Γ. Using the peak rate, we can solve for the quantity Ω in this "self-consistent" fashion. We find that $\Omega = 4.73$ s^{-1}, in excellent agreement with the theoretical estimate considering the crudeness of both estimates.

From the measured rates and the peak rate R_m, we can extract the ratio of Γ to Ω as a function of temperature. These values are plotted in Fig. 2 along with the equilibrium atom density predicted by this analysis. The hopping frequency Ω appears to be thermally activated at the higher temperatures so that we can extract an activation energy, calculate the recombination coefficient α, and compare this result with the direct measurements of Leach and Fitzsimmons. From the fitted line in Fig. 2, we obtain $\Gamma = (1.83\times10^{12}\ s^{-1})\exp[(-303\ K)/T]$ which leads to a recombination coefficient $\alpha = (7.16\times10^{-10}\ cm^3/s)\exp[(-303\ K)/T]$. An activation energy of 303 K for T_2 is reasonable when compared to the value of 195 K found in H_2.

The calculated equilibrium atom density m_a shown in Fig. 2 appears to be "saturating" as the temperature is decreased. Dependent upon the method chosen for the extrapolation, the atom density at 4.2 K could like between 2×10^{20} and 5×10^{20} atoms/cm^3, the smaller estimate being roughly 200 times larger than the density observed by Sharnoff and Pound in D_2. If the atomic recombination rates in D_2 and T_2 were the *same*, we would expect a factor of 10 larger atom concentration simply because the production term in pure T_2 is 100 times larger than they used. In fact, their "production term" was unusually small,[11] most likely indicating that only a small fraction (about 1%) of their T_2 actually was in the cavity. If this is true, then our extrapolated atom density at 4.2 K agrees with the Sharnoff and Pound value and the value of α extracted from their data agrees well with ours.

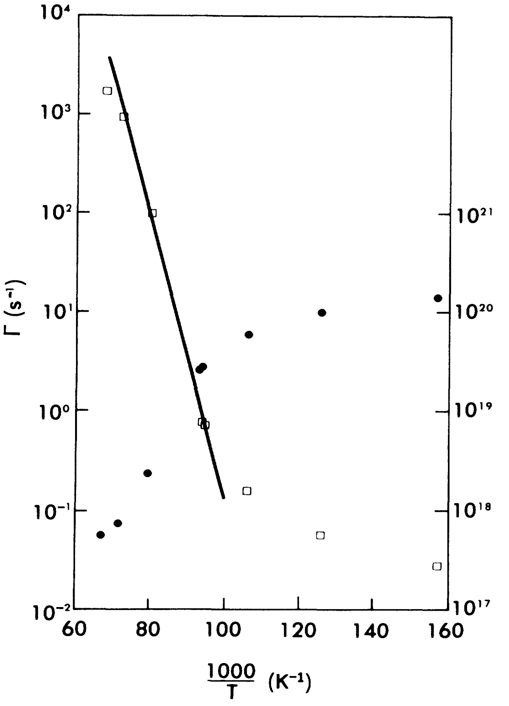

FIG. 2. The hopping (angular) frequency is plotted (open squares) as a function of inverse temperature where the transition probability per unit time, Ω, has been taken equal to 4.73 s^{-1}. The equilibrium number of atoms, m_a (in atoms per cubic centimeter), predicted by the hopping model applied to the data is plotted (filled circles) as a function of inverse temperature. The extrapolated atom density at 4.2 K would be between 2×10^{20} and 5×10^{20} atoms per cubic centimeter.

The ballistic model also leads to an expression for the conversion rate that has a peak in it but the same self-consistent approach applied to this model yields a characteristic frequency of 167 MHz, a frequency that does not correspond to any identifiable frequency in the problem. Moreover, the estimated atom density is orders of magnitude too small to reconcile with the Sharnoff and Pound measurements.

Our interpretation of the data thus suggests the presence of a "gas" of mobile atoms. The temperature dependence of the hopping frequency of the atom gas indicates that the atoms become *localized* or condense below 11.4 K. The condensation of this gas is a "real-space" condensation and not a "momentum-space" one such as the Bose condensation. The atom gas reaches a density of about 1% of the solid density and through its motion is responsible for the enhanced ortho-to-para conversion in the solid.

Scientifically, this interpretation is promising and the present study affords a novel way of inferring quantities such as the temperature-dependent hopping rate. Such a high-density electron-spin gas is an interesting magnetic system in its own right for future study.

The implications for the production of spin-polarized targets for fusion work are not very optimistic. For instance, the value of the equilibrium o-T_2 concentration obtained at our lowest temperatures is about 1.5% and does not appear to be decreasing. For such a concentration, nuclear relaxation is very fast making it difficult to obtain an overall T spin-relaxation time in DT of as much as 1 s. To obtain very low o-T_2 concentrations (and hence long nuclear relaxation times), it will be necessary to inhibit the atom recombination. This might be possible in larger magnetic fields than we used (0.7 T) if the recombination results from two-body interactions. Because of the inferential nature of this work, we plan to observe the atoms directly from their characteristic ESR signals.

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[9] Yue Cao, J. R. Gaines, P. A. Fedders, and P. C. Souers, to be published. The calculation of Berlinsky and Hardy has been modified and used to estimate both the intrinsic two-phonon and one-phonon ortho-to-para conversion rates in solid T_2. In addition, the conversion rate due to both fixed and diffusing paramagnetic impurities (atoms) has been calculated.

[10] The relationship between α and Γ was given by Leach and Fitzsimmons who assumed that $\alpha = \pi R_0 D$, where D is the diffusion coefficient and R_0 is the distance within which recombination is assured. They chose $R_0 = 5$ Å, the value we will use. The diffusion coefficient, D, is taken equal to $\langle r^2 \rangle \Gamma/2$, where we use $r = 3.53$ Å for our estimates. This gives for the peak rate

$$R_m = [\gamma_{\mathrm{solid}} \Omega / 4 N_T (\pi R_0 \langle r^2 \rangle)]^{1/2}.$$

[11] Sharnoff and Pound estimated from the time dependence of their signal intensity that they were getting 22 atoms per tritium disintegration. This is a factor of 35 *below* the gas-phase value. Our results in the solid indicate that we obtain 3 times more atoms per disintegration in the solid than in the gas. Thus their production term is a factor of 100 below ours *for the same assumed amount of* T_2. If only 1% of their T_2 condensed in the cavity, then the two sets of data agree very well.