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Ortho-to-para conversion in solid tritium. II. Experimental values

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Nuclear-magnetic-resonance signal heights at a Larmor frequency of 30 MHz are used to monitor the ortho-T_2 concentration as a function of time at fixed temperature in solid T_2. The ortho-T_2 concentration decreases with time due to ortho-to-para conversion in the solid. From our measurements, we find that the difference between the instantaneous signal height and the equilibrium signal height decays exponentially with time. The time constant of this decay has a minimum near 11.4 K indicative of a peak in the conversion rate near 11 K. The equilibrium signal height is observed to be larger than expected from the Boltzmann distribution. The conversion-rate data are interpreted in terms of a model where the conversion is due to electron spins (on atoms) capable of translational diffusion. The peak in the conversion rate is used to determine the characteristic frequency of the problem and the temperature dependence of the correlation time of the electron spins. The enhanced equilibrium signal is interpreted as arising from a preferential pumping of the $J=1$ ortho-T_2 level due to atom recombination. A model-dependent recombination coefficient for the atoms is extracted from the data, predicting an equilibrium number of atoms that is strongly temperature dependent.

I. INTRODUCTION

The molecular solid, tritium (T_2), is very similar to the molecular solid H_2 if solid H_2 is under constant irradiation by a suitable electron flux. The most notable differences between these two isotopic solids appears to come from the β decay of the tritium nucleus. Since the half-life of this decay is 12.3 y, for an experimental period of order days, the electron flux can be considered constant. In the steady state, this flux is responsible for a heat current of 1 W per mole of tritium in the solid that must be removed to maintain thermal equilibrium.

Our knowledge of solid H_2, under conditions of irradiation, is very sketchy as the few experiments, to date, have not explored many of the critical questions in any depth. There have been a few experiments[1-5] that do provide substantial clues regarding the differences between the behavior of ordinary molecular hydrogens and those irradiated by electrons[1,2] or protons[6] or doped with radioactive isotopes such as DT or T_2 (Refs. 3-5) (where the flux cannot be turned off).

One of the most illuminating experiments was performed by Leach and Fitzsimmons[1] on molecular H_2 irradiated by 200-keV pulses of electrons from an electron gun. The pulsed irradiation produced H atoms, easily identified by ESR techniques from their characteristic hyperfine splitting of 509 G. At a fixed sample temperature, between 8.1 and 6.5 K, measurement of the EPR intensity as a function of time after the electron beam was switched off yielded the recombination coefficient $\alpha(T)$ for the atoms. This coefficient is defined by

$$\frac{dm}{dt}=-\alpha(T)m^2 , \tag{1}$$

where m is the atomic H concentration (in an applied magnetic field of 3 kG). As defined here, the recombination coefficient was found to be an exponential function of the sample temperature,

$$\alpha(T)=\alpha_0\exp(-E_A/kT) , \tag{2}$$

where $\alpha_0=4.1\times10^{-8}$ $\text{cm}^3\,\text{s}^{-1}$ and $E_A/k=195\pm10$ K. Using simple arguments from kinetic theory, they deduced the diffusion coefficient for the *atoms* to be

$$D_{\text{atom}}=(0.07\ \text{cm}^2\,\text{s}^{-1})\exp(-195\ \text{K}/T) . \tag{3}$$

Incidentally, the activation energy, E_A, they obtained for atom diffusion, agrees with the NMR determination of the activation energy for *molecular self-diffusion.*[7] This result suggests that H_2, in the presence of a constant electron flux such as that obtained with their electron gun on, would acquire an equilibrium number of atoms that would increase exponentially with decreasing temperature. This increase would be due to the exponentially decreasing recombination coefficient so that the larger the electron flux, the larger the equilibrium number of atoms.

Using the Leach and Fitzsimmons estimates of atom production with their beam on and their measured recombination coefficient gives predictions of steady-state atom concentrations at $T=4$ K and below that are enormous. Experiments that extend down to the vicinity of 1 K[2] show no such large increase in atom concentration and thus indicate that some different diffusion process, possibly a quantum diffusion process, takes over near 5 K. The transition from one diffusion process to another below 8 K is not surprising as the solid by this temperature contains a large number of atoms and probably many defects that have been produced by radiation damage. These latter experiments, while not in complete quantitative agreement with those of Leach and Fitzsimmons, do confirm their general tendencies at higher temperatures and warn us to use care in extrapolating the high-temperature results to lower temperatures.

These general ideas were extended by our earlier experiments on solid molecular T_2,[5] where NMR techniques were used to measure the ortho-to-para conversion rate at various temperatures. In H_2, the intrinsic deexcitation rate (k) from the $J=1$, $I=1$ level (the lowest ortho level) to the $J=0$, $I=0$ level (the lowest para level), where J and I are the rotational quantum number and the nuclear spin, respectively, is independent of temperature and characterizes the decay:

$$\frac{dx_1}{dt}=-kx_1^2 , \tag{4}$$

where x_1 is the $J=1$ concentration. Experimental determinations of k agree rather well with theoretical predictions where k is found to be $1.95\%\,\mathrm{h}^{-1}$.[8] When this corresponding rate, at fixed sample temperature, was measured in solid T_2 by observing the time dependence of the NMR signal (only ortho-T_2 contributes to the resonance), it was found that[5]

(i) the kinetic equation differed from Eq. (4) and was given by

$$\frac{dx_1}{dt}=-\Omega x_1 , \tag{5}$$

resulting in an exponential decay of the $J=1$ excited state to the ground state.

(ii) The parameter characterizing the decay of the $J=1$ population, Ω, in the previous equation was found to increase exponentially, with decreasing temperature.

(iii) The magnitude of Ω was such, that at 10 K, the half-life of the ortho-T_2 population was about 1 h, a vastly larger rate than that expected from intrinsic conversion such as that seen in H_2 or D_2.

These experiments concluded that the transition was radiation catalyzed and that most likely it was atoms, seen directly by Leach and Fitzsimmons in H_2, and Sharnoff and Pound[3] in D_2, that caused this large, temperature-dependent $J=1$ to $J=0$ conversion rate.

Our earlier experiments were flawed in that the internally generated β radiation produced more self-heating that our sample cell geometry could handle, resulting in sample temperatures, measured from NMR signals, that different significantly from the sensor temperatures. In fact, in a subsequent study,[9] we utilized this difference between sensor temperature and sample spin temperature (combined with the known heating rate from solid T_2) to estimate the thermal conductivity of our samples. Accordingly, we have redesigned the sample cell geometry and chosen different cell materials to eliminate the temperature gradients in our sample.

Motivation for the present study comes from the possibility of using molecular DT with both species of nuclear spins polarized as a target for laser fusion. If the nuclear-spin polarization in molecular DT is to be achieved by one of the dynamic methods that involves a transfer of polarization from a system of electron spins, the details of the ortho-T_2 to para-T_2 conversion process are crucial. The nuclear spin-lattice relaxation times for both D and T nuclei will depend on the final concentrations of ortho-T_2 and para-T_2 in the sample.[10] The time dependence of these concentrations is thus important to dynamic polarization experiments on molecular DT.

In addition, in fairly diverse fields such as studies of conducting polymers by NMR techniques, a central problem is that of obtaining information about electron-spin translational motion by observations of NMR properties. Because of the parallel goals of these two studies, the present experiments, with their large populations of electrons spins embedded in a nuclear-spin system, take on added significance.

The remaining sections of this paper are organized in the following way: the details of the experiment are given in Sec. II; in Sec. III, we present the data on $J=1$ to $J=0$ conversion collected in these experiments; in Sec. IV, we present our analysis and interpretation of the data, and in Sec. V we discuss the conclusions reached by this work.

II. EXPERIMENTAL DETAILS

The sample cell geometry was redesigned. A sapphire cell was used and the sample shape was chosen to be a flattened circular shape to minimize the temperature difference over the sample, which due to self-heating, depends on the square of the sample thickness. The large diameter of the cell was dictated by signal requirements as we anticipated working with samples with very small concentrations of nuclear spins.

The cell as shown in Fig. 1 was cooled from the bottom. The cooling was provided by a continuous ^{4}He transfer cryostat. Copper clamps, with aindium inserts, were used to ensure that the bottom of the sapphire cell was in good thermal contact with the cold tip of the flow cryostat. A calibrated germanium resistance thermometer (GRT), inserted in the bottom of the sapphire, was used to monitor the sample temperature.

The amount of T_2 sample was carefully metered into the cell at $T\approx 22$ K. This ensured that we could compare signal heights from run to run. The sample admitted was observed via NMR in the liquid state and then the temperature reduced to solidify the sample. The entire sample was contained within the NMR coil so that a "spin count" could be obtained. This spin count was aided by a second coil (and transmission line) attached below the regular NMR coil. This auxiliary coil was used to inject a calibration signal into the spectrometer. Thus using a known sample volume, completely containing the sample within the NMR coil, and a calibration signal, meant that we could make accurate signal determinations as a function of time at fixed temperature and compare the signals obtained from run to run.

To obtain an accurate spin count, it is necessary to measure the NMR transient signal accurately at $t=0$, as

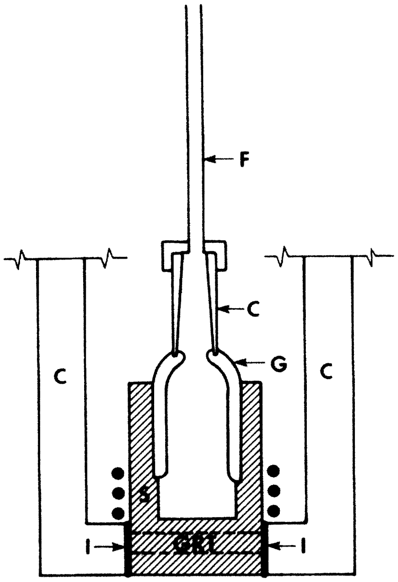

FIG. 1. A sketch of the sample cell used for these experiments. The sapphire cell (S) is epoxyed to the glass portion (G) of a copper (C) to glass (housekeepers) seal. There is a hole in the sapphire for the germanium resistance thermometer (GRT). A small pad of indium (I) is used between the copper (C) shroud and the sapphire. The shroud is connected to the cold tip of a continuous helium transfer cryostat. The NMR coil is indicated. The fill line (F) is stainless steel.

it is this signal that is proportional to the magnetization that existed just before the 90° pulse was applied. This means, in any transient experiment, that some method must be found to extrapolate the signal actually observed for $t>0$ to $t=0$. The problem of extrapolation occurs because the system exhibits a certain "deadtime" after the large rf pulse and there is no universal NMR line shape that can be used unambiguously for the extrapolation.

We used, for these experiments, a commercial NMR spectrometer manufactured by NOVEX, Inc. This phase-coherent spectrometer utilized quadrature detection. Optimum performance is obtained when all components (probe included) are matched to 50-Ω, resistive, loads. Since we had included no mechanical adjustments in our probe, to maintain a 50-Ω resistive load, we had to shift (slightly) our resonant frequency between 77 and 20 K. Below 20 K, temperature changes in the probe became negligible. Nonetheless, the second coil permitted us to check the gain of the system at all temperatures with a known calibration signal.

The quadrature detected signals were (i) phase corrected, (ii) frequency corrected, and (iii) baseline corrected. After these corrections, we fitted the "real" part of the signal to two different analytical forms to obtain the signal at $t=0$. At high ortho-T_2 concentrations, the FID (free induction decay, the NMR signal following the rf pulse in our experiment) resembled a damped oscillation like that observed for normal H_2 by Metzger and Gaines.[11] Accordingly, there the FID was fitted to the "modified Gaussian,"

$$S(t)=A\exp(-a^2t^2/2)\frac{\sin(bt)}{bt}\ , \tag{6}$$

in order to obtain the signal at $t=0$, A. For FID's that showed no such oscillation, the function used for the fit was

$$S(t)=A\exp\{-\omega_p^2\tau_c^2[\exp(-t/\tau_c)-1+t/\tau_c]\}\ . \tag{7}$$

This response function was derived for the case of Brownian motion but has more generality and provides a smooth transition between Gaussian and exponential FID's. In our experiments, we do see such a change in the FID shape, so the above function gives us an unbiased way to extract A, the signal at $t=0$. The actual fits to the above function, when there was no oscillation, were pretty good. The actual values of τ used in the above fit are not quoted in this paper.

Because of the temperature gradient problems encountered in the previous experiments, considerable attention was given, in these experiments, to the comparison of the sensor temperature and the nuclear-spin temperture determined from the signal at $t=0$ and use of Curie's law. We found that when we used H_2 for the sample, there was no detectable difference between these two temperatures. For normal-T_2, our most radioactive sample, the relative nuclear-spin temperature, obtained from the initial signal height, indicated a slightly higher temperature than the sensor did. Thus we apply a correction to our sensor temperature to obtain a more representative value of the real sample temperature. We arrive at this correction by calculating the temperature increment, ΔT, that must be added to the sensor temperature from the known heat generated (1 W per mole T) and the estimated thermal conductivity of the sample at our highest temperature, 14.5 K. The other temperatures are then obtained by requiring conformity to the Curie law. In practice, this amounts to a temperature correction of about +0.5 K at our highest temperature, increasing to about 1 K at our lowest temperatures.

III. EXPERIMENTAL DATA

The samples were analyzed by means of a high-resolution magnetic sector mass spectrometer before and after our experiments. This analysis revealed that small amounts of HT and DT impurities were present. In a gas analysis before the experiments, it was found that the sample contained ^{3}He (0.56%), HT (1.52%), DT (1.53%), T_2 (96.39%). After the experiments, the analysis gave ^{3}He (1.34%), HT (2.62%), DT (1.74%), T_2 (94.11%) and CT_4 (0.18%). The HT and DT impurities contribute to the NMR signal but this contribution is constant, in time, so it contributes nothing to the determination of the decay time of the ortho-T_2 population since the signal difference at two times is the important quantity in finding the ortho-to-para conversion time. The impurity signal does, however, make an important contribution to the "equilibrium" signal, so to obtain the equilibrium signal due to the remaining ortho-T_2, we must subtract the impurity signal. We obtain the correction for the signals from HT and DT by assuming

TABLE I. Experimental data. See text for details.

T (K)	T_s (K)	% HT + DT	τ (min)	$x_1(0)$	$x_1(\infty)$	x_B
6.4	5.3	3.1	137	0.67	0.023	0.0002
8.0	7.0	3.7	98	0.64	0.018	0.0025
9.5	8.4	3.9	59	0.63	0.018	0.0098
10.6	10.0	3.3	31	0.63	0.029	0.026
10.7	10.0	4.1	29	0.65	0.029	0.028
12.6	12.0	3.4	43	0.67	0.077	0.068
14.0	13.3	4.6	119	0.68	0.124	0.107
15.0	14.5	4.3	221	0.66	0.181	0.145

our initial signal is the combination of a signal from T_2 with a known ortho-T_2 concentration and the known amount of impurities. We then use the known concentrations and the spin specific heats to calculate the fraction of the signal coming from the impurities. All our quoted "equilibrium" signals have the impurity contribution removed and thus represent the amount of ortho-T_2 remaining in the sample. The data are presented in tabular form in Table I.

The sensor temperature is indicated by the column labeled T_s whereas the *corrected* sample temperature is simply labeled T. Because we pick up a signal from all T nuclear spins, the HT and DT impurity concentrations are listed for each experiment. The time constant, τ, that characterizes the *exponential* ortho-to-para decay is given in minutes. Other quantities listed in this table are (1) the ortho-T_2 concentration at the beginning of the experiment, $x_1(0)$, that is calculated from the sample's thermal history, the initial signal height, and the impurity concentration; (2) the ortho-T_2 concentration at infinite time after the start of the experiment, $x_1(\infty)$, that is found from the long-time limit of the signal height and the impurity concentration; and (3) the calculated equilibrium concentration, x_b, based on the Boltzmann distribution averaged over the sample's temperature distribution that arises from the self-heating.

In Fig. 2 we plot the log of the signal difference (instantaneous signal minus the equilibrium signal) as a function of time to show the exponential decay. In Fig. 3, we plot the observed decay time, τ, as a function of the inverse temperature showing the minimum in the decay time near 11 K.

IV. ANALYSIS OF THE DATA

In the analysis given below, two different models are tested. In both models, only one type of atom is assumed to exist. By casting the ortho-T_2 to para-T_2 conversion in terms of this one-atom model, it is possible to extract the equilibrium number of atoms and their diffusion coefficient (in addition to the recombination coefficient). A second approach is possible where the atoms are divided into two groups, mobile and trapped. This approach was suggested by Rosen[12] as a means of understanding the Webeler experiments. We do not use this model but instead distinguish between various types

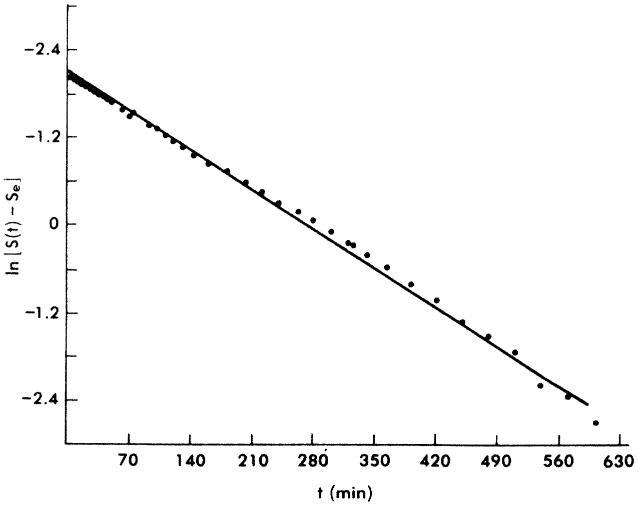

FIG. 2. The logarithm of the difference between the signal at time t and the equilibrium signal (as determined experimentally) is plotted as a function of t (in min). The decay is seen to be exponential.

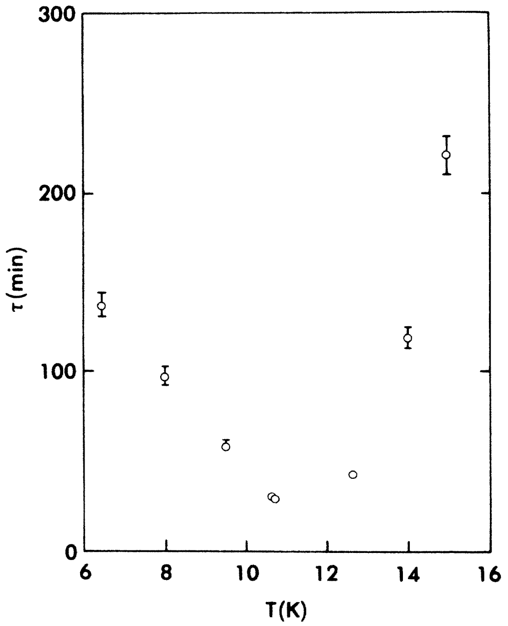

FIG. 3. The time constant of the exponential signal decay (τ), in min, is plotted as a function of the temperature. A minimum is obtained near 11.4 K.

of motion by means of the translational correlation time or the hopping frequency. Clearly when the hopping frequency is small, the atoms spend a large fraction of their time at a given site and thus trapped. Using this single type of atom approach, we obtain simple kinetic behavior.

The constant radiation from the β decay of tritium produces atoms at a constant rate, K, which then can recombine to form molecules with a recombination coefficient, $\alpha(T)$. The rate of atom production depends on the number of tritium molecules per unit volume but should be independent of temperture. If m is the number of atoms, then

$$\frac{dm}{dt}=K-\alpha(T)m^2 , \tag{8}$$

where the recombination is assumed to be quadratic in m (following the work of Leach *et al.*). If the atom population is in equilibrium, the steady-state number of atoms present in the sample, m_a, is given by

$$m_a=\sqrt{K/\alpha(T)} . \tag{9}$$

The production of atoms by the β decay and the subsequent recombination of these atoms to form molecules modifies the rate equations for ortho-to-para conversion. The radiation, first of all, shatters molecules of both types with probability per unit time, γ, and then atoms recombine to form ortho-T_2 at a rate 3 times larger than the rate to form para-T_2, using the high-temperature equilibrium ratios. These two effects, incorporated into the rate equations for the numbers of ortho molecules, N_1, and para molecules, N_0, yield

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

$$\frac{dN_0}{dt}=W_{10}N_1-W_{01}n_0-\gamma N_0+\tfrac{1}{8}\alpha(T)m_a^2 , \tag{11}$$

since it requires two atoms to make one molecule. If the number of molecules, $N_T=N_1+N_0$, is constant in time (the rate of breaking molecules and the recombination rate is the same), then from the addition of the two previous equations and the condition that N_T is constant, we obtain

$$2\gamma N_T=\alpha(T)m_a^2=K . \tag{12}$$

Therefore only one new parameter is needed in the gain-loss equations for the numbers of ortho and para molecules to describe the effects of radiation on the system. Choosing this parameter to be γ, we rewrite the rate equations as

$$\frac{dx_1}{dt}=W_{01}x_0-W_{10}x_1-\gamma x_1+\tfrac{3}{4}\gamma , \tag{13}$$

$$\frac{dx_0}{dt}=W_{10}x_1-W_{01}x_0-\gamma x_0+\tfrac{1}{4}\gamma , \tag{14}$$

where the concentrations x_1 and x_0 have been introduced by dividing by N_T. In the steady state, $dx_1/dt=0$, and we can solve for the *steady-state* population of the $J=1$ level, x_e:

$$x_e=\frac{W_{01}+(3/4)\gamma}{W_{01}+W_{10}+\gamma} . \tag{15}$$

In terms of this new quantity, the rate equation now is

$$\frac{dx_1}{dt}=-(W_{01}+W_{10}+\gamma)(x_1-x_e) , \tag{16}$$

which integrates to

$$x_1(t)-x_e=[x_1(0)-x_e]\exp(-t/\tau) , \tag{17}$$

where the time constant of this exponential decay, τ, is defined to be

$$\frac{1}{\tau}=W_{01}+W_{10}+\gamma . \tag{18}$$

Equations (17) and (18) are the principal ones used in the data analysis since the ortho-concentration is linearly proportional to the NMR signal from the ortho-T_2 molecules.

The Boltzmann equilibrium $J=1$ concentration, x_B, can be related to the transition probabilities per unit time that would exist in the absence of the selective repopulation (due to atomic recombination) of the ortho state through the equation

$$x_B=\frac{W_{01}}{W_{01}+W_{10}} . \tag{19}$$

The quantity x_B can be *calculated* from the Boltzmann factor appropriate to the two-level problem that uses only the lowest ortho state and the lowest para state with a separation of these two states of 58.3 K. If we regard x_e, x_B, and τ as the "knowns" in this problem, we can solve for the unknowns, namely W_{01}, W_{10},and γ. We actually will determine x_e and τ from the data and calculate x_B from the splitting of the rotational levels and the temperature. These solutions are

$$W_{10}=\frac{(1-x_B)(\frac{3}{4}-x_e)}{(\frac{3}{4}-x_B)\tau} , \tag{20}$$

$$\gamma=\frac{x_e-x_B}{(\frac{3}{4}-x_B)\tau} , \tag{21}$$

with a similar expression for W_{01}.

The results of the above analysis on the data points given in Table I are given in Table II. It should be noted that the peak value for W_{10} is more than 2 orders of magnitude larger than the intrinsic ortho-to-para conversion rate in solid H_2.

The value of γ can be estimated from knowledge of the atom production in the gas phase. In a sample of solid tritium, there are 1.15×10^{14} disintegrations per s per cm^3. If each disintegration produces 155 ion pairs per β decay and there are 5 atoms per ion pair, as in the gas phase, then

$$\begin{aligned}K_{\text{gas}}&=(1.15\times10^{14}/\text{cm}^3\,\text{s})(155)(5)\\&=8.91\times10^{16}\text{atoms/cm}^3 s .\end{aligned} \tag{22}$$

TABLE II. Results of analysis on data points

T (K)	T_s (K)	$1000(T^{-1})$ $(\mathrm{K})^{-1}$	$10^4(\tau^{-1})$ (s^{-1})	$10^6\gamma$ (s^{-1})	$10^4 W_{10}$ (s^{-1})
6.4	5.3	157	1.268	3.86	1.23
7.9	7.0	126	1.756	3.64	1.72
9.5	8.4	106	2.93	3.26	2.87
10.6	9.94	94.2	5.59	1.70	5.42
10.7	10.0	93.4	5.79	0.56	5.62
12.6	12.0	79.3	3.62	4.78	3.32
14.0	13.3	71.6	1.289	3.41	1.12
15.0	14.5	67.1	1.038	6.18	0.832

To obtain the predicted value of the constant γ, we divide K by twice the total number of molecules per cm^3, $2N_T=6.42\times10^{22}$, to obtain $\gamma_{\mathrm{gas}}=1.39\times10^{-6}\ \mathrm{s}^{-1}$. The *mean* of the above results of γ is

$$\gamma_{\mathrm{solid}}=(3.4\pm1.6)\times10^{-6}\ \mathrm{s}^{-1}\ ,$$

quite representative of the low-temperature values. This gives a value for the "production term," K, of

$$K_{\mathrm{solid}}=(1.09\pm0.5)\times10^{17}\ \mathrm{atoms/cm^3}\,s\ . \tag{23}$$

The agreement between the gas-phase calculation and the experimental values obtained from the solid data is poor, indicating that the atom production processes may be modified in the solid. We would need to form about 1900 atoms per β decay (or 2.4 times more than in the gas) to account for our mean value of γ. The three higher-temperature data points yield values of γ that are higher than the three low-temperature data points but the high-temperature points are more susceptibile to error since the calculated quantity x_b used in the analysis is nonzero at high temperatures.

Webeler[4] carried out an interesting set of experiments that have bearing on the above anomalously large value of γ. These experiments, involving low-temperature studies of H_2 doped with as much as 1.2% T_2 by weight, stimulated several theoretical papers[12–14] directed towards modeling the results. In a private communication to Rosen,[14] it was revealed that the real heat load on his dilution refrigerator was 9 μW when 37 μW was the expected load from the tritium β decay heating. He postulated $\frac{3}{4}$ of the available energy from the β decays in T_2 was being used to make atoms which were then stored in the lattice. This large energy conversion efficiency (about 75%) seen by Webeler agrees very well with our high values of γ that imply an energy conversion efficiency of 77%. This indicates that many more atoms are formed per β decay in the solid than in the gas.

Regardless of the details of the recombination process, ortho-T_2 molecules are being formed in the solid at a rate considerably in excess of that estimated from the available gas-phase data. This pumping of molecules into the excited rotational level does not have a large effect on the conversion rate. For the five data points at 10 K or below, the contribution of the term γ to the rate τ^{-1} is 3% or less. In the most extreme case, the contribution from the term γ, at 15 K, amounts to 10% of the total rate.

An essential assumption in the derivation of Eq. (17) and (18), used in this analysis, is that the transition probabilities per unit time, W_{10} and W_{01}, are independent of the $J=1$ concentration, x_1. For the intrinsic conversion process, the quantities W_{10} and W_{01} are proportional to x_1, so that the time dependence of x_1 is different from that in Eq. (17). In this case, Eq. (17) is changed to yield

$$\Delta x=\frac{\Delta x_0\exp(-\alpha t)}{1+W'_{10}\alpha^{-1}\Delta x_0[1-\exp(-\alpha t)]}\ , \tag{24}$$

where $\Delta x=x_1(t)-x_e$, $\Delta x_0=x_1(0)-x_e$, α is a decay rate, and W'_{10} is the concentration-independent transition probability per unit time. At low temperatures, $W'_{10}\approx\alpha/2x_e$. The time dependence predicted by Eq. (24) is distinct enough from the simple exponential dependence we observe that we can conclude that the transition probabilities we observe are independent of x_1. Thus intrinsic conversion is ruled out by the time dependence of x_1 as well as by order-of-magnitude theoretical considerations. Since there are no other nuclear spins to produce the magnetic field gradients needed for ortho-to-para conversion, the gradients must be produced by unpaired electronic spins in the solid. Although there are other possibilities for unpaired electron spins in the T_2 solid, in the analysis that follows we will assume that these spins reside on T atoms.

One other assumption made was that the number of atoms was appropriate to the equilibrium distribution. From the values of K and α obtained from our analysis, we can check that assumption. The time constant that characterizes the atoms approach to equilibrium varies from 10 μs at 15 K to about 100 μs at 6.4 K, confirming that the atoms are in equilibrium.

Several comments about this model are now in order.

(i) We use the experimental result that the signal decay is exponential to infer that the transition probabilities per unit time are independent of x_1;

(ii) the steady-state population of the ortho-T_2 level, as observed from the "long-time limit" of the NMR signal height, is larger than the value expected from the Boltzmann distribution;

(iii) the calculation of γ from the data is sensitive to details particularly the sample temperature at high temperatures as the calculated value of x_B is appreciable.

At low temperatures, since x_B is essentially zero, the value of γ is obtained mainly from the two directly measured quantities, τ and $x_1(\infty)$ and hence is much more reliable;

(iv) the value obtained for W_{10} is insensitive to most details as it is approximately equal to τ^{-1} in all cases.

In Fig. 4, we plot $\ln(W_{10})$ as a function of the inverse temperature. The fitted straight lines through the data points will be used to find the maximum rate of conversion, $R_m = 8\times 10^{-4}\ \mathrm{s}^{-1}$, but not used otherwise in the analysis. We will now focus on the main result: the transition probability per unit time, W_{10}, is independent of x_1 and peaks in the vicinity of 11.4 K with a peak magnitude that is 200 times larger than the intrinsic ortho-to-para conversion rate in H_2. We will examine two (or three) interpretations of this result.

In the preceding paper concerned with theoretical models of the ortho-to-para transition, it was concluded that the peak in the rate occurs because some motional correlation frequency becomes comparable to the characteristic frequency of this problem. Here the word motion is used in a very general sense; spin diffusion, for instance, could be the motion in question.

Two different types of motion were considered in paper I. In the first process, the time dependence of the Hamiltonian was supplied by the phonons with atomic hopping from site to site enhancing the overall conversion rate (the "hopping model"). In the second process considered, the time-dependent magnetic field gradient came from the translational motion of the electron spins themselves (the "ballistic model"). In the first process, the hopping could just as well be molecular hopping with the electron spins fixed in space. If the electron spins were *localized,* a maximum in the conversion rate such as we see near 11.4 K would be due to *molecular diffusion.* To test this possibility, we measured the molecular self-diffusion coefficient in solid T_2 by conventional NMR techniques. By fitting the data to a thermally activated form, we obtained an activation energy of 407 K. This seems very reasonable, as in H_2 Bloom[7] found an activation energy of 190 K and Horst Meyer *et al.*[15] found an activation energy of 276 K in D_2. From our measurements of the nuclear self-diffusion coefficient, we can estimate that the correlation time for molecular self-diffusion at 10.6 K is 48 s and 4×10^{12} s at 6.4 K. Relative to the atoms, the molecules are *localized* at the temperature where the measured rate is 30 min. The atoms, at half the mass, and with initial kinetic energy from their formation, are much better candidates for significant translational motion in the solid. Based on the considerations, we rule out molecular motion as the cause of the peak in the conversion rate and consider only motion of the unpaired electron spins (atoms).

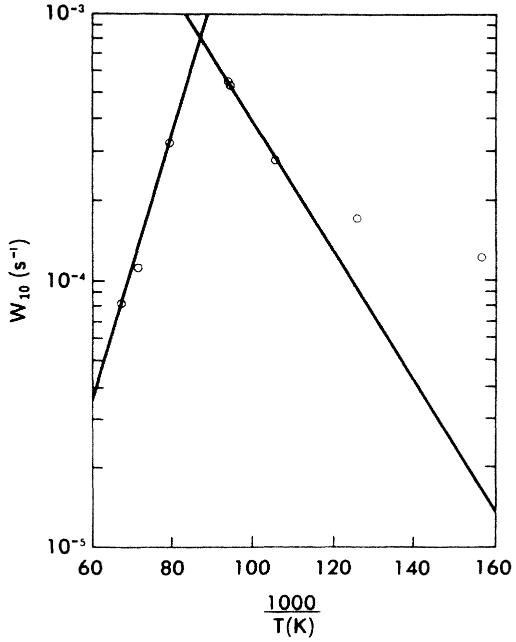

FIG. 4. The transition probability per unit time from the $J=1$ to the $J=0$ state, W_{10}, as deduced from τ, the equilibrium concentration x_e, and the concentration obtained from the Boltzmann distribution, x_B is plotted as a function of the inverse temperature, $1000/T$. A peak is evident near 11.4 K. The fitted lines indicate a peak rate of $8\times 10^{-4}\ \mathrm{s}^{-1}$.

Having reduced the problem to one where only the unpaired electron-spin motion is considered, we should note that this problem is very similar to the problem encountered in explaining the NMR data on conducting polymers. There, an uncharged excitation, a neutral soliton, carries an electron spin and relaxes nuclear spins via the hyperfine coupling, a contact interaction. By comparing the experimental data to a theoretical model, the translational motion of the soliton can be inferred from the NMR relaxation rates. We now consider the two models proposed in paper I for ortho-to-para conversion due to moving electron spins.

A. The hopping model

For the first case where the essential time dependence is supplied by the coupling with the phonons, the conversion rate, R, in the low-concentration limit, can be written as (see paper I)

$$R = \frac{cz\Omega_0\Gamma}{z\Omega_0 + \Gamma} . \tag{25}$$

In this expression, c denotes the concentration of unpaired electron spins, Γ is the rate for an electron spin to hop to a single-neighboring site, z is the number of neighboring sites, and Ω_0 is the conversion rate for a single molecule next to an electron spin. The product $z\Omega_0$, calculated on the assumption that the atoms are in the large interstitial positions between hops to nearby interstitial positions, was found to have the value $z\Omega_0 = 14.1\ \mathrm{s}^{-1}$ when $z=6$ (there are six such interstitial positions for the central molecule). We will denote the product $z\Omega_0$ by Ω.

Since the recombination coefficient, α, also depends on the electron-spin hop frequency, Γ, the equilibrium number of atoms and hence the atom concentration will depend on Γ. Taking $c \propto \Gamma^{-1/2}$, the maximum rate is obtained when $\Gamma=\Omega$. The maximum rate can be written simply as

$$R_m = c\frac{\Omega}{2} . \tag{26}$$

For c, the atom concentration, we can combine Eq. (9) with Eq. (12) to find

$$c = \left[\frac{2\gamma}{\alpha N_T} \right]^{1/2} , \tag{27}$$

where α can in turn be expressed in terms of Ω. To obtain the relationship between α and Γ, we use the assumptions of Leach and Fitzsimmons, namely that the diffusion coefficient and recombination coefficient are related by $\alpha=4\pi R_0 D$, where 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, will be taken equal to $\langle r^2\rangle\Gamma/2$, where we will use $r=3.53$ Å for our estimates. At the peak in the rate, $\Gamma=\Omega$, leading to

$$R_m = \left[\frac{\gamma_{\text{solid}}\Omega}{4N_T(\pi R_0\langle r^2\rangle)} \right]^{1/2} . \tag{28}$$

From this expression, we can evaluate Ω in a self-consistent manner using just the extrapolated rate at the peak, the value of γ obtained in the analysis, and the above stated choices for R_0 and $\langle r^2\rangle$ (that are reasonable though not actually established). Substitution into Eq. (27) yields the value

$$\Omega=4.73\ \text{s}^{-1} , \tag{29}$$

which compares very favorably with the theoretical value of 14.1 s^{-1} obtained in paper I from the Debye model.

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 listed in Table III and plotted in Fig. 5 where the above self-consistent choice for Ω has been made. The hopping frequency, Ω, appears to be thermally activated at the higher temperatures so that we can extract an activation energy. We can then calculate the recombination coefficient, α, for comparison with the direct measurements of Leach and Fitzsimmons.

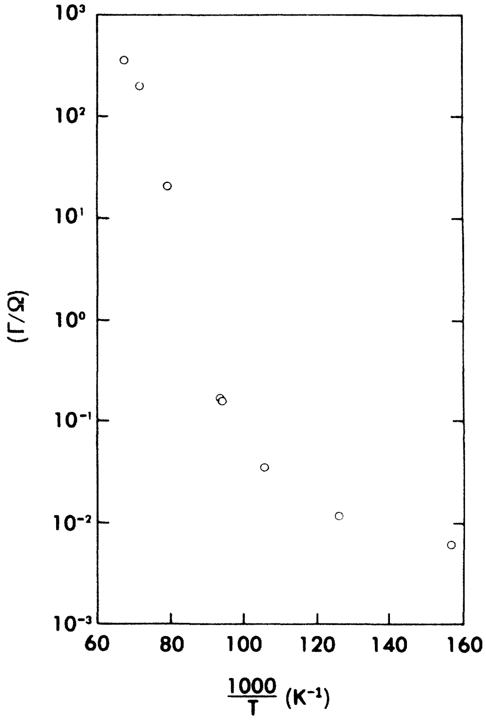

FIG. 5. The ratio of the hopping (angular) frequency to the transition probability per unit time, Ω, as introduced in Eq. (25) is plotted as a function of inverse temperature.

A fit of the five points at the highest temperatures shown in Fig. 5 (the points at low temperatures depart from the thermally activated form) can be made to obtain an activated hopping frequency,

$$\Gamma=(1.83\times10^{12}\ \text{s}^{-1})\exp(-303\ \text{K}/T) . \tag{30}$$

This leads to a recombination coefficient

$$\alpha=(7.16\times10^{-10}\ \text{cm/s})\exp(-303\ \text{K}/T) , \tag{31}$$

that can be compared with the Leach and Fitzsimmons measurement, Eq. (2). The higher activation energy obtained here appears reasonable but the prefactor we obtain is a factor of 50 smaller than theirs in H_2. Lacking a theory of the recombination process *in the solid,* there is little we can say about this comparison. It should be noted that the hopping objects are 3 times more massive and that our magnetic field is 2.3 times larger than theirs. There is no evidence to support the idea that the magnetic field is important in the recombination process in the solid. Following the extensive work on spin-

TABLE III. Values of parameters used in the hopping model.

T (K)	Γ/Ω	D (cm^2/s)	α (cm^3/s)	m_a (atoms/cm^3)
6.4	6.0×10^{-3}	1.8×10^{-17}	1.1×10^{-23}	1.4×10^{20}
7.9	1.2×10^{-2}	3.5×10^{-17}	2.2×10^{-23}	1.0×10^{20}
9.5	3.4×10^{-2}	1.0×10^{-16}	6.4×10^{-23}	5.8×10^{19}
10.6	0.512	4.5×10^{-16}	2.8×10^{-22}	2.8×10^{19}
10.7	0.168	5.0×10^{-16}	3.1×10^{-22}	2.6×10^{19}
12.6	21.2	6.2×10^{-14}	3.9×10^{-20}	2.4×10^{18}
14.0	202	6.0×10^{-13}	3.7×10^{-19}	7.6×10^{17}
15.0	368	1.1×10^{-12}	6.8×10^{-19}	5.7×10^{17}

polarized hydrogen by Silvera *et al.*,[16] we might expect the atom recombination coefficient will decrease as the square of the applied magnetic field for two-body recombination processes. Thus if we increased our magnetic field from 0.7 T to 10 T, we would expect an increase in the atom density by the factor 14 (the ratio of 10 to 0.7 T). Experimental evidence does not support this expectation at this time with the one result indicating that *no change* in recombination coefficient is observed up to fields of 5 T^2.

B. The ballistic model

The second mechanism for conversion, where the time-dependent magnetic field gradient is due to moving electron spins also yields an expression for the rate that has a peak. Again, taking into account the dependence of the equilibrium concentration, c, on the correlation time τ, the peak in the rate is found to occur when $\omega^2\tau^2=3$. The peak rate can be written

$$R_m=(1.63\times10^{13}\ \mathrm{s}^{-2})c\tau_p\ . \tag{32}$$

If the characteristic frequency in the problem, $\omega=\omega_{10}$, then $\tau_p=2.25\times10^{-13}$ s and the atom concentration is $c=2.2\times10^{-4}$, leading to an atom density of $m=7\times10^{18}$ atoms per cm^3. Unfortunately, this choice for τ_p yields such a large recombination coefficient that the predicted atom density from Eq. (9) is 6 orders of magnitude lower than the above estimate. If we use the same self-consistent approach we used with the hopping model, we can solve for that value of τ_p that gives the *same* atom density from Eqs. (32) and (9). In this case, the characteristic frequency in the conversion problem turns out to be 167 MHz, a value that has no apparent significance in this problem. We did perform the following test of this model: At the temperature where we observe the peak rate, we measured the signal at $t=0$, then turned the field off until we remeasured the signal so that the holding field was zero. There was no detectable difference in the conversion rate.

The atom density, at the peak, using the self-consistent approach was found to be $m_p=9.6\times10^{14}$ atoms per cm^3. Based on the unlikely characteristic frequency obtained by the self-consistent solution and the extremely low predicted atom density, we rule out this ballistic model as a possible explanation of the conversion rate peak.

The calculated equilibrium atom density, m_a, is plotted as a function of inverse temperature in Fig. 6. The atom density appears to be saturating as the temperature is decreased. Depending on the method chosen for the extrapolation, the atom density at 4.2 K should be between 2×10^{20} and 5×10^{20} atoms/cm^3, the smaller estimate being roughly 70 times larger than the density observed by Sharnoff and Pound in D_2. Sharnoff and Pound *observed* 3×10^{18} atoms per cm^3 in D_2 at 4.2 K. If the atom 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 that term in a sample containing only 1% T_2 (Sharnoff and Pound were not sure that all the T_2 ended up in their microwave cavity so 1% represents an upper limit on the actual T_2 concentration.) Our extrapolated atom density at 4.2 K is more than 10 times larger than the Sharnoff and Pound value, probably indicating that the recombination coefficients are not the same in D_2 and T_2. Our estimated recombination coefficient for T_2 is lower than the corresponding H_2 value.

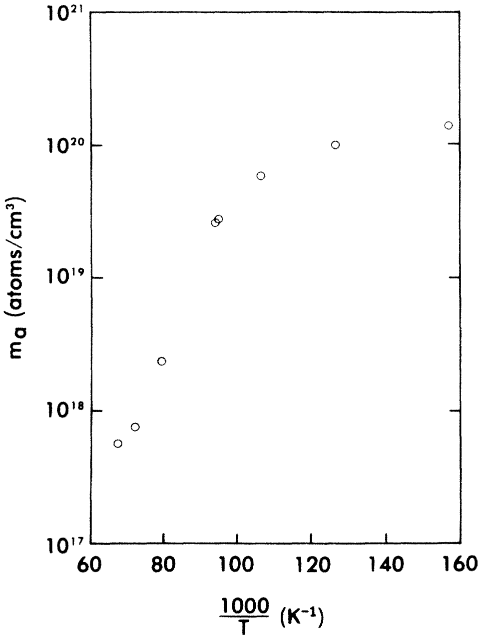

FIG. 6. The equilibrium number of atoms, m_a, (in atoms per cm^3) predicted by the hopping model applied to the data, is plotted as a function of inverse temperature. The extrapolated atom density at 4.2 K would be between 2×10^{20} and 5×10^{20} atoms per cm^3.

V. CONCLUSIONS

By measuring the NMR signal amplitude of a constant volume sample as a function of time, at fixed temperature, the ortho-to-para conversion rate in solid T_2 has been determined. The decay of the difference between the instantaneous signal and the equilibrium signal for the ortho-T_2 spins is *exponential in time,* ruling out intrinsic conversion processes that would give transition probabilities per unit time proportional to the $J=1$ concentration (x_1). The equilibrium signal, after removal of the HT and DT impurity contributions, is much larger, at low temperatures, than the value predicted by the Boltzmann distribution for the $J=1$ and $J=0$ rotational levels.

Using gain-loss equations containing concentration-independent transition probabilities and terms that allow for destruction of molecules by radiation and recombination of atoms into molecules (selectively populating the excited level due to its larger degeneracy), we obtain equations that are used to extract the desired transition probability per unit time from the $J=1$ level to the $J=0$ level, W_{10}, by using as known quantities the observed decay time, τ, the observed equilibrium signal, and the equilibrium signal calculated from the Boltzmann distribution. As a check on the consistency of the procedure, we can extract the atom production term. The value obtained is not in satisfactory agreement with estimates based on gas-phase data but does agree with a previous observation by Webeler and indicates that we have limited knowledge of the production of atoms from β decay in the solid. The equilibrium signal is observed to be larger (significantly in some cases) than that predicted by the Boltzmann distribution. This is interpreted, in our analysis, as resulting from selective repopulation of the excited state ($J=1$, $I=1$) by atom recombination.

The transition probability per unit time, W_{10}, has a maximum near 11.4 K, reflecting the sharp minimum in the decay time, τ. The rate, at this peak, is 2 orders of magnitude larger than the intrinsic conversion rate in solid H_2. By comparing the data with the calculations contained in paper I where the translational motion of atoms in the molecular solid is incorporated into the conversion rate, we extract the atom diffusion coefficient, the recombination coefficient, and the equilibrium number of atoms in the solid, all as functions of temperature. Of the two models tested, we conclude that the hopping model is more nearly correct than the ballistic model. This conclusion is based on the following. (i) The self-consistency test applied to both models yields the characteristic frequency of the model using the peak rate and the observed atom production term in the solid. For the hopping model, this frequency agrees well with that calculated in paper I, but for the ballistic model the characteristic frequency does not correspond with ω_{10} nor any other identifiable frequency in the problem. (ii) The recombination coefficient and the equilibrium atom density obtained from the hopping model seem to agree reasonably with the actual measured quantities in H_2 and D_2, whereas the corresponding values from the ballistic model are orders of magnitude different from the measurements.

The interpretation of the data thus suggests the presence of a gas of mobile atoms. The hopping frequency that characterizes this atom gas is extracted as a function of temperature. The temperature dependence of this motional frequency indicates that the atoms become *localized* below 11.4 K. The atom gas has a density of about 1% of the solid density and is responsible for the enhanced ortho-to-para conversion in the solid.

In a sense, the NMR measurements have been used to probe the electron-spin system of the atoms—a situation analogous to the NMR studies of soliton motion in conducting polymers. It must be anticipated that in T_2, as in H_2, that extrapolation of the high-temperature results to the region below 4 K will be incorrect due to quantum diffusion processes unobservable at our high temperatures.

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