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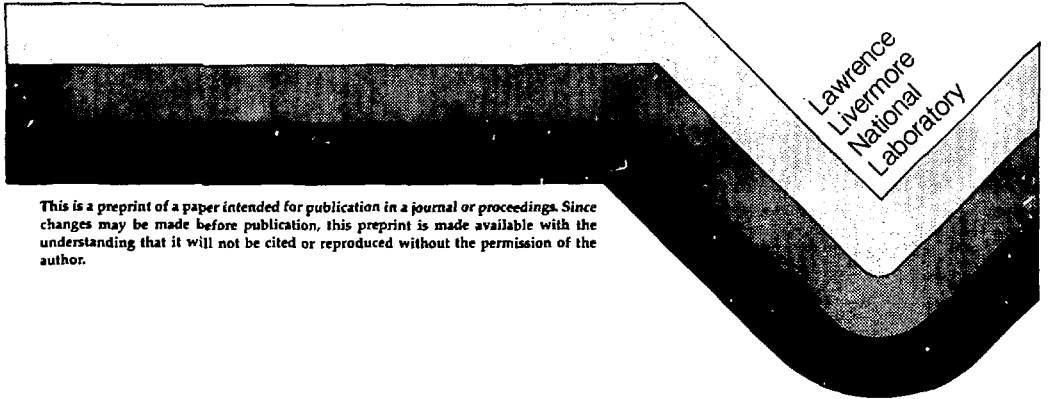# ENHANCING ATOM DENSITIES IN SOLID HYDROGEN BY ISOTOPIC SUBSTITUTION

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ENHANCING ATOM DENSITIES IN SOLID HYDROGEN BY
ISOTOPIC SUBSTITUTION

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Atomic hydrogen inside solid H_2 increases the energy density by 200 MegaJoules/m^3, for each percent mole fraction stored. How many atoms can be stored in solid hydrogen? To answer this, we need to know: (1) how to produce and trap hydrogen atoms in solid hydrogen, (2) how to keep the atoms from recombining into the ground molecular state, and (3) how to measure the atom density in solid hydrogen. We will address each of these topics in this paper.

Hydrogen atoms can be trapped in solid hydrogen by co-condensing atoms and molecules, external irradiation of solid H_2, or introducing a radioactive impurity inside the hydrogen lattice. Tritium, a heavy isotope of hydrogen, is easily condensed as a radioactive isotopic impurity in solid H_2. Although tritium will probably not be used in future rockets, it provides a way of applying a large, homogenious dose to solid hydrogen. In all of the data presented here, the atoms are produced by the decay of tritium and thus knowing how many atoms are produced from the tritium decay in the solid phase is important. Solid T_2 generates about 100,000 W/m^3. In the gas phase each triton decay produces about 155 ion pairs resulting in 780 atoms. We have recently measured the number of atoms that are produced in the solid phase by measuring the exchange time for the reaction

$$D_2 + T_2 <-> 2DT$$
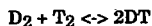
at 6 K^1. We found that tritium produces the same number of atoms in the solid phase as in the gas phase ($K = f_t \cdot 9 \cdot 10^{23}$ atoms/$m^3 \cdot$sec in solid hydrogen, where K is the atom production rate constant and f_t is the mole fraction of tritium).

We will now focus our attention on reducing the recombination rate of the atoms. The quantum nature of atomic hydrogen allows the atoms to move through the lattice and recombine rapidly, even at low temperatures (~1 K). This rapid quantum diffusion and recombination has limited the atom concentration in solid H_2 in previous experiments. Yu Kagan and L. M   mov have developed a theory of quantum diffusion of H and D atoms in H_2 and D_2 respectively[2,3,4,5.] Simply stated the theory treats the diffusion of atoms in solid hydrogen as a band type of diffusion[6]. The tunneling bandwidth, Δ, is directly *related to the tunneling probability. Δ decreases with increasing mass of the diffusing* particle and host. Interaction with other defects cause the energy levels for atoms at neighboring sites to shift. If the level shift, ∂, is larger than the tunneling bandwidth, band diffusion is impossible without the aid of phonons. The phonons move the energy levels at neighboring sites allowing the energy bands to overlap and the trapped atoms to tunnel. This creates a temperature dependence on the tunneling rate of atoms. To relate the atom density to the recombination coefficient we assume that to first order

$$\frac{d[H]}{dt} = K[H_2] - \alpha[H]^2$$

[1]G. W. Collins, E. M. Fearon, E. R. Mapoles, P. C. Souers and P. A. Fedders, "J=1-to-0 Conversion in Solid D-T", submitted to Phys. Rev. B.

[2]Kagan, Yu and M. I. Klinger, J. Phys. C:Solid State Phys., 7 (1974).

[3]Kagan, Yu and L. A. Maksimov, Sov. Phys. JETP, 38, 2 (1974).

[4]Kagan, Yu and L. A. Maksimov, Sov. Phys. JETP, 57, 2 (1983).

[5]Kagan, Yu and L. A. Maksimov, Sov. Phys. JETP, 52, 4 (1980).

[6]Andreev, A. F. and I. M. Lifshitz, Soviet Phys. JETP, Vol. 29, No. 6 (1969).

where K is the atomic production rate described above, α is the recombination coefficient which is proportional to the tunneling rate, [H] is the atom concentration, and t is the time. The solution to the differential equation is

$$[H] = \sqrt{\frac{K}{\alpha}}\ \tanh(\sqrt{K\alpha}\ t)$$

which increases while $t \leq 1/\sqrt{K\alpha}$ and then saturates to a steady state atom concentration

$$[H]_{ss} = \sqrt{\frac{K}{\alpha}}.$$

Even though, as we will show later, the atom density cannot be described by this simple rate equation, the atom density will increase as the recombination rate decreases. Thus we can increase the atom concentration by (1) decreasing the temperature (2) increasing the mass of the diffusing particle and host lattice, and (3) increasing the energy level shifts, ∂, by creating a disordered lattice.

We will now focus on ways to measure the atom concentration. We begin by discussing atom densities which are measured directly with electron spin resonance (ESR) (that is atom densities obtained by integrating the ESR absorption and comparing with a calibrated standard). Figure 1 shows the atom density vs dose for $H_2 + 2\%T_2$, $D_2 + 2\%T_2$, HD $+ 2\%T_2$, D-T ($25\%T_2$-$50\%T_2$-$25\%D_2$), and T_2, at about 4 K. This figure shows that atom densities vs dose, measured directly with ESR, is lower in H_2 than the other isotopic mixtures of hydrogen. Figure 2 shows the atom concentrations vs dose of the same mixtures at about 2 K. This figure shows that the atom density increases with decreasing temperature and again the atoms densities are lower in H_2 than the other isotopic mixtures of hydrogen. Moreover, in the mixture, D-T, the atom density is the largest. This fits well with the theory of Kagan since this mixture has the greatest degree of lattice disorder.

Figures 1 and 2 also show that the simple tanh function solution that we arrived at above cannot be used to model the atom concentration because the atom density does not saturate with time. For most of the atom buildup data, the nonsaturating part can be considered as a small perturbation of the total atom buildup. To account for the nonsaturating part we assume that a separate process is leaking atoms into the ESR spectrum at a rate proportional to the dose. The simple equation we used to fit to our data was

$$[H] = \sqrt{\frac{K_{ESR}}{\alpha}}\ \tanh(\sqrt{K_{ESR}\alpha}\ t) + mt$$

where m is a constant and K_{ESR} is the production rate for atoms seen with ESR and not nessecarily the total atom production rate. One can obtain this same solution by assuming that there is a small time dependent part to the production term and solving the differential equation peturbativly. When we use this equation to fit to our data, and solve for K_{ESR}, α, and m from the adjustable parameters used in the fit, we find that the recombination coefficient, α, is close to values found from previous experiments on H_2 and D_2 but K_{ESR} is temperature dependent and orders of magnitude smaller than the true solid phase value for the atomic production term! Moreover K_{ESR} can be fit to an exponential function

$$K_{ESR} = k_0 \exp\left[\frac{E_a}{k_b T}\right]$$

where k_0 is a constant, k_b is Boltsmann's constant, E_a is the binding energy for trapped atoms seen with ESR, and T is the temperature. Figure 3 shows the plot of K_{ESR}/K vs inverse temperature for D-T and T_2, and the exponential fit to the 4 warmest data points. From this fit we find a binding energy for trapped atoms seen with ESR, E_a, of 33 K in T_2 and 14.5 K in D-T. This is strong support for a two atom model. One type of atom can be counted directly with ESR and is trapped in the lattice with energy E_a, and a second type of atom that is unobserved directly with ESR. The obvious question then becomes, is the concentration of "hidden atoms" large enough to make atomic hydrogen a vehicle for energy density enhancement of solid hydrogen for use as a next generation rocket fuel propellent?
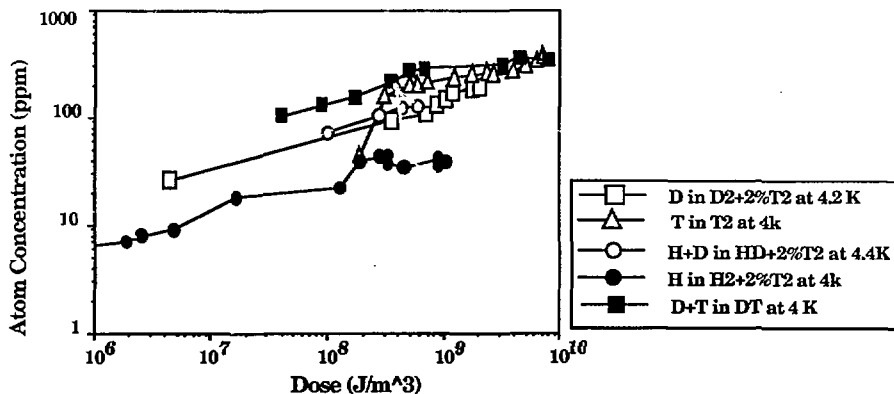
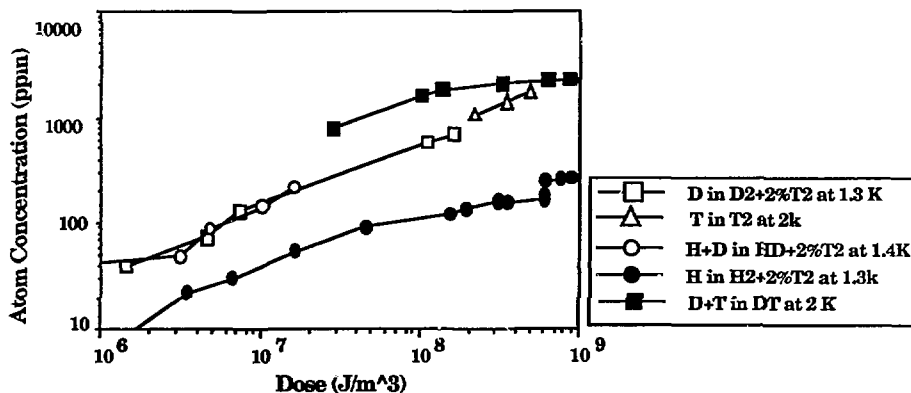Fig 1: Atom concentrations in the solid hydrogens vs dose at about 4 K.

Fig. 2: Atom concentrations in the solid hydrogens vs dose at about 2 K.

To measure the number of "hidden atoms" we have began a series of experiments and analyses. We are currently setting up a magnetization experiment using a differential loop squid magnetometer. This will measure the total concentration of magnetic species in our tritiated hydrogen samples. We have also used nuclear magnetic resonance to measure the J=1 to 0 conversion in solid T_2 and D-T[7,] and we are presently extending these experiments to H_2, D_2, and HD containing tritium. From the J=1 to 0 conversion one can calculate a model dependent atom concentration. Finally, the dipolar

[7]J. D. Sater, J. R. Gaines, E. M. Fearon, P. C. Souers, F. E. McMurphy, and E. R. Mapoles, Phys. Rev. B37, 1482 (1988).

broadening of the ESR spectrum can be analyzed to obtain an atom concentration. We will discuss some of our recent results from NMR and ESR experiments below.

The J=1 to 0 conversion experiments have proved that the atom concentration measured with ESR is a small fraction of the total number of paramagnets in the lattice. The J=1 to 0 conversion in solid $H_2 + 2\%T_2$ is catalyzed by the unpaired atoms in the same way as in solid T_2 and D-T. The time for atom buildup, as measured by ESR, is relatively slow as compared to pure T_2. The rate equation describing J=1 to 0 conversion in solid $H_2 + 2\%T_2$ can be written as

$$\frac{d[J=1\ H_2]}{dt} = -k[J=1\ H_2][H] + \frac{3}{4}\alpha[H]^2$$

where $[J=1\ H_2]$ is the J=1 H_2 concentration and k is the rate characterizing the decay of J=1 molecules due to atoms. The second term on the right hand side shows that J=1 molecules are constantly created due to the recombination of atoms. The first term on the right hand side shows that if the atom concentration is a constant, then the decay of J=1 molecules will be a perfect exponential. If the atom concentration is not constant, t.. · decay of the J=1 concentration will be a convolution of the time dependent atom concentration and an exponential. Figure 4 shows the atom concentration measured by ESR and the J=1 H_2 concentration measured by NMR in solid $H_2 + 2\%T_2$ at about 1.5 K. The J=1 concentration decays in as perfect exponential while the atom density measured with ESR is not at all a constant! If the atoms are the magnetic centers catalyzing the J=1 to 0 conversion, Figure 4 proves that the atom concentration seen by the molecules is essentially a constant by the time our ESR or NMR experiments begin.

We have also started analyzing the linewidth of the ESR lineshape. The linewidth of the hydrogen atoms in solid hydrogen is due to the distribution of local magnetic fields seen by the atoms. Because the local magnetic fields are produced by all the magnetic centers in the lattice, the linewidth provides a way of quantifying the atom density indirectly with ESR without the concern of a limited bandwidth. Because the linewidth is due to both magnetic molecules and paramagnetic atoms we must first calculate and remove the nuclear part to the ESR linewidth. We will first discuss only the results for $H_2+2\%T_2$. Using NMR we have measured the concentration of magnetic molecules ($[J=1\ H_2]$). When the concentration of magnetic molecules is large ($[J=1\ H_2] > 1\%$) the linewidth due to the molecules can be calculated almost exactly. We use the expression[8]

$$\Delta H(\text{nuclear}) = \sqrt{\frac{3.87}{a^6}\gamma_n^2\gamma_e^2h^2I(I+1)[J=1\ H_2]}$$

where γ_n is the nuclear gyromagnetic ratio, γ_e is the electron gyromagnetic ratio, a is the lattice distance in H_2 (~3.8E-10 m), I is the nuclear spin quantum number (I=1 for J=1 H_2), and h is Plank's constant. After subtracting out the nuclear contribution to ΔH we are left with the dipolar broadening from the atoms. When we calculate the atom concentration needed to yield the measured ΔH, we obtain about an order of magnitude larger atom density than that obtained directly with ESR. Figure 5 shows the number of atoms calculated from the linewidth in $H_2 + 2\%T_2$ and T_2 as a function of dose. The atom density is larger than that measured directly with ESR and we find that the heavier isotope, T_2, has a much larger atom density/dose than H_2.

[8]C. P. Poole, Electron Spin Resonance, 2nded. (John Wiley, New York, 1983), chapter 13.
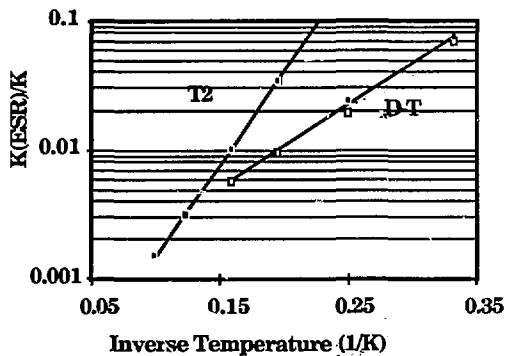
Fig. 3: Ratio of the atom production rates from ESR to gas-solid values in T_2 and D-T.
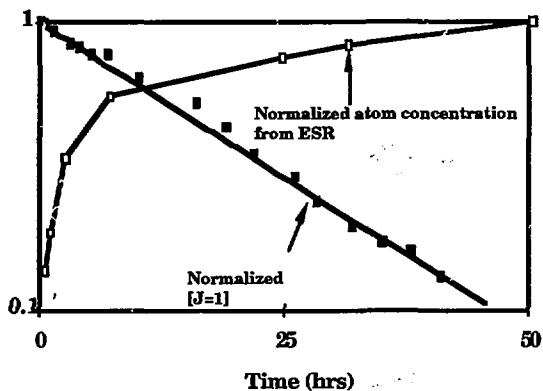

Fig. 4: Normalized decay of the J=1 concentration and the normalized atom concentration measured directly with ESR in Solid H_2 + 2%T_2 at 1.5 K.
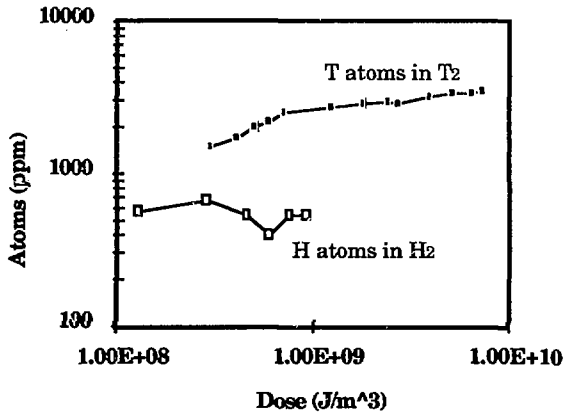
Fig. 5: Atom densities calculated from the linewidth of the ESR spectrum in $H_2 + 2\%T_2$ at 1.5 K and T_2 at about 2 K.

Finally, we have started a series of new experiments, injecting impurities into the hydrogen lattice, creating lattice stains to trap larger atom densities. Figure 6 shows the results of an ESR linewidth study of D-T and D-T containing 2% Neon. The linewidth in D-T + 2%Neon is about twice as large as in regular D-T. Although the linewidth is not completely understood, it does imply that the hydrogen lattice contains possibly twice as many atoms when doped with only 2%Neon.
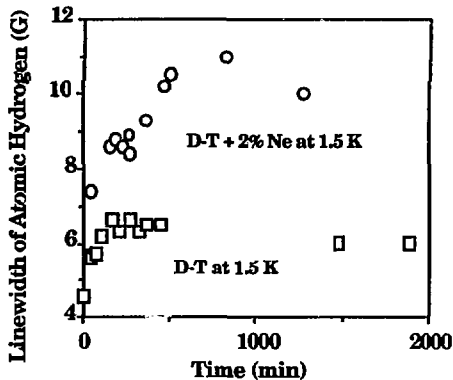

Fig 6: ESR linewidth in D-T and D-T + 2%Ne at about 1.5 K.