Triggered Energy Releases in Solid Hydrogen Hosts Containing Unpaired Atoms

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(Received 29 March 1990)

We have observed both triggered and spontaneous energy releases in tritiated solid hydrogens at temperatures above 1.2 K in several different experiments. These energy releases, which can be triggered by a temperature increase, were observed by monitoring the temperature excursion ("heat spike") versus time, the atom spin density, and nuclear-magnetic-resonance signal heights. The heat spikes correlate with a disappearance of free-atom spin density so that fast atomic recombination is the probable cause. The spontaneous heat spikes may be suppressed by improved heat extraction.

PACS numbers: 67.80.Mg, 61.80.Lj

The molecular solid hydrogen isotopes can store large numbers of unpaired atoms. The atoms are usually produced in one of three ways: (i) by electron beams,[1] (ii) by condensation of rf-gas-discharge products at low temperatures,[2] or (iii) by the β decay of tritium present in the hydrogen host as an isotopic impurity.[3] If the atoms are produced continuously, as is the case here, where the samples contain tritium, a steady-state atom population exists where the constant atom production is balanced by atomic recombination. Since recombination depends on diffusion, the stored-atom concentration increases as temperature decreases and can be quite large, approaching (or surpassing) 0.1% in our experiments.[4]

This steady-state population of atoms can lead to some very interesting physical effects such as the enhanced ortho-to-para conversion we reported earlier,[4] additional breadth to NMR lines,[5] and an unusual response to a sudden temperature increase (the subject of this paper). When the temperature of the hydrogen host plus atoms is quickly increased (say, from 3 to 4 K), the temperature *continues to increase* indicative of what we will call a "triggered heat spike." We have observed the temperature to rise to 8 K or higher before returning to the set temperature. Heat spikes were seen in four different experiments on tritiated solid hydrogens similar to those first reported by Webeler[6] in a study of H_2 solid containing 0.02% T_2 and subsequently interpreted by Rosen[7] and Zeleznik.[8]

In all of our experiments, the hydrogen atoms were produced in the solid by the tritium β decay. In the gas phase, the β particle (with mean energy of 5.6 keV) ionizes about 156 hydrogen molecules along its path,[9] producing five atoms per ion pair.[10] The most elementary way of observing heat spikes is by monitoring the sample thermometer. In Fig. 1, we show the reading on a germanium resistance thermometer following an attempt to ramp the sample temperature. The sample itself was 2.3 mmol of solid D-T (i.e., 25 mol% D_2, 50 mol% DT, 25 mol% T_2) in the shape of a cylinder of 2.0 mm radius and 3.5 mm height. In Fig. 1, the sample controller was changed from 3.7 to 4.9 K at 15 s. The unusual thermal response is seen for a D-T sample but not for a sample of pure HD (where there is no radiation source) under the same conditions. Thus, heat spikes can be triggered by a sudden increase in sample temperature. Alternatively, they can be triggered by a sufficiently rapid magnetic-field sweep or they can occur without any apparent cause, i.e., spontaneously. It is not possible at this time to say whether it is the field sweep itself or resultant eddy-current heating that triggers the spikes.

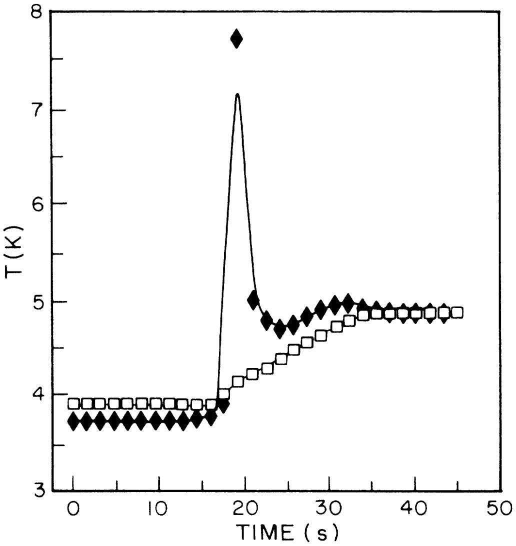

FIG. 1. A temperature spike in a solid D-T sample (◆) with a sudden temperature change from 3.7 to 4.9 K. The sample had aged 16.2 h before the spike, and the spike height is thought to represent the recombination of about 115-ppm hydrogen atoms. The thermal response of the sample cell to the same temperature change (3.7 to 4.9 K) for an equimolar sample of HD solid containing no atoms (□).

The most illuminating experimental observation of the heat spikes came from our X-band (9.4-GHz) electron-spin-resonance (ESR) experiments. We placed a ruby sleeve about the center of the sapphire cell so that the chromium-ion concentration in the ruby could be measured at room temperature using a diphenylpicrylhydroxyl (DPPH) standard. The ruby was then used as the low-temperature spin calibration standard. The ESR signature of each kind of hydrogen atom is unmistakable because of the hyperfine splitting. In a molecular beam extrapolated to zero magnetic field, the H and T atoms have a doublet ESR spectrum with a splitting of 1420 and 1517 MHz, respectively,[11,12] and the D atom forms a triplet with a splitting between adjacent lines of 218 MHz.[11] The basic identity of these spectra in the solid state was confirmed by Sharnoff and Pound.[3] In the solid, we found the splittings for the H, D, and T atoms to be 1433, 214 to 224, and 1532 MHz, respectively.

For our samples, the steady-state atom density, as measured by ESR, increases with decreasing temperature. This is shown in Fig. 2(a). During the course of the ESR measurements of the atom spin density, heat spikes could be observed by monitoring the sample temperature. Figure 2(b) shows the total atom concentration in parts per 10^6 (atoms to molecules) for solid D_2 containing 2 mol% tritium as measured by ESR, with times where heat spikes occur indicated. While it is expected that the atom density would decrease when the temperature is ramped from 4 to 5 K, we observe that, as a result of a heat spike, the atom density becomes immeasurably small. We have also seen spikes in solid D-T and T_2 below 2.2 K as well as in HD containing 2% T_2 between 1.2 and 1.4 K. Only in H_2, to temperatures as low as 1.7 K were no spikes seen. *The correlation of the heat spikes with the decrease in ESR spin count indicates that the thermal spikes result from rapid hydrogen-atom recombination.*

In addition to triggered heat spikes, we also observe heat spikes when we do not intentionally trigger them. These spontaneous heat spikes are usually observed when at the minimum sample temperature where there is no reserve cooling power. In an attempt to eliminate these spontaneous heat spikes in our ESR experiments, we filled the remaining volume of the cavity with liquid ^{4}He. Under those conditions, the heat spikes were either unobservable or suppressed by several orders of magnitude. However, when the cavity contained only a small amount of ^{4}He, even with ^{4}He on top of the sample, we still observed heat spikes, both on the germanium resistance thermometer and on the vapor pressure of the liquid ^{4}He above the sample, although the frequency of occurrence was reduced considerably.

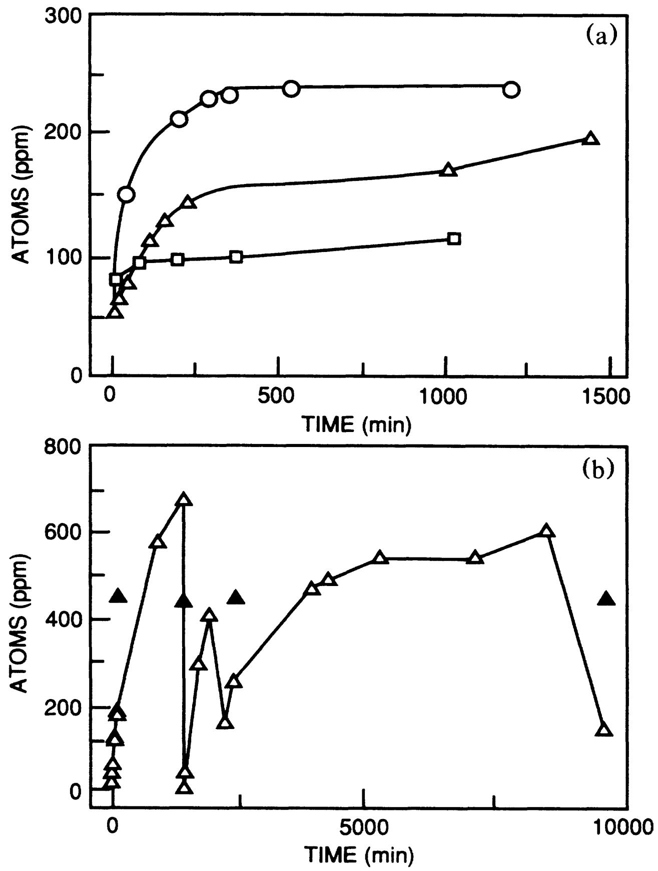

FIG. 2. (a) ESR measurements of the T-atom concentration (in parts per 10^6) in D-T at three different temperatures: (□) 5.1, (△) 4.1, and (○) 3.1 K. (b) The effect of thermal spikes (▲) on the total D-atom concentration (△) as seen by ESR in solid D_2 containing 2% tritium held at 1.3 K. These spikes were not intentionally triggered.

The fact that heat spikes sweep out most of the atoms has a profound effect on the NMR signals from the molecules of the hydrogen hosts containing atoms. In a pulsed NMR experiment, the signal extrapolated to the middle of the rf pulse (S_0) measures the ratio of the number of nuclear spins in the resonance to the spin temperature (Curie's law). When the sample temperature is increased and the H resonance is observed in pure HD (with no atoms), the signal height S_0 decreases as expected and the second moment M_2, a measure of root-mean-square local magnetic field, remains constant. For the *same sample temperature change* in a D-T sample where the T resonance is observed, as seen from Fig. 3, the signal actually increases as the temperature increases following a heat spike, and the second moment is reduced. The most apparent explanation for these two changes is that (i) the number of spins in the resonance increased when the number of electron spins in the sample decreased and (ii) the linewidth narrowed in response to the decreased number of electron spins.

The concept of nuclear spins being unobservable when in the "sphere of influence" of an electron spin is an old one[13] but to our knowledge never demonstrated in the manner that we have. To expand on this, we note that (i) at the lower temperature, when the number of atoms is at its dynamic equilibrium value, many nuclear spins

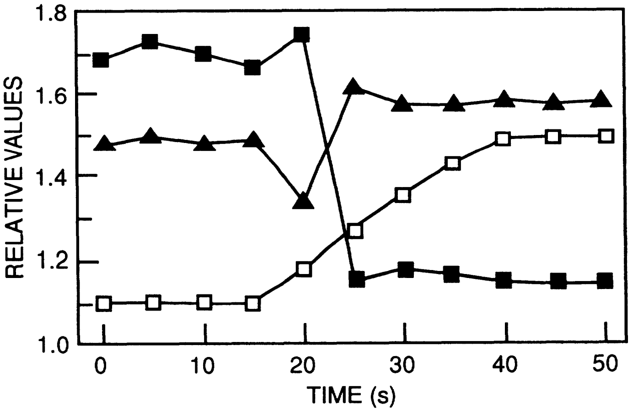

FIG. 3. The temperature ramp (□) for both the HD and DT NMR experiments. The initial temperature is 3.9 K and the final temperature is 5.1 K. The heat spike occurs at about $t=15$ s. S_0 (▲) is plotted in relative units. In a D-T sample (with atoms), when the T resonance is observed, the signal S_0 increases following the temperature increase, and the second moment (■) decreases (as does the atom density).

are removed from the resonance line due to dipolar broadening from the electron spin, and (ii) those nuclear spins remaining in the resonance have a line-broadening contribution from the electron spins. We estimate that the number of nuclear spins removed from the resonance is about 200 per electron spin. After a heat spike, the atoms have recombined and these 200 spins per atom are now observable in the resonance line, offsetting the increase in temperature that would normally degrade the signal. The unusual thermal response observed in three experiments described here and also seen in our thermal-conductivity[14] measurements would appear to be a very general phenomenon. The requisite features of a system with this behavior would be (i) the steady-state number of metastable entities increases with decreasing temperature and (ii) the destruction rate of metastables increases with temperature.

A simplified version of the Rosen[7] and Zeleznik[8] explanation of the Webeler[6] experiment can be used to reproduce most of the features of our experiments. The instantaneous sample temperature (T) is determined by the sample's coupling to an external heat bath and the atomic recombination heating by

$$\frac{dT}{dt}=-\left(\frac{T-T_0}{t_c}\right)+\alpha k m^2, \qquad (1)$$

where T_0 is the temperature the apparatus would cool to if there were no external heating, $2k$ is the atom recombination coefficient, α is the ratio of q, the heat liberated per recombination (4.5 eV), to the heat capacity of the solid hydrogen per molecule (C_{Debye}/N), m is the atom concentration, and t_c is the relaxation time, given by the ratio C_{Debye}/h, where h is the heat-transfer coefficient of the thermal link[15] between the sample and the apparatus heat sink assumed to be at temperature T_0.

If we consider all atoms to be equivalent (and mobile so that they can recombine) and assume the atom density is spatially homogeneous (this amounts to ignoring diffusion, except for its role in recombination), then the atom concentration is governed by

$$dm/dt=K-2km^2, \qquad (2)$$

where K in this equation is the production term per molecule.[16] In the presence of heating, either due to tritium β decay, atom recombination heating, or power from a temperature controller, a steady-state temperature (T_{ss}) is reached.

If the temperature is increased to a higher value, $T_{\text{ss}}+\Delta T$, the temperature may "overshoot," producing a heat spike or a temperature spike. When the sample temperature is increased, the diffusion coefficient (D) increases by a large amount [i.e., $D=D_0\exp(-E_A/k_BT)$]. The recombination coefficient ($2k$), assumed to be proportional to the diffusion coefficient, will increase, promoting rapid atom recombination. Since the atom concentration is initially much too large at the higher temperature, the second (positive) term in Eq. (1) can be larger than the first (negative) term so that the first derivative of the temperature *can* be positive, leading to a heat spike. This analysis indicates that improving the thermal contact between the sample and the bath (reducing t_c) can suppress heat spikes.

In fact, if we use our data[15] to obtain values for the relevant parameters in Eqs. (1) and (2), we can numerically simulate a heat spike with the magnitude and duration of those observed. While this treatment can produce a triggered-heat-spike response and indicate how spontaneous heat spikes can be suppressed, it is overly simple. More complicated, nonlinear processes in the solid probably produce an avalanche effect immediately following a temperature increase. A more detailed theoretical approach is indicated but the above analysis demonstrates the essential features of the observed heat spikes.

The decrease in ESR spin count can be quantitatively related to the temperature changes seen by the thermometer. Our NMR cell was by design strongly coupled to a heat bath so the spikes seen there are difficult to analyze quantitatively. However, in our ESR cell, the coupling was much weaker and we could calibrate the power needed to produce a given temperature change of the cell.[15] Experiments on HD containing 2% T_2 allowed us to compare the actual atom spin decrease following a heat spike as measured by ESR with the observed temperature rise of the sample cell. In both cases, an atom concentration of 300 ppm ± 10% was obtained.

While this agreement was gratifying, it may be fortuitous. Our preliminary observations indicate that some electromagnetic radiation that could escape the cell is also produced during a heat spike, so that using the heat produced to calculate the atom density that recombined may be in error. In addition, the ESR measurement does not detect *all* the spins as some have an ESR signal broadened and shifted so as to be undetectable in our experiment. The order of magnitude of this effect can be obtained from the recent work of Drabold and Fedders[17] on the line shape of dilute spin systems. Our estimate based on their calculation is that at least two-thirds of the atom spins could not be observed (by ESR) at the densities we measure. Thus both determinations that yield an atom spin decrease of 300 ppm may be lower limits.

There may be some practical applications of these effects. The stored energy can be recovered in short bursts by triggering a heat spike, sweeping out all the stored atoms. The increase in power possible could prove useful for certain propulsion applications. Also, we observed that after many spikes, the atom spin count was frequently reduced to the point where apparently only a small fraction of the original sample was left in the region of the cell where the rf field is a maximum. Thus, heat spikes could lead to actual mass redistribution of the sample which might be advantageous for producing uniform layers of D-T fuel for fusion targets.

In conclusion, we have experimentally observed both triggered and spontaneous energy releases in solid hydrogen hosts containing metastable atomic excitations. The energy released by the continuous tritium β decay can be temporarily stored in solid molecular hydrogen in the form of hydrogen (H, D, or T) atoms; the amount of energy that can be stored increases with decreasing temperature. Since the stored energy can be much larger than the lattice energy and the steady-state atom density decreases with increasing temperature, an unusual thermal response (heat spike) is obtained following a positive temperature step. In practice, spontaneous heat spikes can be suppressed by improved thermal coupling with the heat bath.

We would like to thank Chris Gatrousis and Tom Sugihara of the Chemistry and Materials Science Department, John Holzrichter and John Nuckolls of the Institutional Research and Development Fund, and Erik Storm of the Inertial Confinement Fusion Program, all at LLNL, for their support of this work. This work was performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under Contract No. W-7405-ENG-48. We also gratefully acknowledge partial support from the Air Force Avionics Laboratory under Contract No. F04611-88-K-0048. G.W.C. and J.R.G. were under contract to LLNL during the course of this work.

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