Rapid Decay Mechanisms for Bulk Spin-Aligned Atomic Hydrogen at $T = 0$ K in Large Magnetic Fields

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Solid spin-aligned atomic hydrogen is shown to be unstable against spontaneous magnon creation due to electronic dipole-dipole and hyperfine interactions even at $T=0$ K for magnetic fields less than $H_c \approx 7.3\tilde{J}/\mu_e$, where $\tilde{J}$ is the motionally averaged exchange interaction. For an fcc crystal at 50 cm^3/mole, $H_c \approx 10^6$ G. Similar considerations apply to the fluid state where the relevant parameter is again $\tilde{J}$ which is proportional to the density in the low-density limit.

Recently there has been a great deal of theoretical interest in the possible condensed states of spin-aligned hydrogen (H↑) and hydrogen isotopes (D↑ and T↑).[1-4] At low temperature and pressure H↑ is expected to be a nearly ideal Bose fluid,[1,2] while at pressures above 100 atm, corresponding to a density of about 50 cm^3/mole,[1,2] a quantum solid is predicted.

Rather less attention has been paid to the stability of these condensed phases against decay mechanisms which disturb the spin alignment and hence allow a tendency toward the formation of molecular hydrogen. Stwalley[3] has discussed the effect of two-particle scattering in large magnetic fields. He finds that the probability for a single spin flip is proportional to $\exp(-\mu_e H/kT)$ which can be made extremely small by applying large fields at low temperatures. We will show that this argument is not relevant to the condensed phases even at $T=0$ K, except at very low densities or at very high fields. The critical factor is, instead, the product of the field and the molar volume, HV, which must be greater than about 10^7 G cm^3/mole in the low-density limit.

An earlier, comprehensive study of the stability of H was performed by Jones *et al.*[5] The most important conclusions of this work may be summarized as follows: (a) Three-body collisions are a very efficient mechanism for recombination if one of the electron spins is reversed; (b) in the high-field limit the lowest-energy hyperfine state of an H atom contains a fraction $\alpha \approx a/2\mu_e H$ of reversed electron spin, where $a = 0.047$ cm^{-1} is the hyperfine coupling constant, and hence $\alpha = 25\%/$kG; (c) consequently, except at very low densities or extremely high fields, rapid recombination involving three particles will occur. This process is not thermally activated because the attractive final-state interactions more than the compensate for the cost in Zeeman energy. The extra energy is carried off by the third atom.

The work of Jones *et al.*, although suggestive, is based mainly on gas kinetic theory and hence is not directly applicable to the condensed phases of H↑. A particular shortcoming of their theory is that it does not contain a proper description of the elementary excitations of the system, namely, phonons and spin waves in the solid and spin- and mass-density excitations in the Bose fluid. In this Letter we present microscopic calculations of the initial decay rate for the magnetization in the solid. The analogous processes and conditions for the stability in the fluid phase are also discussed.

We begin by considering the zero-temperature solid in the presence of a magnetic field $\vec{H}$ and assume, at least initially, that the electron spins are all aligned antiparallel to $\vec{H}$ and that the proton spins are parallel to $\vec{H}$ (since the electron g value is negative). We write the spin Hamiltonian as

$$\mathcal{H} = \mathcal{H}_0 + V, \tag{1}$$

where

$$\mathcal{H}_0 = \tfrac{1}{2}\tilde{J}\sum_{i,\delta}\vec{S}_i\cdot\vec{S}_\delta + H\sum_j(\mu_e S_j^z - \mu_p i_j^z), \tag{2a}$$

$$V = \tfrac{1}{2}\mu_e^2\sum_{i,j}[\vec{S}_i\cdot\vec{S}_j - 3(\vec{S}_i\cdot\hat{r}_{ij})(\vec{S}_j\cdot\hat{r}_{ij})]/r_{ij}^3 + a\sum_j\vec{S}_j\cdot\vec{i}_j. \tag{2b}$$

In Eq. (2a) $\tilde{J}$ is the motionally averaged nearest-neighbor exchange interaction and is positive, and δ labels a nearest neighbor of atom i. μ_e and $\vec{S}$ are, respectively, the absolute value of the magnetic moment and the spin of the electrons, and μ_p and $\vec{i}_j$ are the analogous quantities for the protons.

If V is neglected the fully aligned state is metastable, even though some of its elementary excitations can be at negative energy, because none

of the terms in Eq. (2a) can create a spin deviation. If the number of spin excitations is small, then it is appropriate to write $\mathcal{H}_0$ in terms of spin-wave operators:

$$\mathcal{H}_0 = \sum_{\vec{k}} \epsilon(\vec{k}) C_{\vec{k}}^{\dagger} C_{\vec{k}}, \tag{3}$$

where

$$\epsilon(\vec{k}) = \mu_e H - \tfrac{1}{2}\tilde{J}\sum_{\delta}[1 - \exp(i\vec{k}\cdot\vec{R}_{\delta})]. \tag{4}$$

To simplify the algebra we will use the spherical average of Eq. (4),

$$\epsilon^{s}(k) = \mu_e H - 6\tilde{J}[1 - j_0(kR_0)], \tag{5}$$

where $j_0(x) = x^{-1}\sin x$, R_0 is the nearest-neighbor distance, and we have set $z = 12$ for an fcc lattice. To conserve phase space, k is restricted to be less than $(3/\pi)^{1/3}(2\pi/\sqrt{2}R) = 4.375/R_0$. The magnon bandwidth is thus about $7.3\tilde{J}$ in this model, compared to the value $8\tilde{J}$ which can be obtained from Eq. (4).

For fields less than $7.3\tilde{J}/\mu_e$ some spin waves have negative energies and hence the system is unstable. Thus it is crucial to determine an accurate value for $\tilde{J}$. If the exchange interaction is small compared to a typical phonon frequency then this renormalization is straightforward. The radial dependence of the exchange interaction $J(r)$ is well known from the work of Kolos and Wolniewicz.[6] Since $J(r)$ has a very strong radial dependence, it is clear that the renormalization due to zero-point motion is important. In particular, the renormalization is quite sensitive to how the wave function cuts off at small distances. We have calculated $\tilde{J}$ as a function of density in the solid using a wave function obtained from the dynamic-field approximation of Etters and Danilowicz[7] and in the self-consistent phonon approximation.[8] At 50 cm^3/mole the ratio $\tilde{J}/J(R_0)$, where R_0 is the average lattice spacing, is about 15. Our results are shown in Fig. 1 by circles and squares where we have plotted the quantity $z\tilde{J}/2\mu_e$ versus $1000/V$. The vertical axis thus represents the approximate field which is necessary to stabilize the spin-wave excitation spectrum. To demonstrate the importance of motional averaging we show the corresponding result for a rigid fcc lattice (dotted line). Also shown by the crosses in Fig. 1 is $\frac{1}{2}\langle zJ\rangle$ for the fluid state where $\langle zJ\rangle$ is the average exchange interaction of one atom with its neighbors,

$$\langle zJ\rangle = 4\pi\rho\int g(r)J(r)r^2\,dr, \tag{6}$$

where $\rho = N/V$ and $g(r)$ is the liquid pair-distribution function which we have calculated in the hypernetted-chain (HNC) approximation. The pair wave function itself was obtained by solving for the two-body, zero-energy, s-wave, reduced Schrödinger equation in the manner of McGee and Murphy.[9] In the low-density limit $g(r)$ goes to the square of the Jastrow function which is independent of ρ and thus $\langle zJ\rangle$ is proportional to ρ at low densities. This linear dependence is represented by the dashed line in Fig. 1 of which the slope is about 10^7 G cm^3/mole.

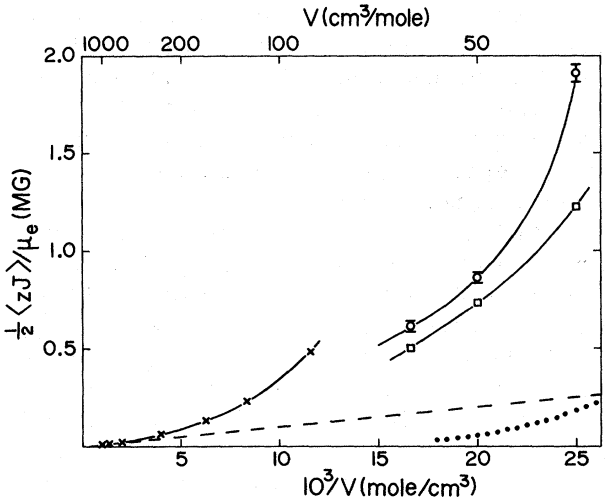

FIG. 1. Average exchange energy per particle as a function of density. The circles and squares are calculated in the local-field and self-consistent-phonon approximations, respectively. The dotted line represents the value for a rigid fcc lattice. The crosses have been calculated in the hypernetted-chain approximation for the fluid. The dashed line is an extrapolation of the low-density behavior. The solid lines are simply smooth curves drawn through the calculated points.

One problem with the treatment given above is that the condition that the exchange interaction be small compared to typical phonon frequencies is not very well fulfilled. One might wonder then whether the contributions to $\tilde{J}$ from the large short-range part of $J(r)$ are valid. Intuitively one might expect for a ferromagnetic system (i.e., one for which $J < 0$) that at short distances the spins would respond to the large negative value of $J(r)$ by improving their alignment. To neglect this "nonadiabatic" correction would lead to an overestimate of $\tilde{J}/J(R_0)$. In our case $J(r)$ is positive, and the response of the spins at close distances would be to increase their relative misalignment, which could be interpreted as an extra positive contribution to the renormalization

of J. Consequently, our method of renormalization, even though it gives a very large result, probably still underestimates $\tilde{J}$. This assumes of course that it is possible to define a $\tilde{J}$, and that the system does not, for example, tunnel directly into the singlet molecular state.

Returning now to the solid calculation, it is clear that, given the current state of technology, H will always be less than $7.3\tilde{J}/\mu_e$, which is about 1 MG at the lowest solid density, and thus some spin waves with $k>0$ will have zero energy. If k_0 is the wave vector for which $\epsilon^s(k_0)=0$, then the spin waves with this wave vector will be created spontaneously by interactions contained in Eq. (2b). Spin waves with wave vectors greater than k_0 can also be created by interactions involving the emission of one or more phonons. However, for simplicity, we consider explicitly only those processes which occur without phonon creation. These are described by the interaction V_1 which may be written as

$$V_1=(\mu_e)^2\textstyle\sum_{\vec{k}}S^{(2)}(\vec{k})C_{\vec{k}}^{\dagger}C_{-\vec{k}}^{\dagger}+(a/2)\sum_{\vec{k}}C_{\vec{k}}^{\dagger}, \quad (7)$$

where

$$S^{(2)}(\vec{k})=-(3\pi/10)^{1/2}\textstyle\sum_{\delta}e^{-i\vec{k}\cdot\vec{R}_\delta}Y_2^{\,2}(\Omega_\delta)/R_\delta^{\,3} \quad (8)$$

is a dipolar sum, $Y_2^{\,2}(\Omega_\delta)$ is a spherical harmonic, and we have taken the nuclear spin matrix element in the hyperfine term since the Zeeman energy involved is negligible. The main effect of the nuclear spins in this term is to act as a sink for crystal momentum. The dipolar sum can be approximated by an integral which gives

$$S^{(2)}(k)\approx\tfrac{4}{3}\pi\rho Y_2^{\,2}(\Omega_k). \quad (9)$$

This approximation overestimates $S^{(2)}(k)$ by, at most, a factor of 2 along certain directions near the zone boundary.

The initial rate of spin-wave creation is obtained by a "golden rule" calculation. We find

$$1/\tau_{dd}=(\pi^2/15\hbar)\mu_e^{\,4}\rho^2D_s(0), \quad (10a)$$

$$1/\tau_{\rm hf}=(\pi/2\hbar)a^2D_s(0), \quad (10b)$$

where the density of final spin-wave states at zero energy is

$$D_s(0)=(R_0k_0)^2/[12\sqrt{2}\pi^2\tilde{J}j_1(k_0R_0)], \quad (11)$$

where $j_1(x)=\sin x/x^2-\cos x/x$. $D_s(0)$ is strongly dependent on the field H which determines the value of k_0 through Eq. (5). Our results for the total transition rate for $V=50$ cm^3/mole are shown in Fig. 2 as a function of H. The hyperfine and dipolar transition rates are almost equal at this density. Their ratio $(1/\tau_{dd})/(1/\tau_{\rm hf})$ is proportional to ρ^2 as can easily be seen by comparing Eqs. (10a) and (10b).

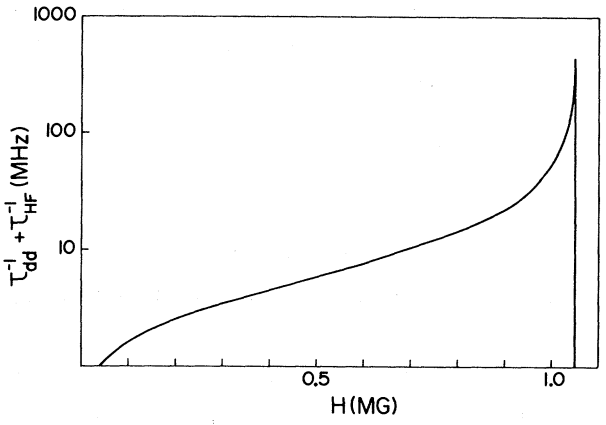

FIG. 2. Initial rate for the decay of the magnetization at 50 cm^3/mole due to the electronic dipole-dipole and hyperfine interactions. At this density the two contributions are roughly equal.

Once a k_0 spin wave is created, it quickly decays via the spin-phonon interaction which results from the radial dependence of $J(r)$. A phonon expansion of the full exchange interaction contains terms in which a phonon is emitted while a spin wave is scattered into a lower energy state, thus providing an efficient mechanism for transfer of exchange energy to the lattice.

From the discussion of the solid given above, it is clear that a proper treatment of the stability of the superfluid phase will require a knowledge of the spectral response of the elementary density and spin-density excitations of the Bose fluid. This problem has been studied recently by Berlinsky[10] who finds that the spin excitations lie at positive energy for $\mu_eH>\frac{1}{2}\langle zJ\rangle$ as we had guessed by analogy to the solid problem. Thus, we would estimate that a fluid at 200 cm^3/mole can probably be stabilized at $T=0$ K by 100 kG and that 10 kG is sufficient to stabilize a fluid at 10^3 cm^3/mole. These estimates certainly represent lower bounds for the necessary magnetic fields since other microscopic processes may also lead to recombination. The effects of finite temperature will also be destabilizing and calculations of these effects for the low-density fluid in a high magnetic field would be of interest from many points of view.

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Elementary Excitations of Bose-Condensed, Spin-Aligned Atomic Hydrogen

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Ground-state properties and elementary excitations of superfluid spin-aligned atomic H are studied using methods adapted from the theory of liquid ^{4}He. The ground state is a $k=0$ condensate of the $|\downarrow$ (electron), $\downarrow$ (proton)$\rangle$ hyperfine state with a small admixture of $|\uparrow\uparrow\rangle$ due to the hyperfine interaction. Excitations can also be labeled approximately by their hyperfine states. $\varphi_{\downarrow\downarrow}(k)$ excitations are phononlike. $\varphi_{\downarrow\uparrow}(k)$ and $\varphi_{\uparrow\downarrow}(k)$ are free-particle–like with energy gaps, and $\varphi_{\uparrow\uparrow}(k)$ excitations resemble spin waves.

Two ground-state hydrogen atoms, in a relative spin triplet state, interact via a potential which is qualitatively similar to, although slightly weaker than, that of helium. When a collection of hydrogen atoms is forced into a spin-aligned state by the application of a very large magnetic field at low temperature, the effective pair interaction is again the triplet potential. This potential is quite accurately known from the variational calculations of Kolos and Wolniewicz.[1]

Since H atoms are very light bosons and since the system is weakly interacting in the low-density limit, Bose condensation is expected to occur at fairly high temperatures (e.g., 1°K at 1000 cm^3/mole). Properties of perfectly spin-aligned, Bose-condensed atomic H have been calculated by Dugan and co-workers,[2] Stwalley and Nosanow,[3] and Miller and Nosanow.[4] There is general agreement among these authors concerning the equation of state of the superfluid. In addition, they predict a fluid-solid transition at about 50 atm for $T=0$.

The stability of spin-aligned H in a finite field, against spin flips and recombination transitions to molecular states, is much less well understood. Jones *et al.*[5] suggested that the nuclear hyperfine interaction would seriously perturb the relative spin alignment of the atoms and thus lead to rapid recombination. Stwalley[6] claims that spin-flip transition rates due to hyperfine interactions are proportional to $\exp(-\mu H/kT)$ and can thus be made negligibly small with available laboratory fields and temperatures. Quite recently, Berlinsky *et al.*[7] have shown that *solid* atomic H is unstable, even at $T=0$, for fields less than about 1 megagauss because the spin-wave excitations lie at negative energy and thus provide a direct channel for decay of the magnetization. These calculations suggest, however, that the gas may be stable in available laboratory fields at densities for which the Bose-condensation temperature is easily accessible.

The purpose of this Letter is to present new theoretical results concerning the ground-state properties and elementary excitations of Bose-condensed, spin-aligned atomic H in a large but