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Electron-spin resonance, nuclear polarization, and spin relaxation of spin-polarized atomic hydrogen

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Electron-spin-resonance measurements of spin-polarized hydrogen are presented. Excellent signal-to-noise ratio, previously obtainable only in pressure studies, allows quantitative fits to the separate a and b (proton up and down) decays of the nuclear-spin-polarized samples, yielding separate temperature dependences of the recombination rate constants K_{aa} and K_{ab}. Spin relaxation due to magnetic particles in the substrate is studied for different thicknesses of solid H_2 wall coating, and the results are compared with a new theoretical model.

In 1980 we predicted[1] that an electron-spin polarized gas of H atoms at temperatures below 1 K would exhibit spontaneous nuclear polarization because the intrinsic T_1 processes which equilibrate the two lowest hyperfine levels (a and b) are slow compared with the recombination processes which deplete the population of the a state. The electron-spin polarized states a and b are given at high field by $|a\rangle = |\downarrow\uparrow\rangle - \epsilon|\uparrow\uparrow\rangle$ and $|b\rangle = |\downarrow\uparrow\rangle$, where $\uparrow, \downarrow$ ($\uparrow, \downarrow$) represent electron (proton) spins and ϵ is 2.5% divided by the magnetic field in tesla or, equivalently, half the ratio of the hyperfine constant to the electronic Zeeman splitting. Cline, Greytak, and Kleppner[2] were the first to observe the so-called "T_1 bottleneck" and demonstrate that very high nuclear polarization $n_b/(n_a+n_b) > 0.99$ is readily obtainable at low temperature. An earlier experimental attempt to observe the bottleneck[3] was frustrated by extrinsic relaxation processes which were later attributed to magnetic particles buried in the walls of the sample chamber.[4]

Experiments in which nuclear polarization is inferred from measurements of pressure as a function of time[2,4,5] can in principle also determine the two separate rate constants K_{aa} and K_{ab}, where the subscripts specify the hyperfine states of the atoms which form a molecule. (Note that nuclear polarization develops because $K_{bb}=0$.) However, the determination of rate constants requires a multiparameter fit to K_{aa}, K_{ab}, G_1, G_2, $n_a(0)$, and $n_b(0)$ where G_1 and G_2 are one and two-body relaxation rates, related to T_1 by $1/T_1 = 2G_2(n_a+n_b)+2G_1$, and $n_a(0)$ and $n_b(0)$ are the initial densities of a and b atoms. All earlier studies, except one, attempted to extract this large number of constants by fitting a single curve, the decay of the total density n_a+n_b with time. The one exception, the earlier electron-spin-resonance (ESR) study of van Yperen *et al.*,[6] yielded only a ratio of rate constants $2 < K_{aa}/K_{ab} < 8$, with much larger error bars than were obtained from pressure studies. The large uncertainty in this result has been attributed to systematic error and inadequate signal to noise.[7]

In this Rapid Communication we report the first quantitative measurements by ESR of the separate decays of the densities n_a and n_b as determined from the integrated intensities of the $a \rightarrow d$ and $b \rightarrow c$ ESR transitions. The additional information available in these separate decay curves allows an accurate determination of the separate temperature dependence of the two recombination rate constants K_{aa} and K_{ab}. We have also studied the one-body surface relaxation rate G_1 due to magnetic particles in the substrate. G_1 depends sensitively on the thickness of the solid H_2 layer on the surface of the metal substrate below the ^{4}He film. Both the thickness and temperature dependence of G_1 are described by the theory presented below. By varying the thickness of the film we were able to vary G_1 in a controlled manner.

Electron-spin resonance was done using a cylindrical microwave cavity, 3 mm in diameter and 2 mm high, resonant at 114 GHz in the TM_{011} mode. Atoms, generated by a low temperature (~ 0.3 K) source, enter through a small, 0.3-mm tube at the bottom of the cavity which can be closed by means of a fountain pump valve of the type developed at Cornell.[5] In order to minimize microwave-induced recombination, a sensitive low power ($P_i \simeq 4\times 10^{-12}$ W) heterodyne spectrometer with an intermediate frequency of 1460 MHz was used. Typically, 0.07% of the atoms in one of the lower levels are excited per sweep through the line, whose duration is ~ 0.1 s. Temperatures are measured by means of a Matsushita resistance thermometer mounted on the cell, which has been calibrated with respect to a ^{3}He melting curve thermometer.[8]

The ESR line is obtained by observing the cavity reflection coefficient Γ as the atomic resonance is swept through the fixed microwave frequency by varying the field. The fractional change $\delta_c = (\Gamma/\Gamma_0)-1$, where Γ_0 is the unperturbed reflection coefficient, is given by

$$\delta_c = \eta \frac{\gamma'' + (\gamma'')^2 + (\gamma')^2 + i\gamma'}{(1+\gamma'')^2 + (\gamma')^2} , \quad (1)$$

where $(\gamma' + i\gamma'') = 4\pi Q(\chi' + i\chi'')$, Q is the loaded Q of the cavity, $\chi' + i\chi''$ is the complex, frequency-dependent susceptibility of the sample, and $\eta = (\Gamma_0 - 1)/\Gamma_0$ is the cavity coupling parameter. When $|\gamma' + i\gamma''| \ll 1$, only the linear terms in Eq. (1) are important and δ_c simply measures the susceptibility. However, for our experiments it was found that at the higher densities, $n_a + n_b \approx 10^{15}/\text{cm}^3$, the peak of the line corresponded to $|\gamma' + i\gamma''| \approx 1$, which caused the measured line shape, $\text{Re}\delta_c$, to exhibit large wings from the $(\gamma')^2$ term in the numerator of Eq. (1). After a careful determination of η, it was possible to use Eq. (1) and the Kramers-Kronig relation between γ' and γ'' to extract γ'' from our measurements of $\text{Re}\delta_c$. The integrals of γ'' for a and b lines were then used to determine the densities of H atoms in these two states.

Typical decay curves are shown in Fig. 1. Initial measurements showed no nuclear polarization. A method was then devised to systematically coat the cell by running the atom source with a high level of microwaves at the ESR frequency incident on the cavity. This led to fast recombination inside the cavity ensuring that most of the resulting H_2 was deposited on the cavity walls. The a,b pair labeled "large G_1" shows a decay in which the nuclear polarization is very small. To obtain even this small polarization required coating the walls of the cell with solid H_2. After further coating, the a,b pair labeled "small G_1" were obtained.

Decays were fitted to the rate equations

$$\dot{n}_a = -2K_{aa}n_a^2 - K_{ab}n_a n_b - [G_2(n_a+n_b)+G_1] \times [(n_a-n_b)-n_a^{eq}-n_b^{eq})] \ , \quad (2a)$$

$$\dot{n}_b = -K_{ab}n_a n_b + [G_2(n_a+n_b)+G_1] \times [(n_a-n_b)-(n_a^{eq}-n_b^{eq})] \ , \quad (2b)$$

where G_2 is the (fixed) theoretical two-body relaxation rate[1] for H atoms in the gas and n_a^{eq} and n_b^{eq} are the values of n_a and n_b for a given n_a+n_b which would result if the relaxation rate were much faster than the recombination rates. A surface contribution to G_2 was not included in the fit since this contribution is thought to be unmeasureably small.[9,10] However, a correction was made for microwave-induced recombination.

Fits were obtained by integrating the rate equations and by a nonlinear least-squares fit for the variables K_{aa}, K_{ab}, and G_1 and the initial densities $n_a(0)$ and $n_b(0)$. Typical fits are shown by the solid lines in Fig. 1. In general the large-G_1 data were not useful for determining K_{aa}/K_{ab}. Instead the small-G_1 data were used to determine K_{aa} and K_{ab} separately. Then interpolated values of K_{ab} were held fixed in the analysis of the large G_1 data from which additional values of K_{aa} and G_1 could be determined. Recombination rate constants determined in this manner are shown in Fig. 2(a). Fits to these data give an average binding energy $E_B = 1.10 \pm 0.02$ K. The average surface recombination rate constant was found to correspond to $K_s T^{-1/2} B^2 = 5.7 \pm 0.8$ $cm^2 s^{-1} K^{-1/2} G^2$, assuming the standard adsorption isotherm, in reasonable agreement with earlier results.[2,5,11] The temperature dependence of $\gamma = K_{aa}/K_{ab}$ is shown in Fig. 2(b). We find that γ is slightly larger than earlier measurements and that it slopes in the opposite direction.

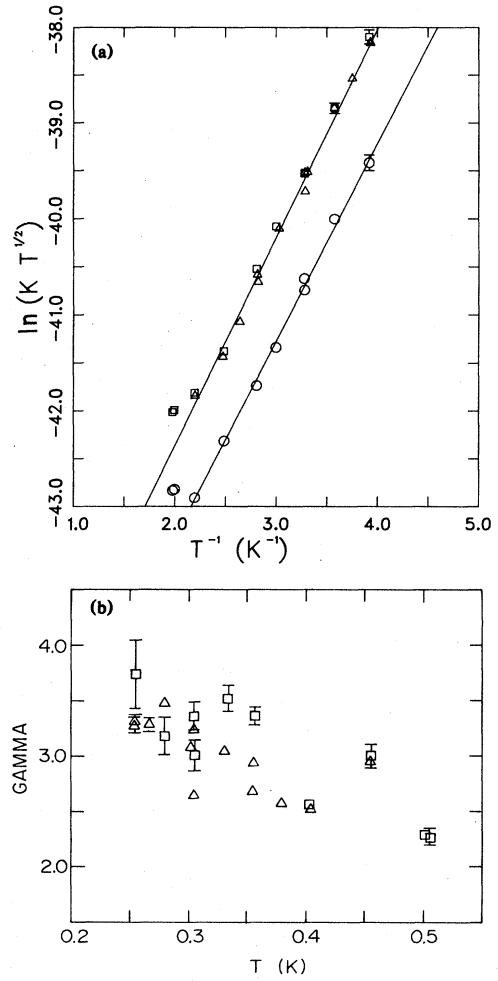

FIG. 2. (a) Temperature dependence of K_{aa} and K_{ab}. Circles and squares represent data from low-G_1 data; triangles are from high G_1 data. (b) Temperature dependence of $\gamma = K_{aa}/K_{ab}$. Squares and triangles represent data from the low-G_1 and high-G_1 data sets, respectively.

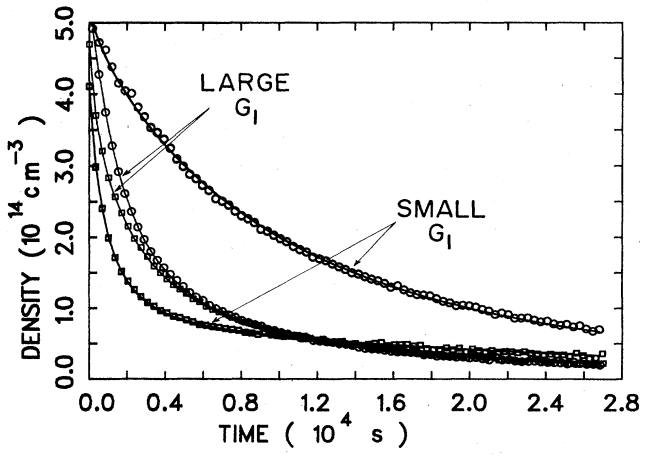

FIG. 1. Typical decay curves for density of a atoms (squares) and b atoms (circles). The pair labeled "large G_1" is for high surface relaxation rate G_1. The temperatures are 501 and 456 mK, respectively.

The measured surface relaxation rates for the two data sets are shown in Fig. 3. We conjecture that this relaxation results from inhomogeneous magnetic fields at the surface produced by ferromagnetic particles in the copper cell. If $\mathbf{H_q}$ is a Fourier component of the field at the surface with spatial dependence $\exp(i\mathbf{q}\cdot\mathbf{r})$, where $\mathbf{q}$ and $\mathbf{r}$ are vectors in the plane of the surface, then an atom moving with velocity $\boldsymbol{v}$ on the surface sees a time-dependent field with frequency $\omega = \boldsymbol{v}\cdot\mathbf{q}$. The amplitude of the contribution to $\mathbf{H_q}$ of a magnetic dipole a distance z below the surface is proportional to $\exp(-qz)$. We have calculated the rate of relaxation due to such magnetic particles, randomly distributed in the metal substrate but displaced from the helium surface by a total thickness d of solid H_2 plus liquid He. Our results can be written in the form

$$G_1 = (3\pi^2\gamma_1^2/4)M_2 A(\theta)\int_0^\infty C_q(\omega)q^2 dq \ , \quad (3)$$

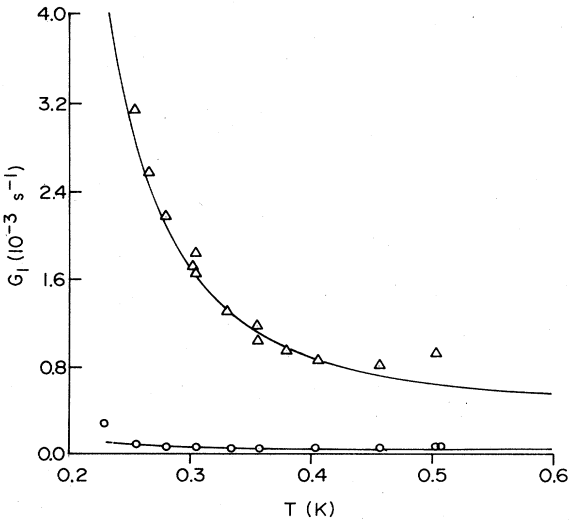

FIG. 3. One-body relaxation rate G_1 from both data sets.

where $\hbar\gamma_\perp$ is the transition moment for the a-b transition, $A(\theta)$ a weak function of order unity of the angle θ between the external field and the normal to the surface, and M_2 the average of the squared magnetic moments of the iron particles per unit volume, $M_2=(\sum_i \mu_i^2)/V$.

The correlation function $C_q(\omega)$ contains two contributions: one from atoms on the surface and another from atoms near the surface. The complete result is

$$C_q(\omega)=(\Lambda A/V)\left(\Lambda e^{\beta E_B}+\frac{1}{2q}\right)(m/2\pi\hbar q)\times e^{-2qd}\exp\left(-\frac{\beta m\omega^2}{2q^2}-\frac{\beta\hbar^2q^2}{8m}+\frac{\beta\hbar\omega}{2}\right), \quad (4)$$

where $\beta=1/kT$ and Λ is the thermal de Broglie wavelength. For the conditions of temperature and thickness d of this experiment, the last two terms in the exponential can be ignored. The exponential factors are then equal to $\exp(-2qd-\beta m v^2/2)$ where $v=\omega/q$. Further details of this theory will be presented elsewhere. However, it is worth noting the prediction of a minimum in G_1 at a temperature where the effect of the atoms slowing down is overtaken by the effect of increasing surface density. The temperature dependences of G_1 calculated from Eqs. (3) and (4) for two thicknesses $d_1=350$ Å and $d_2=610$ Å are shown by the solid lines in Fig. 3. The value of M_2 used to fit both data sets corresponds to 0.1 at.% of iron in the form of 75-Å particles, values that are consistent with other observations on OFHC copper.[12]

An important feature of the analysis described above is that, unlike most situations in nuclear magnetic resonance where the short correlation time limit is appropriate, here the spectral function is decreasing rapidly over the experimental frequency range. Thus, the details of the dynamics, in this case two-dimensional free flight, are important and must be treated correctly.

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