OBSERVATION OF ELECTRON SPIN RESONANCE OF NEGATIVE IONS IN LIQUID HELIUM

by

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ABSTRACT

Electron spin resonance signals of negative ions in liquid helium have been observed. The line width and g-value have been measured. Electrons injected into helium by field emission from ferromagnetic tips are shown to be polarized. A new technique for the measurement of electron spin polarization is presented.

1

Excess electrons injected into liquid helium form a uniquely simple system which has been the object of extensive study over the past decade. The wealth of experimental data so far accumulated has been interpreted using the generally accepted model of the electron trapped in a helium void, a bubble of approximately 17 Å radius.[1] Such an isolated unpaired electron will form a two level system when placed in an external uniform magnetic field, and transitions between these two states should be detectable by standard magnetic resonance techniques. Such measurements probably would have been made long ago if it were not for the extremely low ion densities one can reasonably obtain due to space charge limitations ($\sim 10^{10}$ spins/cm^3) and the predicted long spin–lattice relaxation times of this bubble state.[2]

This letter reports the first measurements of a single, unsplit, ESR absorption line from negative ions injected into helium by field emission from both ferromagnetic (iron) and nonferromagnetic (tungsten) tips. Recent experiments have demonstrated that electrons ejected from ferromagnetic tips by field emission are polarized.[3]

Our spectrometer was a superheterodyne type operating at Ku band. The pressure sealed TE_{102} mode rectangular cavity had special microwave chokes which prevented leakage of microwave radiation. They also provided support and electrical insulation for both an electrolytically etched metallic tip and a collector electrode. The collector served to focus the ion beam into the region of the maximum microwave magnetic field. Typical operating conditions were the following: negative 5,000 V on the tip, positive 2,500 V on the collector, I_t (tip current) = 2.5 μA, and I_c (collector current) = 1.5 μA.

2

A standard phosphorous doped silicon sample was placed on the wall of the cavity to tune and calibrate the spectrometer.[4] The resonance signals were not clearly discernible on single sweep and had to be averaged by a multichannel analyzer over many sweeps, requiring a period of about an hour. Because of the narrowness of these ESP lines, a superstabilizer was constructed which locks the magnetic field to the NMR resonance of protons in mineral oil.[5] The NMR radio frequency field was provided by a synthesizer whose frequency was programed by the multichannel analyzer.

Figure 1a shows an observed absorption signal from a polarized beam of ions (electrons from a tip etched from an iron whisker). Figure 1b shows a similar run with no ion current. This demonstrated that the observed signal did not originate from some unknown impurity within the cavity. Experiments demonstrated that the signal was proportional to the ion current. Figure 1c shows an experimental spectrum of the negative ion beam originating from a paramagnetic tungsten tip at the same temperature and pressure. A compilation of the reduced reproducible data, taken over several months with various tips, yielded a linewidth, ΔH, of (45 ± 10) mG and a residual g shift, Δg, after field corrections were applied of $(1.8 \pm 1.0) \times 10^{-5}$. Here ΔH is the half width at maximum derivative, and $\Delta g = g_{neg.ion} - g_{free}$ (2.0023193). These parameters were identical to within experimental error for ion beams from both types of tips. The line width and g value were independent of pressure (50-225 psi) and temperature (1.4 - 2.0 K) to within experimental error. The iron tip beam produced a signal intensity per unit current which was approximately six times the signal intensity from the tungsten beam. A careful search around the region of $g = 2$ was carried out in an attempt to observe spin resonance

signals from positive ions created by field ionization,[6] but no signal was observed.

Significant corrections must be made to the raw data. These corrections involve the nonuniform magnetic field around the ferromagnetic tip through which the negative ions drift under the influence of the applied dc electric field, and a measured temperature dependent field shift due to what appeared to be paramagnetic impurities in the cavity walls. Extreme care was taken to make the tips as small as possible and still retain their necessary structural strength. A typical iron tip was about .25 cm long with a shank diameter of 2.5×10^{-3} cm. Such a tip produced an increase in the magnetic field at the center of the cavity of ∿16 mG. A NMR probe was constructed to measure the field intensity and inhomogeneity with the iron tip in the cavity. These measurements were used to calibrate the field and to verify our estimates of the perturbations on the applied magnetic field due to the iron tip. This same probe was used to measure the magnetic field at the center of the cavity as a function of the temperature of the cavity walls. The probe was thermally insulated with styrafoam and maintained at 300 K with a tungsten heater. A thermistor was used to monitor the temperature of the probe. A field shift with a hyperbolic tangent dependence on T^{-1} was observed. This shift was (95 ± 5) mG at 1.5 K. These corrections were applied to the data. Attempts are being made to remove the source of the paramagnetic shifts so that the g shifts can be confirmed with greater confidence.

Even with these corrections the question remained as to whether the observed signal came from ions which undergo a spin transition within a few millimeters of the iron tip (where the field gradient and magnitude due to

the tip are appreciable), or whether these transitions occur near the collector where these quantities can be neglected. One can present several arguments to show that a negligible portion of the signal came from spin flipping near the tip. The time spent by the electrons within 2 mm of the tip was small compared to the spins' nutation time because of the large electric field in this region. The measured g-shift was found to be independent of the microwave field (H_1). The magnetic field gradient near the tip further reduces the fraction of spins undergoing transitions, because in this region H_1 is much less than the line width ΔH. The strongest corroborative evidence is the experimental fact that the measured line widths and g-values for signals from both kinds of tips are the same within experimental error.

The analysis of the signal from the tungsten tip beam depends on whether or not the electrons are injected into the helium with an initial polarization. Under the assumption that the beam is initially <u>unpolarized</u>, the observed signals from the tungsten tip beam can be used to estimate the spin lattice relaxation time, T_1, of the negative ion. The theoretical framework employed has been worked out for NMR signals of flowing liquids.[7] Using the notation of Ref. 7, we write the observed signal, which is proportional to the time average of the magnetization $\overline{M}$ of the ions over the transit time τ across the cavity, as

$$S \propto \overline{M} = X_o H_o Z + \frac{ZT_1}{\tau} (M_{en} - X_o H_o Z)(1 - e^{-\tau/ZT_1}) \quad , \qquad (1)$$

where $Z = (1 + \gamma^2 H_1^2 T_1 T_2)^{-1}$ is the saturation factor, and M_{en} is the initial magnetization of the spins after field emission. Substituting the

measured values of cavity Q, volume, incident power, and line width (T_2), our saturation factor becomes

$$Z = (200 \ T_1 + 1)^{-1} \quad . \tag{2}$$

For an unpolarized beam $(M_{en} = 0)$ in the limit where $\tau (ZT_1)^{-1} < 1$, Eq. (1) becomes

$$\overset{..}{M}(X_o H_o)^{-1} = \tau (2T_1)^{-1} \quad . \tag{3}$$

From our standard silicon sample signals, we estimate that our observed signal intensities correspond to the equivalent of 3.3×10^7 spins/μA (in thermal equilibrium) compared with 2.5×10^9 spins/μA in the cavity $(\tau = 4 \times 10^{-4}$ sec). Thus, Eq. (3) allows us to estimate $T_1 \approx 1.5 \times 10^{-2}$ sec. Using this estimated T_1 and Eq. (2) we obtain $Z = 0.25$ and $\tau (ZT_1)^{-1} \approx 0.1 \ll 1$. This short relaxation time is surprising in view of the past theoretical estimates.[2]

Our data can be interpreted equally well by assuming an initial polarization of the tungsten beam and a long $T_1 > 10^{-1}$ sec. With these assumptions we have $(ZT_1)^{-1} = 200$ sec^{-1}, and to first order Eq. (1) becomes $\overline{M} = M_{en}$. This analysis yields an initial electron spin polarization (ESP) of the beam of $(0.25 \pm 0.13)\%$. Recent measurements on electrons field emitted from polycrystalline tungsten[8] at 80 K show an ESP of 18% at a field of 12 kG, while Müller et al.[9] reported no ESP for tungsten to within their experimental uncertainty of 5%. Our tips were made from commercial tungsten wire. We plan to investigate the question of the initial polarization of the tungsten

beam and a possible measurement T_1 by a careful study of the signal amplitude as a function of the transit time and H_1 and a comparison with signals from other metallic tip beams.

We interpret the experimental fact that the iron tip signals are six times larger than the ones from tungsten tips (per unit ion current) as clear evidence that these electrons are injected into the liquid helium with polarized spins. Our analysis of the signals from iron tip beams yield an initial ESP of the beam of $(1.6 \pm 0.8)\%$. The polarization was the same for all iron tips to within experimental error. The orientation of the surface at the tip was not measured.

It is of interest to compare our measured polarizations with the Mott scattering measurements on electrons field emitted from iron tips[10] and photo-ejected from polycrystalline iron films,[11] and with the spin polarization of tunneling electrons from amorphous films of iron into superconducting aluminum.[12] These polarizations at large fields were $(2-4)\%$, 54%, and 44% respectively. The polarization is reduced by a factor of three at the 4800 kG field used here.[11]

The study of the electron spin polarization (ESP) has become an important current topic in solid state physics, because it gives useful information about the band structure of ferromagnetic materials near the Fermi surface. The technique presented here can be used to measure ESP of metals if it can be determined that the initial polarization of the beam as measured is consistent with the ESP of electrons field emitted into a vacuum from a clean metallic surface.

A clean metallic surface is essential for such measurements. Although no care was taken to remove the surface oxide layer, the observed

blunting of our tips, which we attribute to positive ion bombardment, indicates an, in situ, cleaning of the surface. Thus we do not believe surface contamination was important. Positive ion bombardment of the tip suggests the possibility that the beam could consist of a majority of unpolarized secondary electrons created in a discharge near the field emission tip. The comparison of our results with those of Regenfus[10] suggest that the primary polarization is not appreciably diminished. A further comparison of our results on various tips with Mott scattering measurements will determine whether this technique yields an absolute value for ESP from metals. If the polarization of the ion beam is equal to the ESP of the electrons field emitted into a vacuum, then this technique provides an order of magnitude increase in sensitivity over other techniques. If the primary beam is reduced with unpolarized secondaries, then our technique still provides an alternate method for measuring the relative ESP.

Experiments are in progress which will extend the range of temperature and pressure to the solid phase of helium. Such measurements vary the transit time over many orders of magnitude and allow more precise determinations of T_1. We also plan to study the negative ion in ^{3}He in an attempt to observe the electron-nuclear hyperfine interaction. Thus far attempts to achieve a theoretical understanding of our measured parameters of this system have been unsuccessful. We considered the possibility that we were not observing the trapped electron, but rather an "exotic" ion species.[13] A search was made for ions with different mobilities using field emission tips in a velocity spectrometer. To less than one part in 10^3 no such ions were detected.
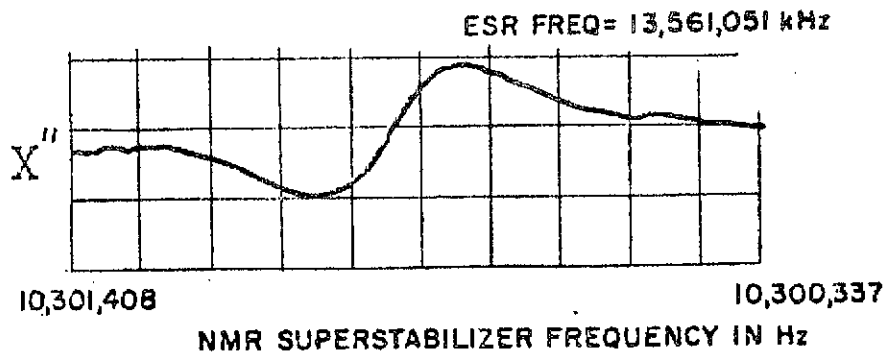
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FIGURE CAPTIONS
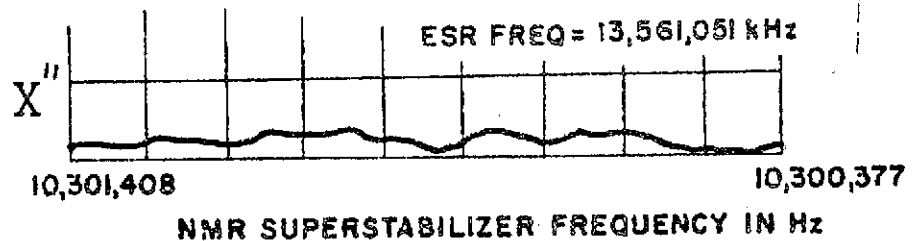
Figure 1. ESR absorption versus magnetic field.

a) Iron tip beam I_t = 2.5 µA, 40 psi pressure at 1.5°K.

b) $I_t = I_c = 0$, otherwise same conditions as (a).

c) Tungsten tip beam I_t = 3.0 µA, 49 psi at 1.5°K.

ESR FREQ= 13,561,051 kHz

1a

X''

10,301,408   10,300,337

NMR SUPERSTABILIZER FREQUENCY IN Hz

ESR FREQ = 13,561,051 kHz

1b

X''

10,301,408   10,300,377

NMR SUPERSTABILIZER FREQUENCY IN Hz

ESR FREQ= 13,423,196 kHz

1c

X''

10,196,755   10,195,470
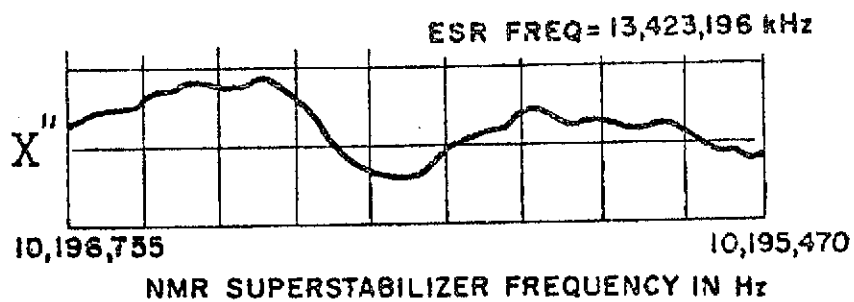
NMR SUPERSTABILIZER FREQUENCY IN Hz

PRL LL403

Figure 1a, 1b, 1c

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