Pulse ESR Studies of Impurity-Helium Condensates Containing Kr, H, and D Atoms

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Abstract. Hydrogen and deuterium atoms trapped in impurity-helium condensates (IHCs) formed by condensing krypton, hydrogen, and deuterium atoms in superfluid $^4$He were studied with pulse electron spin resonance. We have used electron spin echo envelope modulation (ESEEM) to probe the magnetic interactions between atoms of hydrogen isotopes and $^{83}$Kr nuclei. Modeling of the ESEEM spectra suggests that the vast majority of the hydrogen and deuterium atoms reside at the surface of the Kr clusters. This conclusion is in agreement with that from continuous wave ESR experiments with IHCs of similar composition.

1. Introduction

Impurity-helium condensates (IHCs) are formed by directing a beam composed of helium and impurity gases through the surface of superfluid $^4$He. The impurity gases cool and condense into nanoclusters that aggregate to form a low-density gel within the liquid helium\textsuperscript{[1]}. The nanoclusters are favorably wetted by helium, which forms a solid monolayer on their surfaces. Previous x-ray scattering experiments with IHCs formed by condensing helium and krypton show that the nanoclusters of krypton atoms are compact spheroids approximately 5 nm in diameter and constituted of 1000-3000 atoms\textsuperscript{[2]}. These samples are stable indefinitely, provided that they remain immersed in superfluid helium.

Krypton nanoclusters can be doped with hydrogen atoms (radicals) by introducing a small fraction (relative to Kr) of molecular hydrogen into the gas mixture and passing this through an electrical discharge. The resulting condensate contains concentrations of hydrogen atoms ($\sim 4 \cdot 10^{18}$ cm$^{-3}$) that are much larger and much more stable than those obtained by condensing mixtures in which molecular hydrogen is the predominant impurity\textsuperscript{[3, 4]}. Pulsed electron spin resonance is uniquely sensitive to the nuclear environment around the hydrogen atoms and allows us to locate them relative to the krypton clusters. The magnetic dipolar interaction between $^{83}$Kr nuclei (11.49\% natural abundance) and the electron spins of the hydrogen atoms provides the basis for the measurements and conclusions of this paper.

2. Results and Discussion

This paper concerns two impurity-helium solid samples. In sample one, a mixture of H$_2$, Kr and He gases in the ratios of 1:5:1000 was condensed into the superfluid helium at a temperature of 1.5 K. Immediately prior to condensation, the mixture was passed through a 50 W radiofrequency
discharge to dissociate the molecular hydrogen. Sample two was similarly formed but the ratios of H$_2$, Kr and He were 1:50:10000. Both samples produced strong electron spin echoes when the high field hydrogen line was excited with pairs of 9 GHz microwave pulses at a magnetic field of $\approx$ 3300 G. We measured two-pulse electron spin echo envelope modulation (ESEEM) spectra (figure 1, curves a and e) by incrementing the time $\tau$ between the microwave pulses and recording the resulting spin echo amplitudes sequentially[5].

The magnetic environment of the electron spins associated with the hydrogen atoms in our samples results from the dipolar fields produced by surrounding nuclei and other unpaired electrons. The ESEEM effect results from the magnetic coupling of electronic spins to nuclear spins. Microwave pulses induce sudden changes in the orientation of electronic spins that cause changes in the magnetic fields at nearby nuclei. This induces precession in these nuclei at their Larmor frequencies, which are about 540 KHz for the $^{83}$Kr nuclei in the applied magnetic fields used in these experiments. The changing magnetic fields produced by the precessing nuclei act on the electronic spins and modulate their electron spin echoes at the Larmor frequency of the nuclei, as well as at harmonics of this frequency[5]. The “dipole - induced dipole” mechanism responsible for ESEEM causes the modulation depth of the echo signal due to a nucleus at a distance $r$ from the electron spin to scale as $r^{-6}$. Modulation signals from multiple nuclei interacting with the same electron simply multiply. This causes ESEEM to be a very sensitive probe of the nuclear environment immediately surrounding the hydrogen and deuterium atoms in our samples. Two types of magnetic nuclei are present in our samples: $^{83}$Kr nuclei and protons. The spins of the protons present in H$_2$ molecules are strongly coupled into ortho (parallel) and para (antiparallel) configurations. Only the magnetically inert para configuration exists near unpaired electron spins at low temperatures. Therefore only $^{83}$Kr contributes to the modulation of our ESEEM signals.

The dipolar magnetic coupling between unpaired electron spins causes attenuation of the echo amplitude with increasing $\tau$ through a process called “instantaneous diffusion”, which results from changes in the magnetic fields due to the action of the second microwave pulse on the electron spins[6]. The ESEEM spectra is a product of the nuclear modulation signal and unwanted attenuation due to instantaneous diffusion. This complicates the analysis of the nuclear modulation in samples with high concentrations of electron spins, where the instantaneous diffusion effect is most pronounced.

In sample one, which contained a 1:5 ratio of H$_2$:Kr, the concentration of hydrogen atoms was so large that the attenuation of the electron spin echoes by instantaneous diffusion prevented the measurement of a signal that was suitable for the analysis of the $^{83}$Kr nuclear modulation. However, a small concentration of deuterium atoms was present in the sample due to the use of isotopically impure H$_2$ gas in the sample condensation. The ESEEM spectrum of the D atoms in sample one is shown as curve (e) in figure one. Curve (h) shows the spectrum after attenuation due to instantaneous diffusion has been partially removed by assuming an exponential attenuation function. In sample two, which contained a 1:50 ratio of H$_2$:Kr, it was possible to reduce the effects of instantaneous diffusion by shortening the duration of the second microwave pulse. The ESEEM spectrum of the H atoms in sample two is shown as curve (a) in figure one. Curve (d) shows the spectrum after attenuation due to instantaneous diffusion has been partially removed by assuming an exponential attenuation function. In both samples the concentrations of the H and D atoms remained constant over a measurement period of 8 hours.

Hydrogen and deuterium atoms are strongly repelled by superfluid helium and thus reside in the solid component of impurity-helium condensates[7]. Deuterium atoms react with neighboring hydrogen molecules to form hydrogen deuteride in a timescale of 5 minutes[8]. The stability of the D atom population in sample one indicates that these atoms do not reside in molecular hydrogen. Similarly, the stability and high concentration of the H atoms observed in sample two implies that these atoms do not reside in molecular hydrogen, where diffusion and loss of the atoms
Figure 1. Two-Pulse ESEEM spectra and simulations from hydrogen (left) and deuterium (right) atoms in krypton containing IHCs. a, e) ESEEM spectra obtained from the high magnetic field microwave resonances of the hydrogen (left) and deuterium (right) atoms. The first and second microwave pulses were separated by a time interval $\tau$. For the hydrogen spectra, the pulses were each of 16 ns duration. For the deuterium spectra, the durations of the first and second microwave pulses were 48 ns and 96 ns, respectively. b, f) Simulated nuclear modulation spectra of hydrogen (left) and deuterium (right) atoms substitutionally positioned within an fcc krypton lattice. c, g) Simulated nuclear modulation spectra of hydrogen (left) and deuterium (right) atoms positioned above an fcc (111) krypton surface. d, h) The nuclear modulation component remaining after the attenuation due to instantaneous diffusion was removed from experimental spectra (a, e).

to recombination would occur[4]. Bulk solid krypton has an FCC crystal structure in which photochemically introduced hydrogen atoms are known to preferentially occupy substitutional sites [9]. The energetic minimum of the van der Waals potential between a Kr atom and an H atom is at an interatomic distance of 3.65 Å, close to the nearest neighbor distance of 4.04 Å in solid krypton[10].

The above considerations indicate that hydrogen and deuterium atoms occupy sites that can be broadly categorized as either positioned within the interior of the krypton nanoclusters or adhered to the surface of the krypton nanoclusters. We simulated the ESEEM signals from hydrogen and deuterium atoms within two simple models that are broadly representative of these sites. In modeling the site within the interior of the clusters, the atom was substitutionally positioned in an unstrained krypton lattice. In modeling the site at the cluster surfaces, the atoms were positioned above a 111 Kr crystal surface at the position of the minimum in the hydrogen-krypton van der Waals potential. (An analogous model using a 100 surface produced very similar results.) Most of the ESEEM signal results from interactions between the atoms of
hydrogen or deuterium with their krypton nearest neighbors, which number 12 in the interior model and 3 in the surface model. However, contributions to the signal from the first ten coordination spheres were included in the models. Averages over isotopic composition and relative orientations of the applied magnetic field and the crystal lattice were made using standard methods[5, 11]. Figure one shows simulated ESEEM spectra for the interior model (curves b, f) and surface model (curves c, g).

The ESEEM spectra measured from both hydrogen and deuterium atoms show weak but unmistakable $^{83}$Kr nuclear modulation signals. The modulation depth is far less than is calculated for atoms substituted in the interior of the Kr nanoclusters, and somewhat less than is calculated for atoms adhered to the cluster surfaces. Unlike the calculated signals, the measured modulation signal is strongly damped and it is impossible to discern troughs in the modulation after three periods of the $^{83}$Kr Larmor precession. This damping is due to coupling of the electric quadrupole moment of the $^{83}$Kr nuclei to electric field gradients within the krypton nanoclusters[12]. These couplings dephase the precession of the krypton nuclei and damp the nuclear modulation signal[5]. We do not include a first principles model of the quadrupolar coupling in our ESEEM simulations because it involves the introduction of several unknown parameters. Besides the quadrupolar damping, inconsistencies between the measured ESEEM modulation signal and the surface site model arise from errors in estimating the attenuation of the ESEEM signal due to instantaneous diffusion.

3. Conclusion
The persistence of observable nuclear modulation through three Larmor precession periods suggests that the depth of the first nuclear modulation trough is not dramatically affected by the quadrupole coupling. This allows us to conclude that most of the hydrogen and deuterium atoms in our samples are not located in the interior of the krypton nanoclusters. Therefore, we conclude that the light hydrogen and deuterium atoms are adhered to the surfaces of the nanoclusters of heavier krypton atoms. The likelihood of this arrangement has been previously described by Gordon[13]. This result is consistent with the conclusions of our CW ESR measurements of the same samples, which are also presented in these proceedings[3], and is similar to the results of our previous work on D atoms in D$_2$-He samples, which showed that a majority of stabilized D atoms reside on the surfaces of D$_2$ clusters[11].

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