CW ESR Studies of Impurity-Helium Condensates Containing Krypton and Hydrogen Atoms

J Järvinen\textsuperscript{a}, E P Bernard\textsuperscript{a}, R E Boltnev\textsuperscript{b}, V V Khmelenko\textsuperscript{a,b,\ast}, and D M Lee\textsuperscript{a}

\textsuperscript{a} Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, NY 14853, USA
\textsuperscript{b} Branch of Institute of Energy Problems of Chemical Physics, Russian Academy of Sciences, Chernogolovka, Moscow Region, 142432, Russia
E-mail: \textsuperscript{\ast}khmel@ccmr.cornell.edu

Abstract. Impurity-Helium condensates (IHCs) containing krypton and hydrogen atoms have been studied in superfluid helium-4 via CW ESR techniques. The IHCs studied in this work are gel-like aggregates of nanoclusters composed of krypton and hydrogen atoms. We have found that such samples contain very high average concentrations of hydrogen atoms ($\sim 10^{18}$ cm$^{-3}$) as obtained by integration of the microwave absorption signal. Local concentrations ($\sim 10^{19}$ cm$^{-3}$) of H atoms were calculated from the ESR line width. Detailed studies of the ESR line shapes lead to the conclusion that a large fraction of the H atoms lies on the krypton cluster surfaces.

1. Introduction
We have performed CW electron-spin resonance (ESR) experiments on krypton-hydrogen impurity-helium condensates (also known as impurity-helium solids). An impurity-helium condensate (IHC) is a gel-like substance formed when a mixed beam of an impurity gas and helium gas penetrates through a superfluid helium surface. The impurities (in our case Kr and atomic and molecular hydrogen) form nanoclusters (linear dimension 5 nm) each surrounded by a thin layer of solid helium\cite{1, 2, 3}. These clusters aggregate to form a gel-like substance (similar to light aerogels in structure) with superfluid helium in the interstices between the impurity strands. A detailed discussion of the structure of these gels is given by Kiselev \textit{et al}\cite{4}. The atomic hydrogen free radicals are formed when the incident beam is passed through a radiofrequency discharge en-route to the sample cell, where the IHC is formed. ESR studies of H atoms in bulk samples of solid krypton have previously been reported. In earlier work, the atomic H free radicals were prepared via photolysis of HI, HCl, and HBr\cite{5, 6} or by condensation of H atoms on a cold finger\cite{5, 7}. The confined geometries associated with the clusters in our IHC sample led to rather different behavior than that observed in previous work. We observed new sets of ESR lines which were assigned to the H atoms on the surfaces of Kr clusters.

2. Apparatus & Procedure
Details of sample preparation have been discussed elsewhere\cite{8}. After formation of the H-Kr IHC, the beaker containing the sample was lowered into a TE\textsubscript{011} X band resonant cavity. A conventional Varian CW ESR spectrometer was employed to obtain derivative spectra of the free radical H atoms. The steady magnetic field $H_0$ was measured accurately via an NMR
Figure 1. a) ESR spectra of low and high field lines of H atoms stabilized in as-prepared H-Kr-He sample (thick lines). Each of experimental lines was fitted by three Lorentzians (1-3 thin curves). Sums of fitting curves are shown by dashed lines. b) ESR spectra of low and high field lines of H atoms that survived in the sample after annealing to \( T = 14.5 \) K (thick lines). Each of the experimental lines was fitted by the sum of a broad Lorentzian (4) and a sharp Gaussian (5) (thin curves). Sums of fitting curves are shown by dashed lines. Amplification during registration of annealed sample was increased by 40 times.

magnetometer (Sentec type 1001), and the microwave frequency was monitored by a precision frequency counter (EIP 545). These measurements allowed us to determine the g-factor and the hyperfine constant, \( A \), for H atoms in the H-Kr-He sample from the Breit-Rabi equation[9].

The average concentrations of H atoms in H-Kr-He samples were calculated by comparing the intensity of hydrogen atomic signals (obtained by double integration of derivative spectra) with the intensity of the signal from a ruby crystal with a known number of spins. The ruby crystal was glued at the bottom of the ESR cavity. Under the assumption that dipole-dipole interactions are the principle line broadening mechanism, the local concentration of H atoms was determined from the line width of the ESR signals.

An external gas handling system outside the cryostat was employed to carefully meter the Kr, \( \text{H}_2 \) and He gases introduced into the sample cell during sample preparation.

3. Results
The ESR spectrum of atomic hydrogen consists of two lines, the high field line (HFL) and the low field line (LFL) separated by approximately 508 gauss for an applied microwave frequency of 9.07 GHz. Figure 1a shows derivative spectra for the LFL on the left and the HFL on the right for a H-Kr IHC sample at 1.36 K immediately following preparation (an as-prepared
sample). The initial gas mixture was composed of \( \text{H}_2 \), Kr and He gas in the ratio \([\text{H}_2]:[\text{Kr}]:[\text{He}]=1:1:200\). Figure 1b shows plots of the ESR derivative spectra after the sample was annealed to a temperature of 14.5 K and then cooled down to 1.36 K. Because a large fraction of the H atoms in the sample was lost during the annealing process, the amplification required for registration of the annealed sample data presented in figure 1b was 40 times larger than for the as-prepared sample shown in figure 1a.

The low and high field spectra shown in figure 1a for the as-prepared sample were each fitted with a sum of Lorentzians. Although the figure shows only two rather well resolved peaks for the low field line, three Lorentzians were required to fit the data adequately, as indicated by the arrows in the figure 1a. The centers of the Lorentzians were significantly displaced from one another only for the case of the LFL. Table 1 shows the g-factors and the hyperfine constants as calculated for each pair of fitting curves for hydrogen spectra (connected by arrows in figure 1) by using the Breit-Rabi equation[9]. Corresponding values obtained from previous work on H in \( \text{H}_2 \) and Kr matrices are also listed in Table 1 for comparison.

### Table 1. Hyperfine structure constants, \( A \), and g-factors for H atoms in \( \text{H}_2 \), Kr matrices and in H-Kr-He condensates.

| Matrix                        | \( A \), MHz | \( \Delta A/A \),% | g-factor |
|-------------------------------|--------------|------------------|---------|
| Free state[10, 11]            | 1420.40573(5)| 2.002256(24)     |         |
| \( \text{H}_2 \)[12]         | 1417.13(45)  | -0.23            | 2.00243(8) |
| Kr (substitutional sites)[5]  | 1411.799(30) | -0.61            | 2.00179(8) |
| Kr (substitutional sites)[6]  | 1409         | -0.803           | 2.0013   |
| Kr (substitutional sites)[7]  | 1408.97(21)  | -0.805           | 2.00164(12) |
| H-Kr-He, curve 1              | 1416.28(11)  | -0.29            | 2.00231(3) |
| H-Kr-He, curve 2              | 1416.59(24)  | -0.27            | 2.00220(5) |
| H-Kr-He, curve 3              | 1409.76(5)   | -0.755           | 2.00175(2) |
| H-Kr-He, curve 4              | 1409.60(5)   | -0.77            | 2.00160(2) |
| H-Kr-He, curve 5              | 1407.88(11)  | -0.882           | 2.00178(3) |

Lines 1 and 2 (see figure 1a) have been observed for the first time in this work. The resolved line 3 corresponds to H atoms in bulk Kr lattices[5, 7].

Annealing drastically changed the shape and intensity of the ESR signals. The signals after annealing were fitted with one Gaussian and one Lorentzian curve. The centers of the Gaussian and the Lorentzian were almost identical for the LFL fit but they were very slightly displaced for the HFL fit. The Lorentzian curve was much broader than the rather narrow Gaussian curve as shown in figure 1b. The reduction in intensity of these lines relative to the lines in figure 1a indicated that the average concentration of H atoms was decreased from \( 1.2 \times 10^{18} \) cm\(^{-3} \) to \( 6.4 \times 10^{16} \) cm\(^{-3} \). It is especially noteworthy that the center of the smallest Lorentzian signal corresponding to the LFL (curve 3) in figure 1a almost exactly coincides with the center of the LFL signal in figure 1b. Thus the signal that remains after annealing can be identified with the smallest Lorentzian signal in figure 1a. Therefore, annealing destroys the H atoms corresponding to the larger Lorentzians in figure 1a. It is reasonable to conclude that the ESR signals corresponding to lines 1 and 2 are associated with H atoms residing on the surfaces of the Kr clusters. This result may be an indication that a very large fraction of the H atoms lies on the cluster surfaces. During the annealing process these atoms can diffuse rapidly, leading to recombination, so that only the H atoms more deeply embedded in the Kr clusters remain. This conclusion is supported by measured \( g \) and \( A \) values presented in Table 1.
The lowest two entries in Table I, corresponding to curves 4 and 5, shown in figure 1b give the values of g and A found for the annealed samples. These values of g and A are close to the values corresponding to curve 3 of figure 1a and for H atoms embedded in bulk Kr matrices[5, 7]. The intensity of line 3 in figure 1a was only 10 % of the total H signal in the as-prepared sample. After annealing, the signal corresponding to curves 1 and 2 disappeared and only at the position of line 3 (assigned to H atoms in Kr matrix) was a signal (curves 4 and 5) found. The sum of the double integrals calculated from curves 4 and 5 was only half the corresponding magnitude of line 3 (assigned to H atoms in Kr matrix) was a signal (curves 4 and 5) found. The sum of the double integrals calculated from curves 4 and 5 was only half the corresponding magnitude for curve 3, indicating some recombinational loss even within the interior of the nanoclusters.

We have also studied H-Kr-He samples formed by injection of gas mixtures with different ratios of H$_2$/Kr from 1/5 to 1/200. The shapes of the ESR spectra of all as-prepared samples were almost identical to the sample described above. The average concentrations obtained for different samples varied. The largest concentration of H atoms, of order $\sim 4 \cdot 10^{18}$ cm$^{-3}$, was attained in these experiments. From the line width of the ESR lines ($\Delta H = 0.8$ G) the local concentration of H atoms $\sim 2 \cdot 10^{19}$ cm$^{-3}$ was calculated.

In addition, we observed decay of H atoms in H-Kr-He samples during storage at $T = 1.36$ K. The results show linear dependence of the reciprocal concentration of H atoms on time, indicating a second order recombination process for the H atoms. To obtain the recombination rate constant $K_H(T)$, we used equation $K_H(T) = (2 \cdot n_0 \cdot \tau_{1/2})^{-1}$, where $n_0$ is the initial concentration of H atoms and $\tau_{1/2}$ is time needed for decreasing concentration to the value equal to half of the initial concentration. Starting with an initial concentration $n_0 = 1.2 \cdot 10^{18}$ we found a value of $\tau_{1/2} = 161$ min, leading to a rate constant $K_H(1.36)=4.3 \cdot 10^{-23}$ cm$^3$/sec, which is significantly slower than that of H atoms in H$_2$ clusters[13].

4. Conclusions

Very large concentrations ($4 \cdot 10^{18}$ cm$^{-3}$) of atomic hydrogen have been attained in H-Kr impurity-helium condensates at $T = 1.36$ K. It has been shown in this work that a vast majority ($\sim 90\%$) of these atoms reside on the surfaces of the krypton nanoclusters comprising the impurity-helium condensates. Only a small portion ($\sim 5\%$) of the initial population of H atoms survived annealing to 14.5 K. This portion corresponds to H atoms embedded in the interior of the krypton clusters.

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