Two-Pulse Electron Spin Echo Study of Deuterium-Helium Solids

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Abstract. We measured electron spin echoes from deuterium atoms within deuterium-helium solids with an X-band pulse ESR spectrometer. Our two-pulse electron spin echo envelope modulation (ESEEM) measurements are well described by a model that places 50% – 60% of the deuterium atoms at the interface between the molecular deuterium nanoclusters and the superfluid liquid helium. The remainder of the atoms lie in substitutional sites within the nanoclusters. We also report the spin-lattice relaxation times T_1 for these atoms.

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INTRODUCTION

Deuterium-helium (D_2-He) solids form when a mixture of D_2 and He gases is injected into superfluid helium at 1.5 K. If the mixture is subject to an RF discharge immediately prior to injection, deuterium atoms are produced that become embedded in the resulting solid. Studies of D_2-He solids by x-ray scattering show that these solids are composed of nanoclusters of molecular deuterium that are loosely aggregated into a gel within the superfluid helium.[1] A typical cluster is 90 Å in diameter and contains a blend of FCC and random close packed structures, with several stacking faults. In samples made with an RF discharge, deuterium atoms are present at average concentrations of ~ 10^{18} cm^{-3}. Measurements by CW ESR show that these atoms reside within the molecular clusters, so that local radical concentrations exceed average concentrations by at least a factor of ten[1]. Our recently constructed X-band pulse ESR spectrometer allows for electron spin echo envelope modulation (ESEEM) to provide a sensitive probe of the nuclear environment immediately surrounding the D atoms[2].

EXPERIMENT

We formed two D_2-He samples with stabilized atoms from gas mixtures with the ratio D_2:He = 1:20 according to the method described in our previous work.[1] We used a 90°-τ-180°-τ-echo primary echo sequence, with a 90° pulse time of 40 ns. For T_1 measurements, τ was held fixed at 800 or 1312 ns while the recovery time t between subsequent pulse pairs was varied from 500 μs to 50 s. For ESEEM measurements, τ was varied from 460 ns to 12 μs, with t held constant at 400 ms. All three deuterium hyperfine lines were separately excited at a frequency of 8930 MHz and magnetic fields of 3105.5, 3182.5 and 3261.1 Gauss.

RESULTS

Our recovery time data are modeled by the Bloch-type recovery function $V(t) \propto 1-\exp(-t/T_1)$, where V is the echo amplitude and T_1 is the spin-lattice relaxation time.[3] Fits to the data from the middle field hyperfine line give T_1 values of 64 ms and 87 ms for samples 1 and 2, respectively. The other hyperfine lines give similar times. The fit for sample 2 is inset in figure 1. Our sampled echo signals are processed by a blend of boxcar and phase corrected methods as described by our group and Astashkin *et al.*[2,4] The resulting ESEEM data is fit by the product of a sum of two decaying exponentials and a sum of two oscillatory modulation terms (see figure 1):

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$$E(\tau) = A\left(Qe^{-\tau/T_{2Q}} + (1-Q)e^{-\tau/T_{2L}}\right)\left(BE_B(\tau) + (1-B)E_S(\tau)\right)$$

where A, Q, T_{2Q} and T_{2L} parameterize the echo decay and B weights the modulation functions E_B and E_S. The function E_B simulates the ESEEM signal of D atoms *within* the solid clusters by assuming they are substituted in an FCC lattice of D_2 molecules. The function E_S is produced by the same model, but with the population of each coordination shell reduced by one-half. This simulates D atoms at the *surfaces* of the clusters in contact with the helium. We incorporate work by Kumada *et al.*[5] showing that D atoms reside in substitutional sites within solid D_2, that they have a 70 kHz isotropic coupling to their nearest molecular neighbors, and that the D atoms do not distort their immediate environment from the x-ray determined nearest neighbor spacing of 3.60 Å.[6] We calculate E_B and E_S using the "spherical approximation" of Mims *et al.*[7], which simplifies powder averaging over all crystalline orientations by ignoring the angular structure of the molecular lattices surrounding the radicals. At the 3.60 Å nearest neighbor distance this causes minimal distortion of the ESEEM signals.[8] Least-squares fitting finds the parameters A, Q, T_{2Q}, T_{2L} and B. Table 1 shows the four relevant parameters.

TABLE 1. Optimum fitting parameters of the two-population model for the three deuterium ESR lines.

Sample, hyperfine line	Q	T_{2Q}/μs	T_{2L}/μs	B
1, low field	0.648	1.12	5.26	0.394
1, middle field	0.672	1.13	5.51	0.403
1, high field	0.647	1.11	5.24	0.377
2, low field	0.793	0.689	2.96	0.477
2, middle field	0.792	0.732	3.04	0.457
2, high field	0.774	0.649	2.85	0.504

DISCUSSION

The failure of single population models—those that place all of the D atoms either in the interior or at the surface of the clusters—to fit the data necessitates the complexity of the two-population model described above. The presence of faults and randomly stacked structures in the clusters implies a great variety of environments around the deuterium atoms within the clusters. However, the angular insensitivity of this ESEEM method suggests that all these environments produce modulation signals very similar to E_B. Similarly, we assume that the great variety of environments surrounding the D atoms on the cluster surfaces produce ESEEM signals that, when averaged, resemble E_S. The parameter B then estimates the fraction of atoms located *within* the clusters to be 40% - 50%. The form of the echo decay term was found empirically and the fitting parameters T_{2Q} and T_{2L} should not be associated with either the bulk or surface atom populations. The much less concentrated samples of Kumada *et al.*[5] showed much longer decay times, which suggests that our signal decay is dominated by interactions among the D atoms.

Pulse ESR methods offer the first indication that a large fraction of the atomic radicals within impurity-helium solids reside on the cluster-helium interface, as suggested by Gordon.[9]

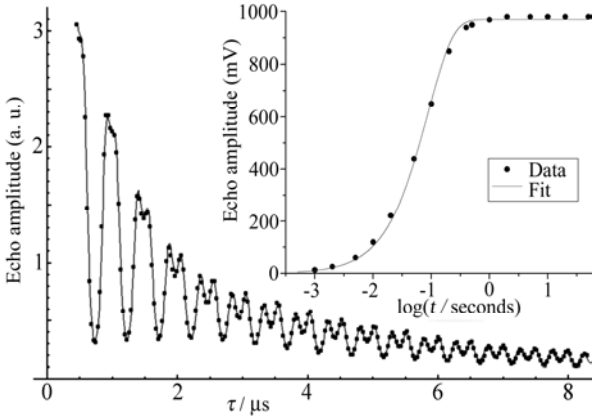

FIGURE 1. Two-pulse ESEEM data from the low field hyperfine line of sample 1. Dots show every fourth data point. The line shows the best fit of the two population model $E(\tau)$; see also table 1. Inset: Fit of $V(t)$ to recovery time data from the middle hyperfine line of sample 2.

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REFERENCES

1. E. P. Bernard, R. E. Boltnev, V. V. Khmelenko, V. Kiryukhin, S. I. Kiselev and D. M. Lee, *Phys. Rev. B* **69**, 104201 (2004).
2. E. P. Bernard, V. V. Khmelenko, E. Vehmanen, P. P. Borbat, J. H. Freed and D. M. Lee, these proceedings.
3. A. Schweiger and G. Jeschke, *Principles of Pulse Electron Paramagnetic Resonance*, Oxford: New York, 2002, p. 225.
4. A. V. Astashkin, V. V. Kozlyuk and A. M. Raitsimring, *J. Mag. Res.* **145**, 357-363 (2000).
5. T. Kumada, T. Noda, J. Kumagai, Y. Aratono and T. Miyazaki, *J. Chem. Phys.* **111**, 10974-10978 (1999).
6. A. F. Schuch and R. L. Mills, *Phys. Rev. Lett.* **16**, 616-618 (1966).
7. W. B. Mims, J. Peisach and J.L. Davis, *J. Chem. Phys.* **66**, 5536-5550 (1977).
8. M. Iwasaki, K. Toriyama and K. Nunome, *J. Chem. Phys.* **86**, 5971-5982 (1987).
9. E. B. Gordon, *Low Temp. Phys.* **30**, 756-762 (2004).