NUCLEAR MAGNETIC RESONANCE SHIFT OF Xe^{129} IN SOLID XENON*

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(Received 14 July 1964)

Nuclear magnetic resonance studies have revealed that the local magnetic field at a Xe nucleus changes as the density of the xenon sample is varied in a constant external magnetic field H_0. We define a shift ΔH as the difference between the local field in our sample and the local field in a dilute gas sample (isolated atoms) when both samples are located in the same H_0. In this manner ΔH describes only the change in the local field resulting from interactions with other atoms. This type of shift was first discovered and studied in the gas and liquid phases of xenon[1-4] where it was found to be directly proportional to both the density ρ and H_0. Recently Yen and Norberg[5] have studied the local magnetic field for the solid phase of xenon at one value of H_0 and found it to vary linearly with density.

We have now measured the dependence of ΔH on both H_0 and ρ for the solid. We find that ΔH is directly proportional to H_0. Although we have confirmed that ΔH varies linearly with ρ we observe a rate of change of ΔH with ρ which is approximately four times smaller than that reported by Yen and Norberg. In addition, we have determined the change in ΔH at the triple point transition between the liquid and solid phases.

In our measurements we have used the same samples previously used in this laboratory.[1,2] In the present work the temperature of these samples was varied between 77°K and 150°K such that the solid was always in equilibrium with its own vapor pressure. The densities of the solid were determined from the solid-vapor coexistence curve.[6] To determine ΔH we measure the difference in the frequencies of the free-precession decay signals following 90° pulses[7] applied to our reference sample at room temperature and to our second sample contained in a cryostat. We measure this frequency difference by first adjusting H_0 such that it is precisely at the resonant value for the reference sample —i.e., we obtain a zero beat frequency between the decay signal of the reference sample and the stable radio-frequency signal of the continuously operating oscillator within the gated pulse apparatus. Then, after having moved the cryostat sample quickly and accurately to a position where the value of H_0 is identical to that used for the reference sample, we apply the 90° pulse to the cryostat sample and observe the new beat frequency between the new decay signal and the stable oscillator signal. Since the gyromagnetic ratio of the Xe^{129} nucleus is well-known, this provides a direct measurement of ΔH.

Because of the small signal-to-noise ratio and the long spin-lattice relaxation time of a dilute gas sample, we use a fast relaxing (slightly doped with oxygen) gas sample of density 310 amagats as our reference in the actual measurements. (For xenon one amagat unit of density is 4.49×10^{-5} mole/cm^3.) We denote the shift for a sample of density ρ relative to this reference sample by $\Delta H(\rho/310)$. The shift $\Delta H(310/0)$ of our reference sample relative to the dilute gas is well known [see Eq. (2) below], and therefore the absolute values of ΔH for the solid are easily determined.

Measurements of $\Delta H(\rho/310)$ were made for three values of the external field, 4.28 kG, 8.52 kG, and 12.10 kG. Our results are indicated in Fig. 1 where we have plotted the shift relative to a new arbitrary reference point (583 amagats) in order to limit the numerical range of the figure. The shifts $\Delta H(583/310)$ of this reference

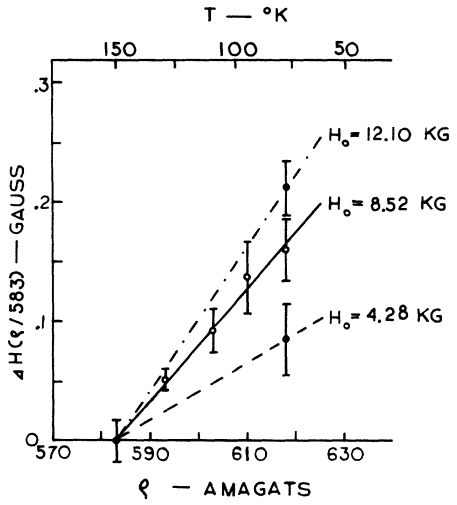

FIG. 1. The shift $\Delta H(\rho/583)$ of Xe^{129} for a solid xenon sample relative to a sample of density 583 amagats, as a function of density ρ (or temperature T) for three values of the external field H_0.

point relative to 310 amagats at the three different H_0 values are (0.677 ± 0.016) G, (1.267 ± 0.016) G, and (1.804 ± 0.018) G, respectively. The indicated errors are root-mean square deviations.

The measurements at $H_0 = 8.52$ kG indicate within the experimental errors that $\Delta H(\rho/583)$ is proportional to the density. If the external field is changed the shift per unit density also is found to be proportional to H_0. A least-squares fit gives

$$(\partial \Delta H/\partial \rho)_{\text{solid}} = +(5.3 \pm 0.3)10^{-7} H_0 \qquad (1)$$

for the density rate of change. This rate is slightly greater than the value

$$\partial \Delta H/\partial \rho = (4.22 \pm 0.05)10^{-7} H_0 \qquad (2)$$

reported for the gas and the liquid[2] or the value $(4.63 \pm 0.14)10^{-7} H_0$ obtained for the gas,[4,3] but it is nearly four times smaller than $20.4 \times 10^{-7} H_0$ which is the rate of change Yen and Norberg[5] obtained in the solid between 4.2°K and 160°K at $H_0 = 8920$ G.

If we plot the shifts $\Delta H(583/310)$ as a function of the external field we find them to be proportional to H_0. A least-squares fit yields

$$\Delta H(583/310) = (1.50 \pm 0.05)10^{-4} H_0. \qquad (3)$$

From this equation we can calculate the shift of the solid phase at the triple point 161°K (density 576 amagats[6]) with respect to 310 amagats by using Eq. (1):

$$\Delta H(576/310) = (1.46 \pm 0.05)10^{-4} H_0.$$

This result may be compared with the value we obtain by extrapolating the gas and liquid results [Eq. (2)] up to 576 amagats. We find that this value (relative to 310 amagats) is only $(1.12 \pm 0.03)10^{-4} H_0$. The difference between the experimental value for the solid and this extrapolated value for the gas-liquid line is $(0.34 \pm 0.06)10^{-4} H_0$. Thus, in addition to having a slope different from that of the gas-liquid line, the solid line is displaced relative to the extrapolated gas-liquid line at the triple-point density.

Finally we calculate the shift ΔH of a xenon atom in the solid phase at density ρ relative to the isolated atom by using Eqs. (1), (2), and (3):

$$\Delta H_{\text{solid}} = \Delta H_{\text{gas}}(310/0) + \Delta H(583/310) + (\partial \Delta H/\partial \rho)_{\text{solid}}(\rho - 583)$$

$$= (-2.9 \pm 2.0)10^{-5} H_0 + (5.3 \pm 0.3)10^{-7} \rho H_0. \qquad (4)$$

Although there is a displacement and a change in slope upon going to the solid, the line describing the data for the solid [Eq. (4)] nearly passes through the origin as does the line describing the data for the gas and liquid [Eq. (2)]. Whether or not this has physical significance remains an open question, particularly in light of our limited understanding of the density proportionality of the shift in the liquid and solid.

The discrepancies between our results and those of Yen and Norberg are not understood. The experimental methods differ at several points, particularly in the measurement of changes in the local magnetic field.[8] The samples also differ in impurity content. Our cryostat sample which was very slightly contaminated by oxygen for experimental convenience was replaced in one measurement by a very pure sample. However, no change in the shift could be observed. Some of Yen and Norberg's samples were contaminated with air, but they also have experimental data[8] to indicate that this impurity, including nitrogen,[9] does not affect the result.

The author wishes to thank Professor H. Y. Carr and Professor H. C. Torrey for placing the nuclear magnetic resonance apparatus at his disposal. He gratefully acknowledges valuable discussions with Professor H. Y. Carr who proposed the problem. He also wishes to thank Professor R. E. Norberg and Mr. W. W. Warren for some helpful comments and for communicating details about the shift measurements at Washington University.

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*This work was supported by the National Science Foundation.

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