

## Nuclear Magnetic Resonance of $\text{Xe}^{129}$ in Solid and Liquid Xenon\*†

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Self-diffusion coefficients, resonance shifts, and nuclear spin-spin relaxation times are reported for  $\text{Xe}^{129}$  in solid and liquid xenon. In the solid, the  $T_2$  data indicate  $D = (7.3_{-0.2}^{+0.4}) \exp[-(7400 \pm 50)/RT]$  cm<sup>2</sup>/sec. In the liquid, direct external gradient-diffusion measurements yield  $D = (2.3_{-0.7}^{+0.8}) \times 10^{-3} \exp[-(1400 \pm 150)/RT]$  cm<sup>2</sup>/sec. Density-dependent resonance shifts are found to occur in both the liquid and the solid.

### I. INTRODUCTION

WITH the exception of  $\text{He}^3$ , the condensed phases of the rare gases have not been thoroughly investigated by means of nuclear magnetic resonance. Low abundances of magnetic species, weak-magnetic moments and long-relaxation times combine to make the resonance experiments difficult. Nevertheless, the simplicity of the rare-gas solids and liquids makes such measurements of particular interest. A theoretical prediction of the coefficient of self-diffusion in a rare gas solid recently has appeared<sup>1</sup> and nuclear magnetic resonance (NMR) experiments can provide a direct test of the predictions.

In the present work,  $\text{Xe}^{129}$  has been the subject of line shape, shift, and diffusion studies via pulsed resonance techniques. The data have been obtained in liquid and solid samples over the temperature range from 4°K to 227°K and at pressures between saturated vapor pressures (SVP) and 20 atm. The samples were of natural abundance in which  $\text{Xe}^{129}$  occurs with 26.24% abundance and the only other abundant magnetic isotope is  $\text{Xe}^{131}$  with an abundance of 21.24%. The spin of  $\text{Xe}^{129}$  is  $\frac{1}{2}$  and that of  $\text{Xe}^{131}$  is  $\frac{3}{2}$ .

Previous NMR work with  $\text{Xe}^{129}$  has dealt mainly with the gas,<sup>2-5</sup> although some liquid data have been reported.<sup>4</sup>

### II. APPARATUS AND MEASUREMENTS

The pulsed nuclear magnetic resonance measurements were made at a radio frequency of 10.5 Mc/sec and in a

field of 8920 Oe. A Carr-Purcell-Meiboom<sup>6</sup> 90°-180° pulse train was used for the spin-echo sequences. The pulses gated a Blume buffer amplifier<sup>7</sup> between a crystal oscillator and a three-stage class C power amplifier. It was found that a Hughes 104A Memoscope was particularly convenient for preliminary examination of the data because of the long  $T_1$  values encountered. Detailed analyses were made from photographs of oscilloscope traces.

In some of the data runs temperatures between 90°K and 230°K were maintained by blowing cold nitrogen gas past the sample. The gas was passed through a heat exchanger cooled by liquid nitrogen and then mixed with a controlled amount of warm gas and directed past the sample. Gas temperatures in the vicinity of the sample were monitored by a Cu-Constantan thermocouple. Gas-stream temperatures were calibrated against sample temperatures by means of a dummy sample containing thermocouples. A sample one-inch long typically showed a 1° temperature differential over its length at 90°K. Other experimental runs between 160°K and 4°K were made with the sample chamber mounted within a helium gas heat exchanger can which was immersed in liquid helium. The sample temperature was controlled by means of the exchange gas pressure and also via resistive heaters mounted near the sample.

Xenon gas (natural abundance) was obtained from Linde Gas Company and was reported to be 99% pure. The solid samples used had volumes of about 5 cm<sup>3</sup>. Most of the data were taken with a nylon cylindrical sample cell 1 in. long and  $\frac{1}{2}$  in. i.d. The sample cell was connected to the gas storage system with a nylon to brass threaded thermal compression seal. In general, the samples used were intentionally contaminated with small amounts of atmospheric oxygen in order to reduce the spin-lattice relaxation times. Pressures were applied to the samples through a medium of helium gas. The helium was delivered from a storage cylinder via a Hoke-Phoenix 512B high-pressure regulator with range 0-3000 psi. Pressures were controlled manually and could be held to within  $\pm 5$  psi as monitored by a No. 1400 U. S. Test Gauge.

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<sup>1</sup> R. Fieschi, G. F. Nardelli, and A. Repanai Chiarotti, *Phys. Rev.* **123**, 141 (1961).

<sup>2</sup> W. G. Proctor and F. C. Yu, *Phys. Rev.* **81**, 20 (1951). E. Brun, J. Oeser, H. H. Staub, and C. G. Telschow, *ibid.* **93**, 904 (1954).

<sup>3</sup> R. L. Streever and H. Y. Carr, *Phys. Rev.* **121**, 20 (1961).

<sup>4</sup> E. R. Hunt and H. Y. Carr, *Bull. Am. Phys. Soc.* **7**, 293 (1962).

<sup>5</sup> D. Brinkmann, E. Brun and H. H. Staub, *Helv. Phys. Acta.* **35**, 431 (1962).

<sup>6</sup> H. Y. Carr and E. M. Purcell, *Phys. Rev.* **94**, 630 (1954); S. Meiboom and D. Gill, *Rev. Sci. Instr.* **29**, 688 (1958).

<sup>7</sup> R. J. Blume, *Rev. Sci. Instr.* **32**, 554 (1961).

For direct measurements of the coefficient of self diffusion, a pair of coils nearly in a Helmholtz configuration was used to provide a reasonably uniform field gradient over the sample. The sixty-turn coils were wound with a  $5\frac{1}{4}$  in. i.d. and were separated by  $2\frac{1}{2}$  in. The field gradient-current characteristics were determined via the shape<sup>8</sup> observed for a proton spin echo from a sample of benzene contained within the sample cell. Analysis of the Bessel function echo shape yielded the relation  $G = (1.95 \pm 0.04)I$  G/cm, where  $I$  is in amperes. A theoretical value of  $G$  was calculated using the method of magnetic images and yielded the approximate result  $G = 2.1I$  G/cm. A final check on the gradient coil system was provided by a determination of the coefficient of self-diffusion in water. The measurement was made at room temperature for water contained in the nylon sample cell and with the same gradients as were used in the xenon run (1.97 G/cm). The result was  $D = 2.43 \times 10^{-5}$  cm<sup>2</sup>/sec, which agrees with the literature values.<sup>9,10</sup>

### III. RESULTS AND INTERPRETATION

#### A. Rigid Lattice

Xenon crystalizes in an fcc lattice with cube edge 6.13 Å (4°K).<sup>11,12</sup> The rigid-lattice dipolar linewidth for Xe<sup>129</sup> can be computed via the Van Vleck second moment expression<sup>13</sup> for a crystalline powder.

$$\begin{aligned} \sigma_A^2 &= \sigma_{AA}^2 + \sigma_{AB}^2 \\ &= \frac{3}{5} \gamma_A^4 \hbar^2 I_A (I_A + 1) \sum_k r_{jk}^{-6} \\ &\quad + (4/15) \gamma_A^2 \gamma_B^2 \hbar^2 I_B (I_B + 1) \sum_{k'} r_{jk'}^{-6}. \end{aligned} \quad (1)$$

Here<sup>2</sup>

$$\gamma_A = \gamma_{129} = 7.401 \times 10^3 \quad (\text{G sec})^{-1}$$

$$\gamma_B = \gamma_{131} = 2.19 \times 10^3 \quad (\text{G sec})^{-1}$$

$$I_A = I_{129} = \frac{1}{2}, \quad I_B = I_{131} = \frac{3}{2}.$$

The  $r^{-6}$  lattice sums, taken over the appropriate sites in the fcc lattice, are given by  $7.225fn^2$ , where  $n$  is the atom density and  $f$  is the isotopic abundance. The normal abundances are (129) 26.24% and (131) 21.24%.

At 103°K the calculation yields

$$\sigma_{AA}^2 = 0.765 \times 10^6 \text{ sec}^{-2}, \quad \sigma_{AB}^2 = 0.120 \times 10^6 \text{ sec}^{-2}$$

and thus  $\sigma_{129}^2 = 0.885 \times 10^6 \text{ sec}^{-2}$ .

Since the observed rigid lattice line shape is nearly Gaussian, we define a rigid-lattice spin-phase memory time as  $T_2 = 1/\sigma$ . Thus, the dipolar  $T_2$  corresponding to the calculated  $\sigma_{129}^2$  at 103°K is 1.06 msec. The nearly horizontal solid line in Fig. 1 corresponds to this theoretical rigid lattice  $T_2$ , including the small correction

associated with the thermal coefficient of volume expansion.<sup>12,14</sup> The predicted dipolar  $T_2$  decreases to 1.00 msec at 4.2°K.

The free induction decays observed below 117°K were found to be closely Gaussian in shape. Figure 2 shows a decay signal obtained at 4.2°K plotted against  $t^2$ . These data, analyzed as  $F(t) \propto \exp(-t^2/2T_2^2)$ , yield  $T_2 = 0.83$  msec. Correction for the field inhomogeneity measured over the sample region brings this result into satisfactory agreement with the theoretical dipolar  $T_2$  of 1 msec.

Sher and Primakoff<sup>15,16</sup> have predicted that Lowe beats<sup>17</sup> should occur for an isotopically pure single crystal sample when the temperature is reduced to below the Debye temperature. In a xenon sample of natural abundance, the random location of the magnetic Xe<sup>131</sup> species would be expected to wash out the Xe<sup>129</sup> beat structure.

A few measurements of the spin-lattice relaxation time  $T_1$  were made in the solid. A sample in which great care had been taken to avoid contamination provided only the limiting value  $T_1 > 7 \times 10^3$  sec at 125°K. Prohibitively long waiting times were required in order to work with such samples so various paramagnetic impurities usually were introduced to reduce  $T_1$ . Activated charcoal suspended in glass wool was used in some runs and produced  $T_1$  values of the order of 900 sec at 125°K. Most of the data were taken with samples contaminated with air, for which  $T_1$  was typically about 600 sec. The  $T_1$  reductions did not produce any observable effect on  $T_2$  (which was never more than three seconds in the solid).

#### B. Diffusion

##### 1. Solid

Above 117°K the Xe<sup>129</sup> resonance line exhibits motional narrowing (Fig. 1) which extends over three decades of  $T_2$  before the melting point is reached. The  $T_2$  values recorded in this temperature range were measured from the envelopes of Carr-Purcell echo trains.<sup>5</sup> These envelopes were observed to be good exponentials above 125°K.  $T_2$  data were taken on runs at SVP, 10 atm and 20 atm. No variation of  $T_2$  with pressure was observed in this range. (None would have been expected, within experimental error, from the reported compressibilities.<sup>14</sup> The purpose of the pressure application was to extend the temperature range of the liquid phase.)

The diffusion-narrowing analysis of the  $T_2$  data, to be discussed below, indicates that the correlation time characteristic of the internal motions in the solid at the melting point is about  $0.5 \times 10^{-6}$  sec. Thus, the 10 Mc Larmor frequency implies that the product  $\omega_0 \tau_c$  is about

<sup>8</sup> R. L. Garwin and H. A. Reich, Phys. Rev. **115**, 1478 (1959); J. R. Gaines, thesis, Washington University, 1961 (unpublished).

<sup>9</sup> J. H. Simpson and H. Y. Carr, Phys. Rev. **111**, 1201 (1958).

<sup>10</sup> J. H. Wang, J. Am. Chem. Soc. **73**, 510 (1951).

<sup>11</sup> A. J. Eatwell and B. L. Smith, Phil. Mag. **6**, 461 (1961).

<sup>12</sup> R. D. Sears and H. P. Klug, J. Chem. Phys. **37**, 3002 (1962).

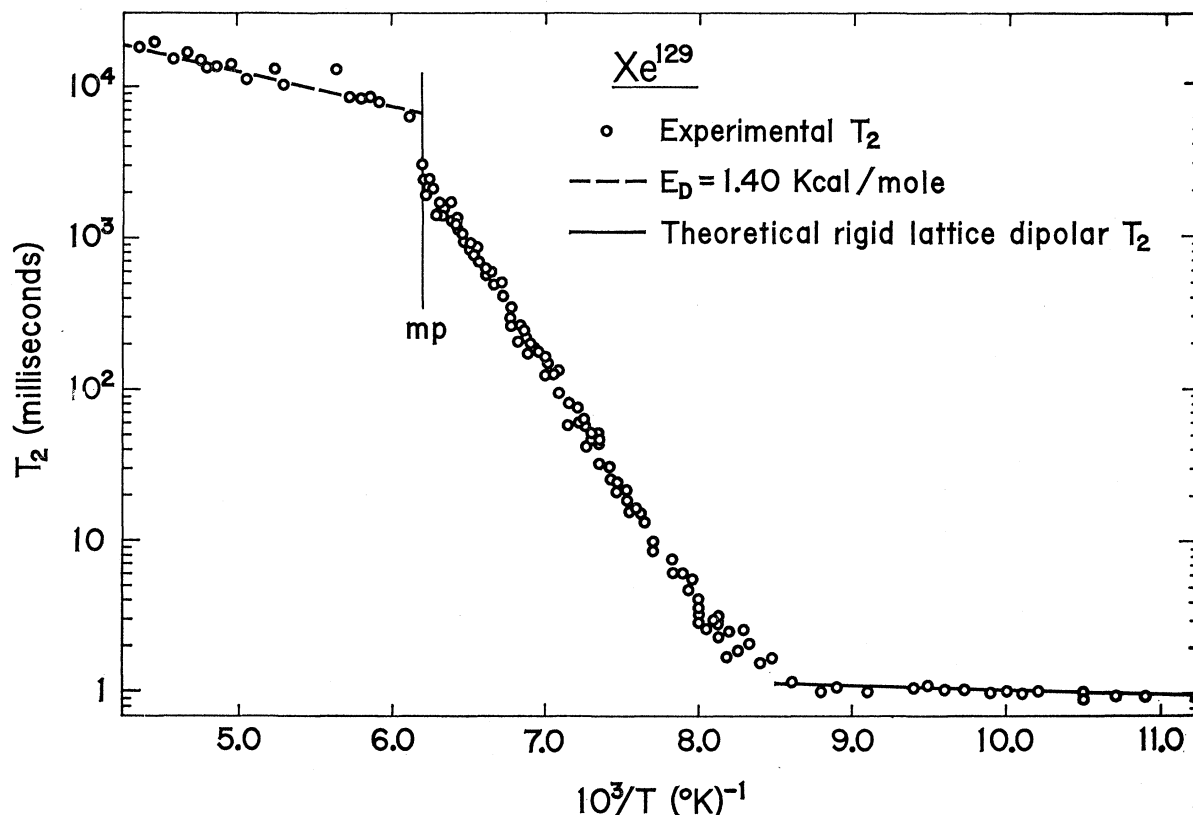
<sup>13</sup> J. H. Van Vleck, Phys. Rev. **74**, 1168 (1948).

<sup>14</sup> J. R. Packard and C. A. Swenson (to be published). We are grateful to Professor Swenson for communicating their results in advance of publication.

<sup>15</sup> A. Sher and H. Primakoff, Phys. Rev. **119**, 178 (1960).

<sup>16</sup> H. Primakoff and A. Sher (private communications).

<sup>17</sup> I. J. Lowe and R. E. Norberg, Phys. Rev. **107**, 46 (1957).

FIG. 1. Spin-spin relaxation times for Xe<sup>129</sup> in liquid and solid xenon.

30 at the melting point and, therefore, we may take  $\omega_0\tau_c \gg 1$  throughout the solid range. The fact that  $T_1$  is observed to remain much larger than  $T_2$  at all temperatures in the solid supports this interpretation. Thus, the motional narrowing in the solid is confined to the adiabatic region and we need consider only the secular contributions to the dipolar line width.

Kubo and Tomita<sup>18</sup> have discussed motional narrowing and, in the adiabatic limit, obtain the result

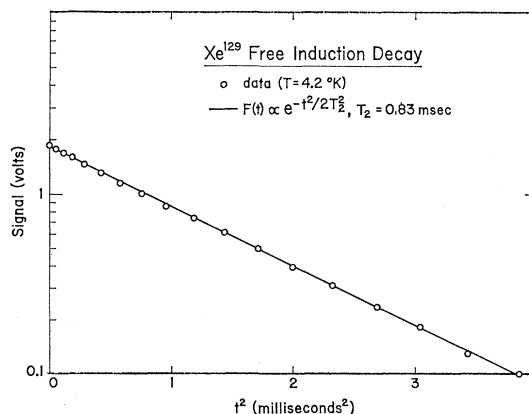
$$\left(\frac{1}{T_2}\right)^2 = \frac{4 \ln 2}{\pi} \sigma^2 \arctan \left\{ \frac{\pi \tau_c}{(4 \ln 2) T_2} \right\}. \quad (2)$$

Here the quantum theory of irreversible processes has been used to refine the semiclassical treatment of Bloembergen, Purcell and Pound.<sup>19</sup> A correlation function of the form  $\exp(-|t|/\tau_c)$  has been assumed and the dipolar rigid lattice lineshape has been taken to be gaussian.

The asymptotic behavior of Eq. (2) is reasonable. For the rigid lattice,  $\sigma\tau_c \gg 1$  and (2) becomes  $1/T_2 = (2 \ln 2)^{1/2} \sigma$  while for the well-narrowed line  $\sigma\tau_c \ll 1$  and  $1/T_2 = \sigma^2 \tau_c$ , the adiabatic Anderson-Weiss

width<sup>20</sup> of a Lorentzian line. Flynn and Seymour<sup>21</sup> have demonstrated the validity of Eq. (2) in the region of incipient narrowing and line shape change ( $\sigma\tau_c \geq 1.5$ ) by analysis of the results of experiments on Cu<sup>63</sup>.

The  $T_2$  data presented in Fig. 1 show an exponential

FIG. 2. Xe<sup>129</sup> free induction decay in solid xenon at 4.2°K.

<sup>18</sup> R. Kubo and K. Tomita, J. Phys. Soc. Japan 9, 888 (1954).

<sup>19</sup> N. Bloembergen, E. M. Purcell and R. V. Pound, Phys. Rev. 73, 679 (1948).

<sup>20</sup> P. W. Anderson and P. R. Weiss, Rev. Mod. Phys. 25, 269 (1953).

<sup>21</sup> C. P. Flynn and E. F. W. Seymour, Proc. Phys. Soc. (London) 77, 922 (1961).

TABLE I. Correlation times and self-diffusion coefficients for solid xenon.

Temp. (°K)	$10^3/T$ (°K) <sup>-1</sup>	$T_2$ (msec)	$\tau_c$ (μsec)	$a$ (Å)	$D$ (cm <sup>2</sup> /sec)
160	6.25	2150	0.508 <sup>a</sup>	6.35 <sup>b</sup>	$6.62 \times 10^{-10}$
154	6.50	855	1.28	6.33	$2.62 \times 10^{-10}$
148	6.75	335	3.26	6.33	$1.02 \times 10^{-10}$
143	7.00	135	8.09	6.32	$4.11 \times 10^{-11}$
138	7.25	52	21.0	6.31	$1.58 \times 10^{-11}$
133	7.50	21	52.0	6.30	$6.36 \times 10^{-12}$
129	7.75	8.2	133	6.30	$2.48 \times 10^{-12}$
125	8.00	4.3	254	6.29	$1.30 \times 10^{-12}$

<sup>a</sup> Calculated using Eq. (2).

<sup>b</sup> Calculated from the zero-pressure molar volume data of J. R. Packard and C. A. Swenson (reference 14).

variation over a factor of  $10^3$ . Thus, it appears that the internal diffusive motion at a given temperature in xenon may be characterized by a single correlation time  $\tau_c$ . In the region between  $10^3/T=8.0$  and  $6.1$ , the  $T_2$  data have been analyzed according to  $1/T_2 = \sigma^2 \tau_c$ . The resulting correlation times are given in Table I. For an fcc lattice, we may write  $\tau_c = a^2/12D$ , where  $a$  is the cube-edge lattice parameter. The corresponding values of  $D$  are also given in Table I. In the calculation, we have again used the molar volume data of Packard and Swenson.<sup>14</sup>

The tabulated  $D$  values, when plotted against  $1/T$ , show an exponential temperature dependence with an activation energy of  $7.40 \pm 0.05$  kcal/mole. A least-squares fit of the diffusion data between 130 and 160°K yields the following result for the coefficient of self-diffusion in solid xenon:

$$D = (7.3_{(-0.2)}^{(+0.4)}) \times \exp[-(7.40 \pm 0.05) \times 10^3/RT] \text{ cm}^2/\text{sec.}$$

## 2. Liquid

The self-diffusion coefficient of Xe<sup>129</sup> in liquid xenon was measured directly by means of spin echoes and a calibrated magnetic-field gradient (cf. Sec. II). Pressures

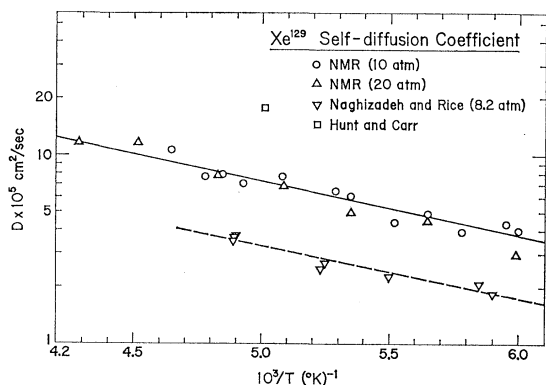


FIG. 3. Coefficient of self-diffusion in liquid xenon. The solid line is a least-squares fit of an exponential to the NMR data reported in this work.

up to 20 atm were used in order to extend the temperature range of the liquid state.

The experimental results are given in Fig. 3 as are the 8.2 atm Xe<sup>133</sup> radioactive tracer data of Naghizadeh and Rice<sup>22</sup> and a single Xe<sup>129</sup> magnetic resonance point reported by Hunt and Carr.<sup>4</sup>

*Note added in proof.* More recent data reported by these authors [E. R. Hunt and H. Y. Carr (to be published)] fall between the solid and dashed lines in Fig. 3. We are grateful to Professor Carr for communicating his results in advance of their publication.

The solid line is a least-squares fit of an exponential to our data. The line corresponds to the result  $D = (2.3_{(-0.6)}^{(+0.8)}) \times 10^{-8} \exp[-(1.40 \pm 0.15) \times 10^3/RT] \text{ cm}^2/\text{sec}$ . The dashed line corresponds to the tracer result reported by Naghizadeh and Rice,  $D = 0.70 \times 10^{-8} \exp(-1.21 \times 10^3/RT) \text{ cm}^2/\text{sec}$ .

The factor of 2 discrepancy between our  $D$  values and the tracer data is not understood. The absence of alternations in our successive echo amplitudes leads us to believe that no appreciable convection existed in our samples.

The  $T_2$  data reported in Fig. 1 display a sudden increase accompanying the melting transition. The increase presumably is associated with increased motional averaging of the dipolar broadening. In the liquid the  $T_2$  data show an exponential increase with temperature with an activation energy near 1.40 kcal/mole. The dashed line through the liquid data in Fig. 1 is drawn with that slope.

The diffusion data indicate that, in the liquid at the melting point,  $D = 3.9 \times 10^{-5} \text{ cm}^2/\text{sec}$ , which corresponds to a correlation time of the order of  $10^{-11} \text{ sec}$ . Thus,  $\omega_0 \tau_c \ll 1$  in the liquid and the conditions of extreme narrowing hold. However, the extreme-narrowed version of Eq. (2), including a correction for the "10/3 effect" predicts that, in the liquid at the melting point, the dipolar  $T_2$  is  $8 \times 10^5 \text{ sec}$ .

The values of  $T_2$  observed in the liquid presumably are limited by spin lattice relaxation arising from interaction with paramagnetic impurities. No reliable  $T_1$  measurements were made in the liquid samples; however, the  $T_1$  values were typically somewhat longer than  $T_2$ , but of the same order of magnitude. The fact that the dashed line drawn with activation energy 1.40 kcal/mole fits the liquid  $T_2$  data indicates that the observed  $T_2$  is proportional to  $D$ . If the correlation times for self-diffusion were much less than the Larmor periods  $1/\omega_s$  of the paramagnetic impurities, then one would expect<sup>23</sup> a  $T_1$ -limited line with  $T_2 \propto D$ . However, assuming  $g_s = 2$  and using our  $D$  values,  $\omega_s \tau_c$  at the melting point is about 2. Thus, the apparent coincidence

<sup>22</sup> J. Naghizadeh and S. A. Rice, *J. Chem. Phys.* **36**, 2710 (1962). We are indebted to Professor Rice for communicating their data in advance of publication.

<sup>23</sup> A. Abragam, *The Principles of Nuclear Magnetism* (Clarendon Press, Oxford, 1961), Chap. VIII.

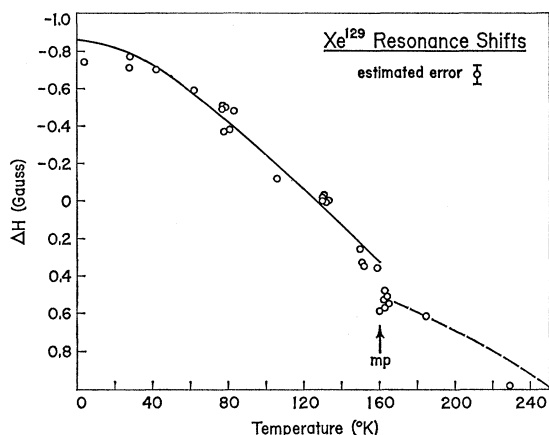


FIG. 4. Xe<sup>129</sup> resonance shifts at 8920 G as a function of temperature. The solid line is a least-squares fit of a linear density dependence (Fig. 5). The dashed line corresponds to the result of Carr, Streever, and Hunt (see references 3 and 4).

of the  $T_2$  temperature dependence with the diffusion activation energy may be fortuitous.

The observation of a line-narrowing accompanying the melting transition is to be contrasted with the apparent broadenings reported for alkali metals.<sup>24</sup> In this connection, it will be of interest to investigate the behavior of Xe<sup>131</sup>, which has a quadrupole moment.

### C. Resonance Shifts

Substantial shifts of the external magnetic-field corresponding to the Xe<sup>129</sup> resonance were found to occur as the temperature was varied in the liquid and solid samples. A shift of about 0.2 G. accompanied the melting transition. In all cases the static magnetic field required for resonance increased as the temperature was increased.

The shifts were measured as beat frequencies by beating the free-induction decay signals against a stable reference oscillator (which was monitored by a frequency counter). The results of shift measurements between 4.2°K and 229°K are given in Fig. 4. The 130°K point was adopted as an arbitrary experimental zero. The beat frequency determinations were rather crude and an estimated error of  $\pm 0.05$  G must be assigned to each point. No pressure dependence of the shifts was observed between SVP and 20 atm.

Carr, Streever and Hunt<sup>3,4</sup> and Brinkman, Brun and Staub<sup>5</sup> have reported the observation of Xe<sup>129</sup> resonance shifts in gaseous and liquid xenon. They find the shifts to be proportional to the sample density and to the external magnetic field. Hunt and Carr<sup>4</sup> give the result,

$$\Delta H = 4.3 \times 10^{-7} \rho H_0, \quad (3)$$

in which  $\rho$  is in amagats,  $H_0$  is in gauss and the shift

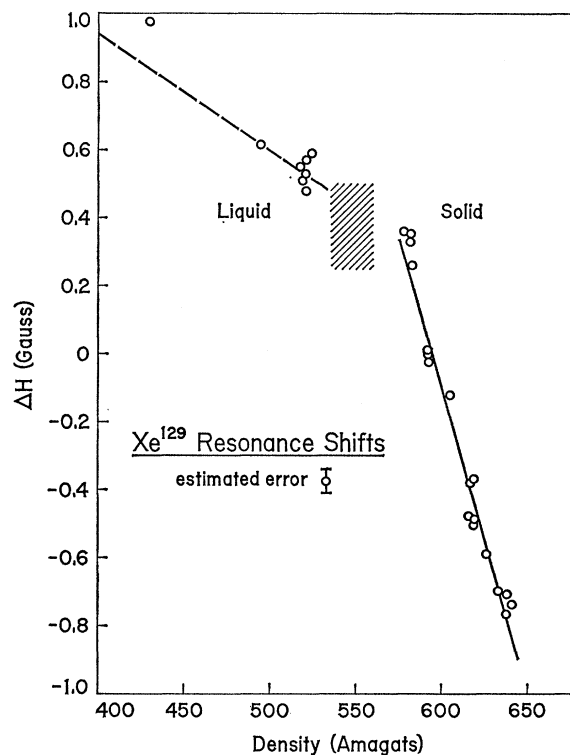


FIG. 5. Xe<sup>129</sup> resonance shifts as a function of density. Results of Carr, Streever, and Hunt (references 3 and 4) are represented by the dashed line, which has been normalized to the 495 amagat point. The solid line is a least-squares fit of a linear density dependence to the shift data in the solid.

relative to the isolated atom has been determined from extrapolation of the observed density dependence.

The shifts observed in the present work are plotted as a function of sample density in Fig. 5, using the molar volume data of Packard and Swenson<sup>14</sup> and values tabulated by Hollis Hallett.<sup>25</sup> The solid line represents a least-squares fit of a linear density dependence to the shift data in the solid. The same line is also drawn in Fig. 4 and corresponds (using our arbitrary reference zero) to the result  $\Delta H = 10.82 - 20.4 \times 10^{-7} \rho H_0$ . The dashed lines shown in Figs. 4 and 5 correspond to Eq. (3) normalized to our 495 amagat point in the liquid.

If the resonance shifts in solid xenon obey a relation of the form  $\Delta H = c \rho H_0$ , then our data indicate that  $c$  is some five times larger in the solid than the value reported<sup>3,4,5</sup> for the liquid and gas. Thus far however, we have data only at 8920 G. Measurements are being undertaken in this laboratory at 2550 G to investigate the field dependence of the shift in solid xenon.

### IV. DISCUSSION: SELF-DIFFUSION IN THE RARE GAS SOLIDS

Studies of atomic self-diffusion in simple metals have led to the development of semiempirical relations cor-

<sup>24</sup> D. F. Holcomb and R. E. Norberg, Phys. Rev. **98**, 1074 (1955).

<sup>25</sup> A. C. Hollis Hallett, in G. A. Cook, *Argon, Helium and the Rare Gases* (Interscience Publishers, Inc., New York, 1961), Vol. 1, Chap. IX.

TABLE II. Comparison of diffusion parameters.

	$L_M$ (cal/mole)	$T_M$ (°K)	$E_D(N)=16.5L_M$ (kcal/mole)	$E_D(VL)=32T_M$ (kcal/mole)	Experimental data		Corresponding states		$2L_0$ (kcal/mole)
					$D_0$ (cm <sup>2</sup> /sec)	$E_D$ (kcal/mole)	$D_0$ (cm <sup>2</sup> /sec)	$E_D$ (kcal/mole)	
Ne	80.1 <sup>a</sup>	24.5 <sup>b</sup>	1.32	0.78	...	...	5.0	1.2	0.9 <sup>d</sup>
Ar	280.8 <sup>a</sup>	84.0 <sup>b</sup>	4.63	2.69	350 <sup>c</sup>	4.15 <sup>c</sup>	8.1	4.0	3.7 <sup>d</sup>
Kr	390.7 <sup>a</sup>	116.6 <sup>b</sup>	6.45	3.73	...	...	7.0	5.5	5.4 <sup>d</sup>
Xe	548.5 <sup>a</sup>	161.2 <sup>b</sup>	9.05	5.16	7.3	7.40	⟨7.3⟩	⟨7.40⟩	7.6 <sup>d</sup>

<sup>a</sup> Values quoted at the triple point (reference 25).

<sup>b</sup> Chemical Rubber Handbook (Chemical Rubber Publishing Company, 1962), 44th ed.

<sup>c</sup> Tracer data (reference 29).

<sup>d</sup> Tabulated in reference 25.

relating the observed activation energies for self-diffusion with various thermodynamic properties of the metals. Nachtrieb and co-workers<sup>26</sup> have used

$$E_D(N) = 16.5L_m \quad (4)$$

where  $L_m$  is the latent heat of melting in cal/mole. This relation has been somewhat more successful than has the earlier expression of Van Liempt,<sup>27</sup>

$$E_D(VL) = 32T_m \quad (5)$$

where  $T_m$  is the melting temperature in °K. In many metals, however, the observed activation energies lie between the two empirically-predicted values.<sup>28</sup> [Usually  $E_D(N) > E_D(VL)$ .]

It is of some interest to examine the predictions of these relations for the rare gas solids. The predicted activation energies for Ne, Ar, Kr, and Xe are given in the third and fourth columns of Table II. Recently, Boato and co-workers<sup>29</sup> have reported tracer diffusion measurements in solid argon. Their results, together with the xenon data of the present work, are tabulated in the fifth and sixth columns. It is evident that in each case, the observed activation energy for self-diffusion lies between the values predicted by the Nachtrieb and Van Liempt relations.

The diffusion coefficients deduced for solid xenon in the present work can be compared with theoretical and experimental results in other rare gas solids by application of the theorem of corresponding states.<sup>30,31</sup> If one

characterizes the short-range two-body interaction by a Lennard-Jones (6-12) interatomic potential with the usual molecular parameters  $\epsilon$  and  $\sigma$ , then  $E_D$  is proportional to  $\epsilon$  and  $D_0$  is proportional to  $\sigma(\epsilon/m)^{1/2}$ , where  $m$  is the atomic mass.<sup>30</sup> In columns seven and eight of Table II we have used the values tabulated by Hollis Hallett<sup>25</sup> and our xenon coefficients,  $D_0=7.3$  cm<sup>2</sup>/sec and  $E_D=7.40$  kcal/mole, to predict the diffusion parameters for neon, argon, and krypton. The predicted values have not been corrected for zero point effects. As Boato *et al.*<sup>29</sup> already have pointed out, the  $E_D$  measurements in xenon and argon correlate reasonably well, but the evident  $D_0$  discrepancy is difficult to understand.

A theoretical estimate of  $D_0$  and  $E_D$  for solid argon has appeared.<sup>1</sup> The analysis, based on the assumption of a vacancy-diffusion mechanism and on the absolute-rate model, yields  $D_0=4.2 \times 10^{-4}$  cm<sup>2</sup>/sec and  $E_D=3.2$  kcal/mole, in disagreement with the argon-tracer results<sup>29</sup> and the corresponding states extrapolation of our xenon data. In the calculation, the  $D_0$  factor depends upon the Einstein vibrational frequency, the lattice parameter and an entropy factor. Since the Einstein approximation should be reasonably good, it appears that the entropy estimate is off by several orders of magnitude.

Finally, it is of interest to consider the cohesive energies of these rare gas solids. The 0°K sublimation energies,  $L_0$ , have been summarized<sup>25,31</sup> and are determined from experimental specific heat and heat-of-vaporization data.  $L_0$  represents the work required to separate all the lattice atoms to infinity. Thus, the work to remove a single atom to infinity, leaving the rest of the lattice undisturbed, is  $2L_0$  (neglecting zero-point energy). The quantity  $2L_0$  is tabulated as the final column of Table II. One observes a rather close correspondence between the energies for removal of an atom from the lattices ( $2L_0$ ) and the activation energies for self-diffusion ( $E_D$ ) observed and anticipated in the various rare-gas solids. This correspondence is in sharp contrast to the situation in metals, for example, where, with more complicated binding,  $L_0$  itself is usually considerably larger than  $E_D$ .

<sup>26</sup> N. H. Nachtrieb, J. A. Weil, E. Catalano, and A. W. Lawson, *J. Chem. Phys.* **20**, 1189 (1952).

<sup>27</sup> J. Van Liempt, *Z. Physik* **96**, 534 (1935).

<sup>28</sup> D. Lazarus, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1960) Vol. 10.

<sup>29</sup> A. Bernè, G. Boato, and M. DePaz, *Nuovo Cimento* **24**, 1179 (1962). We are indebted to Professor Boato for correspondence on the comparison of our data. The xenon  $D_0$  value previously communicated to Professor Boato was in error by about a factor of 2.

<sup>30</sup> E. Helfand and S. A. Rice, *J. Chem. Phys.* **32**, 1642 (1960).

<sup>31</sup> E. R. Dobbs and G. O. Jones, *Rept. Progr. Phys.* **20**, 516 (1957).

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## Nuclear Magnetic Relaxation by Intermolecular Dipole-Dipole Interactions\*

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The contribution of intermolecular dipole-dipole interactions to the nuclear magnetic relaxation of identical spin- $\frac{1}{2}$  nuclei at equivalent positions in spherical molecules in a liquid is calculated. The assumptions made are that: (1), the effect of cross correlations of different dipole-dipole interactions is negligible, so that the relaxations of the longitudinal and transverse components of the nuclear magnetization are simple exponential decays with relaxation times  $T_1$  and  $T_2$ , respectively; (2), the motions of the molecules can be considered to be translational and rotational diffusion; and (3), the correlation time  $\tau_0 \equiv (2a^2/D)$ , where  $a$  is the radius of a molecule and  $D$  is the translational diffusion coefficient, is sufficiently short that  $(\omega_0\tau_0)^2 \ll 1$ , where  $\omega_0$  is the Larmor frequency of the nuclei. As a result of the short correlation time assumption (3), the contributions of the intermolecular interactions to  $(1/T_1)$  and  $(1/T_2)$  are found to be the same and are given by an infinite series, the first three terms of which are

$$\left(\frac{1}{T_1}\right)'' = \left(\frac{1}{T_2}\right)'' = \frac{n\pi\gamma^4\hbar^2}{5aD} \left[ 1 + 0.233 \left(\frac{b}{a}\right)^2 + 0.15 \left(\frac{b}{a}\right)^4 + \dots \right],$$

where  $n$  is the number of spins per unit volume,  $\gamma$  is the gyromagnetic ratio of each nucleus, and  $b$  is the distance of each nucleus from the center of the molecule in which it is contained. The first term in the series is the result obtained in previous calculations in which the effect of the rotations of the molecules was neglected. In a typical case in which  $(b/a) \approx \frac{1}{2}$ , the second and third terms are 6.8% of the first term.

## 1. INTRODUCTION

THE dipole-dipole interactions between the magnetic moments of spin- $\frac{1}{2}$  nuclei in molecules in a liquid contribute significantly to the nuclear magnetic relaxation of the liquid. The dipole-dipole interaction between a pair of spins depends upon the position vector of one spin with respect to the other. The relative position of nuclei in liquid molecules changes with time as a result of the translational and rotational motions of the molecules. The dipole-dipole interactions thus act as time-dependent perturbations on the Zeeman energy levels of the nuclei and produce transitions between these energy levels, which results in the relaxation of the nuclear magnetization.

Since the distance between nuclei in the same molecule is effectively constant, the time dependence of intramolecular dipole-dipole interactions in liquid molecules is due just to the rotational motion of the molecules. The time dependence of the relative position of two nuclei in different molecules depends on the translational motion of the molecules and also on the rotational motion of the molecules, unless both nuclei are at the

centers of their respective molecules. Hence, the contribution of intermolecular dipole-dipole interactions to the nuclear magnetic relaxation of polyatomic molecules in a liquid depends on both the translational and rotational motions of the molecules.

Previous treatments of the contribution of intermolecular dipole-dipole interactions to nuclear magnetic relaxation in liquids have taken into account only the translational motion of the molecules, on the assumption that the nuclei can be considered to be at the centers of spherical molecules which approach each other no more closely than a molecular diameter.<sup>1-4</sup> This assumption is valid only for liquids containing monatomic molecules. In the case of liquids containing polyatomic molecules, the distance of closest approach of nuclei in different molecules is less than the diameter of a molecule, which means that a correct treatment might give a greater contribution to the relaxation rate, since the magnitude of the dipole-dipole interaction varies inversely as the cube of the distance between the spins. On

<sup>1</sup> N. Bloembergen, E. M. Purcell, and R. V. Pound, *Phys. Rev.* **73**, 679 (1948).

<sup>2</sup> H. C. Torrey, *Phys. Rev.* **92**, 962 (1953).

<sup>3</sup> I. Oppenheim and M. Bloom, *Can. J. Phys.* **39**, 845 (1961).

<sup>4</sup> A. Abragam, *The Principles of Nuclear Magnetism* (Clarendon Press, Oxford, 1961), p. 300.

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