cloud. Hence each ion around the La^{3+} ion produces a dipole field at the La nucleus. (B) The La^{3+} ions also polarize in the presence of such optical phonons. This produces a change in the field gradient at the nucleus which cannot be explained by the torsional-oscillation mode. This effect is not present if the electron cloud is spherical but this spherical symmetry certainly does not exist in LaF_3. (C) During either an acoustic or optical vibration, the charge distribution about the La nucleus distorts relative to the equilibrium shape of the distribution. This distortion originates as hard core repulsions become important. This introduces a dynamical change in the crystal field gradient. The quantum-mechanical analog to this classical description is the Stark effect. Whereas the Sternheimer effect involves the absence of an electric field and the presence of a finite electric field gradient, this dynamic effect requires the presence of both the field and the field gradient.

Until the problem of the crystal structure of LaF is resolved,[2] it is impossible to attempt any calculations involving the three mechanisms A, B, C. Even when the structure is realized, the calculations would not be trivial because the structure is far from being cubic.

In summary, the temperature dependence of the pure quadrupole transitions of La^{139} in LaF_3 have been studied from 88 to 447°K. The simple Bayer and Einstein models give good agreement with the form of the temperature dependence of the field gradients but the magnitude of the dependence is much larger than calculated from these two models. A discussion is presented to show that the Sternheimer factor does not explain the large observed dependence and that this dependence must be explained by a dynamic enhancement. Mechanisms capable of producing this dynamic enhancement are discussed.

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We wish to thank Professor A. L. Schawlow, who suggested the Bayer mechanism, and to Mrs. A. Wehlau for her help in programming the numerical computations. We are particularly indebted to Professor M. W. Muller for several illuminating discussions

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Local Magnetic Field Shift in Liquid and Solid Xenon*

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Additional nuclear-magnetic-resonance measurements have been made of the temperature and density dependence of the average local magnetic field at Xe^{129} nuclei in liquid and solid xenon samples in an external magnetic field H_0. We have extended the temperature range of our solid measurements down to 21°K, and a computer of average transients has been used to improve the signal-to-noise ratio and reduce the effects of random errors. Our new liquid data covering the density range from 423 amagat to the triple point at 523 amagat show a linear dependence of the local field on density. The rate of increase of this local field with liquid density is $5.66\times10^{-7} H_0$ G/amagat. The new data for the extended solid range from 577 amagat (triple point) to 639 amagat (21°K) show a nonlinear density dependence. The rate of increase of the local field with solid density ρ is $5.10\times10^{-6}H_0-7.42\times10^{-9}\rho H_0$ G/amagat. The new data confirm the previously established discrepancy between the solid density dependence measured in this laboratory and the dependence measured by Yen, Norberg, and Warren. This discrepancy remains unexplained.

I. INTRODUCTION

WHEN an atom is isolated in an external magnetic field H_0, the screening resulting from the electron circulations induced when H_0 was applied causes the nucleus to experience a local magnetic field significantly smaller than H_0. This shielding of nuclei in *atoms* was first calculated by Lamb.[1] Indeed, for dilute xenon gas in an external field of 10 000 G, the xenon nuclei see a local field approximately 56 G smaller than 10 000 G.

While observing nuclear-magnetic-resonance signals from xenon nuclei in gas samples at room temperature, Streever and Carr[2] found that samples in the same external magnetic field, but having different gas densities, have different average values of the local field at the nuclei. Specifically, with increasing density this average local field shifts nearly linearly to larger values.

Using Ramsey's theory of magnetic shielding of nuclei in *molecules*[3] and measured values for this density-proportional shift, Torrey[4] was able to determine the spin-rotational coupling which exists while two xenon atoms collide. This, in turn, enabled him to

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account for the previously unexplained nuclear-spin relaxation times of gaseous xenon. Subsequently, Adrian[5] was able to show that this shift itself can be accounted for by the short-range exchange forces between colliding atoms in contrast to the longer range van der Waal's forces.

This shift has now been measured as a function of density and temperature in several laboratories for all phases of xenon[6–11] There exist no major discrepancies between the various measurements for the gas and liquid phases, but measurements for the solid have produced remarkably different results.

Yen and Norberg,[8] and Warren and Norberg[10,11] working at one laboratory, and Brinkmann[9] working at this laboratory, have all studied solid xenon in equilibrium with its vapor in sealed samples. The average local field at the nucleus has been measured as a function of temperature (and hence density). The first two groups of workers found the rate of change of the local field with density to be approximately *three* times larger than the rate measured in this laboratory. Although the precision of the measurements of the shift in the solid is less than in the liquid, the above discrepancy lies well outside the expected limits of error.

In an effort to resolve this discrepancy we have made additional measurements which are both more extensive and more precise.

II. MEASUREMENTS AND APPARATUS

If a nondilute sample is placed in a constant external magnetic field H_0, the difference between the average local magnetic field at the nuclei in this sample and that at the nucleus of an isolated molecule (dilute gas sample) in the same external field may be designated by the symbol ΔH. Defined in this way, the shift ΔH describes only the effect of interactions with the *other* molecules. This is in contrast to both the shielding calculated by Lamb for isolated atoms and the usual chemical shift determined primarily by the internal electronic configuration of a molecule.

In our experiments, local fields can in principle be determined from the known gyromagnetic ratio[12] for the Xe^{129} nuclei and the measured radiofrequencies of the free-precession signals following the application of 90° rf pulses[13] to the xenon samples. But in practice we measure changes in ΔH by observing the audio difference frequency (beat frequency) between the free-precession signal from the sample being studied and an arbitrary but stable reference signal. This reference signal may, for example, come from a xenon sample of *fixed* density and temperature. Or it may come from a stable reference oscillator.

There are several major differences between our present work and the work previously reported from our laboratory.

(1) In our earlier measurements[9] we used a standard xenon sample of fixed density (gas at room temperature having a density of 310 amagats) as our reference signal. Because the free-precession signals, one from the sample being studied and the other from the reference sample, were not obtained simultaneously, it was necessary to compare their frequencies by beating them separately with a stable comparison oscillator. By quickly and accurately replacing the reference sample, which was located in the most homogeneous position in our magnet, by the sample to be studied, we ensured that the two samples were in the same external field. Moreover, this exchange was accomplished in a time short compared to the time required for significant drifts in the value of the external field or the frequency of the comparison oscillator. Of course, during a long series of measurements, the external magnetic field and the comparison oscillator can drift by an amount comparable to the shift being measured; but long-term drifts did not affect our measurements of the *difference* frequency—the effect of a long-term drift on the measured frequency for the sample being studied was compensated for by an equal effect on the frequency for the reference sample.

In the present work, however, the external magnetic field is stabilized by a separate crystal-controlled proton resonance. The drift of the external field is small compared to the shifts measured even for the times required for a long series of measurements. Although the most homogeneous position in the magnet is reserved for the cryostat holding the xenon sample, the proton field control can be set with a precision of ±0.04 G. The maximum variation in H_0 due to the frequency drift of the proton crystal-controlled oscillator (monitored by an electronic counter) is less than ±0.01 G.

With the external magnetic field stabilized, the shift in the local field for a given sample is determined directly from the audio beat frequency between an arbitrary reference signal and the free-precession signal of the sample studied. The electronic counter is also used to ensure the constancy of the reference frequency. Variations in this frequency are less than ±10 cps or about one part in 10^6. For our external magnetic field of 7.10 kG, this contributes a maximum error in the local field shift of ±0.007 G.

(2) The beat signal is observed both on the screen of a cathode-ray oscilloscope and with an electronic computer of average transients. Our 400-channel digital computer sums a large number of signals from a given sample. The desired xenon signals add coherently while the undesired noise adds randomly.[14] Indeed, there is

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partial canceling of both (a) the random noise of the electronic circuits and (b) any random error due to the limited precision with which the external field value and reference signal frequency can be continually reset to a constant value. The signal-to-noise ratio is improved by a factor equal to the square root of the number of individual transient signals added. Moreover, our averaged signals are recorded in printed digital form, making the measurement of the beat frequencies and the estimation of the errors more reliable.

(3) In the present work two different cryostats are used. One cryostat (I) is the same as that used in our previous work. In this cryostat the Pyrex tube containing the xenon is submerged in petrol ether contained in a copper can. The temperature of the xenon is controlled by varying the contact between the lower part of the copper can and a liquid-nitrogen bath. This cryostat can be used for temperatures down to 77°K. The temperatures are measured with a pentane thermometer calibrated with a copper-constantan thermocouple.

Most of the present work, however, uses a more elaborate cryostat (II) in which the Pyrex sample container is placed in a copper can filled with helium exchange gas. The upper part of the can is connected thermally to a bath, either liquid nitrogen or liquid helium. The copper can is surrounded by a separate copper radiation shield kept at liquid-nitrogen temperature. With this apparatus, temperature gradients are reduced and the temperature can be determined more accurately. Moreover, the temperature range can be extended down to 21°K. The higher temperatures are measured with a copper-constantan thermocouple and the lower temperatures with a carbon resistance thermometer.

(4) The measurements reported here have been obtained using three different samples. Samples A and B are of the type used in our previous work. They are sealed Pyrex containers with a volume of about 0.2 cm^3 filled with high-pressure gas (pressures about 100 atm) at room temperature. They are so constructed that the liquid or solid portion of a sample at low temperatures nearly fills the bulb at the bottom of the sample holder; the vapor is almost entirely confined to the long small capillary extending above the bulb.

Sample C has approximately the same volume (3.2 cm^3) and shape (cylindrical) as the samples used by Yen and Norberg,[8] and Warren and Norberg.[10,11] The xenon in this sample was continuously kept in the solid phase, even between experiments. In samples A and B, however, the xenon is allowed to return to the gaseous phase at room temperatures between different runs.

The bulbs of samples B and C are completely filled with liquid or solid xenon when the temperature is below the boiling point, but in sample A the liquid or solid fills the bulb only about three-quarters full. All samples are slightly doped with oxygen to reduce the relaxation times to convenient values. Our earlier measurements established that the observed shift is insensitive to small amounts of oxygen. In all measurements the liquid or solid xenon is in equilibrium with its vapor pressure.

III. RESULTS AND DISCUSSION

The data from our present set of measurements are listed in Table I; and the data from run No. 1 representing the most favorable conditions of sample size and magnetic field homogeneity (sample A), as well as the most reliable temperature measurements (cryostat

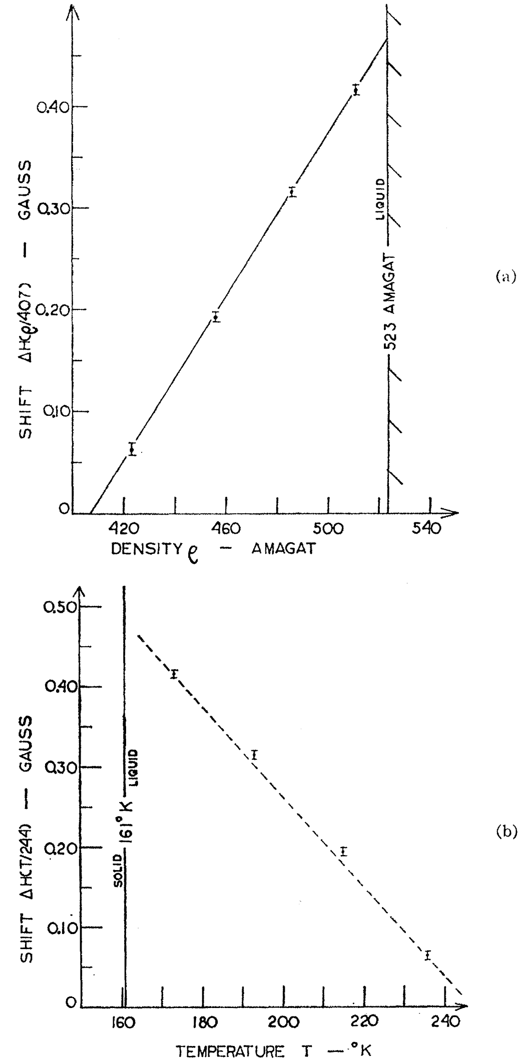

FIG. 1(a) Shift of the average local field at Xe^{129} nuclei in a sealed sample of *liquid* xenon in equilibrium with its vapor. The external field is 7.10 kG and ΔH is the difference between the local field in a sample of density ρ and the local field in a liquid reference sample of density 407 amagat and temperature 244°K. The solid line, a least-squares linear fit to the data, passes within 0.002 G of each experimental point. (b) The same experimental points as in Fig. 1(a) but plotted as a function of temperature. The dashed straight line emphasizes, by contrast, the nonlinearity of this temperature dependence.

TABLE I. Local field shift in an external field of 7.10 kG.

Run		Temperature T (°K)	Density ρ^{a} (amagats)	Shift ΔH (gauss)
No. 1. Sample A, Cryostat II	liquid	244±1	407±2	0(reference)
		236	423	0.063±0.006
		215	456	0.193±0.005
		193	486	0.315±0.005
		173	511	0.416±0.005
	solid	158±1	579±2	0.802±0.007
		133	591	0.865±0.009
		105	605	0.939±0.033
		80	617	0.977±0.036
		21	639	1.052±0.039
No. 2. Sample B, Cryostat I (ΔH normalized to ΔH for 158°K point in Run No. 1)	solid	158±1	579±2	0.802±0.008
		124	598	0.895±0.010
		80	618	0.968±0.031
No. 3. Sample C, Cryostat I (ΔH normalized to ΔH for Run No. 1 at 583 amagat point)	solid	152±2	583±4	0.822±0.025
		80	618	0.957±0.032

[a] Liquid densities from Hollis Hallet (Ref. 16) and solid densities from Packard and Swenson (Ref. 15).

II), are plotted in Figs. 1 and 2. The densities for the solid are determined from the solid-vapor coexistence curve of Packard and Swenson,[15] and those for the liquid phase are obtained from the data tabulated by Hollis Hallett.[16] The external magnetic field H_0 is 7.10 kG and all shifts are relative to the local field corresponding to a liquid sample of density 407 amagat in equilibrium with its saturated vapor. This reference was determined by the arbitrary frequency of a stable oscillator. The improved precision of this present data is primarily the result of the use of the computer of average transients. Each liquid datum point at a given temperature and density in run No. 1 corresponds to the average of approximately *ten* transient signals. The number of transient signals averaged for each solid datum point in this run varies from 10 at the higher temperatures where the nuclear resonance linewidth is still relatively narrow, to 20 at the lower temperatures where the linewidth is broad (broader than the contribution to the linewidth by the inhomogeneity of the magnet). A broader linewidth corresponds to a free-precession signal of shorter duration; this, in turn, means a reduction in the precision with which the frequency difference and field shift can be determined. For our liquid samples, where the linewidth was determined by the inhomogeneity of the external magnet, a typical free-precession signal lasted for approximately 100 msec; but for the solid samples at lower temperatures, where the linewidth is determined by local fields of the rigid solid, the free-precession signals lasted for approximately 1 msec.

The errors listed in Table I come directly from the printed read-out of the computer of average transients; thus they represent the improved precision *after* the individual signals have been averaged.

The data for the liquid can be described well by a linear variation of the shift ΔH with density ρ. A least-squares analysis of the data yields

$$\Delta H(\rho/407) = -2.306\times10^{-4}H_0 + 5.66\times10^{-7}\rho H_0\,, \quad (1)$$

where ρ is in amagats. We use the symbol $\Delta H(\rho/407)$ to denote a shift relative to a reference sample of density 407 amagat rather than relative to an isolated atom (or a gas sample of near-zero density). This least-squares line passes within ±0.002 G of each datum point and is plotted in Fig. 1(a). The slope of this line is between 25% and 30% greater than that previously observed for the gas at room temperature. The present data, however, are restricted to a relatively small region of the high-density liquid in equilibrium with its vapor pressure (the total volume is constant—thus the temperature and density vary simultaneously). The previous measurements[2,6,7] were primarily for the gas at room temperature, but they included a few liquid points which indicated that the shift had an approximately linear dependence on density throughout the gas and liquid regions. The present, more precise, measurements indicate that the rate of change of the shift with density has a different value in the dense liquid from that in the gas at room temperature. Use of the computer of average transients in future measurements will undoubtedly reveal more precise details of the transition between these regions. The liquid data plotted as a function of temperature are shown in Fig. 1(b); the dashed straight line is drawn simply for reference to help show that the data cannot be fitted well to a linear curve.

The data of our present work with its extended temperature range are also sufficiently precise to indicate that the shift in *solid* xenon as a function of either density or temperature is not well described by a linear

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curve.[17] A least-squares fit of a quadratic curve to our most reliable data (run No. 1) yields

$$\Delta H(\rho/407) = -15.98\times10^{-4}H_0 + 5.10\times10^{-6}\rho H_0 - 3.71\times10^{-9}\rho^2 H_0, \quad (2a)$$

where again ρ has the units of amagats and $\Delta H(\rho/407)$ is the shift relative to a 407-amagat liquid sample. Or as a function of temperature the same data are described by

$$\Delta H(T/244°) = 1.499\times10^{-4}H_0 - 5.80\times10^{-8}TH_0 - 1.12\times10^{-9}T^2 H_0, \quad (2b)$$

where T is in degrees Kelvin and $\Delta H(T/244°)$ is again the shift relative to our 407-amagat liquid sample which has a temperature 244°K.

In Fig. 2(a) the solid-xenon shift data from run No. 1 are plotted as a function of density. The solid curve is our least squares expression, Eq. (2a). The dashed curve shows the results of Yen and Norberg[8] and Warren and Norberg[10,11] normalized to our data at the triple point (576 amagats). In Fig. 2(b) the same data are plotted as a function of temperature and the solid curve is the least-squares expression, Eq. (2b). Both least-squares curves for the solid pass within ±0.006 G of the five data points (H_0=7.10 kG).

The above shifts can also be given relative to an isolated atom instead of a 407-amagat liquid sample. Streever and Carr[2] measured the shift of a 480-amagat sample in a 8.06 kG external field and found it to be (1.64±0.05) G relative to the isolated atom (dilute gas of nearly zero density). Hunt and Carr[6] made measurements using a liquid sample of the same density in fields of 4.58 and 12.2 kG and found the respective shifts to be (0.94±0.05)G and (2.41±0.05)G. These three measurements give an average shift $\Delta H(480/0) = (2.02\pm0.05)\times10^{-4}H_0$. In our present work [Eq. (1)] we find that the shift between a 407-amagat and a 480-amagat sample is $\Delta H(480/407) = (0.41\pm0.01)\times10^{-4}H_0$. Therefore the shift of our 407-amagat reference sample relative to an isolated atom is

$$\Delta H(407/0) = \Delta H(480/0) - \Delta H(480/407) = (1.61\pm0.06)\times10^{-4}H_0.$$

In this calculation it is necessary to assume a density-proportional shift only for the dilute gas at constant temperature, not for the entire gas-liquid range.

Thus the shifts given in Eqs. (1) and (2) relative to a 407-amagat reference sample can be converted to shifts relative to an isolated xenon atom simply by adding the constant term $1.61\times10^{-4}H_0$. The precision of this additive term which is based in part on our earlier work is not as good as the precision of Eqs. (1) and (2), which reflect the improvements obtained by using the computer of average transients. In particular, the average local field for a solid sample at 0°K in an external field of 7.10 kG is 2.20±0.08 G larger than for an isolated atom.

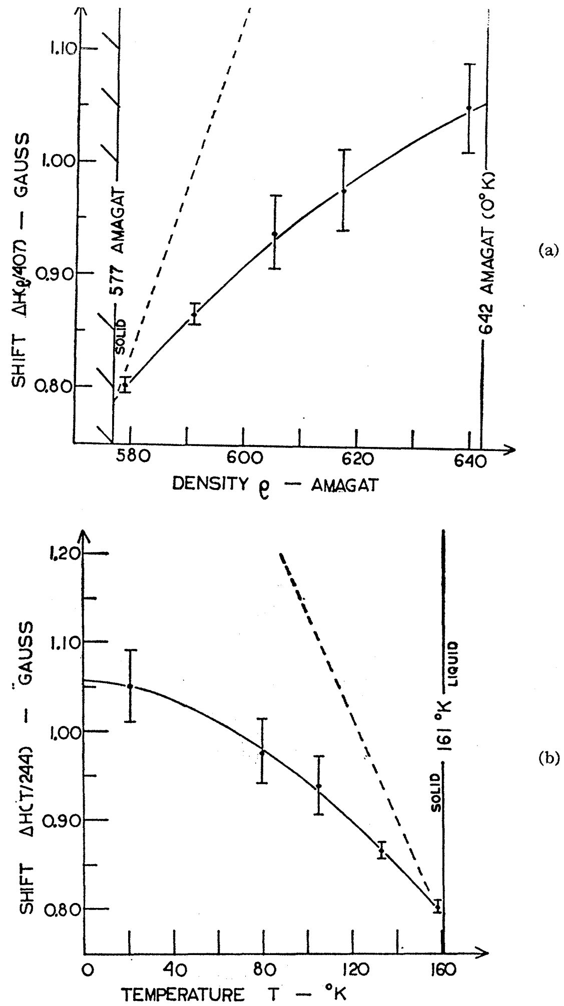

FIG. 2(a) Shift of the average local field at Xe^{129} nuclei in a sealed sample of *solid* xenon in equilibrium with its vapor. The external field is 7.10 kG and ΔH is the difference between the local field of the sample of density ρ and the local field in a liquid reference sample of density 407 amagat and a temperature 244°K. The solid curve, the least-squares quadratic fit to the data, passes within 0.006 G of each experimental point. The dashed curve is from the results of Yen and Norberg, and Warren and Norberg (±0.05 G). (b) The same experimental points as in Fig. 2(a) but plotted as a function of temperature. The solid curve, a least-squares quadratic fit to the data, passes within 0.006 G of each experimental point.

There is a discontinuity in the shift at the liquid-solid transition. This 0.33±0.02 G discontinuity is not related simply to a change of density. If supercooled liquid xenon could be described by Eq. (1), then the shift of a supercooled liquid sample having a density of 576 amagats—that is, the density of the solid[15] at the triple point—would be $(0.13\pm.02)\times10^{-4}H_0$ less than the solid at the same density.

The improved precision of the present measurements indicates that at 161°K the rate of change of the local

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field shift with density is $8.0\times10^{-7}H_0$ G/amagat, while at 21°K the rate has decreased to $3.5\times10^{-7}H_0$G/amagat. In our earlier but less precise measurement we obtained an average rate of $5.3\times10^{-7}H_0$ G/amagat for the less dense solid between 77 and 150°K. But our present result, like our earlier result, is in major disagreement with the rate observed by Yen and Norberg[8] ($20.4\times10^{-7}H_0$ G/amagat), and Warren and Norberg[10,11] ($18.2\times10^{-7}H_0$ G/amagat) for about the same range of solid densities.

It has been established in both laboratories that the values of ΔH are independent of the isotope, Xe^{129} or Xe^{131}, used in the magnetic-resonance measurement. Moreover, it has also been shown that the small amounts of impurity used to reduce the spin-lattice relaxation times[9,11] do not affect the value of ΔH.

There is no major disagreement between the various measurements of the density dependence of the local field shift for *liquid* samples. Somewhat different methods have been used at the two laboratories to control the external magnetic field and to measure the shift ΔH in the *liquid*, and *no discrepancy* exists between the two sets of measurements. But these same methods have been used in the respective laboratories to measure the shift in the *solid* where the *large discrepancy* does exist. This suggests that the discrepancy is not likely to be due to differences in the control of the external field or the measurement of ΔH. This conclusion, however, may not take adequate account of the more severe requirements placed on these measuring techniques as the temperature of the solid is lowered and the line is broadened.

We have checked our temperature measurements and controls. An entirely different cryostat is used in our run No. 2—the temperature gradients are changed in magnitude and direction, and the speed with which the sample temperature is changed is increased. Yet the data from this run when fitted with a straight line give a slope of $6.0\times10^{-7}H_0$ G/amagat which lies between the lowest and highest values for the first run, the limit of error being considerably less than the large discrepancy we seek to understand. We have no evidence that differences in the temperature history can account for this discrepancy.

Sample B used in run No. 2 is different from Sample A in run No. 1, although it does have the same shape and volume. However, in run No. 3 the much larger sample C is used, its volume being equal to that used in the other laboratory. The slope from this run, $5.6\times10^{7}H_0$ G/amagat, is again in agreement with that of our first run, the limit of error also being much less than the unexplained discrepancy. We conclude that variations in our sample size can not account for the discrepancy.

In an effort to identify the origin of the unexplained discrepancy, we are proceeding with optical and x-ray analyses of solid samples frozen under a variety of conditions.[18]

Lurie and Feldman,[19] using Adrian's[5] expression for the shift in the local magnetic field, have recently calculated the temperature dependence of the shift ΔH for the solid. They treat in detail the combined effects of thermal expansion and lattice vibrations in a fcc structure. Their result, described in the following paper,[20] is in good agreement with our observed temperature dependence.

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