Temperature Variation of La^{139} Nuclear Quadrupole Resonance in LaF_3

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The temperature dependence of the pure quadrupole transitions of La^{139} in LaF_3 has been studied from 88 to 447°K. La^{139} has a nuclear spin of $\frac{7}{2}$, so three $|\Delta m|=1$ transitions were observed. A spectrometer of crossed-coil geometry was used. The Bayer torsional-motion mechanism and an Einstein phonon spectrum are used to interpret the measurements. The characteristic (or Einstein) temperatures are 465 and 641°K. Values for the quadrupole coupling constant, asymmetry parameter, and electric-field-gradient components at the La sites are tabulated. The observed temperature variation is approximately two orders of magnitude larger than predicted by the simple theory employed. Mechanisms are discussed to account for this discrepancy.

I. INTRODUCTION

THE "pure" quadrupole resonance frequencies of La^{139} in a single crystal of LaF_3 were measured as a function of temperature in the range from 88 to 447°K. These measurements can be used to determine the temperature variation of the average crystal-field gradient at the La sites. The crystal field sensed by this method is a time average caused by vibrational motions which are fast compared to the quadrupole resonance frequency. As the Debye temperature, or temperatures associated with other characteristic frequencies, are reached and many phonons are excited, the changes in the average field gradient become more pronounced. The measurements are interpreted in terms of the Bayer[1] torsional-motion mechanism and an Einsetin phonon spectrum. Torsional oscillations can be tentatively identified with high-wave-number transverse phonons. However, no attempt has been made to work out the details of the phonon spectrum of LaF_3, which is quite a complicated crystal.[2] The shape of the temperature variation can be explained if only two branches of the phonon spectrum are effective in the temperature range studied. The characteristic temperatures (Einstein temperatures) which best fit the data are 465 and 641°K. These temperatures lie in the range of values obtained from optical,[3] heat-capacity,[4] and transport studies.[5] The effective moments of inertia deduced from these experiments are anomalously small ($\sim 10^2$ smaller than predicted). The observed consequence of this is that the temperature variation of the field gradient is much faster than predicted by this simple model. However, one does not expect improvements in the theory which replaces the Einstein approximation by a Debye model or which include Sternheimer anti-shielding effects[6] to account for the enhanced temperature variation.

II. EXPERIMENTAL TECHNIQUE AND RESULTS

The pure quadrupole transitions of La^{139} with a nuclear spin of $I=\frac{7}{2}$ were observed with a Varian variable-frequency VF-16 nuclear-magnetic-resonance (NMR) spectrometer. The VF-16 employs the "crossed-coil" method of nuclear induction but, with no external magnetic field applied, there can be no nuclear induction into a receiver coil whose axis is orthogonal to the transmitter coil. However, the small perturbing magnetic modulation field normally used in NMR detection is sufficient to remove the energy-level degeneracy responsible for this lack of induction. This small oscillating magnetic field always satisfies the condition that the quadrupole coupling constant $e^2Qq \gg \hbar\gamma H_m$, where H_m is the magnitude of the oscillating magnetic field and γ is the nuclear magneto-mechanical ratio.

The first mention of the use of the "crossed-coil" geometry in zero magnetic field (other than the modulation field) was made by Haering and Volkoff.[7] Subsequently Bloom, Robinson, and Volkoff,[8] and Robinson[9] demonstrated theoretically[8] and experimentally[9] the complete gradual transition of a nuclear-spin-resonance spectrum from a pure quadrupole spectrum slightly perturbed by a magnetic field to the opposite limiting case of a Zeeman spectrum slightly perturbed by the electric quadrupole interaction. The measurements cited were made with a "crossed-coil" spectrometer. The authors have also solved a set of modified Bloch equations which describe the behavior of the magnetization

[1] H. Bayer, Z. Physik **130**, 227 (1951).
[2] L. O. Andersson and W. G. Proctor, Z. Krist. (to be published); M. Mansmann, Z. Anorg. Allgem. Chem. **331**, 99 (1964); A. Zalkin, D. H. Templeton, and T. E. Hopkins (to be published).
[3] W. M. Yen, W. C. Scott, and A. L. Schawlow, Phys. Rev. 136, 271 (1964); R. A. Buchanan and H. H. Caspers (private communication).
[4] D. T. Teaney (private communication).
[5] K. Lee and A. Sher, Phys. Rev. Letters **14**, 1027 (1965); A. Sher, R. Solomon, K. Lee, and M. W. Muller, Phys. Rev. 144, 593 (1966).
[6] R. M. Sternheimer, Phys. Rev. **84**, 244 (1951); **86**, 316 (1952); **95**, 736 (1954). For a brief and clear discussion see N. F. Ramsey, *Molecular Beams* (Clarendon Press, Oxford, England, 1956), Chap. XI.
[7] R. R. Haering and G. M. Volkoff, Can. J. Phys. **34**, 577 (1956).
[8] M. Bloom, L. B. Robinson, and G. M. Volkoff, Can. J. Phys. **36**, 1286 (1958).
[9] L. B. Robinson, Can. J. Phys. **36**, 1295 (1958).

vector of a two-level system when transitions are induced by an oscillating magnetic field. Smith[10] has extended the Bloch-type theory[8] to describe the dependence of line shape, width, and amplitude upon magnetic modulation, static magnetic field, and rf field. He finds good agreement with experiment. Recently Hartmann, Fleissner, and Sillescu,[11] and Proctor and Lee[12] discussed the observation of pure quadrupole transitions using the Varian VF-16 (formerly V-4200) spectrometer.

A cylindrically-shaped single crystal of LaF_3 with a diameter of $\frac{3}{8}$ in. and a length of $\frac{1}{2}$ in. was cut so that the c axis and a axis were, respectively, perpendicular and parallel to the cylinder axis. The crystal was placed in the 2–4 MHz probe with the c axis parallel to the axis of the transmitter coils and the a axis parallel to the axis of the receiver coil. A Varian V-4540 variable-temperature unit was incorporated to control and vary the temperature. In order to provide a more uniform temperature across the sample, a thin-wall, ground-quartz Dewar with an outside dimension of 0.669 in. and an inside dimension of 0.561 in. was used. Using a copper-constantan thermocouple, the temperature was calibrated at the sample to within ±3°K. No detectable temperature gradient was observed across the length of the sample. The frequency was swept by connecting the fine-frequency control shaft of the variable-frequency unit (V-4210) to a synchronous motor and a set of reduction gears. The spectra were recorded on a Varian F-80 X-Y recorder in which the X axis was calibrated linearly in frequency units. This was accomplished by taking the frequency output from the crystal synchronization connector of the V-4210 and introducing it into a Hewlett-Packard HP-5245L frequency counter, which in turn was coupled to an HP-580A digital-to-analog converter. The output of the HP-580A was then introduced into the X axis of the F-80. An 80-Hz modulation field with a peak-to-peak amplitude of either 10 or 27 G was normally used.

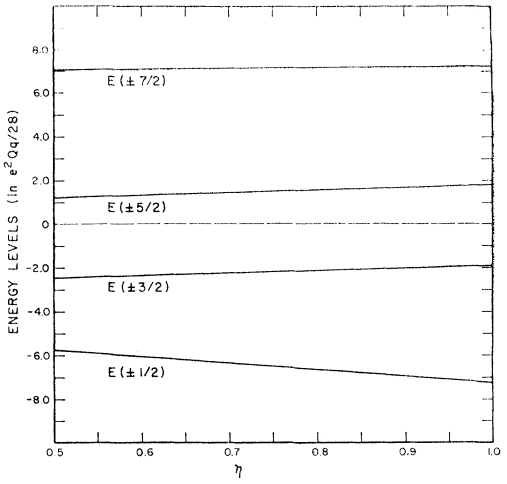

FIG. 2. Calculated energy levels for a nucleus with spin $I=\frac{7}{2}$ versus η. The energy levels are in units of $e^2Qq/28$.

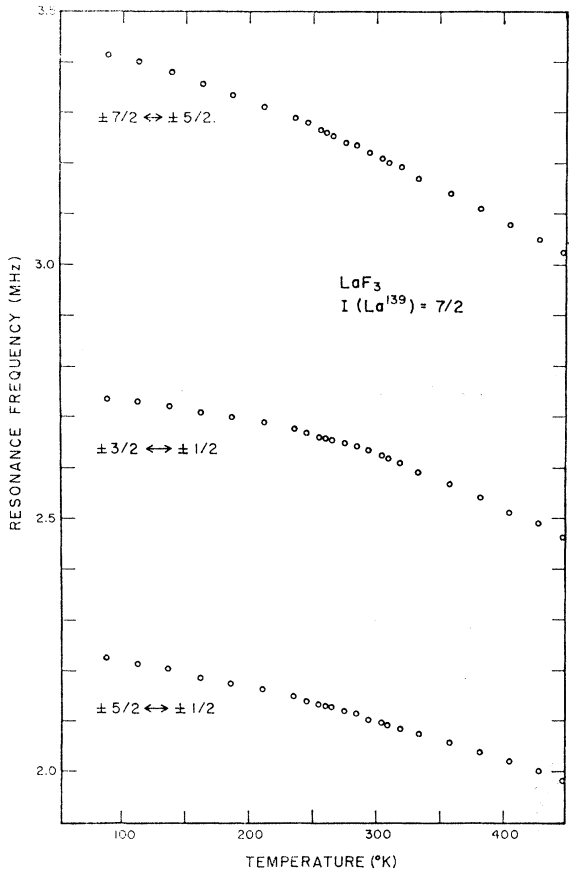

FIG. 1. Observed pure quadrupole transitions of La^{139} ($I=\frac{7}{2}$) versus temperature. The corresponding $|\Delta m|=1$ transitions are indicated.

Since La^{139} has a nuclear spin of $\frac{7}{2}$, three $|\Delta m|=1$ transitions were observed from 88 to 447°K. Figure 1 is a plot of the three nuclear-quadrupole-resonance (NQR) frequencies as a function of temperature. The frequency was usually swept at a rate of 20 kHz in 1 min, but at high temperatures the signal intensity decreases and the scanning rate was decreased to 10 kHz per minute. The position of the resonance lines was measured to an accuracy of better than ±0.002 MHz.

The quadrupole coupling constant e^2Qq, where eQ is the quadrupole moment and $eq=V_{zz}$ is the gradient of the electric field along the z direction, and the asymmetry parameter $\eta=(V_{xx}-V_{yy})/V_{zz}$, where it is assumed that $|V_{xx}|<|V_{yy}|<V_{zz}|$, are determined at

[10] G. W. Smith, Bull. Am. Phys. Soc. **11**, 221 (1966) and private communication.

[11] H. Hartmann, M. Fleissner, and H. Sillescu, Naturwiss. **50**, 591 (1963); Theoret. Chim. Acta **2**, 63 (1964); H. Hartmann and H. Sillescu, *ibid.*, **2**, 371 (1964).

[12] W. Proctor and K. Lee, Varian Technical Information Bulletin, Fall, 1965, p. 6 (unpublished).

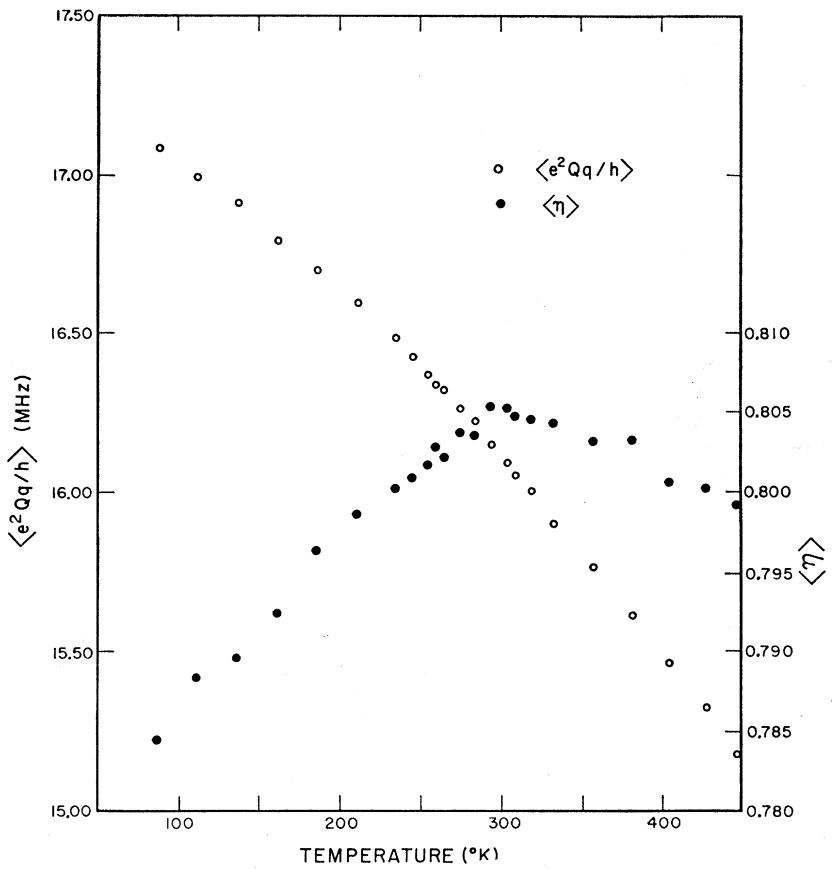

FIG. 3. Average quadrupole coupling constant $\langle e^2Qq/h\rangle$ and average asymmetry parameter $\langle\eta\rangle$ versus temperature.

each temperature by taking the ratios of the observed resonance frequencies and comparing them with the ratios of the calculated $|\Delta m|=1$ transitions. The calculated energy levels are obtained by solving the fourth-order secular equation[13] corresponding to a nuclear spin of $I=\frac{7}{2}$;

$$E^4-42(1+\eta^2/3)E^2-64(1-\eta^2)E+105(1+\eta^2/3)^2=0,$$

where the energy eigenvalue E is in units of

$$3e^2Qq/4I(2I-1)=e^2Qq/28.$$

Cohen[14] has solved this equation numerically and has tabulated the eigenvalues for values of η from 0.1 to 1.0 in intervals of 0.1. Since the full range of the measured values of η varied only by about 0.15, it was difficult to interpolate between Cohen's points. Therefore, the secular equation was solved numerically for values of η from 0.5 to 1.0 in intervals of 0.005. Figure 2 is a plot of the four doubly degenerate eigenvalues (or energy levels) as a function of η. Wang[15] has also solved this equation and has plotted the energy levels for values of η from 0 to 0.6. Comparing the ratios of the

[13] H. G. Dehmelt and H. Kruger, Z. Physik **130**, 385 (1951).
[14] M. H. Cohen, Phys. Rev. **96**, 1278 (1954).
[15] T. C. Wang, Phys. Rev. **99**, 566 (1955).

TABLE I. Measured values for the quadrupole coupling constant, the asymmetry parameter, and the three components of the electric field gradient.

T (°K)	$\langle e^2Qq/h\rangle$ (MHz) ±0.01	$\langle\eta\rangle$ ±0.0010	$+\langle V_{zz}\rangle$ (statvolt/cm²) ×10¹⁴	$-\langle V_{yy}\rangle$ (statvolt/cm²) ×10¹⁴	$-\langle V_{xx}\rangle$ (statvolt/cm²) ×10¹⁴
88	17.08	0.7845	4.711	4.204	0.507
112	16.99	0.7884	4.688	4.192	0.496
137	16.91	0.7897	4.665	4.175	0.490
162	16.79	0.7925	4.663	4.153	0.480
186	16.70	0.7964	4.606	4.137	0.469
211	16.59	0.7987	4.578	4.118	0.460
235	16.48	0.8003	4.547	4.093	0.454
245	16.42	0.8010	4.531	4.080	0.451
255	16.37	0.8018	4.516	4.068	0.448
260	16.33	0.8029	4.506	4.062	0.444
265	16.32	0.8022	4.502	4.057	0.445
275	16.26	0.8038	4.485	4.045	0.440
284	16.22	0.8036	4.474	4.035	0.439
294	16.14	0.8054	4.454	4.021	0.433
304	16.09	0.8053	4.438	4.006	0.432
309	16.05	0.8048	4.428	3.996	0.432
319	16.00	0.8046	4.415	3.984	0.431
333	15.90	0.8044	4.386	3.957	0.429
358	15.76	0.8032	4.349	3.921	0.428
382	15.61	0.8033	4.306	3.883	0.423
405	15.46	0.8007	4.265	3.840	0.425
428	15.32	0.8003	4.225	3.803	0.422
447	15.17	0.7993	4.185	3.765	0.420

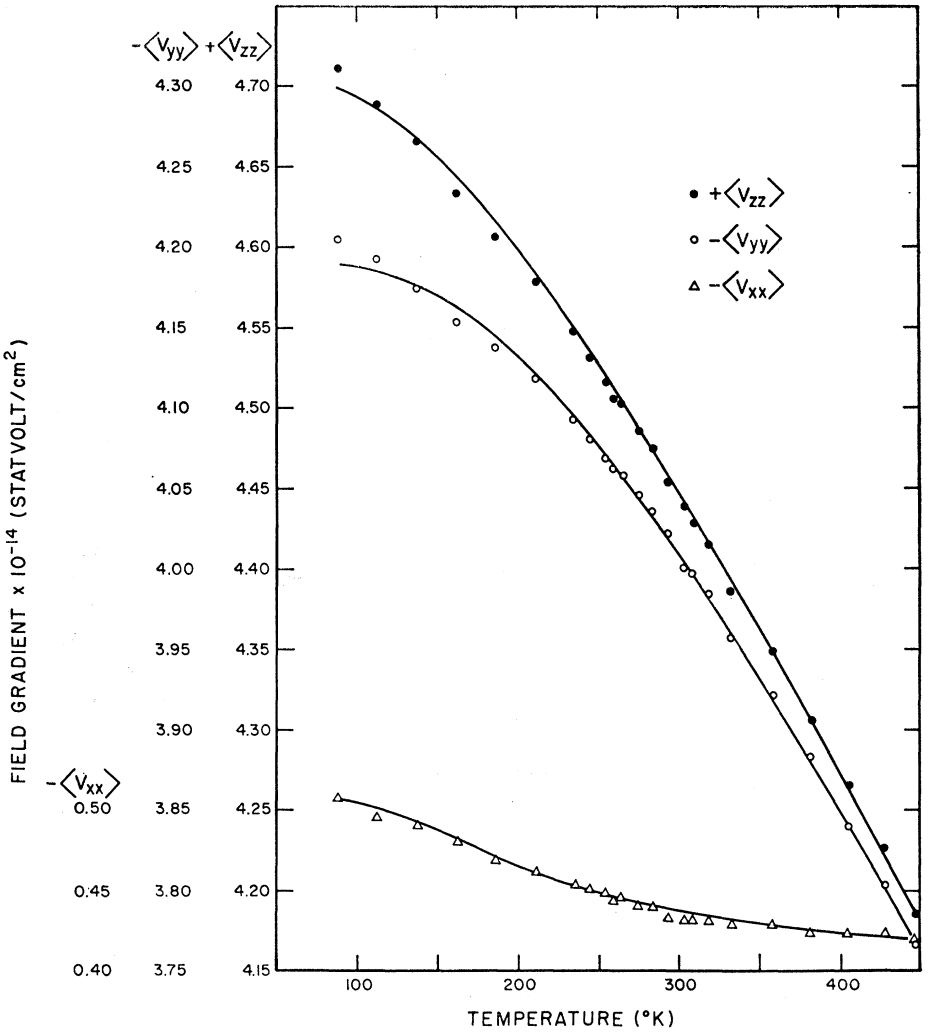

FIG. 4. Average field gradient components versus temperature for LaF_3. A value of $Q=0.5\times10^{-24}$ cm^2 was used. The values of $\langle V_{zz}\rangle$ are positive and the values of $\langle V_{xx}\rangle$ and $\langle V_{yy}\rangle$ are negative. The solid curves are calculated from Eqs. (1) and (2) and the parameters given in the text.

three observed transitions with the three calculated transitions, it was simple to correlate each of the observed transitions with the corresponding energy levels. This is indicated in Fig. 1. Since the $m=\pm\frac{7}{2}$, $\pm\frac{5}{2}$, and $\pm\frac{3}{2}$ levels[16] are nearly parallel, only the two ratios involving the $\pm\frac{1}{2}$ energy level were used to determine η, and consequently e^2Qq, for each temperature. That is, only the ratios $(\frac{3}{2}-\frac{1}{2})/(\frac{7}{2}-\frac{5}{2})$ and $(\frac{5}{2}-\frac{3}{2})/(\frac{3}{2}-\frac{1}{2})$ were used. The average values of $\langle\eta\rangle$ and $\langle e^2Qq/h\rangle$ are listed in Table I and are plotted in Fig. 3.

Neglecting the effect of the atomic core on the nuclear quadrupole coupling[6] and taking the value [17] for the nuclear quadrupole moment of La^{139} to be

$$eQ=0.5e\times10^{-24}\text{ cm}^2=2.40\times10^{-34}\text{ cm}^2\text{ esu},$$

the values for the electric field gradients $\langle V_{jj}\rangle$, where $j=x, y, z$, may be determined at each temperature. $\langle V_{zz}\rangle$ is determined from the quadrupole coupling constant and $\langle V_{xx}\rangle$ and $\langle V_{yy}\rangle$ are then obtained from the definition of the asymmetry parameter and Laplace's equation. These values are given in the third, fourth, and fifth columns in Table I. They are also plotted in Fig. 4. The signs of $\langle V_{xx}\rangle$ and $\langle V_{yy}\rangle$ must be opposite to that of $\langle V_{zz}\rangle$. The sign of $\langle V_{zz}\rangle$ is arbitrarily taken positive, so $\langle V_{xx}\rangle$ and $\langle V_{yy}\rangle$ are negative. The values of $\langle V_{xx}\rangle$, $\langle V_{yy}\rangle$, $\langle V_{zz}\rangle$ in Table I are quoted to four significant figures. Since Q is only known to one figure, the four figures are significant only to within a multiplicative constant. The data in Fig. 4 and Table I are presented in this manner because the physical situation is easier to visualize and analyze.

[16] These energy levels are identified by $m=\pm\frac{7}{2}$, $\pm\frac{5}{2}$, $\pm\frac{3}{2}$, $\pm\frac{1}{2}$, but they are eigenvalues of I_z only for $\eta=0$.

[17] K. Murakawa and T. Kamei, Phys. Rev. **105**, 671 (1957). The effect of the electron core on the quadrupole coupling has not been evaluated for La. If the shielding correction for the $5d$ electrons is assumed to be the same as the calculated value for $W(5d^4)$, the uncorrected quadrupole moment is multiplied by the factor 0.66, giving a value $Q=0.33\times10^{-24}$ cm^2. See Ref. 6.

III. INTERPRETATION

The crystal structure of LaF_3 is quite complicated. In fact, there is still controversy about it.[2] However, it is clear from the proposed crystal structures that it will be a monumental task to determine the phonon spectrum. An approximation procedure is adopted here which allows some physical conclusions about the phonon spectrum to be obtained from the data and which suggests further experiments.

Bayer[1] suggested that in molecular crystals, torsional oscillations (or hindered rotations) will average crystal field gradients, and hence cause shifts in quadrupole resonance frequencies. He assumed that torsional oscillations of molecules in a crystal about an axis can be characterized by a single frequency, and hence employed an Einstein model. Independent oscillations about three orthogonal axes[18] are possible and so there can be three independent frequencies. A calculation results in the following expressions for the average components of the field gradient $\langle V_{xx}\rangle$, $\langle V_{yy}\rangle$, $\langle V_{zz}\rangle$ in the principal axis system.

$$\begin{aligned}\langle V_{xx}\rangle &= (1-\langle\theta_y^2\rangle-\langle\theta_z^2\rangle)V_{xx}+\langle\theta_z^2\rangle V_{yy}+\langle\theta_y^2\rangle V_{zz},\\ \langle V_{yy}\rangle &= \langle\theta_z^2\rangle V_{xx}+(1-\langle\theta_x^2\rangle-\langle\theta_z^2\rangle)V_{yy}+\langle\theta_x^2\rangle V_{zz},\\ \langle V_{zz}\rangle &= \langle\theta_y^2\rangle V_{xx}+\langle\theta_x^2\rangle V_{yy}+(1-\langle\theta_x^2\rangle-\langle\theta_y^2\rangle)V_{zz},\end{aligned} \quad (1)$$

where V_{xx}, V_{yy}, V_{zz} are the field-gradient components in the absence of any motion (even zero-point motion) and

$$\langle\theta_j^2\rangle=\frac{\hbar^2}{A_j k_B T_{Ej}}\left[\frac{1}{\exp(T_{Ej}/T)-1}+\frac{1}{2}\right];\quad j=x,y,z, \quad (2)$$

where T_{Ej} = Einstein temperature about the j axis, k_B = Boltzmann's constant, and A_j = moment of inertia about the j axis.

Obviously, it is a rather drastic measure to use an Einstein model of torsional oscillations developed for molecular crystals to explain the behavior of a complicated ionic crystal. However, it is argued below that the Einstein model is justified and that torsional oscillations can be tentatively identified with high-wave-number transverse phonons.

First, the Einstein model is a good approximation for all optical modes. There is no way to distinguish between optical and acoustic modes from these measurements. Next, the acoustic modes must be discussed. The averaging of the crystal-field gradient depends only on the relative displacement between neighboring ions. This relative displacement is approximately the same for long- and short-wavelength phonons of a given acoustic branch. Since the density of states for an acoustic branch varies as the cube of the wave number k^3, nearly all the modes are concentrated in the high wave numbers. Each mode is about equally effective and nearly all modes are near the Debye frequency, so an Einstein single-frequency model should be relatively accurate. Moreover, the lowest temperatures reported here are not so far below the Debye temperature that large deviations from the Einstein model are expected.

The connection between torsional oscillations and high-k transverse phonons is most easily seen from a one-dimensional picture, as shown in Fig. 5. The arrows on the ions marked ○ represent the instantaneous displacements for a transverse oscillation at the edge of the Brillouin zone. If ○ is the ion with the heavier mass then this is an acoustic mode, and if ○ is the lighter mass, it is an optical mode.[19] Clearly this motion looks like a torsional oscillation as viewed from the X sites. If the results of this one-dimensional model are taken seriously, then since the La ions are heavier than the F ions, only the transverse optical modes look like torsional oscillations as viewed from a La ion site. The extension of this simple picture to two dimensions is obvious. The extension to three dimensions for a crystal as complex as LaF_3 is not so obvious. While no rigorous argument is available, it is clear physically that high-wave-number transverse phonons and torsional motion are related.

The data are analyzed as though the motions responsible for averaging the crystal field gradient are torsional oscillations. However, vibrations along the principal axes will also cause changes in the average crystal field gradient. The magnitude of the changes due to modes which look like vibrations and torsional oscillations should be comparable provided they are excited. The only reason for reducing the data in terms of torsional oscillations is that the analysis has already been worked out. The correct way to treat the problem is to determine the phonon spectrum, but this is beyond the scope of this paper.

Equation (1) for $\langle V_{xx}\rangle$, $\langle V_{yy}\rangle$, and $\langle V_{zz}\rangle$ can be substituted into the expression for $\langle\eta\rangle$, the average anisotropy parameter defined by

$$\langle\eta\rangle=\frac{\langle V_{xx}\rangle-\langle V_{yy}\rangle}{\langle V_{zz}\rangle}, \quad (3)$$

to yield

$$\langle\eta\rangle\cong\eta\left[1+(\tfrac{1}{2}-(2/\eta)+\tfrac{1}{2}\eta)\langle\theta_x^2\rangle+(\tfrac{1}{2}+(2/\eta)-\tfrac{1}{2}\eta)\langle\theta_y^2\rangle-3\langle\theta_z^2\rangle\right]. \quad (4)$$

The coefficient in front of $\langle\theta_x^2\rangle$ is a negative number. Therefore, $\langle\theta_x^2\rangle\gg\langle\theta_y^2\rangle$ is not compatible with $\langle\eta\rangle$ increasing with temperature. It turns out that it is also impossible to fit the details of the curve if $\langle\theta_x^2\rangle=\langle\theta_y^2\rangle$. The curves for $\langle\eta\rangle$ and $\langle e^2Qq\rangle=eQ\langle V_{zz}\rangle$ or equivalently $\langle V_{zz}\rangle$ and $\langle V_{yy}\rangle$ can be made to fit the data reasonably

[18] T. P. Das and E. L. Hahn, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1958), Suppl. I, p. 40. (The reader must exercise some care because of numerous errors in this section of the book.)

[19] C. Kittel, *Introduction to Solid State Physics* (John Wiley & Sons, Inc., New York, 1959), 2nd ed., p. 111.

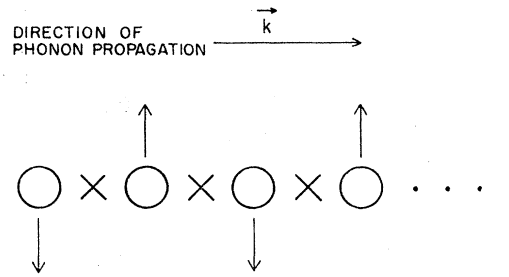

FIG. 5. Drawing of ion displacements for a high-wave-number transverse phonon on a one-dimensional lattice containing two species of ions.

well if $\langle\theta_x^2\rangle \ll \langle\theta_y^2\rangle$ is assumed. It is not certain that this approximation is valid over the entire temperature range investigated since the data are not sufficiently precise. This question would be most easily settled by higher temperature measurements.

The least-squares fit to the $\langle V_{zz}\rangle$ and $\langle V_{yy}\rangle$ curves yield the static lattice values:

$$V_{zz}=5.176\times10^{14}\ \text{statvolts/cm}^2,$$
$$V_{yy}=-4.864\times10^{14}\ \text{statvolts/cm}^2,$$
$$V_{xx}=-0.315\times10^{14}\ \text{statvolts/cm}^2,$$

or

$$e^2Qq/h=18.76\ \text{MHz},$$
$$\eta=0.879,$$

and

$$T_{Ey}=465°\text{K};\quad A_y=1.003\times10^{-40}\ \text{gm cm}^2;$$
$$T_{Ez}=641°\text{K};\quad A_z=0.424\times10^{-40}\ \text{gm cm}^2.$$

These parameters inserted into Eqs. (1) and (2) yield the least-squares fit values for $\langle e^2Qq/h\rangle$, $\langle V_{zz}\rangle$, $\langle V_{yy}\rangle$, and $\langle V_{xx}\rangle$. The electric-field-gradient components are drawn as solid curves in Fig. 4 and it is seen that the agreement is good. The small deviation in the low-temperature region is probably due to the fact that the measurements were not extended far enough below the characteristic temperatures. The fit is expected to be better when lower temperature data are available. The characteristic temperatures T_{Ey}, T_{Ez} lie in the range of temperatures determined from other experiments. However, the moments of inertia A_y and A_z are much smaller than expected. Assuming $A_j=m_Fa_j^2$, where $j=x$, y and m_F is a fluorine mass, then a_j is a distance which should be of the order of a fluorine-lanthanum separation ($\sim$2.3 Å). The numbers which result are $a_y=0.178$ Å and $a_z=0.115$ Å, which are about one order of magnitude too small or A_y and A_z are two orders of magnitude too small. Thus, while the shape of the curves can be made to agree with the measurements, the frequency shifts are much larger than this simple model predicts.

It should first be emphasized that this large enhancement in the rate at which the average crystal field gradient changes is not due to the usual Sternheimer antishielding effect. Classically, the Sternheimer effect corresponds to a distortion of the electron cloud arising from its interaction with the nuclear quadrupole moment and the noncubic crystal field. The distorted electron cloud produces an electric field gradient at the nucleus which is larger (for the heavier nuclei) than the field gradient produced by the presence of the other ions in the lattice. Sternheimer has shown that the field gradients can be enhanced by as much as two orders of magnitude.[6] The distorted electron cloud can be thought of as an electric charge uniformly distributed over the surface of an ellipsoid. In the case of the La^{3+} ion in LaF_3, the axes of the ellipsoid are all different in magnitude. The Bayer analysis treats the torsional oscillations of the ellipsoidal electron cloud as though it were a rigid body attached to the neighboring ions. This leads to Eqs. (1) and (2), which may be written in the form

$$\langle V_{zz}\rangle=V_{zz}[1-K_yf_y(T)], \tag{5}$$

$$f_y(T)=[\exp(T_{Ey}/T)-1]^{-1}+\tfrac{1}{2}, \tag{6}$$

$$K_y=(\hbar^2/A_yk_BT_{Ey})(1-V_{xx}/V_{zz}), \tag{7}$$

where $\langle\theta_x^2\rangle\approx0$. A similar expression can be written for $\langle V_{yy}\rangle$. For a relatively heavy ion such as La^{3+}, the Sternheimer effect causes V_{zz} in Eq. (5) to be larger than the V_{zz} produced by the neighboring ions. While these measurements tend to fit the functional form of Eqs. (5), (6), and (7), a value of K_y is determined which is two orders of magnitude too large. Similarly, K_z is determined to be too large. Since $(V_{xx}/V_{zz})\ll1$ is always valid and T_{Ey} is in reasonable agreement with other measurements,[3-5] the large value for K_y is not due to the static Sternheimer effect but must arise from a dynamic enhancement.

A modification of the simple model which attempts to account for the anomalously large temperature variations in terms of large amplitude motions of the rigid electron cloud can be ruled out. The amplitudes $\langle\theta_y^2\rangle^{1/2}$ and $\langle\theta_z^2\rangle^{1/2}$ implied from the measurements attain values as large as $\approx(\pi/6)$ at the higher temperatures. It is inconceivable that any combination of modes (even if they add coherently) could ever produce such large amplitude motions in the lattice.

There are three separate mechanisms which may lead to large dynamic changes in the crystal field gradient at the La nucleus. Each of these mechanisms for cubic crystals is discussed by Born and Huang[20] and by Wikner, Blumberg, and Hahn.[21] These three are: (A) For long-wavelength optical vibrations, the ions are polarized. The nucleus of an ion, during an oscillation, moves from the center of its electron-charge

[20] M. Born and K. Huang, *Dynamic Theory of Crystal Lattices* (Clarendon Press, Oxford, England, 1954), Chap. II, and references therein.

[21] E. G. Wikner, W. E. Blumberg, and E. L. Hahn, Phys. Rev. 118, 631 (1960).

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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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 5.66×10^{-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 $5.10\times10^{-6}H_0-7.42\times10^{-9}$ ρH_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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