

The low-temperature electrical properties of n -type InAs, measured for the first time in this work, suggest that a pure enough sample of this material should exhibit the electron localization effect in the presence of a strong magnetic field which has been discovered in n -type InSb (sample A).¹¹

¹¹ R. W. Keyes and R. J. Sladek, Phys. Rev. **100**, 1262 (A) (1955).

VII. ACKNOWLEDGMENTS

The stimulating interest of Dr. R. W. Keyes in this work is gratefully acknowledged. Thanks are due to Dr. E. N. Adams for advice and for reading and criticizing the manuscript.

We are indebted to Dr. H. Welker of the Siemens-Schuckertwerke Research Laboratory and to Dr. S. Kurhick of the Chicago Midway Laboratories for providing the material for the samples.

Sodium Nuclear Quadrupole Interactions in NaClO₃ and NaBrO₃†

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 (Received October 8, 1956)

The electric quadrupole splitting of the Na²³ nuclear magnetic resonance has been measured in single crystals as a function of pressure and of temperature for NaClO₃ and as a function of pressure for NaBrO₃. The values for $(1/P)\Delta\nu/\nu$ are $+7.7\times 10^{-6}$ and $+6.0\times 10^{-6}$ kg⁻¹ cm², respectively, and for $(1/T)\Delta\nu/\nu$, -4.2×10^{-4} deg⁻¹. The results suggest that the temperature and pressure dependence of the sodium coupling results mainly from the change with volume of the crystalline field, which also makes an appreciable contribution to the temperature dependence of the chlorine coupling. e^2qQ/h for sodium is found to be 779.2 ± 4 kc/sec in NaClO₃ and 842.4 ± 4 kc/sec in NaBrO₃. In NaClO₃ the electric field gradient at the sodium nuclei varies with volume approximately as V^{-2} indicating the importance of other than simple Coulombic effects.

I. INTRODUCTION

SEVERAL earlier investigations of nuclear electric quadrupole interactions in crystals are particularly pertinent to the present study. Wang *et al.*¹ found the Cl³⁵ pure quadrupole resonance frequency in NaClO₃ to be 29.920 Mc/sec at 26°C; the temperature coefficient of the frequency has also been measured² and corresponds to $(1/T)\Delta\nu/\nu = -1.4\times 10^{-4}$ deg⁻¹. There have been several studies of the effects of hydrostatic pressure, at room temperature, on the Cl³⁵ quadrupole resonance. Livingston³ has given a value of $+0.91\times 10^{-6}$ kg⁻¹ cm² for $(1/P)\Delta\nu/\nu$ in KClO₃ and states that the results for NaClO₃ are very similar. This is confirmed by specific values of $+0.93\times 10^{-6}$ and $(0.93\pm 0.01)\times 10^{-6}$ kg⁻¹ cm² obtained for NaClO₃ by Wang² and by Benedek, Bloembergen, and Kushida.⁴ In addition, the pressure dependence of the chlorine pure quadrupole resonance in *p*-dichlorobenzene has been measured by Dautreppe and Dreyfus.⁵ In all cases, the frequencies increase with pressure.

† Assisted by the Office of Naval Research.

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¹ Wang, Townes, Schawlow, and Holden, Phys. Rev. **86**, 809 (1952).

² T. C. Wang, Ph.D. thesis, Columbia University, 1955 (unpublished).

³ R. Livingston (private communication).

⁴ Benedek, Bloembergen, and Kushida, Bull. Am. Phys. Soc. Ser. II, **1**, 11 (1956).

⁵ D. Dautreppe and B. Dreyfus, Compt. rend. **241**, 795 (1955).

The pressure dependence of the chlorine quadrupole coupling in *p*-dichlorobenzene was ascribed⁶ to an increase in the frequencies of the molecular torsional oscillations. Such thermal vibrations were proposed earlier^{6,7} as the sole mechanism which decreases the coupling upon increasing temperature in molecular crystals. The oscillations average out part of the electric field gradients and reduce the quadrupole coupling by an amount proportional to the mean square displacements. The latter increase with temperature, and decrease with increasing frequency of oscillation and thus with pressure. This model accounts qualitatively for the observations. However, the temperature dependences calculated with the model appear to be invariably smaller than those found experimentally,⁸⁻¹⁰ particularly at higher temperatures. It has been suggested⁹ that this apparent discrepancy results from the temperature dependence of the oscillational frequencies, at least for *p*-dichlorobenzene and *p*-dibromobenzene.

There is also the possibility that some of the effects arise from the contributions of the crystalline field to the field gradients. This contribution would be inversely proportional to the molar volume of the sample and would respond qualitatively to temperature and pres-

⁶ H. G. Dehmelt and H. Krüger, Z. Physik **129**, 401 (1951).

⁷ H. Bayer, Z. Physik **130**, 227 (1951).

⁸ D. W. McCall, Ph.D. thesis, University of Illinois, 1953 (unpublished).

⁹ B. Dreyfus and D. Dautreppe, Compt. rend. **239**, 1618 (1954).

¹⁰ T. C. Wang, Phys. Rev. **99**, 566 (1955).

sure in the manner observed. There is, however, the complication that the thermal vibrations would average out part of the gradients in the crystalline field as well as part of the intramolecular gradients. In a particular solid the relative contributions of the various mechanisms to the temperature and pressure effects depend undoubtedly on the relative contributions of the crystalline and intramolecular fields to the gradients at the nuclei. NaClO_3 is a composite case in that the field gradients at the sodium nuclei result from the crystalline fields of the Na^+ and ClO_3^- ions while the field gradients at the chlorine nuclei occur mainly because of the covalent bonding within the ClO_3^- ion. This type of crystal, with two different atomic species for which the quadrupole coupling can be observed, offers certain advantages in the study of quadrupole interactions. In this research, a comparison of the results for Na^{23} with those for Cl^{35} shows that crystalline field effects contribute to the temperature and pressure dependence of the quadrupole coupling.

II. EXPERIMENTAL

The sodium quadrupole coupling is small so it was observed as a splitting of the Na^{23} nuclear magnetic resonance rather than directly in a pure quadrupole resonance experiment such as that used¹⁰ for chlorine in NaClO_3 . The samples investigated were single crystals of NaClO_3 and NaBrO_3 furnished, respectively, by Dr. Ralph Livingston of the Oak Ridge National Laboratory and Dr. D. W. McCall of the Bell Telephone Laboratories. The crystals employed in the experiments were cubical and about 1 cm an edge.

The magnetic resonance apparatus and cryostat have been described previously¹¹; the permanent magnet with a field of 6300 gauss was used. For Na^{23} , this magnetic field requires a radio-frequency of about 7.1 Mc/sec. The pressure bomb was constructed of austenitic stainless steel with the rf lead introduced through a brass cone with an insulating sleeve of Bakelite. The design of the bomb is conventional¹²; details are given elsewhere.¹³ The hydraulic fluid was Welsh Duo-Seal pump oil. The pressure was developed with a hand pump and was measured with a Bourdon gauge accurate to ± 500 psi.

Two types of experimental procedure were used, one to measure the total Na^{23} quadrupole splitting and the other for the small changes produced in the splitting by the pressure and temperature changes. Na^{23} has a spin of $\frac{3}{2}$ and therefore the quadrupole coupling splits the magnetic resonance into three components.¹⁴ The splitting exceeds the range over which the permanent magnet can be biased conveniently. The splitting was

¹¹ Gutowsky, Meyer, and McClure, *Rev. Sci. Instr.* **24**, 644 (1953).

¹² P. W. Bridgman, *The Physics of High Pressure* (G. Bell and Sons, London, 1949).

¹³ G. A. Williams, Ph.D. thesis, University of Illinois, 1956 (unpublished).

¹⁴ R. V. Pound, *Phys. Rev.* **79**, 685 (1950).

measured by recording the absorption from one satellite as a function of magnetic field at a fixed radio-frequency, and the other satellite at another frequency. The two frequencies were measured and a correction applied for the small difference in magnetic field corresponding to the center of each satellite.

In the pressure and temperature dependence runs, one satellite was observed. The spectrometer was kept at constant frequency by zero-beating with a Collins 51J receiver, the stability of which had been checked against radio station WWV. The absorption of the satellite was recorded as a function of magnetic field, first three or four times at atmospheric pressure, then three or four more at a given high pressure. The atmospheric pressure measurements were then repeated to eliminate any effects of drift in the field of the permanent magnet with changes in room temperature. The pressure effect then corresponds to the differences in position of the center of the resonance from the start of the magnetic field sweep, recorded with and without high pressure. The temperature effects were measured in a similar fashion between 23° and 63°C.

III. RESULTS

In our experiments the magnetic energy was much larger than the quadrupole energy; moreover the electric fields at the sodium nuclei are axially symmetric.^{15,16} The quadrupole splitting of the nuclear magnetic energy levels under these conditions was calculated for a nucleus with $I = \frac{3}{2}$, employing the results of Pound¹⁴ and of Bersohn.¹⁷ The transition energies, to second order, for a given nucleus are

$$E_3 - E_{-3} = \gamma \hbar H_0 \left[1 + \frac{1}{4} (3 \cos^2 \theta - 1) \rho + \frac{3}{8} (\sin^2 \theta \cos^2 \theta) \rho^2 \right], \quad (1)$$

$$E_3 - E_{-1} = \gamma \hbar H_0 \left[1 + \left(\frac{3}{8} \sin^4 \theta - \frac{3}{8} \sin^2 \theta \cos^2 \theta \right) \rho^2 \right], \quad (2)$$

$$E_{-1} - E_{-3} = \gamma \hbar H_0 \left[1 - \frac{1}{4} (3 \cos^2 \theta - 1) \rho + \frac{3}{8} (\sin^2 \theta \cos^2 \theta) \rho^2 \right], \quad (3)$$

where $\rho = e^2 q Q / \gamma \hbar H_0$, θ is the angle between the symmetry axis of the electric field at the nucleus and the direction of applied magnetic field H_0 , eQ is the nuclear electric quadrupole moment in esu cm^2 , eq is the electric field gradient in esu cm^{-3} , and γ is the nuclear magnetogyric ratio.

The magnetic resonance of one nucleus consists of a center component, near $\gamma \hbar H_0$, and two satellites symmetrically placed near $\gamma \hbar H_0 \pm \frac{1}{4} e^2 q Q (3 \cos^2 \theta - 1)$. Therefore, $e^2 q Q$ can be measured by observing the splitting of the satellites, and changes in $e^2 q Q$ can be measured by measuring shifts in the position of one of the satellite lines, providing θ is known. NaClO_3 and NaBrO_3 are isomorphous.¹⁶ The unit cell is a cube, containing four

¹⁵ J. Itoh and R. Kusaka, *J. Phys. Soc. Japan* **9**, 434 (1954).

¹⁶ R. Wyckoff, *Crystal Structures* (Interscience Publishers, New York, 1951), Vol. 1, Sec. VII.

¹⁷ R. Bersohn, *J. Chem. Phys.* **20**, 1505 (1952).

ion pairs. The edges of the unit cells are 6.55 and 6.69 Å, respectively. The Na-Cl and Na-Br directions of the four ion pairs are parallel to the body diagonals of the unit cube and are also the symmetry axes of the electric fields. Thus there is a maximum of twelve possible transitions, three for each of the four different sodium nuclei, for an arbitrary orientation of a single crystal with respect to H_0 .

The absorption spectrum was used to obtain an orientation of the crystals suitable for our measurements. If a (0,1,1) plane is perpendicular to H_0 , two of the Na-X axes make angles of 90° with H_0 , and two make angles of $35^\circ 16'$ or $144^\circ 44'$. This reduces the spectrum to two sets of lines, each with three components. The field of the magnet is horizontal and the bomb was suspended from a vertical rod. The crystal was mounted with one face parallel to the bottom of the bomb, so the orientation desired could be attained simply by rotating the bomb about the mounting axis. As the bomb is rotated the splittings, measured from $\gamma\hbar H_0$, go through a maximum. At this point the four sets of three lines should coalesce into the two sets characteristic of the orientation desired. The outermost satellites are the 90° lines. The 35° lines do not always coalesce, indicating a small deviation between the horizontal face of the crystal and H_0 , usually less than 1° . The effect of this upon the splitting of the 90° lines is smaller than for the 35° lines; it was calculated to be less than 1 part in 1000 which is small compared with other experimental errors.

The 90° satellites are exactly $\pm \frac{1}{4}e^2qQ(3\cos^2\theta - 1) = \mp \frac{1}{4}e^2qQ$ from the center of the absorption, $\gamma\hbar H_0$. The total separation of the satellites is thus $\frac{1}{2}e^2qQ$, which fact was used to determine e^2qQ . The central region of the spectrum for the (0,1,1) orientation has two lines, one the coalesced 90° pair and the other the 35° pair. $\gamma\hbar H_0$ lies above the lower frequency, 35° line by $\frac{5}{8}$ of the separation between the 35° and the 90° line. The values of e^2qQ which were obtained are 779.2 ± 4 kc/sec for NaClO_3 and 842.4 ± 4 kc/sec for NaBrO_3 . Itoh and Kusaka¹⁵ have reported values of 801 ± 8 kc/sec and 864 ± 8 kc/sec.

The measurements of the pressure dependence of the Na^{23} quadrupole coupling in the two single crystals are plotted in Fig. 1. The values found for $(1/P)\Delta\nu/\nu$, the fractional change with pressure of the quadrupole coupling at room temperature, are $7.7 \times 10^{-6} \text{ kg}^{-1} \text{ cm}^2$ and $6.0 \times 10^{-6} \text{ kg}^{-1} \text{ cm}^2$ for NaClO_3 and NaBrO_3 , respectively. The temperature dependence of the Na^{23} coupling in NaClO_3 was observed between 23° and 63°C at atmospheric pressure, giving $(1/T)\Delta\nu/\nu = -(4.2 \pm 0.1) \times 10^{-4} \text{ deg}^{-1}$.

Prior to measuring the pressure and temperature effects, an unsuccessful attempt was made to change the field gradients in NaClO_3 by applying an external electric field. The field gradients necessary to produce an observable interaction with a nuclear quadrupole moment are considerably larger than any which have

been applied in the laboratory. Pound¹⁴ has described an unsuccessful effort to produce artificially an electric quadrupole coupling in a single crystal of KI. NaClO_3 is a more favorable case in that it is piezoelectric and undergoes deformation upon application of an electric field.¹⁸ The deformation produces changes in the field gradients of the crystal which are larger than any gradients which can be produced directly in the applied electric field. However, there was no observable shift at fields up to $20\,000 \text{ volt cm}^{-1}$ in the Cl^{35} pure quadrupole resonance frequency, observed with a super-regenerative spectrometer,⁸ nor in the quadrupole splitting of the Na^{23} magnetic resonance at fields up to $6000 \text{ volt cm}^{-1}$. The observable limit of shifts was about 1 to 2 kc/sec in the Cl^{35} pure quadrupole resonance and about 300 cps in the Na^{23} magnetic resonance.

The piezoelectric effect, at the electric fields we used, produces a deformation corresponding to about 100 atmospheres hydrostatic pressure, so the absence of an observable effect is not surprising in view of the later measurements of the pressure dependence. It does appear that the electric field effects could be detected. It should be possible to go to higher electric fields than we used and also to measure smaller shifts. The latter could be accomplished by plotting the second derivative of the absorption. Moreover, other substances have larger piezoelectric constants¹⁸ and larger quadrupole coupling.

IV. DISCUSSION

The pressure dependence of the sodium quadrupole coupling in NaClO_3 is larger than that in the NaBrO_3 by a factor of 1.3. This appears to be associated mainly

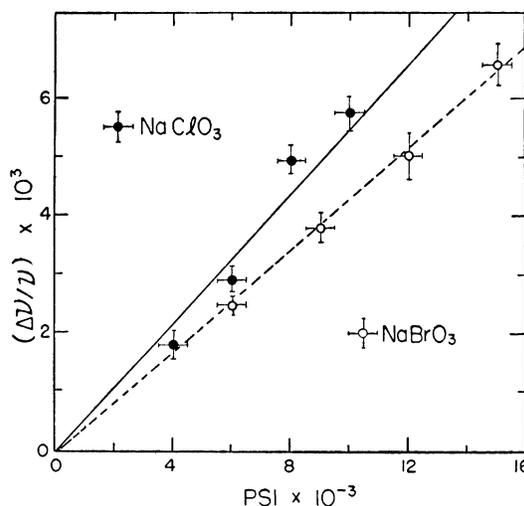


FIG. 1. The fractional change, $\Delta\nu/\nu$, in the quadrupole splitting of the Na^{23} nuclear magnetic resonance observed as a function of pressure at room temperature. The slopes of the lines are $0.54 \times 10^{-3}/1000 \text{ psi}$ and $0.42 \times 10^{-3}/1000 \text{ psi}$ for NaClO_3 and NaBrO_3 , respectively.

¹⁸ W. P. Mason, Phys. Rev. 70, 529 (1946).

TABLE I. The effects of temperature and pressure upon the Na²³ and Cl³⁵ quadrupole coupling in NaClO₃ at 25°C.

Function	Na ²³	Cl ³⁵
$(1/T)(\Delta\nu/\nu)_P$	$-4.2 \times 10^{-4} \text{ deg}^{-1}$	$-1.4 \times 10^{-4} \text{ deg}^{-1}$ ^b
$(1/P)(\Delta\nu/\nu)_T$	$+7.7 \times 10^{-6} \text{ kg}^{-1} \text{ cm}^2$	$+0.93 \times 10^{-6} \text{ kg}^{-1} \text{ cm}^2$ ^b
$(1/T)(\Delta\nu/\nu)_V^a$	$-1.5 \times 10^{-4} \text{ deg}^{-1}$	$-1.1 \times 10^{-4} \text{ deg}^{-1}$

^a Calculated from the observed pressure and temperature dependences using cubical expansion coefficient¹⁹ of $1.32 \times 10^{-4} \text{ deg}^{-1}$ and compressibility¹⁹ of $3.8 \times 10^{-6} \text{ kg}^{-1} \text{ cm}^2$.

^b Values taken from references 2 and 4.

with the difference in the compressibility of the two crystals. The compressibility of NaClO₃ is about¹⁹ $4 \times 10^{-6} \text{ kg}^{-1} \text{ cm}^2$ while that of NaBrO₃ is about^{18,19} $3 \times 10^{-6} \text{ kg}^{-1} \text{ cm}^2$, giving a ratio of 1.35. The close agreement between the ratio of the compressibilities and the ratio of the pressure dependences of the sodium quadrupole coupling is good evidence that the changes in the latter are caused mainly by changes in the crystal-line electric fields with volume. Considerable more data are available for NaClO₃ than for NaBrO₃ and no further discussion is given for the latter.

The various results for NaClO₃ are summarized in Table I. The ratio of the temperature dependence of the sodium coupling at constant pressure to that of the chlorine is 3 while the ratio of the pressure dependences is over 8. This shows that the changes in quadrupole coupling do not arise solely from volume changes and also that different mechanisms are important for the two nuclei. Separation of the contributions from the various mechanisms discussed in the Introduction can be made by extending the calculations of Dautreppe and Dreyfus⁵ to include the effects of volume changes on the crystalline field.

The quadrupole coupling frequency ν is written as a function of the lattice frequencies, ν_i , and of the volume and temperature.

$$\nu = f(\nu_i, V, T). \quad (4)$$

At constant pressure, the temperature dependence is

$$\left(\frac{\partial \nu}{\partial T}\right)_P = \sum_i \frac{\partial \nu}{\partial \nu_i} \left(\frac{\partial \nu_i}{\partial T}\right)_P + \frac{\partial \nu}{\partial V} \left(\frac{\partial V}{\partial T}\right)_P + \left(\frac{\partial \nu}{\partial T}\right)_V. \quad (5)$$

The term $(\partial \nu / \partial T)_V$ represents the pressure- and volume-independent partial averaging out of the field gradients by the lattice oscillations, as proposed in the Bayer model.^{6,7} However, the lattice frequencies themselves change with volume and thus with temperature. This makes $(\partial \nu / \partial T)_V$ different at different volumes; for convenience the effect of this is written separately as the summation term. The middle term represents the change in crystalline fields with volume. The pressure dependence at constant temperature is

$$\left(\frac{\partial \nu}{\partial P}\right)_T = \sum_i \frac{\partial \nu}{\partial \nu_i} \left(\frac{\partial \nu_i}{\partial P}\right)_T + \frac{\partial \nu}{\partial V} \left(\frac{\partial V}{\partial P}\right)_T. \quad (6)$$

Furthermore, for an isotropic crystal, the lattice frequencies depend only on volume, so that

$$\left(\frac{\partial \nu_i}{\partial T}\right)_P = \frac{d\nu_i}{dV} \left(\frac{\partial V}{\partial T}\right)_P \quad \text{and} \quad \left(\frac{\partial \nu_i}{\partial P}\right)_T = \frac{d\nu_i}{dV} \left(\frac{\partial V}{\partial P}\right)_T. \quad (7)$$

Upon substitution in Eqs. (5) and (6), we have

$$\left(\frac{\partial \nu}{\partial T}\right)_P = \left\{ \sum_i \frac{\partial \nu}{\partial \nu_i} \frac{d\nu_i}{dV} + \frac{\partial \nu}{\partial V} \right\} \left(\frac{\partial V}{\partial T}\right)_P + \left(\frac{\partial \nu}{\partial T}\right)_V, \quad (8)$$

$$\left(\frac{\partial \nu}{\partial P}\right)_T = \left\{ \sum_i \frac{\partial \nu}{\partial \nu_i} \frac{d\nu_i}{dV} + \frac{\partial \nu}{\partial V} \right\} \left(\frac{\partial V}{\partial P}\right)_T. \quad (9)$$

Comparison of Eqs. (8) and (9) shows that the Bayer term $(\partial \nu / \partial T)_V$ may be obtained simply by converting the observed constant pressure temperature dependence to constant volume. This was done using the observed pressure dependence, the cubical thermal expansion coefficient¹⁹ and the compressibility.¹⁹ The resulting values for $(1/T)(\Delta\nu/\nu)_V$ are -1.5×10^{-4} and $-1.1 \times 10^{-4} \text{ deg}^{-1}$ for sodium and chlorine, respectively. Thus, of the temperature dependence at constant pressure, 35 and 80% for the sodium and chlorine are caused by the temperature dependence of the amplitudes of the lattice vibrations.

The dependence of the coupling upon volume is determined by changes in ν_i as well as by changes in the crystalline field, as stated in Eq. (9). Of the two terms, that in ν_i is the simplest to analyze. If there is a torsional oscillation about an axis perpendicular to the axis of the field gradient, the resulting fractional change in the quadrupole coupling is given as^{6-8,10}

$$(\nu - \nu_0)/\nu_0 = -\frac{3h}{8\pi^2 I \nu_i} \left(\frac{1}{2} + \frac{1}{\exp(h\nu_i/kT) - 1} \right). \quad (10)$$

ν_0 is the quadrupole coupling at 0°K and I is the moment of inertia associated with the torsional oscillation. Differentiation of Eq. (10) with respect to ν_i gives, upon rearrangement,

$$\frac{\partial \nu}{\partial \nu_i} = \frac{1}{\nu_i} \left[\nu_0 - \nu - T \left(\frac{\partial \nu}{\partial T}\right)_{\nu_i} \right] \cong -\frac{2T}{\nu_i} \left(\frac{\partial \nu}{\partial T}\right)_{\nu_i}, \quad (11)$$

where $(\partial \nu / \partial T)_{\nu_i}$ is the change in the quadrupole coupling produced by the one lattice oscillation ν_i .

To complete the calculation, we need $d\nu_i/dV$. This can be estimated⁹ from the Grüneisen coefficient. Better still, the Raman spectrum and its temperature dependence have been observed²⁰ for NaClO₃. The low-frequency lattice oscillations have temperature coefficients $(1/\nu_i)(\partial \nu_i / \partial T)_P$ of about $-2.5 \times 10^{-4} \text{ deg}^{-1}$ at 25°C. The effects of the different oscillations should be additive, and to the extent that they have the same

¹⁹ S. S. Sharma, Proc. Indian Acad. Sci. 31A, 83 (1950).

²⁰ C. S. Kumari, Proc. Indian Acad. Sci. 31A, 348 (1950).

temperature dependence, we can state that

$$\frac{1}{\nu} \sum_i \frac{\partial \nu}{\partial \nu_i} \frac{d\nu_i}{dV} \left(\frac{\partial V}{\partial T} \right)_P = -2T^{-1} \left(\frac{\partial \nu}{\partial T} \right)_\nu \frac{1}{\nu_i} \left(\frac{\partial \nu_i}{\partial T} \right)_P, \quad (12)$$

where

$$\left(\frac{\partial \nu}{\partial T} \right)_\nu = \sum_i \left(\frac{\partial \nu}{\partial T} \right)_{\nu_i}.$$

The resulting contributions of the temperature dependence of ν_i to $(1/T)(\Delta\nu/\nu)_P$ are -0.23×10^{-4} deg and -0.16×10^{-4} deg $^{-1}$ for sodium and chlorine respectively.

We are now able to calculate $(1/\nu)(\partial\nu/\partial V)(\partial V/\partial T)_P$, the crystalline field contribution to the temperature dependence. The contribution to $(1/T)(\Delta\nu/\nu)_P$ of the Bayer term was found via Eqs. (8) and (9) to be -1.5×10^{-4} and -1.1×10^{-4} deg $^{-1}$ for sodium and chlorine respectively. Subtracting the Bayer term and the contribution of the temperature dependence of ν_i from the values observed for each nucleus, -4.2×10^{-4} and -1.4×10^{-4} deg $^{-1}$, the crystalline field contribution to $(1/T)(\Delta\nu/\nu)_P$ is -2.5×10^{-4} and -0.14×10^{-4} deg $^{-1}$ for sodium and chlorine, respectively.

The field gradients at the sodium no doubt arise in main from the crystalline fields associated with the interionic interactions, even though these fields are averaged out to a considerable extent by torsional oscillations of the ClO_3^- ions and by other lattice motions. Therefore $(1/\nu)\partial\nu/\partial V$ is the fractional change with volume of the crystalline fields at the sodium. To calculate this quantity for chlorine, we would need to know the relative contributions of the crystalline and molecular fields to the total coupling; in general these will not be the same as their respective contributions to the temperature dependence. For sodium, the experimental data lead to a value for $(V/\nu)\partial\nu/\partial V$ of -1.9 . It is encouraging that this value is obtained independently of whether the volume change is from thermal expansion or hydraulic compression. This requires that $\nu \propto V^{-2}$. The dependence of the field gradients upon almost exactly the inverse sixth power of the edge of the unit cube is probably fortuitous in view of the experimental errors and the indirect methods used. None the less, it is clear that the field gradients at the sodium are changed by interactions of fairly high order. The Coulombic fields of ions produce field gradients with a $1/r^3$ dependence for isotropic changes in interionic distances. It thus appears that some other factor is important in NaClO_3 . One possibility is that the interionic repulsions may contribute to the field gradient at the sodium; this contribution would no doubt have a high-order dependence on r . Another possibility is that, upon changing volume, the positions of some of the atoms in the unit cube may be displaced more than others, thereby modifying the $1/r^3$ dependence of the

Coulombic field gradient. This feature of our results will not be considered in detail here, but it does appear to be sufficiently interesting to merit further study.

The most unsatisfactory aspect of the separation made above of the various contributions to the pressure and temperature dependences of the quadrupole coupling is the lack of an independent, experimental check on the results. Similar calculations made for data at several different temperatures are desirable. A partial check can be made by estimating the Bayer term in the temperature dependence of the chlorine coupling from the lattice frequencies. The contribution of a single torsional mode to the temperature dependence is obtained from Eq. (10) to be¹⁰

$$-\frac{1}{\nu_0} \left(\frac{\partial \nu}{\partial T} \right)_{\nu_i} = \frac{3}{2} \frac{\hbar^2}{kT^2 I} \frac{\exp(h\nu_i/kT)}{[\exp(h\nu_i/kT) - 1]^2}. \quad (13)$$

The moment of inertia of the ClO_3^- ion about the axis perpendicular to the symmetry axis is calculated from the x-ray data¹⁶ to be 8.30×10^{-39} g cm 2 .

A detailed assignment of the lattice modes has apparently not been made; but the frequencies have been observed²⁰ and classified as to species. The E species vibrations, at 76.5, 127, and 179 cm $^{-1}$, are doubly degenerate with respect to the four three-fold axes of the crystal and thus appear to be the oscillational modes which would be most important in averaging out the field gradients. The 76.5-cm $^{-1}$ frequency, when introduced in Eq. (13), gives more than twice the temperature dependence observed, which suggests that this frequency corresponds to motions mainly of the Na^+ ions. The other two frequencies give a combined effect of -1.25×10^{-4} deg $^{-1}$ which compares favorably with the observed value of -1.1×10^{-4} deg $^{-1}$.

Little can be said about the Bayer term for Na^+ . If the field gradient at the sodium is developed by the polarization of the ion by interactions with the ClO_3^- ion the torsional oscillations of the ClO_3^- would have about the same effect on the field gradients at the sodium as those at the chlorine. There would also be a contribution from the 76.5 cm $^{-1}$ frequency to make the total Bayer term for sodium larger than that for chlorine, as observed. This is in good agreement with experiment as one could expect without a more detailed consideration of the lattice modes.

ACKNOWLEDGMENTS

We wish to thank Dr. R. Livingston, Dr. D. W. McCall, and Dr. A. N. Holden for supplying the single crystals. Professor H. G. Drickamer furnished the pressure pump and gauge as well as a very generous amount of encouragement and advice on the pressure experiments.