

Nuclear Resonance of Nb^{93} in KNbO_3 [†]

R. M. COTTS AND W. D. KNIGHT

Department of Physics, University of California, Berkeley, California

(Received July 8, 1954)

The nuclear resonance of Nb^{93} in a single crystal of KNbO_3 has been studied in magnetic fields of approximately 5000, 100, and zero oersteds, and at temperatures between -196°C and $+460^\circ\text{C}$. The quadrupole splitting of the magnetic resonance line in strong fields is found to be a sensitive function of crystal structure and, hence, of temperature. Temperatures of the phase transitions found in this way at about -50 , $+220$, and $+430^\circ\text{C}$ are in agreement with other known data for this substance. The splitting $\Delta\nu$ of one satellite line is a continuous function of temperature between 220 and 430°C ; near 430°C $\Delta\nu$ changes abruptly, indicating a first-order phase change. Below the Curie temperature (430°C) KNbO_3 is ferroelectric, with noncubic crystal structure. Above 430° it is cubic and a single resonance line is observed.

Four lines have been identified in the pure quadrupole spectrum in zero magnetic field, and at 20°C . From the four frequencies the quadrupole coupling constant and asymmetry parameter are evaluated to be 23.1 Mc/sec and 0.80, respectively. At -196°C , the frequencies are different from the room temperature values, and the quadrupole coupling is evaluated to be 16.0 Mc/sec and the asymmetry parameter 0.0, the latter appropriate to the rhombohedral crystal structure at this temperature. The Zeeman effect in magnetic fields up to about 100 oersteds is shown to be an aid in identifying the absorption lines and in locating the principal axes of the crystalline electric field gradient. The value of the quadrupole coupling constant is consistent with the existence of a strong covalent character in the chemical bonding to the Nb.

I. INTRODUCTION

PRIOR to the present experiments,¹ the crystal structure of KNbO_3 was studied extensively by both x-ray and optical means,² and four modifications of the perovskite structure (Fig. 1) are known. These are, in order of decreasing temperature, cubic, tetragonal, orthorhombic, and rhombohedral, where one may think of the latter three modifications as being respectively generated by elongations along an edge, face diagonal or body diagonal of the cell shown in Fig. 1. The transition temperatures are about 430, 220, and -50°C . In addition, a large body of data on the electrical properties of this substance is available. Below the Curie point (430°C) it is ferroelectric, and discontinuities in the dielectric constant appear at the three transition temperatures.^{3,4} Around each transition temperature the measured dielectric constant shows a marked hysteresis, and latent heats of transition are observed.⁴ It is known further that a natural twinning² during growth of the crystal prevents one from obtaining a large crystal of one domain only. Thus, any measurements of electrical properties on single crystals are somewhat complicated.

Now, although a good deal of theoretical work⁵ has been done in an attempt to understand the microscopic local field which results in the spontaneous polarization in such ferroelectrics, the theoretical treatments are limited by lack of direct experimental information about the polarizing forces. It is generally agreed that

the ferroelectric state is associated with a displacement of the central ion (in this case Nb) from the center of symmetry of the surrounding oxygen octahedron. This is a complicated cooperative phenomenon, and depends on the potential well affecting the central ion; the surrounding oxygen ions are also supposed to be polarized in such a way as to enhance the Nb polarization by a Lorentz type of local field interaction. Whether or not it is possible to describe this interaction accurately will depend to a large extent on whether or not direct experimental evidence can be found not only for the geometrical displacement of the Nb ion in the crystal, but also for the electrical forces actually causing this displacement.

Since the measurement of the coupling between the nuclear quadrupole moment and the crystalline field gradient should be helpful in this respect, we have undertaken the present series of experiments on the nuclear magnetic resonance (NMR) and the nuclear quadrupole resonance (NQR) in hopes of shedding light

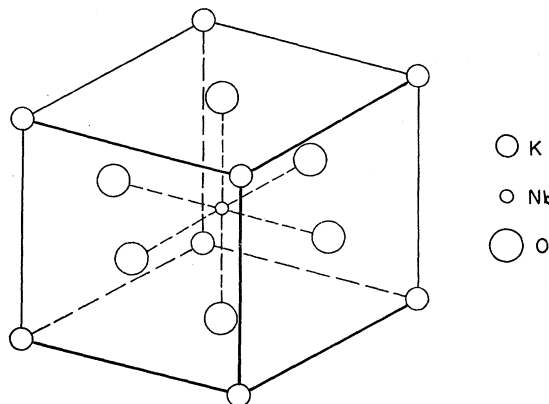


FIG. 1. The perovskite structure.

[†] Supported in part by the Office of Naval Research.

¹ R. M. Cotts and W. D. Knight, Phys. Rev. **93**, 940 (1954); W. D. Knight, Phys. Rev. **94**, 1408 (1954).

² E. A. Wood, Acta Cryst. **4**, 353 (1951).

³ B. T. Matthias and J. P. Remeika, Phys. Rev. **82**, 727 (1951).

⁴ Shirane, Danner, Pavlovic, and Pepinsky, Phys. Rev. **93**, 672 (1954).

⁵ See, for example, E. T. Jaynes, *Ferroelectricity* (Princeton University Press, Princeton, 1953).

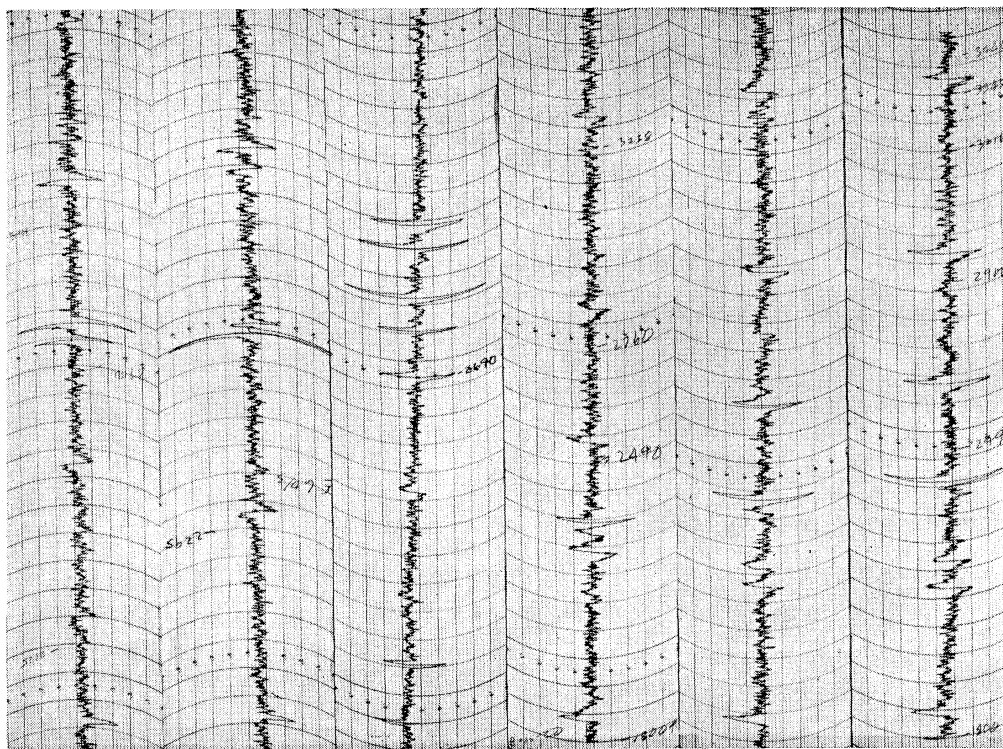


FIG. 2. Nuclear magnetic resonance absorption peaks at several orientations of a single crystal of KNbO_3 . The limits of the spectrum are from about 6 to 8 Mc/sec.

on the problem. To be sure, the interpretation of these results will not be an easy matter, but one may, as we shall show, reasonably expect to extract results which will roughly indicate the relative strength and direction of bonding to the Nb ion in the crystal. The difficulties are briefly the following: The quadrupole coupling constant $e^2qQ/h = (\partial E_z/\partial z)/h$ and asymmetry parameter $\eta = (\partial E_x/\partial x - \partial E_y/\partial y)/(\partial E_z/\partial z)$ are evaluated directly in the experiments, but in order to calculate $eq = \partial E_z/\partial z$, one needs to know Q for the Nb nucleus. At present no experimental value is available and one can only estimate^{6,7} the value for Q . Furthermore, even if the Q were known exactly, the interpretation of the $\partial E_z/\partial z$ is difficult because a complete theory for the wave functions involved in the covalent bonding in such a crystal is not available; nor is the extent of the distortion of the ion core known. Even so, we hope to show that this new approach to the ferroelectric problem can give unique and valuable information.

Following a description of the apparatus, we shall discuss successively the nuclear resonance experiments on KNbO_3 in a strong magnetic field, first as the crystal is rotated in the field, and then as the temperature is changed. This is followed by a description of the experiments in zero magnetic field at two temperatures, and finally in small fields of the order of 100 oersteds at room temperature as the crystal is rotated.

⁶ Townes, Foley, and Low, Phys. Rev. **76**, 1415 (1949).

⁷ K. Murakawa and T. Kamei, Phys. Rev. **92**, 325 (1953).

II. APPARATUS

A Pound spectrometer⁸ was used as a detector of both the NMR and NQR. The NMR of Nb^{93} was observed in a permanent magnet field of 5250 oersteds⁹ which was sine wave modulated at 100 cps with an amplitude about equal to one-half the resonance line width. Temperatures up to 460°C were reached in a stainless steel Dewar with a power dissipation of 70 watts in a heater coil which was wound around the rf head. For low-temperature work, the space below the heater was partially filled with liquid nitrogen and the current through the heater coil was adjusted to obtain an intermediate steady-state temperature.

The 29-turn rf-coil (12.5 mm in diameter and 20 mm long) was held together with Sauer Eisen cement, and was suspended by two 0.100-in.-diameter ceramic tubes which fit inside two 0.125-in.-diameter stainless steel tubes extending downward from the top of the Dewar. One end of the coil was grounded to the tubing and the other ran through the ceramic piece, thus forming a coaxial line. Leads to the heater were carried in double-hole ceramic insulators from the top of the Dewar. Iron and constantan thermocouple wires extended down the inside of a third tube which held the sample crystal in the coil. Because of the magnetic effects of the iron,

⁸ R. V. Pound and W. D. Knight, Rev. Sci. Instr. **21**, 219 (1950).

⁹ The field was about 7000 oersteds during the rotation experiments. For most of the other high-field experiments, the gap was increased, which resulted in the lower field of about 5000 oersteds.

the thermocouple was kept about 1 cm above the coil and crystal during a run. A separate calibration run was performed later to determine temperature at this location in terms of the temperature in the sample.

The NQR was modulated by an on-off antisymmetric square wave H -field¹⁰ of about 100 oersteds amplitude.

Small dc fields for Zeeman splitting were generated by two coils of 9-in.-diameter, spaced 4.5 in. apart. The rf coil, shield, and modulating coils were mounted together as a unit on a turn table between the Zeeman coils. With this arrangement, the angle between the crystal axes and the modulating coils was kept constant at an orientation of the modulating field most effective in splitting the line.

III. ROTATION SPECTRUM IN STRONG MAGNETIC FIELDS

The energy levels for a nucleus of spin $9/2$ in strong magnetic fields have been calculated to the third order of perturbation.¹¹ However, explicit expressions for the orientational dependence have not yet been deduced beyond the second order. One expects in general to see $2I=9$ absorption lines, unequally spaced with respect to the unperturbed Larmor frequency, where the frequencies of all components will vary in a complicated way with the orientation of the crystal in the magnetic field. Furthermore, the relative intensities are expected to be functions of orientation. Since the Larmor frequency in a 7000-oersted field will be about 7000 kc/sec, and the absorption spectrum (see Fig. 2) extends over a 2000–3000 kc/sec range, one expects that any evaluation of the quadrupole coupling must be made on the basis of a third-order theory. It was,

in fact, found that second-order calculations do not agree with the experimental results. Figure 3 shows the results of a 180° rotation of the crystal at 5° intervals, where the polar axis (assumed tentatively to coincide with the axis of symmetry of the crystalline field gradient tensor) was at right angles to the axis of rotation, the latter being perpendicular to the external magnetic field. The following qualitative features are to be noticed. Figure 3 shows two groups of 9 lines which tend toward a partial convergence near 7.2 Mc/sec which is the Larmor frequency. The convergences occur at angles of approximately 70° and 140° of the chosen polar axis with respect to the magnetic field. We see, further, that three pairs of lines, one of each pair apparently being associated with each of the domain twins, cross at 100° . This crossing apparently represents respective orientations for the two domains for which the quadrupole perturbations are the same. The above result is consistent with that of Mrs. Wood,² that the crystals are predominantly of only two domains.

Since any more detailed examination of the above results seemed too difficult to warrant the necessary labor involved, we temporarily abandoned the high-field rotation experiments (until a larger magnetic field is available) in favor of three other lines of investigation. First, it was clear from the results shown in Figs. 1 and 2 that the quadrupole splittings are large enough to allow a measurement of the effects of thermally induced changes in crystal structure which produce appropriate variations in the crystalline field gradient. Thus, if the lattice parameter changes continuously as a function of temperature in a given crystal phase, the quadrupole splitting should exhibit a corresponding

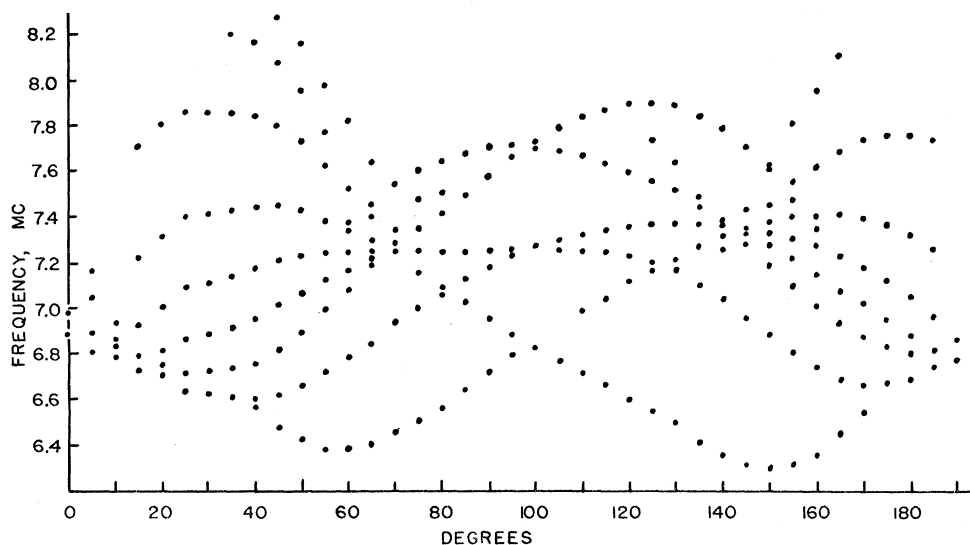


Fig. 3. Rotation pattern for a single crystal of KNbO_3 . Each circle represents an absorption peak. Zero degrees represents an orientation for which the polar axis is parallel to the magnetic field. The rotation is made about an axis perpendicular to the dc magnetic field but parallel to the oscillating (rf) magnetic field.

¹⁰ F. Reif and E. M. Purcell, Phys. Rev. **91**, 631 (1953).

¹¹ R. Bersohn, J. Chem. Phys. **20**, 1505 (1952).

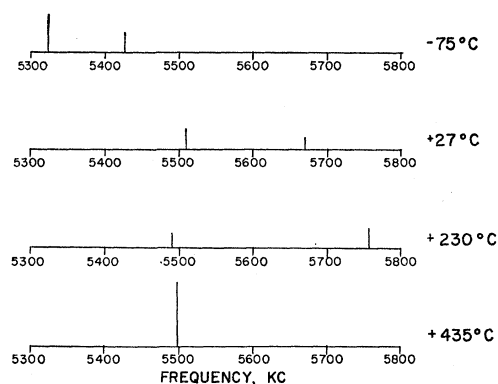


FIG. 4. Partial magnetic absorption spectrum of KNbO_3 at four different temperatures, showing the effects of crystal structure on the quadrupole splitting.

behavior. Also, if the lattice parameter changes more abruptly at a phase transition, the quadrupole splitting would be expected to behave accordingly, the sharpness of the transition being easily observed as a function of temperature in this way. It was clear at the outset that any such changes would be meaningful, even if the value of the quadrupole coupling constant for the crystal was not known. *Second*, the quadrupole splitting seemed large enough so that one could predict that a successful observation of the NQR in zero magnetic field would be possible. In the absence of a strong magnetic field the number of absorption lines to fit into the theoretical spectrum would be smaller (i.e., 4) and the effects of domain structure should become less important. *Third*, the application of a small Zeeman field should split the NQR lines in a predictable way and, except for ambiguities introduced because of the crystal twinning, allow verification of the energy levels and of the principal axes of the crystalline field gradient.

IV. PHASE TRANSITIONS—STRONG-FIELD RESULTS

As we have pointed out previously, the quadrupole coupling should be sensitive to the crystal structure and hence to the temperature. The experiments proceeded as follows. Part of the Nb^{93} NMR spectrum was recorded for a single crystal of KNbO_3 in a magnetic field of 5250 oersteds. The crystal was orientated so that at least two strong lines appeared near the Nb Larmor frequency. Then both the intensities and frequencies of these lines were measured. It was not

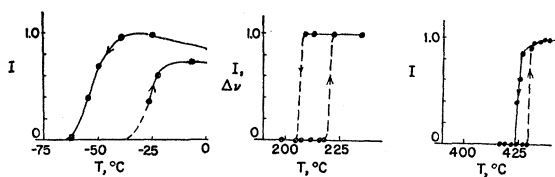


FIG. 5. Hysteresis effects in the KNbO_3 magnetic absorption spectrum near the three phase transitions.

necessary to scan the whole Nb spectrum since any change in the quadrupole coupling would, of course, affect all the lines in the spectrum. At temperatures between phase transitions, the splittings of the lines were observed, while at both sides of the -50°C transition and the low-temperature side of the 430°C transition a combination of change in intensity and frequency occurred. At the -50°C transition the change occurred over a temperature range wide enough to allow measurement of an increase in intensity of lines appropriate to the new phase while the corresponding decrease was measured in lines of the old phase. The crystal was assumed to be in thermal equilibrium during these measurements. At both sides of the 220°C transition and the high-temperature side of the 430°C transition the structure change occurred in range of temperature so small that the intermediate intensities were not seen. Then the change in frequencies alone served as an indicator of phase transitions. The magnitude of frequency changes in the spectrum can be seen in Fig. 4.

In Table I will be found comparative data on the transition temperatures as found by x-ray, optical,² and dielectric measurements,^{3,4} and in our experiments.

TABLE I. Phase transition temperatures ($^\circ\text{C}$) in KNbO_3 as measured by various methods.

| Method | rhombohedral— | orthorhombic — | tetragonal — | cubic |
|----------------------------------|---------------|----------------|--------------|-------|
| X-ray, optical ^a | — | — | 225 | 435 |
| Dielectric constant ^b | —55 to —10 | 210 to 220 | 410 to 435 | |
| Nuclear magnetic resonance | —52 to —27 | 207 to 222 | 426 to 431 | |

^a See reference 2.

^b See references 3 and 4.

The rhombohedral-orthorhombic transition occurs upon heating at -27°C and the reverse transition occurs upon cooling at -52°C . Here the intensity of the absorption lines was used as a criterion of structure change. The temperatures were held constant to $\pm 2^\circ\text{C}$ or better during the runs, which were 20 to 30 minutes long. The line intensity changes gradually over about a 12° range upon heating and about a 20° range upon cooling. This is in contrast to abrupt changes in the dielectric constant seen at this transition.⁴ A plot of line intensity vs temperature appears in Fig. 5.

This transition showed a peculiar annealing effect. At room temperature, the spectrum (a) in Fig. 6 was seen. When the crystal was cooled to -196°C , spectrum (b) was observed. The crystal was then warmed rapidly to room temperature and spectrum (c) was observed. The original (a) spectrum had vanished and a vestige of the (b) spectrum remained, indicating that the low-temperature rhombohedral phase persisted in part. The room-temperature orthorhombic phase is not visible in (c). The crystal was then recooled to -196°C and the spectrum (b) appropriate to the rhombohedral

phase reappeared. Then, when the crystal was heated *slowly* to room temperature, the rhombohedral spectrum disappeared and the original orthorhombic spectrum (a) reappeared in (d) with reduced intensity. The crystal was originally clear, but the above treatment produced a cloudy appearance indicating the presence of gross imperfections in the crystal. The crystal was then used for observations of high-temperature phase transitions where this annealing effect was not observed.

After the high-temperature runs were completed, the exact -50°C transition temperatures were measured. Repeated thermal cycling through this transition increased the cloudiness and actually caused minor splittings in the crystal surface. The persistence of the rhombohedral pattern above -50°C was not again observed after the first runs shown in Fig. 6. Apparently a serious fracturing took place throughout the crystal so that it never completely regained the original structure it had before the first cooling to -196°C .

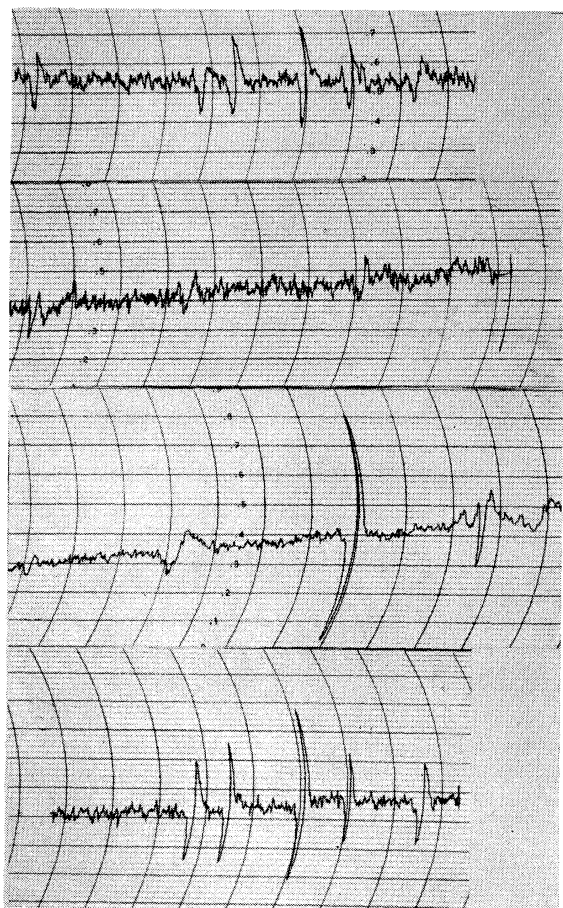


FIG. 6. Partial magnetic absorption spectrum at a single orientation and at temperatures above and below the orthorhombic-rhombohedral transition. (a) 27°C , (b) -196°C , (c) 27°C after rapid heating, (d) 27°C after recooling to -196°C and subsequent slow heating.

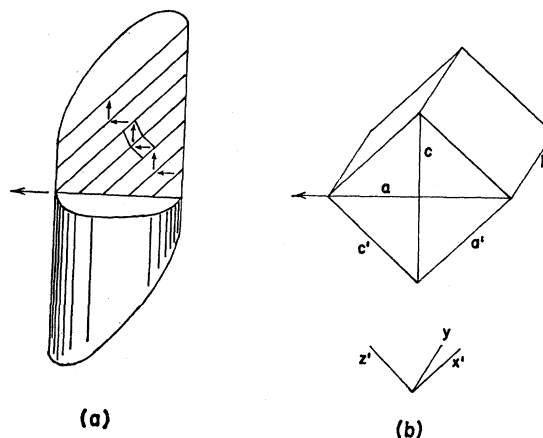


FIG. 7. (a) Cut-out section of the single crystal II, showing direction of laminar twinning. Arrows indicate the polar direction. Two adjacent unit cells are also indicated. (b) Orthorhombic unit cell referred to monoclinic axes a, b, c, a', c' include the obtuse angle $90^\circ 21'$, not drawn to scale here; a and c are orthorhombic cell edges.

The orthorhombic-tetragonal transition, Fig. 5, occurs at $222^\circ \pm 3^\circ\text{C}$ upon heating and at $207^\circ \pm 3^\circ$, on cooling. Here the line intensities change less gradually than in the -50° transitions. Within a range of 5°C , the new lines appeared at full strength and the old lines disappeared. In these runs, the temperature was held constant to $\pm 2^\circ$ and did not vary faster than about $0.2^\circ\text{C}/\text{min}$. Each run required several minutes.

The transition at the Curie point occurs at $430 \pm 1^\circ$ upon heating and at $425 \pm 2^\circ$ upon cooling (Fig. 5). The spectrum changes were observed while the temperature changed less than 1°C per minute. Upon heating, the transition covers a range of less than 2°C and, upon cooling, the transition covers a range of about 7°C .

Since considerable importance may be attached to the behavior of the crystal over the whole temperature range of a single phase, the splitting $\Delta\nu$ of one satellite line from the Nb NMR frequency was measured as a function of temperature throughout the tetragonal phase. $\Delta\nu$ was found to be a smoothly varying function of T up to within 5° of the Curie temperature, in which range about 50 percent of the change in $\Delta\nu$ occurs. This rapid change indicates a discontinuity in ∇E and we therefore suppose that the Curie-point transition is a first-order transition.

It will be interesting to compare the relative change in $\Delta\nu$ with the lattice-constant values $(c/a-1)$ and with values of spontaneous polarization in the tetragonal phase, when reliable values of c/a and P_s are available.

V. PURE QUADRUPOLE SPECTRUM

The pure NQR was observed in the crystal (I) described in Sec. IV as well as in another single crystal (II) which had not been subjected to the fracturing effects of the -50°C transition. Crystal II was placed

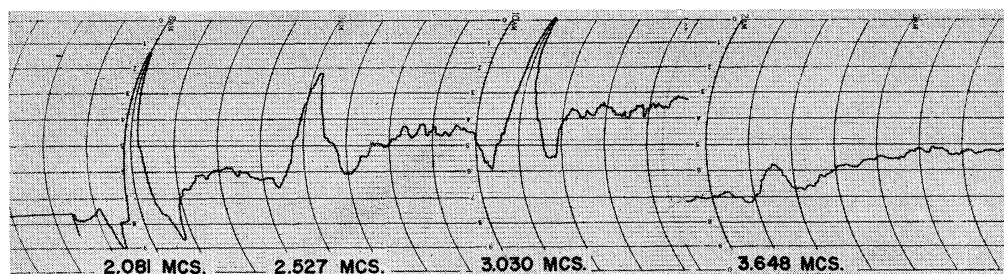


FIG. 8. The pure nuclear quadrupole resonance absorption spectrum at 25°C. The lines are labeled A through D in Table II in order of increasing frequency. The symmetrical wings on the negative side of the no-resonance trace are caused by absorption when the modulating field is on.

in the rf coil with the polar direction, shown in Fig. 7(a), perpendicular to the axis of the coil. In the unfractured crystal II, four lines, Fig. 8, appropriate to a spin of $9/2$, were found at the frequencies given in Table II. The temperature of the crystal was slightly higher than 25°C because of heat generated by the modulating current. A small-temperature coefficient for the resonance frequencies was noticed and is now being studied.

The measured frequencies were fitted to a graph of frequency ratios *vs* axial asymmetry parameter η , and the energy levels for $I=9/2$ as calculated by Cohen¹² (Fig. 9) were used to plot Fig. 10. In Fig. 10 the ratio of the second-lowest frequency to the lowest frequency was plotted as one line. This procedure was followed for each pair of lines at successively higher frequencies. The transition frequencies associated with each ratio are shown on the graph. The measured frequency ratios intersect the calculated ratios in a straight line at constant $\eta=0.806\pm0.002$. From the measured frequencies and the energy-level parameter of Cohen, the quadrupole coupling constant is found to be $e^2qQ/h=23.120\pm0.05$ Mc/sec. With the fit of measured and calculated frequency ratios, the transitions can be identified. The identification is shown in Table II. These lines correspond to $|\Delta m|=1$. Possible $|\Delta m|=2$ lines would be predicted¹² at 4.62 and 5.14 Mc/sec

with lower intensities. However, careful search over the range from 3.7 to 5.7 Mc/sec did not show these lines.

The NQR in the rhombohedral phase was observed in crystal I at -196°C . Before cooling this crystal, the fractured one, the NQR was observed at room temperature and found to agree with crystal II, which has never been taken through the -50°C phase transition. At -196°C , absorption lines are seen in crystal I at 2.674, 2.004, and 1.335 Mc/sec. In this phase $e^2qQ/h=16.0\pm0.1$ Mc/sec and $\eta=0.0$. These three lines fit the frequency ratio chart at $\eta=0$ and do not fit consistently elsewhere. There should also be another line of low intensity at about 0.670 Mc/sec, but this line has not as yet been definitely observed. The signal-to-noise ratio at this frequency is expected to be about unity and a series of attempts to improve the signal were not successful, although some evidence for an absorption around 0.68 Mc/sec was found. A value $\eta=0$ is consistent with the coincidence of the polar axis and the ∇E principal axis in a rhombohedral symmetry.

Experiments on the NQR in the tetragonal phase are under way and will be reported on elsewhere.

VI. WEAK-FIELD ZEEMAN EFFECT

The identification of the principal axes of ∇E is complicated by the twinning of the crystal. The principal axes are identified in NQR from the orientational dependence of line intensity or of the Zeeman splitting of the lines, but any estimate of the relative contribution of each twin to the line intensity is complicated by the fact that the fraction of the total crystal occupied by each twin is not known.

When a small perturbing magnetic field H_0 is applied, each line is split into four components. The magnitude of the splitting is different for each twin, so that there could be eight components for each absorption line in the NQR in small H field. Because of the low intensity and breadth of the lines, all eight components have not been resolved for any one line, although as many as four have been observed.

The transition having the simplest Zeeman dependence is the $(9/2, 7/2)$ 3.65-Mc/sec line. Although this is the weakest line of the four, a measurable symmetric

TABLE II. Identification of zero field nuclear quadrupole spectrum of Nb^{93} in KNbO_3 .

| Crystal structure | Line | Frequency (Mc/sec) | Measured ratio | Calculated ratio $\eta=0.806$ | Identification |
|-------------------|------|--------------------|----------------|-------------------------------|----------------|
| Orthorhombic | D | 3.648 | 1.204 | 1.204 | $(9/2, 7/2)$ |
| | C | 3.030 | 1.198 | 1.196 | $(3/2, 1/2)$ |
| | B | 2.527 | 1.214 | 1.213 | $(7/2, 5/2)$ |
| | A | 2.085 | | | $(5/2, 3/2)$ |
| Rhombohedral | H | 2.674 | | $(\eta=0.0)$ | $(9/2, 7/2)$ |
| | G | 2.004 | 1.335 | 1.333 | $(7/2, 5/2)$ |
| | F | 1.335 | 1.503 | 1.500 | $(5/2, 3/2)$ |

¹² M. H. Cohen, preceding paper [Phys. Rev. **96**, 1278 (1954)].

splitting was observed. For $I=9/2$ and $\eta=0.8$ as for Nb in KNbO_3 , Cohen's results may be used to show that the Zeeman splitting for the $(9/2, 7/2)$ transition has essentially only θ dependence, where θ is the angle between the Zeeman field H_0 and the z principal axis of ∇E . The calculation gives

$$|\Delta\nu| = (g\beta H_0/h)(4.47 \pm 3.34) |\cos\theta|$$

as the splitting from the pure NQR. The + and - signs go with the outer and inner satellites, respectively. For Nb^{93} , $g\beta/h = 1.045$ Kc/sec/oersted. In a dc field of 89 oersteds, the inner satellite lines followed the relation,

$$|\Delta\nu| = (100 \pm 6) |\cos\theta| \text{ Kc/sec,}$$

which is within 6 percent of the predicted dependence at all angles. Analysis shows that the z principal axis of ∇E lies within 5° of the plane $a'c'$ in Fig. 6 and within 20° of the polar direction of the crystal. This Zeeman pattern was somewhat complicated by an outer component of the $(3/2, 1/2)$ transition which, for this H_0 , lies near the $(9/2, 7/2)$ frequency. This satellite, which was of low intensity and tended to broaden the $(9/2, 7/2)$ lines, was a major cause of uncertainty in the assignment of the direction of the z axis of ∇E .

If the polar direction of one domain is the z direction, the z direction of the other domain will always be at 90° with respect to H_0 and the modulating field for the axis of rotation used. Thus the absorption line from the latter domain is not split by either Zeeman or modulation fields, and is not seen at all.

Attempts to analyze the splitting of other lines have so far proved unsatisfactory. No Zeeman splittings have yet been tried in the rhombohedral phase.

VII. LINE WIDTHS

Above the Curie point the structure is cubic and, as would be expected, the quadrupole interaction is drastically reduced and a single resonance line is seen at the Nb NMR frequency. The intensity of this absorption line is about 5 times as large as the individual lines in the tetragonal phase. The line width, measured between peaks of the derivative of the absorption, is 5.0 ± 0.5 kc/sec, which is about half the line width observed in the tetragonal phase. Because the line is narrower and the quadrupole interaction is greatly reduced, one would expect a greater intensity increase than a factor of 5. It is expected that imperfections and strains in the crystal resulted in enough random quadrupole interactions to "wash out" some of the signal.

The calculated magnetic dipolar width given by the formula of Van Vleck¹³ is from 1.6 to 3.6 kc/sec, depending upon the orientation of the crystal axes. Since an arbitrary orientation was used, the direction of the crystal axes was not known. The observed extra width is partially attributed to random static quadrupole

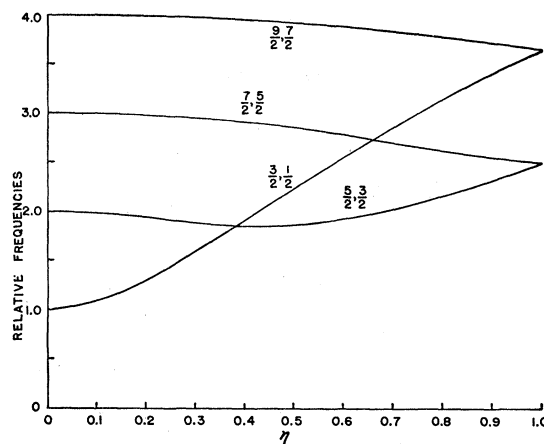


FIG. 9. Pure quadrupole absorption frequencies calculated as a function of the asymmetry parameter, η . (See reference 12.) The ordinates are in units of $6e^2qQ/4I(2I-1)h$.

pole interactions from crystal imperfections. Also, since the resonance could not be saturated with the available rf power from the spectrometer, it is assumed that the spin-lattice relaxation time T_1 is rather short, and that there is probably a line-width contribution from the relaxation mechanism. The contribution to T_1 from thermally induced random quadrupole interactions¹⁴ has been estimated, and this is in reasonable agreement with the observed width, which indicates that T_1 at 450°C is perhaps as short as 10^{-4} sec. The large intensity of the lines at -196°C [Fig. 6(b)] is also evidence for the existence of a strong spin-lattice relaxation mechanism.

The line widths in zero field were found to be three to four times the widths at 5000 oersteds. In the orthorhombic phase the zero field widths at half maximum were 27 kc/sec, 45 kc/sec, 30 kc/sec, 45 kc/sec for lines A, B, C, D, respectively, in Table I, and in the

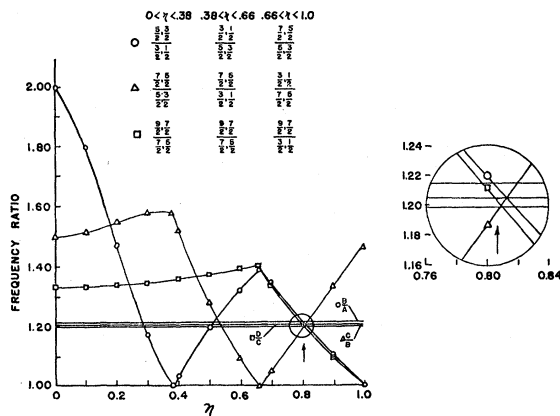


FIG. 10. Determination of the asymmetry parameter, η , from measured frequency ratios. The insert at the right is an expanded view in the region of $\eta=0.8$.

¹³ J. H. Van Vleck, Phys. Rev. 74, 1168 (1948).

¹⁴ N. Bloembergen, *Nuclear Magnetic Relaxation* (Martinus Nijhoff, The Hague, 1948), pp. 118-121.

rhombohedral phase the widths were 25 kc/sec, 30 kc/sec, and 30 kc/sec for the lines *F*, *G*, and *H*. The theoretical problem of NQR line width for spin 9/2 has not yet been solved. Abragam and Kambe¹⁵ show that the NQR line is broader than the NMR line for spins 1 and 3/2, and that there is a greater increase in width over the NMR for the spin 3/2 than for the spin 1 nucleus. The large increase in line width of NQR over NMR which we observed in this experiment might then be expected because of the large spin of Nb, $I=9/2$.

VIII. CONCLUSIONS

We have shown that the quadrupole interaction offers a way of finding and measuring phase transitions in noncubic solids. Furthermore, the measurement of the quadrupole coupling provides a new piece of information, useful in calculations of the microscopic structure of such solids.

With good temperature control, accurate phase-transition temperatures, and associated hysteresis effects can be measured. In addition, information can be gained on the qualitative nature of phase transitions. The quadrupole interaction, being very sensitive to crystal structure, shows whether the transition occurs continuously or discontinuously. A gradual change in quadrupole interaction would indicate a second-order transition, while a discontinuity in the interaction would indicate that the transition was of the first order.

In all of the phase transitions observed the frequency changes and, hence, the quadrupole interaction changes were abrupt. However, the changes in line intensity were not always discontinuous. In the -50°C transition the intensity changed gradually over a range, δT , of about 15°C , Fig. 5. This effect was also seen at the 430°C transition where $\delta T \sim 5^{\circ}\text{C}$. The intensity change in the 220° transition occurred within a 5°C range.

This means that the transition of any given unit cell or small region in the crystal is discontinuous, and that the whole crystal does not change structure at one temperature. If each cell changed continuously with temperature, then the nuclear resonance spectrum would show a gradual shift in frequency at approximately constant intensity. This, as stated above, is not what is observed in KNbO_3 . Therefore, the fact that the transition occurs over a range of temperature δT can be attributed to the fact that different localities of the crystal change at slightly different temperatures. Such a temperature dependence upon the position of a given cell in the crystal could be caused by imperfections in the crystal or, possibly, a temperature gradient in the crystal. If the latter were the determining factor, then one would expect δT to be directly proportional to the gradient in the crystal. Also, the gradient should be, to first approximation, proportional to the difference between the transition temperature and the room temperature. This would give a much bigger δT for the

430°C transition than for the -50°C transition. This certainly is not the case in these measurements.

Local activation energies for nucleation could depend on imperfection concentration. Then if there is some average energy E_I , associated with an imperfection, it will have a greater relative effect on a transition for which the normal activation energy is small. This mechanism would suggest that the temperature range δT decreases as the activation energy increases. The latent heats of these transitions have been measured,⁴ and it is found that the latent heat increases as the transition temperature increases. This would predict a decrease in δT as T increases, in agreement with the observations. Similar arguments may also apply to the widths ΔT of the temperature hysteresis curves.

The problem of accounting for the observed quadrupole coupling for Nb in KNbO_3 in a nearly cubic structure must now be faced. Investigations of atomic hyperfine structure of Nb do not show a deviation from the interval rule because of quadrupole interaction.¹⁶ As yet no upper limit, based on a calculated field gradient in atomic Nb, has been placed on the quadrupole moment of Nb. We estimate however, from the plots of Townes⁶ and of Murakawa,⁷ that Q is of the order of $0.1 \times 10^{-24} \text{ cm}^2$. In order to account for the measured quadrupole coupling in the orthorhombic phase of KNbO_3 , then, the field gradient eq should be about $3 \times 10^{15} \text{ esu/cm}^3$.

Also, any model for this crystal should give an estimate of η and for the direction of the principal axes of ∇E as well as for the magnitude of eq .

In the orthorhombic phase, the calculated field gradient produced a charge of 2 esu in the position of the each six nearest-oxygen neighbors to Nb does not agree with the experimental measurements. The calculated gradient is about $eq \sim 2 \times 10^{13} \text{ esu/cm}^3$, which is too small by a factor of about a hundred. The calculated principal axis of the gradient caused by the oxygens is perpendicular to the rhomb face and the axial asymmetry parameter is about 0.5, neither of which results agrees with experiment. This calculation was made for both a displaced and an undisplaced Nb ion.

Another kind of lattice-point calculation based on the covalent bonding suggested by Megaw¹⁷ was tried. She suggests that Nb forms covalent tetrahedral bonds with the four oxygen atoms nearest to the displaced position of Nb. In this calculation it was assumed that there is an average concentration of charge halfway between niobium and each oxygen atom. Approximately the right magnitude, $2 \times 10^{15} \text{ esu/cm}^3$, for eq results, but the asymmetry parameter, $\eta \sim 0.1$, and the principal axis of ∇E is perpendicular to the rhomb face. So we see that neither of these crude approximations to the measured field gradient fits the observed data at all. An important conclusion to be drawn is that simple lattice-point calculations for ∇E in such a complicated

¹⁵ A. Abragam and K. Kambe, Phys. Rev. **91**, 894 (1953).

¹⁶ W. W. Meeks and R. A. Fisher, Phys. Rev. **72**, 451 (1947); F. A. Jenkins (private communication).

¹⁷ H. Megaw, Acta Cryst. **5**, 739 (1952).

crystal are not capable of giving even qualitative results. Furthermore, it is not expected that a complete lattice-point calculation using appropriate dipole-field factors will be significantly better. It is therefore felt that the large size of the quadrupole coupling which we observe can only be the result of covalent bonding, where the ∇E is generated by valence electrons which penetrate the ion core. Magnification effects¹⁸ may contribute significantly.

It should be pointed out that the large observed quadrupole coupling in the tetragonal phase and the single magnetic resonance line in the cubic phase are inconsistent with the Mason-Matthias¹⁹ model of six equilibrium positions for the central ion.

Perhaps a better correlation between the quadrupole interaction and ferroelectric properties could be made if there were more data available on the ferroelectric properties in the tetragonal phase. A comparison of this interaction, with the lattice constants ($c/a-1$) and with the spontaneous polarization (P_s) would be appropriate. These properties are well known for BaTiO_3 but not for KNbO_3 . The ($c/a-1$) measurements involve extensive x-ray work and the measurement of P_s seems to be inhibited by the high conductivity of KNbO_3 near the Curie temperature⁴ as well as by the twinning.

In order to indicate the range of applicability of the nuclear resonance techniques to problems of this sort, we note that the Curie temperature of NaNbO_3 is not known. (X-ray measurements² indicate a cubic structure above 470°C , while optical data would make this temperature 640°C .) Furthermore, there is evidence

that this substance may be antiferroelectric. Both of these questions can, in principle, be resolved by doing a careful series of nuclear resonance experiments. It will not be easy to do satisfactory experiments on the nuclear resonance in BaTiO_3 . First, it would be necessary to grow crystals containing enriched Ti isotopes. Second, large BaTiO_3 single crystals are usually grown with too much paramagnetic "dope" to expect to see good nuclear resonances. Third, even these crystals are usually in the form of thin plates, which is not convenient for use in the nuclear resonance rf coils.

A study of YAlO_3 would be useful since the nuclear quadrupole moment of Al is known,²⁰ and the quadrupole coupling of Al has been measured^{21,22} in other compounds.

ACKNOWLEDGMENTS

We are happy to express our thanks to Professor C. Kittel, who suggested that we undertake this problem, for many stimulating discussions, and to Dr. M. H. Cohen for his continuing assistance with the theoretical work. We are greatly indebted to Dr. E. A. Wood and Mr. J. P. Reimeika of the Bell Telephone Laboratories for providing us with the KNbO_3 crystals and to Professor A. Pabst of the Department of Mineralogy at the University of California for making an x-ray analysis of a small chip of one of the crystals. Mr. D. F. Abell assisted with some of the measurements on the high-field rotation pattern.

²⁰ Davis, Feld, Carrol, Zabel, and Zacharias, *Phys. Rev.* **76**, 1076 (1949); Hin Lew, *Phys. Rev.* **76**, 1086 (1949).

²¹ R. V. Pound, *Phys. Rev.* **79**, 685 (1950).

²² Hatton, Rollin, and Seymour, *Phys. Rev.* **83**, 672 (1951).

¹⁸ Foley, Sternheimer, and Tycko, *Phys. Rev.* **93**, 734 (1954).

¹⁹ W. P. Mason and B. T. Matthias, *Phys. Rev.* **74**, 1622 (1948).

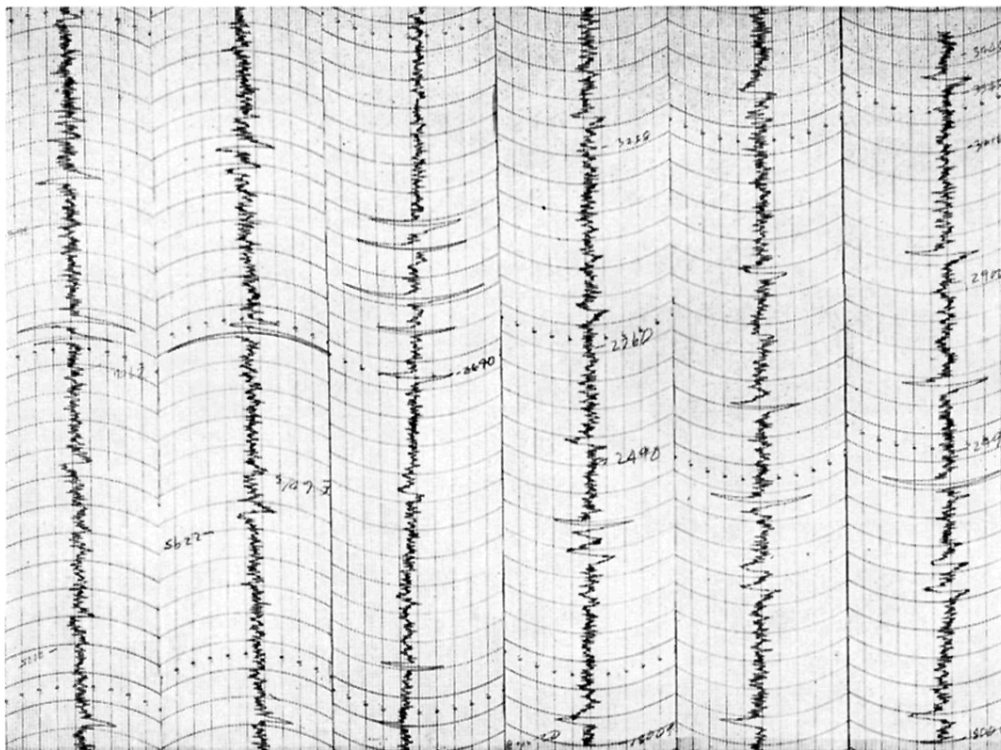


FIG. 2. Nuclear magnetic resonance absorption peaks at several orientations of a single crystal of KNbO₃.
The limits of the spectrum are from about 6 to 8 Mc/sec.

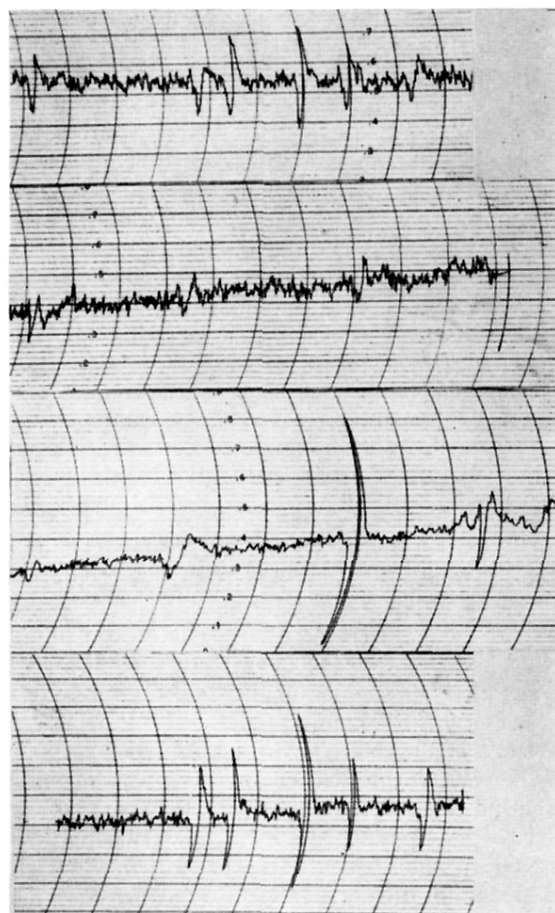


FIG. 6. Partial magnetic absorption spectrum at a single orientation and at temperatures above and below the orthorhombic-rhombohedral transition. (a) 27°C , (b) -196°C , (c) 27°C after rapid heating, (d) 27°C after recooling to -196°C and subsequent slow heating.

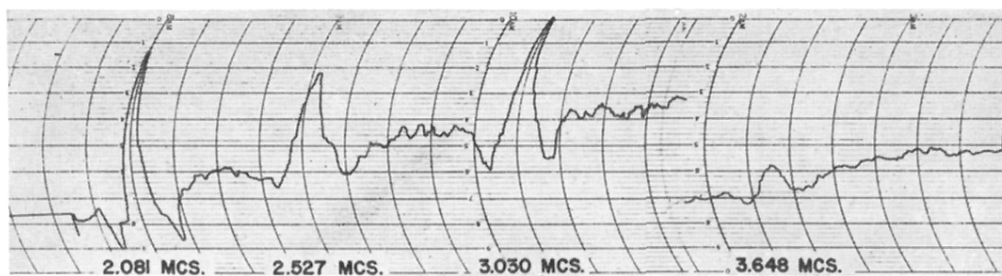


FIG. 8. The pure nuclear quadrupole resonance absorption spectrum at 25°C. The lines are labeled *A* through *D* in Table II in order of increasing frequency. The symmetrical wings on the negative side of the no-resonance trace are caused by absorption when the modulating field is on.