ly χ is rising sharply at the lowest temperatures.

The narrow range of compositions for which ferromagnetism exists in the Sc-In system suggests that this kind of ferromagnetism may be a more general phenomenon than has been thought until now, and may be found to occur in other systems.

We would like to thank Mrs. V. B. Compton for her x-ray investigations of these alloys.

[1]B. T. Matthias, V. B. Compton, and E. Corenzwit, J. Phys. Chem. Solids 19, 130 (1961).
[2]B. T. Matthias and R. M. Bozorth, Phys. Rev. 109, 604 (1958).
[3]S. C. Abrahams, Z. Krist. 112, 427 (1959).
[4]C. E. Olsen, J. Phys. Chem. Solids 19, 660 (1961), and to be published.

SHIFT OF NUCLEAR QUADRUPOLE RESONANCE FREQUENCY BY ELECTRIC FIELD

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It is well known that a static magnetic field splits the nuclear quadrupole resonance (NQR) lines in a single crystal.[1] One might immediately think of the similar effect caused by an electric field applied to the specimen. As a matter of fact, Pound[2] applied a field of about 50 000 v/cm across a thin plated-shaped single crystal of potassium iodide, but no shift in the resonance frequency nor change in the line shape was observed in the I^{127} nuclear resonance line. Gutowsky and Williams[3] tried to observe the effect of an electric field on an NQR line of the Cl nucleus in $NaClO_3$ single crystal without success.

Recently Bloembergen[4] pointed out the possibility of observing the change in the quadrupole coupling constant caused by an external electric field, if the crystal lattice has no local inversion symmetry about the pertinent nucleus.

It is the purpose of this Letter to report the successful observation of this effect for the Br^{81} NQR line in a single crystal of $NaBrO_3$.[5] The resonance frequency and the line shape are observed as a function of applied electric field using a regenerative spectrometer[6] in conjunction with a precise 0°C ice bath in order to keep the temperature of the sample constant during the run. Aluminum film electrodes are evaporated on the surfaces of a thin plate sample which has been cut from a larger single crystal.

The peak frequency of the line shifts linearly with the applied field E when E is parallel to [111], whereas no shift in the center frequency is observed in the case of $E \parallel [100]$. Reversal of the polarity of E reverses the sign of the shift. A typical example of the observed absorption curve is shown in Fig. 1. Here E is along the

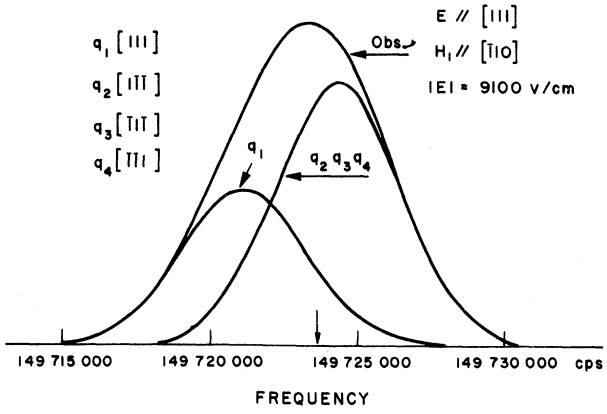

FIG. 1. The effect of the electric field on the Br^{81} resonance in $NaBrO_3$ single crystal. The arrow ↓ indicates the center frequency of the original line without the field.

[111] direction of the crystal, and H_1, an rf magnetic field in a sample coil of the spectrometer, is applied along the [$\bar{1}$10] direction. The vertical arrow ↓ indicates the center frequency without the electric field. The line shape, which was symmetric without an E field, is slightly asymmetric, and the center frequency has shifted by about 500 cps.

A cubic unit cell[7] of $NaBrO_3$ has four physically inequivalent, but chemically equivalent, BrO_3^- radicals. The maximum principal axes of electric field gradients about Br nuclei are parallel to the body diagonals of the unit cell. The field gradients along the [111], [1$\bar{1}\bar{1}$], [$\bar{1}$1$\bar{1}$], and [$\bar{1}\bar{1}$1] directions will be denoted, respectively, by q_1, q_2, q_3, and q_4.

The distortions of the field gradients produced

by the electric field along [111] are the same for q_2, q_3, and q_4 because of the threefold symmetry of the crystal along this direction. Because q_1 distorts differently, a doublet separation of the line would be expected. Since the relative intensity of the component lines is proportional to $\sin^2\angle(H_1, q)$, the intensity ratio of the components of the doublet will be $I_1:I_{234}=3:5$ in the case of $H_1 \| [\bar{1}10]$. Using this intensity ratio the observed asymmetric curve can be decomposed into two components as shown in Fig. 1. When H_1 is along the [111] direction, one observes only the $(q_2q_3q_4)$ line, which does not show any asymmetry nor increase in the linewidth compared with the original line without the E field. The observed shift of each component is

q_1 line $\quad -2500\pm 500$ cps/(10 000 v/cm),

$(q_2q_3q_4)$ line $\quad 750\pm 150$ cps/(10 000 v/cm).

The minus sign for the q_1 line indicates only the fact that the q_1 and the $(q_2q_3q_4)$ lines shift to opposite directions; no attempt has made to determine the absolute sign of these magnitudes.

When E is along [100] and H_1 is along [010], the shift for the (q_1q_2) line is the same as, but opposite in sign to, that for the (q_3q_4) line. Since both lines have the same intensity, no shift in the center frequency is observed up to about 5000 v/cm, where the crystal always breaks down.

The distortion of the field gradient tensor component, $\delta\varphi_{ij}$, may be expressed as

$$\delta\varphi_{ij}=\sum_k(\partial\varphi_{ij}/\partial E_k)E_k; \quad i,j,k=x,y,z. \qquad (1)$$

The third rank tensors, $\partial\varphi_{ij}/\partial E_k$, are zero if local inversion symmetry about the nuclei exists. This is the case for KI. Symmetry requirements of the crystal structure[8] and the traceless property[1] of φ_{ij} generally decrease the number of the independent components of this tensor.

The observed shift of the resonance frequency indicates only the change in q, which is φ_{ii} along the maximum principal axis, because a small asymmetry parameter η produced by the E field changes the resonance frequency only in the second order. From the shift of the q_1 line we obtain

$$\delta\nu_{q_1}/\nu_0=(q_0^{-1}\partial q/\partial E_{\|})E, \qquad (2)$$

and the shift of the $(q_2q_3q_4)$ line gives

$$\delta\nu_{q_2q_3q_4}/\nu_0=(q_0^{-1}\partial q/\partial E_{\perp})\frac{2\sqrt{2}}{3}E-(q_0^{-1}\partial q/\partial E_{\|})\frac{E}{3}, \qquad (3)$$

where ν_0 and q_0 are, respectively, the original resonance frequency and q without the field.

The values of the "field-gradient electrostatic" tensor are derived as

$$q_0^{-1}\partial q/\partial E_{\|}=(1.7\pm 0.3)\times 10^{-5}/(10\,000\ \text{v/cm}), \qquad (4)$$

and

$$q_0^{-1}\partial q/\partial E_{\perp}=(0.0\pm 0.2)\times 10^{-5}/(10\,000\ \text{v/cm}). \qquad (5)$$

The vanishing of $\partial q/\partial E_{\perp}$ is expected from the symmetry requirements of the third rank tensor for this crystal.[4,9]

Since $NaBrO_3$ is piezoelectric,[8] it would be informative to compare the value of $q_0^{-1}\partial q/\partial E_{\|}$ with the q change produced by a piezoelectric strain. The electric field along the [111] direction produces an axial strain along this direction.[8] The resonance frequency change accompanying this axial strain can be estimated from the piezoelectric constant and the pressure (hydrostatic) dependence of the resonance frequency.[10] Since the implicit effect via the piezoelectric strain thus estimated is less than 10% of the observed value of $q_0^{-1}\partial q/\partial E_{\|}$, it may be concluded that the explicit electric effect on q, namely $(q_0^{-1}\partial q/\partial E_{\|})_{\text{const strain}}$, is mainly responsible for the observed effect.

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[1]For instance, T. P. Das and E. L. Hahn, Solid State Physics, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1958), Suppl. 1.

[2]R. V. Pound, Phys. Rev. 79, 685 (1950).

[3]H. S. Gutowsky and G. A. Williams, Phys. Rev. 105, 464 (1957).

[4]N. Bloembergen, Science 133, 1363 (1961).

[5]T. Kushida and K. Saiki, Abstracts of papers presented at the Physical Society Meeting of Japan, April, 1961, Tokyo, Japan (Japanese) (unpublished).

[6]G. B. Benedek and T. Kushida, Phys. Rev. 118, 46 (1960).

[7]R. W. G. Wyckoff, Crystal Structure (Interscience Publishers, Inc., New York, 1951), Vol. II.

[8]For instance, W. P. Mason, Piezoelectric Crystals and Their Application to Ultrasonics (D. Van Nostrand Company, Inc., New York, 1950), p. 41.

[9]The authors are grateful to Professor N. Bloembergen for pointing out this property.

[10]T. Fuke (private communication).