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Stark Shift of Nuclear Spin Levels of ^{9}Be in Beryllium Oxide[†]

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Measurements of the angular variation of the quadrupole splitting in the NMR spectrum of ^{9}Be in single-crystal BeO are reported and give $e^2qQ/h=39.4\pm0.2$ kHz. The dependence of the field-gradient parameter q on an applied external electric field is investigated and interpreted using the phenomenological relation of the form $e(\Delta q)_{ij}=\sum R_{ijk}E_k+\sum\sum T_{ijlm}e_{lm}$, where the first term represents the constant-strain electric-field-induced change and the second term represents the piezoelectric contribution. The strain-induced part of Δq is measured separately and found to be negligible compared with the part due directly to the electric field. We report an experimental value for R_{zzz} of $\pm(1.3\pm0.5)\times10^9$ cm^{-1}. Calculations of R_{zzz} on the basis of ionic and covalent models of the BeO structure give -4.1×10^8 and -8.2×10^8 cm^{-1}, respectively, for the ionic and covalent contributions and a total calculated R_{zzz} of -1.2×10^9 cm^{-1}. It is thus unlikely that the ionic model can account for the observed Stark shift. A determination of the crystal c axis was made using the pyroelectric effect and this, together with the Stark-shift data, indicates that the sign of the field gradient is positive.

INTRODUCTION

The existence of a Stark shift or splitting in the magnetic-resonance spectrum of a nucleus having a quadrupole moment when the nuclear site lacks a center of inversion symmetry was predicted by Bloembergen.[1] This effect was subsequently observed in nuclear quadrupole resonance (NQR)[2] and in nuclear magnetic resonance (NMR).[3] The Stark shift arises from the nuclear electric quadrupole interaction with a field gradient or change in the existing field gradient induced by an applied electric field, and has been described phenomenologically by a relation of the form[2]

$$e(\Delta q)_{ij}=\sum_{k=x,y,z}R_{ijk}E_k+\sum_{l,m,k=x,y,z}S_{ijlm}d_{lmk}E_k\,, \tag{1}$$

for the change in the field-gradient-tensor elements $e(\Delta q)_{ij}$ resulting from the electric field E_k. The first term in Eq. (1) describes the effect due to the electric field at constant strain, while the second term accounts for a strain-induced change in the field gradient for those crystal classes which are piezoelectric. The effect due to the second term can be determined separately by measuring the stress-induced shift and using known elastic compliance and piezoelectric moduli values.

BeO has a hexagonal wurtzite structure with the local symmetry of the oxygen or beryllium ion being $3m$, and is both piezoelectric and pyroelectric. Since the beryllium nucleus in BeO should show a Stark shift in its NMR spectra, a study of the shift was undertaken for a number of reasons. Neutron irradiation of BeO results in the formation of F^+ centers, the model for which is an oxygen vacancy occupied by a single electron.[4] The nuclear quadrupole-coupling constants at the ^{9}Be sites surrounding the F^+ center differ considerably from those at normal ^{9}Be sites. An interpretation of the shift in the quadrupole-coupling constants at the ^{9}Be sites associated with the F^+ center should benefit from measurements of the dependence of the field gradient at normal sites on applied electric field and stress. In addition, interpretation of the Stark-shift data gives information on the covalent nature of the BeO structure and, together with a determination via the pyroelectric effect of the direction of the crystal c axis, allows determination of the sign of the field gradient at the normal ^{9}Be site.

In this paper we report measurements of the angular dependence of the quadrupole splitting in the NMR spectrum of BeO and a value for the quadrupole-coupling constant e^2qQ/h obtained from a least-squares fit to the angular-dependence data. Measurements of the Stark shift and strain-induced shift are then presented and interpreted in terms of the ionic and covalent models for the BeO structure. Determination of the direction of the crystal c axis using the pyroelectric effect, together with the Stark-shift data, then allows the sign of the field gradient to be experimentally determined.

EXPERIMENTAL RESULTS

A cw NMR spectrometer employing magnetic field modulation and a signal averager was used in this study. For the measurement of the angular dependence of the quadrupole splitting in the NMR spectrum, the crystal was mounted on the end of a glass rod with the crystal c axis nominally perpendicular to the rod axis. The rod was then mounted with its axis perpendicular to the magnetic field so that rotation of the mounting rod allowed alignment of the

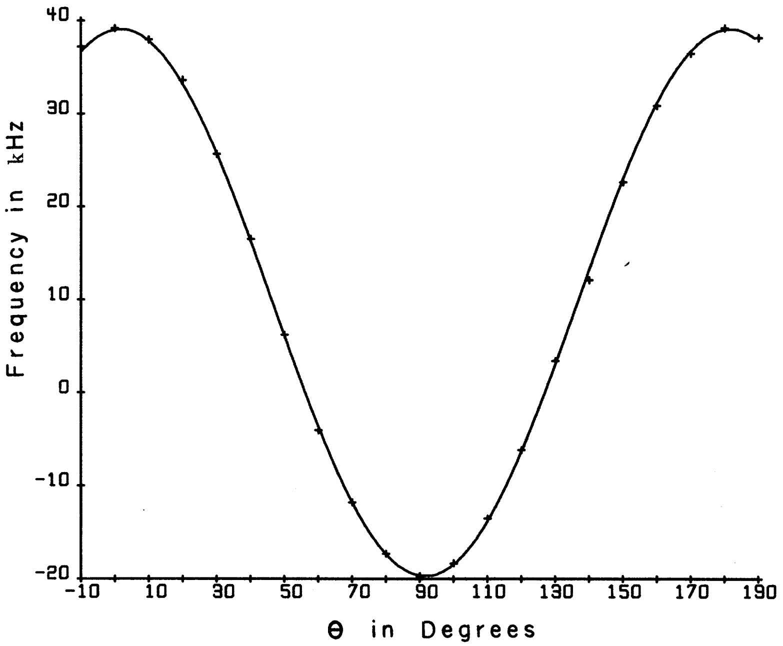

FIG. 1. NMR spectrum of ^{9}Be in BeO with the crystal *c* axis nominally parallel to the external magnetic field. The spectrum is an accumulation of 60 1-min sweeps recorded in the dispersion derivative mode. The NMR frequency of the central line is 5983.05 ± 0.05 kHz and the central-to-satellite splitting is 39.4 kHz. A rf field of ~50 mG and a modulation field of ~5 G at 90 Hz were used.

crystal *c* axis at any angle with the magnetic field. A single crystal with a volume of about 0.1 cm^3 was used. For each orientation of the crystal, the magnetic field was swept through the resonances 30 times at 1 min per sweep and the spectra accumulated in the signal averager. A sample spectrum is shown in Fig. 1.

In order to make absolute measurements of the quadrupole splitting, the field was calibrated as follows. A sample of ^2H_2O was placed in the NMR head and the oscillator frequency was adjusted to give a ^{2}H resonance at the low-field end of the spectrum using the same field sweep as that for the ^{9}Be spectrum. This was repeated with the frequency set to give a ^{2}H resonance at the high-field end of the spectrum. Using the known ^{2}H and ^{9}Be gyromagnetic ratios, the magnetic field sweep was then calibrated in terms of the ^{9}Be resonance.

The ^{9}Be spectrum was recorded at 21 orientations at 10° intervals with the crystal axis nominally from – 10° to 190° with the magnetic field. The quadrupole-splitting data were then fitted to the equation[5]

$$\Delta\nu = \nu_0 [3\cos^2\phi_0 \cos^2(\theta - \theta_0) - 1] , \qquad (2)$$

where $\Delta\nu$ is the observed quadrupole splitting, $\nu_0 = e^2qQ/h$, ϕ_0 is the correction for lack of perpendicularity of the crystal *c* axis with the axis of the mounting rod, θ is the measured angular position of the mounting rod, and θ_0 is the correction for the assumed rod position which makes the crystal *c* axis parallel with the magnetic field. Since the quadrupole term in the Hamiltonian is small compared to the Zeeman term, it is sufficient to treat the quadrupole term as a first-order perturbation resulting in Eq. (2).

A least-squares fit to Eq. (2) was accomplished by calculating the root-mean-square (rms) deviation of the data from the calculated angular dependence for various combinations of ν_0, ϕ_0, and θ_0, and a grid search conducted for the combination of these parameters which gave a minimum rms deviation. A computer plot of the least-squares fit to the data is shown in Fig. 2. Our measured value of $e^2qQ/h = 39.4$ kHz with a standard deviation of 0.2 kHz is to be compared with 38.4 ± 0.4 kHz as reported by Sholl and Walter.[6] The measurements of Sholl and Walter were done with the crystal *c* axis perpendicular to the magnetic field where the quadrupole splitting is one-half that with the *c* axis parallel to the magnetic field.

For the Stark-shift measurements, a crystal with faces parallel to within ~ 2° and with the *c* axis normal to the parallel faces was used. This crystal measured 0.40 cm in its *c*-axis dimension. Electrodes of silver-bearing Epoxy were made on the parallel faces and voltages of up to ±15 kV were applied from a Spellman model RHR-15PN30 power supply. + 25 kV was obtained from an x-ray image-intensifier power supply. NMR spectra for the Stark-shift data were taken at room temperature with the crystal orientation fixed with the *c* axis nominally parallel to the magnetic field. The data for the Stark-shift measurements are shown in Table I. Within the limits of experimental error the shift is linear in applied electric field with $\Delta q/q = (6 \pm 1) \times 10^{-4}$ for 1-kV applied voltage. For the electrode configuration used, the quadrupole split-

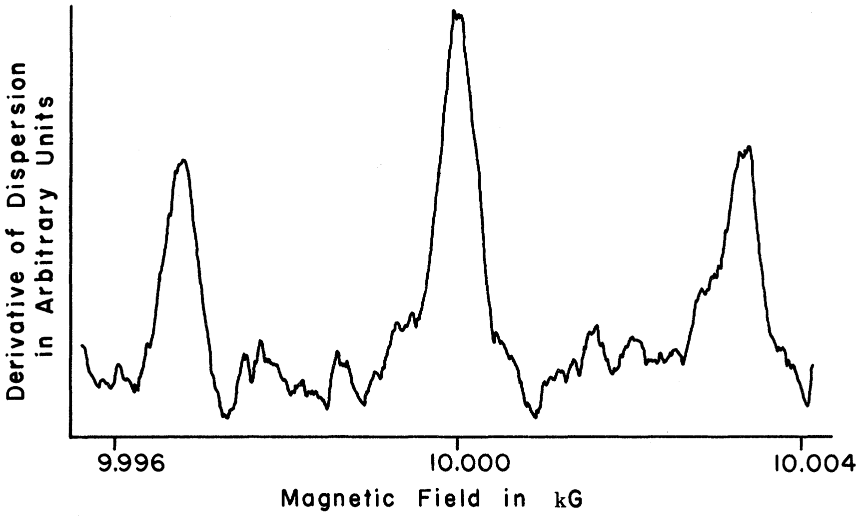

FIG. 2. Angular dependence of the quadrupole splitting in the NMR spectrum. The points are experimental and the solid line is the computed least-squares fit to Eq. (2). In the notation of Eq. (2), $\nu_0 = 9.85$ kHz, $\theta_0 = 1.6°$, and $\phi_0 = 4.5°$.

ting increased; that is, the magnitude of the field gradient increased when a positive voltage was applied to the ungrounded face of the crystal. A measurement of the sign of the pyroelectric-induced charge on the face of the crystal to which the high voltage was applied revealed that the direction of the *c* axis was toward that face of the crystal.[7] Thus we conclude that the field gradient increases in magnitude when the applied electric field is in the direction of the negative *c* axis.

From the known compliance[8] and piezoelectric[7] moduli of BeO, a uniaxial stress along the crystal *c* axis of 9.8×10^6 N/cm^2 results in a strain an order of magnitude larger than the piezoelectric strains at the highest electric fields used in the Stark-shift measurements. Our stress measurements show a shift of less than 1% for a stress of 9.8×10^6 N/cm^2. Thus we conclude that the contribution to the Stark shift from the first term in Eq. (1) is negligible. This is in agreement with such measurements on other materials.[3,9]

With the assumption that the second term in Eq. (1) can be neglected, we have for an electric field along the *c* axis (*z* axis)

$$e(\Delta q)_{zz} = R_{zzz} E_z \,. \tag{3}$$

From the measured value of $\Delta q/q$ and using $e^2qQ/h = 39.4$ kHz, the experimental value for $|R_{zzz}|$ is $(1.3 \pm 0.5) \times 10^9$ cm^{-1}. The sign of *q* could be determined if that of $|R_{zzz}|$ were known.

DISCUSSION

Two mechanisms have been suggested for the origin of the field-gradient shift as given in Eq. (3).[2,3,9] The first is a relative shift of the beryllium sublattice with respect to that of the oxygen and can be related to the ionic part of the dielectric constant. The second mechanism is a distortion of the valence or bonding orbitals and is related to the covalent character of the crystal bonding.

Following Gill and Bloembergen[3] we relate the ionic contribution to the difference between the static and high-frequency dielectric constants. The result is

$$R_{zzz}^{\text{ion}} = -2(1-\gamma_\infty)(\epsilon_{\text{dc}} - \epsilon_\infty)(\pi N r^4)^{-1} \,, \tag{4}$$

where $(1-\gamma_\infty) = 0.811$[10] is the Sternheimer antishielding factor, ϵ_{dc} (= 7.35) and ϵ_∞ (= 2.95)[11] are the static and high-frequency dielectric constants, $r = 1.657$ Å[5] is the Be-O distance, and $N = 7.25 \times 10^{22}$ cm^{-3} is the number of BeO molecules per unit volume. From Eq. (4) we have $R_{zzz}^{\text{ion}} = 4.1 \times 10^8$ cm^{-1} and we see that this can account for about one third of the observed magnitude of R_{zzz}.

TABLE I. Experimental data for the Stark-shift measurements. The vertical columns represent different sets of measurements.

Applied voltage (kV)	Fractional change in q, $\Delta q/q$												
−15	···	···	−0.020	−0.022	−0.005	−0.017	−0.015	+0.002	+0.002	···	···	···	···
+15	+0.028	+0.015	+0.003	+0.005	+0.009	+0.007	+0.007	+0.009	+0.008	+0.021	···	···	···
+25	···	···	···	···	···	···	···	···	···	···	+0.021	+0.022	+0.036

Calculation of the contribution R_{zzz}^{cov} to R_{zzz} from a distortion of the valence orbitals rests on the construction of molecular orbitals for the Be-O bonds. First-order perturbation theory is then applied to obtain the first-order corrected wave functions and the field-gradient shift at the Be site is evaluated using these corrected wave functions.[9] The result for a single bond is

$$R_{zzz}^{\mathrm{cov}} = -2e^2(\Psi_e|z|\Psi_g)(\Psi_e|q_{zz}^{op}|\Psi_g)(E_g-E_e)^{-1}. \quad (5)$$

A BeO pair has eight valence electrons. We assume that these electrons pair to form the distorted tetrahedrally directed bonds required for the $3m$ symmetry. The origin of our coordinate system is taken at the Be site and the z axis is in the direction of the positive c axis. We first look at the contribution of the bond along the positive c axis.

The sp^3 hybrid orbitals on the Be and O ions directed along the c axis are given by

$$\begin{aligned}\Phi_B &= (1-3\beta)^{1/2}\, s^B + (3\beta)^{1/2}\, p_z^B \ , \\ \Phi_O &= (1-3\beta)^{1/2} s^O - (3\beta)^{1/2} p_z^O \ ,\end{aligned} \quad (6)$$

with the hybridization parameter β determined from the angle between the c-axis bond and the other three (basal) bonds.[12]

The atomic hybrids given by Eq. (6) are used to form a bonding and an antibonding orbital for the c-axis bond given by

$$\begin{aligned}\Phi_b &= (1+\lambda^2+2\lambda S)^{-1/2}\,(\Phi_B+\lambda\Phi_O) \ , \\ \Phi_a &= (1+\lambda^2-2\lambda S)^{-1/2}\,(\lambda\Phi_B-\Phi_O) \ ,\end{aligned} \quad (7)$$

where $S=\int\Phi_B\,\Phi_A\,d\tau$ is the overlap integral and λ is related to the covalent nature of the bond. Coulson *et al.*[13] have calculated λ for BeO by a variational method.

The ground-state wave function has two electrons in Φ_b and the excited-state wave function is constructed by promoting one electron to Φ_a. The field-gradient-operator matrix element required in Eq. (5) then gives

$$[\Psi_e(1,2)|q_{zz}^{op}(1,2)|\Psi_g(1,2)] = 2\xi\,[(\zeta+\lambda)(\Phi_B|q_{zz}^{op}|\Phi_B) + (\lambda^2+2\zeta\lambda-1)(\Phi_B|q_{zz}^{op}|\Phi_O) + (\lambda^2\zeta-\lambda)(\Phi_O|q_{zz}^{op}|\Phi_O)] \ , \quad (8)$$

where

$$\begin{aligned}\xi &\equiv 2^{1/2}N\,[(1+\lambda^2)^2-(2S\lambda)^2]^{-1/2} \ , \\ \zeta &\equiv S(\lambda^2-1)(1+\lambda^2+2S\lambda)^{-1} \ , \\ N &\equiv \tfrac{1}{2}\{1+S^2(\lambda^2-1)^2[(1+\lambda^2)^2-(2S\lambda)^2]^{-1}\}^{-1/2} \ .\end{aligned}$$

The result for the dipole matrix element is obtained by substituting z for q_{zz}^{op} in Eq. (8).

The one-electron matrix elements are approximately evaluated as

$$\begin{aligned}&(\Phi_B|q_{zz}^{op}|\Phi_B)\simeq 9\beta q_{at}^B \ , \quad (\Phi_B|q_{zz}^{op}|\Phi_O)\simeq 16S(1-\gamma_\infty)R_{BO}^{-3} \ , \\ &(\Phi_O|q_{zz}^{op}|\Phi_O)\simeq 2(1-\gamma_\infty)R_{BO}^{-3} \ , \quad (\Phi_B|z|\Phi_B)\simeq R_{BO}/3 \ , \\ &(\Phi_B|z|\Phi_O\simeq R_{BO}/2 \ , \quad (\Phi_B|z|\Phi_O)\simeq R_{BO} \ ,\end{aligned} \quad (9)$$

where R_{BO} is the Be-O distance and q_{at}^B is the field gradient at the Be nucleus due to a single p_z atomic electron.[6]

The calculation of the contribution from the basal bonds is most easily accomplished by means of a coordinate transformation applied to Eq. (5). By symmetry the contributions of the three basal bonds are the same and we have

$$R_{zzz}^{\mathrm{cov,\,basal}} = -3e^2\cos\theta(3\cos^2\theta-1)(\Psi_e^b|z|\Psi_g^b) \times(\Psi_e^b|q_{zz}^{op}|\Psi_g^b)(E_e-E_g)^{-1} \ , \quad (10)$$

where the basal-bond wave functions are assumed to have different values of the parameters λ, S, and R_{BO} than the c-axis bond. The required parameters are given in the paper by Sholl and Walter.[6] With the energy denominator taken as the BeO band gap, 11.2 eV,[14] the calculated covalent part of R_{zzz} is -6.8×10^8 cm^{-1}. The ionic part together with the covalent part then gives a calculated R_{zzz} of -1.1×10^9 cm^{-1} in surprisingly good agreement with the observed $\pm(1.3\pm0.5)\times10^9$ cm^{-1}.

The dipole matrix element can also be evaluated from the optical index of refraction.[3] The result is 9.2×10^{-9} cm, while calculation using the assumed wave functions and the approximations of Eqs. (9) gives 7.6×10^{-9} cm. Use of the dipole matrix element calculated from the index of refraction gives a calculated R_{zzz} of -1.2×10^9 cm^{-1}. This also agrees within experimental error with the observed value.

CONCLUSIONS

The strain-induced field-gradient shift being negligible, the experimental value of R_{zzz} is determined to be $\pm(1.3\pm0.5)\times10^9$ cm^{-1}. The calculated value assuming sp^3-type hybridized atomic wave functions and covalent bonding is -1.2×10^9 cm^{-1}. The ionic part alone accounts for only about one third of the observed Stark shift. It is thus unlikely that the Stark shift can be explained assuming a purely ionic model for the crystal structure. This is in agreement with Sholl and Walter,[6] who find that the field gradient in BeO is significantly affected by covalent bonding in the crystal.

The sign of R_{zzz} as calculated on the basis of the model indicates that an electric field in the direction of the positive c axis induces a negative change in the field gradient at the Be site. The experimental fact that such an electric field decreases the magnitude of the field gradient indicates that the normal field gradient has a positive sign. This is in agreement with calculations of the field gradient in BeO.[6,15–18]

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Cs^{133} and Cl^{35} NMR in Antiferromagnetic CsNiCl$_3$[†]

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The nuclear magnetic resonances of Cl^{35} and Cs^{133} in magnetically ordered CsNiCl$_3$ have been investigated to determine the magnetic structure and magnetic properties of this compound. Both the Cs and Cl resonances have been observed in single crystals over a temperature range 300 to 1.3 °K. These data show that CsNiCl$_3$ undergoes two magnetic transitions, one at (4.84 ± 0.03) °K and the other at (4.40 ± 0.03) °K. The higher-temperature transition corresponds to antiferromagnetic alignment of the Ni spin along the *c* axis, while the perpendicular part of the moment is probably paramagnetic. At 4.40 °K, the perpendicular component of the moment becomes ordered. The magnetization curves for the perpendicular and parallel components of the Ni moment have been obtained. When normalized to the appropriate Néel temperature, the reduced magnetization curves represented by components of the internal field parallel and perpendicular to the *c* axis have the same dependence upon temperature, as evidenced by the Cs and Cl resonances. Near the corresponding T_N, the critical exponent β is 0.32 ± 0.03 for both the parallel and perpendicular components.

I. INTRODUCTION

There has been considerable recent interest in compounds of the $AB\text{Cl}_3$ type. The magnetic properties of several of these compounds in which A is represented by Cs or Rb, and B by Cu, Ni, Co, or Fe, have been investigated by Achiwa.[1] His susceptibility data for CsNiCl$_3$ are characteristic of a linear antiferromagnetic chain with a broad peak at about 35 °K in the susceptibility-vs-temperature curve. Achiwa also inferred from the susceptibility data that a paramagnetic-to-antiferromagnetic transition occurs at 4.5 °K.

Several neutron diffraction experiments have been performed on[2–5] CsNiCl$_3$ and the isomorphic compound RbNiCl$_3$,[2,6] and conflicting results have been reported. Achiwa[1] found no antiferromagnetic peak in CsNiCl$_3$ at 1.9 °K. Smith *et al.*[5] saw no evidence of three-dimensional magnetic ordering at 4.6 °K. From powder neutron diffraction data Minkiewicz *et al.*[3] found the Néel temperatures of CsNiCl$_3$ and RbNiCl$_3$ to be 4.5 and 11 °K, respectively, and that the two compounds had the same magnetic structure, which was an antiferromagnetic alignment of spins along the *c* axis with a screw spiral in the basal plane. Single-crystal data by Mekata *et al.*[2] gave