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Principal Axes of the EFG Tensors and Torsional Oscillations in Boron Triiodide

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Synopsis. The Zeeman effect of ^{127}I NQR and the quadrupole effect of ^{11}B NMR on a single crystal of BI_3 were observed in order to investigate the principal axes of the EFG tensors. The frequencies of the torsional oscillations were determined from the temperature dependence of e^2Qq_{ii}/h.

From X-ray analysis, it is well known that the BI_3 molecule has a planar trigonal structure with D_{3h} symmetry.[1] From the molecular symmetry, it can be expected that the z principal axis of the ^{11}B EFG tensor is consistent with the 3-fold rotation axis of the molecule. Using a single crystal, the direction of the principal axes of the ^{127}I and ^{11}B atoms can be determined experimentally from the Zeeman effect of ^{127}I NQR and the quadrupole effect of ^{11}B NMR, respectively.

The infrared and Raman spectra of BI_3 have been observed and the frequencies of the lattice vibrations were estimated.[2] With regard to these results it appears worthwhile to examine the effect of torsional oscillations from the temperature dependence of e^2Qq_{ii}/h.

Experimental

The NQR spectrometer was a self-quenching, super-regenerative oscillator with frequency modulations; the absorption lines were displayed on an oscilloscope. The temperature dependence of the NQR frequencies was found for a sample which was immersed in petroleum ether cooled to a given temperature using liquid nitrogen. The Zeeman effect was examined by the zero-splitting cone method. A magnetic field of *ca.* 250 G was applied by means of a Helmholtz coil.

Using a broad line NMR spectrometer of Japan Electron Optics Lab. Co., Ltd., the measurement of the ^{11}B NMR was made at 13.00 MHz and the magnetic field was varied to observe the resonance.

Results and Discussion

^{127}I NQR. Two resonance lines for ^{127}I NQR were observed and were attributed to the ν_1 and ν_2 lines, corresponding to the $\pm1/2\leftrightarrow\pm3/2$ and $\pm3/2\leftrightarrow\pm5/2$ transitions, respectively.[3] Each of the resonance lines consisted of a doublet with an intensity ratio of *ca.* 2 to 5 and a frequency difference of *ca.* 25 to 30 kHz at room temperature. They were observed at temperatures ranging from −186 to 23 °C. The cause of the doublet has been attributed to the existence of ^{10}B and ^{11}B in BCl_3 and BBr_3.[4] This is true for BI_3 as well.

Figure 1 shows the zero-splitting pattern of the ν_1 line which was observed at room temperature. Since the derived asymmetry parameter η is 0.460 which is greater than the critical value of 0.412, the direction of the axis of the zero-splitting cone is parallel to the y principal axis of the ^{127}I EFG tensor.[5] On the other hand, the direction of the x principal axis of the ^{127}I EFG tensor lies along the 3-fold rotation axis of the molecule. The direction of the z principal axis of the ^{127}I EFG tensor is considered to be parallel to the B–I bond, so that the angle <I–B–I can be obtained from the Zeeman effect, which gives a value of 120±0.6°.

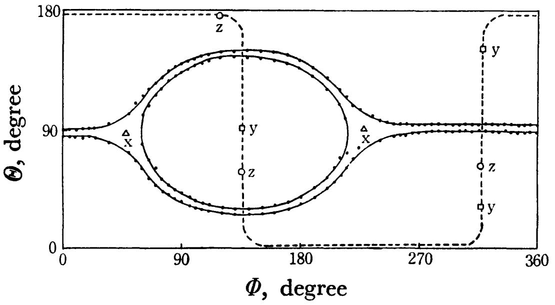

Fig. 1. Zero-splitting pattern of the Zeeman effect on the resonance line, ν_1. The molecular plane is indicated by the broken line.

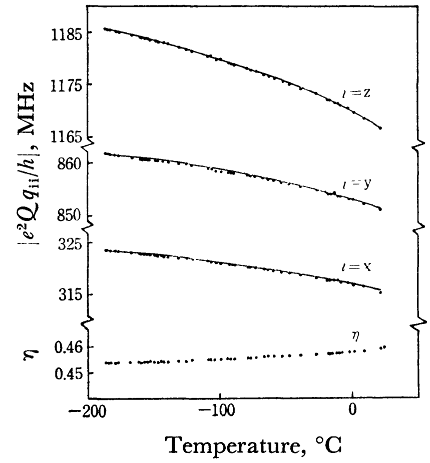

Fig. 2. Temperature dependences of the quadrupole coupling constants and the asymmetry parameter.

The temperature dependence of the quadrupole coupling constants, e^2Qq_{ii}/h (i=x, y, and z) and the asymmetry parameter, η, were derived from the temperature dependence of the ν_1 and ν_2 lines, as shown in Fig. 2. It was found that the absolute temperature coefficients of the quadrupole coupling constants are in the sequence $e^2Qq_{zz}/h > e^2Qq_{yy}/h > e^2Qq_{xx}/h$, and that η increases gradually with temperature. If the amplitudes of the torsional oscillation about the x, y, and z principal axes of the ^{127}I EFG tensor are denoted by ϑ_x, ϑ_y, and ϑ_z, respectively, the averaged principal values of the EFG tensor can be expressed by the following equations,[6]

$$\begin{aligned} V_{xx} &= eq_0[-(1-\eta_0)/2-\langle\vartheta_z^2\rangle\eta_0+\langle\vartheta_y^2\rangle(3-\eta_0)/2], \\ V_{yy} &= eq_0[-(1+\eta_0)/2+\langle\vartheta_z^2\rangle\eta_0+\langle\vartheta_x^2\rangle(3+\eta_0)/2], \qquad (1) \\ \text{and}\quad V_{zz} &= eq_0[1-\langle\vartheta_y^2\rangle(3-\eta_0)/2-\langle\vartheta_x^2\rangle(3+\eta_0)/2], \end{aligned}$$

where q_0 and η_0 are the values in the static lattice, and the $\langle\vartheta_i^2\rangle$ (i=x, y, and z) indicate the mean square amplitudes of the oscillation about each i principal axis of the EFG tensor. If the torsional oscillations are approximated by harmonic oscillations, $\langle\vartheta_i^2\rangle$ is given by[7]

$$\langle\vartheta_i^2\rangle = h\coth(h\nu_i/2kT)/8\pi^2 I_i\nu_i, \qquad (2)$$

where the I_i are the moments of inertia about each i principal axis of the inertia tensor and the ν_i are the torsional frequencies. In order to reflect the effect of thermal expansion of the lattice, the ν_i are expressed empirically by

$$\nu_i = \nu_{i0}(1-\alpha_i T), \qquad (3)$$

where the α_i are coefficients of expansion. In the case of BI_3, the principal axes of the ^{127}I EFG tensor coincide with the principal axes of the inertia tensor. Considering the molecular symmetry it can be assumed that $\langle\vartheta_y^2\rangle=\langle\vartheta_z^2\rangle$. Thus a best fit using the least-squares method was tried.[8] The following results were obtained: $e^2Qq_0/h=1190.6\pm1.1$ MHz, $\eta_0=0.4518\pm0.0003$, $\nu_{x0}=46.1\pm2.6$ cm^{-1}, $\nu_{y0}=\nu_{z0}=34.9\pm1.2$ cm^{-1}, $\alpha_x=0.0012\pm0.0002$ deg^{-1}, and $\alpha_y=\alpha_z=0.0003\pm0.0004$ deg^{-1}. The curves reproduced using these values are shown as full lines in Fig. 2. The standard deviation is between 0.11 and 0.22 MHz. The frequencies of the torsional oscillations obtained above are comparable to those of the R_z and R_{xy} modes of the lattice vibrations.[2] Consequently, it is believed that the effective vibrations for the temperature dependence of the quadrupole coupling constants are in the lattice region.

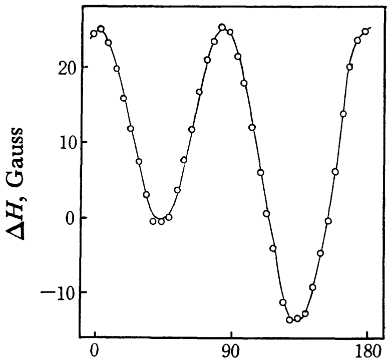

Fig. 3. The rotation pattern of ^{11}B central line.

^{11}B NMR. In ^{11}B NMR, only one central resonance line corresponding to the $m=+1/2\leftrightarrow m=-1/2$ transition was observed and was seen to be affected by the second-order quadrupole interaction. The rotation pattern of the central line was obtained by measuring its shift from the magnetic field corresponding to the Larmor frequency as a function of the rotation angle of the crystal, the results of which are shown in Fig. 3. A second-order frequency shift, $\Delta\nu$, can be represented in terms of the magnetic field by[9]

$$\Delta\nu = -\nu_L(\Delta H/H_L^2)(\Delta H+H_L), \qquad (4)$$

where ν_L and H_L are the Larmor frequency of 13.00 MHz and the corresponding magnetic field, respectively. $\Delta H=H_R-H_L$, where H_R is the resonance magnetic field of ^{11}B shifted by the second-order quadrupole interaction. From the molecular symmetry it can be assumed that the asymmetry parameter for ^{11}B is zero. Accordingly, the frequency shifts of the central transition are given by the following equation for $\eta=0$[10]

$$\Delta\nu = -(\nu_Q^2/16\nu_L)(a-3/4)(1-\mu^2)(9\mu^2-1), \qquad (5)$$

where $\nu_Q=3e^2Qq/2I(2I-1)h$, $a=I(I+1)$, $\mu=\cos\vartheta$, and ϑ is the angle between the direction of the z principal axis of the EFG tensor and that of the applied magnetic field. From this analysis it is found that the direction of the 3-fold rotation axis of the molecule which was determined by the Zeeman effect of the ^{127}I NQR is consistent with the direction of the z principal axis of the ^{11}B EFG tensor within an experimental error of ±0.6°. The quadrupole coupling constant of the ^{11}B atom obtained was 2.32±0.05 MHz at room temperature. This value differs slightly from 2.40±0.04 MHz at −196 °C.[11] The ratio of e^2Qq_{zz} at −196 °C to that at room temperature is 1.03. This ratio can be explained by the torsional oscillations of the ^{11}B atom about the principal axes of the EFG tensor as follows: assuming $\eta_0=0$, the z component of the quadrupole coupling constant, which is averaged over the torsional oscillation, is given by

$$e^2Qq_{zz} = e^2Qq_0(1-\langle\vartheta_x^2\rangle 3/2-\langle\vartheta_y^2\rangle 3/2). \qquad (6)$$

The x and y principal axes of the ^{11}B EFG tensor lie in the plane of the molecule and it can be assumed that $\langle\vartheta_x^2\rangle=\langle\vartheta_y^2\rangle$. The evaluation of $\langle\vartheta_x^2\rangle$ and $\langle\vartheta_y^2\rangle$ can be derived from the results of the temperature dependence of the ^{127}I NQR. The ratio e^2Qq_{zz} (−196 °C)/e^2Qq_{zz} (23 °C) is found to be 1.02 from Eq. 6.

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