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Temperature and Pressure Dependence of ^{209}Bi Nuclear Quadrupole Resonance in $BiCl_3$

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The temperature and pressure dependence of the ^{209}Bi nuclear quadrupole coupling constant and asymmetry parameter in solid $BiCl_3$ have been measured near room temperature. It is not possible to account for the results on the basis of the conventional theory in which the field gradient parameters depend only on the crystal volume.

L'influence de la température et de la pression sur la constante de couplage nucléaire quadrupole du ^{209}Bi et sur le paramètre d'asymétrie du $BiCl_3$ solide, a été mesurée à une température proche de la température ambiante. Il n'a pas été possible d'expliquer les résultats à partir de la théorie classique dans laquelle les paramètres du gradient de champ dépendent seulement du volume du cristal.

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Introduction

Nuclear quadrupole resonance frequencies are dependent upon both volume and temperature, and in order to compare theory with experiment properly it is necessary to separate the explicit volume effects from the frequency measurements made at atmospheric pressure (1). A number of studies of the shift of n.q.r. frequencies under hydrostatic compression have been reported which allows this separation to be made; in addition to the temperature and pressure coefficients of the n.q.r. frequency, the thermal expansion and compressibility coefficients must be known, and in many cases the latter information is not available.

The observed n.q.r. frequencies are determined by two parameters of the effective Hamiltonian, the quadrupole coupling constant (eqQ) and the asymmetry parameter (η). For the common case of a nuclear spin of 3/2, η cannot be determined reliably without measurements of the Zeeman splitting of the resonance in a single crystal which can be re-oriented readily, and so in most high pressure n.q.r. experiments on nuclei of spin 3/2, the asymmetry parameter has been ignored; this assumption is logically consistent since the resonant frequency is almost independent of η except for very large values:

$$\nu_Q = \tfrac{1}{2}eqQ(1+\eta^2/3)^{1/2}$$

Hence in order to obtain information on the temperature and pressure dependence of the asymmetry parameter, it is advantageous to deal with spins other than 3/2. The temperature dependence of the asymmetry parameter has not been measured for many crystals, even though in suitable cases it provides information which is complementary to that obtained from the coupling constant itself.

Bismuth trichloride provides an interesting case for study. The ^{209}Bi resonances have been measured at 299 and 83 K (2), and fall in a convenient frequency range; there are four resonances and η is large enough that two of the resonances lie close together, so the same high pressure bomb may be used to measure both resonance frequencies. Measurement of two of the four resonances suffices to determine the values of eqQ and η using the analysis of the spin 9/2 quadrupolar Hamiltonian given by Cohen (3). The crystal structure (4) and Raman spectrum (5) of solid $BiCl_3$ have been reported. The thermal expansion coefficient has been reported (6) but not the compressibility, and as a result the analysis of the quadrupole spectrum is limited.

The Pure Quadrupole Spectrum for Spin 9/2

There are five energy levels, whose energies may be written in the form (3)

$$[1]\qquad E = x(\eta)(eqQ)/24$$

where $x(\eta)$ are the roots of the equation $f(x,\eta)=0$.

$$[2]\qquad f(x,\eta) = x^5 - 11(3+\eta^2)x^3 - 44(1-\eta^2)x^2 + \tfrac{44}{3}(3+\eta^2)^2x + 48(3+\eta^2)(1-\eta^2)$$

The frequencies of the transitions between adjacent energy levels can therefore be written

$$\nu_i = r_i(\eta)(eqQ)/24h \qquad [3]$$

where $r_i(\eta)$ is the difference between two adjacent roots of eq. 2. In the following, $i = 1$ refers to the $\pm 1/2 \leftrightarrow \pm 3/2$ transition and $i = 2$ refers to the $\pm 3/2 \leftrightarrow \pm 5/2$ transition; in $BiCl_3$ these transitions occur near 31.8 and 25.1 MHz, respectively (2), and are the transitions which were measured as a function of temperature and pressure. The frequencies were found to be linear functions of the temperature and pressure over the ranges investigated, and the subsequent analysis was therefore carried out in terms of the derivatives $(\partial \nu_i/\partial T)_P$ and $(\partial \nu_i/\partial P)_T$. Using eq. 3 these derivatives can be written

$$\left(\frac{\partial \nu_i}{\partial T}\right)_P = \frac{r_i(\eta)}{24h}\left(\frac{\partial eqQ}{\partial T}\right)_P + \frac{\mathrm{d}r_i}{\mathrm{d}\eta}\left(\frac{\partial \eta}{\partial T}\right)_P \frac{eqQ}{24h} \qquad [4]$$

$$\left(\frac{\partial \nu_i}{\partial P}\right)_T = \frac{r_i(\eta)}{24h}\left(\frac{\partial eqQ}{\partial P}\right)_T + \frac{\mathrm{d}r_i}{\mathrm{d}\eta}\left(\frac{\partial \eta}{\partial P}\right)_T \frac{eqQ}{24h} \qquad [5]$$

The derivatives $\mathrm{d}r_i/\mathrm{d}\eta$ are calculated from differences of the derivatives $\mathrm{d}x/\mathrm{d}\eta$, which are obtained from setting the total derivative of $f(x, \eta)$ equal to zero.

$$\frac{\mathrm{d}x}{\mathrm{d}\eta} = -\left(\frac{\partial f}{\partial \eta}\right)\Big/\left(\frac{\partial f}{\partial x}\right) \qquad [6]$$

In evaluating r_i and its derivatives, the value of η at room temperature was used. When $(\partial \nu_i/\partial T)_P$ is known for two resonances, eq. 4 may be solved simultaneously for $(\partial eqQ/\partial T)_P$ and $(\partial \eta/\partial T)_P$, and similarly for the pressure derivatives. It is advantageous to measure the $\pm 1/2 \rightarrow \pm 3/2$ transition no matter which of the other three transitions is measured, for the frequency of this transition varies strongly with the value of η; the frequencies of the other transitions are less sensitive to the value of η and reflect changes in the coupling constant more directly.

Experimental

Spectra were recorded with a self-quenched super-regenerative spectrometer similar to that described by Dean (7); for frequency measurements it was found advantageous to remove the coherence feedback control function in order to allow quick manual change in the quench conditions. Frequency modulation and lock-in detection were used to record the resonances on a chart recorder; the shape of the resonances recorded was complex but was not affected by changes of temperature or pressure so that shifts in the resonance frequency could be measured consistently.

Frequency measurement was performed as follows. The unquenched, unmodulated oscillator was driven slowly in frequency by a synchronous motor, and its frequency as measured by a frequency counter was recorded regularly on the chart record; as the frequency of the oscillator approached the resonance the quench and modulation were switched on, and the resonance was recorded. After the resonance had been passed, further frequency measurements on the unquenched, unmodulated oscillator were recorded. The recorded frequency was fitted to a least squares parabolic function of displacement along the record, and the resonance frequency calculated from this function. A correction for the shift in oscillator frequency with grid time constant was applied by also recording the zero beat of the quenched modulated oscillator with an appropriate harmonic of 100 kHz derived from the frequency counter, either before or after the resonance was recorded; the correction was generally less than 10 kHz. Individual frequency measurements made by this technique appear to be repeatable to within several kHz.

The bomb used for the high pressure measurements was of conventional design, with an O-ring seal which was satisfactory up to a pressure of about 275 MNm^{-2}. The coned electrical seal was insulated with epoxy resin. The pressure coefficients of the resonances were large enough that it was not necessary to carry the measurements to very high pressures, the highest pressure used being about 140 MNm^{-2}; vacuum pump oil was used as a hydraulic medium. The powdered sample was mixed with oil and placed inside a short section of drinking straw with the ends sealed with wax, in order to prevent contact with the stainless steel bomb. The coil of the oscillator was a close fit around the sample. The bomb was thermally insulated, and its temperature was recorded; some temperature drift occurred during the measurements and the frequencies were corrected to 25.0 °C later using the measured temperature dependence.

The temperature dependence was measured using a sample sealed under vacuum. The temperature was varied between 0 and 50 °C using a refrigerated thermostat; the temperature was measured with a mercury thermometer which was compared with a calibrated thermometer in a separate experiment.

Bismuth trichloride from the Matheson, Coleman and Bell Company was dried *in vacuo* at 100 °C over phosphorus pentoxide, before being sealed in an evacuated sample tube, or mixed with oil in a dry atmosphere.

Results and Discussion

The frequencies of both resonances varied linearly with both pressure and temperature over the restricted ranges investigated, with the following coefficients. For the 31.8 MHz resonance,

$$\left(\frac{\partial \nu_1}{\partial T}\right)_P = -10.42 \pm 0.06 \text{ kHz K}^{-1}$$

$$\left(\frac{\partial \nu_1}{\partial P}\right)_T = +1.36 \pm 0.02 \text{ kHz (MN m}^{-2})^{-1}$$

and for the 25.1 MHz resonance

$$\left(\frac{\partial \nu_2}{\partial T}\right)_P = -4.46 \pm 0.03 \text{ kHz K}^{-1}$$

$$\left(\frac{\partial \nu_2}{\partial P}\right)_T = -1.720 \pm 0.008 \text{ kHz (MN m}^{-2})^{-1}$$

The pressure coefficients refer to a temperature of 25 °C. The extrapolated zero pressure frequencies measured for the sample in the high pressure bomb were 31 878.3 ± 1.1 and 25 137.3 ± 0.7 kHz, respectively, while the measurements on the larger sample *in vacuo* at the same temperature (25 °C) were 31 893.8 ± 2.0 and 25 136.6 ± 0.9 kHz, respectively; the value of η derived from these measurements is 0.5544 ± 0.0002, and the quadrupole coupling constant is 318.70 ± 0.15 MHz. The two measurements of the lower frequency resonance are in good agreement, but there is a discrepancy of about 15 kHz in the results for the higher frequency; the latter line was weaker than the former, and the assignment of the central point of the resonance pattern for the sample in the bomb may have been in error, without affecting the value of the derivatives. Substituting these values into eqs. 4 and 5 and solving, the temperature and pressure derivatives of the coupling constant and asymmetry parameter are found to be

$$\frac{1}{h}\left(\frac{\partial eqQ}{\partial T}\right)_P = -40.6 \pm 0.7 \text{ kHz K}^{-1}$$

$$\frac{1}{h}\left(\frac{\partial eqQ}{\partial P}\right)_T = -33.6 \pm 0.2 \text{ kHz (MN m}^{-2})^{-1}$$

$$\left(\frac{\partial \eta}{\partial T}\right)_P = -(1.54 \pm 0.03) \times 10^{-4} \text{ K}^{-1}$$

$$\left(\frac{\partial \eta}{\partial P}\right)_T = +(1.15 \pm 0.07) \times 10^{-4} \text{ (MN m}^{-2})^{-1}$$

These results may be combined in an analysis following the method of Kushida *et al.* (1); the parameters q and η of the electric field gradient tensor are assumed to depend explicitly upon the volume V of a fixed amount of solid, as well as the temperature:

$$[7] \qquad q = q(T, V) \qquad \eta = \eta(T, V)$$

These are fairly drastic assumptions, for it is implied that the effects of thermal expansion and hydrostatic pressure upon the electric field gradient tensor are functions of a single variable, the volume; in a rigorous analysis of a complex crystal, changes of shape and atomic positions within the unit cell must be included as well as the volume, but it is not practical to carry out such an analysis at present. Within the approximations implied by eq. 7, it is found that

$$[8] \qquad \left(\frac{\partial q}{\partial T}\right)_P = -\frac{\alpha}{\beta}\left(\frac{\partial q}{\partial P}\right)_T + \left(\frac{\partial q}{\partial T}\right)_V$$

$$[9] \qquad \left(\frac{\partial \eta}{\partial T}\right)_P = -\frac{\alpha}{\beta}\left(\frac{\partial \eta}{\partial P}\right)_T + \left(\frac{\partial \eta}{\partial T}\right)_V$$

where $\alpha = (1/V)(\partial V/\partial T)_P$ is the coefficient of bulk thermal expansion, and $\beta = -(1/V)(\partial V/\partial P)_T$ is the isothermal compressibility. The value of α has been reported (6) as 2.8×10^{-4} K^{-1}, but the compressibility does not appear to have been measured, and so an approximate value of α/β based upon the Gruneisen–Mie equation of state for solids (8) will be used

$$[10] \qquad \alpha/\beta = \gamma \bar{C}_V / \bar{V}$$

where γ is the Gruneisen constant, generally between 1 and 2, $\bar{C}_V$ is the molar specific heat at constant volume, and $\bar{V}$ is the molar volume. Since $\bar{C}_V$ is not available experimentally, $\bar{C}_p$ may be used together with $\gamma = 2$ to calculate an estimated upper limit for α/β. For $BiCl_3$, $\bar{C}_p = 109$ J K^{-1} mol^{-1} (9) and $\bar{V} = 66 \times 10^{-6}$ m^3 (4), yielding a value $\alpha/\beta \lesssim 3.3$ MNm^{-2} K^{-1}. The compressibility derived from this estimate and the measured value of the thermal expansion coefficient is $\beta \gtrsim 0.8 \times 10^{-4}$ (MNm^{-2})$^{-1}$.

The temperature derivatives of the electric field gradient parameters at constant volume can now be estimated from eqs. 8 and 9

$$\frac{1}{h}\left(\frac{\partial eqQ}{\partial T}\right)_V \cong -150 \text{ kHz K}^{-1}$$

$$\left(\frac{\partial \eta}{\partial T}\right)_V \cong +2 \times 10^{-4} \text{ K}^{-1}$$

The value of $(\partial \eta/\partial T)_V$ is very uncertain, since two terms of opposite sign and comparable magnitude are added together and the uncertainty in the value of α/β is consequently magnified; no further quantitative analysis of the data on the asymmetry parameter is justified.

The large value of η is probably due to the chlorine atoms in the face-bridging positions, and is likely to be very sensitive to the bismuth—chlorine distance, leading to a positive value of $(\partial\eta/\partial P)_T$, as observed. Chihara and co-workers (10) reported the temperature dependence of η for the Sb nucleus in $SbCl_3$ at constant pressure, obtaining a value $(\partial\eta/\partial T)_P$ of about $-1.1 \times 10^{-4}\ K^{-1}$ near 120 °K, which is comparable with the value observed for $BiCl_3$; the attempt to interpret the temperature dependence of η and eqQ/h was not successful, and the present results suggest that the effects of thermal expansion should have been taken into account.

The analysis of the coupling constant data is consistent with these conclusions; the contribution of thermal expansion to the temperature dependence of eqQ/h at constant pressure is considerable, for it cancels out about two-thirds of the Bayer term $(\partial eqQ/\partial T)_V$. It may be concluded that the bridging chlorine atoms reduce the bismuth quadrupole coupling constant appreciably, and are the cause of the negative value of $(\partial eqQ/\partial P)_T$; in other words, the coupling constant is reduced when the intermolecular distances are reduced by hydrostatic pressure.

The interpretation of $(\partial eqQ/\partial T)_V$ in terms of the theory of torsional oscillations (11) is not very satisfactory. If θ_x and θ_y are the angles of rotation about the x and y principal axes of the electric field gradient tensor, q_0 is the coupling constant and η_0 the asymmetry parameter for the solid in the absence of torsional oscillations, then the averaged value of the major component of the electric field gradient tensor is given by eq. 11

$$[11] \quad q = q_0[1 - \tfrac{3}{2}(\langle\theta_x^2\rangle + \langle\theta_y^2\rangle) - \tfrac{1}{2}\eta_0(\langle\theta_x^2\rangle - \langle\theta_y^2\rangle)]$$

The quantities q_0 and η_0 are not accessible experimentally because of zero point vibrations; but for the present purposes, sufficiently accurate values may be obtained by extrapolating q and η measured at room temperature to absolute zero using the measured temperature derivatives

$$(eq_0Q)/h \cong 331 \text{ MHz}$$

$$\eta_0 \cong 0.60$$

Equation 11 may be differentiated at constant volume, treating q_0 and η_0 as constants:

$$[12] \quad \frac{1}{q_0}\left(\frac{\partial q}{\partial T}\right)_V = -1.80\left(\frac{\partial\langle\theta_x^2\rangle}{\partial T}\right)_V - 1.20\left(\frac{\partial\langle\theta_y^2\rangle}{\partial T}\right)_V$$

The left hand side of this equation has the approximate value $-4.5 \times 10^{-4}\ K^{-1}$. In the limit of high temperatures, the temperature coefficient of the mean square amplitude of a torsional oscillator is

$$[13] \quad \left(\frac{\partial\langle\theta^2\rangle}{\partial T}\right)_V = k/4\pi^2\nu^2 I$$

where k is Boltzmann's constant, ν is the frequency of the oscillator and I is the moment of inertia associated with the oscillator. Bismuth trichloride in the solid state contains well-defined $BiCl_3$ groups in a distorted trigonal pyramid; if the distortion is ignored, bond angles taken as 90° and the bond lengths as 0.25 nm, the moment of inertia of this group about an axis perpendicular to the trigonal axis is calculated to be approximately 6×10^{-45} kg m^2. For the lowest frequency line reported in the Raman spectrum of solid $BiCl_3$ (5), namely 37 cm^{-1}, eq. 13 yields

$$\left(\frac{\partial\langle\theta^2\rangle}{\partial T}\right)_V = 0.47 \times 10^{-4}\ K^{-1}$$

and for other, higher frequency, vibrations a smaller value will be obtained. It is therefore not possible to fit the observed value of $(1/q_0)(\partial q/\partial T)_V$ using the Raman spectrum data and eqs. 12 and 13. Although the oscillation which is primarily responsible for the temperature dependence of q may lie at a lower frequency than any reported, a more likely reason for the discrepancy is the restriction placed upon the analysis by the assumptions involved in eq. 7.

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