

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 SbCl₃ at constant pressure, obtaining a value $(\partial\eta/\partial T)_P$ of about $-1.1 \times 10^{-4} \text{ K}^{-1}$ near 120°K, which is comparable with the value observed for BiCl₃; 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

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

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 $-4.5 \times 10^{-4} \text{ K}^{-1}$. 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 BiCl₃ 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 $6 \times 10^{-45} \text{ kg m}^2$. For the lowest frequency line reported in the Raman spectrum of solid BiCl₃ (5), namely 37 cm^{-1} , eq. 13 yields

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

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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