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Pressure and Temperature Dependence of the Nuclear Quadrupole Resonance of ^{79}Br in $NaBrO_3$*

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The theoretical and experimental study of the effects of temperature and pressure on the nuclear quadrupole resonance (NQR) frequency has been the subject of many investigations, some of which are listed in Refs. 1–9. The purpose of this Note is to report some new results of such an investigation of ^{79}Br in $NaBrO_3$.

The data were taken with a regenerative spectrometer similar to that described by Dehmelt[10] and modified by Koi.[11] The frequency measurements were conventional. Because of the very high transition frequency of ^{79}Br, the construction of the high pressure bomb was somewhat unorthodox. It was found that if the electrical feed throughs were seated in Lucite which, in turn, was seated in metal, the spectrometer would perform satisfactorily. (For further details see Ref. 12.) The frequency versus temperature at atmospheric pressure data were taken by Tipsword *et al.*[13] Details of their experimental methods may be found in the references.

In the Bayer[1]–Kushida[2] theory the temperature dependence of the NQR frequency is given by

$$\nu=\nu_Q[1-\tfrac{3}{4}\sum_i (\hbar A_i/\omega_i)\coth(\hbar\omega_i/2kT)], \qquad (1)$$

where ν_Q is the NQR frequency that would occur in the (hypothetical) case of no lattice vibration, A_i^{-1} is the ith moment of inertia of the bromate group, and ω_i is the ith frequency of vibration of the bromate group. The summation on i extends over the two approximately[2] equal low-frequency modes of rotation usually assumed for the bromate group. Following Kushida, Benedek, and Bloembergen[3] (KBB), we expand $\coth(\hbar\omega_i/2kT)$ in Eq. (1) at not too low temperatures to obtain an equation of the form

$$\nu=a(1+bT+c/T). \qquad (2)$$

The three parameters a, b, and c can be found by first

Table I. Quadrupole frequency vs pressure at constant temperature.

Temperature (°K)	Pressure (bar)	Frequency (Hz)
196	1	180 502 100
	345	180 533 600
	690	180 565 700
	862	180 580 300
273	1	179 248 300
	345	179 284 300
	690	179 321 000
	1035	179 358 200
290.5	1	178 940 100
	345	178 975 700
	690	179 011 500
	1035	179 048 400

finding their values at a particular volume and then observing their volume dependence from the pressure data. KBB[3] use this method to deduce the volume variation of ν_Q and certain averages of the A_i's and ω_i's.

The thermal expansion and elastic coefficients of $NaBrO_3$ have been measured by Mason.[14] From our pressure data and the compressibility, $V/\nu(\partial\nu/\partial V)_T$ has been computed. The pressure data are displayed in Table I. At the three temperatures at which the data were taken, the frequency varies with volume approximately as $V^{-0.225}$. This volume variation is relatively quite mild (e.g., Whidden *et al.*[8] found the ^{23}Na frequency in $NaBrO_3$ to vary as $V^{-2.5}$) and it appears to be consistent with the assumptions[8] that the bromate group changes only slightly in size and configuration with pressure and that at the Br nucleus the maximum-moment principal field gradient (to which ν_Q is proportional) is due primarily to the charge distribution within the local BrO_3^- ion. Calculations of the volume dependence of a, b, and c in Eq. (2) indicate that the (small) changes in ν_Q, A_i, and ω_i contribute approximately equally to the volume dependence of ν. Following the method of Gutowsky and Williams,[4] the thermal expansion was fit to an Einstein specific heat curve and adjusted to within 1% of Mason's[14] data, then the constant pressure data, shown by Curve A in Fig. 1, were corrected to constant volume at the three points at which the data were taken and at 0°K. The results are shown by Curve B in Fig. 1. A least-squares fit of these values to Eq. (1) resulted in a standard deviation of 0.0260 MHz with $\nu_Q = 183.8359$ MHz, $\omega_i = 36.455 \times 10^{12}$ sec^{-1}, and $A_i^{-1} = 45.13 \times 10^{-40}$ g·cm^2. These values are relatively close to those obtained by Tipsword *et al.*,[13] for ^{79}Br in $NaBrO_3$ in their case (case "*c*") of no assumed volume (or temperature) dependence for the two equal lattice frequencies. It should be pointed out however that the value of A_i^{-1} calculated from the BrO_3^- ion structure[13] is about 3 times larger than our fitted value, so at least to this extent our model is too simple for the temperature range fitted.

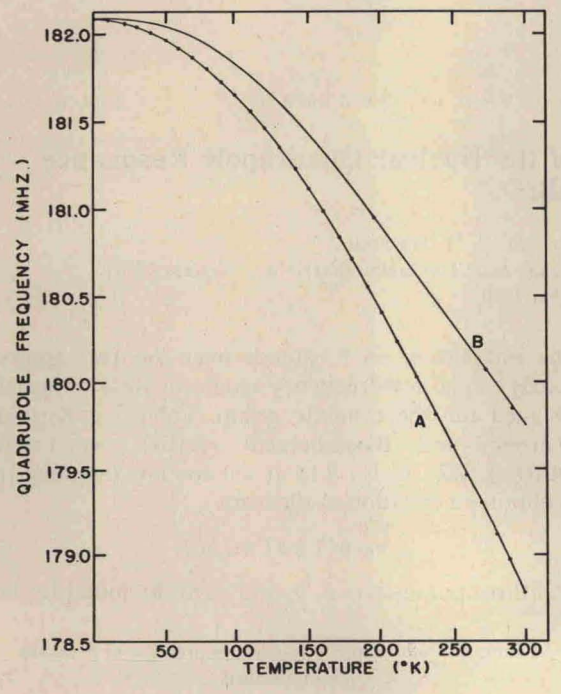

FIG. 1. The quadrupole frequency ν as a function of temperature at constant pressure is shown by Curve (A) and as a function of temperature at constant volume by Curve (B).

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