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 $f(x, \eta) = 0$.

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