Temperature variation of the electric field gradient in mercuric chloride

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Abstract. The temperature dependence of the ^{35}Cl quadrupolar resonance frequency has been measured in a high purity sample of mercuric chloride ($HgCl_2$) over the temperature range 4 K - 460 K. The results allow the temperature dependence of the electric field gradient (efg) at the two inequivalent sites of the chlorine atoms to be determined. Several models were considered to describe the experimental observations, including both librational and vibrational modes. The Bayer model for librational modes provides a satisfactory description of the data over the entire temperature range, when the temperature variation of the lattice modes is taken into account, while the other mechanisms considered provide less convincing descriptions. A single librational mode with a wavenumber of approximately 26 cm^{-1} can account for the variation of the electric field gradient over the temperature range investigated. Our conclusions are consistent with the results of optical spectroscopy investigations.

1. Introduction

$HgCl_2$ crystallises in a distorted rhombohedron structure. It is a molecular solid with essentially straight Cl-Hg-Cl molecules that form herring bone layers in the mirror plane of the *Pnma* space group at ambient pressures [1]. This results in two distinct non-cubic sites for the Cl atoms in the crystal, and hence a unique electric field gradient (efg) at each site. In this paper the two sites will be labeled A and B, where A is the site with the larger electric field gradient. The efg at both sites is known to have small deviations from axial symmetry. The interaction between the efg and the quadrupole moment of the Cl nuclei (both isotopes have $I = \frac{3}{2}$) lifts the degeneracy of the nuclear angular momentum energy levels, giving rise to resonance frequencies in the radio frequency region of the electromagnetic spectrum. Pure nuclear quadrupole resonance (NQR) may therefore be used to probe temperature-induced changes in the efg. For nuclei with $I = \frac{3}{2}$, in an efg with lower than axial symmetry, a single resonance line is observed with a frequency given by:

$$\nu_Q = e^2 q Q \sqrt{1 + \frac{\eta^2}{3}}, \tag{1}$$

where ν_Q is the NQR frequency. The quantities eq and η describe the magnitude and asymmetry of the efg respectively and eQ is the quadrupole moment of the nucleus. The results of a pulsed NQR investigation of the quadrupole resonance frequencies over a wide temperature range (4 K - 460 K) are presented here. From the results the temperature variation of the efg

Table 1. Wavenumbers (in cm^{-1}) for vibrational modes of $HgCl_2$ at ambient pressures as measured by Adams and Appleby [10].

T (K)	Translatory modes				Rotatory modes			ν_1	ν_3
295	18	26	43	74	124		167	315	383
150	18.5	26, 29	48	77	126	134		317	388

at the sites A and B are extracted, and the results compared with theoretical models for the variation of the efg with temperature.

NQR was first used to study $HgCl_2$ by Dehmelt *et al* [2], who established the resonance frequencies for both sites A and B, and both Cl isotopes (^{35}Cl and ^{37}Cl) at 303 K. A subsequent study by Dinesh and Narasimhan [3] (DN) investigated the temperature variation over a limited temperature range at several fixed points, and based their data analysis on the theory of Bayer [4] as modified by Kushida *et al* [5] and Brown [6]. They predicted a low wave number lattice frequency that had not been observed previously using optical spectroscopy. Dinesh and Smith (DS) [7] extended the temperature range of the measurements of the NQR frequencies in $HgCl_2$ to the temperature range 77 K - 400 K. They made no further analysis of the temperature dependence of the efg at the two sites despite the results differing markedly from the results published previously by DN. No further measurements or analysis of the temperature dependence of the NQR frequency have been reported. In particular, the temperature region below 77 K has not been explored at all. The work described here addresses the lack of published data for ν_Q in $HgCl_2$ in this temperature region. A more recent NQR investigation [8] has revisited the asymmetry parameter of the efg at room temperature and provided values consistent with theoretical calculations [9]. It is generally accepted that there are small distortions from axial symmetry in $HgCl_2$, but there is no definitive determination of the temperature dependence of this parameter.

The temperature variation of the efg in molecular solids arises from modulation of the static efg by lattice vibrations. The lattice dynamics of $HgCl_2$ have been studied as a function of temperature and pressure using Raman and infrared spectroscopy by Adams and Appleby [10], who have made a complete assignment of the vibrational spectrum from measurements made at 295 K and 150 K. In a more recent study by Voyiatzis and Papatheodorou [11] Raman spectra of mercuric chloride were taken at 77 K and 545 K. Neither of these data sets were available to DN in their data analysis, but the results confirm their prediction that low wave-number modes play a dominant role in the temperature variation of the efg. The results obtained by Adams and Appleby [10] are summarised in Table 1. The values obtained for the mode at approximately 26 cm^{-1} by Adams and Appleby [10] and Voyiatzis and Papatheodorou [11] are given in Table 2 and are plotted in Fig. 1. The significance of this particular mode will become clear in the discussion of our data that follows.

A more recent X-ray structure study by Subramanian and Seff [12] at room temperature has confirmed the general observations of the crystal structure. In particular, they have shown that the Cl-Hg bond-lengths are marginally larger than the parameters used by Brill *et al* [9] in their calculations.

2. Experimental details

A commercially obtained high purity powder sample of $HgCl_2$ was sealed in a quartz ampoule under vacuum. No further purification of the sample was undertaken. NQR frequencies for the ^{35}Cl and ^{37}Cl nuclei were measured using a standard coherent pulsed radio frequency spectrometer operating in the range 17 - 23 MHz. Quadrupolar spin echoes were obtained using the standard $\pi/2 - \pi$ sequence with a pulse separation of the order of 500 μs. Quadrature

Table 2. The temperature variation of the wavenumber of the mode at approximately 26 cm^{-1} as determined by Adams and Appleby [10] and Voyiatzis and Papatheodorou [11].

T (K)	k_1 (cm^{-1})
77	26.5
150	26.0
295	26.0
545	25.0

detection and phase cycling allowed measurement of the resonance frequency to an accuracy of 1 kHz for the ^{35}Cl nucleus.

Measurements were made using three experimental arrangements. A copper cryostat, fitted with a heater and a copper-constantan thermocouple in thermal contact with the sample, was used to obtain data in the range 77 K - 300 K. The cryostat was placed in an partially sealed nitrogen dewar above the level of the cryogen. A heater was immersed in the liquid to provide dense cold vapour, and hence exchange gas cooling of the cryostat. Temperature control was achieved using the cryostat heater and a copper-constantan thermocouple, together with an Oxford Instruments temperature controller calibrated with respect to the thermocouple. Above room temperature (300 K - 460 K) an oil bath was employed in conjunction with the copper-constantan thermocouple and the temperature controller. An Oxford Instruments continuous flow cryostat (CFC) was used in the low temperature region (4 K - 80 K). In these experiments the temperature was monitored using the Fe+7%Au-chromel thermocouple and a calibrated carbon-glass resistance thermometer. Temperature stability of the CFC was found to be well within 0.1 K in the range 4 K - 100 K, and the sample temperature remained constant during measurements within the precision of ν_Q.

3. Theoretical Models

The variation of the NQR frequency with temperature has been studied extensively in many molecular solids. In most cases a modified form of the Bayer model for molecular librations is sufficient to explain the observed temperature dependence, in the absence of a structural phase transition. In some cases the acoustic phonon contribution to the modulation has been significant. A brief review of the underlying theoretical models is presented.

3.1. Molecular Librations

A model for the temperature variation of the efg due to rotations about the axis of symmetry of the efg for a single mode was first developed by Bayer [4]. For a single mode the expression is of the form

$$\nu_Q(T) = \nu_0 \left[1 - \frac{3\hbar^2}{4Ik_B\Theta_T} \coth\left(\frac{\Theta_T}{2T}\right) \right], \tag{2}$$

where ν_0 is the limiting or static value of the resonance frequency, I is the moment of inertia of the rotating molecule and Θ_T is the characteristic temperature of the oscillation frequency. Kasprzak and Nogaj [13] have provided an illuminating discussion of the various models based on the Bayer model, and these models are presented briefly below. In each of these models the quantity a represents the the resonance frequency at 0 K. The other co-efficients may be determined from fitting the models to the data. These models do not take into account explicitly the asymmetry of the efg. This point will be addressed in more detail in the discussion that follows.

3.1.1. Kushida-Benedek-Bloembergen (KBB) model This model takes into account the effect of changes in the sample volume with temperature. Kushida *et al* [5] have correctly pointed out that NQR measurements are usually made at a constant pressure, not at a constant volume. The model has the following form:

$$\nu_Q(T) = a + bT + \frac{c}{T}. \tag{3}$$

3.1.2. Brown Model Brown [6] accounted for the anharmonicity of the librations by assuming a linear temperature dependence of the mode frequencies. The model has the form:

$$\nu_Q(T) = a + bT + cT^2. \tag{4}$$

3.1.3. Combined Brown and KBB (B-KBB) model This model takes into account both the changes in sample volume and the anharmonicity of the librations as follows:

$$\nu_Q(T) = a + bT + cT^2 + \frac{d}{T}. \tag{5}$$

3.1.4. Extended Brown Model In many measurements of the lattice dynamics a quadratic dependence of the libration frequencies has been observed. In an attempt to take this non-linearity into account a fourth term was added to the Brown model as follows:

$$\nu_Q(T) = a + bT + cT^2 + dT^3. \tag{6}$$

3.2. Acoustic Vibrations

A model for the contribution of acoustic phonons to the temperature variation of the efg has been developed by Stahl [14] and Stahl and Tipsword [15]. More recently this model has been applied to $KBrO_3$ [16]. For an axially symmetric efg the variation of the quadrupolar resonance frequency with temperature is of the form:

$$\nu_Q(T) = \nu_0 \left[1 - S\left(\frac{T}{\Theta_D}\frac{c_v}{9R} + \frac{1}{\exp\frac{\Theta_D}{T} - 1}\right)\right], \tag{7}$$

where the dimensionless quantity S represents the ratio of the Boltzmann energy at the Debye temperature to the rotational energy, Θ_D is the Debye temperature of the solid, and

$$\frac{c_v}{9R} = \left(\frac{T}{\Theta_D}\right)^3 \int_0^{\frac{\Theta_D}{T}} \frac{x^4 e^x}{(e^x - 1)^2}\, dx. \tag{8}$$

In the low temperature limit this model predicts a T^4 dependence, which changes to a linear dependence at high temperatures (for all practical purposes the linear dependence is apparent for $T \geq \Theta_D$).

4. Results and Discussion

The results for the entire temperature range studied for the ^{35}Cl nucleus at both sites A and B are given in Fig. 2. There is a smooth change in the efg with temperature over the entire temperature range, confirming that no phase transitions occur. The results are in excellent agreement with those of DS, but there are large discrepancies with those of DN at high temperatures, and in the region between 77 K and 273 K. All of the models discussed in the previous section were fitted to our data. The KBB and B-KBB models both produce unphysical results at low temperatures,

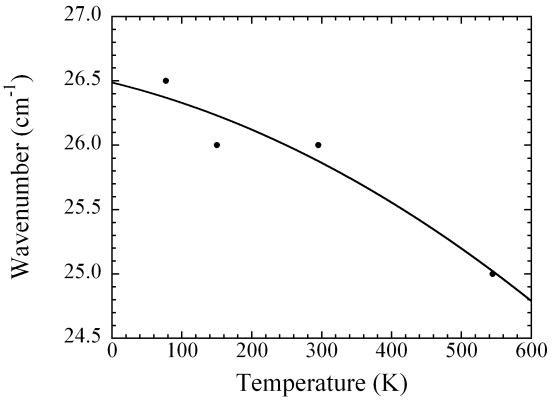

Figure 1. Values for the lattice mode at approximately 26 cm^{-1} obtained by Adams and Appleby [10] and Voyiatzis and Papatheodorou [11]. A quadratic is fitted to the data.

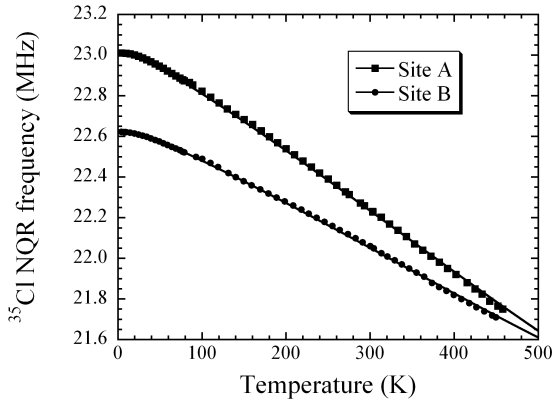

Figure 2. NQR resonance frequency data over the entire temperature range. The Bayer model for a single vibrational mode is fitted to the data. The fit parameters are given in Table 3.

as the $1/T$ term becomes dominant. The Brown model shows significant departures from the data at low temperatures, while the acoustic phonon model provides a markedly better fit in this temperature range. The Debye temperature extracted from the acoustic phonon fits is 120 $\pm$ 5 K. A value for the Debye temperature for $HgCl_2$ could not be sourced from the literature for comparison. Significant discrepancies between the data and the acoustic phonon model at high temperatures were noted, as there is a clear non-linear behaviour within the precision of the data. The Brown model provides a better description of the data at high temperatures. The extended Brown model produces a better fit to the data at low temperatures, as might be expected.

A consideration of the assignment of the symmetry of the Raman modes by Adams and Appleby [10] will allow determination of the modes most likely to contribute to thermal modulation of the efg. The rotatory modes are both of high wave-number and their contribution is insignificant. In addition, there appear to be large changes in the character of these modes with temperature (see Table 1), and this is not reflected in the high temperature measurements of this work and those of DS. Of the low energy translatory modes, the two at approximately 43 cm^{-1} and 74 cm^{-1} have been assigned to modes parallel to the molecule axis, and are therefore unlikely to contribute to rotations about the z-axis of the efg. The two lower modes (approximately 18 cm^{-1} and 26 cm^{-1}) have been assigned to modes perpendicular to the z-axis, and so these may contribute to rotations of the molecules. The presently accepted experimental values of the asymmetry parameter at room temperature are $\eta_A = 0.037$ and $\eta_B = 0.012$ [8]. Setting $\eta = 0$ for further analysis is unlikely to result in significant errors. Assuming that the temperature variation of η is negligible we apply a modified Bayer model for the single mode (2) at 26 cm^{-1} to the data for sites A and B as described below. The geometrical value for the rotational inertia was obtained from the structure data of Subramanian and Seff [12] and is $I = 6.187 \times 10^{-45}$ kg.m^2. The values of k_1 of the mode at approximately 26 cm^{-1} obtained experimentally [10, 11] are plotted against T in Fig. 1 and a quadratic of the form of the form $k_1(T) = a + bT + cT^2$ is fitted to the data to obtain a, b and c. Θ_T is proportional to $k_1(T)$ so Θ_T is of the form

$$\Theta_T = \alpha \left(a + bT + cT^2 \right). \tag{9}$$

We substituted (9) into the Bayer model (2), and the resulting expression was fitted to data

Table 3. Fit parameters for the Bayer model for a single mode over the entire temperature range.

Site	ν_0 (MHz)	α
A	23.070	1.59
B	22.676	1.83

for both lattice sites. The values for α and ν_0 extracted from the fit are given in Table 3. The fit provides an excellent description of ν_Q over the entire temperature range, except for small deviations at the highest and lowest temperatures (above 400 K and below 20 K respectively). We conclude that the temperature-induced changes in the efg at the two lattice sites are dominated by rotations of the molecules about the axis of symmetry of the efg for the mode at approximately 26 cm^{-1}.

5. Conclusions

The temperature dependence of the efg in $HgCl_2$ at the two inequivalent lattice sites has been deduced from measurements of the NQR frequencies over a wide temperature range. The data for the resonance frequency is best described by the model for molecular librations developed by Bayer [4] for a single mode with a wave number of approximately 26 cm^{-1}, although deviations above 400 K and below 20 K are noted. It is probable that these discrepancies are related to the necessary approximations employed in determining the temperature dependence of this mode obtained from the Raman data. None of the other models considered provide a convincing fit to the data over the entire temperature range. Our results suggest that further investigations of the lattice dynamics of $HgCl_2$ at lower temperatures would be of interest.

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