The Lattice Dynamics of Mercuric Chloride

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Abstract.
Measurements of the nuclear spin-lattice relaxation time (T_1) of the ^{35}Cl nuclei in a high purity sample of the molecular solid mercuric chloride ($HgCl_2$) have been made over the temperature range 9 K - 485 K using pure nuclear quadrupole resonance (NQR). Spin-lattice relaxation in this material appears to be dominated by lattice vibrations and/or molecular librations over the entire temperature range investigated. Analysis of the data using available spin-lattice relaxation models has allowed us to estimate the Debye temperature, and to follow changes in the lattice dynamics as a function of temperature. At temperatures above 340 K deviations from the expected quadratic relationship between the spin-lattice relaxation rate and temperature have been noted. Further analysis shows this is a thermally activated process related to the $HgCl_2$ molecules changing their position in a double-well potential. A previously unobserved doublet in the NQR spectrum of the ^{35}Cl nuclei was seen at temperatures above 340 K. The perturbation underlying the changed line-shape appears to be related to hindered re-orientations of the $HgCl_2$ molecules in the crystal lattice. The correlation time of the perturbation was calculated for a range of temperatures. The temperature dependence of the correlation time may be understood by noting the fact that the structure of the unit cell of the lattice is temperature dependent. We conclude that there is a correlation between the high temperature T_1 results and the doublet observed in the NQR spectrum.

1. Introduction

Mercuric chloride ($HgCl_2$) crystallizes in a distorted rhombohedral 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, giving rise to a unique electric field gradient (EFG) at each site [2]. In this paper the two sites will be labelled A and B, where A is the site with the larger EFG. As the temperature of the crystal increases the orthorhombic distortion constants of the crystal lattice decrease [1]. Both the ^{35}Cl and the ^{37}Cl nuclei have a spin of $I = \frac{3}{2}$. The presence of an EFG, and the fact that the nuclei have a quadrupole moment, allow for the use of pure nuclear quadrupole resonance (NQR) to probe the properties of solid $HgCl_2$. The two inequivalent sites in $HgCl_2$ result in two distinct NQR frequencies at a particular temperature. At room temperature the ^{35}Cl resonance frequencies for two sites are 22.2489 MHz (Site A) and 22.0655 MHz (Site B). The difference in frequencies decreases as the temperature increases, and the frequencies approach one another as the temperature moves toward the melting temperature (549 K) [3].

A number of NQR investigations of $HgCl_2$ have been reported. The resonance frequency of the Cl nuclei was first reported by Dehmelt *et al* [2], while the asymmetry parameter η

was investigated by Dinesh and Narasimhan [4] and Negita *et al* [5]. More recently, Keartland and Newby [3] have presented a comprehensive study of the temperature dependence of the quadrupole resonance frequency in $HgCl_2$ over the temperature range 4 K - 500 K. The variation of the spin-lattice relaxation time (T_1) with temperature of the ^{35}Cl nuclei in $HgCl_2$ was reported by Dinesh and Smith (DS) [6] over the temperature range 77 K - 398 K. DS also measured the temperature dependence of the inverse line-width parameter T_2^* of the NQR spectrum. The temperature dependence of T_1 of the ^{35}Cl nuclei in a related material (the molecular solid $NaClO_3$) has been measured by Zamar *et al* [7] over a wide range of temperature.

In this paper we describe measurements of T_1 and the NQR spectrum of the ^{35}Cl nuclei in $HgCl_2$, made using pulsed NQR methods over a wide temperature range (9 K - 485 K). We show that lattice vibrations dominate the measured spin-lattice relaxation rate up to 340 K, and that a thermally-activated process becomes important at higher temperatures. The NQR spectrum splits into a doublet for $T \geq 340$ K. Hindered re-orientation of the $HgCl_2$ molecules is identified as a likely mechanism to describe both the T_1 results, and the changes in the NQR spectrum.

2. Experimental Considerations

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 measurements were made using a standard coherent pulsed radio frequency spectrometer operating in the range 17 - 23 MHz. Averaging, quadrature detection and phase-cycling were used to obtain quadrupolar spin-echoes with an excellent signal-to-noise ratio. Relaxation times were obtained using an inversion-recovery-echo pulse sequence applied at the resonance frequency of the nuclear spin system. Measurements of T_1 were made at both lattice sites for the ^{35}Cl nuclei. Quadrupolar spin-echoes were recorded at each temperature, and the NQR spectra obtained from Fast Fourier Transforms (FFTs) of the spin-echo signals. Temperature control was achieved to an accuracy of better than 0.1 K using two separate arrangements. For measurements between 300 K and 500 K the sample was placed inside a copper can fitted with a heater and copper-constantan thermocouple. The entire can was placed inside a thermally insulated sleeve. Temperature control is via an Oxford ITC503 temperature controller. For temperatures below 300 K an Oxford continuous flow cryostat was used in conjunction with the temperature controller and the built-in cryostat thermocouple. Liquid nitrogen and liquid helium were used as cryogens. The temperature for each measurement was obtained from a previous careful calibration of the NQR frequency [3].

3. Results and Analysis

3.1. Spin-Lattice Relaxation Time

The spin-lattice relaxation times of the ^{35}Cl nuclei in $HgCl_2$ over the entire temperature range (9 K - 485 K), are plotted in Fig. 1. The spin-lattice relaxation times at site A and site B differ slightly at the same temperature. In the discussion that follows we identify three temperature ranges: below 100 K (low temperature), between 100 K and 340 K (intermediate temperature), and above 340 K (high temperature). Where it is appropriate we compare our results to those of DS [6].

Spin-lattice relaxation in the temperature range 9 K - 280 K should be dominated by the vibrational or librational modes of $HgCl_2$. Two models were fitted to the data in this temperature range, and the fits to the models for Site A are shown in Fig. 2. A two-phonon Raman model [8] provides an excellent fit to the data, and the Debye temperature extracted from the fit is 47 ± 5 K. A value for the Debye temperature of $HgCl_2$ could not be sourced from the literature for comparison. The model for molecular librations [9] (assuming a single mode) provides a less satisfactory fit, and gives a characteristic temperature of 31.6 ± 0.4 K (corresponding to a wave number of 22 cm^{-1}). This does not correspond to any lattice modes observed previously

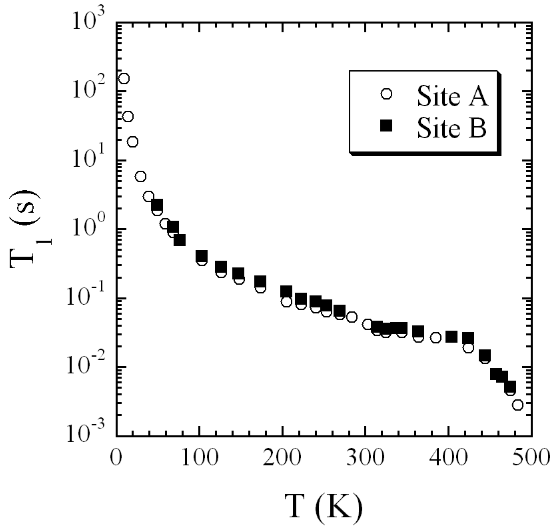

Figure 1. A plot T_1 vs T for the entire temperature range studied (9 K - 485 K). Three regions are identified for analysis: 9 K - 280 K, 100 K - 340 K and above 340 K.

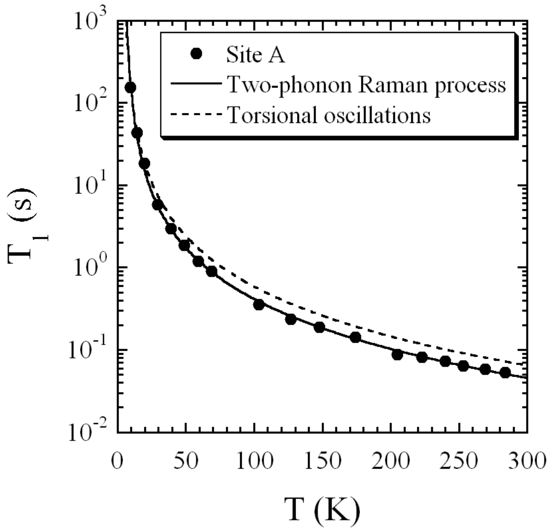

Figure 2. A plot of T_1 vs T for the temperature range 9 K - 280 K. The fits of a two-phonon Raman model [8]and a model for torsional oscillations [9] are shown.

Table 1. Comparison of the values of n obtained in this paper with those obtained by DS [6]

Site	n (this work)	n (DS [6])
A	2.04 ± 0.06	1.79 ± 0.16
B	2.11 ± 0.08	1.89 ± 0.15

using Raman spectroscopy, although there is a mode at 18 cm^{-1} [10]. It is possible that a number of modes contribute, in which case it is the lowest wave number modes that dominate. It is reasonable to ascribe spin-lattice relaxation in this temperature region to acoustic phonons, and to offer the value for the Debye temperature extracted as realistic estimate of the Debye temperature of $\mathrm{HgCl_2}$.

The relaxation rate in the intermediate temperature range 100 K - 340 K was analysed using the well-known relation for the vibrational relaxation rate [11]

$$\left(\frac{1}{T_1}\right)_{vib} = AT^n. \tag{1}$$

It is expected that $n \simeq 2$ in this temperature range. A plot of $-\ln T_1$ vs T for both lattice sites in the intermediate temperature range is shown in Fig. 3, and the extracted results for n are given in Table 1. The T_1 data obtained by DS [6] for the same temperature range were analysed using (1), and the results for n are also given in Table 1. The values of n for site B agree within experimental error, while those for site A show a small discrepancy. The rate parameter A was determined for each site by fitting (1) to the data for 100 K - 340 K for each site using $n = 2$, and the results for A obtained were used in analysis of the high temperature data that follows.

The relaxation rate attributed to the vibrational modes was subtracted from the total relaxation rate for temperatures above 340 K, and the resulting data were fitted to an Arrhenius

Table 2. Values of the activation energy E_A obtained using the Arrhenius model (2) for the spin-lattice relaxation data above 340 K.

Site	E_A ($\mathrm{kJ\,mol^{-1}}$)
A	97 ± 14
B	83 ± 10

model of the form [7]

$$\left(\frac{1}{T_1}\right)_{total} - \left(\frac{1}{T_1}\right)_{vib} = B \exp\left[-\frac{E_A}{k_B T}\right]. \tag{2}$$

The results are shown in Fig. 4. The resulting activation energies E_A are tabulated in Table 2, where E_A is the height of the potential barrier. Zamar *et al* [7] obtained an activation energy of 26.4 ± 1 kJ.mol^{-1} for $NaClO_3$, and proposed that orientational disorder accounts for the deviation from relaxation governed by vibrations. We propose that the increase in the spin-lattice relaxation rate at high temperatures is due to re-orientations of the $HgCl_2$ molecules in a double-well potential. Evidence for this is provided by the changes observed in the NQR spectrum (as discussed below).

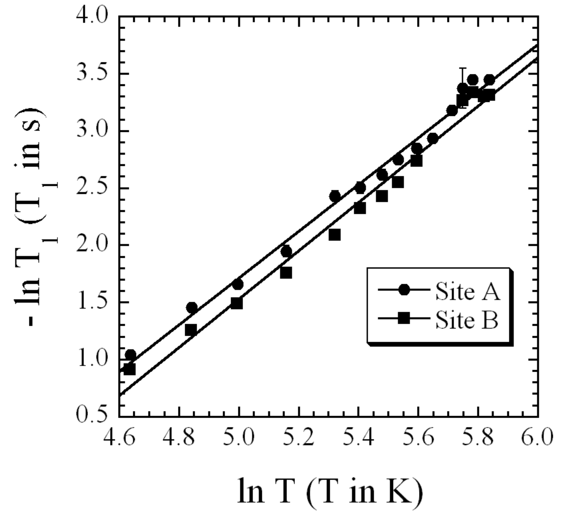

Figure 3. A plot of $-\ln T_1$ vs T for the intermediate temperature range (100 K - 340 K). An expression for the vibrational relaxation rate (1) was fitted to the data, and a value of n for each site was extracted, and the results are presented in Table 1.

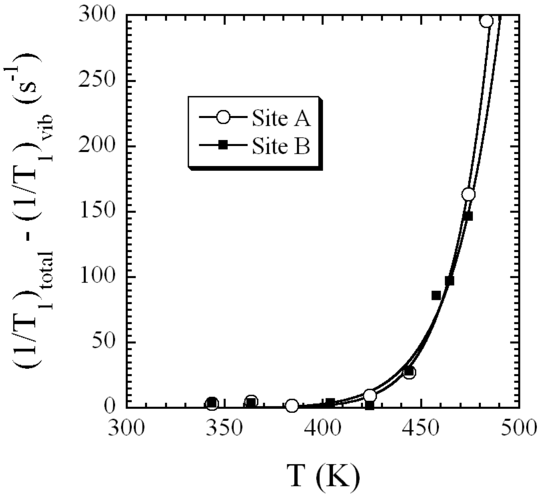

Figure 4. A plot of the total relaxation rate less the vibrational relaxation rate as a function of temperature for the T_1 data in the temperature range $T > 340$ K. An Arrhenius model (2) is fitted to the data, and the results are presented in Table 2.

3.2. NQR Spectrum

The NQR spectra obtained from FFTs of the quadrupolar spin echoes are shown in Fig. 5. Seliger [12] has pointed out that the NQR spectrum will split into a doublet when conditions such as those considered by Zamar *et al* [7] are applicable. Zamar *et al* do not report a doublet in the ^{35}Cl spectra at high temperatures in $NaClO_3$, while the spectra in Fig. 5 show clear evidence of an emerging doublet at 350 K, and the frequency difference between the doublet peaks increase the temperature increases. The doublet arises from a perturbation, in the form of a two-site exchange, to the unperturbed quadrupolar Hamiltonian. The correlation time τ_c of the perturbation causing the change in the observed resonance line may be calculated by manipulating the expressions derived by Seliger [12]. The temperature range was divided into two regions; temperatures below which the doublet is observed (118 K - 332 K), and temperatures above which the doublet is observed (350 K - 425 K). Full details of the calculation will be presented elsewhere. The calculated values of the correlation time of the perturbation for 118 K - 425 K are shown in Fig. 6.

A number of physical phenomena could lead to changes to the NQR resonance line-shape. They include vibration and re-orientation of the $HgCl_2$ molecules, interconversions between molecular conformers, and diffusion of molecules through the crystal lattice [13]. Re-orientation of the $HgCl_2$ molecules is considered to be the most likely underlying mechanism. The molecule re-orientates in a periodic potential arising from inter-molecular forces [13], which restrict the re-orientation. Three types of transitions may be identified; the molecule could make transitions between states in the same potential well, the molecule could tunnel through the potential barrier, or the molecule could be excited to a level above the barrier, rotate classically as a rigid system and drop into another potential well [13]. We suggest that the doublet in the NQR spectrum results from a two-site exchange which eliminates the first type of transition mentioned above. The second type of transition is only significant at low temperatures [13], and may also be eliminated. The third type of transition (two-site exchange) is the most likely mechanism, and we propose that the essentially straight Cl-Hg-Cl molecule rotates through π radians. It can be seen from Fig. 6 that the correlation time of the rotation of the $HgCl_2$ molecule which causes the perturbation decreases as the temperature increases from $T = 118$ K until it reaches a minimum at $T \simeq 300$ K. This occurs because the energy of the molecules in the crystal lattice increases, allowing them to rise above the potential barrier and execute a rotation. It follows that the molecules spend less time in each state and so the correlation time decreases. We suggest that the increase in τ_c above 300 K is related to the change in the orthorhombic distortion constants of the $HgCl_2$ crystal lattice. This results in an increase in the height of the potential barrier between states, making it less likely that a molecule would execute a rotation. The T_2^* measurements of DS [6] also show a turning point at $T \approx 300$ K although their turning point is, as expected, a maximum instead of a minimum (T_2^* is a measure of width in the time domain, and the linewidth is measured in the frequency domain). This behavior of T_2^* was not discussed in any detail by DS. We note that the linewidth in our sample has a minimum at approximately 300 K, in agreement with both the results of DS, and the calculated correlation time.

Fig. 5 shows that the frequency difference between the two peaks in the doublet increases with temperature, in agreement with the decrease in the orthorhombic distortion constants of the crystal. This changes the structure of the potential well, and the resonance frequency of each well changes. The thermally activated increase in the relaxation rate at elevated temperatures, and changes the spectrum line-shape may be traced to the same underlying physical mechanism.

4. Conclusion

A comprehensive study was made of the temperature dependence of the spin-lattice relaxation time of the ^{35}Cl nuclei in $HgCl_2$. It was found that the data could be divided into three temperature ranges and models were successfully fitted to the data in each of the temperature ranges as can be seen in Figs. 2, 3 and 4. The T_1 values in the temperature range 100 K - 340 K were found to agree with the values previously obtained by DS [6]. Hindered re-orientations of the Cl-Hg-Cl molecules are identified as a likely physical model for the appearance of a doublet in the NQR spectrum. The broadening of the split is ascribed to the decrease of the orthorhombic distortion constants of the $HgCl_2$ lattice at high temperatures. The correlation times of the

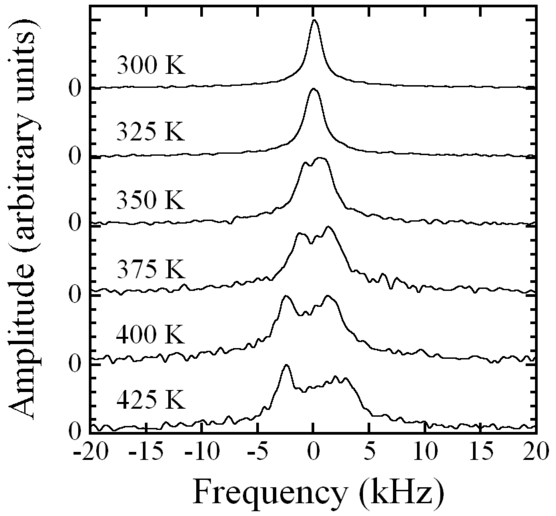

Figure 5. The NQR spectra of ^{35}Cl in $HgCl_2$ for a number of temperatures showing the emergence of a doublet as the temperature increases above 340 K. The linewidth is a minimum at $T \simeq 300$ K.

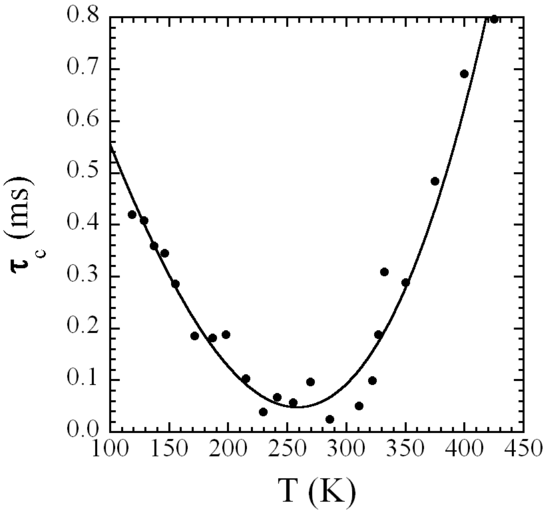

Figure 6. A plot of the extracted correlation time (τ_c) as a function of temperature using a modification of the model suggested by Seliger [12]. The solid line is a guide for the eye.

re-orientations were calculated in the temperature range 118 K - 425 K by assuming that the re-orientations could be modelled as a symmetric two site exchange and making use of the model developed by Seliger [12]. The model considered provides a satisfying description of changes in both the relaxation rate and the resonance line-shape with temperature.

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