

Spectroscopic Modifications of the Pippard Relations for NaNO_2 in the Paraelectric Phase

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We examine here our spectroscopic modification of the first Pippard relation for the paraelectric phase of NaNO_2 . By establishing a linear variation of the specific heat C_P with the frequency shifts $\frac{1}{\omega} \frac{\partial \omega}{\partial T}$ for the $q[010]$, $q[001]$ and $q[100]$ modes of NaNO_2 , we are able to calculate $dT=dP$ values for the paraelectric phase in this crystalline system. Our calculated $dT=dP$ values agree with those given in the literature.

PACS. 63.70.+h Statistical mechanics of lattice vibrations and displacive phase transitions.

I. Introduction

NaNO_2 exhibits a second order transition from the paraelectric phase to the sinusoidal antiferro-electric phase at the Néel temperature $T_N = 165.3 \text{ }^\circ\text{C}$. At lower temperatures this transition becomes a first order transition from the sinusoidal antiferro-electric phase to the ferroelectric phase at the Curie temperature $T_C = 163.9 \text{ }^\circ\text{C}$. These transitions of the second order and the first order type from the paraelectric to the sinusoidal antiferro-electric and eventually to the ferroelectric phases, have been investigated both experimentally and theoretically in the literature. We have reviewed some of those studies in our recent work [1]. Various experimental and theoretical techniques have been used to study the mechanism of phase transitions in the NaNO_2 crystal. Among those experimental studies, some earlier X-ray [2-4], dielectric [5-7] and calorimetric [8, 9] measurements on NaNO_2 have been carried out. Later, another X-ray [10] and another dielectric [11] study on NaNO_2 were reported. Measurements for the thermal expansivity [12] and for the elastic compliances [13] close to the phase transitions in NaNO_2 , have also been reported. Spectroscopic techniques such as NMR [14], neutron scattering [15], infrared [16], Raman [17], ultrasonic [18-20] and Brillouin [21] scattering have been used to study the phase transitions in NaNO_2 .

The mechanism of phase transitions in NaNO_2 has been studied theoretically using some microscopic models. An Ising model analogy of the NaNO_2 system was given earlier in the literature [22]. Some other microscopic models [23, 24] have also been reported in the literature. Recently, we have calculated [1] the Brillouin frequencies of the L-mode [010], [001] and [100] of NaNO_2 in the paraelectric, sinusoidal antiferro-electric and ferroelectric phases, using the experimental data for the thermal expansivity [12] and for the Brillouin frequency [21] in this crystalline system.

In this study we modify the Pippard relations spectroscopically in the paraelectric phase of NaNO_2 . For this modification we relate the specific heat C_P to the frequency shifts $\frac{1}{\omega} \frac{\partial \omega}{\partial T}$ close to the Néel temperature T_N in the paraelectric phase of NaNO_2 .

In Section 2 we give an outline of the theory. In Section 3 we present our calculations and results. Discussion and conclusions are given in Sections 4 and 5, respectively.

II. Theory

The critical behaviour of the thermodynamic functions can be studied close to phase transitions. In the vicinity of the T_N -transition point Pippard related the specific heat C_P to the thermal expansivity α_P and also α_P to the isothermal compressibility β_T [25]. The Pippard relations can be expressed as

$$C_P = T \left(\frac{dP}{dT} \right)_V \alpha_P + T \left(\frac{dS}{dT} \right)_P ; \quad (1)$$

and

$$\alpha_P = \left(\frac{dP}{dT} \right)_V \cdot T + \frac{1}{V} \left(\frac{dV}{dT} \right)_P ; \quad (2)$$

In these expressions the variations of the entropy ($dS=dT$) and the volume ($dV=dT$) with the temperature are taken as constants at the T_N transition point. Eq. (1) assumes that the specific heat varies linearly with the thermal expansivity. Also, a linear variation of the thermal expansivity with the isothermal compressibility is assumed in Eq. (2). Thus, in the vicinity of the T_N point it is assumed that the thermodynamic functions such as the specific heat C_P , the thermal expansivity α_P and the isothermal compressibility β_T exhibit similar critical behaviour according to Eqs. (1) and (2).

We have modified spectroscopically the Pippard relations in our earlier studies [26, 27] by defining the isobaric mode Grüneisen parameter

$$\alpha_P^{\circ} = \frac{1}{\alpha_P} \left(\frac{1}{\omega} \frac{\partial \omega}{\partial T} \right)_P ; \quad (3)$$

and the isothermal mode Grüneisen parameter

$$\beta_T^{\circ} = \frac{1}{\beta_T} \left(\frac{1}{\omega} \frac{\partial \omega}{\partial P} \right)_T ; \quad (4)$$

This definition of the mode Grüneisen parameter α_P° is essentially the variation of the volume and the frequency with the temperature at constant pressure. Similarly, β_T° defines the variation of the volume and the frequency with the pressure at constant temperatures. By assuming that the mode Grüneisen parameters α_P° and β_T° remain constant right through the phase transitions, we can modify spectroscopically the Pippard relations (Eqs. 1 and 2) by means of Eqs. (3) and (4). Those spectroscopic modifications of the Pippard relations are then expressed as

$$C_P = T V \left(\frac{dP}{dT} \right)_V \alpha_P^{\circ} \left(\frac{1}{\omega} \frac{\partial \omega}{\partial T} \right)_P + T \left(\frac{dS}{dT} \right)_P ; \quad (5)$$

and

$$\alpha_p = \frac{1}{V} \left(\frac{\partial \mu}{\partial T} \right)_P + \frac{1}{V} \left(\frac{\partial \mu}{\partial P} \right)_T + \frac{1}{V} \left(\frac{\partial \mu}{\partial T} \right)_P \quad (6)$$

as we have also expressed previously [26, 27]. Thus, the above relations relate the specific heat C_p to the frequency shifts with temperature (Eq. 5) and the thermal expansivity α_p to the frequency shifts with pressure (Eq. 6) in the vicinity of the T_c -point. As a result of the Pippard relations (Eqs. 1 and 2) the specific heat C_p varies linearly with the frequency shifts $\left(\frac{\partial \omega}{\partial T} \right)_P$ and also the thermal expansivity α_p varies linearly with the frequency shifts $\left(\frac{\partial \omega}{\partial P} \right)_T$ according to Eqs. (5) and (6). As assumed for the Pippard relations (Eqs. 1 and 2), we also assume here that C_p and $\left(\frac{\partial \omega}{\partial T} \right)_P$ exhibit similar critical behaviour near T_c (Eq. 5). Accordingly, we assume that a similar critical behaviour is exhibited by α_p and $\left(\frac{\partial \omega}{\partial P} \right)_T$ near T_c (Eq. 6).

Our spectroscopic modifications of the Pippard relations (Eqs. 5 and 6) can be applied to NaNO_2 . For this application we require the temperature dependence of the specific heat C_p and of the frequency shifts $\left(\frac{\partial \omega}{\partial T} \right)_P$ for NaNO_2 according to Eq. (5). Also, we require the temperature dependence of the thermal expansivity α_p and of the frequency shifts $\left(\frac{\partial \omega}{\partial P} \right)_T$ for NaNO_2 according to Eq. (6).

In this study we apply our spectroscopic modification of the first Pippard relation (Eq. 5) to NaNO_2 in its paraelectric phase ($T > T_N$). By means of Eq. (3), the temperature dependence of the frequency can be expressed as

$$\ln \omega(T) = \ln \omega_0 - \int_{T_N}^T \alpha_p(T) dT; \quad (7)$$

as we have also expressed in our recent study [1]. In Eq. (7) ω_0 is the value of the frequency at a constant temperature T_0 and T_N is the Neél temperature ($T_0 > T_N$). The temperature dependence of the thermal expansivity can be expressed as

$$\alpha_p(T) = A_1 2^{i_1} + B_1; \quad (8)$$

where i_1 is the critical exponent for the thermal expansivity, A_1 and B_1 are constants, and the reduced temperature is $2 = \frac{T - T_N}{T_N}$ with the Neél temperature T_N . For NaNO_2 in the paraelectric phase Eq. (8) has been given by Ema *et al.* [12]. So, the frequencies can be calculated using the temperature dependence of the thermal expansivity (Eq. 8) by means of Eq. (7). This then gives the temperature dependence of the frequency shifts $\left(\frac{\partial \omega}{\partial T} \right)_P$ for Eq. (5). On the other hand, the temperature dependence of the specific heat C_p has been given [28] for the paraelectric phase of NaNO_2 as

$$C_p = A_c^+ 2^{i^+} + B_2 + B_0; \quad (9)$$

where i^+ is the critical exponent for the specific heat, and A_c^+ , B and B_0 are constants.

III. Calculations and results

We established here the first Pippard relation, which we modified spectroscopically (Eq. 5) using the specific heat C_p data [28] and our calculated frequency shifts $\left(\frac{\partial \omega}{\partial T} \right)_P$ for the $q[010]$,

q[001] and q[100] modes of NaNO₂ [1] in the paraelectric phase ($T > T_N$). For this phase we used the specific C_P data according to Eq. (9) where the value of the critical exponent was $a^+ = 0.38$ with the Néel temperature $T_N = 437.7$ K and the values of the coefficients were taken as $A_c^+ = 0.77$ cal/mol.K, $B = 36.3$ cal/mol.K and $P_0 = 18.8$ cal/mol.K [28].

For calculating the frequency shifts $\frac{1}{\omega} \frac{\partial \omega}{\partial T} \bigg|_P$, we first obtained the temperature dependence of the Brillouin frequencies, which we calculated [1] using the experimental frequency data [21] for the q[010], q[001] and q[100] modes of NaNO₂. For this calculation we used Eq. (7), where the experimental data for the temperature dependence of the thermal expansivity α_P [12] were used according to Eq. (8) [1].

As indicated above, the specific heat C_P and the thermal expansivity α_P should exhibit similar critical behaviour in the vicinity of the ω_c point, according to the Pippard relation (Eq. 1). In fact, for NaNO₂ it has been reported that the values of the critical exponents are $\alpha_1 = 0.36$ for the thermal expansivity α_P [12] and $a^+ = 0.38$ for the specific heat C_P [21]. This indicates that the thermal expansivity α_P and the specific heat C_P show similar critical behaviour, as expected. On the other hand, the above argument indicates that the frequency shifts $\frac{1}{\omega} \frac{\partial \omega}{\partial T} \bigg|_P$ should also exhibit similar critical behaviour as C_P and α_P , according to a spectroscopic version of the Pippard relation (Eq. 5). Since the temperature dependences of the thermal expansivity α_P and of the specific heat C_P in the vicinity of the ω_c point can be expressed as Eqs. (8) and (9), respectively, we can express the temperature dependence of the frequency shifts $\frac{1}{\omega} \frac{\partial \omega}{\partial T} \bigg|_P$ as

$$\frac{1}{\omega} \frac{\partial \omega}{\partial T} \bigg|_P = a_c \tau^{1-a} + a_1 \tau + a_0 \quad (10)$$

This is the same functional form as the specific heat C_P (Eq. 9), with the exponent a , amplitude a_c , a_1 and a_0 as constants. In Eq. (10) the reduced temperature is $\tau = \frac{T - T_N}{T_N}$, as before. By means of Eq. (10), we were then able to determine the frequency shifts for each mode for the paraelectric phase in the NaNO₂ crystal.

III-1. Analysis of the q[010] mode of NaNO₂

In order to obtain the temperature dependence of the Brillouin frequency shifts $\frac{1}{\omega} \frac{\partial \omega}{\partial T} \bigg|_P$ for the q[010] mode of NaNO₂ in the paraelectric phase ($\omega_0 = 20.32$ GHz at $T_0 = 444$ K, Eq. 7), we employed Eq. (10) within the temperature interval of $438 \text{ K} < T < 442 \text{ K}$, with the values of the coefficients a_c , a_1 and a_0 , which are tabulated in Table I. For this analysis we used the value of the critical exponent for the frequency shifts $\frac{1}{\omega} \frac{\partial \omega}{\partial T} \bigg|_P$ as $a = 0.38$, which is the same value of a^+ for the specific heat C_P [28]. By calculating the frequency shifts $\frac{1}{\omega} \frac{\partial \omega}{\partial T} \bigg|_P$ for the q[010] mode as a function of temperature, we examined our spectroscopic modification of the first Pippard relation (Eq. 5) using the specific heat C_P data [28]. We established a linear variation of the specific heat with the frequency shifts for the q[010] mode of NaNO₂ in the paraelectric phase ($T > T_N$), as shown in Fig. 1. From this plot, we calculated the slope value of $dT = dP = 6.57$ mK/bar for the paraelectric phase of NaNO₂, according to Eq. (5) where we used our value of the isobaric mode Grüneisen parameter $\gamma_P = 7.32$ for the q[010] mode [1], $T = T_N = 437.7$ K and $V = V_c = 33.2$ cm³/mol as the critical value of the crystal volume [12]. We also obtained from this plot the intercept value of $dS = dT = 0.032$ cal/mol.K², as given in Table I.

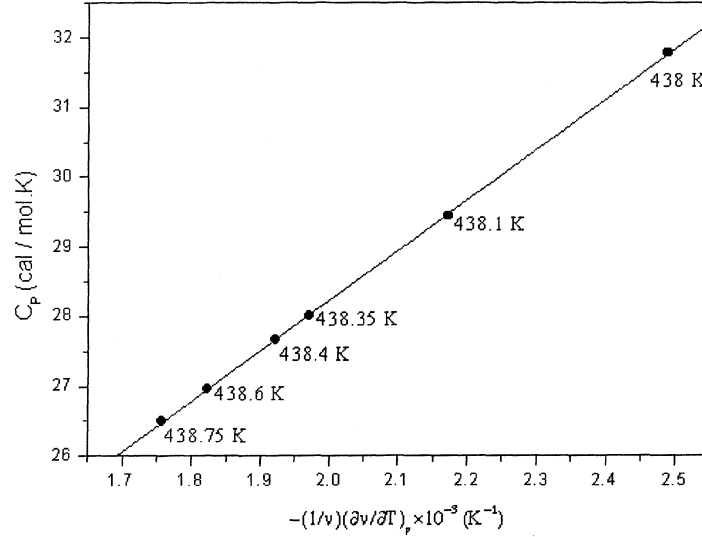


FIG. 1. The specific heat C_P as a function of the frequency shifts $\frac{1}{\nu} \frac{\partial \nu}{\partial T}$ for the $q[010]$ mode of NaNO_2 in the paraelectric phase ($T > T_N$) close to the Neél temperature ($T_N = 437.7$ K) according to Eq. (5). The C_P data are taken from Ref. (28).

TABLE I. Values of the coefficients a_c , a_1 and a_0 for the modes indicated according to Eq. (10). The values of the isobaric mode Grüneisen parameter α_p given here, are taken from our recent study [1]. The values of the slope $dT=dP$ and the intercept $dS=dT$ due to the Brillouin frequencies of the modes considered according to Eq. (5), are given for the paraelectric phase ($T > T_N$) of NaNO_2 .

Mode	$a_c (K^{-1})$	$a_1 (K^{-1})$	$a_0 (K^{-1})$	α_p	$dT=dP$ (mK/bar)	$dS=dT$ (cal/mol.K ²)
$q[010]$	$-1 \text{ } \epsilon \text{ } 10^i \text{ } 4$	$5.6 \text{ } \epsilon \text{ } 10^i \text{ } 3$	$-7.7 \text{ } \epsilon \text{ } 10^i \text{ } 4$	7.32	6.57	0.031
$q[001]$	$-9.8 \text{ } \epsilon \text{ } 10^i \text{ } 5$	$6.9 \text{ } \epsilon \text{ } 10^i \text{ } 3$	$-7.4 \text{ } \epsilon \text{ } 10^i \text{ } 4$	7.01	6.54	0.031
$q[100]$	$-8.6 \text{ } \epsilon \text{ } 10^i \text{ } 6$	$8.6 \text{ } \epsilon \text{ } 10^i \text{ } 4$	$-6.7 \text{ } \epsilon \text{ } 10^i \text{ } 5$	0.62	6.48	0.031

III-2. Analysis of the $q[001]$ mode of NaNO_2

The frequency shifts were determined for the $q[001]$ mode of NaNO_2 as a function of temperature within the same temperature interval ($438 \text{ K} < T < 442 \text{ K}$) in the paraelectric phase ($\nu_0 = 17.94 \text{ GHz}$ at $T_0 = 444 \text{ K}$, Eq. 7). For this determination according to Eq. (10), using $a = 0.38$ as before, the values of the coefficients a_c , a_1 and a_0 are given in Table I. Using Eq. (5), the specific heat C_P data [28] were plotted against our calculated frequency shifts $\frac{1}{\nu} \frac{\partial \nu}{\partial T}$ for the $q[001]$ mode of NaNO_2 close to the Neél temperature in the paraelectric phase. Our plot is

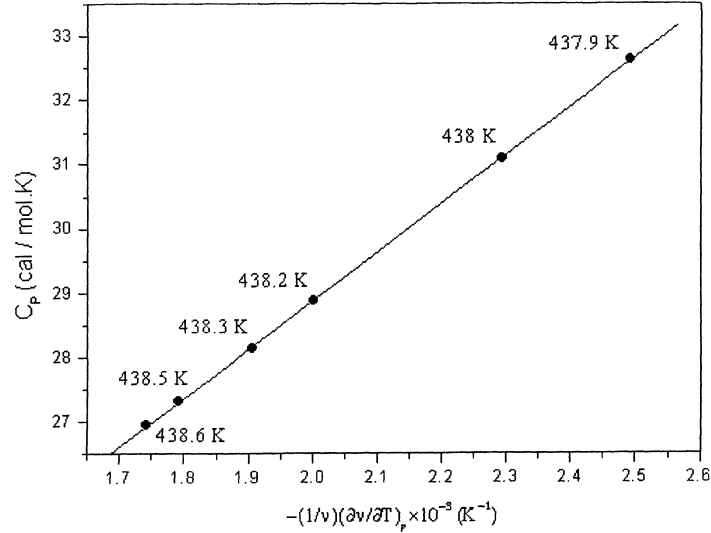


FIG. 2. The specific heat C_p as a function of the frequency shifts $\frac{1}{\nu} \frac{\partial \nu}{\partial T}$ for the $q[001]$ mode of NaNO_2 in the paraelectric phase ($T > T_N$) close to the Neel temperature ($T_N = 437.7 \text{ K}$) according to Eq. (5). The C_p data are taken from Ref. (28).

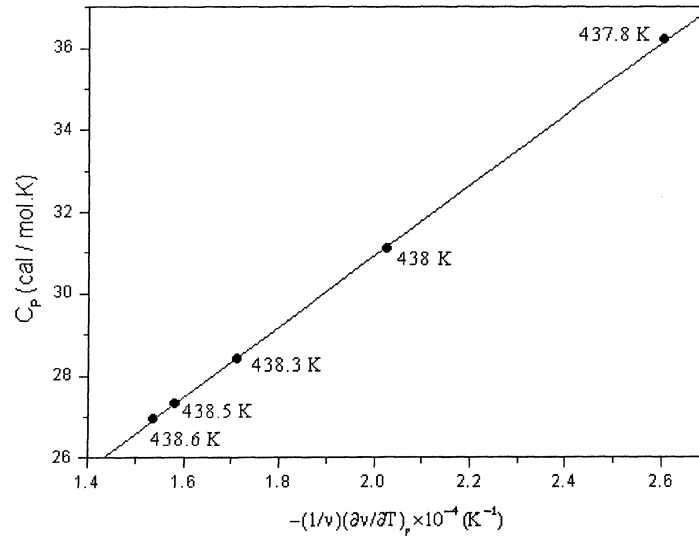


FIG. 3. The specific heat C_p as a function of the frequency shifts $\frac{1}{\nu} \frac{\partial \nu}{\partial T}$ for the $q[100]$ mode of NaNO_2 in the paraelectric phase ($T > T_N$) close to the Neel temperature ($T_N = 437.7 \text{ K}$) according to Eq. (5). The C_p data are taken from Ref. (28).

given in Fig. 2. Within the temperature region indicated, we were able to calculate the slope and the intercept which had the values of $dT=dP = 6.54 \text{ mK/bar}$ and $dS=dT = 0.031 \text{ cal/mol.K}^2$, respectively, according to Eq. (5), which we give in Table I. In Eq. (5) we used our value of

the isobaric mode Grüneisen parameter $\alpha_p = 7.01$ [1], $T = T_N = 437.7$ K and $V = V_c = 33.2$ cm³/mol [12], as before.

III-3. Analysis of the q[100] mode of NaNO₂

We determined here the Brillouin frequency shifts for the q[100] mode of NaNO₂ as a function of temperature in the paraelectric phase. For this determination of the frequency shifts $\frac{1}{\omega} \frac{d\omega}{dT}$ for the q[100] mode, the values of the coefficients a_c , a_1 and a_0 were obtained according to Eq. (10) within the temperature interval of 438 K $< T < 442$ K, as before. Their values are tabulated in Table I. The specific heat C_p data [28] were then plotted as a function of our frequency shifts $\frac{1}{\omega} \frac{d\omega}{dT}$ for the q[100] mode close to the Néel temperature T_N in the paraelectric phase, as given in Fig. 3. This plot gave us the slope of $dT=dP = 6.48$ mK/bar and the intercept value of $dS=dT = 0.031$ cal/mol.K² which were due to the q[100] mode of NaNO₂ in the paraelectric phase ($T > T_N$), according to Eq. (5). For this determination of the slope and the intercept, we used in Eq. (5) the value of the mode Grüneisen parameter $\alpha_p = 0.62$ for the q[100] mode of NaNO₂ [1], $T = T_N = 437.7$ K and $V = V_c = 33.2$ cm³/mol [12] for this crystal, as before.

IV. Discussion

We examined in this study our spectroscopic modification of the first Pippard relation (Eq. 5), by plotting the specific heat C_p as a function of the frequency shifts $\frac{1}{\omega} \frac{d\omega}{dT}$ for the Brillouin frequencies of the q[010], q[001] and q[100] modes of NaNO₂. We obtained those plots for the paraelectric ($T > T_N$) phase of NaNO₂, as given in Figs. 1-3. As seen from those figures, the specific heat varies linearly with the frequency shifts within the temperature regions for the paraelectric phase in the NaNO₂ crystal. By means of those linear plots, we were able to obtain the values of the slope $dT=dP$ and the intercept $dS=dT$ according to Eq. (5), where we used a constant value of the isobaric mode Grüneisen parameter α_p for each mode for the paraelectric phase in NaNO₂. This is the assumption we had made across the phase transitions, as we have also assumed in calculating the Brillouin frequencies of those modes studied for NaNO₂ in our recent work [1].

For the paraelectric phase of NaNO₂ ($T > T_N$) our values of $dT=dP$ due to the q[010], q[001] and q[100] modes, as given in Table I, are almost equal to each other, namely, ≈ 6.5 mK/bar. Our value can be compared with the value of $dT_N=dP = 8.9$ mdeg/bar for NaNO₂ due to Ema *et al.* [12], the value of $dT_N=dP = 6.2$ mK/bar due to Hamano and Ema [13] and also the experimental value of $dT_N=dP = 5.6$ mK/bar due to Gesi *et al.* [29]. Although the α_p value of the q[100] mode is much smaller than those for the q[010] and q[001] modes (Table I), we get the $dT=dP$ value for the q[100] mode, which is closer to those values due to the q[010] and q[001] modes. So our spectroscopic modification of the first Pippard relation is also valid, which uses the Brillouin frequencies of the q[100] mode of NaNO₂ (Fig. 3) in the paraelectric phase of this crystal. In this phase of NaNO₂ our values of the intercept $dS=dT$, as given in Table I, are also equal to each other, namely, 0.031 cal/mol.K².

Our slope values of $dT=dP$, which we calculated using the Brillouin frequencies of the q[010], q[001] and q[100] modes of NaNO₂ in the paraelectric phase, can also be compared with our $dP=dT$ values for the ammonium halides [26, 27]. Our $dT=dP$ value (Table I), or alternatively $dP=dT$ value, is ≈ 153 bar/K for all the modes studied for NaNO₂ in the paraelectric phase ($T > T_N$). Our value of 153 bar/K can be compared with our $dP=dT$ values of 62.1 bar/K

for the $\nu_5\text{TO}$ (134 cm^{-1}) and 90.1 bar/K for the $\nu_5\text{LO}$ (177 cm^{-1}) Raman modes of NH_4Br at zero pressure [27]. They can also be compared with our $dP=dT$ values of 105.5 bar/K ($P = 0$) for the $\nu_5\text{TO}$ (174 cm^{-1}) and 94.9 bar/K ($P = 0$) for the ν_2 (1708 cm^{-1}) Raman modes of NH_4Cl [26, 27].

In our analysis for obtaining the frequency shifts $\frac{1}{\nu} \left(\frac{\partial \nu}{\partial T} \right)_P$ according to Eq. (10), we assumed a similar critical behaviour of $\frac{1}{\nu} \left(\frac{\partial \nu}{\partial T} \right)_P$ as the specific heat C_P , as pointed out earlier. Therefore, this non-linear behaviour of the specific heat C_P (Eq. 9) was also assumed for the frequency shifts $\frac{1}{\nu} \left(\frac{\partial \nu}{\partial T} \right)_P$ according to Eq. (10). This then provided us a linear relationship between C_P and $\frac{1}{\nu} \left(\frac{\partial \nu}{\partial T} \right)_P$ according to Eq. (5).

Our spectroscopic modification of the second Pippard relation (Eq. 6) can also be tested by means of the experimental data for the thermal expansivity α_P and for the frequency shifts $\frac{1}{\nu} \left(\frac{\partial \nu}{\partial P} \right)_T$ of NaNO_2 . Those frequency shifts can be obtained from the Brillouin frequencies measured as a function of pressure at constant temperatures for the modes considered in the paraelectric ($T > T_N$) phase of NaNO_2 . When those data for the thermal expansivity and the frequency shifts for NaNO_2 are available in the literature, Eq. (6) can be examined in the paraelectric phase of this crystalline system.

V. Conclusions

We established here a linear variation of the specific heat C_P with the frequency shifts $\frac{1}{\nu} \left(\frac{\partial \nu}{\partial T} \right)_P$ for NaNO_2 in the paraelectric phase. For the verification of our spectroscopic modification of the first Pippard relation, we used the Brillouin frequencies for the $q[010]$, $q[001]$ and $q[100]$ modes of NaNO_2 in the paraelectric phase. From our linear plots of C_P against $\frac{1}{\nu} \left(\frac{\partial \nu}{\partial T} \right)_P$ the $dT=dP$ values which we obtained for this phase in NaNO_2 are in good agreement with the literature values.

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