# Specific heat of ferroelectric NaNO$_2$ at low temperatures

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Specific-heat measurements on a single crystal (unpoled) of NaNO$_2$ from 1.7 to 74 K are reported for the first time. Two non-Debye features are found, similar to previous findings on other ferroelectrics: a $T^{3/2}$ contribution below about 4 K, and a broad maximum in $C/T^3$ at 17 K describable by a single Einstein term of frequency 56.4 cm$^{-1}$. The Debye temperatures determined in these two regions are 302 and 298 K, respectively. No evidence is found for the mode at 195 cm$^{-1}$ suggested by recent analyses of low-temperature pyroelectric data on NaNO$_2$.

## I. INTRODUCTION

The low-temperature specific heats of ferroelectrics are proving to be a fruitful research area. A low-lying mode (or modes) gives rise to a large maximum in $C/T^3$ below $\sim 30$ K in these crystals, and the contribution from this mode generally dominates the specific heat at low temperatures.[1] An unusual $T^{3/2}$ specific-heat contribution has been found in several ferroelectrics below $\sim 4$ K, and evidence for this contribution has also been seen in pyroelectric measurements on BaTiO$_3$, LiNb$_2$O$_3$, and triglycine sulfate (TGS). Paraelectric, antiferroelectric, and quantum-ferroelectric crystals do not display this $T^{3/2}$ term.[2] Finally, the relaxation ferroelectric PbMg$_{1/3}$Nb$_{2/3}$O$_3$ has recently been found to display *glasslike* behavior in all its thermal and dielectric properties, 0.1 − 30 K.[3] A recent study[4] of the $T^{3/2}$ term in TGS definitely eliminated a domain-wall explanation and yielded strong evidence for an explanation based on surface layers.

Recent pyroelectric measurements on NaNO$_2$ at low temperatures[5] suggest two specific-heat contributions: a $T^n$ contribution where $n$ lies between $\frac{3}{2}$ and 2, and an Einstein contribution characterized by $\Theta_E = 281$ K (frequency 195 cm$^{-1}$). This latter term would be expected to make its largest contribution to the specific heat around 50 − 60 K, in contrast to what has been found calorimetrically in other ferroelectric crystals. The purpose of this study was to measure the specific heat of NaNO$_2$, 1.7 − 70 K, and to examine these contributions. NaNO$_2$ undergoes an incommensurate phase transition at 163 °C from an orthorhombic (*Immm*) phase to a ferroelectric orthorhombic (*Im2m*) phase. Molecular reorientations of the NO$_2$ groups around the crystallographic $c$ axis are coupled to acoustic-lattice vibrations, and lattice-dynamic studies of the phase transition have recently been done by Michel.[6] Spectroscopic studies of NaNO$_2$ have been reported,[7] and a second transition at 168 K to another ferroelectric phase has also been reported.[8]

## II. EXPERIMENTAL RESULTS AND ANALYSES

The NaNO$_2$ single crystal was in the form of a cylinder, approximately 1 cm diam $\times$ 2 cm long, and was from the same growth batch as the crystal used in the pyroelectric measurements. The crystal was carefully etched with warm distilled water to remove any strained surface regions, and weighings before and after indicated that a $\sim 0.05$-cm-thick layer had been removed. The crystal was dried overnight at 100 °C and subsequently kept in a desiccator except for fixturing and loading in the calorimeter. The final crystal dimensions yielded a surface-to-volume ratio of 4.81 cm$^{-1}$. No effort was made to pole the crystal because the TGS studies[4] clearly indicate that domain walls do not contribute to the specific heat in the temperature range of interest.

The crystal (3.12 g) was outfitted with a heater (341 Ω) and a carbon-chip resistor thermometer (12 mg) using a small amount of G.E. 7031 varnish, and the specific-heat measurements were made in the adiabatic pulse calorimeter described previously.[9] The addenda constituted 1.43 wt. % and con-

tributed 5.6 to 0.6 % of the total heat capacity be-
tween 1.7 and 74 K, respectively. Temperature
rises $\Delta T/T$ were maintained $\sim 2-4\%$, and the
carbon-chip resistor was calibrated *in situ* during
the run. Two runs were made, the first run from
1.7 to 27 K, the second run from 38 to 74 K. The
crystal was kept at helium temperatures between
the two runs, and the carbon-chip resistor was cali-
brated independently in the two temperature re-
gions.

The experimental data measured in the lower
temperature range are shown in Fig. 1 where the
data are plotted as $C/T^3$ to display the non-Debye
features. Two such features are evident, as have
been found with other ferroelectric crystals: a
broad maximum in $C/T^3$ at about 17 K, and a
rapid rise in $C/T^3$ with decreasing temperature
below 4 K. The data in Fig. 1 below about 3 K
were fitted to the $T^{3/2}$ model used previously for
ferroelectrics,

$$C = mT^3 + BT^{3/2} , \qquad (1)$$

where the first term in Eq. (1) is the familiar De-
bye term (i.e., $m \propto \Theta_D^{-3}$). This fit is shown in Fig.
2, and Eq. (1) gives a highly accurate representa-
tion of the experimental data. The fitting parame-
ters are $\Theta_D = 301.6$ K, $B = 19.13$ erg g$^{-1}$ K$^{5/2}$ .
(The Debye temperatures reported here are normal-
ized to one atom per formula weight.)

The broad maximum in $C/T^3$ at 17 K in Fig. 1
was analyzed according to the single-Einstein-
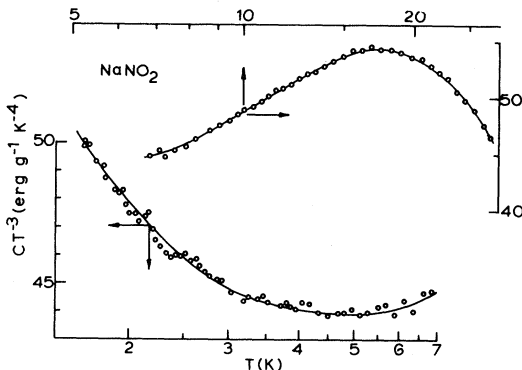oscillator model previously employed for ferroelec-
trics,



FIG. 1. Specific-heat data on NaNO$_2$ plotted as
$C/T^3$ to illustrate the non-Debye features, two of which
are evident: the rapid rise in $C/T^3$ with decreasing
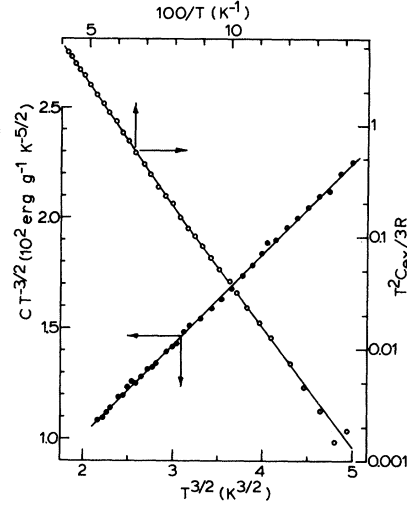temperature below 4 K, and the broad maximum in
$C/T^3$ at 17 K.



FIG. 2. Fitting results for the NaNO$_2$ specific-heat
data according to the $T^{3/2}$ model, Eq. (1), and the Ein-
stein model, Eq. (2). The $T^{3/2}$ term was subtracted
from the specific-heat data prior to the Einstein-model
fitting. The Debye temperatures from these two fits
agree well, 302 and 298 K, respectively.

$$C = C_D(\Theta_D/T) + 3Rrx^2 e^x/(e^x - 1)^2 ,$$

$$x = \Theta_E/T \qquad (2)$$

where $C_D$ is the Debye specific-heat function, $\Theta_D$
is the Debye temperature, $r$ is the number of Ein-
stein oscillators per formula weight, and $\Theta_E$ is the
Einstein temperature. A three-parameter fitting
program was used for $\Theta_D$, $\Theta_E$, and $r$, and the
$BT^{3/2}$ term was subtracted from the total specific
heat prior to this fitting. A tabulation of the De-
bye function was used in the fitting program.[10]
The results of this fitting procedure are shown in
Fig. 2 where $C_{ex} = C_{expt} - C_D$, and, as has been
found for all other ferroelectrics, Eq. (2) gives a
very accurate description of the $C/T^3$ maximum.
The fitting parameters from this procedure are the
following: $\Theta_D = 297.8$ K, $\Theta_E = 81.30$ K (56.4
cm$^{-1}$) and $r = 7.59 \times 10^{-2}$. The Debye tempera-
tures determined from the two regions agree very
well (avg., $\Theta_D = 299.7 \pm 0.90\%$) and lend confi-
dence to the data analyses.

The experimental data measured in the higher
temperature range are shown in Fig. 3, again plot-
ted as $C/T^3$. There is no evidence for an anomaly
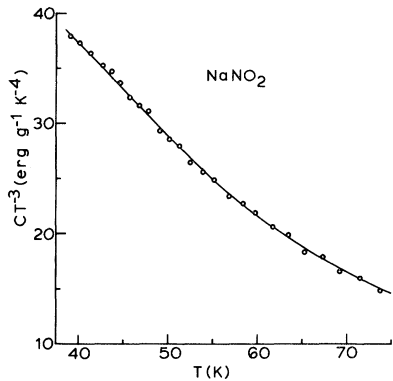in $C/T^3$ around $50 - 60$ K as suggested by the py-

FIG. 3 Specific-heat data for $NaNO_2$ at higher temperatures. No evidence is seen for the pyroelectric mode at 195 $cm^{-1}$ which would make its largest contribution to $C/T^3$ at $\sim 50-60$ K.

roelectric data.[5] The $C/T^3$ data in Fig. 3 smoothly join the (extrapolated) $C/T^3$ data in Fig. 1, and the effective Debye temperatures estimated from the Fig. 3 data vary from about 300 to 330 K between 40 and 70 K, respectively. It is not unusual to find a $\pm 5\%$ variation in the effective Debye temperature in this temperature range (the specific-heat data at lower temperatures are far more accurate, uncertainty $< \pm 2\%$). Also, a significant Einstein-type contribution to the specific heat causes a distinct *minimum* in the effective Debye temperature, which is not found for $NaNO_2$ between 40–70 K.

## III. DISCUSSION

The results presented here are consistent with what has been found previously for a number of ferroelectric crystals.[1,9] The Einstein mode in $NaNO_2$ at 56.4 $cm^{-1}$ compares closely with the corresponding modes found in (multidomain) single crystals of TGS (46.9 $cm^{-1}$) and potassium dihydrogen phosphate (KDP) (59.6 $cm^{-1}$) from calorimetric studies.[9] There is evidence that this mode is independent of the domain walls present because pyroelectric data on a single-domain crystal of TGS yielded 45.7 $cm^{-1}$ for this mode.[11]

The $B$ coefficient of the $T^{3/2}$ term, Eq. (1), for

$NaNO_2$ ($1.32 \times 10^3$ erg $mole^{-1} K^{-5/2}$) is approximately the same as the coefficients found for large crystals of TGS ($2.47 \times 10^3$ erg $mole^{-1} K^{-5/2}$) and KDP ($2.10 \times 10^3$ erg $mole^{-1} K^{5/2}$). However, the TGS studies[4] indicated that for surface-to-volume ratios $(S/V)$ *below* 5 $cm^{-1}$ the $B$ coefficient is essentially *zero*. These studies also indicated that the $T^{3/2}$ term arises from a 0.02-cm thick surface layer. The $NaNO_2$ crystal studied here was the largest crystal $(S/V = 4.8$ $cm^{-1})$ of a ferroelectric measured to date, and these results suggest that the $B$ coefficient for $NaNO_2$ may become very large for small crystals, by analogy with the TGS studies.

It is difficult to reconcile the results here with the analysis of the pyroelectric data on $NaNO_2$ (Ref. 5). The pyroelectric and calorimetric measurements sample the same modes because, by Radebaugh's thermodynamic arguments,[12] the spontaneous polarization and specific heat follow the same temperature dependence. Therefore, it is troublesome that the pyroelectric data analysis did not yield the 56.4-$cm^{-1}$ mode, in contrast to the TGS case. A possible explanantion for this discrepancy may lie in the relative *strengths* of these modes in $NaNO_2$ and TGS. That is, the amplitude $r$ in Eq. (2) is an order of magnitude smaller in $NaNO_2$ (0.076) than in TGS (0.79), (Ref. 9), so that the other contributions to the pyroelectric coefficient in $NaNO_2$ may mask the contribution from this mode. The $T^n$ ($n = \frac{3}{2}$ to 2) term in the pyroelectric data was reported to be very weak, again in contrast to the case of TGS. This was explained[5] as due to possible masking by the $T^4$ secondary-pyroelectric contribution at the lowest temperatures. Both the pyroelectric[5] and spectographic[7] data reveal the 195-$cm^{-1}$ mode in $NaNO_2$. The absence of this mode in the calorimetric data may simply be a resolution problem because the Debye background specific heat is large above 50 K.

## ACKNOWLEDGMENTS

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