Analysis of the temperature-dependent lattice modes in sodium nitrite by infrared spectroscopy

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Abstract. The temperature dependence of the infrared reflectivity spectra of NaNO$_2$ is reported for the ferroelectric and paraelectric phases, over a wide temperature range (10–500 K). Reflectivity spectra from 5 to 600 cm$^{-1}$ have been fitted with a model of the factorised form of the dielectric function including the relaxational mode. The temperature dependence of the lattice mode frequencies, damping factors and oscillator strengths in the two phases is reported. The ionic effective charges are calculated from the TO–LO splitting of the polar modes. The study confirms the activity of five lattice modes in the ferroelectric and paraelectric phases and shows the existence of dielectric relaxation in the low-frequency region consistent with the order–disorder nature of the phase transition.

1. Introduction

Since the discovery of ferroelectricity in sodium nitrite by Sawada et al (1958), a considerable amount of experimental and theoretical work has been carried out on the ordered and disordered phases. Interest in performing research on NaNO$_2$ has been stimulated partly because it has a relatively simple structure for a ferroelectric and partly by the discovery that between the ordered ferroelectric phase ($T < T_C = 436.6$ K) and the high-temperature disordered paraelectric phase ($T > T_N = 437.7$ K) an incommensurate antiferroelectric phase exists. Sodium nitrite is actually a model substance of an order–disorder structural phase transition.

There have been numerous studies of the spontaneous polarisation and dielectric constant (Sawada et al 1958, Hatta 1968, Yamada et al 1968). The dynamical properties of NaNO$_2$ have been studied mainly above room temperature, by means of infrared, Raman and neutron spectroscopy. An infrared analysis of sodium nitrite at room temperature has been performed by Axe (1968) and Vogt and Happ (1966) reported infrared reflectivity measurements from 293 K up to 503 K. Barnoski and Ballantyne (1968) and Suzuki et al (1969) have analysed the infrared reflectivity spectra using the classical oscillator model; their results have provided the temperature dependence of the TO lattice mode parameters. The effects of heating on the frequencies and linewidths of the NaNO$_2$ Raman-active modes were also studied from 300 up to 500 K (Chisler and Shur 1966, Hartwig et al 1972, Castelluci et al 1976, Prasad Rao and Porto 1976). The neutron scattering measurements made by Sakurai et al (1970) complete these studies and give the phonon dispersion curves for sodium nitrite.
Up to now, the temperature dependence of zone-centre phonon frequencies has not been completely established down to lower temperatures. Infrared reflectivity appears to be a very efficient technique to detect these modes and to determine their frequencies and damping factors.

The research reported here supplements previous lattice dynamical studies on NaN02; it extends the temperature range down to 10 K and the frequency range down to 5 cm\(^{-1}\). Thus, the analysis of the temperature-dependent lattice mode frequencies and dampings can be achieved over a wide temperature range: 10 up to 500 K, in the frequency range 5 to 600 cm\(^{-1}\), for the three crystallographic orientations.

2. Crystal structure and lattice modes

2.1. Structure

Sodium nitrite has a body-centred orthorhombic structure (C\(_{2h}\), Im2m) in the ferroelectric phase, with one formula unit per primitive cell (Ziegler 1931, Kay and Fraser 1961). The spontaneous polarisation is parallel to the \(b\) axis.

The transition from the ferroelectric phase to the high-temperature disordered paraelectric phase occurs in two steps. At the Curie temperature \((T_C = 436.6 \text{ K})\) the ferroelectric structure transforms to a sinusoidal antiferroelectric phase (Tanisaki 1961, 1963). This in turn transforms at the Néel temperature \((T_N = 437.7 \text{ K})\), to an orientationally disordered paraelectric phase. In this phase, the random orientation of the NO\(_2\) ions along either +\(b\) or −\(b\), introduces a statistical mirror plane perpendicular to the \(b\) axis. By means of x-ray analysis an orthorhombic space group symmetry \((D_{2h}^{25}, \text{Immm})\) has been assigned to this non-polar phase, with one formula unit in the primitive cell (Strijk and McGillavry 1943, 1946, Kay et al 1962).

Experimental studies have shown that the disorder does not appear at the Curie temperature, but it is manifest at about 350 K in the ferroelectric phase. The heat capacity and molar volume begin to rise anomalously above 350 K (Sakiyama et al 1965) and the thermal expansion coefficients above 370 K (Ema et al 1975). Large-amplitude oscillations of the Na atoms along the \(b\) axis about their mean position at \((0, \frac{\pi}{2}, 0)\) and large-amplitude librations of the NO\(_2\) anions about the crystallographic axis are observed, below and above the phase transition (Kay et al 1975). The recent theoretical works of Ehrhart and Michel (1981, 1982) and Klein et al (1982) have examined the reorientation mechanism of the NO\(_2\) anions.

2.2. Optical modes of vibration

The primitive cell of sodium nitrite contains four atoms in both phases; there are thus nine optical modes of vibration in each phase. From the group theoretical selection rules, the optical modes are distributed in the symmetry species of the space groups C\(_{2h}^{20}\) and D\(_{2h}^{25}\) as shown in table 1. We should expect the compatibility relations between the modes across the phase transition given in table 1.

The symmetry coordinates of sodium nitrite have been determined by Chisler and Shur (1966). The normal modes of vibration consist of three internal vibrations, movements of deformation of the NO\(_2\) ions, and six lattice modes. The B\(_1\) and B\(_2\) lattice modes have mixed translation and libration character (Sakurai et al 1970); the A\(_1\) lattice mode has a pure translational character. A TO-LO splitting is expected for the five
Table 1. Correlation chart for optical modes, between the low- and high-temperature phases of sodium nitrite. The upper indices indicate the infrared (+) and Raman (×) activities. The direction of the dipole moment for the polar modes is indicated in brackets.

<table>
<thead>
<tr>
<th>Ferroelectric phase</th>
<th>Paraelectric phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$\text{S}_\text{f}$</td>
<td>D$\text{S}_\text{f}$</td>
</tr>
</tbody>
</table>
| [010] 3A$^+_g$ | 1 A$^+_g$
| 1A$^+_g$ | 1B$^+_g$
| [001] 3B$^+_g$ | 1B$^+_g$
| 2B$^+_g$, [001] | 2B$^+_g$, [001] |

infrared-active lattice modes and observed by neutron scattering (Sakurai et al. 1970) and Raman spectroscopy (Hartwig et al. 1972).

3. Experimental techniques

The sodium nitrite single crystals were grown by the Bridgman method. Several plates of (101) and (010) orientation were cut and polished to optical quality.

Infrared reflectivity measurements, between 10 and 500 K, were performed with an angle of incidence of 10°, in the frequency range 10–600 cm$^{-1}$, by means of two different far-infrared grating spectrometers. One is equipped with a Golay detector for the temperature range 300–500 K, the second with a gallium-doped germanium bolometer for the low-temperature range 10–270 K (Wyncke et al. 1983). The incident radiations were polarised by means of a wire-grid polariser. (101) plates were used for the spectra polarised along the $b$ axis, and (010) plates for the $a$ and $c$ spectra. The crystal temperature is controlled with a precision of ±1 K from 10 to 500 K. Thus the narrow temperature phase between $T_C$ and $T_N$ was not studied by this research. The dimensions of the samples were 16 × 16 × 5 mm$^3$ for temperatures higher than 300 K, and 12 × 12 × 8 mm$^3$ for temperatures lower than 300 K.

Precise dielectric measurements were performed by Kozlov et al. (1985) and Wyncke et al. (1984). The amplitude and phase of the complex transmission at normal incidence were measured independently and the complex dielectric functions were calculated. The data obtained are used to calculate the low-frequency values of the far-infrared reflectivity spectra from 3 up to 30 cm$^{-1}$.

4. Experimental results

4.1. Far-infrared reflectivity spectra

The temperature dependence of the reflectivity spectra of sodium nitrite is displayed in figure 1, for the three crystallographic orientations from 10 up to 500 K. Below 250 K the reflectivity spectra are recorded in the frequency range 10–400 cm$^{-1}$. The number
of observed modes and their polarisations agree with those predicted by group theoretical predictions for lattice modes in the ferroelectric phases: one $A_1$ mode in the $b$ polarisation, two $B_1$ modes in the $c$ polarisation and two $B_2$ modes in the $a$ polarisation (figure 1). The five lattice modes are active above 436 K in the paraelectric phase. The two $B_1$ and $B_2$ lattice modes are discernible up to 500 K, though an increasing overlapping of the two $B_1$ reflection bands is observed above 450 K (figure 1).

The nearly flat reflectivity level below 60 cm$^{-1}$, increases with temperature for the three orientations, from 0.125 to 0.20, 0.11 to 0.17 and 0.18 to 0.24 for the $a$, $b$ and $c$ directions respectively at 10 and 495 K (figure 1). At low temperatures ($<90$ K) the low-frequency reflectivity spectra below 100 cm$^{-1}$ are affected by a systematic positive error caused by the reflectivity of the sample holder. The reflectivity measurements have been corrected by measuring the transmission of the sample.
4.2. Dielectric function model

An accurate determination of the lattice mode parameters could be achieved by a fit to the experimental reflectivity data with the factorised form of the dielectric function (Gervais 1983).

In the case of sodium nitrite it is impossible to obtain a good fit to the experimental data below 100 cm$^{-1}$, for the three crystallographic directions, by only taking account of the lattice modes. An additional relaxation mode is necessary at any temperature to obtain a good fit to experimental data throughout the frequency range 5–600 cm$^{-1}$ (figure 1).

Such a relaxation can be introduced by adding a damped oscillator characterised by the damping factors $\gamma_F^E$ and $\gamma_F^K$, with $\gamma_F^E > \gamma_F^K$, the frequency of which would be zero, as proposed by Chaves and Porto (1973). With this model, the dielectric function is written...
in the form:

\[ \varepsilon(\omega) = \varepsilon_\infty \left( \frac{\omega - i\gamma_j}{\omega - i\gamma_j} \right)^2 \prod_j \frac{\Omega_j^{2\text{LO}} - \omega^2 + i\gamma_{j\text{LO}}\omega}{\Omega_j^{2\text{TO}} - \omega^2 + i\gamma_{j\text{TO}}\omega} \]  

(1)

where \(\Omega_j\) and \(\gamma_j\) are the frequencies and damping factors of the transverse and longitudinal polar lattice modes \(j\) and \(\varepsilon_\infty\) is the high-frequency dielectric constant deduced from the measurement of the refractive index. The reflectivity level \(R(\omega)\) is related to the dielectric function \(\varepsilon(\omega)\) by the formula

\[ R(\omega) = \left| \frac{\sqrt{\varepsilon(\omega)} - 1}{\sqrt{\varepsilon(\omega)} + 1} \right|^2. \]  

(2)

We can also use the Debye dispersion function:

\[ \varepsilon(\omega)_D = S_D/(1 + i\omega\tau) \]  

(3)

for the relaxation mode.

We have fitted the experimental data to the reflectivity spectra from 10 to 600 cm\(^{-1}\), and the complex dielectric permittivity from 7 to 18 cm\(^{-1}\), for the \(a\) and \(c\) directions with equations (1) and (2). For the \(b\) direction we have used equation (2) and (4):

\[ \varepsilon(\omega) = \frac{S_{D1}}{1 + i\omega\tau_1} + \frac{S_{D2}}{1 + i\omega\tau_2} + \varepsilon_\infty \frac{\Omega_{\text{LO}}^2 - \omega^2 + i\gamma_{\text{LO}}\omega}{\Omega_{\text{TO}}^2 - \omega^2 + i\gamma_{\text{TO}}\omega}. \]  

(4)

In the latter model we have considered three contributions to the dielectric permittivity: one is the \(A_1\) lattice mode, the other two are relaxations. The first Debye relaxation represents the low-frequency mechanism used to describe the radiofrequency dispersion (Hatta 1968, Yamada et al. 1968), a second Debye relaxation describes the submillimetre dispersion between 5 and 30 cm\(^{-1}\) (Kozlov et al. 1985). Good fits to the experimental data were obtained as shown in figure 1.

The validity of these models is proved by the good agreement which is achieved between the values of the real and imaginary parts of the dielectric permittivity obtained from a Kramers–Kronig analysis and those deduced from the best fit to the experimental data (figure 2). The values of \(\varepsilon'\) and \(\varepsilon''\) calculated with these models in the frequency range 3–30 cm\(^{-1}\) agree to within ±5% with those found experimentally by dielectric measurements (Kozlov et al. 1984, Wyncke et al. 1984).

Lattice mode parameters which yield the best fit are reported in figures 3 and 4. In table 2 the values of the lattice mode parameters at 300 K are listed, together with previous results for comparison.

5. Analysis of the results

5.1. Lattice mode frequencies

Figure 3 displays the temperature dependence of \(\text{TO}\) and \(\text{LO}\) lattice mode frequencies obtained by fitting the reflectivity spectra.

The frequencies decrease slowly with increasing temperature in the ferroelectric phase. They are shifted from their low-temperature value to within 10% at 420 K (figure 3). This behaviour is common since the effects of lattice thermal expansion, which tends to lower the force constants, and the cubic anharmonic coupling contribute to the
Figure 2. Comparison between the real $\varepsilon'$ and imaginary $\varepsilon''$ parts of the dielectric permittivity calculated with the factorised form of the dielectric function for NaNO$_2$ including relaxation (full curves) and the result of a Kramers-Kronig analysis of the experimental data (dots) at 293 K. (a) B$_{1}$ spectra, $E \parallel a$, (b) A$_{1}$ spectra, $E \parallel b$, (c) B$_{1}$ spectra $E \parallel c$. 
downshift of the phonon frequency on heating. In the paraelectric phase, six frequencies continue to decrease, while the other four maintain the value attained at $T_C$.

Our infrared results agree satisfactorily with the Raman data studied between 300 and 400 K for the $B_1$ and $B_2$ modes; but we observe a lower downshift of the frequencies above 400 K (Hartwig et al 1972, Prasad Rao and Porto 1976).

The frequency of an anharmonic crystal, $\omega_j(T)$, is given as follows:

$$\omega_j(T) = \omega_j(0) + \Delta \omega_j$$

in which $\omega_j(0)$ represents the harmonic frequency and $\Delta \omega_j$ the anharmonic frequency shift.

With a good approximation $\omega_j(0)$ may be obtained from the extrapolation to 0 K of the data of figure 3.

From the observed temperature dependence of the lattice mode frequencies which

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**Figure 3.** Temperature dependences of the $T_O$ and $L_O$ lattice mode frequencies of NaNO$_2$. Full curves are fits to the data with equation (6).
Temperature-dependent lattice modes in NaNO₂

Figure 4. Temperature dependence of the lattice mode dampings. Full curves are fits to the data with equation (7).

decrease with increasing temperature (figure 3), it is possible to assume that the main contribution to the anharmonic frequency shift is due to the volume change of the crystal by thermal expansion.

Within the limits of the quasi-harmonic oscillator model, the contribution to the frequency shift of the jth normal mode due to volume expansion may be expressed by:

\[
\omega_j(T) = \omega_j(0) \left[ \exp \left( -G_j \int_0^T \alpha_v(T) \, dT \right) \right]
\] (6)

where \( \alpha_v(T) \) is the thermal volume expansion, and \( G_j \) the mode Grüneisen parameter for the jth mode. \( G_j \) is expected to be constant (Mitra 1969).

Equation (6) fits the temperature dependence of the frequencies with the \( G_j \)-values listed in table 3 in the ferroelectric phase well, but the agreement is poorer in the paraelectric phase (figure 3). The values of \( \alpha_v(T) \) are taken from the work of Ema et al.
Table 2. Frequency and damping of each TO and LO lattice mode of sodium nitrite at room temperature (in cm\(^{-1}\)). Our results are compared with previous results obtained by infrared, neutron and Raman spectroscopy at room temperature. A, this work; B, Axe (1968); C, Barnoski and Ballantyne (1968); D, Sakurai et al (1970); E, Hartwig et al (1972).

<table>
<thead>
<tr>
<th>Mode</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>TO</td>
<td>149</td>
<td>145.7</td>
<td>234</td>
<td>180</td>
<td>149.5</td>
</tr>
<tr>
<td>LO</td>
<td>193</td>
<td>12.6</td>
<td>234</td>
<td>180</td>
<td>149.5</td>
</tr>
<tr>
<td>TO</td>
<td>153</td>
<td>234</td>
<td>180</td>
<td>149.5</td>
<td>149.5</td>
</tr>
<tr>
<td>LO</td>
<td>180</td>
<td>234</td>
<td>180</td>
<td>149.5</td>
<td>149.5</td>
</tr>
</tbody>
</table>

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Table 3. The mode Gruneisen parameters for NaNO\(_2\).
anharmonic processes, respectively. \( \gamma_i(0) \) and \( \gamma'_i(0) \) are adjustable parameters which give the value of the damping for \( T = 0 \) K. The temperature dependence of \( \gamma_i(T) \) is linear above the Debye temperature (Gervais 1983).

The damping of all the TO and LO lattice modes of NaN\(_2\)O can be satisfactorily described with the model given by equation (7) in the ferroelectric phase up to 400 K, as shown in figure 4, with only the cubic anharmonic contribution (table 4). In four cases a small quartic contribution (\( \gamma'_i(0) \neq 0 \)) is added to improve the fits, but it is not significant in view of the experimental uncertainty (table 4). This result proves that the lifetime of each phonon mode is essentially limited by the anharmonic third-order phonon coupling in the ordered ferroelectric phase.

From 400 up to 500 K, in the paraelectric phase, we observe that the damping of the modes labelled A\(_1\) TO, LO, B\(_1\) TO\(_1\), LO\(_1\), TO\(_2\), and B\(_2\) TO\(_1\), LO\(_1\) increases more rapidly than expected from equation (7) (figure 4). On a log–log scale we found that the damping of these modes has a \( T^3 \) temperature dependence above 400 K (the Debye temperature of sodium nitrite is 300 K), indicating the contribution of anharmonic higher-order phonon coupling. This may be due to the increase of the weight of the low-frequency excitations in the anharmonic coupling term due to increasing dynamical disorder in the crystal structure above 370 K (Brehat et al. 1982). It is to be noted that the damping of the B\(_1\) LO\(_2\) and B\(_2\) TO\(_2\) modes are satisfactorily described by equation (7) up to 500 K in the paraelectric phase, and that the damping of the B\(_2\) LO\(_2\) mode displays an unusual behaviour above 400 K (figure 4).

### 5.3. Oscillator strengths

From the expression for the factorised form of the dielectric function, the oscillator strengths of the phonon polar oscillator associated with each of the five transverse lattice modes can be calculated from the TO–LO splitting through the relation (Gervais 1983):

\[
\Delta \varepsilon_j = \varepsilon_\infty \left( \frac{\Omega^2_{jLO}}{\Omega^2_{jTO}} - 1 \right) \prod_{j \neq k} \frac{\Omega^2_{jLO} - \Omega^2_{jTO}}{\Omega^2_{kTO} - \Omega^2_{jTO}}.
\]

The temperature dependences of the oscillator strengths are displayed in figure 5.

The dielectric contribution of the relaxational processes (equation (1)) introduced to fit the experimental data in the low-frequency range for the \( a \) and \( c \) directions can be calculated from:

\[
S_R = \varepsilon_\infty \frac{\gamma^R_i}{\gamma^R_i - 1} \prod \frac{\Omega^2_{jLO}}{\Omega^2_{jTO}}.
\]

We have observed (Wyncke et al. 1984) that, for the \( a \) and \( c \) polarisations, the dielectric...
contribution $S_R$ is smaller than the oscillator strength of the corresponding lattice modes below 300 K, and that it increases with temperature and becomes stronger than the oscillator strengths above 400 K.

For the $b$ direction, we used equation (4); the dielectric contribution $S_{D2}$ is always smaller than the oscillator strength of the lattice mode $A_1$, while $S_{D1}$ is stronger. $S_{D1}$ increases considerably in the paraelectric phase since it is responsible for the dielectric dispersion in the radiofrequency range (Hatta 1968, Yamada et al 1968, Kozlov et al 1985).

A complete discussion of the additional relaxation-like modes is published elsewhere (Kozlov et al 1984, Wyncke et al 1984). They yield a good fit of both low-frequency dielectric data between 3 and 30 cm$^{-1}$ and reflectivity measurements between 10 and 600 cm$^{-1}$. At 300 K, the relaxation times are: $4.93 \times 10^{-13}$, $6.67 \times 10^{-13}$ and $2.11 \times 10^{-13}$ s for the $a$, $b$ and $c$ directions respectively. It appears clearly that they are ‘extra’ in the group theoretical sense, because all the expected lattice modes are observed.

5.4. Temperature dependence of effective charges

The effective ionic charge can be calculated from the TO and LO optical-mode frequencies, according to the procedure proposed by Scott (1971) and demonstrated by Gervais and Arend (1983):

$$\frac{1}{\varepsilon_0 V} \sum_k \frac{(Z_k e)^2}{m_k} = (2\pi c)^2 \sum_j (\Omega_{j,LO}^2 - \Omega_{j,TO}^2).$$  \hspace{1cm} (10)
Here $e$ is the elementary electric charge, $\varepsilon_r$ the dielectric constant of the vacuum, $c$ the velocity of light and the index $\alpha$ denotes the polarisation direction. The summation on the left-hand side is taken over all ions $k$ of mass $m_k$ located in the elementary volume $V$, and on the right-hand side over all infrared-active optical modes in the $\alpha$-direction.

Equation (10) has been derived in the harmonic approximation and is applicable under the condition of an isotropic effective field for each ion. In the case of NaN02, the mode damping remains much smaller than the corresponding mode frequency at any temperature, and the nitrite ion is located at the centre of the octahedron formed by the six nearest sodium ions. This allows the use of equation (10) for NaN02.

A second relation is required by the charge neutrality of the cell:

$$\sum_k Z_k = 0 = 2(Z_{Na} + Z_N + 2Z_O).$$

(11)

Since there are three unknown parameters in equation (11) and only two equations, some assumption must be made about the ionic charge of the sodium ion to solve the problem. From the molecular orbital calculation of Goddard et al (1983), it appears that sodium nitrite is nearly but not completely ionic; the calculated charge of the Na$^+$ ion is $Q_{Na} = 0.95|e|$. From the calculation of Pullman and Berthod (1981) the nitrite ion has a slightly positive nitrogen atom, the negative charge being shared by the two oxygens. The sodium ion polarisability is much smaller than that of the nitrite ion (Kinase and Ohi 1968).

To obtain a positive value for the charge of the nitrogen ion we ought to take $Z_{Na} = 0.9$, for the effective charge of the sodium ion. This value can be compared with the Szigetti effective charge $Z'_{Na} = 0.96$, calculated by Axe (1968), which is related to $Z_{Na}$ via the equation:

$$Z'_{Na} = 3(\varepsilon_x)^{1/2}Z_{Na}/(\varepsilon_x + 2).$$

(12)

With the three values of $\varepsilon_x$ listed in table 2 and $Z_{Na} = 0.9$ we obtain a mean value $Z'_{Na} = 0.954$, in agreement with the value calculated by Axe.

The effective charges $Z_N$ and $Z_O$ are calculated for each temperature using equations (10) and (11) and $Z_{Na} = 0.9$. The $\text{TO}$ and $\text{LO}$ frequencies are those obtained from the best fit to our experimental data, and those of Axe (1968) and Barnoski and Ballantyne (1968) for the high-frequency modes. The volume $V$ in equation (10) is calculated from the lattice parameters measured by Kucharczyk (1976).

The effective charge depends strongly on the polarisation direction (figure 6). A correlation can be made between this result and the calculated polarisability of the NO$_2^-$ ion along the three crystallographic directions. It has been found that $\pi_c > \pi_b > \pi_a$ (Kinase and Ohi 1968). We observe that the effective charge of the N and O ions changes in the same way: $Z_c > Z_b > Z_a$ (figure 6).

The effective charges $Z_N$ and $Z_O$ are nearly constant over the entire temperature range 0–500 K for the $a$ and $c$ directions (for instance the value $Z_N$ at 500 K is only 5% higher than at 10 K for the $c$ direction), without any discontinuity at $T_c$. This is what is expected in the case of an order–disorder phase transition in which the distances of all possible sites of flipping ions remain the same. However, in the $b$ direction we observe an important increase of the effective charges $Z_O$ and $Z_N$ above 400 K which can be related to the increase of the Na–N bond distance with temperature as observed by Kay et al (1975).
Figure 6. Temperature dependence of the effective charges along the three crystallographic axes, calculated with equations (10) and (11). The curves are: A, $E \parallel a$; B, $E \parallel b$; C, $E \parallel c$.

6. Discussion

The infrared reflectivity spectra of sodium nitrite are in agreement with the group theoretical predictions based on $C_{2v}^0$ space group symmetry, with one formula unit per primitive cell, confirming its use for the ferroelectric phase. In the paraelectric phase, five lattice modes are active up to 500 K (figure 3).

Infrared and Raman spectroscopy did not reveal any appearance of a statistical mirror in the paraelectric phase of NaN02, because these two techniques can observe the disordered microdomains which do not have a real inversion centre (Hartwig et al 1972).

The nature of the sodium nitrite phase transition can be characterised by the temperature dependences of the lattice mode parameters displayed in figures 3, 4, 5 and 6.

Below 400 K, in the ferroelectric phase, all the lattice mode parameters behave ‘normally’ with temperature, confirming the ordered structure of this phase. The tem-
perature dependence of the TO and LO frequencies is explained by the thermal volume expansion (figure 3) and phonon coupling by cubic anharmonicity explains the lattice mode damping (figure 4). No significant change of the oscillator strengths and effective charges is observed from 10 to 400 K (figure 5 and 6).

However, the occurrence of disorder in the structure is manifested by the temperature dependences of the relaxation-like modes of B₁ and B₂ symmetries whose dielectric contributions begin to increase significantly at about 350 K (Wyncke et al 1984). This is the temperature at which the librations of the NO₂ ions around either the c or the a axes most probably both begin to increase. For these reasons we have assigned these two relaxation-like modes to the large-amplitude libration of the NO₂ ions about the c axis (B₂ spectra) and about the a axis (B₁ spectra) (Wyncke et al 1984). This confirms the theoretical calculation of Ehrhart and Michel (1982).

Above 400 K, the considerable increase of the dielectric contribution of these relaxation-like modes together with the divergence of the damping of most lattice modes (figure 4) indicate the reorientational disorder of the high-temperature phase. In the paraelectric phase an important contribution to the low-frequency dielectric permittivity for the a and c directions arises from the relaxation-like modes.

All these results are consistent with a transition of the order-disorder type, starting gradually at about 350 K, which is due to the increase of the large-amplitude librations of the NO₂ ions about the crystallographic axis together with the large-amplitude oscillations of the Na⁺ ions along the b axis about their mean position at (0, ½b, 0). The increasing disorder affects the TO and LO frequencies of the B₁ and B₂ lattice modes in particular, while the TO and LO frequencies of the A₁ mode, which is of pure translation type, behaves normally even in the high-temperature disordered phase.

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