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Orientation and temperature dependence of the spin–lattice relaxation of ^{23}Na in NaNO_2

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Abstract. The spin–lattice relaxation of ^{23}Na has been studied in single crystals of NaNO_2 at temperatures between 130 K and 462 K and at various crystal orientations relative to an external magnetic field = 1.3 T. The technique involved applying a selective 180° pulse to the centre line and monitoring the subsequent recovery of the spin system. The relaxation is predominantly magnetic below 145 K and seems to be caused by a nuclear dipole–dipole interaction. The quadrupole relaxation rate increases very rapidly above 145 K and is dominant above 235 K. The orientation dependence of the quadrupole relaxation probability W_1 , measured at 235 K, 298 K, 350 K, 432 K and 448 K, is in excellent agreement with the theoretical form, showing that the relaxation is both quadrupolar and homogeneous at all these temperatures. Comparison of the ratios of the six independent \mathbf{M} -tensor components obtained by fitting these data show that the relaxation is caused by the *same* mechanism at 235 K, 298 K, and 350 K. Quite different ratios are found at 432 K and 448 K, a manifestation of the relaxation caused by critical fluctuations associated with the ferroelectric order–disorder phase transition at 438 K. Ratios of the \mathbf{M} -tensor components calculated using simple point-charge dynamical models of the lattice are in poor agreement with the measured ratios at 235 K, 298 K and 350 K, so the cause of the relaxation at these temperatures is still not known. Four of the five ratios of the \mathbf{M} -tensor components associated with critical fluctuations at 432 K and 448 K are in rough agreement with theoretical estimates derived using a simple point-charge model of reorienting NO_2 groups. The fifth ratio seems to indicate that the NO_2 groups do not reorient by rotating through 180° about the a axis of the crystal, as is widely assumed.

1. Introduction

The spin–lattice relaxation of nuclei with $I > \frac{1}{2}$ in non-metallic crystalline solids of high purity is usually dominated by the interaction of the nuclear electric quadrupole moment with thermal fluctuations in the electric field gradient (Pound 1950, Cohen and Reif 1957, Abragam 1961). For $I = \frac{3}{2}$ nuclei, such as ^{23}Na , the allowed quadrupole transitions are $m = \pm\frac{1}{2} \leftrightarrow \pm\frac{3}{2}$ ($\Delta m = \pm 1$) with a probability denoted by W_1 , and $m = \pm\frac{3}{2} \leftrightarrow \mp\frac{1}{2}$ ($\Delta m = \pm 2$) with a probability W_2 . These probabilities are of the same order of magnitude but have a different dependence on the orientation of the crystal relative to a strong external magnetic field. If the nuclei are situated at identical sites in a single crystal, the relaxation is homogeneous and described by the components of a fourth-rank tensor, the

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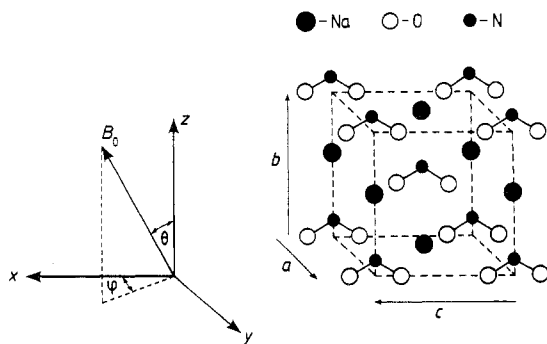


Figure 1. Unit cell of NaNO_2 and the coordinate system used to specify the direction of the external magnetic field B_0 .

so-called **M**-tensor (Pietila 1968). Snyder and Hughes (1971) derived general expressions for the orientation dependence of W_1 and W_2 for the various point-group symmetries.

The temperature dependence of the spin–lattice relaxation of ^{23}Na in a single crystal of NaNO_2 was first measured by Bonera *et al* (1970). It has since been studied by Avogadro *et al* (1971, 1975) and Buchheit and Petersson (1981) in the vicinity of the order–disorder transition from the ferroelectric phase to the paraelectric phase which occurs via an antiferroelectric phase near 438 K. The anomalous behaviour between 170 K and 300 K has been largely ignored. Also, apart from the initial work of Bonera *et al* (1970) and some room temperature measurements made in our laboratory (Hughes and Spencer 1982), the orientation dependence of the relaxation has received little attention.

In this paper, we present the results of a systematic study of the orientation dependence of the spin–lattice relaxation of ^{23}Na in NaNO_2 , carried out using pulsed double resonance over the temperature range 145 K to 448 K. Bonera *et al* (1970) found the relaxation time of this spin system to be independent of the magnetic field strength, indicating that the correlation time of the fluctuations is much shorter than the Larmor period. In such a regime, W_1 and W_2 are described by the *same* **M**-tensor, in which case no new information will be obtained by measuring both quantities (Snyder and Hughes 1971). For reasons of experimental convenience, we measured the orientation dependence of W_1 instead of W_2 .

The aims of our work were, firstly, to measure the temperature dependence of the **M**-tensor components, secondly, to attempt to correlate these with dynamical processes believed to occur in the material and, thirdly, to try to shed some light on the anomalous behaviour observed below room temperature.

A preliminary report of our work has been presented earlier (Towta and Hughes 1986).

2. Theoretical orientation dependence of W_1 for ^{23}Na in NaNO_2

In the ferroelectric phase, sodium nitrite crystallises in the orthorhombic system, space group C_{2v} , ($\text{Im}2m$). The unit cell, shown in figure 1, contains two formula units of NaNO_2 . Both sodium sites are identical and possess $\text{mm}2$ symmetry. In the high temperature

paraelectric phase, the NO_2 dipoles are oriented with equal probability along the positive and negative directions of the b axis so that the space group is D_{2h} (Immm). In this case, both sodium sites are, on average, identical and possess mmm symmetry.

It can be shown using the general expressions of Snyder and Hughes (1971) that the \mathbf{M} -tensor of the ^{23}Na nuclei in NaNO_2 is characterised by six independent components. The additional symmetry elements possessed by the paraelectric phase do *not* reduce the number of independent \mathbf{M} -tensor components and the orientation dependence of W_1 in *both* phases is given by

$$\begin{aligned} W_1 = & (e^2 Q^2 / 96) [4M_{1111} + 4M_{1133} + M_{3333} + 4M_{2323} + 4M_{3131} + 4M_{1212} \\ & + 6(3M_{3333} - 2M_{2323} - 2M_{3131}) \cos^2 \theta \\ & - (4M_{1111} + 4M_{1133} + 19M_{3333} - 16M_{2323} - 16M_{3131} + 4M_{1212}) \\ & \times \cos^4 \theta - 12(2M_{1133} + M_{3333}) \cos 2\varphi \sin^2 \theta \cos^2 \theta \\ & - 4(M_{2323} - M_{3131}) \cos 2\varphi \sin^2 \theta (1 - 4 \cos^2 \theta) \\ & - (4M_{1111} + 4M_{1133} + M_{3333} - 4M_{1212}) \cos 4\varphi \sin^4 \theta]. \end{aligned} \quad (1)$$

Here, eQ is the nuclear quadrupole moment, and θ and φ are the polar and azimuthal angles of the external magnetic field relative to a principal coordinate system whose z axis coincides with the twofold b axis and whose x and y axes lie in the mirror planes. As before (Hughes and Spencer 1982), we choose the x and y axes to coincide with the c and a axes respectively of the unit cell as shown in figure 1. Our coordinate system is therefore the same as that used to describe the time-averaged electric field gradient at the ^{23}Na sites at room temperature (Weiss 1960, Weiss and Biedenkapp 1962).

The $\alpha\beta\alpha'\beta'$ component of the \mathbf{M} -tensor can be expressed quantum-mechanically (Snyder and Hughes 1971) as

$$\begin{aligned} M_{\alpha\beta\alpha'\beta'} = & (2\pi/\hbar) \sum_{nn'} \exp(-\beta E_n) \langle n' | V_{\alpha\beta} | n \rangle^* \langle n' | V_{\alpha'\beta'} | n \rangle \\ & \times \delta(E_{n'} - E_n + E_{m+\mu} - E_m) \left(\sum_{nn'} \exp(-\beta E_n) \right)^{-1} \end{aligned} \quad (2)$$

where $\beta = 1/kT$, T is the temperature of the lattice, $V_{\alpha\beta}$ is $\partial^2 V / \partial x_\alpha \partial x_\beta$, E_n and E_m are eigenvalues of the lattice and spin system, n and n' are initial and final lattice states, and μ is 1 and 2 for W_1 and W_2 respectively. $M_{\alpha\beta\alpha'\beta'}$ can also be expressed classically as

$$M_{\alpha\beta\alpha'\beta'} = (\hbar)^{-2} \int_{-\infty}^{\infty} \overline{V_{\alpha\beta}(t+\tau) V_{\alpha'\beta'}(t)} \exp[-i(E_{m+\mu} - E_m)\tau/\hbar] d\tau \quad (3)$$

where the bar signifies a time average.

3. Choice of method to study the orientation dependence of the quadrupole relaxation

Because of quadrupole splitting, the NMR spectrum of ^{23}Na in a single crystal of NaNO_2 consists of three lines (Weiss 1960, Weiss and Biedenkapp 1962), the satellites being, to first order, equidistant from the centre line (Cohen and Reif 1957). The quadrupole spin-lattice relaxation of such a spin system with $I = \frac{3}{2}$ is in general described by three relaxation rates, $2W_1$, $2W_2$ and $2(W_1 + W_2)$ (Andrew and Tunstall 1961). If the spin

system is perturbed by selective excitation of the centre line alone, it can be shown that the satellites relax exponentially with a rate $2W_1$, while the recovery of the centre line is non-exponential, of the form

$$A + B(\exp(-2W_1t) + \exp(-2W_2t)). \quad (4)$$

If, on the other hand, one of the satellites is selectively excited, the centre line relaxes exponentially with a rate $2W_1$ and the relaxation of the satellites is of the form $A + B \exp(-2W_1t) + C \exp(-2(W_1 + W_2)t)$. Since the extraction of relaxation rates from non-exponential decays is difficult when the rates are nearly equal, the preferred method is to study the orientation dependence of W_1 , either by perturbing the centre line and monitoring the recovery of one of the satellites or, conversely, by perturbing one of the satellites while monitoring the recovery of the centre line.

Both approaches were compared in preliminary experiments carried out at room temperature (Towta 1986). Discrepancies of up to three percent in the values of W_1 , measured at the *same* crystal orientation, were found using the two methods. When the measurements were repeated at other crystal orientations, it was found that the sign of the discrepancy seemed to depend upon the sign of $(W_2 - W_1)$ which was known from earlier work (Hughes and Spencer 1982). The discrepancy can be explained by the fact that the pulses used to perturb the spin system were not perfectly selective and therefore weakly perturbed the other two components of the spectrum, thereby creating double- and triple-quantum coherences (Bodenhausen 1981). It is readily shown by a consideration of the spin dynamics (Towta 1986) that the satellites should relax exponentially with a rate $2W_1$, even if the pulse applied to the centre line is not selective. This is because the satellites are approximately equidistant from the centre line and therefore experience essentially the *same* perturbation. On the other hand, if a satellite is excited by a non-selective pulse, the other two resonances will be unequally perturbed and the centre line will *not*, in general, relax exponentially with a rate $2W_1$.

Most of the measurements described in this paper were therefore carried out by perturbing the centre line and monitoring the subsequent recovery of a satellite.

4. Experimental details

Our NMR system consisted mainly of Matec instrumentation, interfaced to form a pulsed double-resonance spectrometer. Resonances were detected at a fixed frequency of 14.5 MHz by means of a single-coil NMR probe equipped with a Faraday shield (Pandey and Hughes 1984) to suppress piezoelectric ringing (Hughes and Pandey 1984). Since the Q of the coil was about 30 and the separation of the centre line from the satellites never exceeded 600 kHz, the frequencies of the two RF fields applied to the spin system were generally within the bandwidth of the NMR circuit. Thus, no double tuning was required.

Most of our measurements were made on a cylindrical single crystal $\approx 2 \text{ cm}^3$ in volume, though, for comparison, a few measurements were made on a smaller cleaved crystal. The crystals, referred to as A and B respectively and described elsewhere (Hughes and Spencer 1982), were mounted in the probe in such a way that the angles θ and φ could be varied independently. These angles were determined, to within $\pm 0.3^\circ$

and $\pm 1^\circ$ respectively, from the readings of angular scales which were calibrated by comparing the measured satellite separation at room temperature with the relation

$$\Delta\nu = (549.0 \pm 0.1)[3 \cos^2\theta - 1 + (0.109 \pm 0.001) \sin^2\theta \cos 2\varphi] \text{ kHz} \quad (5)$$

found by Hughes and Spencer (1982).

The duration τ_p and the amplitude B_1 of the rotating field associated with the pulses should ideally satisfy the condition $\delta\omega\tau_p \ll 1$ where $\delta\omega$ is the resonance linewidth, as well as $\gamma B_1\tau_p = \pi/2$ and π for the 90° and 180° pulses respectively. To be selective, the pulses should also satisfy the condition $\omega_Q\tau_p \gg 1$, where ω_Q is the quadrupole splitting. It was not possible to satisfy all these conditions simultaneously. By keeping $\omega_Q/2\pi \geq 200$ kHz (by avoiding values of θ between 45° and 70°) and using 90° and 180° pulses of duration $\approx 30 \mu\text{s}$ and $\approx 150 \mu\text{s}$ respectively, the condition $\omega_Q\tau_p \gg 1$ was well satisfied. The pulses, especially the 180° pulse, were therefore quite selective. On the other hand, since $\delta\omega\tau_p$ was ~ 1 , some resonance amplitude was lost due to transverse relaxation which occurred during the pulses. This is not expected to introduce any systematic error in the measured relaxation rates.

To determine all six independent components of the \mathbf{M} -tensor, W_1 must be measured at a minimum of six different crystal orientations, including at least three different values of $\cos 4\varphi$. However, to see how well the data obeyed equation (1), we measured W_1 at a minimum of thirteen different orientations at each temperature.

Temperatures below room temperature were achieved by passing a stream of cold nitrogen gas through the cryostat. The temperature of the crystal was kept constant to within $\pm 0.2^\circ\text{C}$ over extended periods, both above and below room temperature, such stability being required to achieve the desired precision of better than $\pm 2\%$ in W_1 . There was a significant temperature inhomogeneity across the crystal at the highest temperature (462 K). This had little effect on our values of W_1 , but it meant that our cryostat was not suitable for making measurements very close to the ferroelectric phase transition.

5. Results and discussion

5.1. Temperature dependence of the relaxation

The temperature dependence of the ^{23}Na relaxation in crystal A was studied between 130 K and 462 K at $\theta = 0^\circ$ by applying a selective 180° pulse to the centre line and monitoring the subsequent recovery of the high frequency satellite with a selective 90° pulse. Apart from small deviations near 170 K, the recovery was exponential and all the data were fitted to the form $A + B \exp(-2W_{\text{sat}}\tau)$, where τ is the interval between the 180° and 90° pulses. W_{sat} , which is equal to W_1 if the relaxation is entirely quadrupolar, is shown as a function of temperature in figure 2.

The peak near 438 K is obviously associated with critical phenomena which accompany the ferroelectric phase transition (Bonera *et al* 1970, Avogadro *et al* 1971, 1975). However, the minimum that occurs near 160 K was unexpected and led us to make measurements using crystal B for comparison. As can be seen in figure 2, there is no significant difference between the behaviour of the two crystals, indicating that the minimum in W_{sat} may be an intrinsic property of the material.

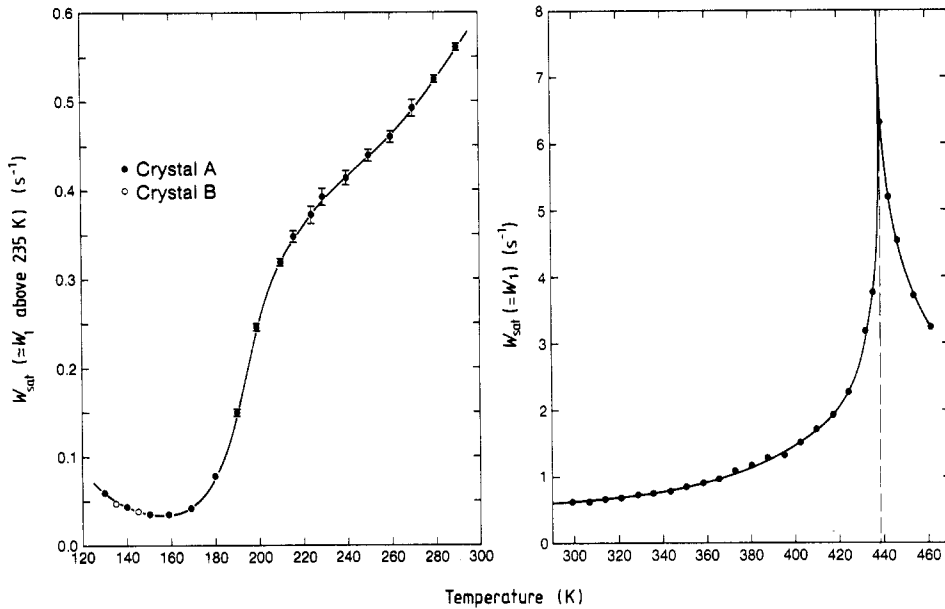


Figure 2. Temperature dependence of W_{sat} , half the relaxation rate of the high-frequency satellite, following selective excitation of the centre line measured at $\theta = 0^\circ$. Full (open) data points refer to crystal A (B). The broken vertical line shows the location of the transition from the ferroelectric to the paraelectric phase.

5.2. Orientation dependence of W_{sat}

The orientation dependence of W_{sat} was measured with crystal A at 145 K, 170 K, 235 K, 298 K, 350 K, 432 K and 448 K, the last two temperatures being selected because of their proximity to the ferroelectric transition. For measurements at 298 K, the centre line was perturbed by saturation with a ‘comb’ of closely spaced 90° pulses and the recovery of each satellite was monitored in turn. Since there was no difference between the values of W_{sat} in the two cases, only the high-frequency satellite was monitored at the other temperatures. Also, in these other measurements, the centre line was inverted by means of a selective 180° pulse, instead of being saturated. In principle, this gives a factor of two increase in the ‘signal’. The observed increase was between 1.5 and 1.9, because of the failure to satisfy the condition $\delta\omega\tau_p \ll 1$ as noted in section 4.

The data are shown in figure 3. The curves represent least squares fits to equation (1), except at 145 K where they were drawn by eye through the data points. Since the uncertainty in W_{sat} was known from the fitting of the raw data, meaningful values of χ^2 could be derived. Values of the reduced χ^2 lie between 0.7 and 1.2 at 298 K, 350 K, 432 K and 448 K, showing that W_{sat} is equal to W_1 and the relaxation of the ^{23}Na nuclei is both quadrupolar and homogeneous at these temperatures.

The non-exponential recovery of the centre line after inversion by a selective 180° pulse was measured at 298 K at the orientations $\theta = 0^\circ$, and $\theta = 90^\circ$, $\varphi = 90^\circ$. The data were fitted to equation (4), giving values of W_1 of 0.61 ± 0.01 at $\theta = 0^\circ$, and 0.50 ± 0.01 at $\theta = 90^\circ$, $\varphi = 90^\circ$. These are in agreement with the corresponding values of W_{sat} in figure 2. The values of W_2 were 1.10 ± 0.02 at $\theta = 0^\circ$ and 2.45 ± 0.03 at $\theta = 90^\circ$, $\varphi = 90^\circ$. These are in very good agreement with values of W_2 obtained by substituting the

M-tensor components, found by fitting the W_1 data at 298 K, in equation (4), of Hughes and Spencer (1982). This confirms that W_1 and W_2 are governed by the *same* **M**-tensor components at 298 K, and shows that the correlation time of the fluctuations causing the relaxation is much shorter than the Larmor period. It can be seen that the ratio W_2/W_1 at 298 K is roughly 2 at $\theta = 0^\circ$ and 5 at $\theta = 90^\circ$, $\varphi = 90^\circ$. At other orientations, it is as small as 0.6 (Hughes and Spencer 1982). Such a large orientation dependence is in marked contrast to that found for ^{23}Na in NaNO_3 (Spencer and Hughes 1978) and is mainly due to the very different locations of the near neighbours of the ^{23}Na nuclei in the unit cells of the two materials.

Agreement between theory and the data in figure 3 becomes progressively poorer as the temperature is reduced. Values of χ^2 are 1.5, 6.7 and 85 at 235 K, 170 K and 145 K respectively, showing that another relaxation mechanism is dominant at low temperatures. It was also noticed that the values of W_{sat} measured near $\theta = 75^\circ$ at 170 K and 145 K were not as reproducible as those taken at other orientations. They were sometimes significantly larger than anticipated. Inconsistent behaviour at low temperatures was also observed by Petersen and Bray (1976). These phenomena may be due to cross-relaxation to another spin system, e.g. ^{17}O , at certain crystal orientations.

5.3. Interpretation of the behaviour of W_{sat} at low temperatures

The anomalous low-temperature relaxation was studied further by monitoring the recovery of both the centre line and the high-frequency satellite after inversion of the centre line by a selective 180° pulse. This was done at 135 K and 145 K using the two crystals. In contrast to the behaviour at 298 K, the recovery of the centre line was exponential in each case; all attempts to fit the data to equation (4) were unsuccessful. Values of W_{cl} , obtained by fitting the data to $A + B \exp(-2W_{\text{cl}}\tau)$, are shown in table 1, together with corresponding values of W_{sat} . Exponential recovery of the centre line would, of course, occur if W_1 and W_2 were coincidentally equal. The fact that the recovery was exponential at *all* orientations indicates that the relaxation is magnetic rather than quadrupolar at 135 K and 145 K. Quadrupole relaxation will undoubtedly occur because of the interaction with phonons (Van Kranendonk and Walker 1967, 1968), but it seems to be negligible in comparison with the magnetic relaxation at these temperatures.

Magnetic relaxation of a spin system characterised by well-resolved quadrupole splitting does not seem to have been treated in the literature. As shown in the appendix, selective excitation of the centre line of an $I = \frac{3}{2}$ spin system which experiences homogeneous magnetic relaxation, leads to a recovery of the centre line of the form

$$A + B(\exp(-2W_3\tau) + 9 \exp(-12W_3\tau)). \quad (6)$$

The corresponding recovery of the satellites is of the form

$$A + B(\exp(-2W_3\tau) - 6 \exp(-12W_3\tau)). \quad (7)$$

When the raw data used to obtain the values listed in table 1 were refitted to a function of the form $A + B(\lambda \exp(-2W_3\tau) + \exp(-12W_3\tau))$, λ was found to be -0.05 ± 0.05 instead of $\frac{1}{3}$ for the centre line and 0.00 ± 0.05 instead of $-\frac{1}{3}$ for the high-frequency satellite. When all of the 145 K data in figure 3 were similarly reanalysed, the mean of the fourteen values of λ was found to be 0.00 ± 0.04 .

It is not clear why we did not observe the $\exp(-2W_3\tau)$ behaviour. One possibility is that the low-temperature relaxation involves spin diffusion (Abragam 1961) to distant

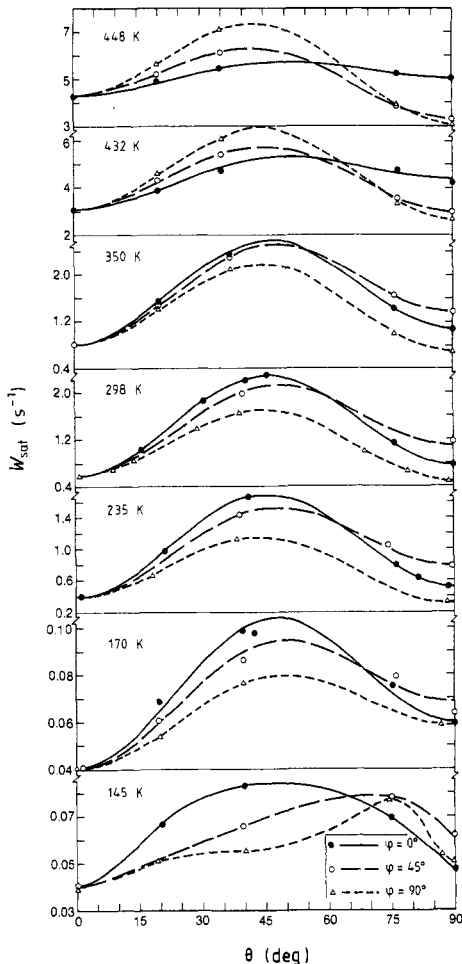


Figure 3. θ dependence of W_{sat} , half the relaxation rate of the high-frequency satellite (mean of high- and low-frequency satellites at 298 K), following selective excitation of the centre line, measured at various temperatures. The full circles (open circles, triangles) refer to $\varphi = 0^\circ$ (45° , 90°). The full (broken, short-dash) curves refer to $\varphi = 0^\circ$ (45° , 90°) and represent least-squares fits of the data to equation (1), except at 145 K where the curves were drawn by eye through the data points. Note the different ordinate scales at the various temperatures. Error bars are not shown since they are smaller than the data points in most cases.

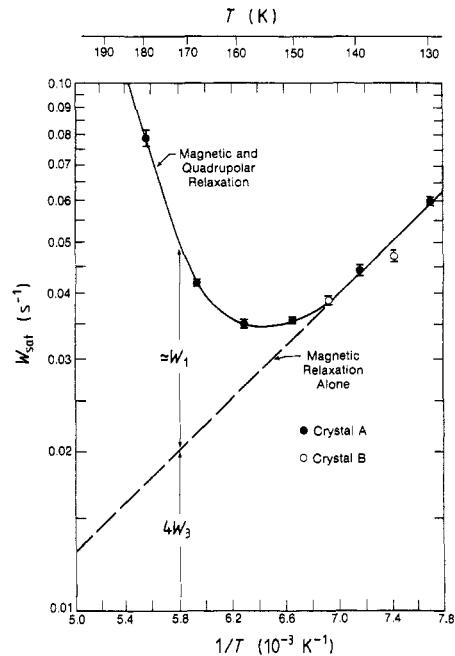


Figure 4. Logarithmic plot of W_{sat} , measured at $\theta = 0^\circ$, as a function of the reciprocal of the absolute temperature. The full curve is drawn through the data points. The straight line represents the magnetic contribution to the relaxation. The full (open) data points refer to crystal A (B).

relaxation sites, even though we found that the theoretical orientation dependence of the diffusion coefficient of the spin system is quite different from the observed orientation dependence of W_{sat} at 145 K. Since the ^{23}Na satellites in NaNO_2 experience substantial inhomogeneous quadrupole broadening (Betsuyaku 1969, Hughes and Pandey 1987), spin diffusion via the satellites may be severely inhibited. As shown in the appendix, if

Table 1. W_{cl} , half the relaxation rate of the centre line, and W_{sat} , half the relaxation rate of the high frequency satellite, of ^{23}Na in NaNO_2 , measured at various orientations and temperatures.

Temperature (K) ± 1 K	θ (deg) $\pm 0.3^\circ$	φ (deg) $\pm 1^\circ$	W_{cl} (s^{-1}) ± 0.001 s^{-1}	W_{sat} (s^{-1}) ± 0.001 s^{-1}
135	4.0	0	0.059	0.056
135	42.9	0	0.092	0.100
135	90.0	0	0.063	0.060
135	0.0	0	0.051†	0.047†
145	0.0	0	0.042†	0.039†
145	0.0	90	0.045	0.040

† Obtained using crystal B.

spin diffusion, and hence relaxation, occurs only via the centre line, the recovery of both the centre line and the satellites should be exponential of the form $A + B \exp(-8W_3\tau)$. As can be seen in table 1, W_{cl} tends to be slightly larger than W_{sat} . This may be because the satellite resonances from nuclei close to the relaxation sites are not observed on account of quadrupole broadening. This, in turn, suggests that the low-temperature relaxation may possibly be caused by paramagnetic centres or impurities.

A brief ESR investigation of crystal B was therefore carried out. It showed only a small concentration, $\sim 10^{-8}$, of paramagnetic spins, far smaller than the concentration of 10^{-4} to 10^{-5} needed to account for the observed relaxation rates. We therefore believe that the relaxation near 145 K is intrinsic and is related to the anomalous relaxation observed by Abe *et al* (1972) in a NQR study of ^{14}N in NaNO_2 .

These workers found that the ν_- and ν_+ ^{14}N resonances exhibited strong minima in T_1 at 36 K and 64 K, and at 36 K and 80 K respectively, which they attributed to a quadrupole relaxation mechanism. We believe that the minima are caused by a magnetic relaxation mechanism, with the characteristic frequency of the fluctuations being ≈ 1.17 MHz (the frequency of the difference line (Marino and Bray 1968)) at 36 K, ≈ 3.76 MHz (the frequency of the ν_- line) at 64 K, and ≈ 4.93 MHz (the frequency of the ν_+ line) at 80 K.

The work of Abe *et al* (1972) indicates that the increase in W_{sat} below 160 K in figure 2 is almost certainly the high-temperature 'skirt' of a thermally activated ' T_1 -minimum' centred below 130 K. (We were unable to extend our measurements much below 130 K to check this because of the design of our cryostat.) Figure 4 shows $\log W_{\text{sat}}$ plotted as a function of $1/T$. A straight line consistent with a single thermal activated process has been drawn through the data points below 145 K. The slope of the line is similar to that found by measuring W_{sat} at $\theta = 4^\circ$, $\varphi = 0^\circ$ at seven different temperatures between 130 K and 145 K (Towta 1986) and points to an activation energy ≈ 4 kJ mol $^{-1}$. Values of the activation energy derived from the data of Abe *et al* (1972) indicate a value closer to 2 kJ mol $^{-1}$. Such a large discrepancy between the two values of the activation energy merits further investigation.

The exact cause of the magnetic relaxation is not yet known but would seem to involve a nuclear magnetic dipole-dipole interaction. Since the orientation dependence is known from the 145 K data in figure 3, it should be possible to identify the mechanism involved. This problem is currently being addressed.

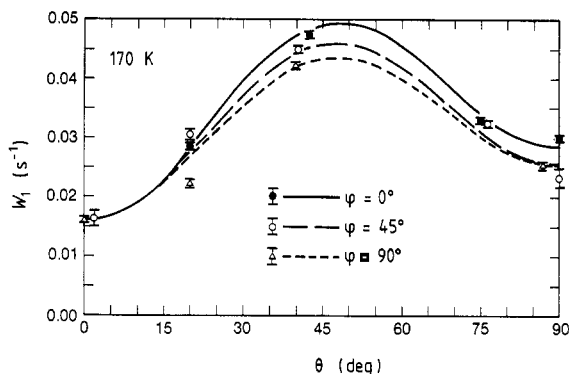


Figure 5. θ -dependence of W_1 at 170 K, obtained by removing the magnetic contribution from W_{sat} measured at 170 K. The full circles (open circles, triangles) refer to $\varphi = 0^\circ$ (45° , 90°). The solid (broken, short-dash) curves refer to $\varphi = 0^\circ$ (45° , 90°) and represent a least-squares fit of the data to equation (1).

Table 2. **M**-tensor components of ^{23}Na in NaNO_2 at various temperatures, obtained by fitting the orientation dependence of W_1 to equation (1). Values are in s^{-1} and the errors limits are random errors. (Systematic errors are believed to be small.)

Components	170 K	235 K	298 K	350 K	432 K	448 K
$(e^2Q^2/96)M_{1111}$	0.0044 ± 0.0003	0.186 ± 0.003	0.241 ± 0.002	0.263 ± 0.005	0.362 ± 0.018	0.322 ± 0.011
$(e^2Q^2/96)M_{1133}$	-0.0038 ± 0.0002	-0.173 ± 0.003	-0.222 ± 0.002	-0.236 ± 0.006	-0.385 ± 0.019	-0.411 ± 0.010
$(e^2Q^2/96)M_{3333}$	0.0063 ± 0.0002	0.237 ± 0.003	0.326 ± 0.002	0.375 ± 0.005	0.831 ± 0.020	0.927 ± 0.011
$(e^2Q^2/96)M_{2323}$	0.0008 ± 0.0001	0.0106 ± 0.0007	0.0197 ± 0.0005	0.028 ± 0.001	0.088 ± 0.007	0.147 ± 0.004
$(e^2Q^2/96)M_{3131}$	0.0012 ± 0.0001	0.0381 ± 0.0007	0.0531 ± 0.0005	0.074 ± 0.001	0.301 ± 0.007	0.389 ± 0.005
$(e^2Q^2/96)M_{1212}$	0.0023 ± 0.0001	0.0252 ± 0.0007	0.0421 ± 0.0005	0.061 ± 0.001	0.250 ± 0.007	0.241 ± 0.004

The rapid increase in W_{sat} which occurs at 160 K in figure 4 must be due to quadrupole relaxation and it is evident that the magnetic and quadrupole contributions are comparable at 170 K. Such a situation is treated in the appendix. By fitting our 170 K relaxation data to the non-exponential form, equation (A13), we extracted approximate values of W_1 which are shown in figure 5. To do so, it was necessary to know the orientation dependence of W_3 at 170 K. We assumed that it was of exactly the same form as at 145 K and that the scaling factor $(W_3)_{170\text{K}}/(W_3)_{145\text{K}}$ is 0.57, as obtained from the slope of the straight line representing magnetic relaxation alone in figure 4. A fit of the W_1 data to equation (1) is shown in figure 5; the agreement between experiment and

theory is quite good, considering the uncertainties involved in removing the large magnetic contribution.

It was found that values of W_1 at 170 K, obtained by the above procedure, are quite similar to those obtained by simply subtracting estimated values of $4W_3$ at 170 K from W_{sat} measured at that temperature. Thus, as indicated in figure 4, the difference between the full curve and the broken line can be used as a rough estimate of W_1 . The magnetic contribution to W_{sat} , found by extrapolating the straight line in figure 4, is small but significant at 235 K. Values of W_{sat} at that temperature were therefore corrected by simply subtracting the magnetic contribution. It is reassuring that applying such a correction led to a small decrease in the χ^2 of the fit to equation (1). No correction was applied to the 298 K data, since the magnetic relaxation makes a negligible contribution at that temperature.

5.4. Orientation and temperature dependence of the quadrupole relaxation

The temperature dependence of W_1 at $\theta = 0^\circ$, illustrated in figures 2 and 4, is anomalous in two respects. Firstly, its magnitude at temperature ≥ 200 K is much larger than that of other ionic sodium compounds at the same temperature. Secondly, its temperature dependence is very different from the T^2 -behaviour, characteristic of a phonon interaction (Van Kranendonk and Walker 1967, 1968), displayed by most other ionic sodium compounds. Indeed, the initial increase in W_1 is exponential over the temperature range 145 K to 170 K, showing that the dominant quadrupole relaxation at these low temperatures is not caused by phonons.

Values of the **M**-tensor components, found by fitting the W_1 data at the various temperatures, are listed in table 2 and plotted in figure 6 where the curves were drawn using figure 2 as a guide. The components satisfy the relations derived by Snyder and Hughes (1971). The only 'cross-component', M_{1133} , is negative. All the other components are of the form $M_{\alpha\beta\alpha\beta}$ and are necessarily positive as found experimentally.

Ratios of the **M**-tensor components, which govern the *form* of the orientation dependence of W_1 , are shown in table 3. They are of interest since they depend only on the relative configuration of near neighbours in the lattice and on the type of relative motion of these neighbours (Hughes and Reed 1971, Hughes and Spencer 1982). It can be seen in table 3 that the ratios are quite similar at 235 K, 298 K and 350 K, indicating that the quadrupole relaxation is almost certainly caused by the *same* mechanism at all these temperatures. The small temperature dependence of the ratios is probably caused, in part, by anisotropic thermal expansion (Gesi 1969), as in the case of sodium nitrate (Hughes and Reed 1971).

The ratios of the **M**-tensor components at 170 K are markedly different from those found at 235 K, 298 K and 350 K. This may mean that relaxation at 170 K is caused by a different type of dynamical process. On the other hand, since the differences are not large, they may be caused by systematic errors introduced by the removal of the magnetic relaxation, compounded by the uncertain values of W_{sat} obtained near $\theta = 75^\circ$.

Ratios of the **M**-tensor components of ^{23}Na in sodium nitrate, NaNO_3 , were surprisingly well accounted for by a simple point-charge dynamical model of near neighbours (Hughes and Reed 1971, Spencer and Hughes 1978). In an attempt to identify the quadrupole relaxation mechanisms which occur in NaNO_2 , we list, in table 3, ratios of the components found by making similar point-charge calculations for NaNO_2 using four different dynamical models (Hughes and Spencer 1982, Towta and Hughes 1986). The theoretical ratios are in poor agreement with the experimental ratios obtained from

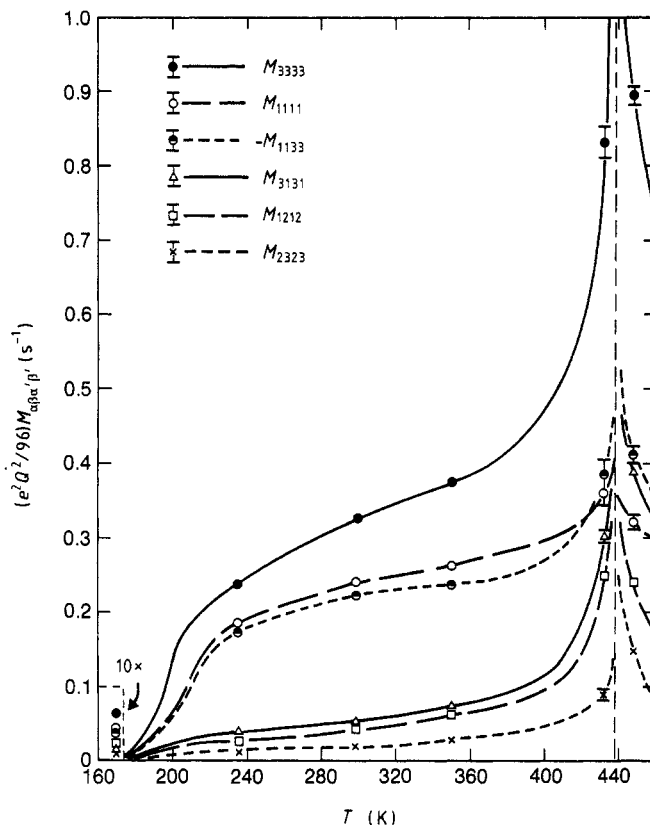


Figure 6. The six quadrupole relaxation **M**-tensor components plotted as a function of temperature. Note that M_{1133} is negative at all temperatures and that the components at 170 K are shown magnified by a factor of 10. The curves were drawn through the data points using figure 2 as a guide. The broken vertical line shows the location of the transition from the ferroelectric to the paraelectric phase.

170 K to 350 K, so it is not obvious which dynamical process is responsible for the relaxation in this temperature range.

It can be seen from table 3 that the ratios of the **M**-tensor components at 432 K and 448 K are quite different from those at lower temperatures. This is not unexpected, since the relaxation near the ferroelectric phase transition is caused by critical fluctuations (Bonera *et al* 1970, Avogadro *et al* 1971, 1975), in addition to the mechanism which is dominant at lower temperatures. It is probably a reasonable approximation to assume that these two relaxation mechanisms are independent of one another, so that the observed **M**-tensor components are simply the sums of the corresponding components associated with each mechanism. In order to determine $(M_{\alpha\beta\alpha'\beta'})_{\text{crit}}$ —the **M**-tensor components associated with the critical fluctuations alone—it is necessary to estimate the contribution of the 'low-temperature' mechanism at 432 K and 448 K.

It is evident in figure 6 that critical fluctuations cause a substantial increase in five of the six **M**-tensor components, even at a temperature as low as 350 K. However, M_{1111} seems to be hardly affected. We therefore linearly extrapolated M_{1111} from the range 298 K to 350 K out to 432 K and 448 K. We also assumed that the other 'low-temperature'

Table 3. Ratios of the M -tensor components of ^{23}Na in NaNO_2 measured at various temperatures. Also shown are theoretical estimates based on four point-charge dynamical models of the lattice. (Details are given by Hughes and Spencer (1982).)

Ratios	Experimental values							Theoretical values			
	170 K	235 K	298 K	350 K	432 K	448 K	a	b	c	d	
M_{111}/M_{333}	0.69	0.79	0.74	0.70	0.44	0.35	0.27	0.09	0.19	0.24	
M_{113}/M_{333}	-0.60	-0.73	-0.68	-0.63	-0.46	-0.44	-0.35	-0.30	-0.43	-0.69	
M_{223}/M_{333}	0.13	0.05	0.06	0.08	0.11	0.16	0.48	0.43	1.18	0.06	
M_{313}/M_{333}	0.19	0.16	0.16	0.20	0.36	0.42	0.25	0.37	5.77	0.16	
M_{121}/M_{333}	0.37	0.11	0.13	0.16	0.30	0.26	0.31	0.02	0.73	0.13	

^a Isotropic uncorrelated vibration of equal amplitude of each Na ion and its seven nearest neighbours.

^b Uncorrelated sudden reorientation of individual NO_2 groups within the bc plane.

^c Small uncorrelated angular oscillations of the NO_2 groups about the a axis.

^d Small uncorrelated angular oscillations of the NO_2 groups about the c axis.

Table 4. Ratios of the **M**-tensor components of ^{23}Na in NaNO_2 associated with critical fluctuations measured at 432 K and 448 K. Also shown is a theoretical estimate assuming uncorrelated sudden reorientations of individual NO_2 groups within the bc plane.

Ratio	Experimental values		Theoretical value
	432 K	448 K	
$(M_{1111})_{\text{crit}}/(M_{3333})_{\text{crit}}$	0.15	0.03	0.09
$(M_{1133})_{\text{crit}}/(M_{3333})_{\text{crit}}$	-0.26	-0.25	-0.30
$(M_{2323})_{\text{crit}}/(M_{3333})_{\text{crit}}$	0.15	0.24	0.43
$(M_{3131})_{\text{crit}}/(M_{3333})_{\text{crit}}$	0.55	0.63	0.37
$(M_{1212})_{\text{crit}}/(M_{3333})_{\text{crit}}$	0.46	0.37	0.02

M-tensor components experience the same fractional increase as M_{1111} , between 298 K and 448 K. Using this extrapolation procedure, we obtained the values of $(M_{\alpha\beta\alpha'\beta'})_{\text{crit}}$ shown in table 4. It can be seen that there are no large differences between the ratios in the ferroelectric (432 K) and paraelectric (448 K) phases.

Also shown in table 4 is a theoretical estimate obtained by assuming that the relaxation is entirely caused by individual NO_2 groups which are suddenly reorienting (reversing their orientation) in the bc plane (Hughes and Spencer 1982). Bearing in mind the crudeness of the model and the extrapolation procedure, the agreement between the two sets of data and the theoretical estimate is probably as good as could be expected, except in the case of $(M_{1212})_{\text{crit}}/(M_{3333})_{\text{crit}}$. The large experimental value of this ratio can be accounted for on the point-charge model if the a or c coordinates of the oxygen atoms change significantly as a result of the reorientation of the NO_2 groups. (In the model, it was assumed that reorientation causes a change in only the b coordinate of the atoms (Hughes and Spencer 1982).) This implies either that the NO_2 groups do not rotate through exactly 180° , or that the axis of rotation is not parallel to the a axis. In either case, this may be because of the presence of other nearby disordered NO_2 groups.

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Appendix

We first consider the homogeneous magnetic spin-lattice relaxation of a system of $I = \frac{3}{2}$ nuclei which experience first-order quadrupole splitting by being situated at identical non-cubic sites in a single crystal. The probability of $m = \frac{1}{2} \leftrightarrow -\frac{1}{2}$ transitions is $4W_3$, and that of $m = \frac{3}{2} \leftrightarrow \frac{1}{2}$ and $m = -\frac{1}{2} \leftrightarrow -\frac{3}{2}$ transitions is $3W_3$. If the population differences associated with the $m = \frac{3}{2} \leftrightarrow \frac{1}{2}$ satellite, the centre line and the $m = -\frac{1}{2} \leftrightarrow -\frac{3}{2}$ satellite

are denoted by N_1 , N_0 and N_{-1} respectively, then, in the absence of externally applied RF fields, the rate equations are

$$dN_1/dt = 4W_3N_0 - 6W_3N_1 + 2W_3n_0 \quad (\text{A1})$$

$$dN_0/dt = 3W_3N_1 - 8W_3N_0 + 3W_3N_{-1} + 2W_3n_0 \quad (\text{A2})$$

$$dN_{-1}/dt = 4W_3N_0 - 6W_3N_{-1} + 2W_3n_0 \quad (\text{A3})$$

where n_0 is the difference in the populations of adjacent levels in thermal equilibrium. (It can be shown (Towta 1986) that it is not necessary to take account of unequal population differences in thermal equilibrium arising from first-order quadrupole splitting.) By solving (A1), (A2) and (A3), it is found that N_1 , N_0 and N_{-1} are, in general, given by expressions of the form

$$n_0 + A \exp(-6W_3t) + B \exp(-2W_3t) + C \exp(-12W_3t). \quad (\text{A4})$$

The relaxation rates are $2W_3$, $6W_3$ and $12W_3$, in accordance with the general rule given by Andrew and Tunstall (1961).

If the spin system is initially in thermal equilibrium and the centre line only is perturbed by a selective pulse, the recovery is given by

$$N_0 = n_0 + A(\exp(-2W_3t) + 9 \exp(-12W_3t)) \quad (\text{A5})$$

$$N_{\pm 1} = n_0 + A(\exp(-2W_3t) - 6 \exp(-12W_3t)) \quad (\text{A6})$$

where A is a constant which depends on the initial perturbation and is equal to $-n_0/5$ for a 180° pulse. It can be seen from (A5) and (A6) that the recovery of the centre line and satellites is significantly non-exponential.

If the relaxation involves spin diffusion to distant relaxation sites and inhomogeneous quadrupole broadening suppresses spin diffusion via the satellites, only the $m = \frac{1}{2} \leftrightarrow -\frac{1}{2}$ transitions will cause relaxation. An analysis similar to the above shows that the recovery of the spin system following selective perturbation of the centre line is, in this case, given by

$$N_0 = n_0 - 2A \exp(-8W_3t) \quad (\text{A7})$$

$$N_1 = n_0 + A \exp(-8W_3t) \quad (\text{A8})$$

where A is n_0 if the perturbation is a 180° pulse. It can be seen that the centre line and satellites recover exponentially with the *same* rate, $8W_3$.

We now consider the situation where a $I = \frac{3}{2}$ spin system experiences both magnetic and quadrupole relaxation. The case where magnetic relaxation occurs via the satellites as well as the centre line has been considered by Niemela (1967). We extend his analysis to cover the situation where the magnetic relaxation occurs only through the centre line because spin diffusion via the satellites is inhibited by inhomogeneous quadrupole broadening. The appropriate rate equations are

$$dN_1/dt = W_2N_{-1} + 4W_3N_0 - (2W_1 + W_2)N_1 + n_0(2W_1 - 4W_3) \quad (\text{A9})$$

$$dN_0/dt = (W_1 - W_2)N_{-1} - (2W_2 + 8W_3)N_0 + (W_1 - W_2)N_1 + n_0(4W_2 - 2W_1) + 8W_3 \quad (\text{A10})$$

$$dN_{-1}/dt = -(2W_1 + W_2)N_{-1} + 4W_3N_0 + W_2N_1 + n_0(2W_1 - 4W_3). \quad (\text{A11})$$

If the spin system is initially in thermal equilibrium and the centre line alone is perturbed

by a selective pulse, it can be shown by solving (A9) to (A11) that the recovery is non-exponential of the form

$$N_0 = n_0 + A[(4W_3 - P)/P] \exp(\lambda_1 t) - A[(4W_3 + P)/P] \exp(\lambda_2 t) \quad (\text{A12})$$

$$N_{\pm 1} = n_0 + A[(W_2 - W_1 + 4W_3 + P)(4W_3 - P)/2(W_1 - W_2)P] \exp(\lambda_1 t) \\ - A[(W_2 - W_1 + 4W_3 - P)(4W_3 + P)/2(W_1 - W_2)P] \exp(\lambda_2 t) \quad (\text{A13})$$

where A is a constant which depends on the perturbation and

$$\lambda_1 = - (W_1 + W_2 + 4W_3 - P) \quad (\text{A14})$$

$$\lambda_2 = - (W_1 + W_2 + 4W_3 + P) \quad (\text{A15})$$

$$P = [(W_1 - W_2)^2 + 16W_3^2]^{1/2}. \quad (\text{A16})$$

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