Interpretation of the temperature dependence of the quadrupole spin-lattice relaxation of ^{23}Na in NaNO$_2$

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Abstract. It is shown theoretically that the quadrupole relaxation probabilities W_1 and W_2 of ^{23}Na in the ferroelectric material NaNO$_2$, caused by random 180° reorientations of the NO$_2$ groups associated with the order–disorder transition, should be proportional to $(1 - S^2)(1 - S)\exp(\Delta U/kT)$, where S is the order parameter that characterizes the orientation of the NO$_2$ groups and ΔU is the associated potential barrier. By using a theoretical expression for the temperature dependence of S derived by Yamada *et al*, and the values of W_1 recently measured in our laboratory, it is found that the above proportionality is accurately obeyed between 230 K and the critical temperature, 437 K. This shows that reorientations of the NO$_2$ groups are essentially random in this temperature range. The agreement between experiment and theory becomes progressively worse as the temperature is reduced below 230 K, indicating that the reorientations are no longer random in that range. Below 150 K, spin–lattice relaxation of the ^{23}Na nuclei occurs by spin diffusion to relaxation centres, believed to be reorienting NO$_2$ groups situated about 3 nm apart. Our analysis should be applicable to other materials that undergo a similar order–disorder transition.

1. Introduction

Sodium nitrite is a ferroelectric material (Sawada *et al* 1958) which undergoes an order–disorder transition, first to a sinusoidal antiferroelectric phase at 437 K and then to a paraelectric phase at 438 K (Tanisaki 1961, Yamada *et al* 1963). At low temperatures, the NO$_2$ groups are believed to be aligned in the *bc* plane of the orthorhombic unit cell (Ziegler 1931), shown in figure 1, with their electric dipole moments pointing along one direction of the ferroelectric *b* axis. The transition from the ferroelectric phase occurs by progressive reversal of the orientations of the NO$_2$ groups, so that, in the paraelectric phase, their dipole moments are oriented with equal probability along the two directions of the *b* axis (Strijk and Macgillavry 1943, 1946).

The ^{23}Na NMR spectrum obtained from a single crystal of NaNO$_2$ is a well resolved quadrupole-split triplet (Weiss 1960). The ^{23}Na nuclei relax primarily via the quadrupole transitions $m = \pm 3/2 \leftrightarrow \pm 1/2$ and $m = \pm 3/2 \leftrightarrow \mp 1/2$, with probabilities W_1 and W_2, respectively, which vary quite strongly with the orientation of the crystal relative to the external magnetic field (Hughes and Spencer 1982, Towta and Hughes 1990).

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● - Na   ○ - O   ● - N
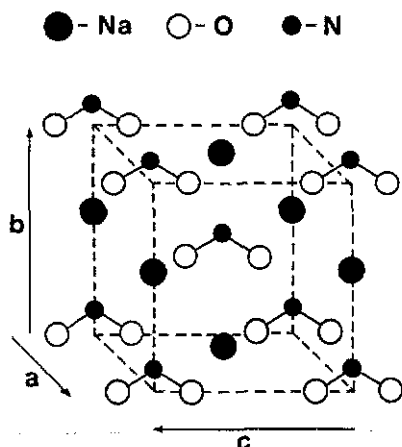
Figure 1. Unit cell of $NaNO_2$.

Bonera *et al* (1970) measured the spin–lattice relaxation rate $T_1^{-1} = (2/5)(W_1 + 4W_2)$ of ^{23}Na between 150 K and 530 K by orienting their $NaNO_2$ crystal so that the three resonances approximately overlapped each other (the angle between the external magnetic field and the *b* axis then being roughly 54° (Hughes and Spencer 1979)). They found a very rapid increase of T_1^{-1} between 150 K and 230 K, followed by a much slower rise from 230 K to about 350 K, and another rapid increase to a critical peak at 437 K. The behaviour near the peak has been studied in more detail by Avogadro *et al* (1971, 1975) and Buchheit and Petersson (1981).

Towta and Hughes (1990) have recently studied the temperature dependence of the spin–lattice relaxation of ^{23}Na in $NaNO_2$ by observing the approach to equilibrium of one of the satellites, following selective excitation of the central resonance. They fitted their data to the form $[A + B \exp(-2W_{sat} t)]$, where W_{sat} is equal to W_1 in the absence of magnetic relaxation. Their results, which were obtained with the magnetic field parallel to the *b* axis, are reproduced in figure 2. The data above 150 K are qualitatively similar to those of Bonera *et al* (1970), but are quantitatively different because of the different crystal orientation used, and because W_1 and W_2 do not exhibit quite the same temperature dependence. The increase in the relaxation rate below 150 K is believed to be the high-temperature skirt of a 'T_1 minimum' centred well below 130 K, similar to anomalies in the relaxation rate of ^{14}N observed by Abe *et al* (1972) in an NQR study of $NaNO_2$.

Previous workers (Bonera *et al* 1970, Avogadro *et al* 1971, 1975) interpreted the relaxation behaviour near the critical region in terms of long-wavelength fluctuations in the electric polarization caused by the 180° reorientations of the NO_2 groups; they paid little attention to the anomalous relaxation observed at lower temperatures. Our purpose in the present paper is to present a new way of interpreting the relaxation data through the entire temperature range up to the critical point. Our approach shows that individual NO_2 groups are undergoing essentially random 180° reorientations above 230 K. As the temperature is reduced below 230 K, the reorientations become less random until, at about 150 K, the reorienting NO_2 groups seem to be situated at fixed sites roughly 3 nm apart.

In section 2, we derive simple theoretical expressions for the contributions to W_1 and W_2 caused by reorientations of the NO_2 groups. The experimental data of Towta and Hughes (1990) are compared with the theory in section 3.
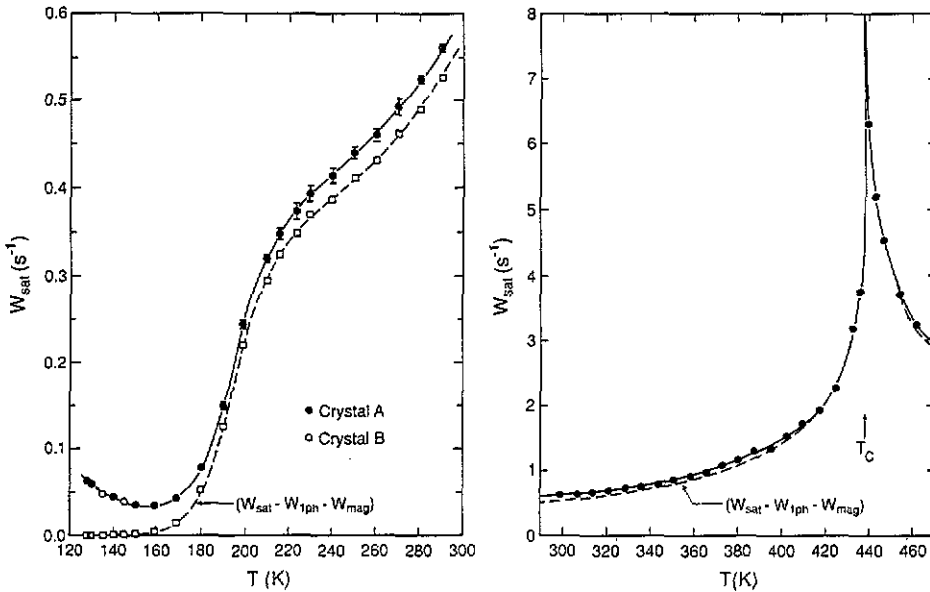
Figure 2. Temperature dependence of the relaxation probability W_{sat} of ^{23}Na nuclei in single crystals of NaNO$_2$, measured by Towta and Hughes (1990). The full (open) circles refer to crystal A (B) (Hughes and Spencer 1982) and the solid curves are drawn smoothly through the data. The open squares in the left-hand graph and the smooth broken curve drawn through them, show $(W_{sat} - W_{1ph} - W_{mag})$, the raw data with the phonon and magnetic contributions removed. Only the broken curve is shown in the right-hand graph, since the points representing $(W_{sat} - W_{1ph} - W_{mag})$ lie too close to the raw data.

2. Theory

For a system of $I = 3/2$ nuclei situated at identical sites in a single crystal and relaxing via a direct quadrupole relaxation process, W_1 can be written as

$$W_1 = \hbar^{-2}(e^2 Q^2/12) \int_{-\infty}^{\infty} \overline{[V_{xz}(t) + iV_{yz}(t)][V_{xz}(t+\tau) + iV_{yz}(t+\tau)]^*} e^{-i\omega\tau} \, d\tau \tag{1}$$

where eQ is the nuclear quadrupole moment, ω is the frequency of the $\Delta m = \pm 1$ transitions involved, and $V_{xz}(t)$ and $V_{yz}(t)$ are time-dependent components of the electric field gradient tensor at the nuclear sites in a coordinate system whose z axis is parallel to the magnetic field.

To evaluate $\overline{V_{xz}(t)V_{xz}(t+\tau)}$, we suppose, for the moment, that each ^{23}Na nucleus is influenced by just one neighbouring NO$_2$ group, and that V_{xz} changes suddenly from $(V_{xz})_1$ to $(V_{xz})_2$ when the neighbouring group flips from the parallel (lowest energy) orientation to the antiparallel one. If $p_1(\tau)$ and $p_2(\tau)$ are the probabilities that $V_{xz}(t)$ is equal to $(V_{xz})_1$ and $(V_{xz})_2$, respectively, at time τ in an ensemble where $V_{xz}(t)$ is equal to $(V_{xz})_1$ at $\tau = 0$, then they satisfy the equations (Susuki and Kubo 1968)

$$dp_1/d\tau = -w_{12}p_1 + w_{21}p_2 \qquad dp_2/d\tau = w_{12}p_1 - w_{21}p_2. \tag{2}$$

Here, w_{12} and w_{21} are, respectively, the probabilities that an individual NO_2 group will flip from the lower energy state 1 to the higher energy state 2, and vice versa. The appropriate solution to (2) is

$$2p_1(\tau) = 1 + [w_{21} - w_{12} + 2w_{12}e^{-(w_{21}+w_{12})\tau}](w_{21} + w_{12})^{-1} \qquad (3)$$

$$2p_2(\tau) = 1 - [w_{21} - w_{12} + 2w_{12}e^{-(w_{21}+w_{12})\tau}](w_{21} + w_{12})^{-1}. \qquad (4)$$

For an ensemble where $V_{xz}(t)$ is equal to $(V_{xz})_2$ at $\tau = 0$, the corresponding probabilities, $p_1'(\tau)$ and $p_2'(\tau)$, say, are given by (3) and (4) with the signs of the exponential terms reversed. Since

$$\overline{V_{xz}(t)V_{xz}(t+\tau)} = (V_{xz})_1[p_1(\tau)(V_{xz})_1 + p_2(\tau)(V_{xz})_2]$$
$$+ (V_{xz})_2[p_1'(\tau)(V_{xz})_1 + p_2'(\tau)(V_{xz})_2] \qquad (5)$$

it is found, using (3), (4) and (5), that the τ-dependent part of $\overline{V_{xz}(t)V_{xz}(t+\tau)}$ is given by

$$\overline{V_{xz}(t)V_{xz}(t+\tau)} = \left\{(1 - S^2)[(V_{xz})_1 - (V_{xz})_2]^2 e^{-i(w_{21}+w_{12})|\tau|}\right\}/4. \qquad (6)$$

Here, S is the order parameter defined as $(N_1 - N_2)/(N_1 + N_2)$, where N_1 and N_2 are the number of NO_2 groups with parallel and antiparallel orientations, respectively. A corresponding expression is obtained for $\overline{V_{yz}(t)V_{yz}(t+\tau)}$. For the situation in figure 2 where the magnetic field is parallel to the b axis, cross terms such as $\overline{V_{xz}(t)V_{yz}(t+\tau)}$ vanish because of the $mm2$ point group symmetry of the sodium sites, if the x and y axes are taken to be parallel to the c and a axes (Hughes and Spencer 1982).

In reality, the ^{23}Na nuclei will relax because of the reorientations of several neighbouring NO_2 groups. If the reorientations of individual NO_2 groups are assumed to be uncorrelated with those of their near neighbours, but are thermally activated across a potential barrier ΔU so that $w_{12} = A\exp(-\Delta U/kT)$, it is found, using (1) and (6) and the relation $w_{21}/w_{12} = N_1/N_2 = (1+S)/(1-S)$, that

$$W_{1fl} = (2\hbar^2)^{-1}(e^2Q^2/12)(1 - S^2)(1 - S)\left\{\sum[(\delta V_{xz})_i]^2 + \sum[(\delta V_{yz})_i]^2\right\}$$
$$\times A^{-1}\exp(\Delta U/kT). \qquad (7)$$

Here, W_{1fl} denotes the contribution to W_1 caused by the 180° flips or reorientations of the NO_2 groups, $(\delta V_{xz})_i$ and $(\delta V_{yz})_i$ are changes in V_{xz} and V_{yz} at a ^{23}Na site caused by a reorientation of the ith NO_2 group, and the summation extends over all NO_2 groups. In deriving (7), it has been assumed that $\omega^2 \ll (w_{12} + w_{21})^2$, i.e. that the correlation time of the reorientations is short, as found by Bonera *et al* (1970). It is evident from (7) that the temperature dependence of W_{1fl} is essentially governed by the temperature dependence of the order parameter and of the exponential term.

A similar derivation to the above shows that W_{2fl}, the contribution to W_2 caused by random 180° reorientations of the NO_2 groups, is given by (7) with

$$\left\{\sum[(\delta V_{xz})_i]^2 + \sum[(\delta V_{yz})_i]^2\right\}$$

replaced by

$$\left\{ \sum[(\delta V_{xx})_i]^2 + \sum[(\delta V_{xy})_i]^2 + \sum(\delta V_{xx}\delta V_{zz})_i + \left(\sum[(\delta V_{zz})_i]^2/4 \right) \right\}$$

when the magnetic field is parallel to the *b* axis.

For other orientations of the magnetic field and for spin systems situated at sites with a different point group symmetry, W_{1fl} and W_{2fl} are given by equations of the same form as (7), but with different derivatives in the curly brackets. These can be evaluated or, equivalently, expressed in terms of M-tensor components, using the method of Snyder and Hughes (1971).

3. Comparison of the temperature dependence of W_{1B} with theory

Before comparing the W_{sat} data in figure 2 with (7), it is necessary to remove any magnetic relaxation and the quadrupole relaxation caused by phonons (Van Kranen-donk 1954, Van Kranendonk and Walker 1968), which we denote by W_{1ph}. Since it is difficult to measure W_{1ph} directly in NaNO$_2$, we estimate it by comparison with other similar sodium salts. For ^{23}Na in NaNO$_3$, W_{1ph} at room temperature varies between 0.068 and 0.086 s^{-1} (Spencer and Hughes 1978), depending upon the orientation of the magnetic field relative to the crystal. For ^{23}Na in NaCl, W_{1ph}, averaged over all orientations (Snyder and Hughes 1971), is 0.035 s^{-1} at room temperature. For ^{23}Na in NaClO$_3$, the results of Hovi and Punkkinen (1966) imply that W_{1ph} at room temperature is about 0.049 s^{-1}, when the magnetic field is parallel to a fourfold symmetry axis. For ^{23}Na in NaNO$_2$, a point charge calculation (Hughes and Spencer 1982) indicates that W_{1ph} varies markedly with the orientation of the magnetic field, and is a minimum when the magnetic field is parallel to the *b* axis. We therefore estimate that W_{1ph} of ^{23}Na in NaNO$_2$ is approximately 0.036 s^{-1} at room temperature for that orientation. Since the phonon relaxation rate is proportional to the square of the absolute temperature T except at very low temperatures (Van Kranendonk 1954, Van Kranendonk and Walker 1968), we shall take W_{1ph} to be $(4 \times 10^{-7}T^2)$ s^{-1}, with estimated (68% confidence) error limits of about ±30%. Since the relaxation caused by phonons and by reorienting NO$_2$ groups should be independent of each other, at least to first order, we shall assume that the phonon contribution can be removed by subtracting calculated values of W_{1ph} from W_{sat} at each temperature.

The increase in W_{sat} observed below 150 K was attributed by Towta and Hughes (1990) to a magnetic interaction. A double-resonance experiment, which will be described elsewhere (Hughes 1992), has shown that the relaxation seems to be entirely magnetic at 130 K. A logarithmic plot of $(W_{sat} - W_{1ph})$ versus $1/T$ is shown in figure 3. Since the graph is quite linear below 150 K, it seems that the remaining relaxation below this temperature can be entirely attributed to a magnetic interaction which gives rise to a T$_1$ minimum centred at a much lower temperature. The slope of the line corresponds to an activation energy of 0.057 eV, with error limits of about ±0.01 eV because of the uncertainty in W_{1ph}.

The deviation from linear behaviour above 150 K in figure 3 is evidently caused by reorientations of the NO$_2$ groups. For simplicity, we shall assume that the magnetic contribution to $(W_{sat} - W_{1ph})$, which we denote by W_{mag}, is given by the extrapolation represented by the broken line in the figure and that its effect can be removed
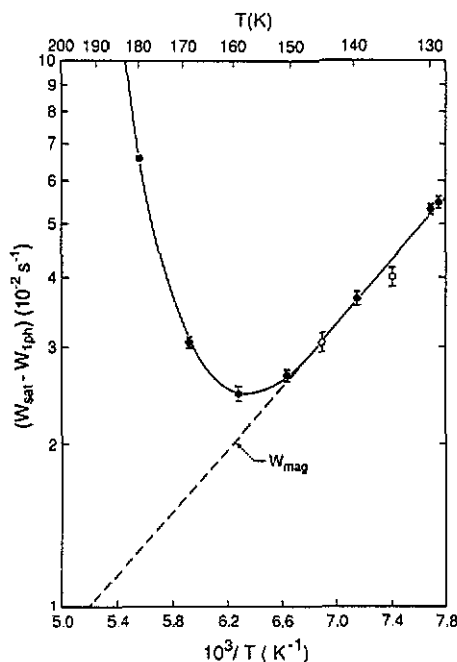
Figure 3. Logarithmic plot of $(W_{sat} - W_{1ph})$ against the reciprocal of the absolute temperature. The curve is drawn through the data points. The broken line represents W_{mag} alone. The full (open) circles refer to crystal A (B) (Hughes and Spencer 1982).

by simple subtraction. Values of $W_{1fl} = W_{sat} - W_{1ph} - W_{mag}$ obtained in this way are shown in figure 2 and will now be compared with the theoretical prediction, as given by (7).

The order parameter, S, was evaluated at various temperatures using the relation

$$S = \tanh[(T_C/T)(S + S^3 \Delta)] \tag{8}$$

derived by Yamada *et al* (1963). In (8), T_C is the critical temperature (437 K) and Δ is a parameter which was found to be 0.39 from studies of x-ray diffraction (Yamada *et al* 1963), and the temperature dependences of the dielectric susceptibility (Gesi 1965) and of the ^{23}Na quadrupole splitting (Betsuyaku 1969).

According to (7), $\ln[(W_{sat} - W_{1ph} - W_{mag})/(1 - S)(1 - S^2)]$ should vary linearly with $1/T$. As can be seen in figure 4, the linear relation is obeyed very closely between 230 K and T_C, and, from the fit, one obtains an activation energy ΔU of (0.209 ± 0.005) eV or $(5.55 \pm 0.13)kT_C$, where the error limits are mainly governed by the uncertainty in W_{1ph}. Our value of ΔU is in excellent agreement with the $5.42kT_C$, found by Hatta (1970) from dielectric measurements.

It can be seen from (7) that the intercept of the linear fit to the data should equal

$$(2\hbar^2)^{-1}(e^2 Q^2/12)\left\{ \sum[(\delta V_{xz})_i]^2 + \sum[(\delta V_{yz})_i]^2 \right\} A^{-1}.$$

The point charge calculations of Hughes and Spencer (1982) indicate that

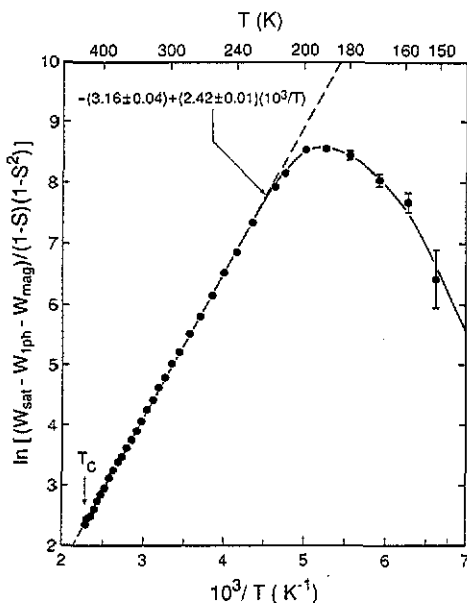$$\left\{ \sum[(\delta V_{xz})_i]^2 + \sum[(\delta V_{yz})_i]^2 \right\}$$

Figure 4. $\ln[(W_{sat} - W_{1ph} - W_{mag})/(1 - S^2)(1 - S)]$ plotted against the reciprocal of the absolute temperature. The straight line represents a least squares fit of the data between 230 K and T_C to equation (7). The error bars are associated with a $\pm 30\%$ uncertainty in the values of W_{1ph}.

caused by random 180° reorientations of NO_2 groups, is roughly 2.3×10^{41} V^2 m^{-4} at each ^{23}Na nucleus, when the antishielding factor of sodium is assumed to be 4.53 (Das and Bersohn 1956) and the charges on the nitrogen and oxygen sites are taken to be $+0.124e$ and $-0.562e$, respectively. From the intercept of the linear fit in figure 4 and by taking the quadrupole moment of ^{23}Na to be e $(0.087 \times 10^{-28}$ $m^2)$ (Bernheim and Gutowsky 1960), the frequency factor A is found to be 4×10^{13} s^{-1}. Since the NO_2 groups flip by rotation about the c axis (Shibuya *et al* 1970, Ehrhardt and Michel 1981), A should be of the same order of magnitude as the librational frequency of the NO_2 groups about the c axis, namely 7.1×10^{12} Hz, found by Sakurai *et al* (1970). The agreement is satisfactory in view of the uncertainties involved in the calculations, especially since the neglect by Hughes and Spencer (1982) of any 'relaxation' of the lattice when NO_2 groups flip, will almost certainly lead to an overestimate of

$$\left\{ \sum [(\delta V_{xz})_i]^2 + \sum [(\delta V yz)_i]^2 \right\}.$$

We therefore deduce that the NO_2 groups are executing essentially random 180° reorientations between 230 K and T_C.

The progressive departure from linearity in figure 4, which becomes very pronounced below 200 K, may well be associated with anomalies in the thermal expansion coefficient (Gesi 1969) and in the NQR frequency of ^{14}N (Singh and Singh 1974), observed between 200 K and 170 K, which have led to suggestions that there may be a phase transition in this temperature range.

The departure from linearity in figure 4 is much too large to be attributed to uncertainty in W_{1ph} or to an inappropriate value for Δ in equation (8). Nor, as

will be discussed later, does it seem to be caused by a serious breakdown in the validity of equation (8). A more likely explanation is that, as the temperature is reduced below 230 K (at which temperature the order parameter is 0.989 and 0.54% of the NO_2 groups are disordered at any one time), the disordered NO_2 groups are increasingly confined to fixed sites quite far apart from each other. The relaxation of the ^{23}Na nuclei in this temperature range is therefore inhomogeneous and occurs by spin diffusion (a magnetic mechanism) to ^{23}Na nuclei which are relaxing rapidly because of their proximity to the reorienting NO_2 groups. We cannot totally rule out paramagnetic centres as the cause of the low-temperature relaxation. However, that is unlikely to be the case since essentially the same relaxation behaviour was observed in two different crystals, as can be seen in figure 3. Moreover, the observed relaxation rates are much larger than would be expected from the concentration of paramagnetic centres indicated by spectroscopic analysis and an ESR study (Towta and Hughes 1990).

In the absence of a theoretical treatment of the spin diffusion of quadrupolar nuclei in a non-cubic environment, we shall estimate the density of relaxation centres by using the relation

$$T_1^{-1} = 4\pi N b D \qquad (9)$$

(Abragam 1961), which was derived for the relaxation of spin-1/2 nuclei by paramagnetic centres. In (9), N is the number of centres per unit volume, D is the spin diffusion coefficient and b is the temperature dependent scattering amplitude of a single relaxation centre, which is equal to $0.7(C/D)^{1/4}$, where $C = r^6/T_1'$, T_1' being the relaxation time, due to the direct quadrupole interaction, of nuclei situated at a distance r from a centre.

For the ^{23}Na satellites in $NaNO_2$, D is estimated to be 1.1×10^{-17} m^2 s^{-1} from the dipolar second moment of $0.27 G^2$. Assuming that the relaxation centres are individual reorienting NO_2 groups, b is found to be 2.7×10^{-2} nm at 130 K, using the approach given by Abragam (1961). By substituting this value and the corresponding $T_1^{-1} = 2W_{\mathrm{mag}} = 0.106$ s^{-1} in equation (9), N is found to be $\sim 3 \times 10^{25}$ m^{-3}. Such a density corresponds to about one relaxation centre for every seven hundred NO_2 groups and an average separation between centres of roughly 3 nm. Instead of being individual reorienting NO_2 groups, the relaxation centres may be small aggregates of reorienting NO_2 groups, perhaps situated adjacent to sodium vacancies, which would occur if there was a small departure from strict stoichiometry.

If the essential features of the above interpretation are correct and N is independent of temperature below 150 K, the temperature dependence of W_{mag} arises from the temperature dependence of b, which, in turn, is governed by the temperature dependence of the correlation time, τ_c, of the fluctuations associated with the reorienting NO_2 groups. From the relations $\omega_{12} = A\exp(-\Delta U/kT)$ and $\omega_{21}/\omega_{12} = (1+S)/(1-S)$, it follows that the correlation time is given by

$$\tau_c = (\omega_{12} + \omega_{21})^{-1} = (2A)^{-1}(1-S)\exp(\Delta U/kT). \qquad (10)$$

By substituting known values of A, ΔU and S (obtained from equation (8)) in equation (10), the correlation frequency, τ_c^{-1}, of the fluctuations is found to be 9.1×10^7 s^{-1}, corresponding to the angular frequency of the $\Delta m = \pm 1$ transitions in the work of Towta and Hughes (1990), at a temperature of 107 K. $W_{1\mathrm{A}}$ should

therefore exhibit a maximum at roughly that temperature; such a situation is not inconsistent with the data in figure 2 and with the ^{14}N relaxation data of Abbe *et al* (1972). It thus appears that (8) is a reasonable approximation at low temperatures, so that the deviation from linearity in figure 4 must be attributed to the

$$\left\{ \sum [(\delta V_{xz})_i]^2 + \sum [(\delta V_{yz})_i]^2 \right\}$$

term in equation (7), as assumed earlier.

Equation (10) enables an independent estimate of the activation energy associated with W_{mag} to be made. By substituting calculated values of S at 130 K and 150 K in equation (10), it is found that the activation energy associated with τ_c is 0.104 eV. Since C is proportional to τ_c in the short-correlation time limit (Abragam 1961), and b is proportional to $C^{1/4}$, the activation energy associated with W_{mag} should be 0.104/4 or 0.026 eV. This is substantially smaller than the value (0.057 ± 0.01) eV found from the data in figure 3. Part of the discrepancy is probably due to the fact that W_{1ph} falls off faster than T^2 at low temperatures. The remaining discrepancy may be due to assumptions made in deriving equation (9).

We conclude by noting that our method of analysis using (7) is not restricted to $NaNO_2$, but should be applicable to other materials that undergo a similar order–disorder transition.

Acknowledgments

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