Orientation Dependence of the Nuclear Quadrupole Spin-lattice Relaxation of ^{23}Na in NaNO$_2$ *

S. Towta and D. G. Hughes

Department of Physics, University of Alberta, Edmonton, Alberta, Canada

Z. Naturforsch. **41 a,** 370–373 (1986); received July 23, 1985

The nuclear quadrupole relaxation probability W_1 of ^{23}Na in a single crystal of NaNO$_2$ has been studied by applying a selective 180° pulse to the centre line and monitoring the exponential approach to equilibrium of the satellites. The orientation dependence of W_1 at 170 K is similar in form to that at 298 K, indicating that the lattice motions responsible for the relaxation are similar at both temperatures. Ratios of the M-tensor components obtained by fitting the W_1 data have been compared with the results of various point charge calculations. It indicates that the relaxation is primarily caused by interaction with the four nearest oxygen atoms and confirms that the NO$_2$ groups oscillate and reorient primarily about the c axis.

1. Introduction

The first detailed study of the quadrupole relaxation of ^{23}Na in NaNO$_2$ was carried out by Bonera, Borsa and Rigamonti [1] who measured the temperature dependence of $T_1^{-1} = (2/5)(W_1 + 4W_2)$ [2], where W_1 and W_2 are the probabilities of the $\Delta m = \pm 1$ and ± 2 transitions respectively. They observed a critical point anomaly in $T_1{}^{-1}$ at the ferroelectric transition temperature of 436 K and a sudden unexplained decrease in T_1^{-1} between 220 K and 170 K. In many subsequent investigations of the critical point anomaly, the orientation dependence of W_1 and W_2 was not properly taken into account. To extract maximum information from quadrupole relaxation data requires the determination of all the independent components of the fourth-rank M-tensor [3]. Their temperature dependence should be of interest since there is no a priori reason why they should scale identically with temperature, and, indeed, we have shown [4] that the ratios of the M-tensor components of ^{23}Na in NaNO$_2$ change significantly near the ferroelectric transition.

We have therefore begun an investigation of the orientation dependence of the quadrupole relaxation of ^{23}Na in NaNO$_2$. In this paper, we describe our method of determining the M-tensor components, and we present some results obtained at room temperature and 170 K.

2. Theoretical Orientation Dependence of W_1 for ^{23}Na in NaNO$_2$

The unit cell of NaNO$_2$, shown in Fig. 1, contains two identical sodium sites with mm2 point group symmetry. For homogeneous spin-lattice relaxation, the theoretical orientation dependence of W_1 for ^{23}Na is given by [3, 4]

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

Here, θ and φ are the polar and azimuthal angles of the magnetic field relative to a coordinate system whose x, y and z axes coincide with the c, a and b axes respectively of the unit cell (see Figure 1). The

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Reprint requests to Dr. D. G. Hughes, Department of Physics, University of Alberta, Edmonton, Alberta T6G 2J1, Canada.

* Presented at the VIIIth International Symposium on Nuclear Quadrupole Resonance Spectroscopy, Darmstadt, July 22–26, 1985.

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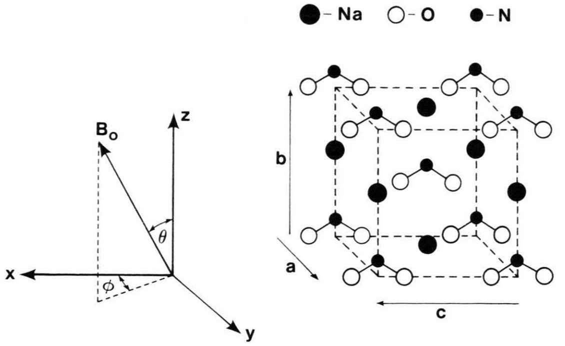

Fig. 1. Unit cell of $NaNO_2$ and coordinate system used in this work.

M-tensor components are defined classically by [3]

$$M_{\alpha\beta\alpha'\beta'} = \hbar^{-2} \int_{-\infty}^{+\infty} \overline{V_{\alpha\beta}(t+\tau)\, V_{\alpha'\beta'}(t)} \cdot \exp\{-i(E_{m+1}-E_m)\,\tau/\hbar\}\, \mathrm{d}\tau, \quad (2)$$

where $\alpha, \beta, \alpha', \beta' = 1, 2, 3 = x, y, z$ and $V_{\alpha\beta}$ is $\partial^2 V/\partial x_\alpha\, \partial x_\beta$.

3. Measurement of W_1

The quadrupolar spin-lattice relaxation of a system of $I = 3/2$ nuclei which experience quadrupole splitting, in general involves three relaxation rates $2\,W_1$, $2\,W_2$ and $2(W_1 + W_2)$ [2]. However, if the spin system is perturbed by selective excitation of the centre line alone, it can be shown that each satellite should relax exponentially with a rate $2\,W_1$. Also, if one of the satellites is selectively excited, the centre line should relax exponentially with the same rate $2\,W_1$. These experiments for determining W_1 are to be preferred, since it is difficult to extract accurate values of relaxation rates from multi-exponential decays. (It is not necessary to measure both W_1 and W_2 to determine the M-tensor components, provided the correlation time of the fluctuations is short [3].)

In a preliminary study, we selectively saturated the centre line of ^{23}Na in a single crystal of $NaNO_2$ with a comb of weak 90° pulses, and monitored the subsequent approach to equilibrium of one of the satellites with a weak 90° pulse. Similar experiments were performed in which a satellite was saturated and the centre line was monitored. In both types of experiments, the relaxation was essentially exponential. Also, the rates were the same at crystal orientations where W_2/W_1 was $\cong 1$. However, they differed by about three percent at orientations where W_2/W_1 was approximately 0.5 or 2, and the discrepancy was of opposite sign in the two cases. We attribute this to the fact that our excitation pulses were not sufficiently selective. For the "symmetrical" case where a pulse applied to the centre line partially excites the satellites, it can be shown that the satellites should still approach equilibrium exponentially with a rate $2\,W_1$. The most accurate values of W_1 should therefore be obtained from experiments in which the centre line is excited and one of the satellites is observed. Data reported in this paper were obtained in this way. However, for improved accuracy, an inversion-recovery method was used in which a weak 180° pulse, instead of a comb of 90° pulses, was applied to the centre line. At all crystal orientations, the magnetic field was adjusted so that the frequency of the satellite being monitored was 14.5 MHz.

4. Results and Discussion

Values of W_1 measured at room temperature (298 K) are shown in Figure 2. The curves, which represent a least squares fit to (1), are in very good agreement with the data. The M-tensor components obtained from the fit are listed in Table 1, normalized with respect to M_{1111}. (Absolute values can be found from the ratios, given that $e^2 Q^2 M_{1111}/96 = (0.242 \pm 0.002)\ \mathrm{s}^{-1}$.) Also shown in Table 1 are corresponding values obtained earlier in our laboratory with the same crystal but using a very different steady-state enhancement technique [4].

Measurements at 170 K, i.e. below the low temperature anomaly, showed that the approach of the satellites to equilibrium was quite exponential at all crystal orientations. This showed that magnetic relaxation effects were small at that temperature so that the measured relaxation rate could be taken to be $2\,W_1$ [5]. (Our earlier work [4] showed that magnetic relaxation was negligible in the crystal at room temperature.) Values of W_1 at 170 K are shown in Fig. 3, together with curves representing the best fit of the data to (1). The corresponding M-tensor components, normalized with respect to M_{1111} (where $e^2 Q^2 M_{1111}/96 = (0.0109 \pm 0.0005)\ \mathrm{s}^{-1}$),

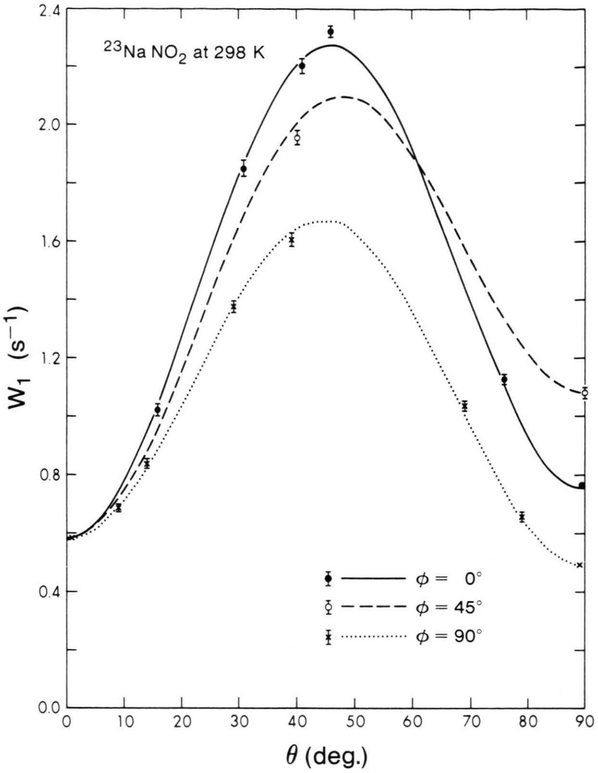

Fig. 2. Orientation dependence of W_1 for ^{23}Na in NaNO$_2$ at 298 K. The curves show the best fit of the data to (1).

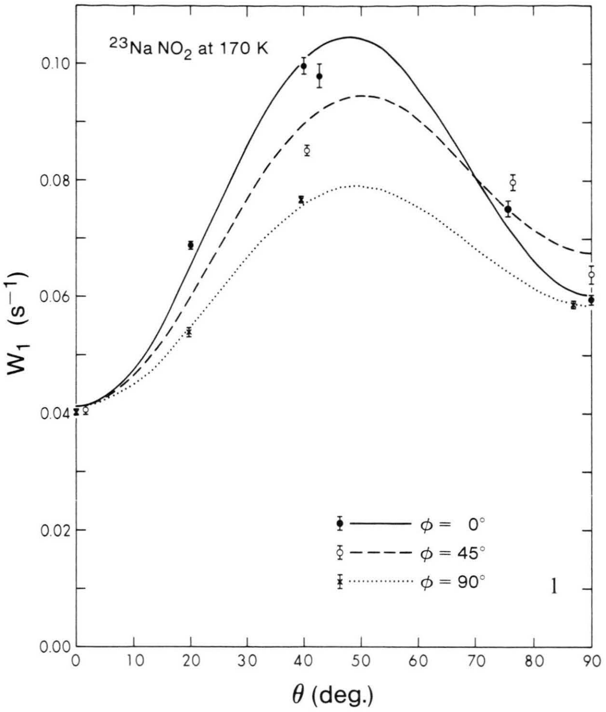

Fig. 3. Orientation dependence of W_1 for ^{23}Na in NaNO$_2$ at 170 K. The curves show the best fit of the data to (1).

are listed in Table 1. It is not yet known why the agreement between experiment and theory is so much poorer at 170 K than at 298 K, though we have evidence that the low temperature relaxation rates may depend on the previous treatment of the sample, as reported elsewhere [6]. Nevertheless, it is clear that the orientation dependence of W_1 at 170 K is qualitatively similar to that at 298 K, indicating that the low temperature anomaly is not caused by two very different relaxation mechanisms as we suggested earlier [4]. It can also be inferred that the relaxation at 170 K does not occur pre-

Table 1. Experimental and theoretical ratios of the M-tensor components. a) Isotropic vibration of Na only [4]. – b) Reorienting NO$_2$ groups only [4]. – c) Small angular oscillation of NO$_2$ groups about the a axis only. – d) Small angular oscillation of NO$_2$ groups about the c axis only. – e) Combination of a small angular oscillation of NO$_2$ groups about the c axis and isotropic vibration of Na ions as described in the text.

Ratios	Theoretical					Experimental		
						170 K	298 K	
	a	b	*c*	*d*	*e*	this work	this work	Ref. [4]
M_{1133}/M_{1111}	– 1.27	– 3.28	– 2.31	– 0.67	– 0.85	– 0.71 ± 0.06	– 0.92 ± 0.01	– 0.89 ± 0.03
M_{3333}/M_{1111}	3.68	10.85	5.32	0.45	1.00	1.01 ± 0.02	1.35 ± 0.02	1.50 ± 0.01
M_{2323}/M_{1111}	1.75	4.64	6.30	0.12	0.30	0.22 ± 0.01	0.08 ± 0.01	0.08 ± 0.01
M_{3131}/M_{1111}	0.91	3.97	30.65	0.27	0.36	0.24 ± 0.01	0.22 ± 0.01	0.28 ± 0.01
M_{1212}/M_{1111}	1.15	0.18	3.86	0.36	0.32	0.45 ± 0.01	0.17 ± 0.01	0.20 ± 0.01

dominantly by spin diffusion to rapidly-relaxing nuclei in domain walls for example, since, in that case, the relaxation rate should be a maximum at the orientation $\theta = 90°$ and $\varphi = 90°$ where the dipolar interaction is strongest.

Table 1 shows ratios of the M-tensor components calculated for various types of lattice motions using a point charge model (cf. [4]). For all cases except reorientation of the NO_2 groups, fluctuations in $V_{\alpha\beta}$ were assumed to be linear in the atomic displacements. The calculations took into account the seven nearest neighbours. Agreement between experiment and theory is generally poor, except for the model where it is assumed that the NO_2 groups oscillate (independently of one another) about the c axis, and only the four nearest neighbour oxygen atoms contribute significantly to $V_{\alpha\beta}$. (When the two next-nearest oxygen atoms were also taken into account, M_{2323}/M_{1111} was found to be 1.00, much larger than the observed value.) Our results therefore support the conclusion of others [7] that polarization reversal occurs by reorientation about the c axis, rather than about the a axis as indicated by IR absorption and Raman experiments [8, 9]. Also, our tentative finding that the dominant contribution comes from the four nearest oxygen atoms, presumably indicates that the main contribution to the fluctuating electric field gradient is caused by overlap of the electron clouds of the Na ions and these four atoms. As can be seen in the last column of Table 1, even better agreement with experiment can be obtained by combining two models and supposing that the sodium ions vibrate isotropically with a rms amplitude which is 35% larger than the amplitude of the motion of the oxygen atoms associated with the rotation of the NO_2 groups about the c axis.

Acknowledgements

The authors wish to acknowledge financial support provided by the Natural Sciences and Engineering Research Council of Canada.

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