Temperature Dependence of ^{14}N NQR and Phase Transitions in KNO_2 Powder *

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The temperature dependence of ^{14}N NQR, measured at 77 to 300 K, is in better agreement with the model proposed by Blinc et al. than the Bayer theory. The nuclear quadrupole coupling constant and asymmetry parameter show a discontinuity at about 160 K and 230 K, respectively. The linewidths are broadened at these temperatures up to 22 kHz and 18 kHz, respectively. These results indicate that KNO_2 undergoes phase transitions at these two temperatures.

Introduction

^{14}N NQR in KNO_2 at 4.2 to 50 K has been studied by Matukhin et al. [1]. At room temperature KNO_2 is rhombohedral [2, 3] and above 320 K it is cubic (Fm3m) with rotational disorder of the nitrite group [2, 3]. More phase transitions of KNO_2 are reported [4, 5]. Parry et al. [6] and Rao et al. [7] reported that the room temperature phase is ferroelectric and the phase above 320 K is paraelectric. According to other authors, however, the room temperature phase is not ferroelectric [8, 9]. A big dielectric anomaly has been found at 230 K [9]. Seven phases of KNO_2 have been identified by Raman spectroscopy using various combinations of temperature and pressure [10]. Adams et al. [11] have found nine phases of KNO_2, using Raman spectroscopy. Some phases and corresponding crystal structures are listed in Table 1.

In this work, the temperature dependence of the ^{14}N NQR line positions and linewidths were measured in the temperature range from 77 to 300 K for the first time.

Table 1. Crystallographic data of some phases of KNO_2.

Phase	Temperature (K)	Structure	Symmetry
I	above 320 K	cubic	Fm3m
II	320–260 K	rhombohedral	R3m
III	260–230 K	monoclinic	$P2_1/c$
IV	below 230 K	unknown	

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I. Experimental

The employed KNO_2 powder with 97% purity was commercially available (Jassen Chemica GEEL, Belgium). This powder was packed in a pyrex tube and sealed. The NQR measurements were made with an FET-adopted Robinson type spectrometer [12]. The temperature of the sample was measured with an alumel-chromel thermocouple, the reference junction being kept at the boiling point of liquid nitrogen at the ambient pressure.

II. Results and Discussion

The ^{14}N ($I = 1$) NQR spectrum consists of two resonance lines (ν_+ and ν_-) [13]:

$$\nu^{\pm} = \frac{3\,e^2\,qQ}{4\,h}\left(1 \pm \frac{\eta}{3}\right), \tag{1}$$

where $e^2\,qQ/h$ and η are the quadrupole coupling constant and the asymmetry parameter, respectively. Figure 1 shows the temperature dependence of the two ^{14}N NQR lines in KNO_2, where the data at 4.2 K stand for the values reported by Matukhin et al. [1]. According to Bayer [14], the temperature dependence of NQR lines may be approximated by a simple harmonic motion of a molecule around an equilibrium position with the torsional oscillation frequency. Both the amplitude and the number of vibrational modes of the molecule increase with temperature, resulting in a reduction of the time averaged electric field gradient (efg). Considering only one vibrational mode around the O–O axis of NO_2^-, one may express the change in

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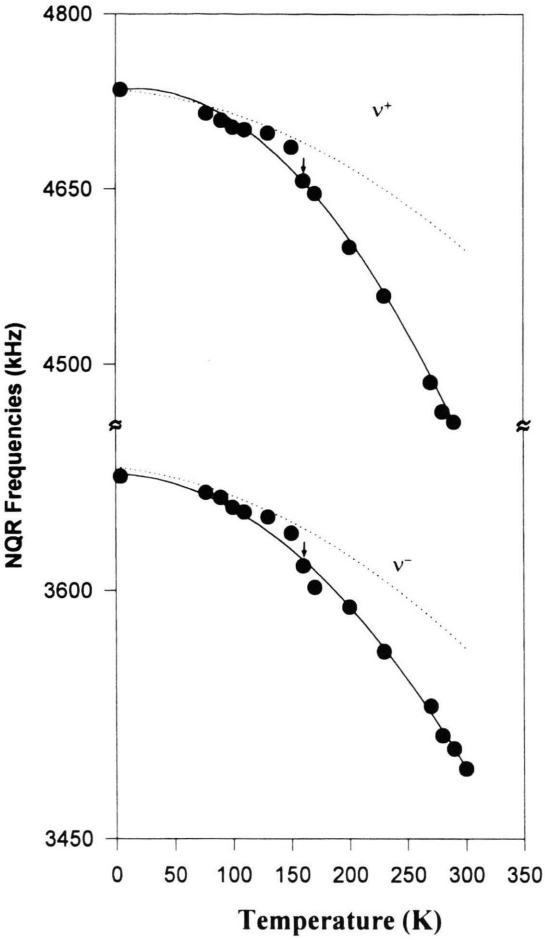

Fig. 1. Temperature dependence of the two ^{14}N NQR lines (ν^+ and ν^-) in KNO_2; the dotted line stands for the result calculated with Bayer's theory and the solid line with the model proposed by Blinc et al. The arrows indicate the phase transition temperature 160 K.

frequencies due to temperature by

$$\nu^{\pm} = \nu_B^{\pm}|_0 \left[1 - \frac{3\hbar}{2A\omega}\left\{\frac{1}{2} + (\exp(\hbar\omega/kT) - 1)^{-1}\right\}\right], \quad (2)$$

where $\nu_B^{\pm}|_0$ is the NQR frequency at 0 K, A is the moment of inertia of NO_2^- around the O–O axis, and ω is the torsional frequency (for KNO_2; $A = 29.4 \times 10^{-40}$ g · cm^2, $\omega = 120$ cm^{-1} [11]). As can be seen from Fig. 1, Bayer's theory (the dotted line) with parameters of $\nu_B^{\pm}|_0 = 4799$ and $\nu_B^{-}|_0 = 3718$ kHz, can not explain the experimental data at higher temperatures. In order to reduce the difference between the experimental data and Bayer's theory, we have introduced an order parameter p ($0 \le p \le 1$), being the reduced spontaneous polarization. The spontaneous polarization (P_s) of KNO_2 at 298 K is known to be 2.8 μC/cm^2 [15], but its temperature dependence is not known. We assumed that it might be a function of $P_s(T) = 5.44 \times (1 - T/320)^{1/5}$, where the 1/5-power was taken from that in $NaNO_2$ [16]. Then the temperature dependence of ν^+ and ν^- in KNO_2, like in case of $NaNO_2$, can be approximated by the model proposed by Blinc et al. [17]:

$$\begin{aligned} \nu^{\pm}|_{\text{exp}} &= \nu^{\pm}|_{\text{Bayer}} + \nu^{\pm}|_{\text{pol}}, \\ \nu^{\pm}|_{\text{Bayer}} &= 2D^{\pm}[\exp(\hbar\omega/kT) - 1]^{-1}, \\ \nu^{\pm}|_{\text{pol}} &= \nu^{\pm}|_0 + \alpha p^2 + \beta p^4, \end{aligned} \quad (3)$$

where the Bayer-term is due to the torsional vibration of NO_2^- around the axis of the O–O bond in KNO_2, whereas the contribution $\nu^{\pm}|_{\text{pol}}$ arises from the ferroelectricity. $\nu^{\pm}|_{\text{pol}}$ is an even function of $p(=P_s(T)/P_s(0))$, $\nu^{\pm}|_0$ is the frequency at 0 K, and $\alpha^{\pm}$, $\beta^{\pm}$ and $D^{\pm}$ are constants. In Fig. 1, the solid line denotes the best fit of (3) to the experimental data with following parameters, all in units of kHz; for the $\nu^{\pm}$ line, $\nu^+|_0 = 4636$, $D^+ = -130.4$, $\alpha^+ = 17.3$ and $\beta^+ = -0.5$, and for the ν^- line, $\nu^-|_0 = 3632$, $D^- = -74.6$, $\alpha^- = 7.2$ and $\beta^- = -0.2$. Figure 1 shows that the Blinc model explains the experimental results better than the Bayer theory in the high temperature range.

The NQR frequencies and P_s values of KNO_2 and $NaNO_2$ [17–22] at room temperature and 77 K are listed in Table 2. The fitting parameters of (3) for KNO_2 are compared with those for $NaNO_2$ in Table 3. The coefficients $\alpha^{\pm}$ and $\beta^{\pm}$ in (3) are related to the contribution of the spontaneous electric polarization, and the factor $D^{\pm}$ to the torsional vibration of NO_2^-. As can be seen from Table 3, the temperature dependence of ^{14}N NQR in KNO_2 is slightly different from that in $NaNO_2$. Incidentally, the absolute values of $\alpha^{\pm}$ and $\beta^{\pm}$ for KNO_2 are even smaller than those for $NaNO_2$. This implies that the changes in nuclear

Table 2. The ^{14}N NQR frequencies and P_s values of KNO_2 and $NaNO_2$ at two temperatures.

Material	ν^+ (kHz)	ν^- (kHz)	P_s (μC/cm^2)	Temp. (K)	Ref.
KNO_2	4432	3429	2.7	300	present work
	4735	3670	5.1	77	
$NaNO_2$	4645	3606	9.0	300	[16–18]
	4929	3757	12.0	77	

Table 3. Comparison of the fitting parameters in (3) for KNO_2 and $NaNO_2$.

NQR lines (kHz)	Parameters (kHz)	KNO_2	$NaNO_2$ [19]
ν^+	$\nu^+\|_0$	4636	4485
	α^+	17.3	215
	β^+	−0.5	−250
	D^+	−130.4	−140
ν^-	$\nu^-\|_0$	3632	–
	α^-	7.2	–
	β^-	−0.2	–
	D^-	−74.6	–

quadrupole interaction in KNO_2 due to the temperature arise mainly from the torsional motion of NO_2^- rather than the ferroelectricity.

The transition temperatures of this material were reported by many investigators [2–10]. With structural phase transformations, the resonance frequencies generally display abrupt changes at the transition temperature. These frequency-changes are due to the electron distribution within the molecules affected by intermolecular forces. This environmental alteration results from the change in crystal structure and causes a discontinuity of the resonance frequencies. The broadening effects are due to the fluctuation of the efg and dipole-dipole interaction at the phase transition.

For the magnetic dipole-dipole interaction, the dipolar broadening is given by [23]

$$\Delta\nu = \mu_{ne}\gamma/(r^3 \times 2\pi), \tag{4}$$

where γ is the magnetogyric ratio of the resonant nucleus, μ_{ne} is the magnetic moment of the neighboring nucleus, and r is the distance between the two nuclei. For the interaction between ^{14}N and ^{17}O nuclei in NO_2^- one has

$$\gamma = 0.193 \times 10^4, \quad \mu_{ne} = -1.89\,\mu_n \quad \text{and}$$
$$r = 2.07\ \text{Å} \quad \text{and then} \quad \Delta\nu = 0.3\ \text{kHz},$$

Thus, the major contribution is from the fluctuation at the resonant nucleus at the temperature of the phase transition. Also, this fact induces the order-disorder reorientation in NO_2^-, proposed as the transition mechanism for the crystal as shown in Figure 2. The linewidth shows a remarkable broadening at about 160 K and 230 K, respectively, as shown in Figure 3. The phase transition at 230 K agrees with previous Raman studies [3, 24], but the phase transition at 160 K has not been reported yet.

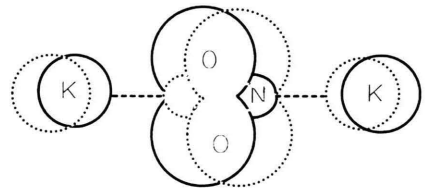

Fig. 2. Order-disorder arrangement of the molecular unit.

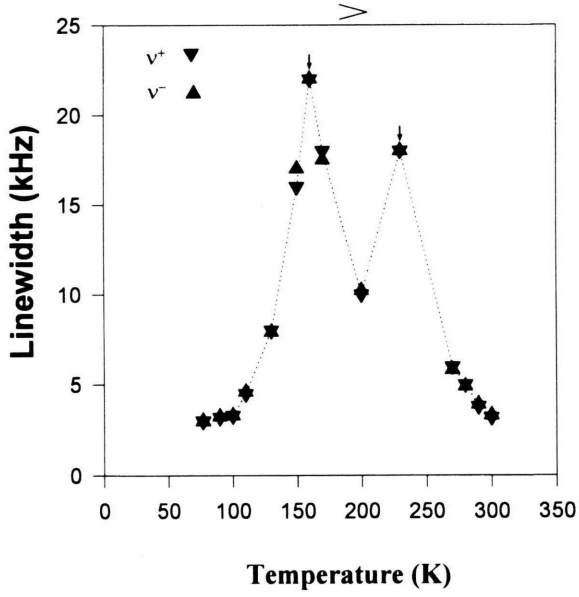

Fig. 3. The resonance linewidths (ν^+ and ν^-) vs. temperature.

III. Conclusion

The present work gives for the first time the temperature dependence of ^{14}N NQR in KNO_2 above 50 K. The two resonance lines (ν^+ and ν^-) decrease with increasing temperature. Though this material has two phase transitions in the range of 77 to 300 K, the temperature dependence of ^{14}N NQR in KNO_2 could be well explained by the Blinc model, assuming that $P_s(T) = 5.44(1 - T/320)^{1/5}$ and the torsional frequency ω is independent of temperature. This fact implies that the efg change at ^{14}N due to the temperature dominately originates from the torsional motion of NO_2^-.

Our experimental results indicate two phase transitions near 160 K and 230 K. These transitions induce

a considerable increase in inhomogeneity of the electric field gradient near the resonant nucleus, which causes the line broadening as observed. The phase transition near 160 K is newly observed in KNO_2.

Acknowledgement

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