Anomalous Temperature Dependence of Spin-lattice Relaxation Time of the ^{14}N-NQR Line in $NaNO_2$ *

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Z. Naturforsch. **45a**, 523–526 (1990); received September 11, 1989; in revised form November 6, 1989

The temperature dependence of the ^{14}N-NQR spin-lattice relaxation time T_1 of a powder sample of $NaNO_2$ prepared from saturated aqueous solution could be fitted by a monotonic curve. When this sample was annealed, two minima of the $T_1 - T$ curve appeared around 35 K and 77 K. The origin of this phenomenon is discussed.

1. Introduction

The temperature dependence of the spin-lattice relaxation time T_1 of the ^{14}N-NQR line of $NaNO_2$ was reported in two papers [1, 2]. There are three characteristic features: 1) a very narrow minimum at 35 K, 2) a broad minimum around 77 K, 3) a very rapid decrease above 140 K.

Among those, 3) is common to every sample but 1) and 2) depend on the sample preparation. Figure 1 shows the temperature dependence of T_1 observed for samples obtained by precipitation from aqueous solution (sample 1) and prepared by a type of Bridgman method (sample 2) [3]. The T_1 vs. T curve of sample 1 is monotonuous while that of sample 2 has two minima around 77 K and 35 K. When sample 1 was held under good vacuum at a high temperature below the melting point, its temperature dependence of T_1 became similar to that of sample 2. In this study, we observed the change of the recovery curve of the nuclear magnetization due to annealing.

2. Experimental

We prepared the powder sample 1 of $NaNO_2$ from ca. 1 kg of the starting material using the method 1 and dried it by evacuating ambient gas for more than a week at room temperature. Glass ampoule containing powder samples of about 15 g were evacuated at various temperatures below 270 °C for a few days and then sealed without breaking the vacuum.

We observed the magnetization recovery of the ^{14}N-NQR line (frequency 4.931 MHz) of the samples at 77 K using a pulsed NQR spectrometer. The temperature dependence of T_1 was measured between 28 K

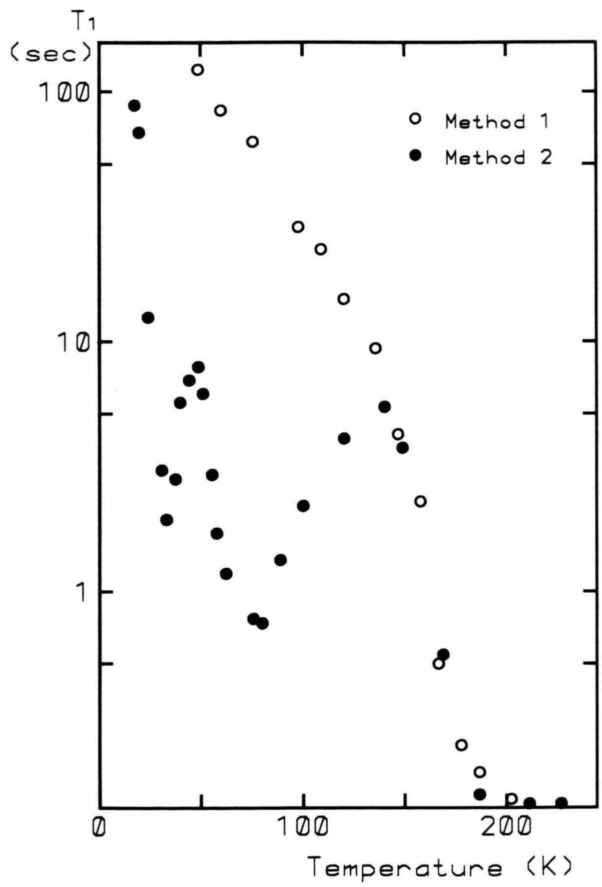

Fig. 1. Temperature dependences of T_1 of the ^{14}N-NQR line in $NaNO_2$. Method 1: Precipitating from aqueous solution. Method 2: Solidifying from the melt by the Bridgman method.

* Presented at the Xth International Symposium on Nuclear Quadrupole Resonance Spectroscopy, Takayama, Japan, August 22–26, 1989.

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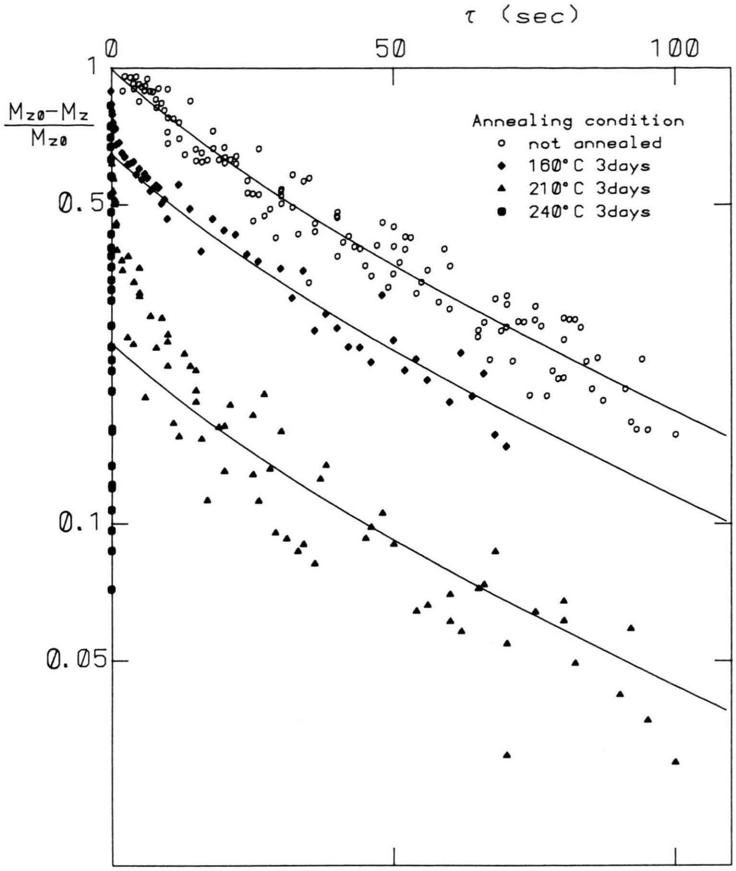

Fig. 2. Recovery curves of the nuclear magnetization of the ^{14}N-NQR line in $NaNO_2$ at 77 K.

and 120 K with a sample prepared by the method 1 where annealing was carried out at 240 °C.

3. Results and Discussion

The magnetization recovery curves of samples prepared by the method 1 and then annealed are shown in Figure 2. The recovery curve of the starting material was least squares fitted by the equation

$$f(t) = 0.325\, e^{-t/20} + 0.675\, e^{-t/74}. \quad (1)$$

The effect of annealing is characterized by the appearance of a rapidly relaxing component in addition to the curve recorded for the starting material. We concluded that the relaxation behaviour of the unannealed part of the sample is common to all the samples. According to the time dependence of (1), we fitted the recovery curves of the annealed samples for the slow relaxing part using the least squares method. The solid lines in Fig. 2 are the best fitted curves. Figure 3 shows the annealing temperature versus the fraction of the slow relaxing component determined by the intercepts of these fitting with the ordinate, and Fig. 4 shows the heating duration versus the same fraction. They show that these values decrease as the annealing temperature and duration increase.

The lower curve in Fig. 5 shows the temperature dependence of the long time component T_1 of the powder sample annealed under vacuum for 3 days at 240 °C. This T_1 describes the relaxation due to the nitrogen nuclear spin system. In the figure, there is also shown the temperature dependence of T_1 observed on a single crystal of the sample 2 [3]. This crystal was yellow and transparent having the size of $15 \times 15 \times 25\ \mathrm{mm}^3$ and grown in an open glass container by use of the Bridgman method. In the temperature region below 100 K, T_1 of the annealed sample was shorter by one order of magnitude than that of the single crystal. But the two T_1 curves are closely similar

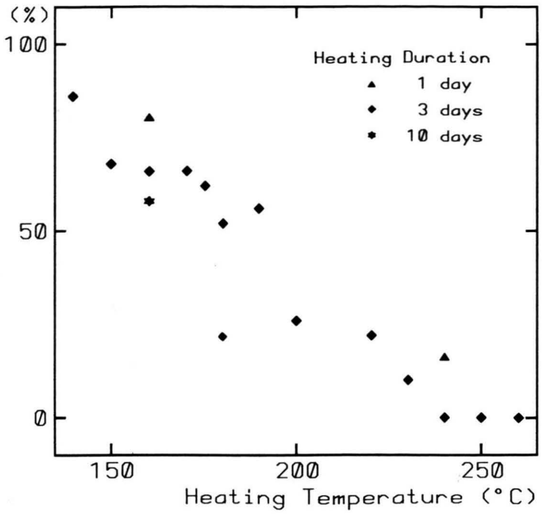

Fig. 3. Percentage of the slowly relaxing component versus annealing temperature.

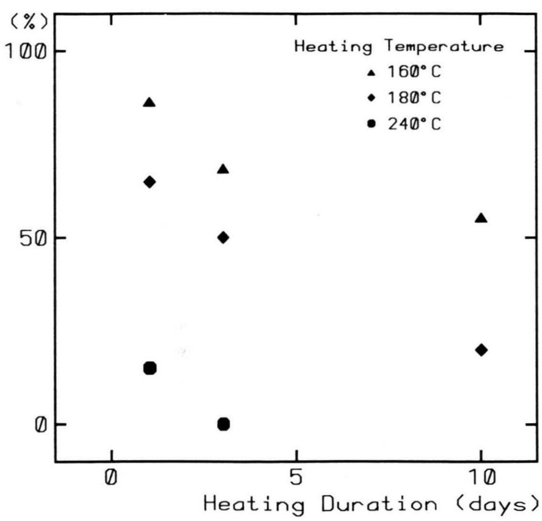

Fig. 4. Percentage of the slowly relaxing component versus annealing duration.

to one another. The temperatures of the two minima and the slopes around the minima are approximately the same. Therefore, also the mechanism which causes the two minima seems to be the same. Present investigation suggests that the mechanism giving rise to the rapid relaxation is the same for every sample.

The temperature dependence of T_1 of the starting material is expressed by a simple curve below 140 K

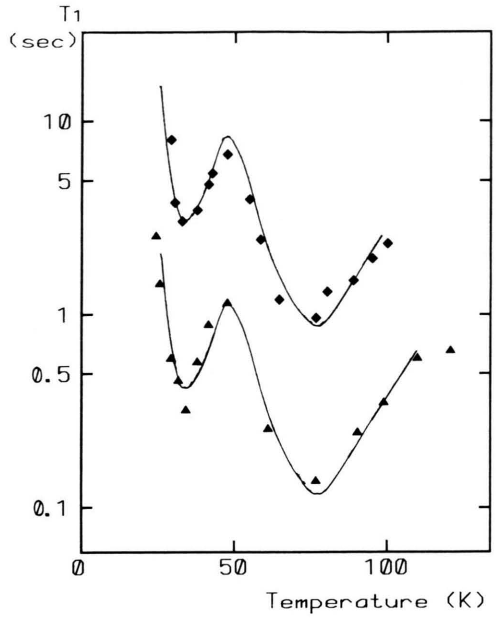

Fig. 5. Temperature dependences of T_1 of the ^{14}N-NQR line in $NaNO_2$. ◆: Single crystal prepared by method 2. ▲: Powder sample prepared as described in text. The annealing temperature was 240 °C. Solid lines in the figure are eye guides.

which decreases gradually as the temperature rises. This temperature dependence agreed well with that of sample 1 within the experimental errors. Sample 1 was sealed in a glass ampoule and consisted of about 20 colourless transparent crystals having an average size of $1 \times 1 \times 3$ mm^3. When either the powdered or crystalline samples are annealed at a certain temperature below the melting point, the temperature dependence of T_1 of each sample shows two minima. This result suggests that the intrinsic temperature dependence of T_1 for the nitrogen nuclear spin system in $NaNO_2$ is expressed by the curve shown in Fig. 1 for the sample 1 and that the relaxation mechanism which causes the two minima can be ascribed to some relaxation centers which are introduced by the annealing process. When the concentration of the relaxation centers increases as the annealing temperature rises, the volume fraction corresponding to the rapid relaxation mechanism increases and the overall relaxation time of the ^{14}N nuclear spin system should become short. This is seen in Figs. 3 and 4. The well annealed yellow sample clearly shows two minima in the T_1 versus T curve. Dietrich et al. [4] observed the ESR signal of isolated spins in$NaNO_2$. Unpaired electrons trapped at vacancies of the host lattice seem to be relaxation centers, and the fluctuation of the local magnetic field caused by the trapped paramagnetic spins seems to be the reason for the rapid relaxation of the ^{14}N nuclear-spin system in $NaNO_2$. However, identification of a lattice vacancy giving rise to the minima of the $T_1 - T$ curve still remains as a problem to be solved. The study of NMR of ^{23}Na in $NaNO_2$ is now under way, and detailed discussion about this origin will be reported soon.

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