Relaxation of Lattice Imperfections as Studied by Chlorine NQR *

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Z. Naturforsch. **41 a,** 374–377 (1986); revised version received October 12, 1985

The intensities, linewidths, and frequencies of ^{35}Cl NQR signals in 6-nitro-2,4-bis(trichloromethyl)-benzo[1,3]dioxine were found to vary remarkably depending on the crystallization methods and annealing. This finding was correlated to the degree of crystal disorder. For a sample obtained by slow crystallization from an ethanolic solution of the compound, the growth of the height of the NQR absorption signal due to annealing was measured as a function of the isothermal annealing time. A kinetic analysis of the growth process gave an activation energy of approx. 110 kJ/mole for the relaxation process of the imperfection dominating the NQR signals. The dimorphism of the compound and the magnitude of the activation energy suggest the presence of misoriented molecules accompanied by vacancies in the crystal lattice of the stable phase.

Introduction

Real crystals are more or less disordered. The frequency, intensity, and linewidth of nuclear quadrupole resonance (NQR) signals reflect this disorder. From this point of view, NQR spectra [1–7] and apparent spin-spin relaxation times T_2^* [8–13] of several compounds have been investigated. Generally, the more disordered the crystal the broader is the NQR signal.

In studying derivatives of chloral, we found that 6-nitro-2,4-bis(trichloromethyl)-benzo[1,3]dioxine is dimorphic and that the intensities, linewidths, and frequencies of the ^{35}Cl NQR signals in the stable phase depend markedly on the methods of crystallization. Furthermore, when a sample was annealed near the melting point, the intensity increased and the linewidth narrowed.

Changes in the intensity of NQR signals have been used in studies of phase transitions [14, 15]. In the present work we attempted to get information about the annealing process.

Experimental

6-nitro-2,4-bis(trichloromethyl)-benzo[1,3]dioxine (TMB-NO_2), was prepared by the method of Chattaway [16]. The sample was purified by recrystallizations from ethanol of spectroscopic grade. The last crystallization was carried out slowly so that small, transparent plates (ca. $1 \times 0.5 \times 0.1\ \mathrm{mm}^3$ in average) could be obtained. The solvent was removed in vacuo. The plates thus obtained will be called "SC samples" throughout this paper. For the NQR measurements, the samples were sealed in a glass tube.

The ^{35}Cl NQR spectra were observed by a frequency modulated, regenerative spectrometer [17, 18]. For the NQR measurements the sample tube was immersed in a liquid nitrogen bath. The first derivatives of the NQR absorption signals were recorded on strip charts through a lock-in amplifier (time constant 1 s). The peak-to-peak deviations of the derivatives (I) and maximum slope widths (w) were determined from the recorded spectra. The sensitivity of the spectrometer was frequently checked by measuring the ^{35}Cl NQR of a standard SC sample and was found to vary within ± 4%. The NQR frequencies were determined with an accuracy of ± 0.2 kHz. In some cases, the output voltage of the lock-in amplifier was fed into a microcomputer (HP-85) through an A/D converter and the numeric data were used for the line shape analysis.

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

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To study the polymorphism and to check the purity of the compound, thermal analysis was made by using a commercial differential scanning calorimeter, Rigaku DSC 8058.

Results

The thermal analysis evidenced that TMB-NO_2 is at least dimorphic with a metastable and a stable phase under normal pressure at room temperature. On rapid cooling of molten TMB-NO_2 a glass was obtained. On heating, after a glass transition at about 290 K, the metastable phase was formed at about 350 K and the stable phase at about 380 K. The dimorphism was confirmed by powder x-ray diffraction. The purity of the sample deduced from the DSC curve of fusion was better than 99.9%. The melting point of the stable phase was 417.3 K.

The stable phase of TMB-NO_2 (SC sample) gave six ^{35}Cl NQR lines (39.9493, 39.8556, 39.6018, 39.4431, 39.2917, and 38.7547 MHz) at 77 K. The signal to noise (S/N) ratio of the spectrum was fairly good. When the SC samples were annealed in a relatively high temperature region of $373 \leqq T_a/\mathrm{K} \leqq 403$ (T_a: annealing temperature), an increase in I accompanied by decrease in w was observed. To investigate the changes in I and w with the annealing time (t_a), the highest frequency signal (ν_1) was monitored at various t_a. Figure 1 shows these changes. At the beginning of the annealing ($t_a \leqq$ ca. 0.2 h), the changes in I and w were rather abrupt. At $T_a = 373$, 393, and 403 K, the same tendency was observed, although the higher T_a, the sooner the changes. When an SC sample was annealed at 403 K for a long time ($61 \leqq t_a/\mathrm{h} \leqq 110$), I reached saturation at 22.0 ± 0.6 (in the units used in Fig. 1) and w at 2.0 ± 0.2 kHz, which agreed well with T_2^* (ca. 200 μs at 77 K) determined by pulse NQR method [19]. The shape of the recorded NQR signals approximated the derivative of a Gaussian curve: $A \cdot \exp(-2\nu^2/w^2)$.

From the metastable phase no ^{35}Cl NQR signal was observed. A sample of the stable phase obtained by solid-solid transformation (abbreviated as MG sample) gave a broad ^{35}Cl NQR spectrum ($w = 5 \pm 1$ kHz for ν_1). Moreover, the NQR frequency ν_1 in the MG sample was shifted by ca. 1.3 kHz from that in the SC sample. After the MG sample was annealed for 256 h in the temperature range $393 \leqq T/\mathrm{K} \leqq 411$, the signal was still broad ($w = 3.3 \pm 0.2$ kHz) and the shift of the frequency was ca. 0.5 kHz.

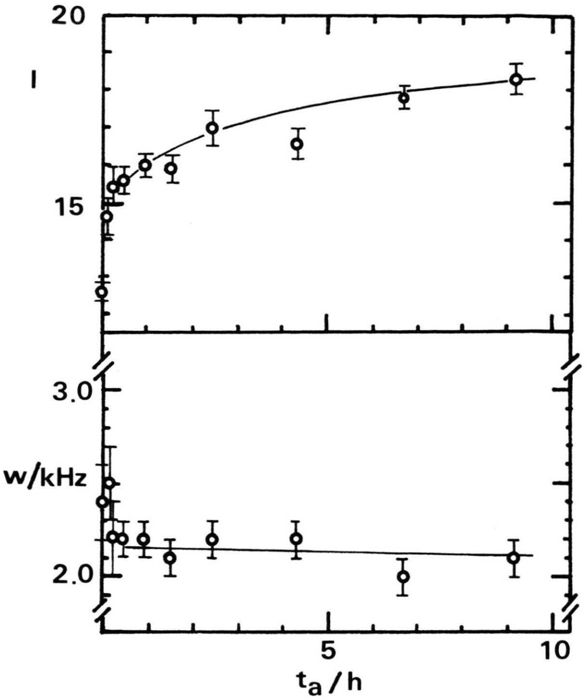

Fig. 1. Changes in I and w of a ^{35}Cl NQR signal (ν_1) of TMB-NO_2 during annealing at 383 K. I in arbitrary units; t_a: annealing time.

Discussion

The MG samples are obtained by formation of the metastable phase from the melt and subsequent solid-solid transition. Such a sample should be less ordered than an SC sample obtained by slow crystallization from a solution. Indeed the former sample exhibited broader NQR signals than the latter. The imperfections in the MG sample are probably dislocations and grainboundaries.

Both the SC and MG samples showed relaxation of imperfections during annealing. The structure of the imperfections in the SC samples seems to be simpler than that in the MG samples, therefore the annealing process of the SC samples was studied as will be shown below.

According to Monfils and Grosjean, and Kojima et al. [1, 2], the height of the NQR absorption line (A) is correlated to the molar concentration of an impurity (c) by the relation

$$A = A_\infty \exp(-Nc)\,, \tag{1}$$

where N is a characteristic number which represents the number of resonant nuclei around an impurity whose resonance frequencies have been so shifted that they can no longer contribute to the central portion of the NQR line. In the present case, c will be regarded as the concentration of the imperfections which most affect the NQR signals in the SC sample.

For simplicity one may assume a first order law for the decrease of c during annealing:

$$-\mathrm{d}c/\mathrm{d}t_a = k\,c\,, \tag{2}$$

where t_a is the annealing time and k is the rate constant.

From (1) and (2) one obtains

$$\ln\ln(A_\infty/A) = -k\,t_a + \ln(N c_0)\,, \tag{3}$$

where c_0 is the concentration of the imperfection in the original SC sample without annealing. A_∞ is the height of the absorption line at $t_a = \infty$. For such a sample the amount of the imperfection is assumed to be negligible.

As long as the observed first derivative is approximated by a Gaussian, A is proportional to the product of the peak-to-peak deviation of the derivative (I) and the maximum slope width (w). Then, in place of A_∞/A in (3) one may use the quantity, $I_\infty\, w_\infty / I w$, where I_∞ and w_∞ stand for I and w corresponding to a sample annealed for $t_a = \infty$. Furthermore, in the range of t_a where $w \cong w_\infty$, A_∞/A may be approximated by I_∞/I. The k values obtained from the $\ln\ln(I_\infty/I)$ vs. t_a plots shown in Fig. 2 were in good agreement with those deduced from $\ln\ln(I_\infty w_\infty/I w)$ vs. t_a plots.

As shown in Fig. 2, the points observed at longer t_a deviate from the straight line predicted by (3). In general, the higher the temperature, the earlier the onset of the deviation. This suggests that the first order approximation (2) is too simple to cover a wide range of t_a at higher temperatures. Furthermore, the deviation would be associated with the decomposition of the material. Although because of these reasons the k values at higher temperatures deduced from Fig. 2 are considered to be less reliable, one can see that the k values tend to increase with increasing temperature. The Arrhenius plots of k's gave an activation energy of (110 ± 20) kJ/mole.

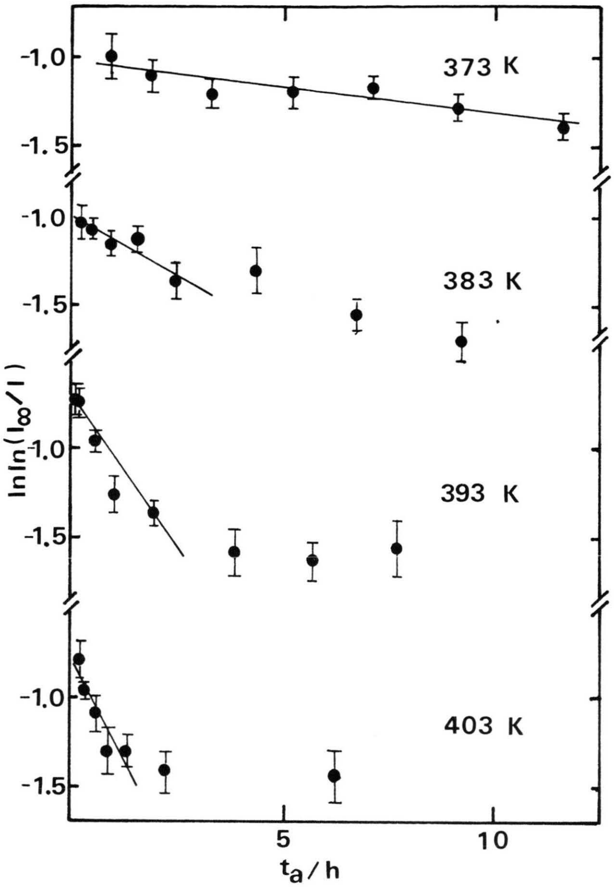

Fig. 2. $\ln\ln(I_\infty/I)$ vs. t_a plots obtained for ν_1 signal in the SC sample of TMB-NO$_2$ annealed at 373, 383, 393, and 403 K.

Since TMB-NO$_2$ is dimorphic, there are at least two ways of molecular alignment in crystal lattices having almost the same free energy. Therefore, in the crystal lattice of the stable phase of TMB-NO$_2$, as in the case of p-dichlorobenzene [20], there would be misoriented molecules accompanied by vacancies. It has been shown for several organic crystals that the vacancy formation enthalpy ranges from 0.5 to 1.2 of the triple point sublimation enthalpy [21]. The value of the activation energy mentioned above is considered to be comparable to the heat of sublimation of TMB-NO$_2$, as judged from those of other molecular crystals [22]. Thus, the dimorphism and the magnitude of the activation energy suggest that the dominant imperfection in the SC sample is caused by misoriented molecules accompanied by vacancies.

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