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^{14}N nuclear quadrupole resonance study of the structural phase transition in phenothiazine

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Abstract. ^{14}N nuclear quadrupole resonance frequencies have been measured in both the low-temperature and the high-temperature phase of phenothiazine by a ^1H - ^{14}N nuclear quadrupole double-resonance technique. The proton spin-lattice relaxation time was measured in both crystallographic phases as well. The NQR data show the presence of large thermal librations of the phenothiazine molecules in both crystallographic phases. The NQR data are consistent with an order-disorder phase transition associated with the reorientations of the phenothiazine molecules around the orthorhombic b axis. The reorientation angle is at T_c equal to $9 \pm 2^\circ$. The long proton spin-lattice relaxation times above and below T_c seem to rule out any large translation or butterfly motions associated with the phase transition.

1. Introduction

Tricyclic aromatic non-planar molecules of phenothiazine ($\text{C}_{12}\text{H}_9\text{SN}$) form molecular crystals which under atmospheric pressure undergo structural phase transitions at $T_c = 251$ K. The high-temperature phase is orthorhombic with the space group $Pbnm$ [1] whereas the ferroelastic low-temperature phase is monoclinic with the space group $P2_1/n$ [2]. X-ray [2], Brillouin scattering [3] and proton magnetic relaxation [4] experiments suggest that the ferroelastic phase transition is of the order-disorder type. However, the entropy of transition is so small that this phase transition may not be a pure order-disorder phase transition [5]. Sircar *et al* [6] measured the proton NMR spectra and they observed large changes in the proton second moment between 220 and 320 K suggesting large reorientational motion of phenothiazine molecules. Criado and Luty [7] proposed a mechanism of the phase transition where the thermal motion molecular probability distribution of the low-temperature ordered phase broadens as the temperature rises, turning to a two-site double-peaked distribution at the phase transition.

The microscopic mechanism of the ferroelastic phase transition in phenothiazine is not yet completely understood. We therefore decided to perform the ^{14}N nuclear quadrupole resonance (NQR) measurements both in the high-temperature orthorhombic phase and in the low-temperature monoclinic phase of phenothiazine. We believed that the NQR data which in the case of phenothiazine reflect the local properties of the phenothiazine molecules may contribute to the understanding of the microscopic mechanism of the phase transition. The temperature dependence of the proton spin-lattice relaxation time was measured in phenothiazine for the same reason.

2. Experimental details

A polycrystalline sample of phenothiazine was purchased from the Sigma Chemical Co. in the form of a pale-yellow powder. The sample was recrystallized once from methanol. Small crystals in the form of pale-yellow platelets were obtained. The NMR and NQR measurements were performed both on the original substance and on the recrystallized substance.

The proton spin-lattice relaxation time T_1 was measured at the Larmor frequency ν_L equal to 32 MHz with the sequence saturation-time- 90° pulse-acquisition. The accuracy of the measurements was estimated as being $\pm 5\%$.

^{14}N has a spin $I = 1$. It has thus three nuclear quadrupole energy levels in zero magnetic field with the energies

$$\begin{aligned} E_1 &= \frac{1}{4}eQV_{ZZ}(1 + \eta) \\ E_2 &= \frac{1}{4}eQV_{ZZ}(1 - \eta) \\ E_3 &= -\frac{1}{2}eQV_{ZZ}. \end{aligned} \quad (1)$$

Here eQ is the nuclear quadrupole moment, V_{ZZ} is the largest principal value of the electric-field-gradient (EFG) tensor at the nitrogen site and η is the asymmetry parameter of the EFG tensor. The EFG tensor is a symmetric second-rank tensor composed of the second derivatives $\partial^2 V(\partial x_i \partial x_j)$ of the electrostatic potential V with respect to the coordinates. It has three principal values V_{XX} , V_{YY} and V_{ZZ} which are ordered in the following way: $|V_{XX}| \leq |V_{YY}| \leq |V_{ZZ}|$. The asymmetry parameter η of the EFG tensor is defined as the ratio $\eta = (V_{XX} - V_{YY})/V_{ZZ}$. It ranges between zero and one.

The NQR measurements give three resonance frequencies

$$\begin{aligned} \nu_{1,3} &= \nu_+ = eQV_{ZZ}(3 + \eta)/4h \\ \nu_{2,3} &= \nu_- = eQV_{ZZ}(3 - \eta)/4h \\ \nu_{1,2} &= \nu_0 = eQV_{ZZ}\eta/2h \end{aligned} \quad (2)$$

which depend on the quadrupole coupling constant eQV_{ZZ}/h and on the asymmetry parameter η of the EFG tensor.

The ^{14}N NQR frequencies were measured with a highly sensitive ^1H - ^{14}N nuclear quadrupole double-resonance technique based on magnetic field cycling and two-frequency irradiation [8-10].

A magnetic field cycle consists of the following steps. The proton spin system is first polarized in a high static magnetic field B_0 . Then the static magnetic field is adiabatically reduced to a low value B for a time τ . After the demagnetization is completed, the proton magnetization relaxes towards the new equilibrium value which is smaller by a factor B/B_0 than the equilibrium proton magnetization in the high magnetic field B_0 . After the time τ the static magnetic field is adiabatically increased to the initial value B_0 , and the proton NMR signal following a 90° pulse is measured. It is proportional to the proton magnetization and decreases with increasing τ approximately as $\exp[-\tau/T_1(B)]$. Here $T_1(B)$ is the proton spin-lattice relaxation time in the low magnetic field B .

In the first part of the experiment the time τ was chosen as being 1 s and, when the sample was in a zero magnetic field, it was subjected to a RF magnetic field which performed multiple frequency sweeps. The lower limit $\nu_1 = 2.5$ MHz and the upper limit $\nu_u = 4$ MHz, of the frequency sweeps were chosen in such a way that they covered the frequency range in

which the upper two ^{14}N NQR frequencies ν_+ and ν_- are expected to be found. The duration of a single frequency sweep was set to 10 ms and the amplitude of the RF magnetic field was equal to approximately 1.5 mT. The magnetic field cycles were repeated at different values of the low static magnetic field B whereas all other parameters of the magnetic field cycle and of the RF irradiation were kept constant. The step in B between two repetitive magnetic field cycles was set to 0.25 mT. At resonance, i.e. when the proton Larmor frequency $\nu_{\text{H}} = \gamma_{\text{H}}B/2\pi$ in the low magnetic field B was equal to the lowest ^{14}N NQR frequency ν_0 , we observed a smaller proton NMR signal than off resonance. In this case therefore the frequency sweeps of the RF magnetic field cause multiple excitations of the two ^{14}N NQR transitions with the frequencies ν_+ and ν_- . These excitations are similar to a fast spin-lattice relaxation of nitrogen atoms. Owing to the resonant coupling of protons and nitrogen atoms at $\nu_{\text{H}} = \nu_0$ the relaxation time of proton is also shortened, which results in a smaller proton NMR signal at the end of the magnetic field cycle. In this way the lowest ^{14}N NQR frequency ν_0 was roughly determined and B was set to the resonance condition $\nu_{\text{H}} = \nu_0$.

In the second part of the experiment the two upper ^{14}N NQR frequencies ν_+ and ν_- were determined by varying the limits of the frequency sweeps. The additional relaxation of protons via nitrogen atoms is therefore observed only when the frequency sweeps cover both ν_+ and ν_- . When they cover only one of the two frequencies, a quasi-equilibrium population of the nitrogen energy levels is established after a few frequency sweeps. Later the frequency sweeps no longer influence the time evolution of the populations of the proton and nitrogen energy levels.

Finally the two upper ^{14}N NQR frequencies were precisely determined by two-frequency irradiation. The frequency of the first of the two RF magnetic fields was fixed closed to a NQR frequency, say ν_- , and the frequency range around the highest ^{14}N NQR frequency ν_+ was scanned by the second RF magnetic field. The largest drop in the proton NMR signal at the end of the magnetic field cycle was observed when the frequency of the second RF magnetic field was equal to ν_+ . Then the frequency of the first RF magnetic field was fixed at ν_+ and the frequency range around the intermediate ^{14}N NQR frequency ν_- was scanned by the second RF magnetic field. In this way the two upper ^{14}N NQR frequencies ν_+ and ν_- were determined with an accuracy of ± 1 kHz.

3. Results and discussion

The temperature dependences of the ^{14}N NQR frequencies ν_+ and ν_- are shown in figure 1. The corresponding quadrupole coupling constant and asymmetry parameter are shown as functions of temperature in figure 2. As is clearly seen, both the quadrupole coupling constant and the asymmetry parameter η exhibit strong temperature variations. This is presumably the effect of large thermal librations of the phenothiazine molecules.

The quadrupole coupling constant is at room temperature equal to 4189 ± 2 kHz and within the experimental resolution it continuously increases with decreasing temperature. At -125°C it reaches the value of 4233 ± 2 kHz. No change either in the value or in the slope in the temperature dependence of the quadrupole coupling constant is observed at the phase transition temperature. Thus within the experimental resolution the quadrupole coupling constant is not affected by the phase transition.

The asymmetry parameter η , which at room temperature is equal to 0.2261 ± 0.0005 , first decreases with decreasing temperature and reaches a value of 0.2250 ± 0.0005 close to the phase transition temperature. Just below T_c we observed an asymmetry parameter of

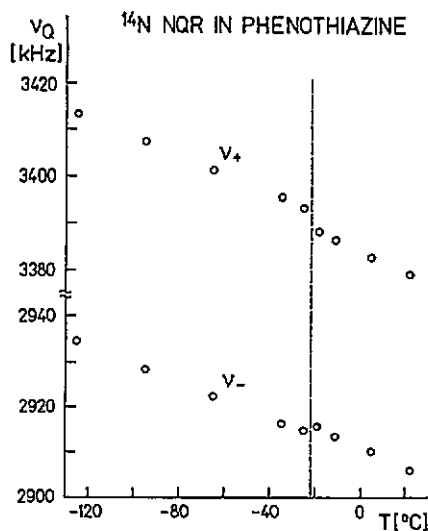


Figure 1. Temperature dependences of the ^{14}N NQR frequencies ν_+ and ν_- in phenothiazine.

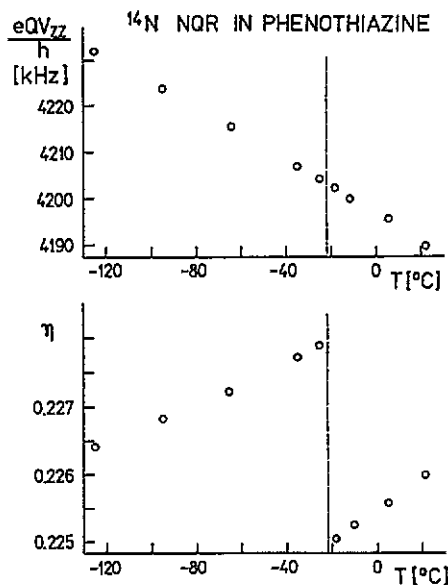


Figure 2. Temperature dependences of the ^{14}N quadrupole coupling constant eQV_{zz}/h and the asymmetry parameter η in phenothiazine.

0.2278 ± 0.0005 . The temperature resolution of our measurements was not high enough to see whether this jump is continuous or discontinuous but other experiments show that the phase transition is of the first order. Thus the jump must be discontinuous. Below T_c the asymmetry parameter η again decreases with decreasing temperature and reaches the value 0.2264 ± 0.0005 at -125°C .

The present values of the quadrupole coupling constant and asymmetry parameter are close to the quadrupole coupling constant $eQV_{zz}/h = 4240 \pm 30$ kHz and the asymmetry parameter $\eta = 0.226 \pm 0.009$, as measured at 77 K by a double-resonance technique [11]. However, the sensitivity and resolution of the experimental technique at present used are much higher than the sensitivity and resolution of the double-resonance technique used in the previous measurement.

In phenothiazine we may safely assume that the EFG tensor at the nitrogen site is mainly determined by the electric charge distribution within the three covalent bonds (two C–N and one N–H) formed by a nitrogen atom. Each bond contributes an axially symmetric EFG tensor with the symmetry axis along the bond direction. The contribution of the N–H bond is not very different from the contribution of a C–N bond. This may be claimed on the basis of the comparison of the ^{14}N NQR data from nitrogen atoms surrounded by three C–N bonds, from other C–NH–C groups, from C–NH₂ groups, from C–NH₂⁺–C ions and from C–NH₃⁺ ions.

If a phenothiazine molecule is planar, then the principal axis Z of the EFG tensor at the nitrogen site would be perpendicular to the molecular plane; one of the other two principal axes (X or Y) would be perpendicular to the molecular plane which passes through both the S and the N atoms and is perpendicular to the plane of the molecule. The third principal axis would in this case be along the S–N axis.

In a phenothiazine crystal the molecules are not planar, but they are folded along the S–N axes. The fold angle is 158.5° . The symmetry element which is left is the molecular

mirror plane. Thus one of the principal axes of the EFG tensor at the nitrogen site is perpendicular to the mirror plane. The C–N and N–H bonds surrounding a nitrogen atom are directed in such a way that the principal axis Z of the EFG tensor at the nitrogen site lies in the molecular mirror plane and is nearly perpendicular to the S–H axis. The third principal axis of the EFG tensor is nearly parallel to the S–H axis. Thus the principal axis Z of the EFG tensor is nearly parallel to the orthorhombic axis *b* of the crystal.

The NQR data show that the quadrupole coupling constant passes through the phase transition nearly continuously whereas the two smaller principal values of the EFG tensor change. This is only consistent with a reorientation of a molecule around the principal axis Z of the EFG tensor. If we assume that above T_c a molecule reorients around the principal axis Z between two equivalent equilibrium orientations separated by an angle Φ (figure 3), then V_{ZZ} does not change whereas the principal values V_{xx} and V_{yy} of the time-averaged EFG tensor are expressed as

$$\begin{aligned} V_{xx} &= V_{XX} \cos^2(\tfrac{1}{2}\Phi) + V_{YY} \sin^2(\tfrac{1}{2}\Phi) \\ V_{yy} &= V_{XX} \sin^2(\tfrac{1}{2}\Phi) + V_{YY} \cos^2(\tfrac{1}{2}\Phi) \end{aligned} \quad (3)$$

and the asymmetry parameter of the EFG tensor changes to

$$\eta = \eta_0 \cos \Phi. \quad (4)$$

Here η_0 is the asymmetry parameter of the EFG tensor at the nitrogen site for a static molecule and η is the asymmetry parameter of the time-averaged EFG tensor.

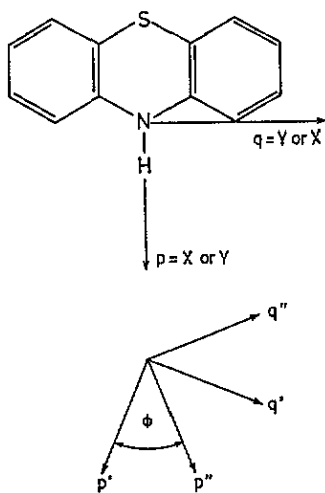


Figure 3. Approximate directions of the principal axes of the EFG tensor at the nitrogen site and the proposed disorder in phenothiazine.

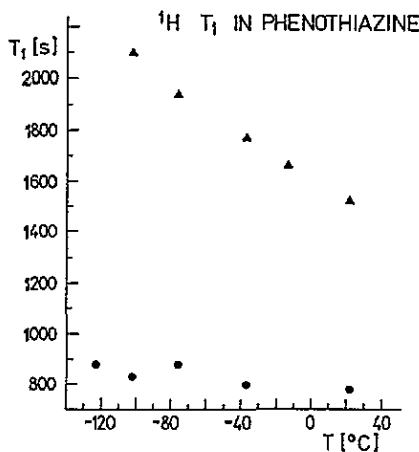


Figure 4. Temperature dependence of the proton spin-lattice relaxation time in an original sample of phenothiazine (▲) and in a sample of phenothiazine once recrystallized from methanol (●).

In phenothiazine the molecules are not static below T_c . The strong temperature dependences of the quadrupole coupling constant and of the asymmetry parameter η suggest that the molecules undergo thermal librations. Nevertheless there is a step in η at T_c . If we

assume that the thermal librations are independent of the reorientations associated with the phase transition, we may use in equation (4) the value of 0.2278 for η_0 and the value of 0.225 for η and calculate the reorientational angle Φ . As a result we obtain $\Phi = 9 \pm 2^\circ$, a result which is in good agreement with the angle 8° obtained from the optical extinction measurements close to T_c [5]. Positional disorder of the molecules as suggested on the basis of the x-ray data [2] is, however, still possible. It therefore has no influence on the NQR frequencies. Thus the reorientations of the phenothiazine molecules may in principle be associated with their displacements.

The ^{14}N NQR data also exclude the possibility of the butterfly motion of the phenothiazine molecules associated with the phase transition. In this case therefore the molecular mirror plane persists and the principal value of the EFG tensor which is perpendicular to the molecular mirror plane (V_{XX} or V_{YY}) does not change. The NQR experiment shows that both V_{XX} and V_{YY} change, which excludes the butterfly up-down motion as the motion associated with the phase transition.

The temperature dependence of the ^1H spin-lattice relaxation time is shown in figure 4. In the original substance it is equal to 1500 s at room temperature and it continuously increases with decreasing temperature. At -100°C , T_1 reaches the value of 2100 s. No change in T_1 is observed at the phase transition within the experimental resolution ($\pm 5\%$). In the substance once recrystallized from methanol the spin-lattice relaxation time is significantly shorter. It is equal to 780 S at room temperature and it slowly increases with decreasing temperature. At -100°C , T_1 reaches the value of 900 s. This large change in T_1 can easily be understood. Methanol contained very small amounts of paramagnetic impurities which in the recrystallized substance shortened T_1 . The spin-lattice relaxation rate T_1^{-1} as measured in the recrystallized substance is expressed as

$$T_1^{-1} = (T_1^{-1})_{\text{original}} + (T_1^{-1})_{\text{impurities}} \quad (5)$$

where $(T_1^{-1})_{\text{original}}$ is the spin-lattice relaxation rate of the original substance and $(T_1^{-1})_{\text{impurities}}$ is the contribution to the spin-lattice relaxation rate caused by the paramagnetic impurities which entered the substance during the process of recrystallization. The value of $(T_1^{-1})_{\text{impurities}} = 1/1600$ s produces the changes observed in T_1 .

The proton T_1 as measured in the present experiment at the Larmor frequency of 32 MHz is nearly an order of magnitude longer than the proton T_1 measured in phenothiazine in a previous experiment at 10, 18.2 and 37 MHz [4]. Moreover no change in the temperature dependence of the proton T_1 was observed at the phase transition contrary to the data of Ishimaru *et al* [4]. The reason for this discrepancy is not known. Nevertheless our samples underwent a structural phase transition at 251 K, i.e. at the same temperature as observed by optical experiments. Also the changes in the orientations of the phenothiazine molecules as determined by NQR are in agreement with the optical measurements.

The very long proton spin-lattice relaxation time (about $\frac{1}{2}$ h)—as observed in our samples—which is within the experimental resolution not affected by the phase transition rules out the possibilities of any large molecular motions such as for example large translational motions as proposed by van de Waal and Feil [2] or the butterfly motions associated with the phase transition. It is of course still possible that there are some large motions which are slow on the NMR time scale. These motions reduce the proton second moment as observed by Sircar *et al* [6] and also shorten the proton spin-lattice relaxation time in very low magnetic fields. The shortening of the proton T_1 in a magnetic field below a few milli teslas was indeed observed in our magnetic field-cycling experiments. The shortening in T_1 is larger than expected for the transition from the Zeeman spin reservoir

to the dipolar spin reservoir [12]. As can be seen from the proton second-moment data of Sircar *et al* [6], the slow motion has already started below T_c and is not affected by the phase transition. This motion is in the transition region (220–320 K) in the kilohertz frequency range. The shifts in the ^{14}N NQR frequencies at the phase transition are caused by a motion (reorientations) which is fast on the NQR megahertz frequency scale [13]. Thus the slow motion which reduces the proton second moment and shortens the proton spin–lattice relaxation time in a low magnetic field is not directly related to the phase transition.

Our NMR and NQR data thus agree with the model of the phase transition as proposed by Criado and Luty [7] in which the phase transition is associated with the thermal librations of the phenothiazine molecules. When the amplitudes of the thermal librations around the orthorhombic axis b become sufficiently large, the single-well potential for a molecule changes to a double-well potential. This change is associated with a first-order phase transition. The angle between the two possible orientations of a molecule is at T_c equal to $9 \pm 2^\circ$ in agreement with the optical data [5]. Any large translational or butterfly motions associated with the phase transition seem to be ruled out by the proton spin–lattice relaxation data.

References

- [1] McDowell J J H 1976 *Acta Crystallogr. B* **32** 5
- [2] van de Waal B W and Feil D 1977 *Acta Crystallogr. B* **33** 314
- [3] Sartwell J and Eckhardt C J 1993 *Phys. Rev. B* **48** 12438
- [4] Ishimaru S, Nakamura N and Chihara H 1991 *J. Phys. Soc. Japan* **60** 2424
- [5] Nakayama H, Ishii K, Chijiwa E, Wada M and Sawada A 1985 *Solid State Commun.* **55** 59
- [6] Sircar R, Mishra S C and Gupta R C 1980 *Indian J. Pure Appl. Phys.* **18** 757
- [7] Criado A and Luty T 1993 *Phys. Rev. B* **48** 12419
- [8] Seliger J, Žagar V, Blinc R, Kind R, Arend H and Milia F 1987 *Z. Phys. B* **67** 363
- [9] Seliger J, Žagar V and Blinc R 1994 *J. Magn. Reson. A* **106** at press
- [10] Seliger J, Žagar V and Blinc R 1994 *Z. Naturf. a* **49** at press
- [11] Koo J C *PhD Thesis* University of California, Berkeley, CA, referred to in Edmunds D T 1977 *Phys. Lett.* **29C** 233
- [12] Goldman M 1974 *Spin Temperature and Nuclear Magnetic Resonance in Solids* (Oxford: Clarendon) ch 3
- [13] Seliger J 1993 *J. Magn. Reson. A* **103** 175