NQR and Phase Transitions in Hexachlorocyclopropane Crystal *

Masahiko Suhara

Department of Chemistry, Faculty of Science, Kanazawa University,
1-1 Maru-no-uchi, Kanazawa 920, Japan

Koichi Mano

Department of Applied Chemistry, Faculty of Engineering, Osaka City University,
Sugimoto, Sumiyoshi-ku, Osaka 558, Japan

Z. Naturforsch. **45a,** 339–342 (1990); received August 23, 1989

^{35}Cl NQR and DSC studies on phase transitions in hexachlorocyclopropane (HCCP), C_3Cl_6, are reported. It is found that HCCP has three solid phases: A high temperature disordered phase (Phase I) above 301 K (no NQR spectrum was observed); a metastable phase (Phase II), which exhibited 6 NQR lines from 77 to 270 K; a low temperature phase (Phase III) in which a 24-multiplet of ^{35}Cl NQR lines at 77 K, the most complex multiplet spectrum ever reported was observed.

DSC measurement shows a λ-type transition at 301 K and a broad transition of very slow rate at 285 K. The structure and mechanism of phase transitions in HCCP crystal are discussed.

Key words: Nuclear quadrupole resonance, Phase transition, Crystal structure, Differential scanning calorimetry, Order-disorder transition.

Introduction

Structural phase transitions of crystals formed by nearly spherical molecules are an interesting field in solid state physics [1]. For example, methane [2] and adamantane [3] form a face-centered cubic lattice which is usually a disordered phase. With decreasing temperature, this lattice transforms to orientationally ordered structures. NQR is very usefull to investigate the crystal structure and phase transition when multiplet lines are originated from the crystallographically inequivalent atoms which belong to chemically equivalent sites in a free molecule. The most striking example so far reported is carbon tetrachloride, which shows a 16-line ^{35}Cl NQR spectrum [4]. This comes from the formation of a large unit cell with 32 CCl_4 molecules. In this paper, we report a very complex multiplet-pattern of an NQR spectrum and several phase transitions found in solid hexachlorocyclopropane (HCCP). The resemblance of the polymorphism in CCl_4 to that in HCCP is also discussed.

Experimental

NQR signals were detected by means of a Kushida type regenerative oscillator detector with a second harmonics detection to avoid the side-band interference in a superregenerative detector. The resonance frequency was measured by means of pip marks at 10 kHz intervals on a chart generated by a frequency counter. Details of the spectrometer have been reported elsewhere [5].

A differential scanning calorimeter (DSC), Rigaku DSC 8058, was employed for thermal analysis.

Results

DSC Measurements

The phase transitions of solid HCCP at atmospheric pressure were observed by measuring DSC curves as shown in Figure 1. Run a shows the heating curve exhibiting a λ-type transition at 301 K. The high and low temperature phases are denoted by I and III, respectively. Run b, the second run, exhibits an anomalous DSC curve which is superimposed with a λ-type transition peak and a broad one. The transition corresponding to the broad peak is very slow and could be observed once at the second run in one sam-

---

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

Reprint requests to Prof. M. Suhara, Department of Chemistry, Faculty of Science, Kanazawa University, 1-1 Maru-no-uchi, Kanazawa 920, Japan.

0932-0784 / 90 / 0300-0339 $ 01.30/0. – Please order a reprint rather than making your own copy.

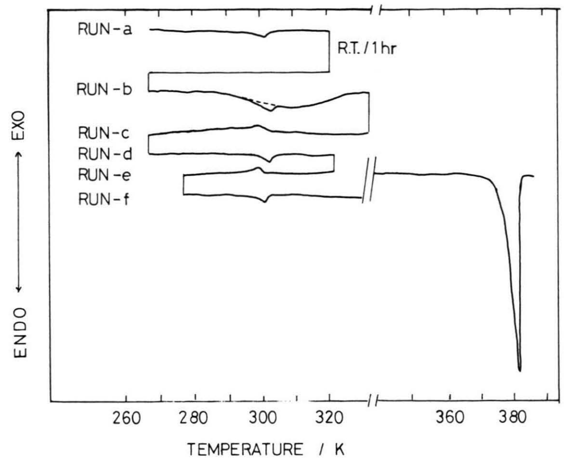

Fig. 1. DSC curves in hexachlorocyclopropane.

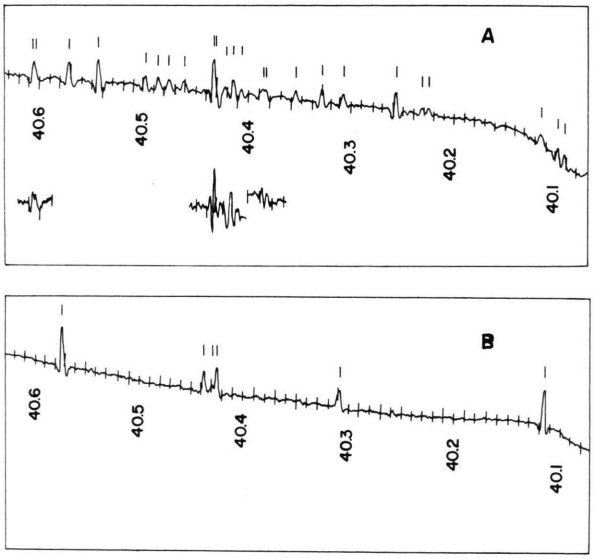

Fig. 2. ^{35}Cl NQR spectrum in (A) Phase III and (B) Phase II of hexachlorocyclopropane at 77 K, together with frequency marks of 10 kHz intervals and frequency in MHz.

ple as seen in Figure 1. Afterward, only the λ-type transition was observed reversively. This new phase is denoted by Phase II. The transition point (T_c) from II to I is 285 K. The melting point (T_m) is 376 K. The enthalpies of transition in run a and run b are 0.21 and 1.26 J mol^{-1}, respectively. This leads to the value of 1.05 J mol^{-1} for the slow transition. The enthalpy and entropy changes at T_m are 18.6 kJ mol^{-1} and 49 J mol^{-1} K^{-1}, respectively.

NQR Measurement

The sample crystallized from n-propane shows no ^{35}Cl signal in I. At 77 K, a very complicated multiplet-spectrum consisting of 24 lines was observed, as shown in Figure 2A. The sample, kept at 343 K over a period of several weeks, showed the same spectrum at 77 K. The sample crystallized from a melt also exhibited the same pattern at 77 K. This 24-lines spectrum is one of the most complex multiplet NQR spectra ever reported. Repeating the heating and/or cooling of the sample, the spectrum pattern turned to a very simple spectrum of 6 lines, as shown in Figure 2B. After the sample of II was kept at 253 K or at room temperatur for a long time, a mixed spectral pattern of two modifications, II and III, was observed, and finally no resonance for II could be observed, no matter how the temperature of specimen was varied. The rate of transition between II and III was quite small and equilibrium was not reached in a reasonable period of time. So, the transition temperature could not be determined from the NQR measurement. The temperature dependence of ^{35}Cl NQR frequencies in II and III is shown in Figs. 3A and 3B, respectively. Most of the resonance lines in III faded out considerably below $T_c = 301$ K, whereas in II the resonance was detected at 270 K, which was slightly below $T_c = 285$ K. The disappearance of the resonance signal can be attributed to the orientational disordering of molecules due to librational motions in the crystal. The resonance lines in III disapper at a lower temperature than those in II. Such a fade-out has also been observed in the case of chloral hydrate crystal [6].

Discussion

From the DSC and NQR observations, we confirmed three phases: a high temperature phase (I), a metastable one (II), and a low temperature one (III), as shown in Figure 4. The HCCP and CCl_4 molecules are nearly spherical and all of the chlorine atoms in a molecule are chemically equivalent. The crystal structure and mechanism of phase transition in HCCP are expected to be similar to those in CCl_4. The phase diagram for CCl_4 was determined by Bridgman [7] and Trapeniers [8], who obtained at least three different solid phases at temperatures of 233 to 458 K and pressures of 0 to 10^4 kg cm^{-2}. The crystal structure of II was determined by Rudman and Post [9] and Weir et al. [10], and that of III by Piermarini and Braun

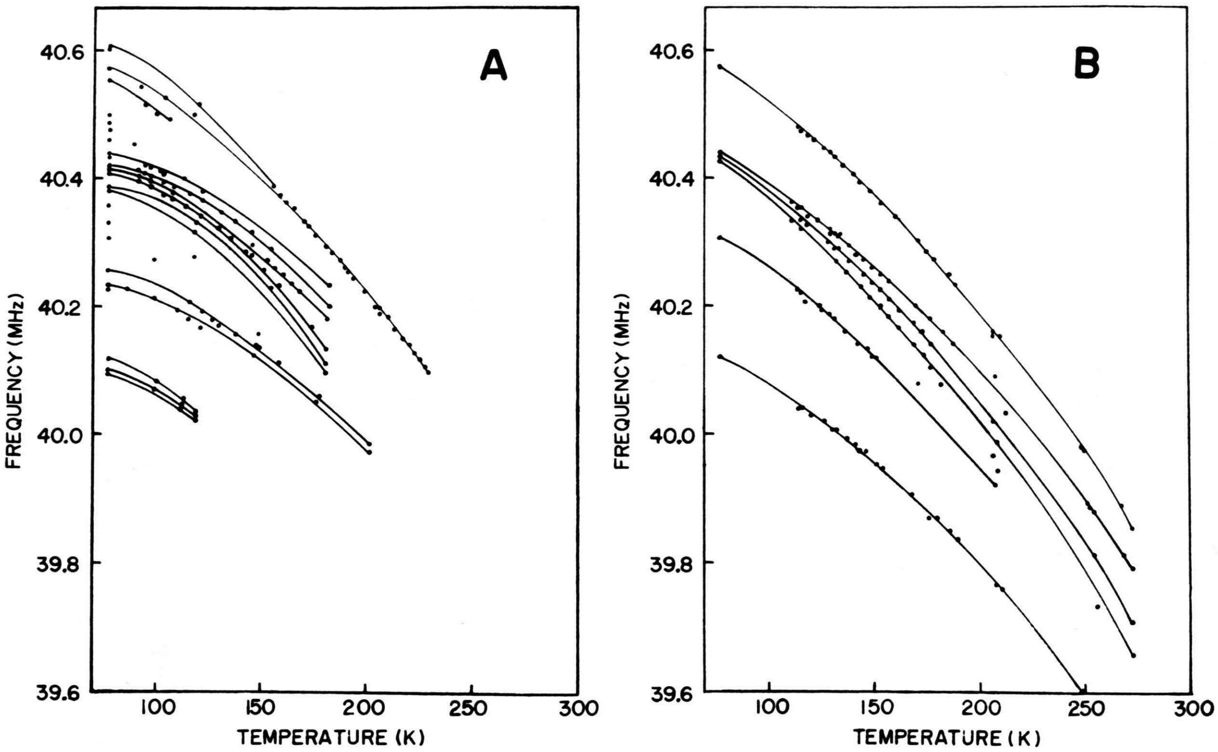

Fig. 3. Temperature dependence of ^{35}Cl NQR frequencies in (A) Phase III and (B) Phase II of hexachlorocyclopropopane

Fig. 4. The phases of hexachlorocyclopropane.

Table 1. Crystal and NQR data for CCl_4 and HCCP.

Compounds	Ordered phases	
	Phase II	Phase III
CCl_4	$0\ \mathrm{kg\ cm^{-2}}$ $T < 225.5$ K $Z = 32$ $N_{NQR} = 16$	$10^4\ \mathrm{kg\ cm^{-2}}$ $T =$ room temp. $Z = 4$ $N_{X\text{-ray}} = 4$
	Phase III	Phase II
cyclo-C_3Cl_6 (HCCP)	$0\ \mathrm{kg\ cm^{-2}}$ $T < 301$ K $Z = 32$ $N_{NQR} = 24$	$0\ \mathrm{kg\ cm^{-2}}$ $T < 285$ K $Z = 4$ $N_{NQR} = 6$

Z and N denote the numbers of molecules and inequivalent chlorine sites in a unit cell, respectively.

[11]. The structure of II obtained at 123 to 248 K and atmospheric pressure is ordered pseudo-cubic monoclinic with a very large cell dimension containing 32 molecules. The structure of III is monoclinic with 4 molecules per unit cell at room temperature and a pressure of 10^4 kg cm^{-2} [11]. Crystal data for HCCP show a pseudo-body-centered monoclinic form containig 4 molecules [12], which has been determined at low temperature and atmospheric pressure. We can compare HCCP and CCl_4. The similarity of the crystal data and the results of NQR measurements are shown in Table 1. The values of 16/24 and 4/6, which are the ratios of the number of equivalent chlorine sites in each pair of phases, are equal to the ratio of the number of chlorine atoms between the two molecules.

This suggests that the structure and polymorphism observed in HCCP crystal are the same as those in CCl_4. The transition mechanism is believed to give a slight change in the packing of molecules whose centers of mass are unaffected by the transition, as suggested for solid CCl_4 [13].

[1] T. H. K. Barron and C. Domb, Proc. Roy. Soc. A **227,** 447 (1965). – T. Kihara, J. Phys. Soc. Japan **7,** 348 (1952). – L. Jansen and E. Lombardi, Disc. Faraday Soc. **20,** 35 (1952).
[2] A. Schallamach, Proc. Roy. Soc. A **171,** 589 (1939). – J. Herczec and R. E. Stoner, J. Chem. Phys. **54,** 2284 (1971).
[3] C. E. Nordman and D. L. Schmitkons, Acta Cryst. **18,** 764 (1965).
[4] R. Livingston, J. Phys. Chem. **57,** 496 (1953). – H. Okuma, N. Nakamura, and H. Chihara, unpublished work refered in: T. Atake and H. Chihara, J. Chem. Thermodyn. **3,** 51 (1971). – S. Murata, K. Fujita and M. Suhara, Chem. Lett. 1067 (1973).
[5] M. Suhara, Sci. Rep. Kanazawa Univ. **17,** 7 (1972).
[6] D. Biedenkapp and Al. Weiss, Z. Naturforsch. **22 a,** 1124 (1967).
[7] P. W. Bridgman, Phys. Rev. **3,** 153 (1914).
[8] N. T. Trappeniers, refered in: J. Timmermans, J. Phys. Chem. Solid **18,** 1 (1961).
[9] R. Rudman and B. Post, Science **154,** 1009 (1966).
[10] C. E. Weir, G. J. Piermarini, and S. Block, J. Chem. Phys. **50,** 2089 (1969).
[11] G. J. Piermarini and A. B. Braun, J. Chem. Phys. **58,** 1974 (1973).
[12] T. Takano, T. Chiba, Y. Sasada, M. Kakudo, S. Nozakura, and S. Murahashi, Bull. Chem. Soc. Japan **38,** 157 (1965) together with the private communications.
[13] B. M. Mogilevskii and V. G. Surin, Sov. Phys. Solid State **13,** 234 (1971).