PHYSICAL REVIEW B VOLUME 54, NUMBER 5 1 AUGUST 1996-I

Finite-size effects on the incommensurate phase transition of bis(4-chlorophenyl)sulphone studied by ^{35}Cl NQR

J. Schneider, C. Schürrer, and A. Brunetti
FaMAF, Universidad Nacional de Córdoba, Medina Allende y Haya de la Torre, Ciudad Universitaria, 5000 Córdoba, Argentina

(Received 18 December 1995; revised manuscript received 4 March 1996)

The temperature behavior of the ^{35}Cl nuclear quadrupolar resonance (NQR) spectrum of thin bis(4-chlorophenyl)sulphone films grown on fine powder samples of TiO_2 was studied. In order to characterize the structural and dynamical changes, a comparative study of the NQR parameters of the film with respect to the bulk samples was performed in the temperature range 80–370 K. A shift of the incommensurate phase-transition temperature from 150 in bulk to 156 K in film was detected. Also, the observed NQR spectra in the incommensurate phase suggest qualitative changes in the modulation. The presence of a central intense peak below the transition temperature indicates important contributions to the NQR spectra from periodic domains in the film. [S0163-1829(96)09129-1]

INTRODUCTION

The study of the characteristic of the phase transition in thin films is a topic of experimental and theoretical interest.[1–3] A wide range of phenomena can occur in thin films, such as surface melting,[4] change of the order of phase transitions,[5] the appearance of new phases,[6] etc. In particular, the interest in the study of thin films of molecular crystals has grown.

On the other hand, biphenyl compounds show interesting structural and dynamical features, like the incommensurate phase transitions in biphenyl[7–9] and in bis(4-chlorophenyl)sulphone (BCPS).[10,11] In BCPS, a second-order phase transition from a monoclinic $I2/a$ structure[12] to an incommensurate phase (IC) was detected by ^{35}Cl nuclear quadrupole resonance (NQR) at 150 K.[11] The IC modulation in this compound involves the dihedral angle between phenyl rings along the crystallographic $\mathbf{b}$ axis.

Until now, there are few studies on biphenyl films.[13,14] Nakayama, Kawahara, and Ishii[14] show, by means of Raman spectroscopy, the apparition of an unknown crystalline phase consisting of twisted molecules. However, the studies were performed at temperatures well above the normal-IC phase transition, thus no conclusion can be obtained about the thin-film second-order phase-transition behavior. In order to analyze how finite-size effects perturb an incommensuration, the IC phase transition of BCPS was studied. This compound has been extensively characterized by x-ray diffraction,[12,15] Raman spectroscopy,[16] calorimetric measurements,[17] neutron scattering,[18] NMR,[19] and NQR.[20,21] Thus, BCPS is a suitable compound to carry out a comparative study between film and bulk behavior of the IC phase.

In this work, the temperature behavior of ^{35}Cl NQR frequencies of thin BCPS films was studied in the temperature range 80–370 K. In order to characterize the structural and dynamical changes, a comparative study of the NQR parameters of the film with respect to bulk samples was performed.

EXPERIMENTAL

The TiO_2 powder was commercial grade. The crystalline structure of TiO_2 fine powder sample is the tetragonal anatase phase. The N_2 adsorption area is 13 m^2/g and the typical particle size obtained by transmission microscopy is 0.2 μm. The TiO_2 powder was dried under vacuum at 250 °C for 48 h. The BCPS compound was the purum grade from Fluka.

Both compounds were outgased and mixed under vacuum in a glass tube. This sample holder was sealed and heated up to 5° above BCPS melting point. The sample was maintained at this temperature for a week, cooled at about 2 °C below the BCPS melting point and annealed for 70 h. Finally, the temperature was gradually lowered to room temperature in a week.

The ratio of BCPS mass over TiO_2 powder surface is 0.5 g/49 $m^2 = 0.01$ g/m^2. The pore volume fraction of a TiO_2 powder filled with BCPS was 23%. The estimated mean thickness of the BCPS film (supposed uniform) was 70 Å.

^{35}Cl NQR measurements were performed from liquid-nitrogen temperatures to 370 K. The NQR spectrometer was described elsewhere.[22] The NQR line shape was obtained from the fast Fourier transform echo $\pi/2-\pi$ reconstruction method.[23] The $\pi/2$ pulse was 23 μs width and 150 W power. Sampling frequencies of the nuclear signal between 200 KHz and 20 MHz were used. The spectrometer temperature control provides temperature stability of the sample better than 0.1 K during the measurements.

EXPERIMENTAL RESULTS AND DISCUSSION

Figure 1 shows some observed NQR spectra of the BCPS film at different temperatures. The frequencies of the peaks in those spectra were obtained from a least-squares spline of the experimental data. The temperature behavior of these frequencies is plotted in Fig. 2. For a comparison, NQR frequencies of the bulk sample are superimposed.[21] From Figs. 1 and 2, a continuous splitting of the NQR line can be observed for temperatures below 156 K. This behavior of the NQR spectra of the BCPS film indicates a continuous structural phase transition as in the bulk sample.[21] Nevertheless, the transition temperature is shifted 6° above that observed in bulk. Thermal hysteresis effects were not detected in the transition temperature or in the spectral features. The characteristics of the two observed phases are described below.

0163-1829/96/54(5)/2972(4)/$10.00

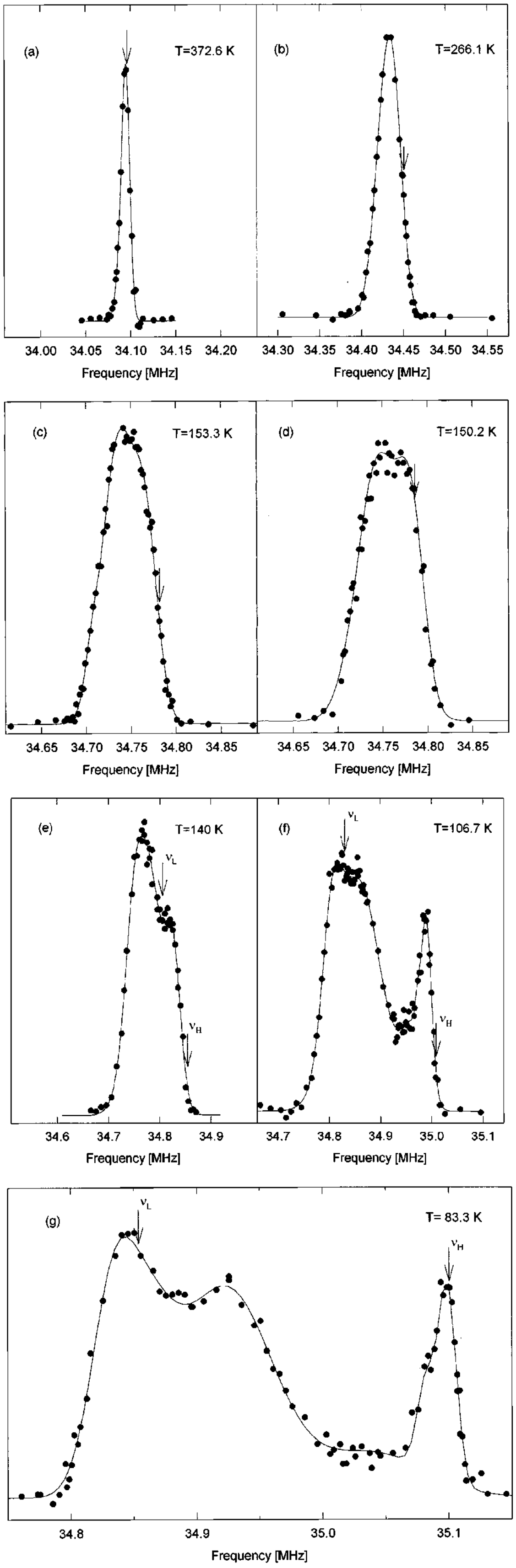

FIG. 1. Some typical ^{35}Cl NQR spectra of bis(4-chlorophenyl)sulphone film observed at different temperatures. The arrows indicate the NQR frequencies measured in the bulk sample at the same temperatures (Ref. 21).

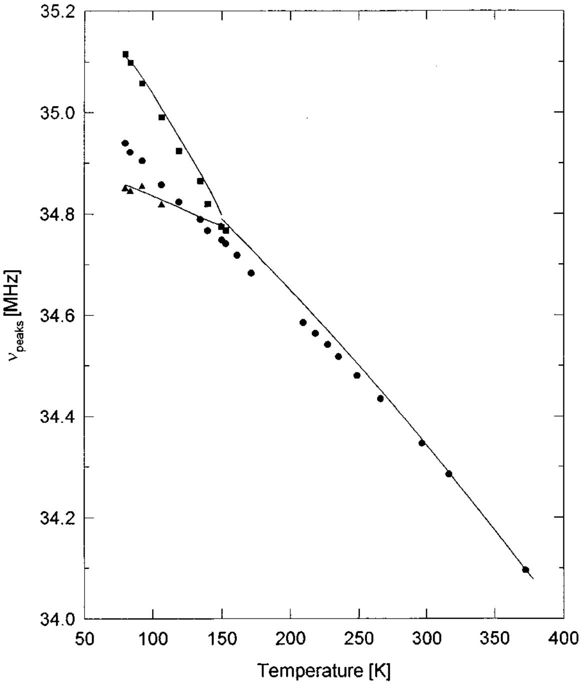

FIG. 2. Temperature behavior of NQR frequencies of the resolved peaks. Points: film data. Solid lines: bulk data (Ref. 21).

High-temperature phase (HTP) $T>156$ K

The NQR spectrum is composed of a single inhomogeneously broadened resonance line. The second moment of this electric-field gradient (EFG) distribution is one order of magnitude greater than that observed in bulk,[21] possibly due to a distribution of film thickness values and different orientations of the film crystalline axis with respect to the substrate. In order to study the temperature behavior of the NQR frequencies, only the first moment of the EFG distribution will be regarded. Figure 3 shows the difference $\Delta\nu$ between the NQR frequencies in the film and bulk samples. Following Brunetti,[24] a comparative study of the frequency temperature behavior can be done. The temperature behavior of the NQR frequency in the high-temperature regime can be expressed as

$$\nu_Q(T)=\nu_0\left(1-\frac{3}{2}k_BT\sum_i\frac{A_i}{\omega_i^2}-3k_BT^2\sum_i\frac{A_i}{\omega_i^2}g_i\right),$$

where the summation ranges over all inter- and intramolecular oscillation modes involved in the average of the electric-field gradient (EFG),[25] $\omega_i(1-g_iT)$ is the frequency of the mode at the temperature T, A_i is a quantity related to the inverse of the moment of inertia, and ν_0 is the limiting static value of the NQR frequency.

Assuming only one dominant oscillation mode in the film and the bulk samples, $\Delta\nu$ can be expressed as

$$\Delta\nu_Q(T)=\Delta\nu_0+aT+bT^2, \tag{1}$$

where

$$a=-\frac{3}{2}k_B\left[\frac{\nu_0^fA^f}{\omega_f^2}-\frac{\nu_0^bA^b}{\omega_b^2}\right],$$

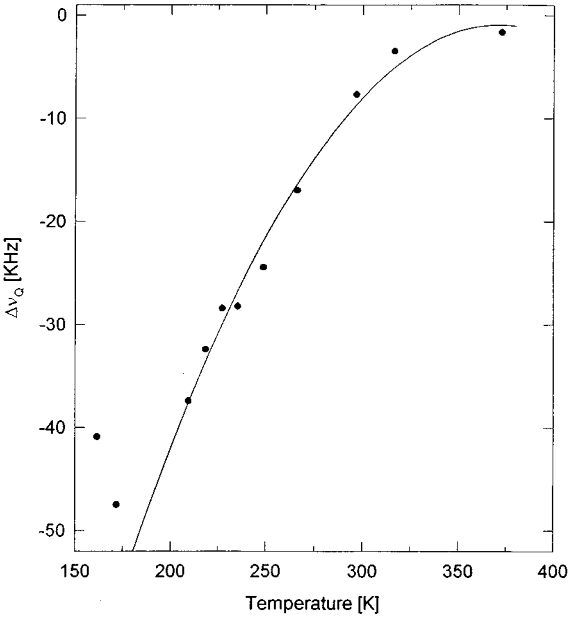

FIG. 3. Temperature behavior of the difference between the NQR frequencies of bulk and film in the high-temperature phase. Points: $\nu_{\mathrm{BULK}}-\nu_{\mathrm{FILM}}$. Solid line: Fitting of expression (1).

$$b=-3k_B\left[\frac{\nu_0^f g^f A^f}{\omega_f^2}-\frac{\nu_0^b g^b A^b}{\omega_b^2}\right],$$

where f and b refer to film and bulk, respectively.

Fitting of expression (1) to the experimental data yields the following parameters:

$$\Delta\nu_Q(T)=(-0.19+0.0010\ \mathrm{T}-1.4\times10^{-6}\ \mathrm{T}^2)\mathrm{MHz}.$$

The sign of the first and second coefficients indicates that $\nu_0^f<\nu_0^b$ and $A_b/\omega_b^2>A_f/\omega_f^2$. The first inequality shows a change in the molecular packing, while the second indicates a modification in the dynamic of the film. The third coefficient gives the relation $g_f>g_b$, indicating larger anharmonicities in the film.

Low-temperature phase (LTP) *T*<156 K

The NQR spectrum in this phase shows three peaks of comparable amplitudes. As can be seen in Fig. 2, the value of the frequency separation between the two lateral peaks is of the same order as that of the observed in bulk. Those peaks can be associated with molecules having the maximum dihedral angle distortion produced by the IC modulation, as in the bulk.[21] Nevertheless, the presence of a third peak shows important structural changes in the incommensurate phase of BCPS films. This broad and intense central peak has approximately 50% of the total area under the NQR spectrum at about 84 K. These features of the central peak indicate that one half of the total number of molecules in the sample have a small dihedral angle distortion with respect to the HTP conformation.

Estimation of the phase-transition temperature

As it was described above, the NQR spectra for temperatures above 160 K show only one peak. Below 150 K, the spectra have two clearly resolved peaks. The measured spectra at 153.3 and 150.2 K, shown in Figs. 1(c) and 1(d) have anomalous shapes. The spectrum at 150.2 K has a flat peak whereas the spectrum at 153.3 K is strongly asymmetric. Taking into account the continuous character of the phase transition, we assumed that both line shapes can be described by the superposition of the two single peaks resolved at lower temperatures. All the spectra in the range 130–160 K were fitted with two Gaussian functions. Figure 4 shows the difference $\Delta\nu$ between the fitted frequencies of the peaks as a function of temperature. In order to estimate the transition temperature, a spline of the experimental data was extrapolated to $\Delta\nu=0$ giving the value $T_1=156\pm1$ K. Although the procedure gives only a rough estimate of the transition temperature in the film, it clearly shows an increase with respect to the bulk. This increase of the transition temperature could be expected if a compression on the BCPS thin film occurs. This compression has been observed in thin metallic and molecular films and small particles[26,27] and its origin lies in the van der Waals interactions between the film and the substrate.[28] In a more open structure than bulk, the molecular conformation could be mainly determined by intramolecular interactions, and consequently the competing intermolecular interactions could not perturb the stability of the periodic structure. Conversely, a more compact structure increases the intermolecular interaction energies. This fact could produce instabilities of the molecular conformation at higher temperatures.

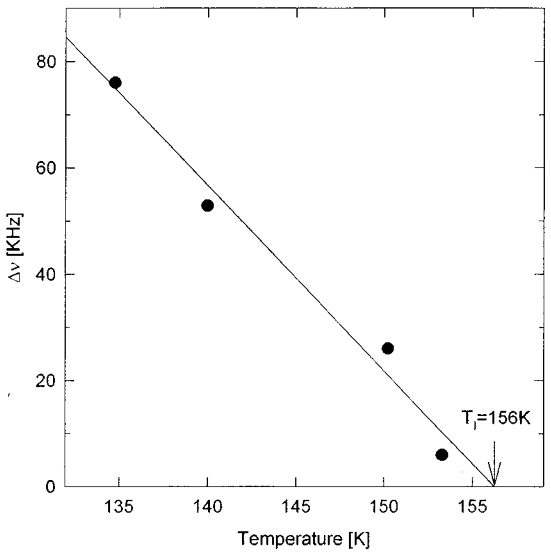

FIG. 4. Temperature behavior of the difference between the frequencies of two Gaussian functions fitted to the NQR spectra. Solid line: linear fit of the data. The extrapolation of the line to $\Delta\nu=0$ was used to estimate the transition temperature $T_1=156\pm1$ K.

CONCLUSIONS

The preceding discussion of the experimental results shows how the van der Waals interactions between the film and the substrate could perturb the crystalline potential. We have not found any report in the literature on the shifting of a second-order phase-transition temperature in molecular crystals thin films. More accurate determination of the transition temperature may be obtained by means of calorimetric measurements. Also, the temperature behavior of the NQR frequencies in the HTP shows structural and dynamical changes with respect to bulk samples. Taking into account the small shifting of the resonance frequencies in the film, the magnitude of the structural change could be small. The observed NQR spectra in the LTP suggest some qualitative change in the incommensurate modulation. The presence of the central intense peak could suggest an important contribution to the NQR spectra from periodic domains inside the film. This behavior resembles the soliton regime of the IC modulation.[29]

ACKNOWLEDGMENTS

J.S. and A.B. thank the Concejo de Investigaciones Científicas y Tecnológicas (CONICET), Argentina for financial support.

---

[1] *Phase Transitions in Surface Films II* (Plenum, New York, 1991), Vol. B267.

[2] S. Dietrich, *Phase Transition and Critical Phenomena* (Academic, New York, 1988), Vol. 112.

[3] J. M. Sanchez, F. Mejia Lira, and J. L. Moran Lopez, Phys. Rev. Lett. **57**, 360 (1986).

[4] J. F. Van der Veen, *Phase Transition in Surface Films II* (Ref. 1), p. 289.

[5] D. Sornette, Phys. Rev. B **31**, 2435 (1973).

[6] R. Mu and V. M. Malhotra, Phys. Rev. B **46**, 532 (1992).

[7] H. Cailleau, J. C. Messanger, F. Moussa, F. Bugaut, C. Zeyen, and C. Vettier, Ferroelectrics **67**, 3 (1986).

[8] H. Cailleau, *Incommensurate Phases in Dielectrics Materials*, edited by R. Blinc and A. P. Levanyuk (North-Holland, Amsterdam, 1986).

[9] V. Heine and S. Price, J. Phys. C **18**, 5259 (1985).

[10] J. Corberó, A. Wolfenson, D. Pusiol, and A. Brunetti, Phys. Lett. **114A**, 105 (1986).

[11] D. Pusiol, A. Wolfenson, and A. Brunetti, Phys. Rev. B **40**, 2523 (1989).

[12] J. G. Sime and D. I. Woodhouse, J. Cryst. Mol. Struct. **4**, 287 (1974).

[13] A. A. Chernov and V. A. Jacovlev, Langmuir **3**, 635 (1987).

[14] H. Nakayama, M. Kawahara, and K. Ishii, Chem. Phys. **178**, 371 (1993).

[15] F. Zúñiga, J. Perez-Mato, and T. Breczewski, Acta Crystallogr. B **49**, 1060 (1993).

[16] K. Ishii, H. Nakayama, T. Sakato, and H. Kano, J. Phys. Soc. Jpn. **61**, 2317 (1992).

[17] T. Tanaka, T. Atake, H. Nakayama, T. Eguchi, K. Saito, and I. Ikemoto, J. Chem. Thermodynamics **26**, 1231 (1994).

[18] J. Etrillard, J. Even, M. Sougoti, P. Launois, S. Longeville, and B. Toudic, Solid State Commun. **87**, 47 (1993).

[19] R. De Souza, M. Engelsberg, and D. Pusiol, Phys. Rev. Lett. **66**, 1505 (1991).

[20] J. Etrillard, B. Toudic, M. Bertault, J. Even, M. Gourdji, A. Péneau, and L. Guibé, J. Phys. (France) **3**, 12 (1993).

[21] J. Schneider, A. Wolfenson, and A. Brunetti, J. Phys. **6**, 11 035 (1994).

[22] D. Pusiol and H. Brunetti, J. Phys. C **17**, 4487 (1984).

[23] G. Jellison, G. Petersen, and P. Taylor, Phys. Rev. B **22**, 3903 (1980).

[24] A. Brunetti, J. Mol. Struct. **58**, 513 (1980).

[25] H. Chihara and N. Nakamura, *Advances in Nuclear Quadrupole Resonance*, edited by J. A. S. Smith (Heyden, London, 1981), p. 1.

[26] F. H. Streitz, R. C. Cammarata, and K. Sieradzki, Phys. Rev. B **49**, 10 699 (1994).

[27] M. Rappaz, C. Solliard, A. Chatelain, and L. A. Boatner, Phys. Rev. B **21**, 906 (1980).

[28] I. E. Dzyaloshinsky, E. M. Lifshitz, and L. P. Pitaewsky, Adv. Phys. **10**, 165 (1961).

[29] R. Blinc, Phys. Rep. **79**, 343 (1981); **79**, 395 (1981).