Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Raman Scattering Studies of the Disorder in A-TCNB and N-TCNB Crystals

Andrzej Mierzejewski [a]

[a] Institute of Organic and Physical Chemistry, Technical University, Wroclaw, Poland

Version of record first published: 04 Jun 2010.

To cite this article: Andrzej Mierzejewski (1993): Raman Scattering Studies of the Disorder in A-TCNB and N-TCNB Crystals, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 229:1, 63-68

To link to this article: http://dx.doi.org/10.1080/10587259308032177

Mol. Cryst. Liq. Cryst. 1993, Vol. 229, pp. 63–68
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

RAMAN SCATTERING STUDIES OF THE DISORDER IN A-TCNB AND N-TCNB CRYSTALS.

Andrzej Mierzejewski
Institute of Organic and Physical Chemistry, Technical University, Wrocław, Poland.

Abstract Raman scattering studies of the low-energy excitations in crystals of weak charge transfer complexes A-TCNB and N-TCNB are presented. The results are discussed in relation to a character of orientational disorder and expected mechanism of lattice instabilities in the measured systems.

INTRODUCTION

Weak charge transfer complexes between 1,2,4,5-tetracyanobenzene (TCNB) and aromatic donors like anthracene (A) and naphthalene (N) form a characteristic mixed-stack structure in the solid state. At room temperature, these crystals are isostructural with C2/m symmetry and one complex unit in the primitive cell[1] . The acceptor molecules build a rigid framework reinforced by dipol-dipol interactions of CN groups belonging to neighbouring TCNB molecules. Donor sublattices are orientationally disordered but the disorder has a different character in each case. It results from a competition between orientational coupling of donor molecules and steric hindrances created by H atoms of donors and CN groups of TCNB[2]. In the A-TCNB crystals, the first type of interactions is dominating and it leads to dynamical disorder of the anthracene molecules in the (102) plane. Thus, a phase transition to the ordered phase of $P2_1/a$ symmetry at 212 K has predominantly the displacive character and it is associated with a softening of a librational mode[3]. A strength of the orientational coupling between naphthalene molecules in the N-TCNB crystals is weak and the disorder has the static character. One can expect, that the phase transition to the ordered phase which occurs in this system at 73 K should be of the order-disorder type.

EXPERIMENTAL RESULTS AND DISCUSSION.

A large-amplitude librations of the anthracene molecules around normal to its plane are responsible for the dynamic disorder in the A-TCNB crystals[2]. In the spectra recorded at room temperature, there is no direct evidence of the disorder except a weak depolarization of the Bg mode at 26 cm^{-1}. A softening of this librational phonon at the M point of the Brillouin zone (BZ) boundry leads to the lattice instability at 212 K. Since the Raman scattering allows to study excitations in the BZ center only, the soft mode in the HT phase cannot be observed by this technic. However, such studies are possible below T_c where the soft mode becomes fully symmetric excitation in the BZ center. An evolution of the Ag symmetry spectrum in (ac) polarization as a function of temperature is presented on Fig. 1. On cooling, a quasielastic scattering is observed in the HT phase from about 240 K. It reaches the strongest intensity close to the phase transition and transforms smoothly into the soft mode band below T_c. The soft mode is strongly overdamped between T_c and about 195 K. Attempts to describe the spectra by a classical damped oscillator profile fail in this temperature range: the fitted soft mode tends to stabilise its frequency at a few wavenumbers and the damping constant diverges when temperature approaches T_c. These features in-

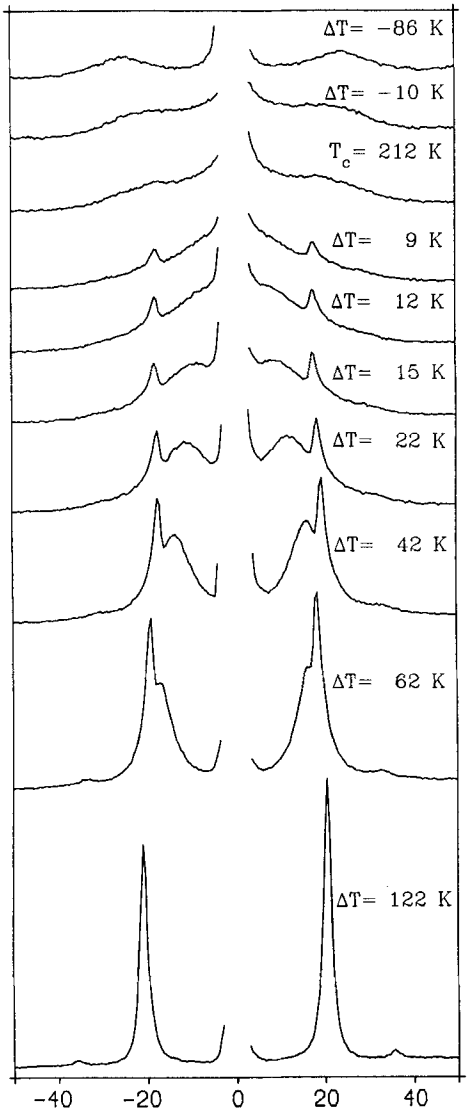

Fig. 1

dicate an important contribution of two-phonon processes to the intensity of Raman scattering in the low-energy spectral range[4]. Since the inelastic neutron scattering allows to probe one-phonon cross sections both above and below T_c, it can be used to testify the temperature range in which the Raman scattering is contaminated by two-phonon processes. According to recently published results of such experiments performed on $A(d_{10})$-TCNB crystals[5], both technics give significantly different energies and widths of the soft mode in the region where it is overdamped.

In the low temperatures (150 K - 90 K), the soft mode interacts with the Ag hard mode at 18 cm^{-1} and both modes gradually exchange their properties. Such anti-crossing phenomena are rarely observed in the Raman spectra.

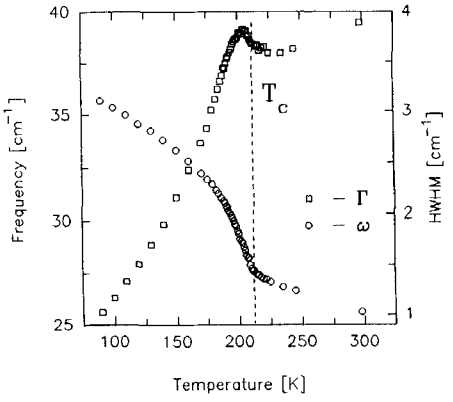

Fig. 2

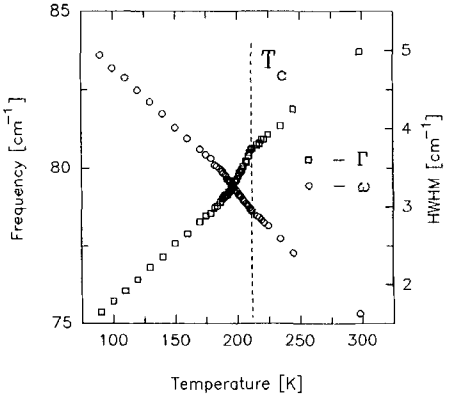

Fig. 3

In the HT phase, the Raman active Bg mode observed at 26 cm^{-1} belongs to the same phonon dispersion branch as the soft mode at the M point and both of them have the identical pattern of motion of the anthracene sublattice. Properties of this phonon below T_c are different than other hard modes (see Fig. 2). The frequency evolution can be explained in terms of biquadratic coupling between the order parameter and the normal coordinate of the Bg mode [6]. However, this type of coupling has no influence on the damping and it cannot be used to interpret anomalous behaviour of the band width in the vicinity of the phase transition. It is worthy to notice, that the band widths of these excitations behave in a similar way, i.e. it approaches a maximum value a few degrees below T_c.

Properties of the other hard modes in the A-TCNB are more or less similar to that ones of Ag mode presented in Fig. 3. The lattice instability has a very small influence on the frequency dependence on temperature changing only a little its inclination over 32 degrees below T_c. Simultaneously, the damping exhibits sligthly more distinct anomaly characteristic of the order-disorder instabilities. It suggests a complicated mechanism of the phase transition like that proposed recently by Luty et al.[7]. The main point of this approach is that the instability is of displacive type in the (102) planes of the anthracene sublattice and a crossover takes place to the order-disorder instability triggered by modulation of interactions between the planes by the soft mode.

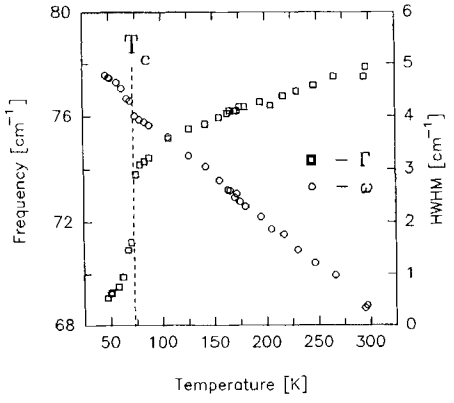

Fig. 4

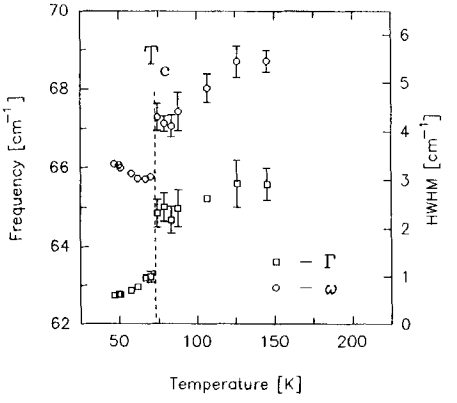

Fig. 5

Polarized spectra of the N-TCNB crystals in the HT phase exhibit several features characteristic of the disordered crystals. The most striking one is a broadness of all low-energy bands. A typical half-width value is found about 5-8 cm^{-1} and it depends strongly on temperature. As an example, the properties of the strongest Ag mode are shown in Fig. 4. Number of observed peaks in the lattice modes region exceeds group theoretical predictions. Intensities of redundant bands are usually small in the HT phase and they increase rapidly below T_c. These bands have been assigned to the fundamental lattice modes of the LT phase. The frequency and damping dependence on temperature observed for one of the redundant Ag band is presented in Fig.5. Moreover, a strong quasielastic scattering is seen in the (ab) polarization i.e. in the Bg symmetry spectrum (see Fig.6). The intensity and the width of the qua-

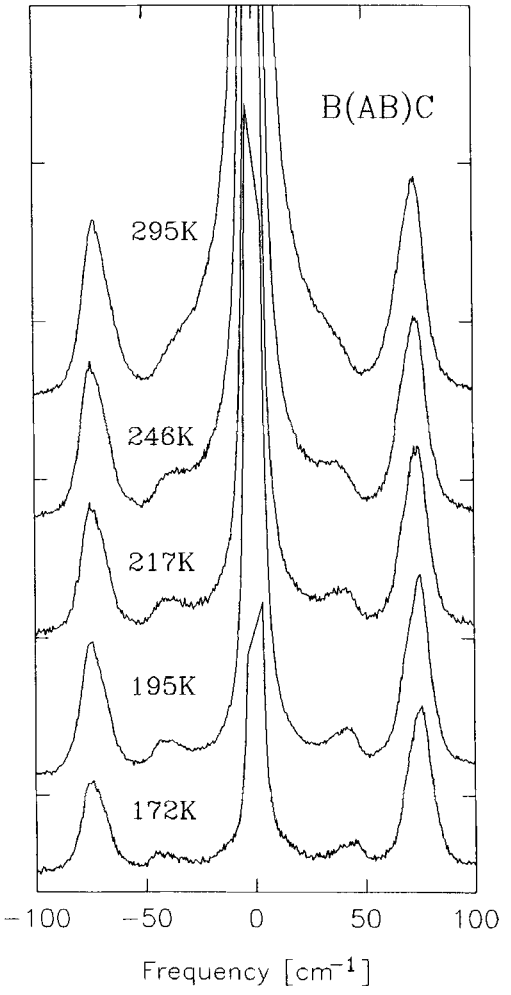

Fig. 6

sielastic peak decreases rapidly at lower temperatures and, finally, it vanishes about 160-170 K.

The above behaviour can be explained assuming a large number of dynamical clusters of the LT phase formed within the HT phase. A rapid jumps between equilibrium orientations of the naphthalene molecules in both phases give rise to the quasielastic peak. This motion slows down when temperature decreases and below 160 K it is no more detectable by the Raman spectroscopy. We suppose that the same phenomenon contributes to the quasielastic scattering already studied by means of the incoherent quasielastic neutron spectroscopy[8].

Further ordering processes lead to the phase transition at 73 K. It is accompanied by abrupt decrease of the damping and small changes of the mode frequencies. As the LT phase has lower symmetry, six new modes is observed below T_c but any of them exhibits soft mode properties. We have not seen any other critical phenomena like central peak in the vicinity of T_c. Spectra of the LT phase exhibit features of well ordered lattice: number of peaks and their polarization properties agree well with the predictions for $P2_1/a$ space group. All bands are sharp indicating small amplitude of the molecular librations.

CONCLUSIONS

Results presented in this paper can be explained in terms of sug-

gested type of disorder for each of the studied systems. Discovery of the soft mode in the A-TCNB is a spectacular confirmation of the displacive character of the phase transition and the dynamic type of disorder in the HT phase of these crystals. However, there are some subtle signs in the spectra which suggest more complicated model of the lattice instability being a combination of the displacive and order-disorder mechanism.

In the N-TCNB crystals, the HT phase structure seen by the Raman spectroscopy is heterogenous, i.e. it containes an important concentration of clusters of the LT phase. Reorientational movement of the naphthalene molecules between their equilibrium positions in "pure" HT and Lt phase is sufficiently fast above 170 K to give rise to the prounanced quasielastic peak observed in the Raman spectra.

REFERENCES

1. J. Lefebvre, G. Odou, M. Muller, A. Mierzejewski and T. Luty, Acta Crystallogr., B45, 323 (1989)
2. T. Luty and B. Kuchta, J.Chem.Phys., 85, 4032 (1986)
3. A. Mierzejewski, C. Ecolivet, G. S. Pawley, T. Luty, A. Girard and M.-H.Lemée, Solid State Commun., 65, 431 (1988)
4. R.A.Cowley in Raman Spectroscopy: Sixty Years On, edited by H. D. Bist, J. R. Durig and J. F. Sullivan, Vibrational Spectra and Structure, Vol. 17A, p. 1, (Elsevier , Amsterdam, 1989)
5. Ph. Bourges, M.-H. Lemée-Cailleau, P. Launois, F. Moussa, C. Ecolivet and A. Mierzejewski, Ferroelectrics, 109, 69 (1990)
6. Ph. Bourges, Thesis, (Rennes, 1989)
7. T. Luty and J. Lefebvre, J.Chem.Phys., 90, 7346 (1989)
8. K. Czarniecka, J. M. Janik, J. A. Janik, J. Krawczyk, I. Natkaniec, J. Wasicki, R. Kowal, K. Pigoń and K. Otnes, J.Chem.Phys., 85, 7289 (1986)