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High resolution Raman study of the soft mode in the incommensurate bis(4-chlorophenyl)sulfone

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Abstract. — The soft optical mode of bis(4-chlorophenyl)sulfone is analysed up to the incommensurate transition temperature T_i with both a tandem of Fabry-Perot interferometers and a triple monochromator. High resolution spectra (~ 4 GHz) of the soft mode reveal a mean field behaviour up to $T_i - 4$ K, but between T_i and this temperature the frequency of the soft mode saturates whereas its linewidth increases and its intensity decreases. The occurrence of second order scattering with a very slow decrease of its intensity above T_i precludes the explanation of the observed soft mode blocking by a divergence of the second order scattering. Different spectral profiles of the soft mode have been recorded in the (**bb**) and ($\gamma\gamma$) polarizations, γ being the principal dielectric axis parallel to the molecular long axis. Within single mode analysis, excess intensity is found between the soft mode and the longitudinal acoustic mode in the ($\gamma\gamma$) polarization. This intensity is assigned to a coupling effect between these modes whereas a phason contribution is ruled out for reasons of symmetry and temperature behaviour.

1. Introduction.

Bis(4-chlorophenyl)sulfone, abbreviated for convenience as BCPS, undergoes at about 150 K an incommensurate phase transition which was first identified by NQR resonance technique [1]. Resonance techniques are, with X-ray or neutron diffraction, among the rare techniques which can reliably detect the signature of an incommensurate order. Later on, 1st order satellites have been observed [2] below 150 K, then higher order ones (up to the 4th) at lower temperatures down to 13 K [3]. Surprisingly, the wavevector modulation $\mathbf{q}_k = \mathbf{a}^* \pm \delta \mathbf{b}^*$ varies very little between $\delta = 0.223$ at 150 K and $\delta = 0.213$ at 13 K. This precludes the attribution of calorimetric anomalies observed around 115 K [4] to a lock-in phase transition. However recent neutron scattering results [3] indicate that the higher order (2nd and 3rd) satellites grow noticeably around 120 K and this could be interpreted as a modification of the shape of the modulation between a sinusoidal regime and more rectangular modulation.

The origin of the incommensurability is still not established but common ideas involve an unstable molecular conformation instability like in biphenyl [5]. But since here the molecules are non-planar, the instability, if its origin is an internal molecular mode, may involve several

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distorsions. It has also been shown by Raman scattering in the gas phase [6] that some internal modes of the molecule can be as low as 25 cm^{-1} , but inside the crystal these modes are probably hardened by the crystalline field which usually strongly restricts internal degrees of freedom. However, additional information obtained in a recent X ray-diffraction study of the modulation [7] indicates a large translational contribution to the modulation pattern. Moreover, lattice dynamics calculations [8] involving the additional twisting of the chlorophenyl rings were able to predict a soft phonon branch at $\mathbf{q}_\pm = \pm 0.8 \mathbf{b}^* \pm 0.2 \mathbf{b}^* + \mathbf{a}^*$ in the first Brillouin zone.

A soft mode was in fact observed by Raman scattering in the incommensurate phase [6] but only at temperatures much lower than $T_i = 150 \text{ K}$. Actually this mode has always a very low frequency : 14 cm^{-1} even at 6 K and this precluded its observation above 130 K. However, its frequency behaviour looks Landau-like at least in this temperature range ($T < 130 \text{ K}$). Nevertheless this study ignored the damping of this mode and its frequency was only obtained from the maximum of intensity, moreover the damping of this mode is an important quantity since it is thought to be of the same order of magnitude as the phason one. The aim of our study is to obtain more quantitative results below 130 K and to follow the disparition of the soft mode as close as possible to T_i in the temperature range where the soft mode cannot be investigated by a conventional grating spectrometer.

2. Experimental.

Two growth methods have been used in order to obtain single crystals of BCPS with good results. Solution grown crystals were usually (**b**, **c**) plates with a longer dimension ($\sim 8 \text{ mm}$) along **b**, the typical thickness of crystals grown in benzene was about 2 mm. Thicker crystals were grown from a Bridgman method with typical dimensions ranging between 6-10 mm. Both kinds of crystals were of very good optical quality and no difference was observed in the thermal behaviour except for a slight difference ($\cong 1 \text{ K}$) in the transition temperature and in the shape of the anomaly which was observed by DSC [9].

BCPS crystallizes in the monoclinic system with the C_{2h}^6 space group. The two fold axis **b** is located on the molecule whereas in the perpendicular plane (**a**, **c**) the chlorine-chlorine axis, i.e. the molecular long axis, is called γ . This direction is also very close to the principal dielectric axis with the largest refractive index. Two cleavage planes were used in the preparation of samples ; (**b**, **c**) planes give very good surfaces but another one (**b**, γ) also gives good quality surfaces. Other faces were cut and polished with the smallest possible amount of damage in particular for those perpendicular to **b** and to α . This rectangular frame (α , **b**, γ) is obviously very close to the principal dielectric frame.

Samples were cooled by a temperature controlled flux of nitrogen inside a cryostat regulated by a three term temperature stabilization with a stability better than 0.1 K. Temperature was measured by GaAs diodes with an accuracy of 0.5 K.

Crystals were illuminated by an argon ion laser at 514.5 nm with a power never exceeding 150 mW. Analysis of the scattered light was either performed by a triple monochromator (DILOR Z 24) with a resolution slightly better than 1 cm^{-1} or by a tandem of Fabry Perot (F.P.) interferometers (SANDERCOCK). In order to reduce to a minimum the length of the optical beam, each interferometer was individually triple passed ; the resulting finesse of each one was about 60 and the individual free spectral range set to 7 cm^{-1} . In such conditions, the resolution was about 0.1 cm^{-1} and a very large Rayleigh rejection was achieved ($> 10^{12}$) with the possibility of observing quasi transverse Brillouin lines at 0.4 cm^{-1} . The stabilization of the tandem was obtained through a second photomultiplier which received a few percent of the main beam diverted by a thin glass plate. Each scan of the tandem, over 2 or 3 spectral ranges, lasted 1 s and was multiscaled in a memory with 512 channels ; typical spectra were obtained

in 3/4 of hour. An interferential filter blocked unwanted Raman lines and laser fluorescence whereas a polarizing prism achieved the polarization discrimination.

Maximization of the scattered light was obtained by matching the shape of the scattered volume to entrance optics : right angle scattering was used with the grating spectrometer and backscattering with the interferometer. At each experiment, data were stored in a PC for further processing.

3. Data reduction.

3.1 SINGLE MODE ANALYSIS. — Up to 135 K the maximum of the soft mode can be detected in the wing of the Rayleigh line by the grating spectrometer ; it is about 10 K higher than in the previous experiment [6] and, up to 141 K it is possible to fit the recorded spectra with a damped oscillator profile convoluted with the apparatus function. The damped oscillator intensity profile is given below in the case of Stokes process and is proportional to the imaginary part of the susceptibility $\chi_o^0(\nu)$:

$$I_R(\nu) = I_o [n(\nu) + 1] \Im m \chi_o^0(\nu),$$

$n(\nu)$ being the Bose factor and $\chi_o^0(\nu)$ being defined by :

$$(\chi_o^0(\nu))^{-1} = m^* [\nu_o^2 - \nu^2 - i \Gamma_o \nu]$$

where ν_o and Γ_o are respectively the frequency and the full linewidth of the oscillator whereas m^* represents its effective mass. In this temperature range, **a(bb)c** spectra recorded on a solution grown crystal show a Landau like frequency variation for the soft mode :

$$\nu_o = (1.2 \pm 0.03) \sqrt{149.8 \mp 0.6 - T} \text{ (cm}^{-1}\text{)}$$

where alternating signs indicate correlations between extreme values compatible with experimental data. In the same temperature range, Γ_o increases steadily from 1.4 cm⁻¹ at 87 K up to 3.3 cm⁻¹ near 130 K and then seems to remain constant.

The soft mode study in the immediate vicinity of T_i requires a more resolving instrument which should particularly present a very high contrast i.e. a very high rejection of the elastically scattered light.

Spectra recorded with the tandem of F.P. interferometers were obtained on Bridgman grown samples, some of them are displayed in figures 1a and 1b. Soft mode characteristics were found identical to those obtained with the Z24 spectrometer at lower temperatures. Several scattering configurations were investigated apart from the **a(bb)ā** or **α(bb)ā** spectra which, in agreement with [6], give the largest soft mode intensity. In particular, noticeable differences are observed between **α(bb)ā** and **α(γγ)ā** between 130 K and 150 K. Very strikingly in figure 1b the soft mode looks overdamped above 141 K in the (γγ) polarization whereas this seems to occur only above 148 K in the (bb) polarization. It looks as if some excess intensity would be located between the longitudinal acoustic mode and the soft mode. In contrast with usual Raman spectra, the wing observed near the soft optical mode does not belong to the Rayleigh line but to the longitudinal acoustic Brillouin line the maximum of which is three orders of magnitude larger than the soft mode one.

The Brillouin line itself should be theoretically described by the imaginary part of the susceptibility $\chi_a^0(\nu)$ of a damped oscillator convoluted by the apparatus function of the interferometer $\mathcal{A}(\nu)$:

$$I_B = I_a \{ [n(\nu) + 1] \Im m (\chi_a^0(\nu)) \} \otimes \mathcal{A}(\nu)$$

$$(\chi_a^0)^{-1} = \frac{p}{q^2} (\nu_1^2 - \nu^2 - i \Gamma_1 \nu)$$

where q is the phonon wavevector and ρ the specific mass, the other terms having a similar meaning as in χ_0^0 . In fact, the optical resolution and data sampling ($\sim 0.15 \text{ cm}^{-1}$) exceed Γ_0 so that the Brillouin lineshape is, to a good approximation, given by the instrumental profile. At low resolution as here, the F.P. tandem profile should be described by an

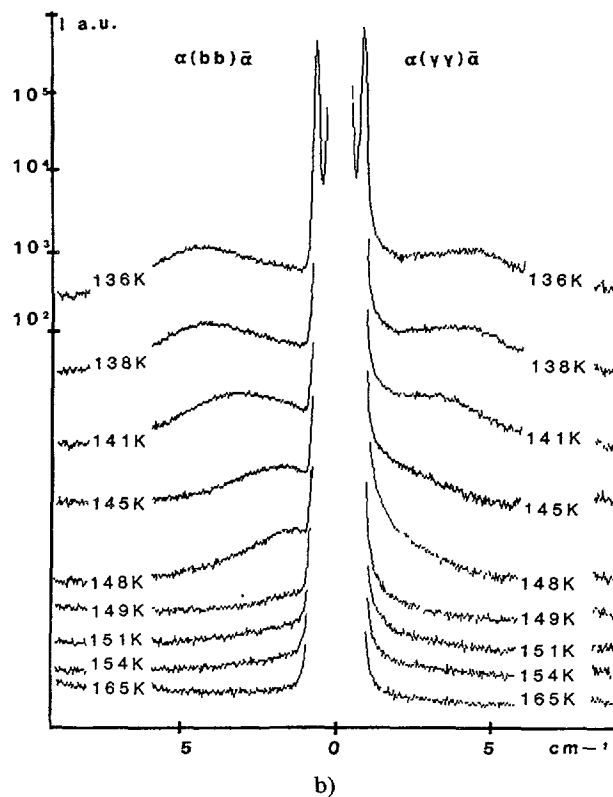
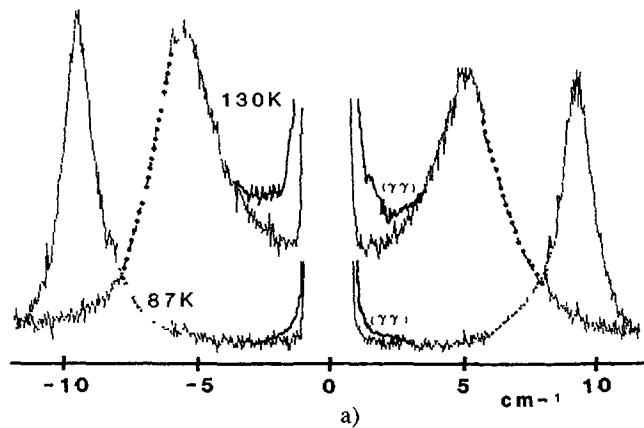


Fig. 1. — a) Low temperature spectra of the soft mode : lower traces at 87 K and higher traces at 130 K. At each temperature, the bolder trace, which differs from the other one between -3^{-1} cm^{-1} and 3 cm^{-1} , comes from $\alpha(\gamma\gamma)\bar{\alpha}$ whereas the other one comes from $\alpha(\text{bb})\bar{\alpha}$; vertical scale is linear. b) Temperature evolution of $\alpha(\text{bb})\bar{\alpha}$ and $\alpha(\gamma\gamma)\bar{\alpha}$ Stokes spectra. The intensity is in a logarithmic scale in order to better show longitudinal Brillouin and Raman components and their interference.

Airy function raised to the 6th power in order to reflect the six beams inside the interferometer, but due to some possible electronic jitter associated to a low sampling, it was found from fits that the instrumental profile was better described by a Lorentzian function raised to the power of 2.92. However, sufficiently steep functions, for example Gaussian functions, may also give an acceptable description. Actually, fits are not excellent over four decades but we always preferred functions which give a good description of the Brillouin wing.

Such a method gives perfect fits of experimental spectra up to 138 K for the **(bb)** polarization whereas the quality of fits decreases between the Raman and Brillouin lines at higher temperatures due to the appearance of a dip : the result of the fit looks like an average ignoring the dip. Then, the frequency and linewidth of the soft mode were mainly determined from the frequency range above the soft mode maximum.

The $(\gamma\gamma)$ spectra cannot be fitted by the same procedure above 140 K since they look like an overdamped soft mode profile in contradiction to the **(bb)** spectra. In fact, when using the soft mode frequency and linewidth derived from **(bb)** spectra for the fit of $(\gamma\gamma)$ spectra, we obtain an excess intensity which slightly increases around 140 K and strongly decreases close to 150 K. Notice that this excess intensity is already detectable at lower temperatures but the difference is so small that it can only be observed on a linear scale as in figure 1a where the upper trace at each temperature is always obtained with the $(\gamma\gamma)$ polarization. However care should be taken when comparing the intensities close to the Brillouin lines since the Brillouin shift is also larger in this polarization.

The **(bb)** fits show first that the soft mode frequency decreases with a Landau like behaviour up to 145 K where it saturates at approximately 2.7 cm^{-1} (Fig. 2). We may also notice a slight shift in the frequency *versus* temperature curve between the Z24 and the tandem results. This shift in the flatter region of the curve may attain 3 K although the 90 K frequencies are

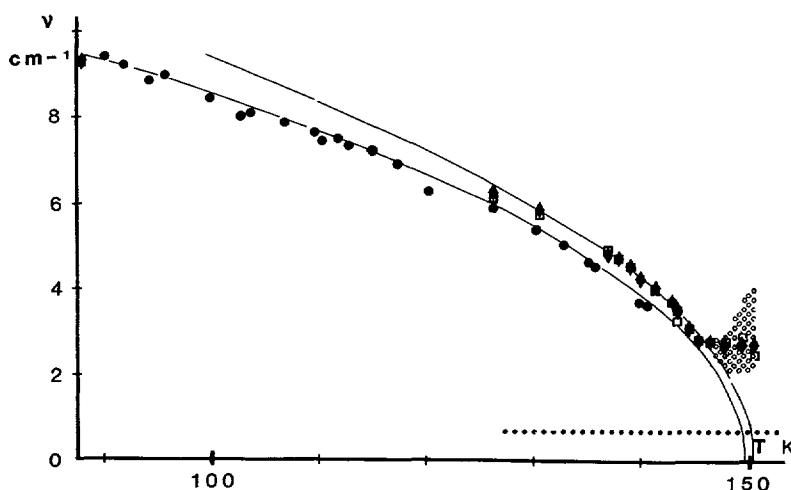


Fig. 2. — Temperature evolution of the soft mode frequency when spectra are fitted to independent oscillators with data obtained with a triple monochromator (\bullet) and the tandem (\square) or to coupled modes (\blacklozenge). There is an almost perfect overlap for these two last kind of points which lie close to the upper curve. At the lowest temperature (87 K) all data coincide. The shaded zone close to 150 K corresponds to the frequency range where fits are visually acceptable. Data from $\alpha(\text{bb})\bar{\alpha}$ experiments. Continuous lines represent the Landau like evolutions described in the text whereas the dotted line shows the Brillouin shift.

evolution of this component is not compatible with that expected for a Landau like phason which is expected to follow :

$$[n(\nu) + 1] \eta^2 / \nu_\varphi^2 \propto T(T - T_1)$$

where η is the order parameter and ν_φ the phason frequency which, for a given wavevector, is temperature independent in contrast to the amplitudon frequency which ideally cancels the order parameter variation in the above formula. So, instead of having a maximum near 140 K we expect one near $T_1/2$. Moreover, according to the theory of light scattering by phasons [10] one expects activity through 3rd order tensor terms R_{ijk} which should remain invariant in the group of the wavevector of the modulation. This group is reduced here to the C_{2v} rotation and identity so that the only finite terms are $R_{\alpha\alpha\gamma}$; $R_{\alpha\gamma\alpha}$, $R_{\alpha\gamma\alpha}$ and those with any permutation or repetition of subscripts involving α and γ which both belong to the (a, c) glide plane. In this notation with three subscripts the first two ones correspond to the dielectric tensor component whereas the last one refers to the component of the phason wavevector. Hence in backscattering the only Raman active configurations for the phason are expected to be : $\alpha(\mathbf{bb})\bar{\alpha}$ and $\mathbf{b}(\gamma\gamma)\bar{\mathbf{b}}$ with the same allowed operations on α and γ . Comparison with polarized spectra shows unambiguously that the excess component in $\alpha(\gamma\gamma)\bar{\alpha}$ is truly of Ag symmetry and incompatible with phason scattering theory.

3.2 COUPLED MODE ANALYSIS. — It is well known that the coupling between longitudinal acoustic modes and damped soft modes can produce dips in the spectrum at the upper wing of the longitudinal mode [11]. This dip requires a high resolution apparatus in order to be observed whereas Raman grating spectrometers often fail to detect this feature. Another consequence of this coupling is a down step at T_1 in the curve of the evolution of the acoustic velocity due to the disappearance of this coupling in the high temperature phase. Here we expect to find a weak coupling since the step in the velocity is quite small as revealed by higher resolution experiments. In the experiment reported here we have observed a relative velocity step of 2.3 ± 0.8 per cent along α in agreement with the higher resolution experiments which will be reported later.

Coupling effects are well described by coupled-mode analysis where the scattered intensity is written as :

$$I(\nu, T) = [n(\nu) + 1] 3m \left(\sum_{i,j=a,o} P_i P_j \chi_{ij}(\nu) \right)$$

where P_a^2 and P_o^2 are the integrated intensities of the acoustic and the optical modes and the χ_{ij} are the coupled susceptibilities defined by :

$$\begin{aligned} \chi_{ii}^{-1} &= (\chi_i^0)^{-1} - A^2(\chi_i^0)^{-1} \\ \chi_{ao}^{-1} &= \chi_{oa}^{-1} = [(\chi_a^0)^{-1} (\chi_o^0)^{-1} - A^2] / A \\ A &= K\eta \end{aligned}$$

where χ_i^0 are the uncoupled susceptibilities of the damped oscillator used in the previous paragraph. A , the coupling constant, was taken proportional to the order parameter which is assumed to vary like $\sqrt{T_1 - T}$ and from the magnitude of the elastic anomalies A is not expected to be much greater than $0.1 \nu_0$.

The essential modification induced by the coupling is due to the interference term $2 P_a P_o 3m (\chi_{ao})$ which introduces an asymmetry of spectral lines, and since the acoustic mode is very narrow, the modification looks like a steep dispersion profile centered on the

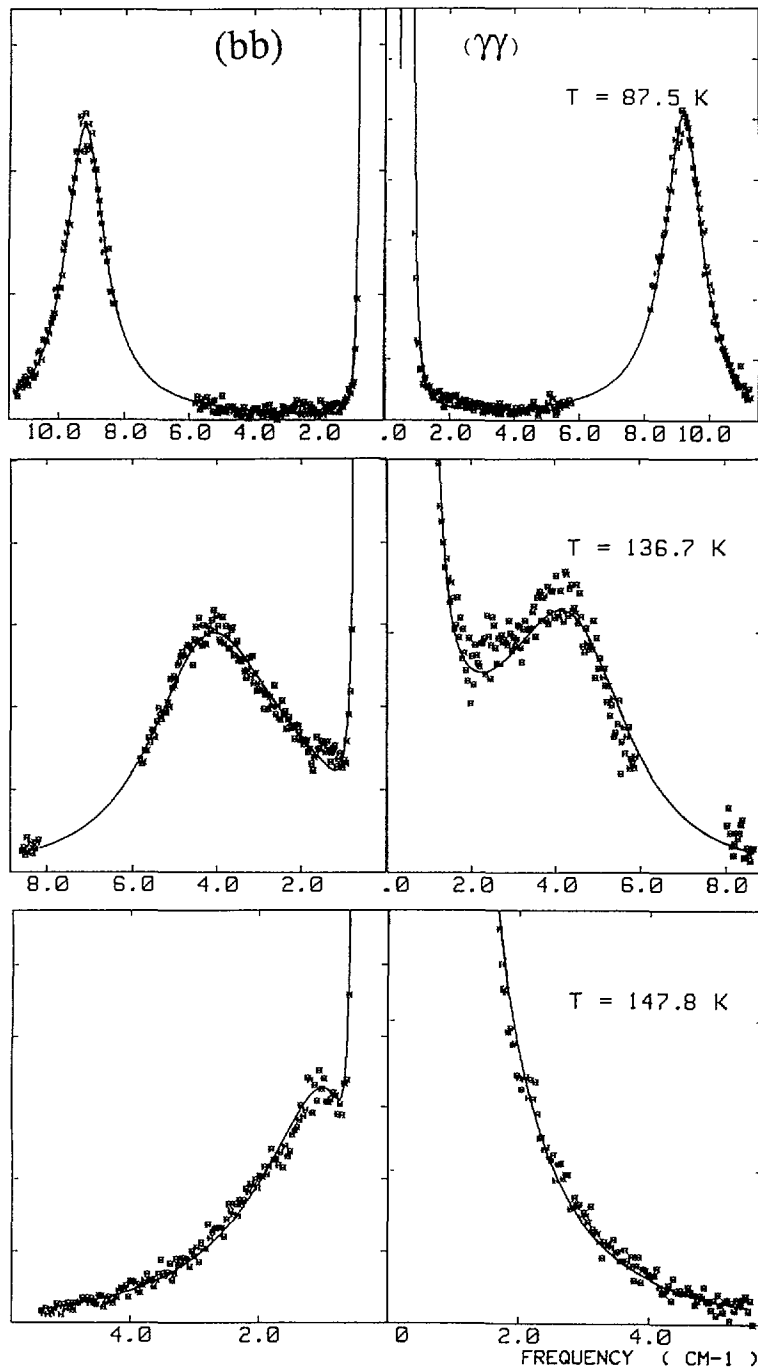


Fig. 4. — (bb) left, and $(\gamma\gamma)$ right, fits of the soft mode spectra by the coupled modes analysis. Soft mode frequency, linewidth and coupling constant are kept fixed in both polarizations. Background has been removed and spectra normalized to the same value of the soft mode maximum. The intensity scale is linear with arbitrary units.

acoustic frequency. This term involves the quantity $Aq\rho^{-1/2} = Kq[(T_1 - T)/\rho]^{1/2}$ which varies proportionally to the phonon wavevector and hence to the refractive index. The effect of the interference term is maximum when the optical mode is close to the acoustic mode but not too close to T_1 since this coupling then vanishes. $\alpha(\mathbf{bb})\bar{\alpha}$ spectra can easily be fitted up to 146 K with a constant coupling factor and free soft mode parameters. Above this temperature, ν_0 is kept constant for reasons that we will justify below and (\mathbf{bb}) spectra are fitted up to T_1 with a very nice agreement (Fig. 4). The most interesting result is that $(\gamma\gamma)$ spectra can also be nicely fitted by assuming that one of the P_{α} or P_{β} may be taken as negative. In that case very good fits are performed by using the same parameters for the soft mode and the coupling constant as those derived from (\mathbf{bb}) spectra (Fig. 4). This proves that the additional scattering is in fact a resonant interference for $(\gamma\gamma)$ polarization whereas this coupling is antiresonant for (\mathbf{bb}) .

The evolution of the soft mode parameters obtained by this procedure is quite similar to the results obtained without coupling except above 136 K where the plateau of constant linewidth is strongly reduced and perhaps even suppressed due to a progressive increase and slightly larger values of the linewidth by one additional wavenumber above 145 K. In fact, above this temperature the soft mode maximum has disappeared and strong correlations exist between the soft mode frequency, its linewidth and intensity so that a large number of solutions exist which give rather good fits with nearly equivalent results with respect to statistical tests. However, when the frequency differs too much from the optimum value, fits are visually less good with large fractions of the spectrum alternately above or below the computed values. It is also possible to determine in which range of the soft mode frequency we obtain good fits. The width of this range is smaller than 1 cm^{-1} at 148 K and although it increases to 2 cm^{-1} at 150 K, the lowest possible values of the soft mode frequency are always higher than 2.3 cm^{-1} and this confirms the saturation detected in the precedent paragraph. For this reason, above 146 K the soft mode frequency is kept at the value found at this temperature.

We should also stress here that the soft mode cannot be described as a relaxor close to T_1 , with a relaxation time $\tau(T) = \Gamma_0(T)/2\pi\nu_0^2$ since ν/ν_0 is not much smaller than unity. However strong correlations exist in this temperature range between ν_0 and Γ_0 but they are not complete like in a relaxor case. The evolution of these correlations is illustrated in figure 2 where close to T_1 the range of frequencies which gives acceptable fits increases like the linewidth.

4. Conclusion.

This study reveals several interesting features. The first one concerns the evolution of the soft mode which behaves almost like a typical mean field soft mode except very close to T_1 where the frequency saturates, the linewidth rapidly increases whereas the integrated intensity falls down to a much lower level. This finite level which remains constant over a few degrees above T_1 can reasonably be assigned to second order scattering by soft phonons. This second order scattering is often considered as the origin of the soft mode saturation when observed by Raman scattering, due to the fact that its intensity is expected to diverge at T_1 [12]. However this divergence should only be observed in the critical regime which usually does not exceed $10^{-3}T_1$. Here the situation is different since this intensity varies very slowly above T_1 and its behaviour is expected to be somewhat similar below T_1 , moreover the temperature range where this saturation occurs is much broader than the critical regime interval. It is possible that a coupling of the order parameter with a relaxing variable characterized by its Debye relaxation time can induce such a saturation which is then associated with the growth of a central peak taking its intensity from the soft mode. However, due to the presence of an intense elastically scattered light, this additional contribution could

not be observed. Such contributions are more likely to be observed with neutrons and a recent experiment has indeed detected an unresolved central peak [13] which, according to this picture, would correspond to a slowly relaxing variable. As usual, the nature of this variable is far from being identified.

This study has also shown the existence of resonant and antiresonant interferences of a longitudinal acoustic mode with the soft optical mode ; if the antiresonance effect, i.e. the dip, is well known, it is to our knowledge the first observation of the resonance or positive interference. This explanation rules out any phason contribution in the recorded spectra.

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