Incommensurate transition effect on a molecular Raman band in thiourea [SC(NH₂)₂] crystal

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Abstract. A molecular Raman band of thiourea [SC(NH₂)₂] crystal was studied as a function of temperature through the incommensurate and ferroelectric phases. The temperature-dependent splitting Δv of the molecular Raman band at $625\,\mathrm{cm}^{-1}$, corresponding to a $\pi(\mathrm{SCN})$ deformation mode of A_g symmetry in the paraelectric phase, was found to be best fitted by $\Delta(v^2) \propto (T_I' - T)^{0.54}$ below the incommensurate transition temperature T_I.

1. Introduction

Thiourea [SC(NH₂)₂] crystal, possessing D_{2h} point group symmetry in the paraelectric normal phase (n phase) above the incommensurate transition temperature $T_I \simeq 202\,\mathrm{K}$, adopts C_{2v} point group symmetry in the ferroelectric phase below the ferroelectric transition temperature $T_C = 169\,\mathrm{K}$. In between the two temperatures $T_I = 202\,\mathrm{K}$ and $T_C = 169\,\mathrm{K}$ the thiourea crystal has a wide temperature range of incommensurate modulation (see, for example, Denoyer and Currat 1986).

Raman spectra of thiourea crystals have been studied by many research workers (Chapelle and Benoit 1977, Delahaigue *et al* 1978, Wada *et al* 1978, Siapkas 1980, Winterfeldt and Schaack 1980, Farhi and Moch 1985) mainly to observe the soft-mode behaviour of the amplitudon associated with the incommensurate phase transition in the crystal. Strictly speaking the soft mode is not at the zone centre but at the incommensurate satellite point, so we can observe this soft-mode Raman band as the amplitudon only in the incommensurate phase (Wada *et al* 1978, Winterfeldt and Schaack 1980). The zone-centre mode of the soft-mode phonon branch in thiourea crystal belongs to the Raman-inactive B_{3u} representation in the paraelectric n phase but the Raman-active A_1 representation in the ferroelectric phase. The A_1 symmetry modes of the ferroelectric phase, where the soft mode belongs to, are derived from both A_g and B_{3u} modes of the paraelectric n phase. We thus expect that the A_g mode vibrations may not couple directly with the soft mode of B_{3u} symmetry in the paraelectric n phase but they may interact with each other in the ferroelectric phase where both A_g and B_{3u} modes merge into the same A_1 modes. The $625\,\mathrm{cm}^{-1}$ band of our present work is an A_g mode in the paraelectric n phase and corresponds to a molecular internal vibration of $\pi(\mathrm{NCS})$ deformation (Winterfeldt and Schaack 1980).

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2. Experimental

Thiourea [$SC(NH_2)_2$] single crystals were grown from saturated solution of thiourea in methyl alcohol at 30°C by a slow evaporation process for about one month to obtain a Raman sample of dimensions of 4 mm×5 mm×7 mm. Raman excitation was made by use of the Ar/Kr mixed-gas ion laser (Spectra Physics 165) operated at 4880 Å and 200 mW. A double-grating spectrometer (Spex 1403) was used to analyse the 90° scattered Raman signals and the signal processing was made by use of the photon counting electronics (EG&G/PAR 1105). Temperature control of the sample was made by use of the closed-cycle helium refrigerator cryostat (Air Products Inc./Displex). Sample temperatures were measured by a calibrated gold–chromel thermocouple and stabilised to within ±0.1 K. Spectral resolution was set to better than 2 cm^{-1}, corresponding to slit widths narrower than 125 μm.

3. Results and discussion

Although the low-frequency external lattice modes have been studied by Raman scattering in details (see §1) with respect to the amplitudon soft-mode problem, Raman studies of the molecular internal modes have not been paid much attention. However, Winterfeldt and Schaack (1980) found a very important phase transition effect on some molecular Raman bands in thiourea crystal, that is, several molecular Raman bands were observed to show a temperature-dependent frequency shift. They attributed this large frequency shift as due to a coupling between the order parameter η and the phonon Q in the form of $\eta Q^* Q$ or $\eta^2 Q^* Q$ in the mean field approximation. This coupling leads to a band splitting of either $\Delta(v^2) \propto \eta$ or $\Delta(v^2) \propto \eta^2$ respectively in the incommensurate phase between T_C and T_I (Winterfeldt and Schaack 1980). A different origin of the band splitting was suggested recently by Poulet and Pick (1986) as due to a NMR-type lineshape effect where the incommensuration-induced coupling between molecules leads to the vibrational band shape of the form

$$g(v) = A \left[1 - \left(\frac{v - v_0}{\eta \Delta v_0} \right)^2 \right]^{-1/2}$$

where η denotes the order parameter, v_0 the vibrational frequency in the paraelectric n phase, and Δv_0 the band width in the n phase. This lineshape effect can be seen to give a band splitting of the form $|\Delta v| \propto \eta$, i.e. $|\Delta v|$ instead of $\Delta(v^2)$ as proportional to the order parameter η.

In figure 1 we show the $b(cc)a$-polarised Raman spectra of thiourea crystal corresponding to the A_g modes of the paraelectric n phase. The weak band at 625 cm^{-1}, indicated by an arrow, corresponds to a molecular vibration of $\pi(SCN)$ deformation (Winterfeldt and Schaack 1980). This 625 cm^{-1} band was observed to show the temperature-dependent band splitting throughout the incommensurate and ferroelectric phases as illustrated in figure 2. We have measured the temperature-dependent Raman shifts of the splitted components v_1 and v_2 derived from the 625 cm^{-1} band as shown in figure 3. A small discontinuity is observed at T_C but a continuous increase of the splitting $\Delta v = v_1 - v_2$ is observed in both incommensurate and ferroelectric phases. No splitting was observed until the temperature was lowered below 200 K. It may be that the incommensuration order parameter η remains too small to give a strong $\eta Q^* Q$-type
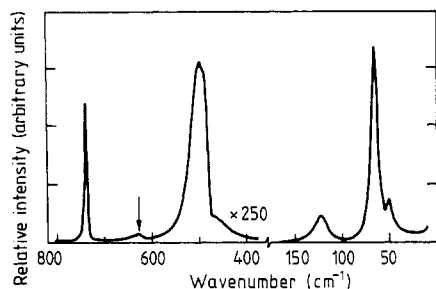
Figure 1. A$_g$-mode Raman spectra [$b(cc)a$] of thiourea crystal observed at room temperature (the 625 cm^{-1} band is indicated by an arrow).
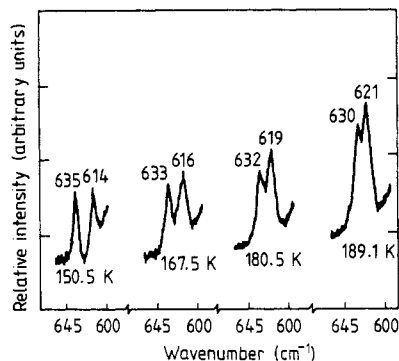

Figure 2. Temperature-dependent splitting of the 625 cm^{-1} Raman band in incommensurate and ferroelectric phases.

interaction for splitting until temperature falls below 200 K. Our crystal was cycled under high bias fields for the field effect study of our previous work (Kim and Kim 1988) and possibility exists for a slightly shifted transition temperature due to memory effects (Lederer *et al* 1986). Chapelle (1986) reports, for example, $T_I = 201$ K. We have presented the temperature dependence of the splitting Δv in log–log plots as shown in figure 4, where the best fit is obtained by $\Delta(v^2) \propto (T'_I - T)^{0.54}$.
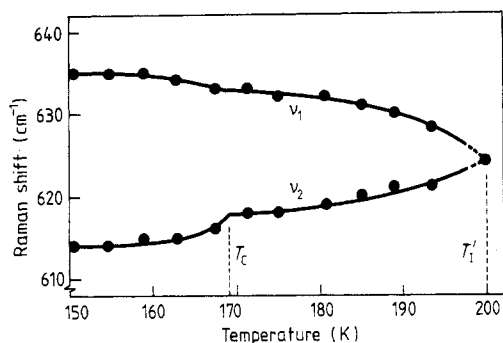

Figure 3. Temperature-dependent frequencies of the split Raman bands in incommensurate and ferroelectric phases. No splitting was observed until the temperature was lowered to below 200 K ($= T'_I$, see text).
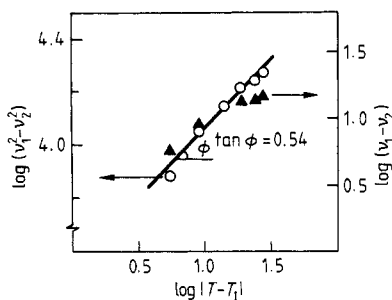

Figure 4. Log–log plot of the splitting dependence on temperature (full triangles represent data points of $\Delta v = v_1 - v_2$; circles represent data points of $\Delta(v^2) = v_1^2 - v_2^2$). Note the different scales for different axes so that tanϕ for the data line-of-fit of the circles is not 1.08 but 0.54.

Our result seems to conform with those of Winterfeldt and Schaack (1980) who obtained $v^2 - v_0^2 \propto (T_I - T)^{0.53}$ for an antisymmetric NH$_2$ stretching band and $v^2 - v_0^2 \propto (T_I - T)^{0.51}$ for a π(NCS) deformation vibrational band at 608 cm^{-1} where v_0 is the unperturbed frequency of the paraelectric n phase. However, some other molecular bands show splittings of $\Delta(v^2) \propto \eta^2$ (Winterfeldt and Schaack 1980) which may not be distinguished from $\Delta v \propto \eta$ of Poulet and Pick (1980) unless we go to much higher resolution in the Raman measurements.

4. Conclusion

Our Raman studies of the $625\,\mathrm{cm}^{-1}$ band, corresponding to the A_g-mode molecular vibration of $\pi(SCN)$ deformation, suggest that the $625\,\mathrm{cm}^{-1}$ band may have the $\eta Q^* Q$-type interaction and thus the band splitting of the type $\Delta(\nu^2) \propto \eta$ of Winterfeldt and Schaack (1980), where η represents the order parameter. Our Raman data of $\Delta(\nu^2)$ near T_C seems to imply that the spontaneous polarisation P_s and the incommensurate modulation amplitude η are proportional to each other at T_C in thiourea since the Raman data $\Delta(\nu^2)$ could be best fitted by the same temperature dependence of $(T'_I - T)^{0.54}$ across T_C, which conforms with the x-ray experimental work (Shiozaki 1971) on the temperature dependence of the order parameter.

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