CROATICA CHEMICA ACTA CCACAA **61** (3) 671—683 (1988)

YU ISSN 0011-1643
CCA-1818 UDC 543.42
Original Scientific Paper

Far Infrared Spectra, Phase Transitions, and Surface Layers

Armand Hadni and Xavier Gerbaux

University of Nancy I, B. P. n° 239, 54506 Vandoeuvre les Nancy

Received April 4, 1988

Measurements of Far Infrared transmission for ferroelectric plates of different thicknesses and orientations have suggested for a few compounds that at 4 K the samples are not homogeneous and can be described in a first approximation as having an absorbing surface layer and a bulk nearly transparent in the Far-Infrared.

A more detailed analysis suggests that the primitive unit-cell in the absorbing phase at low temperature is slightly modified when it is displaced from the center, to the crystal surface. The structure cannot be described simply by the lattice translations applied to one unit-cell and is reminiscent of incommensurate structures.

INTRODUCTION

Most crystals, and among them ferroelectric (FE) ones, show a number of lattice vibrations, the most famous being the soft mode. Some are infrared active and located in the far-infrared, between 10 and 300 cm^{-1}. They are ascribed to external lattice vibrations either translational or rotational ones with a wave vector $q \simeq 0$. In the last case, they are called librations[1]. The translational frequencies of large formula-units may perhaps be the lowest vibrational frequencies, and may be observed optically i. e. with $q \simeq 0$, implying that the primitive unit-cell contains at least two formula-units. It is the case of FE Triglycine Sulphate (TGS) and Guanidine Aluminium Sulphate Hexahydrate (GASH) crystals where at room temperature there are respectively two and three formula-units[2] which exhibit a dozen of absorption lines in the far-infrared.

We have made an extensive study of the far-infrared transmission of TGS and GASH. It is now possible to get a 3% accuracy in transmission measurements with sophisticated Fourier spectrometers, liquid helium cooled detectors, and small computers which not only give the Fourier Transform but also make summation of a number of spectra, averages, etc.... The result is that the era of quantitative measurements is opened in the far-infrared and new results can be expected even for crystals as complicated as TGS and GASH.

In the case of TGS, TGSe and GASH, far-infrared spectroscopy has recently shown some evidence that thick single crystal plates of any orientation are not homogeneous at 4 K, with an absorbing thick surface-layer and a quite transparent bulk.

We shall review the most important experimental facts, sending the reader to more detailed papers,[4-5] to see how different possible artifacts have been rejected, and we shall suggest here the possibility of a new kind of superstructure which should explain the heterogeneities obserwed at 4 K.

I — TGS SINGLE CRYSTALS

Triglycine sulphate, in spite of its complicated structure[2,3], is one of the most studied FE crystals because of an easy growth and a number of interesting properties which have sometimes led to applications.

I.1. — Thick Crystal Plates are not Homogeneous at 4 K for Far-Infrared

Figure 1 gives at 4 K the transmission of a thin crystal plate (thickness $t = 13$ µm) cut parallel to both the monoclinic C_2 axis and the X direction[2]. The electric field E of the far infrared radiations is polarized parallel to C_2. There are clearly fourteen absorption lines in the spectral range considered (20 to 140 cm^{-1}) which are probably due to external vibrations. The spectrum can be reconstructed in terms of pseudo-harmonic damped oscillators and multi-reflections in the parallel planes plate. Table I gives the oscillators parameters for the 21 low frequency infrared active oscillators. Such a large number of oscillators is the burden associated with so complicated crystals as TGS, but it can be handled with a small modern computer. From Table I, the complex refractive index $\overline{n} = n - jk$ is calculated vs frequency, and from n and k, the transmission curve is obtained, taking into account all multiple reflections in the crystal plate. Oscillator strengths and damping coefficients in Table I have been adjusted to get a good fit to Figure 1.

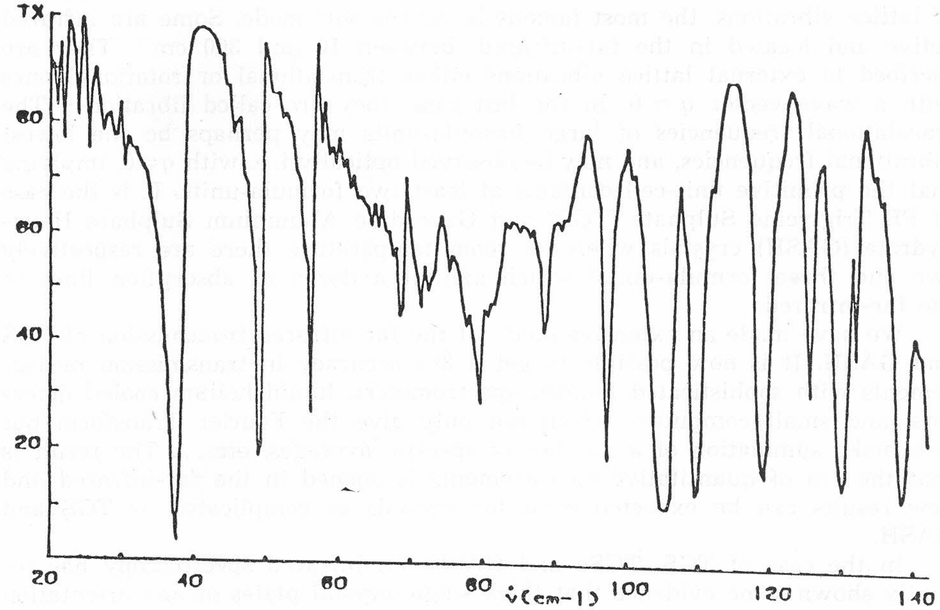


Figure 1. Observed far-infrared transmission spectrum at 4 K for a (C_2, X) plate of TGS, 13 µm thick with the electric field of the far-infrared radiation $E // C_2$.

TABLE I

TGS Oscillators, 4 K, $E // C_2$, $t = 13$ µm. Oscillators with Frequencies Higher than 140 cm^{-1} Give a Very Small Contribution to the Transmission Spectra Considered in the Paper ($\nu < 140$ cm^{-1}). Their Parameters are not Needed with a High Accuracy and are Computed from a Previous Study; $\varepsilon_{RV} = 4.4$

ν cm^{-1}	$\Delta \varepsilon_R$	$\delta \sim d\nu/\nu$
37.3	0.720	0.0078
49.2	0.060	0.0035
56.1	0.040	0.0060
68.9	0.018	0.0080
79.5	0.034	0.0100
88.6	0.010	0.0080
97.1	0.050	0.0100
105.0	0.140	0.0200
109.5	0.040	0.0080
119.0	0.050	0.0110
125.5	0.015	0.0080
129.9	0.055	0.0150
132.3	0.006	0.0040
138.3	0.080	0.0200
149.0	0.014	0.0200
170.0	0.150	0.0200
200.0	0.300	0.0200
215.0	0.700	0.0200
221.0	0.300	0.0200
250.0	0.250	0.0200
301.0	0.250	0.0200

From Table I, transmission spectra for crystal plates of any thickness can be immediately computed assuming only the samples are homogeneous and keep their oscillator parameters when, for instance, the thickness is increased. Figure 2-a gives the computed spectrum for $t = 1$ mm and it is seen that for the 6 lowest frequency lines, transmission T should go to zero, and also for $\nu > 100$ cm^{-1}. The observed spectrum is given in Figure 2-b and shows a much higher transmission in the whole spectral range even from 100 to 140 cm^{-1} where transparency peaks are observed, smaller than 3%, but higher than uncertainties in measurements.

It is thus seen that while thin crystal plates cut parallel to C_2 with $t \leqq 13$ µm are optically homogeneous for far-infrared radiations, thick crystal plates are not. In the simplest model, there is a surface layer with thickness $t_o/2 = 6.5$ µm where oscillator parameters are given by Table I (i. e. the same parameters as in the thin crystal plate considered above), and a quite transparent bulk described by a new table, with same frequencies but smaller strength parameters.

The conclusion is not confined to crystal plates cut parallel to C_2, but has been extended to any cut, and any orientation of E. For instance, Figure 3 gives in full lines the observed transmission of crystal plates cut perpendicular to C_2, with $E//Z$. One plate is 4 µm thick, the other one is 2 000 times thicker ($t = 8\,000$ µm). It is seen that for the lines at 50 and 57 cm^{-1} the transmission is comparable! In contrast, the calculated transmission for $t = 8$ mm is zero not only at 50 and 57 cm^{-1} but also for $\nu > 80$ cm^{-1}.

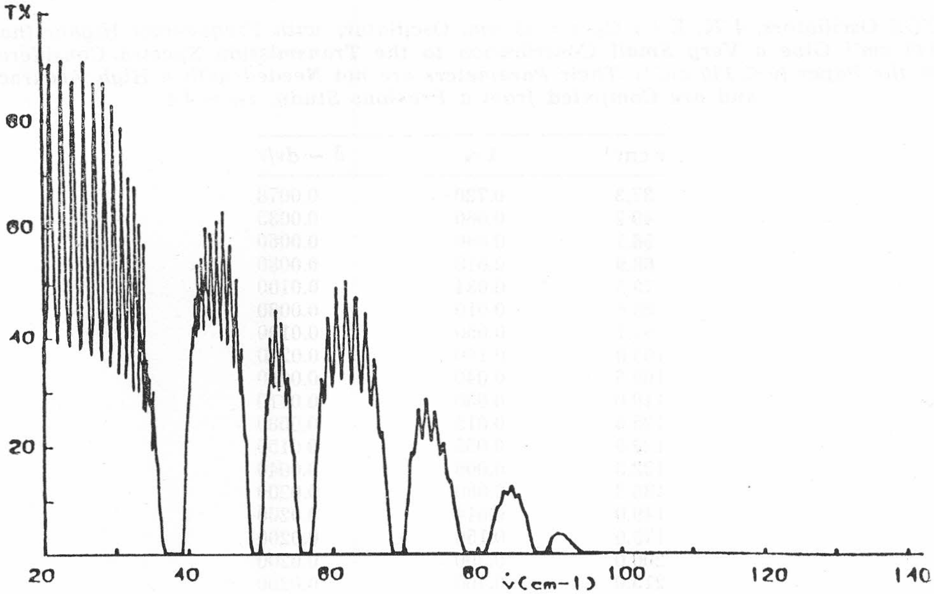


Figure 2a. Calculated spectrum at 4 K for a (C_2, X) plate of TGS, 1 mm thick, $E // C_2$, from Table I.

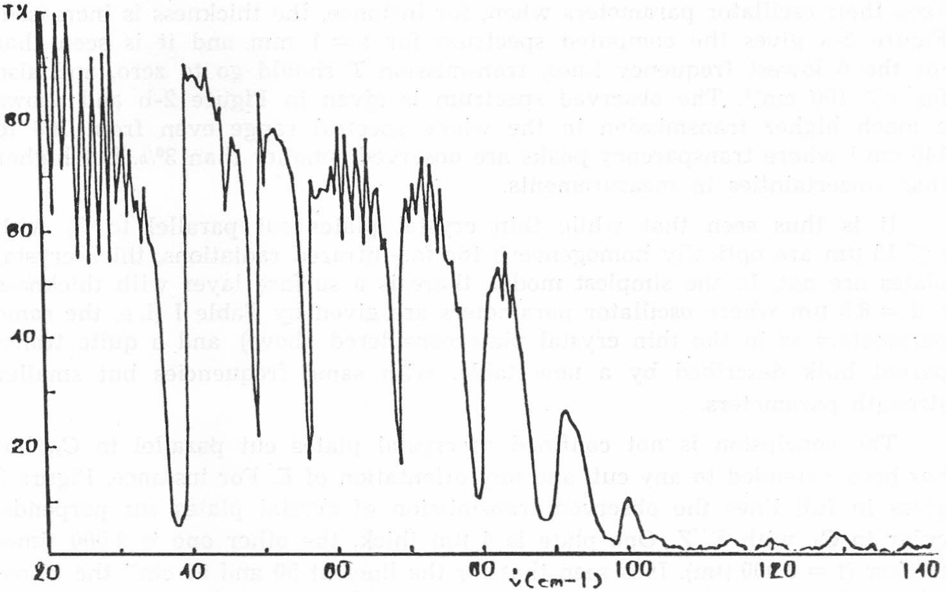


Figure 2b. Observed spectrum for the above considered 1 mm plate: much higher transmission than calculated.

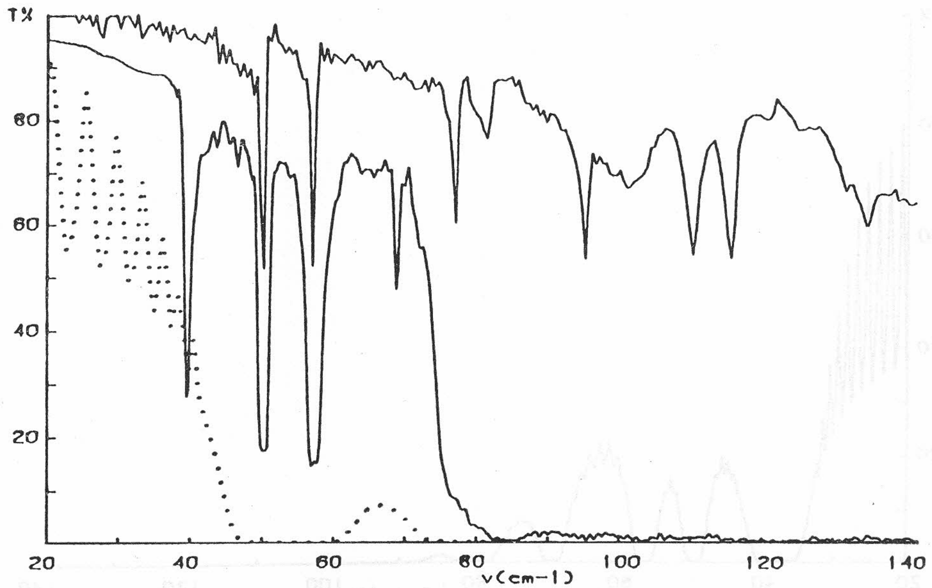


Figure 3. In full lines, observed spectra of (*X*, *Z*) plates of TGS thickness $t = 4$ μm and $t = 8000$ μm, with $E // Z$ and $T = 4$ K. In dotted line the computed spectrum for $t = 8000$ μm, assuming homogeneity and oscillator parameters taken in a suitable table which gives a good fit to the 4 μm thick plate spectrum: the calculated transmision is dramatically smaller than what is observed.

I.2. — Thick Crystal Plates Look Homogeneous at 80 K for Far-Infrared Radiations

Figure 4 gives the computed transmission spectrum at 80 K for the same one mm thick crystal plate considered above. The calculation is made with a new table where the oscillator parameters are the same ones as in Table I ($T = 4$ K), except for a higher damping.

The transmission spectrum at 80 K has been observed, and indeed the fitting given by Figure 4 is fairly good. The conclusion is that the bulk transparent phase we have to consider at 4 K gradually disappears when temperature is increased up to 80 K. At 80 K, the sample looks homogeneous as if it were completely filled with the absorbing phase which at 4 K was confined to the surface layer.

I.3. — Spontaneous Polarization Increasing Smoothly Down to 4 K, Dielectric Permittivity Decreasing With a Step Variation Between 80 K and 4 K

Figure 5 shows that spontaneous polarization P_s is smoothly increased by 1.5 μC/cm² when temperature T decreases from 300 K to 4 K.

Figure 6 gives the dielectric permittivity ε_R and shown a decrease $\Delta\varepsilon_R = 4.5$ from 80 K to 4 K. It has to be compared with the total contribution given by all far-infrared oscillators parallel to C_2 with frequencies ranging

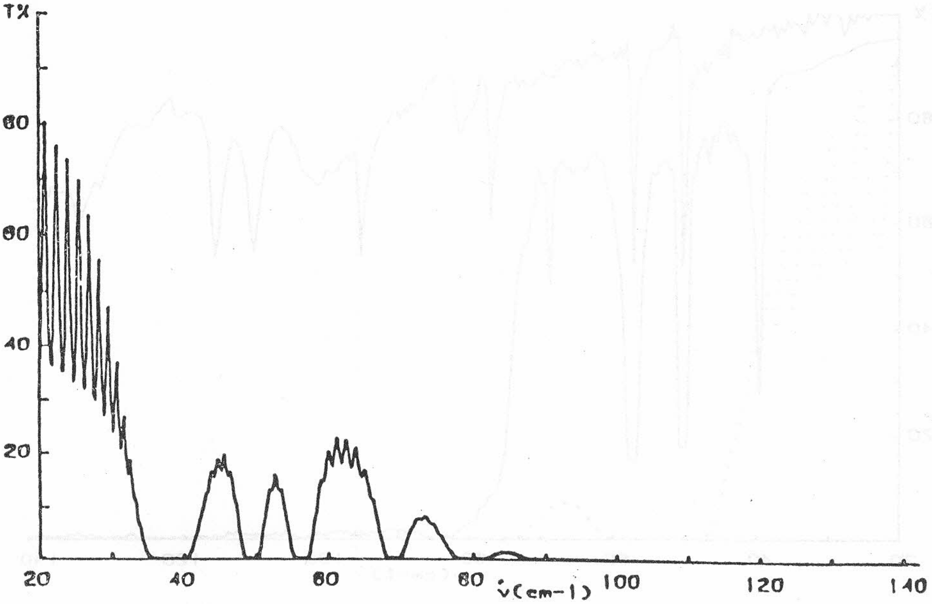


Figure 4. Calculated spectrum at 80 K for the TGS plate 1 mm thick considered above at 4 K, with $E // C_2$, assuming homogeneity and oscillator parameters adjusted to give a good fit to the 13 μm thick TGS plate at 80 K.

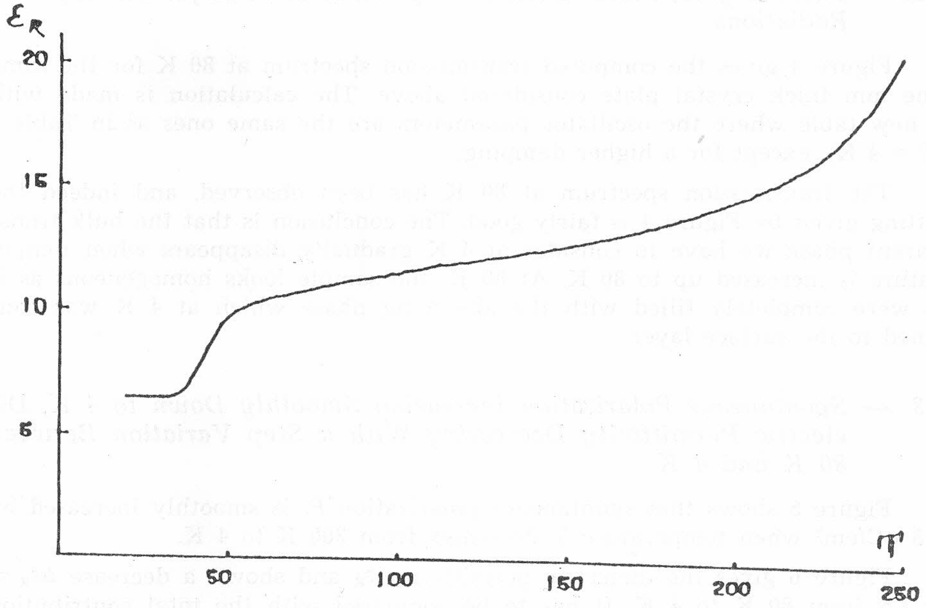


Figure 5. Observed decrease of spontaneous polarization in TGS from 4 K to 300 K.

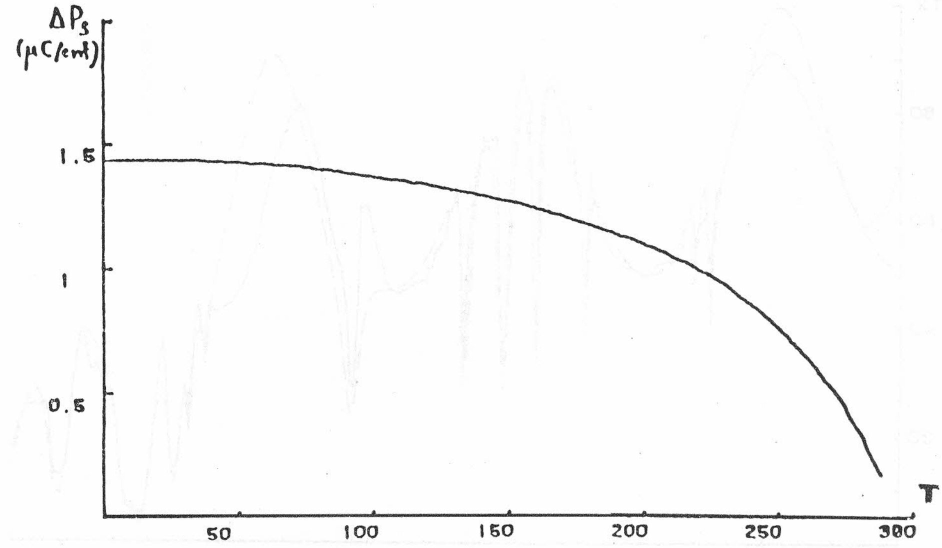


Figure 6. Increase in TGS electric permittivity ε_R from 4 K to 250 K.

from 37 to 301 cm^{-1}: $\Delta\varepsilon_{IR} = 3.5$, plus the Debye contribution $\Delta\varepsilon_D$. Assuming a simple law $\varepsilon_D = \frac{C_F}{T_c - T}$, with $C_F = 672$ K,[7,8], we get $\Delta\varepsilon_D = 0.7$, and $\Delta\varepsilon_{IR} + \Delta\varepsilon_D = 4.2$. This is the right order of magnitude and an additional argument to support our model but the reproducibility of dielectric constant measurements is not good in the case of TGS at low temperatures[7]. However, it shows that the surface layer thickness for a TGS plate cut perpendicular to C_2 is small compared to the total plate thickness ($t = 20$ μm), which is indeed our assumption to explain the far infrared spectra of such plates (see ref. 5 where $t_o/2 = 2$ μm is assumed).

II — GASH CRYSTALS

II.1 — Thick GASH Crystal Plates are not Homogeneous at 4 K for Far-Infrared Radiations

Figure 7 (solid line), gives the observed transmission spectrum of a thin GASH crystal plate cut perpendicular to the C_3 axis ($t = 55$ μm). A number of lines are observed between 20 and 140 cm^{-1}. Table II gives a set of oscillator parameters which allows a good fit to the transmission spectrum (Figure 7, dotted line). It is seen in Table II that oscillator strengths are one order of magnitude smaller than in a TGS plate cut parallel to C_2 (i. e. Table I).

Figure 8 (dotted line) gives the transmission spectrum calculated for a much thicker crystal plate ($t = 8\,500$ μm) assuming it is homogeneous. Transmission goes to zero at 50 cm^{-1}, and stays to zero for $\nu > 70$ cm^{-1}.

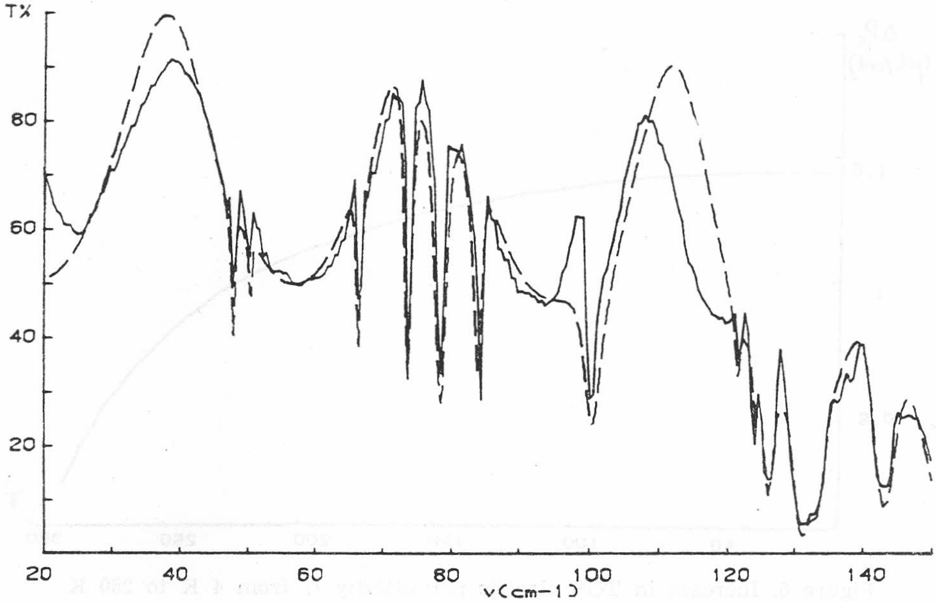


Figure 7. Full line: observed far infrared transmission spectrum at 4 K for a GASH plate 55 μm thick cut perpendicular to the C_3 axis.
Dotted line: calculated spectrum, from Table II whose parameters have been adjusted to give the best fit to the observed transmission spectrum.

TABLE II

GASH Oscillators, 4 K, $E \perp C_3$, $t = 55\ \mu m$, $\varepsilon_{RV} = 5$

ν cm^{-1}	$\Delta\ \varepsilon_R$	$\delta \simeq d\nu/\nu$
48.0	0.0080	0.011
50.5	0.0034	0.007
66.4	0.0075	0.011
73.7	0.0120	0.014
78.5	0.0187	0.021
84.0	0.0084	0.014
100.3	0.0192	0.028
121.5	0.0017	0.007
124.0	0.0012	0.003
126.0	0.0115	0.013
131.0	0.0250	0.018
133.2	0.0150	0.019
143.0	0.0170	0.020
155.0	0.1000	0.045
163.0	0.0080	0.025
172.0	0.0033	0.021
183.0	0.0080	0.042
205.0	0.0750	0.030
250.0	0.3750	0.014

Figure 8 (full line), shows the observed transmission is much higher than computed. We come to the same conclusion as for TGS: thick crystal plates at 4 K show much weaker absorption than expected from thin crystal plates

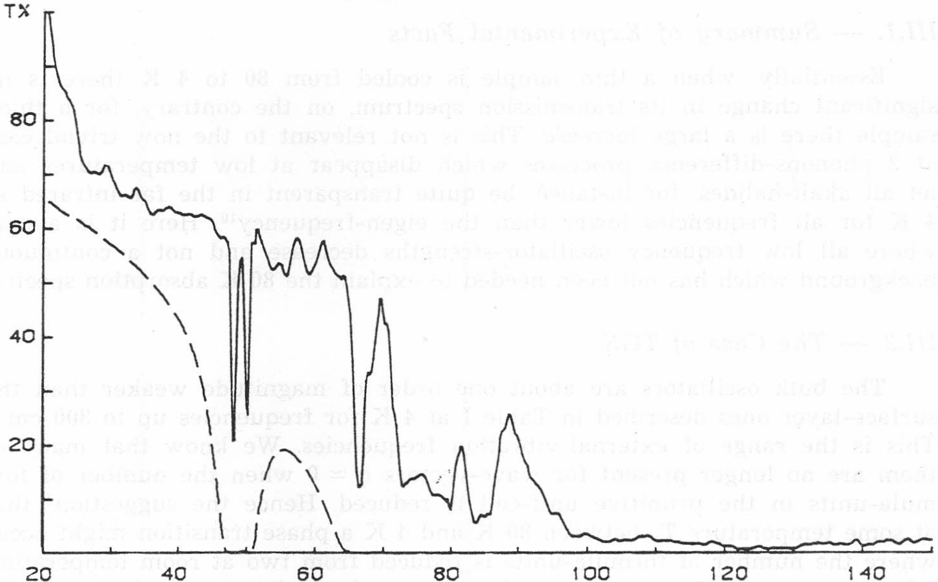


Figure 8. Dotted line: Calculated spectrum at 4 K for a GASH plate 8,500 μm thick, cut perpendicular to C_3

Full line: Observed spectrum at 4 K for the above considered GASH plate 8,500 μm thick, cut perpendicular to C_3: much higher transmission than computed.

data. A surface layer model is again a first approximation with oscillator parameters given by Table II. for the surface layer and a new table for the bulk which is quite transparent, and assuming the surface layer is 100 μm thick, i. e. much thicker than in TGS.

II.2. — Thick GASH Crystal Plates are Homogeneous at 80 K for Far Infrared Radiations

The observed spectrum at 80 K for the same GASH crystal plate 8 500 μm thick considered above is very close to the computed one at 4 K assuming homogeneity (Figure 8, dotted line). We are led to the same conclusion drawn for thick TGS samples: at 80 K the bulk has taken the high values of oscillator strengths which are the privilege of the surface at 4 K.

II.3. — Variation of Spontaneous Polarization and Dielectric Constant Between 80 K and 4 K

We have not yet made any measurement. However, the oscillator strengths being smaller than in the case of TGS, the far infrared contribution to the dielectric constant is small ($\Delta\varepsilon_{IR} = 0.72$ from Table II). The static dielectric constant at room temperature is also much smaller than for TGS, $\varepsilon_R = 5.1$ for E perpendicular to the C_3 axis.

III — TENTATIVE EXPLANATION

III.1. — Summary of Experimental Facts

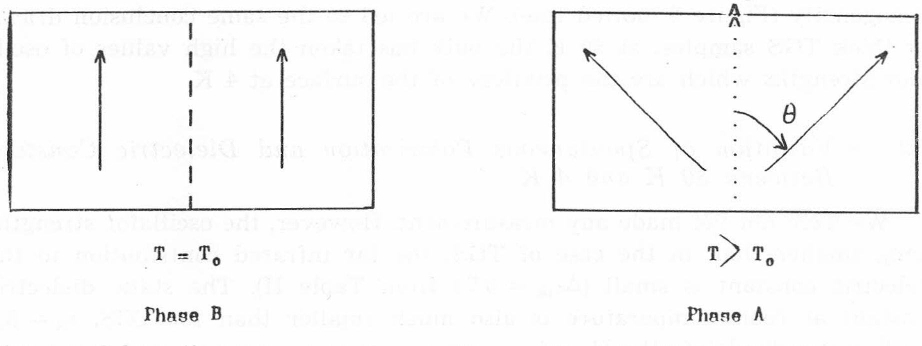
Essentially, when a thin sample is cooled from 80 to 4 K there is no significant change in its transmission spectrum, on the contrary, for a thick sample there is a large increase. This is not relevant to the now trivial case of 2 phonons-difference processes which disappear at low temperatures and let all akali-halides, for instance, be quite transparent in the far infrared at 4 K for all frequencies lower than the eigen-frequency[10]. Here it is a case where all low frequency oscillator-strengths decrease and not a continuous background which has not been needed to explain the 80 K absorption spectra.

III.2 — The Case of TGS

The bulk oscillators are about one order of magnitude weaker than the surface-layer ones described in Table I at 4 K for frequencies up to 300 cm^{-1}. This is the range of external-vibration frequencies. We know that many of them are no longer present for wave-vectors $q \simeq 0$ when the number of formula-units in the primitive unit-cell is reduced. Hence the suggestion[4] that at some temperature T_0 between 80 K and 4 K a phase transition might occur where the number of formula-units is reduced from two at room temperature (phase A), to one. The transition should start from the center of the sample, and only if it is thick enough.

At room temperature we know that the two formula-units are symmetric through the C_2 axis. Each one is bearing an electric dipole moment (Figure 9) and the two dipoles make an angle Θ. The division of the primitive unit-cell at T_0 means that the two dipoles have become parallel at that temperature, i. e. $\Theta = 0$ and the total electric dipole in the double cell is maximum. As we have seen that P_s increases smoothly when temperature is decreased from 300 K to 4 K(Figure 5), this should mean that Θ also decreases monotonously, giving a simple explanation to the increases of polarization down to T_0.

At a temperature lower than T_0, transparent phase B should extend from the centre to the surface of the sample, and at 4 K the absorbing phase A should persist only as a surface-layer (thickness $t_0/2 \cong 6.5$ µm for plates cut parallel to C_2). At lower temperatures, the surface layer thickness should still



$T = T_0$ Phase B

$T > T_0$ Phase A

Figure 9. Schematic approach to the primitive unit-cell in TGS at low temperatures.

decrease and P_s attain its asymptotic value. In this range of temperatures, the TGS crystal is not homogeneous, made with phase B in the center (i. e. $\Theta = 0$), and phase A outside. It is difficult to imagine a sharp boundary but rather a smooth increase of Θ up to the surface. Thus, phase A should not be homogeneous since application of lattice translation is not enough to reproduce the crystal structure, but we must also slightly increase angle Θ when we look at primitive unit-cells closer to the surface. Such a structure for phase A is reminiscent of incommeasurate structures.

At temperatures above T_o, and in a limited range of temperatures, phase A will probably stay inhomogenous with a small but definite value of Θ in the center, and a larger value outside. At $T = 80$ K, the crystal has been shown homogeneous, made of the same phase which has been observed at 4 K in the thinner plates and which has been assumed to constitute the surface layer.

In conclusion, there might be a subtle phase transition in TGS which should start at around 80 K with first some disorder introduced by a decrease of angle Θ in the center of the samples if thick enough, until it is zero at T_o and transparent phase B occurs.

More data are needed to confirm this scheme. The increase of transparency in the far infrared means a decrease in the number of far-infrared active oscillators and a decrease in static dielectric constant. This has been observed and appears in good quantitative agreement with Table I if all its oscillators with frequencies up to 300 cm^{-1} are assumed to become infrared inactive in phase B. The observation of X-Rays diffraction patterns from 80 to 4 K has not shown significant changes but is not a proof there is not some kind of phase transition[13]

III.3. — The Case of GASH

The above considerations are applicable to GASH. The only difference is that oscillator strengths in absorbing phase A are somewhat weaker, and also that the surface layer thickness at 4 K is larger ($t_o/2 \cong 100$ μm). There are 3 formula-units in the primitive unit-cell and the structure is still more complicated than in the case of TGS.

CONCLUSION

There are at least three crystals (TGS, TGSe and GASH) where an extensive study of far-infrared transmission in thick crystal plates has given a hint of a decrease of oscillator strengths when temperature is decreased from 80 to 4 K. It might be due to a lack of homogeneity, with a surface layer practically unchanged from 80 to 4 K, and a quite transparent bulk at 4 K. We have to admit that such high quality crystals are not homogeneous at low temperatures. A few other cases of thick surface layers, i. e. heterogeneities have been uncovered, by elastic measurements in $SrTiO_3$ [14], and $KTaO_3$,[16] or by comparison of Raman scattering and far-infrared reflection on $TlGaCe_2$ [15]. In both crystals the phase transition starts first in the surface when the crystal is cooled. There is also the case of KNO_3 where a thin crystal plate is still FE at room temperature while the bulk one losses its FE properties for $T < T_c = 113$ °C [16]. In this case, the phase transition starts first in the bulk as in the present study on TGS, TGSe and GASH (Figure 10).

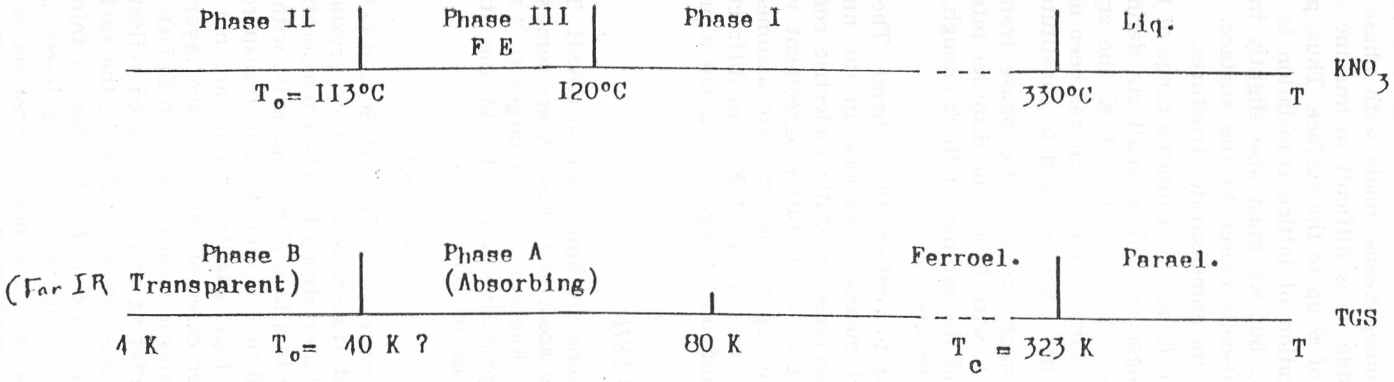


Figure 10. Comparison of phase transition temperatures in KNO$_3$ where the 113 °C transition does not occur in thin films, and in TGS where a similar transition has been suggested around 40 K.

Far IR appears as an interesting tool to look at surface layers. More accurate data with higher resolution are needed, and also electron or neutron diffraction data to confirm these still hypothetic phase transitions in the bulk.

REFERENCES

1. H. Poulet and J. P. Mathieu, *Spectres de vibrations et symétrie des Cristaux,* (Gordon and Breach, N. Y., 1970).
2. F. Jona and G. Shirane, *Ferroelectric Crystals* (Pergamon, N. Y., 1982).
3. M. E. Lines and A. H Glass, *Principles and Applications of Ferroelectrics and Related Materials,* (Clarendon, Oxford, 1977).
4. A. Hadni and X. Gerbaux, *J. Phys. C.* **18** (1985) 4805.
5. X. Gerbaux and A. Hadni, *Feroelectrics* **70** (1986) 175.
6. X. Gerbaux, A. Hadni, and J. Pierron, *Int. J. of Infrared and Millimeter Waves* **8** (1987) 35.
7. Y. Yamada, Y. Fuhi, and I. Hatta, *J. of the Phys. Soc. of Japon,* **24** (1968) 1953.
8. G. Luther, *Phys. Status Solidi* (b) **52** (1972) K41.
9. K. Itoh and T. Mitsui, *J. of Phys. Soc. of Japon* **23** (1967) 334.
10. A. Hadni, J. Claudel, D. Chanal, P. Strimer & P. Vergnat, *Phys. Rev.* **163** (1967) 836.
11. J. F. Scott, M. S. Zhang, R. B. Godfrey, C. Araujo, and L. Mc-Millan, *Phys. Rev.* **B35** (1987) 4044.
12. M. S. Zhang, R. S. Katiyar, and J. F. Scott, *Ferroelectrics* **74** (1987) 309.
13. Mrs Denoyer's private communication (Université de Paris XI, Laboratoire de Physique du Solide, Orsay).
14. U. T. Hochli and H. Rohrer, *Phys. Rev. Letters* **48** (1982) 188.
15. G. N. Zhizhin, E. A. Vinogradov, M. A. Moskalova, and V. A. Yakovlev, *Appl. Spectrosc. Rev.* **18** (1983) 171.
16. J. P. Ansermet, D. Rytz, A. Châtelain, U. T. Höchli, and H. E. Weibel, *J. Phys. C.* **14** (1981) 4541.

SAŽETAK

Daleki infracrveni spektri, fazni prijelazci i površinski slojevi

Armand Hadni i Xavier Gerbaux

Ekstenzivna mjerenja propusnosti dalekoga infracrvenog zračenja za feroelektrične pločice različitih debljina i orijentacija pokazala su da za nekoliko spojeva pri 4 K uzorci nisu homogeni, te se u prvoj aproksimaciji mogu opisati apsorbirajućim površinskim slojem i unutarnjim dijelom, gotovo transparentnim u dalekom infracrvenom području.

Potanja analiza sugerira da je primitivna jedinična ćelija u apsorbirajućoj fazi pri niskoj temperaturi neznatno modificirana kada se pomakne iz središta prema kristalnoj površini. Struktura se ne može opisati jednostavnom translacijom rešetke primijenjenom na jednu jediničnu ćeliju, nego je ostatak nekomenzurabilnih struktura.