

Classification

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## Far infrared response of $\alpha$ - and $\alpha_1$ -(BEDT-TTF)<sub>2</sub>I<sub>3</sub>

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**Résumé.** — On a déterminé la dépendance en température de la réflectivité des phases  $\alpha$  et  $\alpha_1$  de (BEDT-TTF)<sub>2</sub>I<sub>3</sub> dans le domaine 10-700 cm<sup>-1</sup>. En outre, on a étudié les spectres de transmission de la phase  $\alpha$  entre 10 et 33 cm<sup>-1</sup>. La conductivité infrarouge et la permittivité ont été calculées au moyen d'une analyse Kramers-Kronig. Des similarités ont été notées entre les phases  $\alpha_1$  et  $\beta$ . Des transitions à travers un petit gap (dont l'origine reste à discuter) permettent d'interpréter le pic élargi de la phase métallique situé entre 200 et 500 cm<sup>-1</sup>. Une structure foisonnante en pics est attribuée à des effets vibroniques. Nous suggérons que des modes impariellement symétriques de la molécule BEDT-TTF peuvent être couplés aux électrons.

**Abstract.** — The temperature dependence of the reflectivity of  $\alpha$ - and  $\alpha_1$ -(BEDT-TTF)<sub>2</sub>I<sub>3</sub> was determined in the 10-700 cm<sup>-1</sup> range. Moreover the transmission spectra of  $\alpha$ -phase between 10 and 33 cm<sup>-1</sup> were studied. Using Kramers-Kronig analysis the IR conductivity and permittivity were calculated. The similarity of  $\alpha_1$  and  $\beta$ -phases was confirmed. The spectra in the metallic phase are dominated by a broad electronic peak between 200 and 500 cm<sup>-1</sup> which can be understood as due to transitions across the small gap whose origin is discussed. In the spectra a rich phonon peak structure is observed, mostly of vibronic origin. It is suggested that non totally symmetric modes of BEDT-TTF molecule can couple with electrons.

### 1. Introduction.

According to the stoichiometry and conditions of the electrocrystallization the bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF or ET) molecule and iodine yield about ten charge-transfer crystals with different physical properties [1] but the most intensively studied are two modifications with identical stoichiometry:  $\alpha$ - and  $\beta$ -(ET)<sub>2</sub>I<sub>3</sub>. Both modifications are two-



dimensional conductors at room temperature. The  $\alpha$ -(ET)<sub>2</sub>I<sub>3</sub> undergoes a metal-insulator transition at  $T_{MI} = 135$  K [2]. The  $\beta$ -(ET)<sub>2</sub>I<sub>3</sub> preserves metallic properties down to low temperatures and exhibits ambient pressure superconductivity at  $T_c \simeq 1.3$  K (low- $T_c$  state) or  $T_c \simeq 8.1$  K (high- $T_c$  state) depending on the pressure-temperature history of the sample [3, 4] ( $\beta$ -crystals in the high- $T_c$  state are further denoted as  $\beta^*$ -(ET)<sub>2</sub>I<sub>3</sub>). The interest for these two crystals is mainly connected with the nature of the phase transition at  $T_{MI} = 135$  K in  $\alpha$ -(ET)<sub>2</sub>I<sub>3</sub> and the existence of two superconducting states in  $\beta$ -(ET)<sub>2</sub>I<sub>3</sub>.

The phase-transition at  $T_{MI} = 135$  K in  $\alpha$ -(ET)<sub>2</sub>I<sub>3</sub> was studied by many different techniques [2, 5-10]. The crystal structure of  $\alpha$ -(ET)<sub>2</sub>I<sub>3</sub> contains sheets of ET molecules in the  $a$ - $b$  plane separated by layers of I<sub>3</sub><sup>-</sup> anions in the  $c$ -direction. The ET molecules are stacked along the  $a$ -direction with a small dimerization [2, 11]. The crystal structure changes only slightly upon passing through the phase transition. Due to the phase transition the I<sub>3</sub><sup>-</sup> anions are slightly rotated with respect to one another and the increase of the degree of dimerization of one of the ET stacks is observed [12-14]. The mechanism of the phase transition is unknown ; it was suggested that the material above 135 K is a metal or a semiconductor with a very narrow energy gap.

Recently, it was discovered that by a thermal procedure the  $\alpha$ -crystals can be transformed into another modification ( $\alpha_t$ -crystals) with the stable superconducting state at  $T_c \simeq 8$  K [15, 16]. The full crystal structure of  $\alpha_t$ -(ET)<sub>2</sub>I<sub>3</sub> cannot be determined since the thermal procedure reduces the crystal quality [17] (strong mosaicity), however, in Weissenberg-pictures the reflections typical of  $\beta$ -crystals were observed [15]. Taking into account the physical properties one can conclude that  $\alpha_t$ -crystals are very similar to  $\beta$ -crystals in the high- $T_c$   $\beta^*$  state [15, 16, 18, 19].

The polarized reflectivity spectra of  $\alpha$ - and  $\beta$ -(ET)<sub>2</sub>I<sub>3</sub> were studied in the broad frequency range by several authors [9, 10, 20-24]. The pronounced influence of the phase transition in  $\alpha$ -(ET)<sub>2</sub>I<sub>3</sub> on the middle infrared spectra was observed by Meneghetti *et al.* [9] and Yakushi *et al.* [10]. The change of the electronic structure due to the phase transition was seen. For  $\beta$ -(ET)<sub>2</sub>I<sub>3</sub> a cross-over from semiconductor-like infrared properties at 300 K to metallic-like optical properties at 40 K was observed ; it was the first such observation in any organic conductor [24].

The far-infrared (FIR) measurements of conducting charge-transfer crystals are very important considering the fact that the energies of different phenomena observed in these crystals (such as superconductivity, anion-ordering, spin- and charge-density waves, solitons) lie in the FIR or microwave regions. However, it is difficult to measure the FIR-spectra of these materials since single crystals are usually very small. The crystals of  $\alpha$ -(ET)<sub>2</sub>I<sub>3</sub> usually grow as plates, therefore, it is possible to measure the FIR reflectivity from the high-quality single crystal. Because of the thermal procedure, the  $\alpha_t$ -crystals are worse in comparison with the  $\alpha$ -crystals but the surface is still good enough to enable FIR reflectivity measurements. In this paper, we report FIR measurements of  $\alpha$ -(ET)<sub>2</sub>I<sub>3</sub>,  $\alpha_t$ -(ET)<sub>2</sub>I<sub>3</sub> and transmission spectra of  $\alpha$ -(ET)<sub>2</sub>I<sub>3</sub> in the submillimetre range. Recently, the FIR reflectivity of  $\beta$ -(ET)<sub>2</sub>AuI<sub>2</sub> and  $\beta$ -(ET)<sub>2</sub>I<sub>2</sub>Br was measured in the temperature range 30-300 K [25]. These two compounds and  $\beta$ -(ET)<sub>2</sub>I<sub>3</sub> are isostructural, therefore, their spectra can be compared with our spectra of  $\alpha_t$ -(ET)<sub>2</sub>I<sub>3</sub>.

## 2. Experimental.

Large single crystals (ab platelets of area up to  $\sim 0.5$  cm<sup>2</sup>) of the  $\alpha$ -(ET)<sub>2</sub>I<sub>3</sub> were prepared by the standard electrochemical method [2]. The  $\alpha_t$ -modification was prepared by annealing the  $\alpha$ -(ET)<sub>2</sub>I<sub>3</sub> crystals at  $\sim 350$  K for 70 or 115 h [16]. The  $\alpha_t$ -samples have frequently cracked



into smaller pieces and showed a strong mosaicity seen in the visible polarized reflected light, due to internal stresses during the  $\alpha \rightarrow \alpha_1$  transformation. This prevented us from carrying out reflectivity measurements in polarized light in the case of  $\alpha_1$ -samples.

IR reflectivity measurements were performed on a Bruker IFS-113v Fourier-transform interferometer equipped with Ge-bolometer for the detection in the 10-100 cm<sup>-1</sup> range and standard pyroelectric detector for the 30-700 cm<sup>-1</sup> range. Temperature dependences were measured using Oxford Instruments CF 104 continuous flow cryostat equipped with a single warm polyethylene window and with the sample situated on a cold finger in vacuum. This limited our lowest achievable sample temperature to about 20 K (as checked by an independent thermometer close below the sample) and prevented us from investigating the superconducting phase in the case of the  $\alpha_1$  sample. A grid polyethylene polarizer was used for the measurements in polarized light ( $\alpha$ -modification). Reflectivity was measured from natural (001) surfaces of several individual single crystals with a diameter 4-5 mm. The transmission spectra in the 10-33 cm<sup>-1</sup> range were performed using a home-made spectrometer « Epsilon » based on tunable monochromatic backward-wave-oscillator sources [26]. In this technique, the intensity and phase of the radiation are measured using a Mach-Zehnder interferometer and the spectra of the complex dielectric function  $\varepsilon(\nu) = \varepsilon'(\nu) - i\varepsilon''(\nu)$  are directly calculated using standard formulae. The accuracy of this method is much higher than that of the usual reflectivity measurements.

### 3. Results and evaluation.

In figure 1 we compare the room-temperature unpolarized reflectivity of the  $\alpha$ - and  $\alpha_1$ -(ET)<sub>2</sub>I<sub>3</sub> in a broad frequency range (30-5 000 cm<sup>-1</sup>). The  $\alpha$ -phase spectra are similar to those published previously [9, 10]. The pronounced difference between the  $\alpha$ - and  $\alpha_1$ -phase spectra and comparison with the published  $\beta$ -phase spectra [21-24] confirm that the  $\alpha_1$ -modification is closely related to the  $\beta$ -modification. The difference between the  $\alpha_1$ -phase spectra of differently annealed samples shows an effect of deterioration of the sample surface with longer annealing. Therefore, we have further investigated only the samples annealed for 70 h.

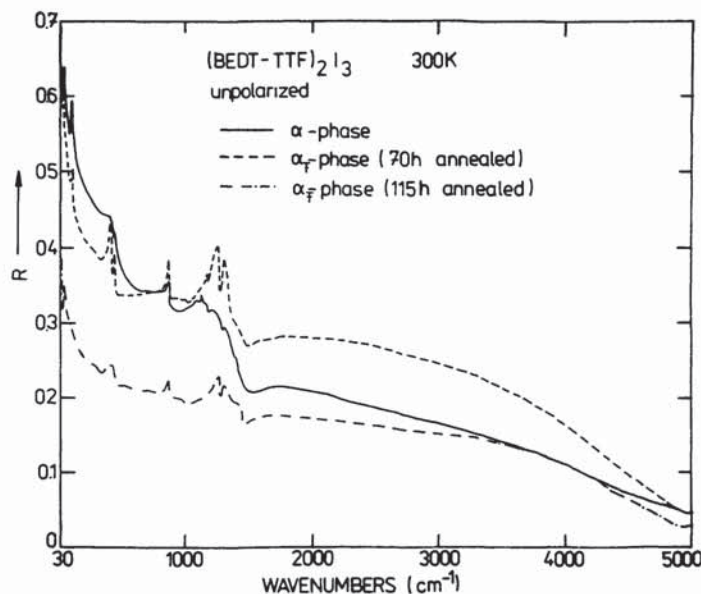


Fig. 1. — Room temperature reflectivity of the  $\alpha$ - and  $\alpha_1$ -modification of (ET)<sub>2</sub>I<sub>3</sub> in unpolarized light.

In figures 2 and 3 the FIR reflectivity of the  $\alpha$ -modification for the electric field parallel to the ET stacking axis ( $E//a$ ) and nearly perpendicular to the stacking axis ( $E//b$ ) is shown as a function of temperature, respectively. The crystal  $b$ -axis coincides with the directions of maximum reflectivity and the direction  $\perp b$  is almost parallel to the  $a$ -axis which coincides with BEDT-TTF stacks [20]. Notice the very pronounced drop of the overall reflectivity at the metal-insulator transition  $T_{MI} = 135$  K in agreement with the observed drop in the middle IR region [9, 10].

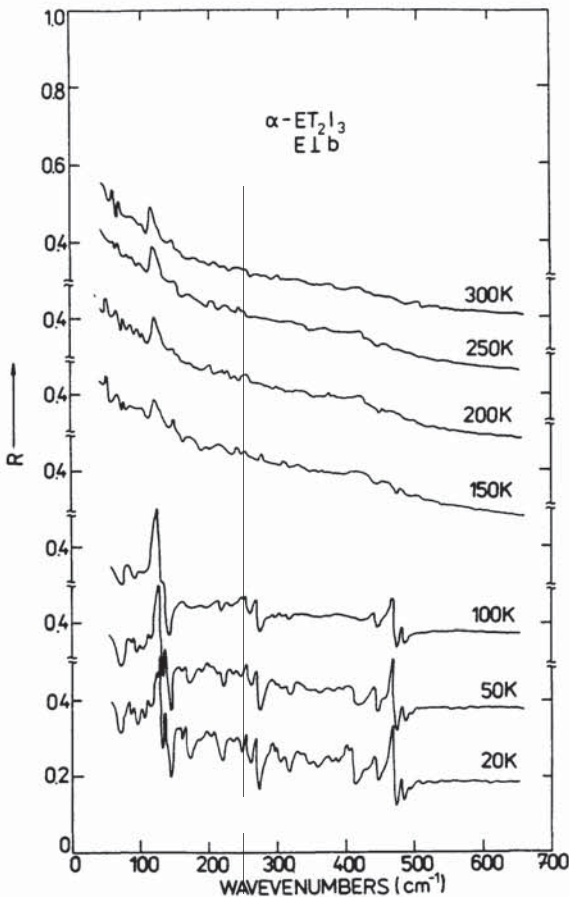


Fig. 2.

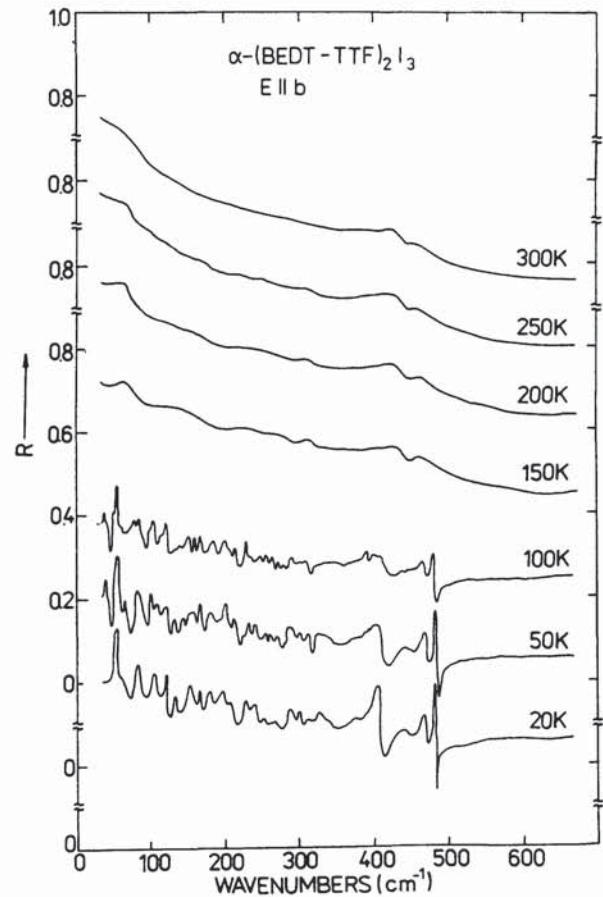


Fig. 3.

Fig. 2. — Temperature dependence of the FIR reflectivity of  $\alpha$ -( $ET$ ) $_2I_3$  for  $E//a$  (dotted lines show the extrapolations for Kramers-Kronig analysis — see text).

Fig. 3. — Temperature dependence of the FIR reflectivity of  $\alpha$ -( $ET$ ) $_2I_3$  for  $E//b$  (dotted lines, see Fig. 2).

The results of transmission measurements of the  $\alpha$ -phase are presented in figures 4 and 5. The extrapolation of  $\epsilon'(\nu)$  and  $\sigma(\nu)$  to the zero frequency gives values close to microwave data at 10 GHz ( $\sigma_{RT,a} = 30-60 \Omega^{-1} \text{cm}^{-1}$  and  $\sigma_{RT,b} = 50-90 \Omega^{-1} \text{cm}^{-1}$  [27]). From the spectra the reflectivity coefficient at  $\sim 30 \text{cm}^{-1}$  was calculated and used for normalization of our FIR spectra (Figs. 2, 3). In figure 6 we show the temperature dependences of  $\epsilon'$  and  $\sigma$  at  $20 \text{cm}^{-1}$ .

In figure 7 we show a set of normalized reflectivity spectra of the  $\alpha$ -modification exhibiting only an overall increase of reflectivity with decreasing temperature but no abrupt phase



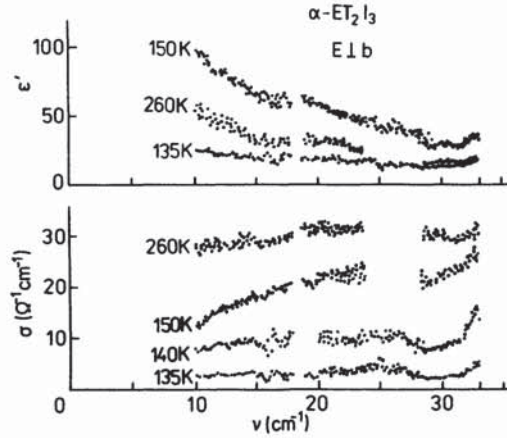


Fig. 4. — Submillimetre permittivity and conductivity of  $\alpha$ -(ET) $_2$ I $_3$  for  $E \parallel a$ .

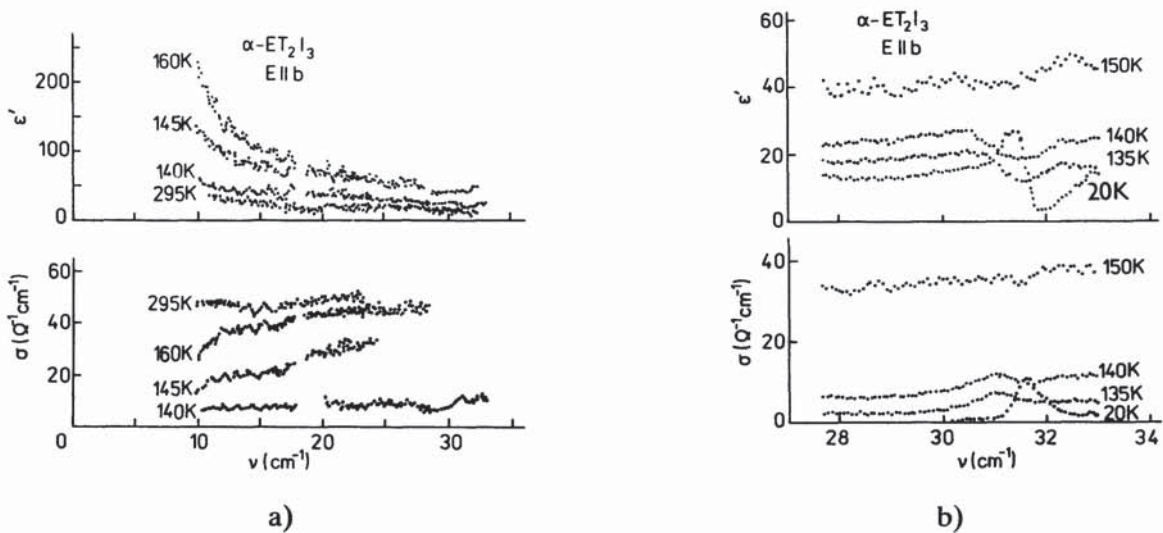


Fig. 5. — Submillimetre permittivity and conductivity of  $\alpha$ -(ET) $_2$ I $_3$  for  $E \parallel b$ : (a) at temperatures above  $T_{MI}$  and (b) the influence of the phase transition on the spectra.

transition. Similar overall increase of  $R$  was observed for  $\beta$ -(ET) $_2$ I $_3$  and the isostructural materials  $\beta$ -(ET) $_2$ AuI $_2$  and  $\beta$ -(ET)I $_2$ Br [25]. To eliminate the influence of surface unflatness on reflectivity spectra the sample covered with an evaporated gold layer was used as a reference. In such a way the low-frequency reflectivity increase and its overall value were influenced as compared with the results obtained with a normal flat reference mirror. To make contact of our unpolarized spectra with the published polarized  $\beta$ -phase spectra in the middle IR ( $E$  parallel to stacks) [21-24] we still multiplied our spectra with a common normalization constant of about 1.6. In this way the high  $R$  values in figure 7 are obtained. The dotted low-frequency part shows the Hagen-Rubens extrapolation used for the Kramers-Kronig analysis.

The reflectivity spectra were analyzed by means of Kramers-Kronig dispersion relations to obtain the phase spectrum of the reflected light and calculate the complex permittivity ( $\epsilon^*(\nu) = \epsilon'(\nu) - i\epsilon''(\nu)$ ) or conductivity ( $\sigma^*(\nu) = \sigma'(\nu) - i\sigma''(\nu) = i\nu c \epsilon^*/2$ ) spectrum. To avoid divergences at zero frequency  $\nu = 0$  in the non-superconducting phase we prefer the representation of real conductivity  $\sigma'$  and real permittivity spectra  $\epsilon'$  for the

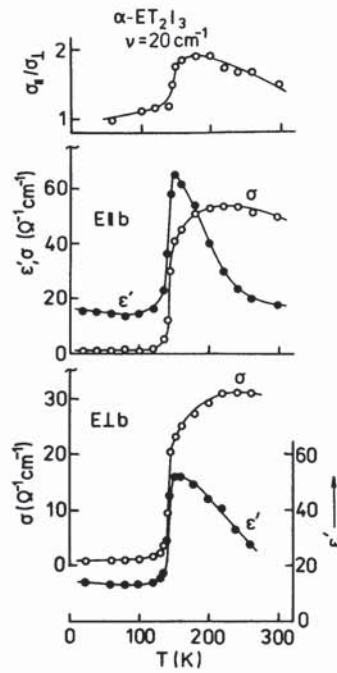


Fig. 6. — Temperature dependence of the submillimetre conductivity and permittivity at  $\nu = 20 \text{ cm}^{-1}$  of  $\alpha\text{-(ET)}_2\text{I}_3$  for two polarizations.

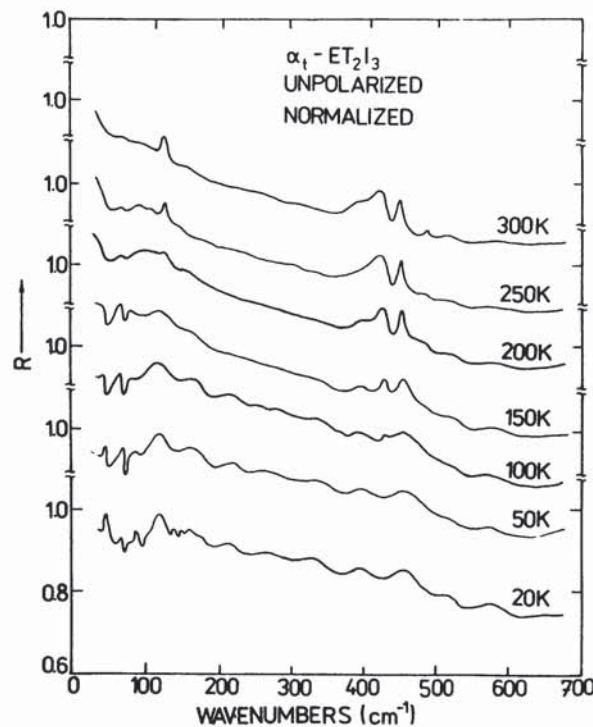


Fig. 7. — Temperature dependence of the normalized FIR reflectivity of  $\alpha_t\text{-(ET)}_2\text{I}_3$  (dotted lines, see Fig. 2).

discussion of the optical response. Outside the measured range the reflectivity spectra were continuously extrapolated from  $\sim 40 \text{ cm}^{-1}$  to  $0 \text{ cm}^{-1}$  by means of the Hagen-Rubens relation  $R(\nu) = 1 - A \sqrt{\nu}$  (the parameter  $A$  was calculated from our low-frequency reflectivity) and to  $5000 \text{ cm}^{-1}$  by the corresponding room temperature reflectivity (see Fig. 1) normalized at

700  $\text{cm}^{-1}$  to the measured value of  $R$ . Above 5 000  $\text{cm}^{-1}$  a constant  $R(\nu)$  was assumed. Different ways of extrapolation lead essentially to the same results. The calculated  $\sigma(\nu)$  and  $\epsilon'(\nu)$  spectra for selected temperatures and both modifications are shown in figures 8-10. It should be noticed that for low symmetry crystals (triclinic and monoclinic) such a simple Kramers-Kronig analysis is strictly speaking incorrect because the reflected light is generally elliptically polarized and therefore the calculated spectra in figures 8-10 have the meaning of some approximate and averaged values.

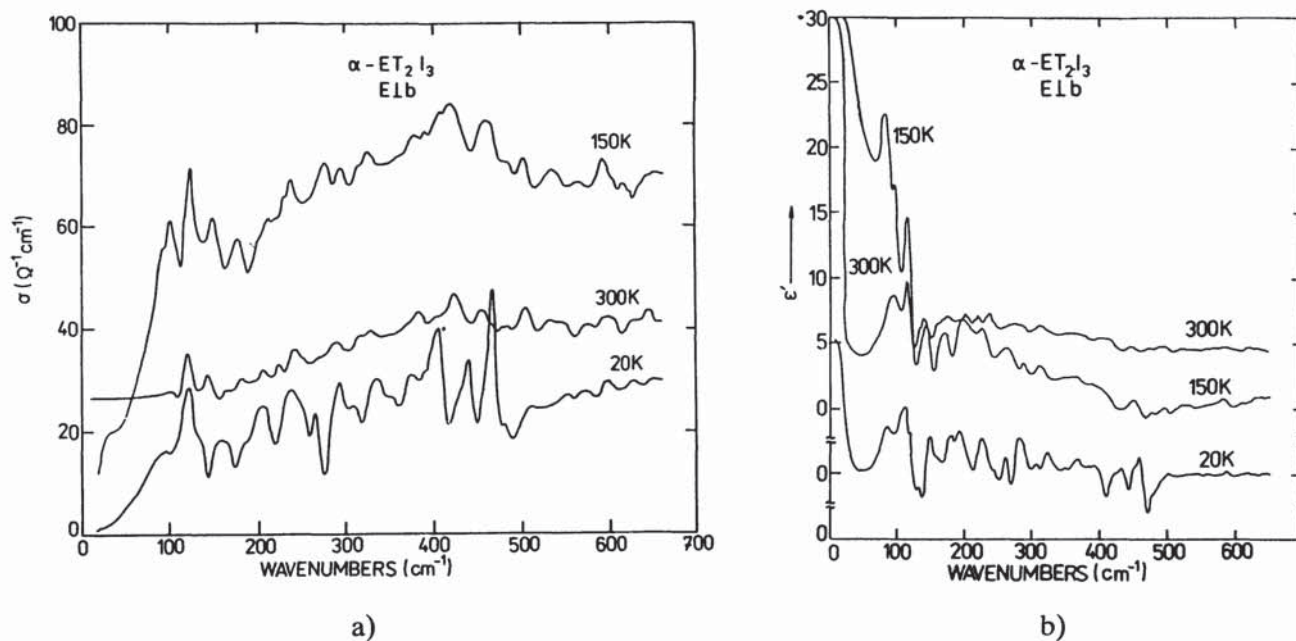


Fig. 8. — FIR response calculated from the spectra in figure 2 : a) conductivity, b) permittivity.

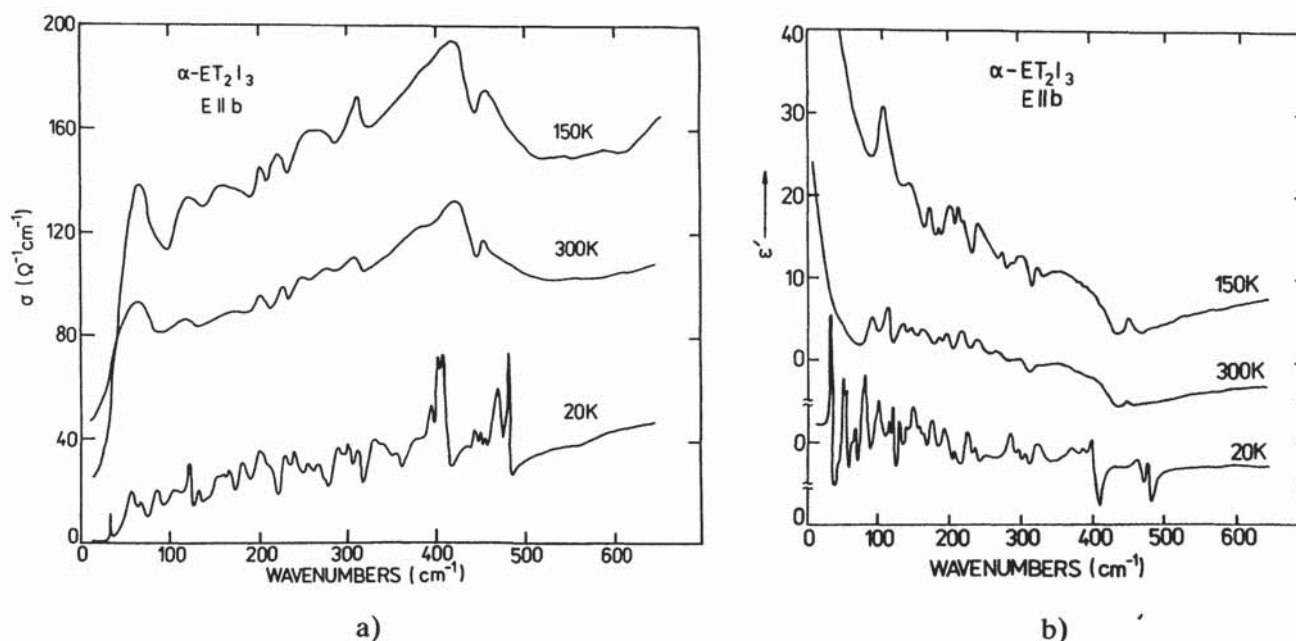


Fig. 9. — FIR response calculated from the spectra in figure 3 : a) conductivity, b) permittivity.



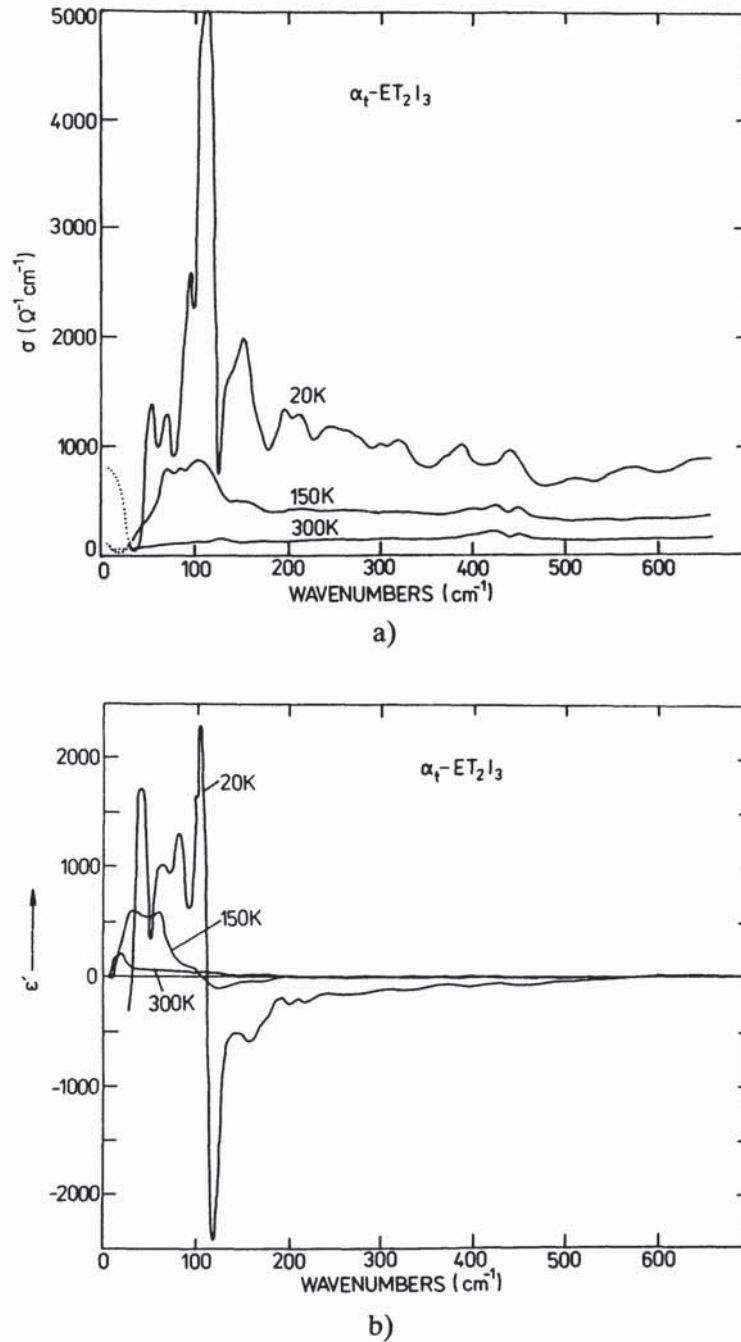


Fig. 10. — Effective FIR response calculated from the spectra in figure 7 : a) conductivity, b) permittivity.

#### 4. Discussion.

The comparison of the  $\alpha_1$ -phase spectra in figure 1 with earlier measurements carried on the  $\beta$ -phase [21-24] has shown that both types of spectra are practically identical. This is in agreement with the belief that  $\alpha_1$ -phase is very similar to the high  $-T_C$   $\beta^*$ -phase [16] and confirms this conclusion. Nevertheless, several spectral features are common for both  $\alpha$ - and  $\alpha_1$ -phase : the plasma edge near 5 000 cm<sup>-1</sup>, the strong and broad electronic band near 2 000 cm<sup>-1</sup>, the phonon peaks between 100 and 1 500 cm<sup>-1</sup> and the reflectivity increase at the low-frequency end. Only the relative strength of individual contributions and the fine structure of the phonon peaks differ for both modifications.



Polarized light is known to reveal another important difference between  $\alpha$ - and  $\beta$ -modification [20, 21, 28]: whereas in the  $\beta$ -modification the maximum IR reflectivity (and conductivity) occurs for electrical vector  $\mathbf{E}$  parallel to the ET stacks, in the  $\alpha$ -modification the maximum IR reflectivity is perpendicular to the stacks in the plane of ET layers. This is also observed in the FIR range of the  $\alpha$ -phase and means that charge-transfer is easier between the ET stacks in the (001) plane than along the ET stacks.

At 300 K the real part of the dielectric function  $\varepsilon'(\nu)$  of  $\alpha_t$ -(ET)<sub>2</sub>I<sub>3</sub> (Fig. 10b) is positive in the whole frequency range. At 20 K the  $\varepsilon'(\nu)$  is negative but below about 120 cm<sup>-1</sup> strong vibrational features make it positive. This differs from the situation in  $\beta$ -(ET)<sub>2</sub>I<sub>3</sub> [24] and  $\beta$ -(ET)<sub>2</sub>AuI<sub>2</sub> [25], where single-zero crossing at the plasma-edge region was observed. When the reflection coefficient  $R$  is close to unity (as for  $\alpha_t$ -phase in the low frequency range) a very small change of  $R$  yields very strong changes of  $\varepsilon'(\nu)$  and  $\sigma(\nu)$ , therefore, the uncertainty of estimation of  $\varepsilon'(\nu)$  and  $\sigma(\nu)$  below 120 cm<sup>-1</sup> is considerable. Nevertheless, there is no doubt about the existence and position of the strong oscillator strength below 120 cm<sup>-1</sup> for  $\alpha_t$ -(ET)<sub>2</sub>I<sub>3</sub> even if their strength might have been overestimated due to the normalization procedure.

We try to fit the reflectivity spectra of the  $\alpha_t$ -phase at 20 K to the Drude model in the broad spectral range (10-5 000 cm<sup>-1</sup>). Neglecting the influence of phonons the best fit was obtained with parameters:  $\varepsilon_\infty = 3.7$ ,  $\sigma_{dc} = 900 \Omega^{-1} \text{cm}^{-1}$  and  $\gamma = 1\,700 \text{cm}^{-1}$ .  $\sigma_{dc}$  is in good agreement with the measured dc value [16]. For these parameters the contribution of the conduction electrons to the static  $\varepsilon$  is  $-30$  and  $\varepsilon'(\nu)$  crosses zero at  $\approx 4\,670 \text{cm}^{-1}$ . This also shows that strong absorption near 100 cm<sup>-1</sup> can change the sign of  $\varepsilon'(\nu)$  in a limited spectral range (Fig. 10b). Nonetheless the overall behaviour can be characterized as a crossover from semiconductor like properties at 300 K to metallic behaviour at low temperatures. Similar conclusions were drawn for  $\beta$ -(ET)<sub>2</sub>I<sub>3</sub> [24] and  $\beta$ -(ET)<sub>2</sub>AuI<sub>2</sub> [25].

The nature of the strong and broad absorption band between 200 and 500 cm<sup>-1</sup> which appears in both modifications in the metallic phase was not yet discussed in the literature of ET salts. Because of its broadness and strong temperature dependence of its strength, especially its near disappearance in the  $\alpha$ -phase below the phase transition, it is clearly of electronic origin. Similar absorption band was also observed at slightly lower frequencies in other organic metals like (TMTSF)<sub>2</sub>X compounds ( $X = \text{PF}_6^-$ ,  $\text{ClO}_4^-$ ,  $\text{SbF}_6^-$ ,  $\text{AsF}_6^-$ ) [29-32] and TTF-TCNQ [33-35]. In the case of (TMTSF)<sub>2</sub>X compounds it was assigned to Holstein scattering processes of free carriers on phonons [30-32], in the case of TTF-TCNQ to transitions across the Peierls pseudogap [33-37], i.e. to interband transitions. Both possibilities should be considered in our case.

The  $\alpha$ -phase above the phase transition temperature  $T_{\text{MI}}$  was considered as a very narrow direct gap semiconductor with a large thermal occupation of the conduction band [12]. Therefore we might assign the conductivity maximum between 200-500 cm<sup>-1</sup> in the  $\alpha$ -phase above  $T_{\text{MI}}$  to excitations across the semiconductor gap. The width of the gap is in acceptable agreement with the results of band structure calculations which give the value  $\sim 13 \text{meV}$  [12]. The disappearance of this maximum should be understood as its pronounced shift to higher frequencies due to the phase transition. In fact, reflectivity measurements in the higher frequency range (700-25 000 cm<sup>-1</sup>) [10] have revealed a splitting of the strong charge transfer mode near 2 600 cm<sup>-1</sup> above  $T_{\text{MI}}$  into two peaks at 2 350 and 2 950 cm<sup>-1</sup> below  $T_{\text{MI}}$ . One of the peaks can be assigned to transitions across this much larger gap of  $\sim 0.2$ - $0.3 \text{eV}$ . This is much more than  $\sim 35 \text{meV}$  calculated by Emge *et al.* [12] but in agreement with the pronounced decrease of the dc conductivity below  $T_{\text{MI}}$  (by about 4 orders of magnitude at 100 K).

Let us comment here on the temperature dependences of  $\varepsilon'$  and  $\sigma$  for the  $\alpha$ -modification.



The decrease of  $\sigma$  below  $T_{MI}$  is in agreement with the metal-insulator nature of the phase transition, but clearly some background electronic absorption essentially temperature independent below  $T_{MI}$  remains present in the whole FIR range down to the lowest temperatures (20 K). The only reasonable explanation for it seems to us a presence of some little semi-metallic inclusions in our samples. A similar suggestion was also made to explain the microwave behaviour below  $T_{MI}$  [27].

Another interesting point is the increase of the overall conductivity spectrum on decreasing the temperature from 300 K to  $T_{MI}$ . An independent proof of this feature (*via* Kramers-Kronig relation between  $\varepsilon'(\nu)$  and  $\sigma(\nu)$ ) is the increase of submillimetre  $\varepsilon'$  near  $T_{MI}$  (see Fig. 6). This seems to be an intrinsic effect of the  $\alpha$ -modification because it is too large to be explainable by small inclusions of the metallic phase. The simple semiconductor picture seems not to be able to explain this feature. It might be understood e.g. in terms of increasing electron-electron correlations near  $T_{MI}$ .

The narrow-gap-semiconductor picture is quite inappropriate for the  $\alpha_t$ -modification because of its metallic behaviour down to the lowest temperatures. Here the similar broad absorption band between 200 and 500  $\text{cm}^{-1}$  which develops especially at low temperatures should be caused either by Holstein processes or by electron-electron correlations which seem to play a very important role in this type of compounds [12, 36]. It is not easy to estimate quantitatively the role of Holstein processes because of unknown one-phonon density of states in this substance. On the other hand, if we consider electron-electron correlations the main band near 2 000  $\text{cm}^{-1}$  could be assigned to transitions across the Hubbard gap (of the order of on-site Coulomb interaction energy  $U$ ), whereas the lower band at 200-500  $\text{cm}^{-1}$  could be of the order of the nearest-neighbour Coulomb interaction energy  $V$  (see e.g. [36]). At the present stage of our knowledge it is impossible to decide which of these mechanisms is dominant.

Let us discuss the phonon features which manifest themselves by the rich fine structure in our spectra. The most pronounced peaks at about 430 and 460  $\text{cm}^{-1}$  for both modifications are clearly of vibronic origin. A similar doublet was observed in the spectra of the salts  $\beta$ -(ET)<sub>2</sub>AuI<sub>2</sub> and  $\beta$ -(ET)<sub>2</sub>I<sub>2</sub>Br at 430-460  $\text{cm}^{-1}$  [25]. In this frequency range two totally symmetric  $a_g$  modes of the ET molecule  $\nu_{12}$  and  $\nu_{13}$  are observed [9, 38] (in Ref. [38] these modes are denoted as  $\nu_9$  and  $\nu_{10}$ ). It is well known that the  $a_g$  modes can couple with electrons leading to IR activity; for the case of  $\alpha$ -(ET)<sub>2</sub>I<sub>3</sub> this was already discussed by Meneghetti *et al.* [9]. The bands at about 430 and 460  $\text{cm}^{-1}$  could be assigned to the  $\nu_{12}$  and  $\nu_{13}$  modes activated by the linear coupling with electrons. However, the calculations have shown that the dimensionless electron-molecular vibration (EMV) coupling constant for the  $\nu_{12}$  mode is  $g_{12} = 0.476$  and for the  $\nu_{13}$  mode is  $g_{13} \approx 0.05$  [39]. Taking into account that the intensities of these bands are nearly the same and that  $g_{12} \gg g_{13}$ , we suggest that origin of the band at about 430  $\text{cm}^{-1}$  might be different. On the other hand, this band is strong, exhibits strong temperature dependence and for the  $\alpha$ -phase it shows dramatic change below the MI transition; this could mean that this band is due to the EMV interaction.

For organic conductors it was usually considered [40] that only totally symmetric  $a_g$  modes can couple with electrons. However, an alternative mechanism of EMV coupling was proposed for TTF compounds [41]. During an out-of-plane vibration of the TTF molecules the electronic overlap (and hence the hopping integral  $t$ ) can be modulated leading to a finite IR activity. Recently, a similar mechanism was discussed for ET and DIMET salts [42]. The ET molecule has an out-of-plane deformation of symmetry  $b_{2g}$  at the frequency close to 430  $\text{cm}^{-1}$  (mode  $\nu_{40}$  in Ref. [38]). Therefore, we relate the band at about 430  $\text{cm}^{-1}$  in  $\alpha$ - and  $\alpha_t$ -(ET)<sub>2</sub>I<sub>3</sub> to the out-of-plane vibration of ET molecule. The broken symmetry is presumably connected with the dimerization of the stacks in these materials. Similar



mechanism could be responsible for the band near 120 cm<sup>-1</sup> in  $\alpha$ -phase and near 110 cm<sup>-1</sup> in  $\alpha_t$ -phase. The ET molecule has an out-of-plane vibration  $b_{2g}$  in this frequency range (mode  $\nu_{43}$  at 127 cm<sup>-1</sup> in Ref. [38]). However, the possibility of mixing of internal and external modes in the low frequency region cannot be neglected. On the other hand, the band at about 150 cm<sup>-1</sup> observed in both modifications could be assigned to  $a_g$  mode of ET molecule activated by EMV coupling (mode  $\nu_{16}$  at 156 cm<sup>-1</sup> in Ref. [9]).

There are a lot of IR active external vibrations (i.e. those where ET and I<sub>3</sub> molecules vibrate or librate as a whole without changing the interatomic distances inside the individual molecules) which are generally expected in the 10-200 cm<sup>-1</sup> range. In table I we give the results of our factor-group analysis of these degrees of freedom (see e.g. [43]). Due to the triclinic symmetry, all the FIR active modes (6 and 15 for the  $\beta$  and  $\alpha$ -modification, respectively) can generally appear in all polarizations. In this way we can understand the dense peak structure in our spectra, especially at low temperatures. (There are 330 vibrational degrees of freedom in the unit cell, but of course some of the minor peaks have origin in the noise.) Below  $T_{MI}$  in  $\alpha$ -phase for E perpendicular to the ET stacks a mode at about 31 cm<sup>-1</sup> is observed (Fig. 5b). Its origin could be an ET-I<sub>3</sub> external vibration. Its changes and gradual disappearance above  $T_{MI}$  indicate some coupling with the free carriers and finally a complete screening of the phonon effective charge.

Table I. — Factor group analysis of external vibrations in (ET)<sub>2</sub>I<sub>3</sub>.

Phase	Acoustic	Transl.	Librat.	No of FIR modes
$\beta$	3 A <sub>u</sub>	3 A <sub>g</sub> + 3 A <sub>u</sub>	5 A <sub>g</sub> + 3 A <sub>u</sub>	6
$\alpha$ -met.	3 A <sub>u</sub>	3 A <sub>g</sub> + 12 A <sub>u</sub>	13 A <sub>g</sub> + 3 A <sub>u</sub>	15
$\alpha$ -ins.	3 A <sub>u</sub>	6 A <sub>g</sub> + 9 A <sub>u</sub>	10 A <sub>g</sub> + 6 A <sub>u</sub>	15

## 5. Conclusions.

1) The IR reflectivity supports the similarity between  $\alpha_t$  and  $\beta$ -modifications of (ET)<sub>2</sub>I<sub>3</sub>.

2) The FIR absorption in metallic phases is dominated by a broad band between 200 and 500 cm<sup>-1</sup> of electronic origin whose intensity increases near  $T_{MI}$  in the  $\alpha$  phase. Its origin may be in transitions across a small gap either of the one-electron band scheme or more probably due to electron correlations, or it might occur due to Holstein electron-phonon scattering processes. This absorption is strongly reduced in the insulating  $\alpha$ -phase which leads to a drastic drop of the FIR reflectivity. The remaining absorption in this phase indicates probably some inclusions of a metallic phase.

3) A rich phonon structure with vibronic features was observed. The band at about 460 cm<sup>-1</sup> and 150 cm<sup>-1</sup> are assigned to  $\nu_{12}$  and  $\nu_{16}$  totally symmetric vibrations of the ET molecule activated through linear coupling with electrons. We suggest that electron-molecular vibration coupling is not only limited to totally symmetric  $a_g$  modes and we assign the bands at about 430 cm<sup>-1</sup> and 120 cm<sup>-1</sup> to the out-of-plane deformation of the ET molecule. Many IR active external (ET)-I<sub>3</sub> modes are expected below 200 cm<sup>-1</sup> of which one  $E // b$  mode was observed at 31 cm<sup>-1</sup> below  $T_{MI}$ .

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