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# Charge ordering in the $\kappa$ -phase BEDT–TTF salts with $\text{Co}(\text{CN})_6$ and $\text{Fe}(\text{CN})_6$ anions studied by infrared and Raman spectroscopies

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## Abstract

We studied the temperature dependence of the Raman scattering spectra of two semiconducting, isostructural charge transfer salts  $\kappa$ -[Et<sub>4</sub>N](BEDT–TTF)<sub>4</sub>M(CN)<sub>6</sub>·3 H<sub>2</sub>O (M = Co<sup>III</sup>, Fe<sup>III</sup>) within the region of C=C stretching vibrations (1200–1700 cm<sup>-1</sup>). Moreover, polarised reflectance spectra (600–10000 cm<sup>-1</sup>) of the Co<sup>III</sup> salt were recorded as a function of temperature and compared with previous infrared studies of the Fe<sup>III</sup> salt. Both salts undergo a phase transition at  $T = 150$  K related to a charge ordering inside the conducting BEDT–TTF layers. Due to the charge ordering, new vibrational bands corresponding to BEDT–TTF<sup>+1</sup> cations are recorded both in Raman and infrared spectra. Infrared electronic bands also experience strong modifications at 150 K: a new energy gap is formed and a new charge-transfer band in the near-infrared region is observed. The most important difference is that the charge redistribution in Fe<sup>III</sup> salt is developed gradually below about 240 K, whereas in Co<sup>III</sup> salt this is an abrupt process related to the phase transition at 150 K. *To cite this article: R. Świetlik et al., C. R. Chimie 6 (2003).*

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## Résumé

Dans nombre de conducteurs organiques, les intégrales de transfert entre molécules voisines sont comparables aux intra-sites ( $U$ ) et inter-sites ( $V$ ) énergies d'interaction coulombiennes ; par conséquent, les corrélations électroniques jouent un rôle important dans ces matériaux. Des études théoriques récentes ont montré que ces énergies  $U$  et  $V$  ainsi que l'anisotropie des intégrales de transfert sont nécessaires à la compréhension du schéma de distribution des charges dans la couche organique conductrice. Les spectroscopies IR et Raman sont d'excellentes méthodes expérimentales pour l'étude du phénomène d'ordre de charge. Les sels à transfert de charge  $\kappa$ -[Et<sub>4</sub>N](BEDT–TTF)<sub>4</sub>M(CN)<sub>6</sub>·3 H<sub>2</sub>O, M = Co<sup>III</sup>, Fe<sup>III</sup> sont isostructuraux et semi-conducteurs. Dans la couche organique, les molécules de BEDT–TTF présentent un arrangement de type  $\kappa$ . Ces composés révèlent des transitions de phase à 240 et 150 K. À température ambiante, la couche organique contient deux dimères indépendants, portant des charges moyennes identiques de +1 chacun ...A<sup>+0,5</sup>A<sup>+0,5</sup>...B<sup>+0,5</sup>B<sup>+0,5</sup>..., alors qu'à basse température, il existe quatre dimères indépendant avec la distribution de charge ...A<sup>0</sup>A<sup>0</sup>...B<sup>+0,5</sup>B<sup>+0,5</sup>...C<sup>+0,5</sup>C<sup>+0,5</sup>...D<sup>+1</sup>D<sup>+1</sup>... Nous rapportons dans cette contribution les études en température des spectres Raman dans la région de vibration de la liaison C=C (1200–1700 cm<sup>-1</sup>) des deux sels. De plus, les spectres de réflectance polarisée (600–10 000 cm<sup>-1</sup>) du sel de Co<sup>III</sup> ont été enregistrés en fonction de la température et comparés avec ceux des composés à base de Fe<sup>III</sup> obtenus antérieurement. Pour les deux composés,

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une nouvelle bande de vibration correspondant au cation BEDT–TTF<sup>+1</sup> a été observée dans les spectres Raman et IR. Les bandes électroniques montrent aussi de grandes modifications à 150 K, révélant la formation d'un gap d'énergie, avec celle d'une nouvelle bande de transfert de charge dans le proche infrarouge. La différence fondamentale entre les deux composés réside dans le fait que la redistribution de charge est graduelle dans le sel à base de Fe<sup>III</sup> en dessous de 240 K, alors qu'elle est abrupte dans le composé de Co<sup>III</sup> en dessous de 150 K. *Pour citer cet article* : R. Świetlik et al., C. R. Chimie 6 (2003).

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*Mots clés* : sels de BEDT–TTF ; ordre de charges ; spectroscopie infrarouge et Raman

## 1. Introduction

In many organic conductors, the transfer integrals between neighbouring molecules are comparable to the on-site ( $U$ ) and inter-site ( $V$ ) Coulomb interaction energies; therefore, electron correlations play an important role in these materials. The inter-site Coulomb interactions in organic conductors can be responsible for changes of average electron density on molecules, i.e. charge ordering (or charge disproportionation) phenomena [1, 2]. The charge ordering states can be widely realised in two-dimensional charge transfer salts formed by the organic donor bis(ethylenedithio)tetrathiafulvalen (BEDT–TTF or ET) with various inorganic anions. In BEDT–TTF salts the inter-site Coulomb repulsion can give rise to stripe-type charge ordered states, where the sites with more and less amount of charge are arranged in rows alternately. As shown by recent theoretical calculations [3], both energies  $U$  and  $V$  together with the anisotropy of transfer integrals are necessary for the understanding of charge distribution patterns inside the conducting BEDT–TTF layers.

Infrared and Raman spectroscopies are good experimental methods for investigations of the charge ordering phenomena [4–6]. In BEDT–TTF salts, the positions of vibrational bands, especially those related to the C=C stretching vibrations of BEDT–TTF, can be used for determination of the charge density [7]. The neutral BEDT–TTF molecule has two Raman active C=C modes:  $\nu_2(a_g)=1551\text{ cm}^{-1}$  and  $\nu_3(a_g)=1493\text{ cm}^{-1}$  [8]. On increasing the average oxidation state of BEDT–TTF, the frequencies of these bands are shifted down, reaching the values  $\nu_2(a_g)=1455\text{ cm}^{-1}$  and  $\nu_3(a_g)=1431\text{ cm}^{-1}$  for BEDT–TTF<sup>+1</sup> cation [9]. As shown recently, for estimation of charge density in the

BEDT–TTF salt, the  $\nu_2(a_g)$  Raman band is more reliable than  $\nu_3(a_g)$ , because of weaker coupling with electrons, which yields an additional frequency shift towards lower frequencies [6]. On the other hand, the charge ordering can be responsible for the formation of a new energy gap in electronic spectrum or the appearance of new charge-transfer bands, and these phenomena can be observed in infrared spectra.

The salts  $\kappa\text{-[Et}_4\text{N]BEDT-TTF}_4\text{M(CN)}_6\cdot 3\text{H}_2\text{O}$  ( $M = \text{Co}^{\text{III}}, \text{Fe}^{\text{III}}$ ) are isostructural and exhibit very similar semiconducting properties [10–12]. In conducting layers, the BEDT–TTF molecules are arranged in almost perpendicular dimers (so-called  $\kappa$ -phase structure) and alternate with insulating layers of hexacyanometalate trianions  $\text{M(CN)}_6^{3-}$ . Both crystals undergo analogous phase transitions at about  $T = 240\text{ K}$  and  $T = 150\text{ K}$ . At room temperature, the organic conducting layer is built of two different kinds of BEDT–TTF molecules forming two kinds of dimers (labelled A and B). At 240 K, the unit cell is doubled and there exist four different kinds of dimers (labelled A, B, C and D). The phase transition at 150 K has no distinguishable influence on the crystal structure; however, it was evidenced by heat-capacity and paramagnetic-susceptibility measurements. The analysis of the bond lengths of BEDT–TTF donors suggested that at room temperature both A and B molecules bear a charge +0.5 (i.e. charge distribution is:  $\dots\text{A}^{+0.5}\text{A}^{+0.5}\dots\text{B}^{+0.5}\text{B}^{+0.5}\dots$ ); but below 240 K a charge redistribution takes place leading to the following pattern:  $\dots\text{A}^0\text{A}^0\dots\text{B}^{+0.5}\text{B}^{+0.5}\dots\text{C}^{+0.5}\text{C}^{+0.5}\dots\text{D}^{+1}\text{D}^{+1}\dots$  [12].

Recently, the charge ordering phenomena in the Fe<sup>III</sup> salt were studied by IR and Raman spectroscopy. The existence of charge redistribution inside BEDT–TTF layers was confirmed by the FT–NIR Raman experiment (excitation:  $\lambda = 1064\text{ nm}$ ) on powdered

crystals dispersed in KBr matrix [13] as well as by the IR reflectance from single crystals [14]. Here, we report on IR and Raman investigations of the  $\text{Co}^{\text{III}}$  and  $\text{Fe}^{\text{III}}$  single crystals. Preliminary spectroscopic data for the  $\text{Co}^{\text{III}}$  salt have been described in [15].

## 2. Experimental

Single crystals of the salts  $\kappa\text{-[Et}_4\text{N] (BEDT-TTF)}_4\text{M(CN)}_6\cdot 3\text{H}_2\text{O}$  ( $\text{M} = \text{Co}^{\text{III}}, \text{Fe}^{\text{III}}$ ) were grown on platinum electrodes by an electrocrystallisation technique, as previously described in [10]. The crystals were in the form of shiny platelets with the best-developed crystal face (001) being parallel to the conducting BEDT-TTF layers.

Raman spectra of the single  $\text{Co}^{\text{III}}$  and  $\text{Fe}^{\text{III}}$  crystals were recorded in the spectral range from 1200 to 1800  $\text{cm}^{-1}$  using a Renishaw Ramascope System 1000. The excitation light from a NIR diode laser ( $\lambda = 785\text{ nm}$ ) was focused on the (001) crystal face. The scattered light was collected in a backscattering geometry. The power of the laser beam was kept below 240  $\mu\text{W}$  to avoid sample overheating.

Polarised reflectance spectra of the  $\text{Co}^{\text{III}}$  single crystals were measured from the (001) crystal face, in the frequency region from 600 to 10 000  $\text{cm}^{-1}$ , using a FT-IR Nicolet Magna 760 spectrometer. The spectrometer was equipped with an IR microscope Spectratech IR Plan. The electrical vector of the polarised light was either parallel ( $E_{\parallel}$ ) or perpendicular ( $E_{\perp}$ ) to the direction corresponding to the maximum of reflected energy. The frequency-dependent conductivity was determined by Kramers–Kronig analysis of the reflectance data. The low-frequency data were extrapolated to zero-frequency assuming a constant value, a common procedure for semiconducting materials. The high-frequency data in the region 10 000–30 000  $\text{cm}^{-1}$  were extended on the basis of room temperature data of the  $\text{Fe}^{\text{III}}$  salt [14] and above 30 000  $\text{cm}^{-1}$  a constant reflectance was assumed.

Low temperature IR and Raman measurements were performed with samples mounted with vacuum grease in helium cryostats. Previous investigations have shown that in both compounds the intensity of the phase transition at 150 K strongly depends on the cooling or warming rates and it is accompanied by a large thermal hysteresis, whereas the transition at 240 K remains unchanged [10–12]. These effects were

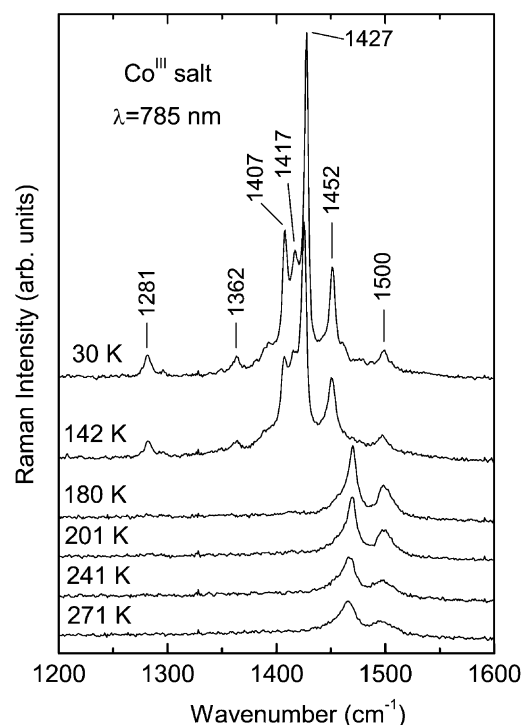


Fig. 1. Temperature dependence of the Raman spectra of  $\kappa\text{-[Et}_4\text{N] (BEDT-TTF)}_4\text{Co(CN)}_6\cdot 3\text{H}_2\text{O}$  salt (NIR excitation:  $\lambda = 785\text{ nm}$ ).

not studied in our experiments: the sample temperature was carefully decreased with the cooling rate below 1  $\text{K min}^{-1}$ . We observed frequently that the crystals cracked in cryostat during evacuation at room temperature. The cracking was related to a process of losing water molecules by sample under vacuum (there are three water molecules in the unit cell). Subsequently, we have found that this problem can be avoided when the sample temperature was reduced down to about 275 K before cryostat evacuation. Our present experiments were carried out following such a procedure.

## 3. Results

Raman spectra of the  $\text{Co}^{\text{III}}$  and  $\text{Fe}^{\text{III}}$  crystals as a function of temperature are shown in Figs. 1 and 2, respectively. At room temperature, the spectra of both salts are very similar. On cooling down they undergo analogous modifications due to the charge ordering, nevertheless, they show different temperature dependence.

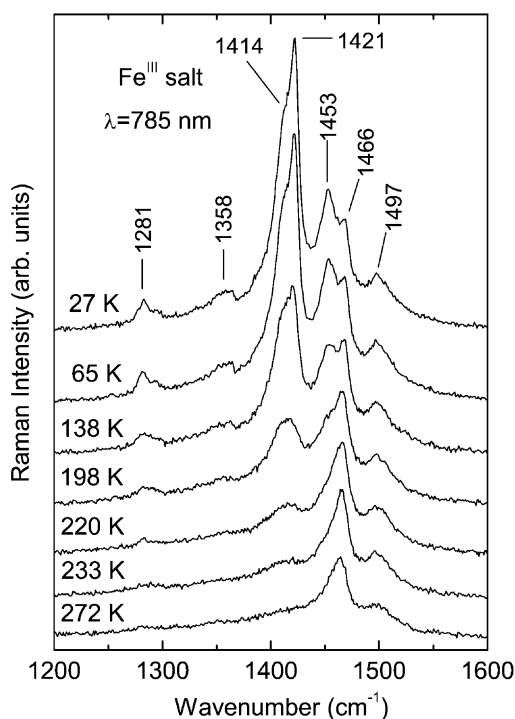


Fig. 2. Temperature dependence of the Raman spectra of  $\kappa$ -[Et<sub>4</sub>N](BEDT-TTF)<sub>4</sub>Fe(CN)<sub>6</sub>·3 H<sub>2</sub>O salt (NIR excitation:  $\lambda = 785$  nm).

As seen in Fig. 1, the room temperature spectrum of Co<sup>III</sup> salt is dominated by two bands at 1495 and 1465 cm<sup>-1</sup>, corresponding to the  $\nu_2(a_g)$  and  $\nu_3(a_g)$  modes of BEDT-TTF molecule with charge +0.5, respectively, in agreement with the stoichiometry and the crystallographic data. In the salt  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu(SCN)<sub>2</sub> containing (BEDT-TTF<sup>+0.5</sup>)<sub>2</sub> dimers, the  $\nu_2(a_g)$  and  $\nu_3(a_g)$  Raman bands were observed at 1491 and 1466 cm<sup>-1</sup> [16].

The phase transition at  $T = 150$  K has a drastic influence on the Raman spectrum of the Co<sup>III</sup> salt (Fig. 1): the bands related to molecules with charge +0.5 nearly disappear and simultaneously new strong lines grow, which are related to molecules with charge +1. Below 150 K, the band  $\nu_3(a_g) = 1465$  cm<sup>-1</sup> is nearly not seen, i.e. the number of molecules with the charge +0.5 decreases considerably. A similar process occurs with the  $\nu_2(a_g) = 1495$  cm<sup>-1</sup> band – we suggest that the spectral feature at about 1500 cm<sup>-1</sup> should be attributed to the  $\nu_3(a_g)$  mode of neutral molecule. Additionally, on closer analysis of the Raman spectra, we find a weak and broad band centred at about 1540 cm<sup>-1</sup>,

related to the  $\nu_2(a_g)$  mode of neutral molecule. Simultaneously, below 150 K we see the appearance of new lines at 1452, 1427, 1417, 1407 cm<sup>-1</sup> related to molecules with charge +1. The bands 1452 and 1427 cm<sup>-1</sup> should be assigned to the  $\nu_2(a_g)$  and  $\nu_3(a_g)$  modes of BEDT-TTF<sup>+1</sup> cation, respectively. The other two lines at 1417 and 1407 cm<sup>-1</sup> should be related to the  $\nu_3(a_g)$  mode of BEDT-TTF<sup>+1</sup>. Our Raman data show that the charge separation is much stronger than that one suggested previously by the X-ray investigations. The nearly disappearance of bands attributed to molecules with charge +0.5 and the existence of three lines related to the  $\nu_3(a_g)$  mode of molecules with the charge +1 proves that not only the molecules D, but also other molecules in the unit cell should bear the charge +1. The existence of three separate  $\nu_3(a_g)$  lines can be due to the following reasons: (1) different (BEDT-TTF<sup>+1</sup>)<sub>2</sub> dimers are not equivalent; (2) different dimers are in non-equivalent positions in the unit cell; (3) different dimers possess different charge. The  $\nu_2(a_g)$  and  $\nu_3(a_g)$  Raman bands were found respectively in a salt with (BEDT-TTF<sup>+0.9</sup>)<sub>2</sub> dimers at 1455 and 1425 cm<sup>-1</sup> [17] and in salts with (BEDT-TTF<sup>+1</sup>)<sub>2</sub> dimers at 1460 and 1418 cm<sup>-1</sup> [18]; or 1451 and 1408 cm<sup>-1</sup> [19] (room-temperature data).

The Raman bands of the Fe<sup>III</sup> salt (Fig. 2) are much broader in comparison to those recorded for the Co<sup>III</sup> salt. This difference can be related to a larger degree of disorder in the Fe<sup>III</sup> crystals; e.g. this disorder can be created by (Et<sub>4</sub>N)<sup>+</sup> cations. As results from the crystallographic investigations, the (Et<sub>4</sub>N)<sup>+</sup> cations show a great disorder, which was not determined even at low temperature [11, 12]. In the room temperature Raman spectrum of Fe<sup>III</sup> salt (Fig. 2), we observe also two bands at 1497 and 1466 cm<sup>-1</sup>, attributed to the  $\nu_2(a_g)$  and  $\nu_3(a_g)$  modes of BEDT-TTF<sup>+0.5</sup>, respectively. The spectral modifications due to charge ordering are analogous to those observed for the Co<sup>III</sup> salt. An important difference is that the modifications in the Fe<sup>III</sup> salt are not directly related to the phase transition at 150 K, but they grow gradually on decreasing temperature below about 240 K. In the Fe<sup>III</sup> spectra, we observe also the appearance of new lines assigned to BEDT-TTF<sup>+1</sup> cations:  $\nu_2(a_g) = 1453$  cm<sup>-1</sup> as well as  $\nu_3(a_g) = 1421$  cm<sup>-1</sup> and 1414 cm<sup>-1</sup>. Similarly to the case of the Co<sup>III</sup> salt, the splitting of the  $\nu_3(a_g)$  band suggests an existence of different BEDT-TTF dimers consisting of molecules with the charge +1. Nevertheless,

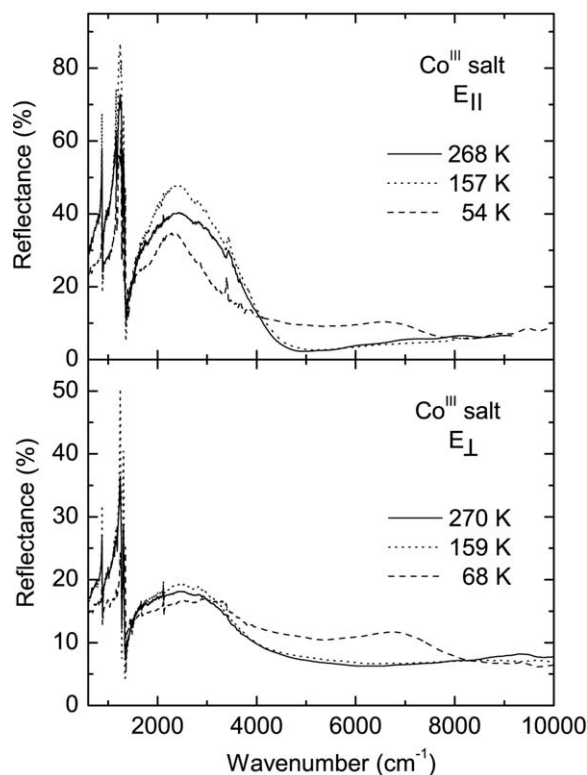


Fig. 3. Temperature dependence of the polarised reflectance spectra of  $\kappa$ -[Et<sub>4</sub>N](BEDT-TTF)<sub>4</sub>Co(CN)<sub>6</sub>·3 H<sub>2</sub>O salt for two perpendicular orientations of the electrical vector of the incident IR beam.

in the Fe<sup>III</sup> salt the line 1466 cm<sup>-1</sup>, attributed to the  $\nu_3(a_g)$  mode of BEDT-TTF<sup>+0.5</sup>, does not disappear even at lowest temperatures, providing thus evidence that the charge separation is not complete.

Fig. 3 displays temperature dependence of the reflectance spectra of Co<sup>III</sup> crystals over the entire spectral range for two perpendicular polarisations, corresponding to the maximum ( $E_{||}$ ) and minimum ( $E_{\perp}$ ) of reflected energy. For polarisation  $E_{||}$  the electrical vector was parallel to the direction [110]. Conductivity spectra obtained by Kramers–Kronig transformation of the reflectance data are shown in Fig. 4. These spectra are very similar to the reflectance spectra of other  $\kappa$ -phase BEDT-TTF crystals [20–22].

In the room-temperature spectra of the Co<sup>III</sup> salt, we observe a broad mid-infrared electronic band with maximum at about 2200 cm<sup>-1</sup> for  $E_{||}$  and 3100 cm<sup>-1</sup> for  $E_{\perp}$ , corresponding to charge transfer transition between charged and neutral BEDT-TTF molecule (CT<sub>2</sub>), as well as several vibrational features below

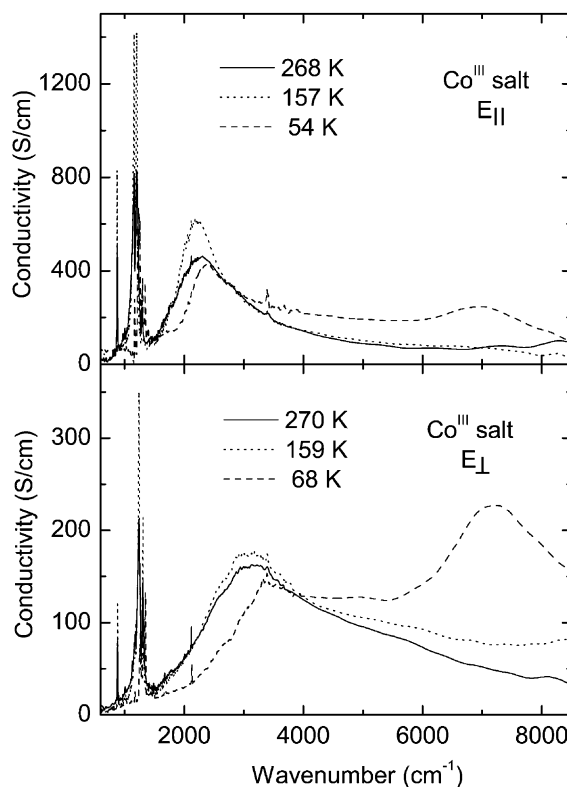


Fig. 4. Optical conductivity spectra of  $\kappa$ -[Et<sub>4</sub>N](BEDT-TTF)<sub>4</sub>Co(CN)<sub>6</sub>·3 H<sub>2</sub>O derived by Kramers–Kronig analysis of the reflectance spectra.

1400 cm<sup>-1</sup>. The phase transition at 240 K causes some modifications of the Co<sup>III</sup> spectra, similarly to those observed previously for the Fe<sup>III</sup> crystals [13]. However, the most important changes occur as a result of the phase transition at 150 K. Below 150 K, the mid-infrared electronic band decreases its intensity, changes shape and shifts towards higher frequency (Fig. 4). This is a consequence of opening of a new energy gap. By fitting the reflectance spectra with a Drude–Lorentz dielectric function (as described previously for Fe<sup>III</sup> salt [13, 14]), we estimated the energy gaps ( $\Delta$ ) for two perpendicular directions: at 160 K,  $\Delta_{||} = 0.27$  eV and  $\Delta_{\perp} = 0.40$  eV, whereas at 120 K  $\Delta_{||} = 0.30$  eV and  $\Delta_{\perp} = 0.48$  eV. However, the most striking spectral change is the appearance of a new near-infrared electronic band with maximum at about 7000 cm<sup>-1</sup> for  $E_{||}$  and 7200 cm<sup>-1</sup> for  $E_{\perp}$ , related to charge transfer between BEDT-TTF<sup>+1</sup> cations (CT<sub>1</sub>), providing thus a proof of existence of (BEDT-TTF<sup>+1</sup>)<sub>2</sub> dimers below 150 K.

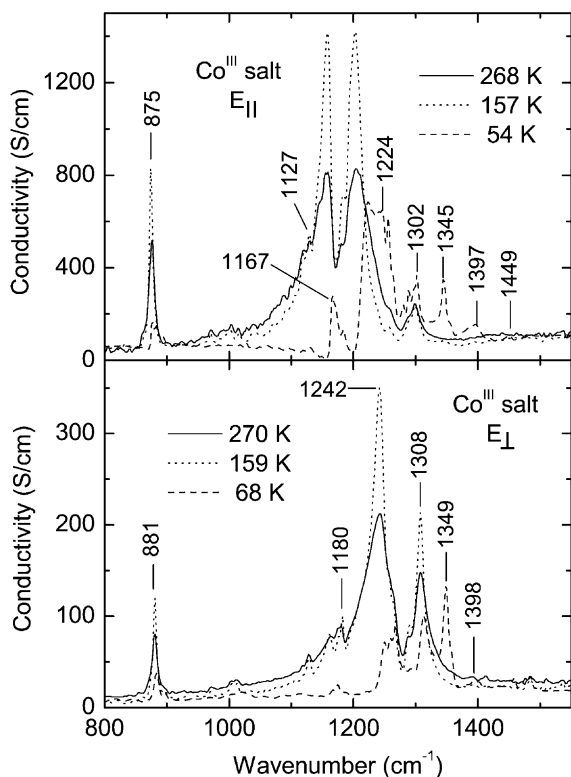


Fig. 5. Optical conductivity spectra of  $\kappa$ -[Et<sub>4</sub>N](BEDT-TTF)<sub>4</sub>Co(CN)<sub>6</sub>·3 H<sub>2</sub>O within the region of strong vibrational bands.

Above 150 K, for both polarisations, the IR spectra of Co<sup>III</sup> salt within the region of strong vibrational bands (Fig. 5) are very similar to those of other  $\kappa$ -phase BEDT-TTF salts [20–22]. The assignment of main vibrational features in the Co<sup>III</sup> spectra is carried out on the basis of references [16, 21–23]. For polarisation  $E_{||}$ , we observe a broad and strong band in the region 1130–1230 cm<sup>-1</sup> related to the  $\nu_3(a_g)$  mode of BEDT-TTF, activated by coupling with the charge transfer transition CT<sub>2</sub>. An antiresonance dip at about 1170 cm<sup>-1</sup> is due to the  $\nu_{67}(b_{3u})$  mode. A doublet at 1286 and 1299 cm<sup>-1</sup> is attributed to the  $\nu_5(a_g)$  mode (CH<sub>2</sub> vibrations), whereas a strong band at 875 cm<sup>-1</sup> is attributed to the activated  $\nu_{60}(b_{3g})$  mode, according to the proposition made in [23]. The charge ordering at 150 K induces considerable modifications of the vibrational bands. Below 150 K the spectral feature related to the  $\nu_3(a_g)$  mode has weaker intensity and lies in the higher-frequency region 1210–1270 cm<sup>-1</sup>; the intensity of this band is nearly temperature independent.

Such a strong effect, together with the Raman data, suggest that (BEDT-TTF<sup>+0.5</sup>)<sub>2</sub> dimers are nearly absent; therefore, the 1210–1270 cm<sup>-1</sup> band can be associated with coupling of the  $\nu_3(a_g)$  mode of charge-poor molecule with charge transfer between neighbouring dimers (CT<sub>2</sub>-type transition). For the mode  $\nu_{67}(b_{3u})$ , we can see a band at 1167 cm<sup>-1</sup> instead of the dip. The band  $\nu_{60}(b_{3g})$  reduces strongly its intensity, confirming thus an interaction of the  $\nu_{60}(b_{3g})$  mode with the CT<sub>2</sub>. Additionally, below 150 K we observe a new band at 1345 cm<sup>-1</sup>, related to the  $\nu_3(a_g)$  mode of BEDT-TTF<sup>+1</sup> cation, which is activated by coupling with the charge transfer transition CT<sub>1</sub>, as well as relatively weaker lines at about 1397 and 1449 cm<sup>-1</sup>, related to the  $\nu_{45}(b_{2u})$  and  $\nu_{27}(b_{1u})$  modes of BEDT-TTF<sup>+1</sup>, respectively. However, it is also possible that the band at 1449 cm<sup>-1</sup> is due to the  $\nu_2(a_g)$  vibration. In the IR spectra of a salt containing (BEDT-TTF<sup>+1</sup>)<sub>2</sub> dimers, the  $\nu_{27}(b_{1u})$ ,  $\nu_2(a_g)$ ,  $\nu_{45}(b_{2u})$ ,  $\nu_3(a_g)$  bands were found at 1454, 1452, 1408, 1343 cm<sup>-1</sup>, respectively [18].

Above 150 K, in the Co<sup>III</sup> spectrum for polarisation  $E_{\perp}$  (Fig. 5), we observe strong bands at 1308 and 1242 cm<sup>-1</sup> related to the  $\nu_3(a_g)$  and  $\nu_5(a_g)$  modes of BEDT-TTF<sup>+0.5</sup>, respectively, and the band  $\nu_{60}(b_{3g})$  at 881 cm<sup>-1</sup>. The phase transition has a strong influence on these bands: the band  $\nu_3(a_g)$  is observed at 1314 cm<sup>-1</sup> and it is of weaker intensity; a spectral feature consisting of three lines (1250, 1259 and 1267 cm<sup>-1</sup>) is related to the  $\nu_5(a_g)$  mode; the band  $\nu_{60}(b_{3g})$  gets much weaker. However, for polarisation  $E_{\perp}$ , the most important spectral change is the appearance of a relatively strong band at 1349 cm<sup>-1</sup> as well as a weak band at 1398 cm<sup>-1</sup>, respectively, related to the  $\nu_3(a_g)$  and  $\nu_{45}(b_{2u})$  modes of BEDT-TTF<sup>+1</sup> cation.

Due to the phase transition at 150 K, the infrared spectra of the Fe<sup>III</sup> salt undergo analogous modifications to those observed for the Co<sup>III</sup> salt (Figs. 6 and 7). In the vibrational spectra of the Fe<sup>III</sup> salt (both above and below 150 K), we find nearly all the spectral features described above for the Co<sup>III</sup> salt: for example, below 150 K we observe the bands at 1342 cm<sup>-1</sup> ( $E_{||}$ ) and 1344 cm<sup>-1</sup> ( $E_{\perp}$ ), related to the  $\nu_3(a_g)$  mode of BEDT-TTF<sup>+1</sup> cation. It is important to emphasise, that in the case of Fe<sup>III</sup> salt, the spectral modifications are directly related to the phase transition at 150 K, although, as shown by Raman experiment, the charge redistribution occurs gradually below 240 K. For example, for polarisation  $E_{||}$ , for bands related to the

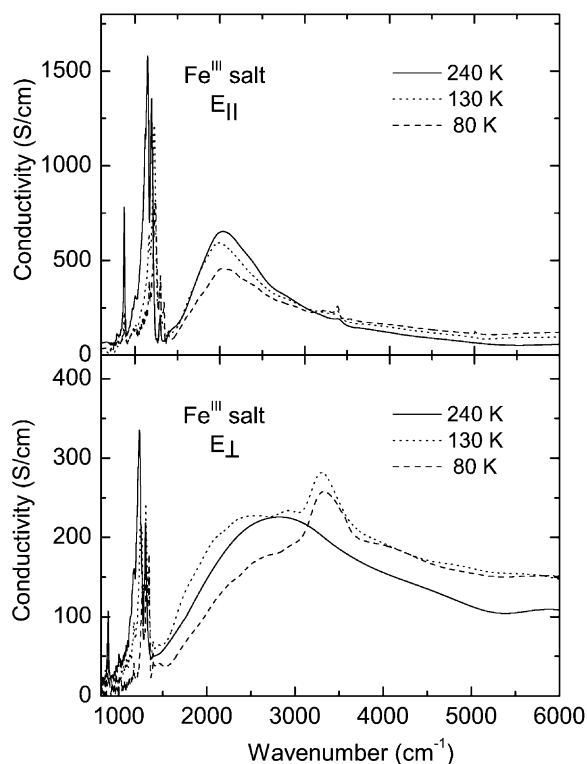


Fig. 6. Optical conductivity spectra of  $\kappa$ -[Et<sub>4</sub>N](BEDT-TTF)<sub>4</sub>Fe(CN)<sub>6</sub>·3 H<sub>2</sub>O salt for two perpendicular polarisations corresponding to the maximum ( $E_{||}$ ) and minimum ( $E_{\perp}$ ) of reflected energy.

$\nu_3(a_g)$  mode, the disappearance of the spectral feature at 1170–1230  $\text{cm}^{-1}$  and the appearance of a peak at 1227  $\text{cm}^{-1}$  occurs at the phase-transition temperature 150 K (Fig. 7). Analogous conclusion results from the analysis of temperature dependence of electronic absorption [14]. Below 150 K, for the Fe<sup>III</sup> salt, the spectral features 1227  $\text{cm}^{-1}$  ( $E_{||}$ ) and 1308  $\text{cm}^{-1}$  ( $E_{\perp}$ ), attributed to the  $\nu_3(a_g)$  mode activated by a CT<sub>2</sub>-type transition, are much stronger than those for the Co<sup>III</sup> salt (see also Fig. 5), and considerably decrease their intensities when temperature goes down. Such behaviour can be related to a process of further charge redistribution intervening in the Fe<sup>III</sup> salt below 150 K.

#### 4. Discussion

The studied salts are isostructural, exhibit very similar physical properties and undergo analogous phase transitions at about 240 and 150 K, but the charge

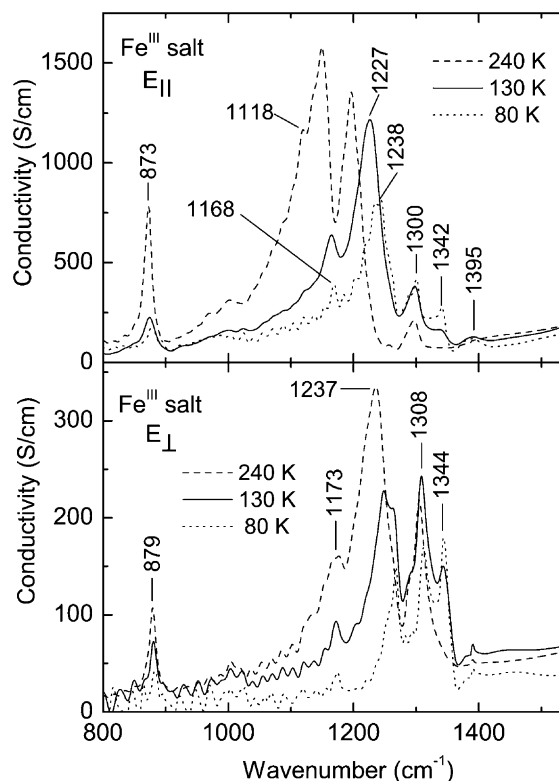


Fig. 7. Optical conductivity spectra of  $\kappa$ -[Et<sub>4</sub>N](BEDT-TTF)<sub>4</sub>Fe(CN)<sub>6</sub>·3 H<sub>2</sub>O salt within the region of strong vibrational bands.

ordering inside conducting BEDT-TTF layers arises in different ways. The Raman spectra show that, in the Co<sup>III</sup> salt, the charge redistribution occurs at the phase-transition temperature, i.e. 150 K. In this salt, above 150 K, the charge is distributed more or less uniformly among BEDT-TTF molecules (charge +0.5), while below 150 K most molecules are either neutral or possess a charge +1. On the other hand, in Fe<sup>III</sup> salt the charge redistribution starts already below 240 K, then develops gradually on temperature lowering and is even further continued below 150 K. In this case, the phase transition at 150 K has no drastic influence on the Raman spectrum. Nevertheless, the charge redistribution in Fe<sup>III</sup> salt seems to lead to analogous charge patterns as in the Co<sup>III</sup> salt.

The differences between charge-ordering mechanisms in the studied compounds, as revealed by Raman experiment, are not directly observed in IR spectra. The IR electronic and vibrational features of both crystals change abruptly at the phase transition temperature

$T = 150$  K. Such an effect should be expected in the  $\text{Co}^{\text{III}}$  salt, but is rather surprising in the  $\text{Fe}^{\text{III}}$  salt. We suppose that in the  $\text{Fe}^{\text{III}}$  salt, in the temperature range 240–150 K, the charge ordering is dynamical and does not lead to the formation of stable  $(\text{BEDT-TTF}^{+1})_2$  dimers. Such stable dimers are just created at 150 K, yielding modifications of the electronic and vibrational spectral features of the  $\text{Fe}^{\text{III}}$  salt. The phase transition at 150 K causes modifications of the electronic structure. On the other hand, the vibrational bands are mainly due to the effect of coupling of BEDT-TTF vibrations with electrons; therefore, they are considerably modified when charge transfer transition between  $\text{BEDT-TTF}^{+1}$  cations is activated. Previous investigations of the ESR spectra and the magnetic susceptibility [10–12] have shown that the results for the  $\text{Fe}^{\text{III}}$  salt were similar to those for the  $\text{Co}^{\text{III}}$  salt, but the experimental signatures of the phase transitions for  $\text{Fe}^{\text{III}}$  salt were less clear and appeared in a wider temperature range. Our spectroscopic measurements confirm these observations.

Now we discuss possible reasons of the charge-ordering effect. The theoretical studies have shown that the insulating state of quarter-filled  $\kappa$ -phase BEDT-TTF salts is stabilised by the strong on-site Coulomb ( $U$ ) interaction and strong dimerisation of conducting BEDT-TTF layers [24]. The presence of relevant values of the inter-site interactions ( $V$ ) can be also expected in  $\kappa$ -phase salts; however, the stability of their insulating state is proved by the mean-field calculations by considering only  $U$  (without  $V$ ). Consequently, the electronic states of these compounds can be considered by taking each dimer as a unit (dimer model). The important parameter of dimer model is the so-called on-site Coulomb interaction energy of the dimer ( $U_{\text{eff}}$ ), which grows when  $t$  increases ( $t$  is intra-dimer transfer integral). Strong dimerisation leads to a phase with half-filled band, in which the Mott insulator is stabilised for strong electron correlations [24]. Consequently, in a typical  $\kappa$ -phase salt, the charge distribution is uniform among BEDT-TTF molecules and no charge-ordering phenomenon is expected.

Within the family of  $\kappa$ -phase BEDT-TTF salts the studied crystals  $\kappa\text{-[Et}_4\text{N](BEDT-TTF)}_4\text{M(CN)}_6\cdot 3\text{H}_2\text{O}$  ( $M = \text{Co}^{\text{III}}, \text{Fe}^{\text{III}}$ ) are exceptional, since the degree of dimerisation of BEDT-TTF molecules is relatively weak [12]. The analysis of the crystallographic data at  $T = 115$  K shows that the intra-dimer interaction is

weaker than that one in typical  $\kappa$ -phase salts; moreover, it is weaker than the interaction between molecules belonging to neighbouring dimers. Consequently, the parameters  $U_{\text{eff}}$  and  $V$  are respectively smaller and larger, in comparison with a typical  $\kappa$ -phase salt; therefore, the Mott insulating state can be unstable. In this situation, the inter-site Coulomb interaction  $V$  plays an important role and gives rise to the charge ordering.

Theoretically, it was argued that inter-site Coulomb interactions ( $V$ ) can stabilise charge ordered states in organic conductors based on BEDT-TTF donor [3]. Therefore, we suggest that, in the studied salts at  $T = 150$  K, the parameter  $V/t$  becomes large enough to induce charge redistribution. If we assume that the degree of disorder in the  $\text{Fe}^{\text{III}}$  salt is higher than in the  $\text{Co}^{\text{III}}$  salt (e.g. due to  $\text{Et}_4\text{N}^+$  cations), the larger distribution of  $t$  can be expected and the charge redistribution can occur at different temperatures in different unit cells of the crystal lattice. In this way, one can explain differences between the charge redistribution phenomena in both compounds. Nevertheless, it is important to emphasise that the phase transition in both salts occurs at 150 K.

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