

## Phase transitions in $\beta$ -(BEDT-TTF) $_2$ XF $_6$ (X = P, Sb or As) salts as seen by Raman Spectroscopy

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Raman spectra of three charge-transfer salts,  $\beta$ -(BEDT-TTF) $_2$ XF $_6$  (where X = P, Sb, As), were measured in the temperature range of 300–80 K. The salts exhibit fluctuations in charge ordering, indicating the formation of Wigner-like crystals.

Key words: *Raman spectroscopy; charge ordering; Wigner crystal*

### 1. Introduction

The nature of phase transitions in low-dimensional organic metals has attracted a lot of interest for many years. In some organic conductors, phase transitions generate a charge ordered (CO) state in the form of charge-rich and charge-poor sites. Such a phase transition is connected with charge localisation on molecules, and a possible explanation of these phenomena is electron correlation effects. In the presence of a strong dimerisation, on-site Coulomb interactions can give rise to a dimer Mott insulating state, while the inter-site Coulomb interactions can stabilize the CO as a Wigner crystal, even in the presence of some weak dimerisation [1].

In the present study, we have investigated vibrational spectra for three salts of the bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) donor molecule:  $\beta$ -(BEDT-TTF) $_2$ PF $_6$ ,  $\beta$ -(BEDT-TTF) $_2$ SbF $_6$ , and  $\beta$ -(BEDT-TTF) $_2$ AsF $_6$ . These salts show a metal–insulator phase transition at 293 K (X = PF $_6$ ), 273 K (X = SbF $_6$ ), and 264 K (X = AsF $_6$ ) [2– 4], respectively. In crystals of the  $\beta$ -(BEDT-TTF) $_2$ PF $_6$  salt, the donor molecules are strongly dimerised [5]. The two other salts,  $\beta$ -(BEDT-TTF) $_2$ SbF $_6$  and  $\beta$ -(BEDT-TTF) $_2$ AsF $_6$ , show only weak dimerisation [3, 5]. It was therefore of interest to check which of the effects (Mott insulator or Wigner crystal) is responsible for the phase transitions.

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Vibrational spectroscopy is an effective method of investigating electron correlation effects and phase transitions in BEDT-TTF salts. The frequencies of some C=C stretching modes in the donor molecule carry information on the charge localised on the molecule making possible the determination of charge spatial distribution in the crystal's unit cell [6]. Charge ordering can be observed in the Raman spectrum as a splitting of the Raman bands sensitive to the charge on the donor molecules. It is well known that for the BEDT-TTF molecule two in-phase ring C=C stretching modes,  $\nu_2$  and  $\nu_3$ , show large charge-dependent frequency shifts. There is also one antiphase ring C=C stretching mode sensitive to the charge,  $\nu_{27}$ , which can be observed in infrared spectroscopy. Nevertheless, the antiphase vibration of molecules forming a dimer can become Raman active and in such a case the mode  $\nu_{27}$  will be visible in the Raman spectrum [6].

## 2. Experimental

Single crystals of the charge transfer salts (BEDT-TTF)<sub>2</sub>XF<sub>6</sub> (where X = P, Sb, As) were synthesized by electro-crystallisation according to the known procedure [4]. Crystallographic X-ray investigations have shown that all the crystals obtained are in the  $\beta$ -phase. The salt  $\beta$ -(BEDT-TTF)<sub>2</sub>PF<sub>6</sub> belongs to the orthorhombic crystal system, with the  $P_{nna}$  space group at room temperature [2]. The salts  $\beta$ -(BEDT-TTF)<sub>2</sub>SbF<sub>6</sub> and  $\beta$ -(BEDT-TTF)<sub>2</sub>AsF<sub>6</sub> belong to the monoclinic crystal system, with a  $C_{2/c}$  space group at room temperature [4].

Raman spectra in the temperature range of 300–80 K were recorded using a Micro-Raman Spectrometer (Jobin-Yvon T64000) and 514.5 nm laser light. Single crystals were mounted with silicon grease on a cold stage in a homemade helium cryostat. The spectra were collected upon cooling in ca. 20 K intervals; the crystals were thermostated at each temperature for ca. 20 minutes. The Raman bands in the characteristic frequency range of the C=C stretching modes (1200–1700 cm<sup>-1</sup>) were recorded for the incident light polarised along and perpendicular to the long axis of the BEDT-TTF molecules.

## 3. Results and discussion

The Raman spectra obtained for all the investigated BEDT-TTF salts show an abrupt change in the C=C stretching band, from a broad band at high temperatures to multiple peaks below the metal-isolator transition temperature. The spectra for all three salts are very similar at room temperature, i.e., in the metal states. Therefore, in Fig. 1 and Fig. 2 we show the spectra at different temperatures only for the salt  $\beta$ -(BEDT-TTF)<sub>2</sub>AsF<sub>6</sub>. For the two other salts, only the spectra obtained at 80 K (i.e., well below their phase transition temperatures) are presented in the insets.

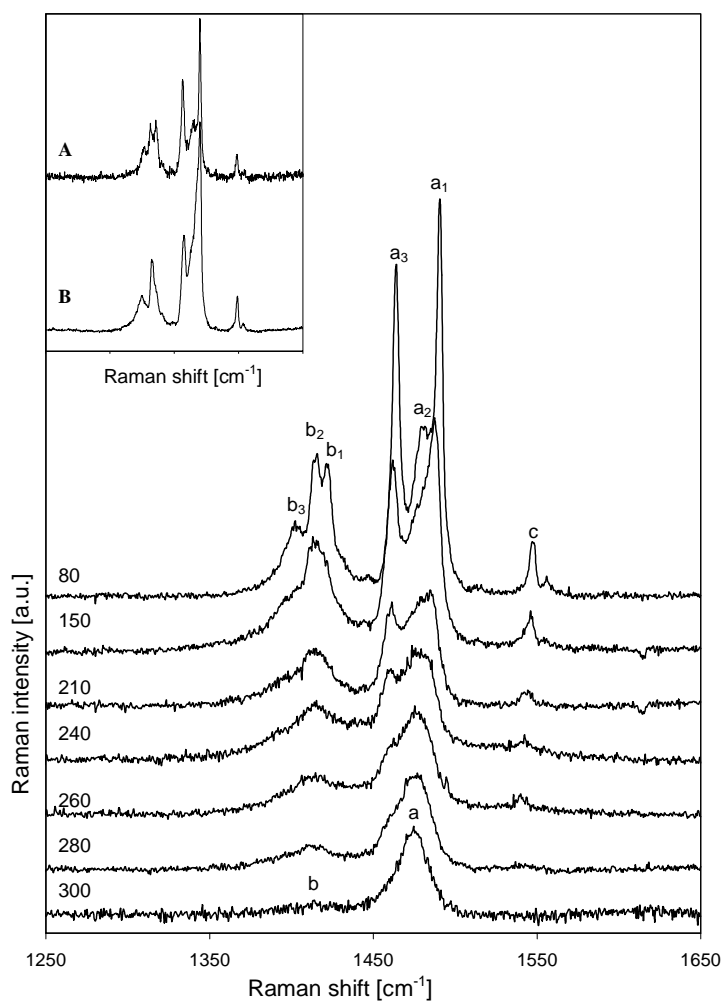


Fig. 1. Temperature dependences of the Raman active C=C stretching modes for  $\beta$ -(BEDT-TTF) $_2$ AsF $_6$  salt, with the laser light polarisation plane parallel to the long axis of the donor molecules. The inset shows spectra for  $\beta$ -(BEDT-TTF) $_2$ PF $_6$  (A) and  $\beta$ -(BEDT-TTF) $_2$ SbF $_6$  (B) salts at 80 K and the same polarisation

Figure 1 shows the spectra obtained for the incident light polarised along the long axis of the BEDT-TTF molecules. The bands marked as  $a$  and  $b$ , observed at 300 K, undergo a splitting at 260 K, i.e. at the metal–insulator transition temperature for  $\beta$ -(BEDT-TTF) $_2$ AsF $_6$ , observed in resistivity and EPR measurements [4]. Among the multiple peaks observed at 80 K, we can attribute the peaks  $c$  (1547 cm $^{-1}$ ) and  $a_1$  (1489 cm $^{-1}$ ) to  $\nu_2$ , the peak  $a_2$  (1482 cm $^{-1}$ ) to  $\nu_{27}$ , and the peak  $a_3$  (1463 cm $^{-1}$ ) to  $\nu_3$ . Since the frequencies of the  $\nu_2$  mode are sensitive to charge, the observed position of

the bands after splitting indicates that peak *c* corresponds to the charge-poor site, while peak *a*<sub>1</sub> corresponds to the charge-rich one. Basing only on the frequency of the  $\nu_2$  mode, we estimated the deviation of the charge on the donor molecules to be 0.16 and 0.84.

An unequivocal assignment of three peaks at lower frequencies (*b*<sub>1</sub> at 1422 cm<sup>-1</sup>, *b*<sub>2</sub> at 1415 cm<sup>-1</sup>, and *b*<sub>3</sub> at 1403 cm<sup>-1</sup>) is difficult. One of them should be assigned to the  $\nu_3$  mode, the others probably to bending ones.

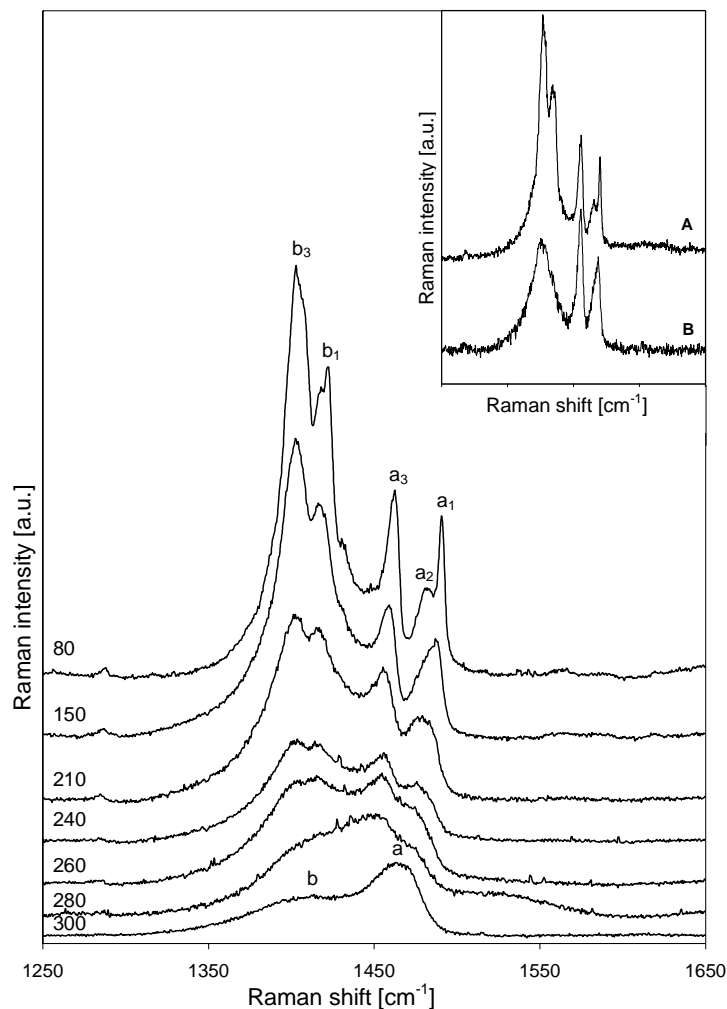


Fig. 2. Temperature dependences of the Raman active C=C stretching modes for the  $\beta$ -(BEDT-TTF)<sub>2</sub>AsF<sub>6</sub> salt, with the laser light polarisation plane perpendicular to the long axis of the donor molecules.

The inset shows spectra for  $\beta$ -(BEDT-TTF)<sub>2</sub>PF<sub>6</sub> (A) and  $\beta$ -(BEDT-TTF)<sub>2</sub>SbF<sub>6</sub> (B) salts at 80 K and the same polarisation

For the  $\beta$ -(BEDT-TTF)<sub>2</sub>PF<sub>6</sub> salt, the splitting of the observed *a* and *b* bands starts at room temperature. This is due to the fact that the metal–insulator phase transition occurs at 293 K in this salt. In  $\beta$ -(BEDT-TTF)<sub>2</sub>SbF<sub>6</sub>, analogous changes were observed at 270 K (the phase transition occurs at 273 K). Comparing the spectra recorded for these two salts at 80 K (see the inset in Fig. 1), one can notice that both are very similar to the spectrum of the salt  $\beta$ -(BEDT-TTF)<sub>2</sub>AsF<sub>6</sub> taken at the same temperatures. The most important difference relates to the *a*<sub>2</sub> band ( $\nu_{27}$ ), which is considerably weaker in the spectrum of (BEDT-TT)<sub>2</sub>SbF<sub>6</sub> than in that of the two other salts (see inset B in Fig. 1).

Figure 2 shows the temperature dependence of the Raman spectrum for the  $\beta$ -(BEDT-TTF)<sub>2</sub>AsF<sub>6</sub> salt, taken with a laser light polarisation plane perpendicular to the long axis of BEDT-TTF molecule. The broad bands, marked *a* and *b*, split at low temperatures, and at 80 K five main bands, *a*<sub>1</sub>, *a*<sub>2</sub>, *a*<sub>3</sub>, *b*<sub>1</sub>, and *b*<sub>3</sub> (1489 cm<sup>-1</sup>, 1482 cm<sup>-1</sup>, 1463 cm<sup>-1</sup>, 1422 cm<sup>-1</sup>, and 1403 cm<sup>-1</sup>, respectively), can be distinguished. We can attribute the peak *a*<sub>1</sub> to  $\nu_2$ , *a*<sub>2</sub> to  $\nu_{27}$ , and *a*<sub>3</sub> to  $\nu_3$ . The *a*<sub>1</sub> band, assigned to the  $\nu_2$  mode, corresponds to the charge-rich site (analogous to the *a*<sub>1</sub> band in Fig.1.). The assignments of the *b*<sub>1</sub> (1422 cm<sup>-1</sup>) and *b*<sub>3</sub> (1402 cm<sup>-1</sup>) bands are not certain, as discussed above in relation to the spectra in Fig.1. Note that the same bands are observed for both light polarisations - only their relative intensities are different.

The spectra for the two other salts for perpendicular incident light polarisation are also similar to the spectrum of the  $\beta$ -(BEDT-TTF)<sub>2</sub>AsF<sub>6</sub> salt – see the inset in Fig. 2. Also in this case, the  $\beta$ -(BEDT-TTF)<sub>2</sub>SbF<sub>6</sub> salt exhibits only a weak *a*<sub>2</sub> ( $\nu_{27}$ ) band, which is shown in inset B.

The results published by Laversanne et al. [4] and Mori et al. [5] indicate that among the three investigated BEDT-TTF salts,  $\beta$ -(BEDTTTF)<sub>2</sub>PF<sub>6</sub> exhibits the strongest dimerisation of the donor molecules, and the two other salts show rather weak dimerisation. Taking into account the relative intensities of the  $\nu_{27}$  bands, we can conclude from our studies that strong dimerisation occurs also in  $\beta$ -(BEDT-TTF)<sub>2</sub>AsF<sub>6</sub>.

The temperature dependence of the Raman spectra for the  $\beta$ -(BEDT-TTF)<sub>2</sub>PF<sub>6</sub> salt has already been published by Ding and Tajima [7]. In contrast to the results obtained by us, they did not observe any splitting of the *b* band. In fact, this band disappears in their spectra at low temperatures. As discussed above, one should expect the second  $\nu_3$  mode in this region, which can appear at low energies due to the *e-mv* interaction.

## 4. Conclusions

The results obtained show that the dimerisation occurs in all three investigated salts, (BEDT-TTF)<sub>2</sub>XF<sub>6</sub> (where X = P, Sb, As), upon cooling below their M–I phase transition temperatures. On the other hand, the splitting of the C=C stretching bands  $\nu_2$  and  $\nu_3$  clearly demonstrates that charge ordering occurs in the insulating state,

indicating formation of a Wigner-like crystal. The splitting of the  $\nu_2$  mode indicates an irregular charge distribution in the unit cell. Therefore, we conclude that the phase transitions in the (BEDT-TTF)<sub>2</sub>XF<sub>6</sub> salts are caused by charge localizations. To verify these conclusions derived from Raman studies, X-ray diffraction investigations at different temperatures are in progress.

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