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Infrared and Raman Studies of the Charge Ordering in the Organic Semiconductor κ-$[Et_4N][Co(CN)_6(ET)_4]\cdot 3H_2O$

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Summary: Polarised infrared reflectance and Raman spectra of the charge transfer salt κ-$[Et_4N][Co(CN)_6\ (ET)_4]\cdot 3H_2O$ were measured as a function of temperature. The salt undergoes a phase transition at 150 K, which is related to a charge ordering inside conducting ET layers. The charge ordering has a considerable influence on vibrational as well as electronic spectra. New vibrational bands related to ET^+ cations are seen below 150 K. Moreover, formation of a new energy gap (charge gap) in electronic excitation spectrum is observed.

Keywords: charge transfer; infrared spectroscopy; Raman spectroscopy; transitions

Introduction

Three isostructural charge transfer salts yielded by the organic donor bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF, ET) with diamagnetic (M = Co^{III}) or paramagnetic (M = Fe^{III}, Cr^{III}) hexacyanometalate trianions $[M(CN)_6]^{3-}$ exhibit very similar semiconducting properties and undergo two phase transitions at 240 K and 150 K.[1,2] A specific feature of their crystal structure is that ET molecules in conducting layers are arranged in nearly perpendicular dimers, in a characteristic manner of the so-called κ-phase structure. At room temperature, two kinds of ET dimers can be distinguished (A and B), whereas below 240 K the unit cell is doubled and there exist four kinds of dimers (A, B, C and D). The charge distribution inside ET layers was studied in the Fe^{III} salt by comparison of the bond lengths of ET donors determined from the X-ray structural data. From these data it results that at room temperature all ET molecules possess a charge +0.5 (both in dimers A and B), but below 240 K a charge redistribution takes place leading to the following charge pattern: $A(ET^0)_2$ $B(ET^{+0.5})_2$ $C(ET^{+0.5})_2$ $D(ET^{+1})_2$. The phase

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transition at 150 K has no distinguishable influence on the crystal structure, suggesting a minor role of structural change at this temperature.

Recently, the phase transitions and in particular charge ordering phenomena in Fe^{III} salts were studied by IR and Raman spectroscopy.[3,4] The existence of charge redistribution inside ET layers was unambiguously confirmed by the Raman experiment on powdered crystals dispersed in KBr. The Raman data showed that the charge redistribution is not an abrupt process but develops gradually below 240 K.[3] Subsequently, the IR experiment on Fe^{III} single crystals provided an evidence that significant changes of electronic and vibrational spectral features, related to charge ordering, occur below 150 K.[4] Here we report on IR and Raman investigations of the phase transition at 150 K in single crystals of the Co^{III} salt.

Experimental

Single crystals of the salt κ-$[Et_4N][Co(CN)_6(ET)_4]\cdot 3H_2O$ were prepared by an electrochemical method, as described elsewhere.[1] The Et_4N^+ cations incorporated in crystal lattice show a great disorder, which is not determined by X-ray experiment even at low temperatures. Polarised reflectance spectra were recorded from the best-developed crystal face (001) in the frequency range (600 – 10000 cm^{-1}) using FT-IR Nicolet Magna 760 spectrometer equipped with an IR microscope. Single-crystal Raman spectra were measured within the region of C=C stretching vibrations (1200 – 1700 cm^{-1}) with NIR excitation (λ = 785 nm) using Renishaw Ramascope System 1000. The experiments were carried out in vacuum cryostats (T = 40 - 300 K). To avoid problems with sample cracking, due to loss of water molecules from crystals under vacuum, the sample temperature was reduced down to about 270 K before cryostat evacuation.

Results and discussion

The phase transition at 150 K has a drastic influence on Raman spectrum of the κ-$[Et_4N][Co(CN)_6(ET)_4]\cdot 3H_2O$ salt within the region of C=C stretching bands (Figure 1). At room temperature we observe two bands at about 1495 and 1465 cm^{-1} which can be related to $\nu_2(a_g)$ and $\nu_3(a_g)$ modes of ET, respectively. Positions of these bands in Raman spectrum are strongly dependent on the degree of ionisation of ET and they are often used for determination of charge residing on ET (for neutral ET^0, $\nu_2(a_g)$ = 1552 cm^{-1} and $\nu_3(a_g)$ = 1493 cm^{-1}; for ET^+ cation,

$\nu_2(a_g) = 1455\ cm^{-1}$ and $\nu_3(a_g) = 1431\ cm^{-1}$).[5] As shown recently, the mode $\nu_2(a_g)$ is even more valuable for this purpose than $\nu_3(a_g)$ because of weaker coupling with electrons, which yields an additional shift towards lower frequency.[6] Using this method we estimate that the frequencies 1495 and 1465 cm^{-1} correspond to the molecules with charges +0.58 and +0.45, respectively. The average charge on ET is close to the value +0.5 estimated from the stoichiometry and crystallographic data. Below 150 K, due to charge ordering, additional strong bands appear in the spectrum at frequencies 1452, 1427, 1417 and 1407 cm^{-1}. The bands at 1452 and 1427 cm^{-1} are assigned to $\nu_2(a_g)$ and $\nu_3(a_g)$ modes of ET^+ cations, respectively. Their positions are very close to the frequencies of Raman bands of ET^+ cations reported elsewhere.[5] The bands at 1417 and 1407 cm^{-1} can be also attributed to the $\nu_3(a_g)$ mode of ET molecules with slightly higher oxidation state than +1 or of the molecules in different environment. An important result is that in the studied Co^{III} salt the charge ordering is not a gradual process as in the Fe^{III} salt but proceeds abruptly at 150 K.

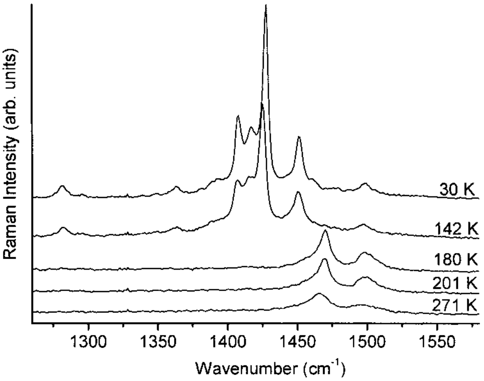

Figure 1. Raman spectra of a κ-$[Et_4N][Co(CN)_6(ET)_4]\cdot 3H_2O$ single crystal as a function of temperature (NIR excitation: $\lambda = 758$ nm).

The IR reflectance spectra were measured for two perpendicular orientations of the electrical vector of polarised light corresponding to the maximum ($E_{\|}$) and minimum ($E_{\perp}$) of reflected energy. For polarisation $E_{\|}$, the electrical vector of polarised light was parallel to the direction [110], which is the direction of strongest side-by-side S···S contacts between neighbouring ET molecules. The reflectance spectra at different temperatures are displayed in Figure 2. Optical conductivity spectra were determined by Kramers-Kronig analysis of the reflectance data (Figure 3). The phase transition at 150 K has a considerable influence on electronic part of the reflectance spectrum. The most striking feature is the appearance of a new electronic band centred at about 7000 cm^{-1} for $E_{\|}$ and 7200 cm^{-1} for $E_{\perp}$. This band is assigned to charge transfer mechanism $ET_I^+ + ET_{II}^+ = ET_I^0 + ET_{II}^{2+}$ and provides an evidence of formation of ET^+ cations below 150 K. In a compound containing quasi-isolated dimers $(ET^+)_2$, this charge-transfer transition was observed at 7000 cm^{-1}.[7] Simultaneously, we observe also important modifications of the band related to charge transfer $ET_I^+ + ET_{II}^0 = ET_I^0 + ET_{II}{}^+$ centred at 2200 cm^{-1} for $E_{\|}$ and 3100 cm^{-1} for $E_{\perp}$ (at about 160 K). Below 150 K, the intensity of this band decreases and its maximum shifts towards higher frequencies. This shift is a consequence of opening of a new energy gap in electronic excitation spectrum (charge gap). By fitting to experimental data, the reflectance calculated with a Drude-Lorentz dielectric function (procedure commonly used for semiconductors), the energy gaps below and above 150 K were estimated: 0.27 eV (at 160 K) and 0.30 eV (at 120 K) for polarisation $E_{\|}$; 0.40 eV (at 160 K) and 0.48 eV (at 120 K) for polarisation $E_{\perp}$.

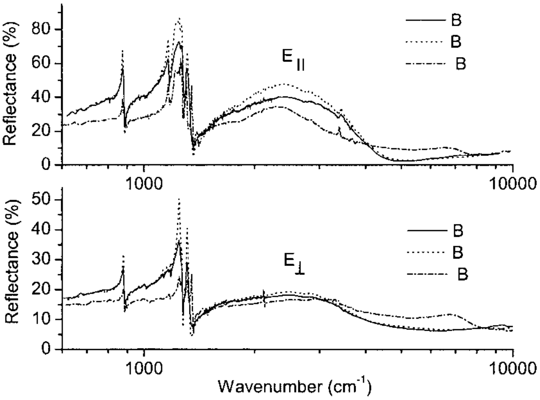

Figure 2. Temperature dependence of the polarised reflectance spectra of the κ-$[Et_4N][Co(CN)_6(ET)_4]\cdot 3H_2O$ crystal for two perpendicular polarisations corresponding to the maximum ($E_{\|}$) and minimum ($E_{\perp}$) of reflected energy (note the logarithmic frequency scale).

In vibrational part of the IR spectrum, we find several bands related to the totally symmetric C=C and C-S stretching vibrations of ET molecule activated by strong coupling with the charge transfer. These bands undergo also significant changes due to the phase transition at 150 K. The most important modification is that below 150 K we observe new bands assigned to the C=C modes of ET^+ cations: $\nu_2(a_g)$=1393 cm^{-1}, $\nu_3(a_g)$=1345 cm^{-1} and $\nu_{27}(b_{1u})$=1451 cm^{-1}. These frequencies are in good agreement with analogous bands observed in the salts containing ET radical cations with charge +1.[7]

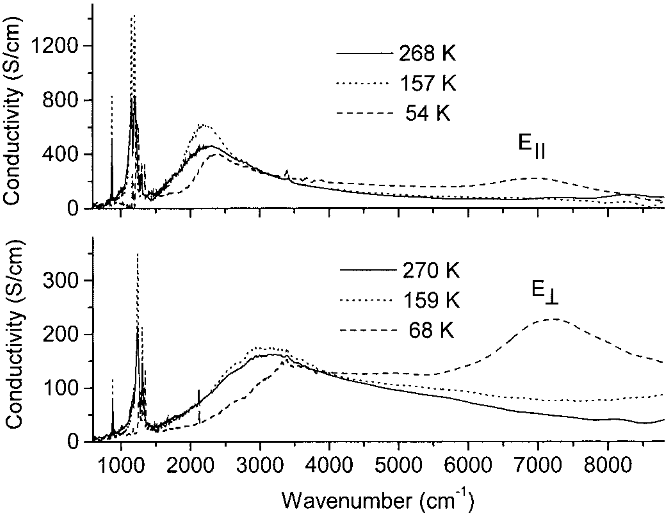

Figure 3. Temperature dependence of the optical conductivity spectra of a κ-$[Et_4N][Co(CN)_6(ET)_4]\cdot 3H_2O$ crystal as obtained from the reflectance spectra by Kramers-Kronig transformation.

The modifications of both IR and Raman spectra of Co^{III} crystals caused by the charge ordering are very similar to those recorded previously for Fe^{III} crystals. The most important difference is that the charge redistribution in the Fe^{III} salt proceeds gradually below 240 K, as proved by Raman studies of powders [3] as well as single crystals [8], but in the Co^{III} salt this is an abrupt process, which is directly related to the phase transition at 150 K. Such different behaviour is not clear at the moment. A possible explanation is that disorder in Fe^{III} crystals is larger than in Co^{III} crystals, as suggested by the fact that C=C bands in Fe^{III} Raman spectra are broader than analogous bands in Co^{III} spectra.

Recent investigations demonstrate that the charge-ordering phenomena are frequently observed in nearly uniform one- and two-dimensional conductors. For understanding of the charge-ordered states in quarter-filled quasi-two-dimensional ET salts, it is necessary to consider both on-site and intersite Coulomb interactions, together with the full anisotropy of transfer integrals.[9] In non-dimerised, nearly uniform salts the intersite Coulomb interactions are responsible for the charge ordering giving rise to various stripe-type charge-ordered states. The presence of the relevant values of the intersite Coulomb interactions can be also expected in the dimerised κ-phase salts; nevertheless, the stability of their insulating state is due to the on-site Coulomb repulsion and large dimerisation of conducting ET layers. In κ-phase salts, the charge distribution is uniform among ET molecules and charge ordering is not expected. Therefore, the transition from uniform to non-uniform charge distribution at 150 K in the κ-phase Co^{III} salt is quite surprising. An explanation of this unexpected phenomenon can be the fact that in Co^{III} salt the intra-dimer interaction between ET molecules is weak in comparison with interactions between neighbouring dimers, whereas in typical κ-phase salts, the situation is opposite, i.e. intra-dimer interactions are much stronger than inter-dimer ones.

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[1] P. Le Maguerès, L. Ouahab, N. Connan, C.J. Gómez-García, P. Delhaès, J. Even, M. Bertault, *Solid State Commun.* **1996**, *97*, 27.
[2] P. Le Maguerès, L. Ouahab, P. Briard, J. Even, M. Bertault, L. Toupet, J. Rámos, C.J. Gómez-García, P. Delhaès, T. Mallah, *Synth. Met.* **1997**, *86*, 1859.
[3] R. Świetlik, M. Połomska, L. Ouahab and J. Guillevic, *J. Mater. Chem.* **2001**, *11*, 1313.
[4] R. Świetlik, A. Łapiński, M. Polomska, L. Ouahab and J. Guillevic, *Synth. Met.*, in press.
[5] J. Moldenhauer, Ch. Horn, K.I. Pokhodnia, D. Schweitzer, I. Heinen, H.J. Keller, *Synth. Met.* **1993**, *60*, 31.
[6] K. Yamamoto, K. Yakushi, K. Miyagawa, K. Kanoda, A. Kawamoto, *Phys. Rev. B* **2002**, *65*, 085110.
[7] G. Visentini, M. Masino, C. Bellitto and A. Girlando, *Phys. Rev. B* **1998**, *58*, 9460.
[8] R. Świetlik, unpublished data.
[9] H. Seo, *J. Phys. Soc. Jpn.* **2000**, *69*, 805.
[10] K. Kino and H. Fukuyama, *J. Phys. Soc. Jpn.* **1995**, *64*, 2726.