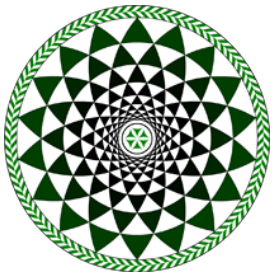

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Spectroscopic studies of the phase transition from Mott insulating phase to charge ordering phase in the charge-transfer salt κ-(ET)₄[Fe^{III}(CN)₆][N(C<sub>

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Organic molecular conductors formed by the bis(ethylenedithio)tetrathiafulvalene (ET) and anions with permanent magnetic moments exhibit various electronic states and physical properties, such as Mott insulator or charge ordering. Some time ago, a new κ-ET salt with Fe(CN)₆³⁻ anions, N(C)₂H)₅))₄⁺cations, and H₂O molecules was synthesized [1]. Along the c axis conducting layers of centrosymmetric ET₂ dimers alternate with insulating layers. Above T = 150 K, the charge is distributed uniformly among ET molecules; due to electronic correlations the holes are localized on ET₂ dimers driving the compound to a Mott insulating state. Below 150 K, a charge-ordered phase is observed where neutral (ET₂)⁰ and ionized (ET₂)²⁺ dimers are present [1, 2].
To gain more insight into the charge disproportionation in kappa;-(ET)₄[Fe^{III}(CN)₆][N(C₂
salt, we have performed comprehensive optical investigations of the infrared and Raman active vibrational features around the phase transition. The polarized reflectivity spectra versus temperature were recorded from 100 to 18 000 cm⁻¹ for single crystals for the electrical field of the incident beam within ab plane. Moreover, we have carried out the investigations in FIR using gold overcoating technique for the mosaic. The complex optical conductivity was obtained from the Kramers-Kronig analysis. The Raman spectra within the wavenumber range of 40-2000 cm⁻¹ as a function of temperature in the region of 10 - 280 K were measured on single crystals using two excitations lambda;_{exc} = 632.8 and 785 nm. To complete the discussion, we add ab-initio quantum-chemical calculations of the frequencies and intensities of the normal modes performed for the neutral (ET₂)⁰ and ionized (ET₂)¹⁺, (ET₂)²⁺ dimers.
As a consequence of the charge ordering the vibrational spectra are strongly modified. From the analysis of our infrared and Raman spectra we have obtained a wealth of information on the nature of the phase transition. Below the phase transition the vibrational band at 1347 cm⁻¹ appears, which is the result of coupling of the C=C mode of ET with the charge-transfer transition within the (ET₂)²⁺ dimer. The mode at approximately 420 cm⁻¹ (nu;₁₀ A_g) reveals very strong enhancement of the electron-phonon coupling due to charge order fluctuactions near the phase transition. The presence of the broad feature at 200-700 cm⁻¹ shows that the charge density strongly fluctuates in this system.

References
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