EXISTENCE OF TWO PHASES IN β-(BEDT-TTF)$_2$I$_3$: PROOF BY RESONANCE RAMAN SPECTROSCOPY

*R. Świetlik, D. Schweitzer and H.J. Keller[1]

Max-Planck-Institut für Medizinische Forschung, Abteilung für Molekulare Physik and [1]Anorganisch-Chemisches Institut der Universität, 6900 Heidelberg, Fed. Rep. Germany

Among various organic metals and superconductors based on the BEDT-TTF molecule [bis(ethylenedithiolo)tetrathiafulvalene] and different polyhalide anions the most intensively studied is β-(BEDT-TTF)$_2$I$_3$. Partially it is caused by the fact that these crystals exhibit the superconductivity with the highest critical temperature reported for organic materials, but the main reason of this interest is the existence of two superconducting states in these crystals. Under ambient pressure the superconductivity in β-(BEDT-TTF)$_2$I$_3$ is observed below $T_c \approx 1.3K$[1-4] (low-T_c phase) but after a particular pressure-temperature cycling procedure the superconductivity can be stabilized under ambient pressure at $T_c \approx 8.1K$[5,6] (high-T_c phase). α-(BEDT-TTF)$_2$I$_3$ is another modification of the salt formed between BEDT-TTF and I_3^-; at ambient pressure α-phase crystals undergo a metal-insulator phase transition at T=135K[4,7]. Recently, it was discovered that by tempering α-phase crystals at about 75°C for several days crystals can be obtained with similar properties as the high-T_c state of the β-crystals[8,9] (these crystals are further denoted as α_t-(BEDT-TTF)$_2$I$_3$).

The existence of two superconducting states in β-(BEDT-TTF)$_2$I$_3$ can be connected with a commensurate superstructure[10] developed below 125K which can be suppressed by an applied pressure. The most important feature of this superstructure is a pronounced distortion of the I_3^- anions (low-T_c phase). However, the pressure-temperature cycling procedure suppresses the development of the superstructure and a completely ordered high-T_c state can be obtained[11]. In other superconductors based on BEDT-TTF the structural situation is simpler in comparison to β-(BEDT-TTF)$_2$I$_3$. For example, in the salt β-(BEDT-TTF)$_2$IAuI only one superconducting state is observed with $T_c \approx 4K$ and the structure is ordered in the whole temperature range below 300K; i.e. the $IAuI^-$ anions are linear and symmetric[12].

The studies of the resonance Raman (RR) spectra of the I_3^- anions in the β-(BEDT-TTF)$_2$I$_3$[13] have shown that below 125K a splitting of the band related to the symmetrical stretching mode ν_1 of the linear and symmetric I_3^- anions into three or two lines (109, 120 and 126cm^{-1} at T=2K) exists (Fig.1). For some crystals the band at 109cm^{-1} disappeared irreversible during the illumination by intense laser light and only one line at about 122cm^{-1} was left (Fig.2). For other crystals the band at 109cm^{-1} did not completely disappear even for long time of irradiation and relatively high laser power but the intensity ratio between the fundamental and split bands I(122cm^{-1})/I(109cm^{-1}) increased. Above 125K the spectra were the same for both kinds of β-(BEDT-TTF)$_2$I$_3$ crystals

*On leave from: Institute of Molecular Physics, Polish Academy of Sciences, 60-179 Poznań, Poland

and only minor changes due to the temperature were observed.

The splitting of the ν_1 band in β-(BEDT-TTF)$_2$I$_3$ can be related to the commensurate superstructure developed below 125K; i.e. to the distortion of the I_3^- anions and the fact that three different anions exist in the unit cell. The irreversible change induced by the laser light can be connected with the disappearence of the distortion of the I_3^- anions[13]. Neutron diffraction studies have shown that the high-T_c phase of β-(BEDT-TTF)$_2$I$_3$ crystals is completely ordered[11]. Therefore, we conclude that the excitation by laser light can induce a transition from the low-T_c to the high-T_c state of β-(BEDT-TTF)$_2$I$_3$, at the surface at least. In the RR experiment the I_3^- and possibly also the donor cations are excited into the first excited singlet state. During the radiationless desactivation of this excited state by internal convertion and vibronic relaxation the I_3^- anion may fall down to the vibronic levels of the ground state S_o in such a way that it reaches either the symmetric or the asymmetric configuration. The efficiency of this process should be proportional to both the time of illumination and the power of the exciting laser light. However, for some crystals the irreversible change by light could not be performed totally (this is not understood in the moment). Nevertheless, the ratio I(122cm^{-1})/I(109cm^{-1}) increases with the power giving evidence that transition takes place in these crystals as well, although it is not complete and is not fully irreversible. It should be emphasized that the splitting could be observed again after temperature cycling when the upper temperature exceeded 125K; i.e. the temperature below which the superstructure is developed.

The investigations of α_t-(BEDT-TTF)$_2$I$_3$ crystals have shown that the split band at about 109cm^{-1} is absent. The α_t-(BEDT-TTF)$_2$I$_3$ is in the high-T_c state for the whole temperature range (i.e. the structure is completely ordered), therefore, only one line at 120cm^{-1} was observed[9] (Fig.3). Similary, only one band assigned to the ν_1 mode of $IAuI^-$ anions was observed for β-(BEDT-TTF)$_2$IAuI crystals (Fig.3), in agreement with the structural studies which have shown that the $IAuI^-$ anions are not distorted and that no structural change takes place in this salt[14]. On the other hand, the ν_1 mode of the I_3^- anions in the RR spectra of the α-(BEDT-TTF)$_2$I$_3$ crystals was split into three lines as well (115, 118 and 121cm^{-1} at T=55K), despite the I_3^- anions are linear and symmetric (Fig. 1). However, this splitting was qualitatively different in comparison with β-(BEDT-TTF)$_2$I$_3$ as was shown by RR measurements as a function of temperature, frequency and

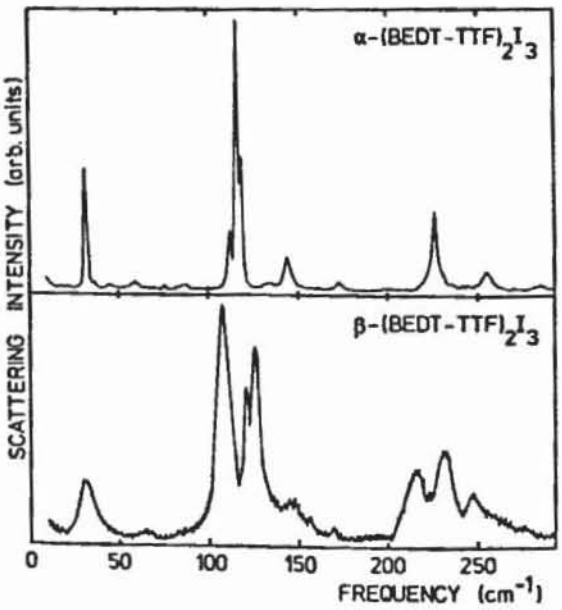

Fig.1. The resonance Raman spectra of α-(BEDT-TTF)$_2$I$_3$ and β-(BEDT-TTF)$_2$I$_3$ (T=2K, λ=4880 Å).

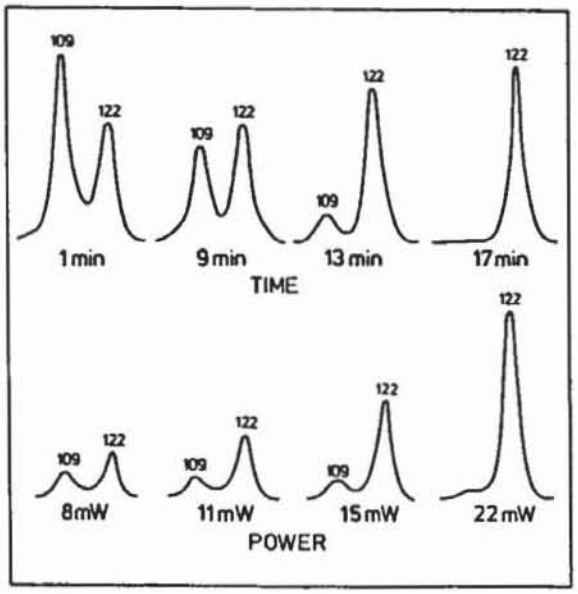

Fig.2. The disappearence of the band at $109cm^{-1}$ in β-(BEDT-TTF)$_2I_3$ crystals, λ=5145Å (top: with time by an illumination with P=15mW, T=20K; bottom: with increasing power of the laser light, T=35K)

power of the exciting laser light. The experimental evidence for α-(BEDT-TTF)$_2I_3$ shows that the splitting cannot be related to the presence of different phases in the crystal but it should be related to the influence of crystal field effects on I_3^- anions[13].

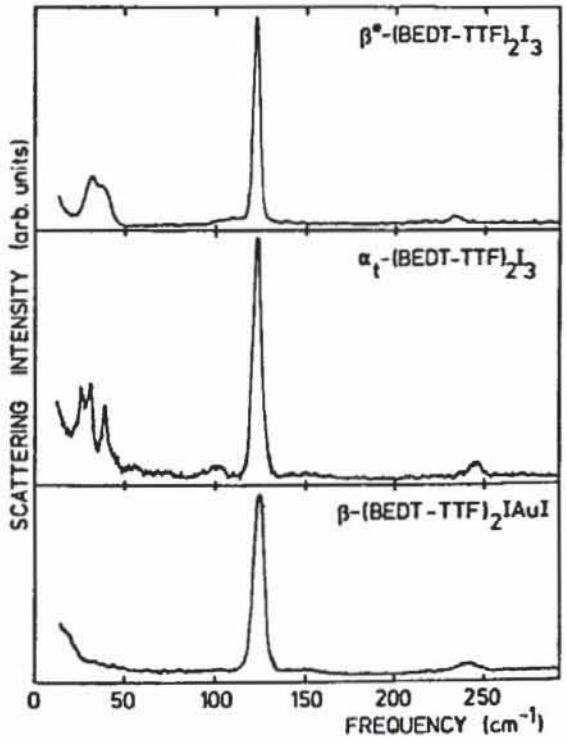

Fig.3. The comparison of the RR spectra of β^*-(BEDT-TTF)$_2I_3$ (for which the irreversible change by light has been performed) α_t-(BEDT-TTF)$_2I_3$ and β-(BEDT-TTF)$_2$IAuI (T=2K, λ=4880Å)

In conclusion, in β-(BEDT-TTF)$_2$I$_3$ two superconducting states exist at ambient pressure: the low-T_c state with $T_c \approx 1.3$K and the high-T_c state with $T_c \approx 8$K. The formation of the high-T_c state is connected with the suppression (by pressure-temperature procedure) of the development of a commensurate superstructure at 125K; without this procedure the crystal stays in its low-T_c state. The existence of the two different states in β-(BEDT-TTF)$_2$I$_3$ crystals was shown by the resonance Raman studies on the I_3^- anions as well. Moreover, on the basis of the observed changes of the RR spectra during illumination by the exciting laser light, one can draw a conclusion that intense light induces the transition between these states as well. The suitable electrical conductivity measurements are under progress.

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