

Original contributions

Resonant Raman scattering from superconducting single crystals of (BEDT-TTF)₂I₃

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Abstract. A study of low energetic resonant Raman scattering of (BEDT-TTF)₂I₃ superconductors was performed. The vanishing of phonon bands accompanied by a decrease of the electronic background was observed below T_c . We propose a theoretical explanation for this novel effect in terms of the Balseiro-Falicov model of phonon-superconducting amplitude mode interaction.

Introduction

The organic superconductors with the highest transition temperatures are all radical salts of the donor bis(ethylenedithiolo)tetrathiafulvalene (BEDT-TTF). Of special interest are the several structural different phases of the radical salt (BEDT-TTF)₂I₃ [1–11]. These (BEDT-TTF)₂I₃ systems have undergone intensive experimental and theoretical scrutiny, most of which have been devoted to the understanding of the nature of the superconducting mechanism in these compounds. The Raman spectroscopy is a useful tool for this purpose because it is based on the electron-phonon interaction and therefore is able to probe sensitively both the phonon and the electronic subsystems as well as their coupling. Abrikosov and Fal'kovskii [12] showed that the presence of an energy gap in the electronic energy spectrum of superconductors leads to the absence of absorption (at $T=0$) of radiation with frequencies less than the threshold frequency, equal to the energy gap 2Δ .

The method to determine the superconducting gap magnitude of the high- T_c superconductors (HTSC) from the Raman scattering spectra is based on this idea. Raman scattering spectra of the HTSC above T_c consist of an almost constant background attributed to electron-

ic excitations and superimposed structures due to scattering from phonons. In the superconducting state the electronic scattering strength decreases for low frequencies, overshoots the normal conducting one in the middle frequency region, and asymptotically approaches unity for high energy transfers [13–16].

Beside this observation a softening of some of the Raman-active modes at T_c in the crystals of $\text{RBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (R is a rare earth) was noticed [17–19]. This fact was interpreted by the existence of the energy gap above the mode frequency. Sometimes a reduced background scattering below T_c at a frequency below the softened mode was observed as well [19]. An anomalous intensity change of Raman-active phonons in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ below the superconducting transition temperature was observed by Friedl et al. [20]. It was explained by a superconductivity-induced resonant Raman process originating from the resonance of the phonons with the superconducting gap. From the above remarks one can see that Raman scattering from superconducting gap excitations in HTSC can give information of the pairing mechanism as well as of the nature and the value of the gap.

(BEDT-TTF)₂I₃ is a unique system for Raman scattering investigations. Several phases with rather high T_c exist inside this family which are suitable for Raman measurements. First of all, it is the α_r -phase with a $T_c = 8\text{--}8.5\text{ K}$ which can be produced from the α -phase by tempering the crystals at temperatures higher than $75\text{ }^\circ\text{C}$ [10, 11], and the β_H -phase ($T_c = 8\text{ K}$) which appears on the surface of β -phase crystals due to irradiation with a laser [9].

Perhaps the most important feature for Raman investigations of this system is the existence of several low energetic optical phonon bands assigned to I₃ anion stretching modes as well as of librations of the BEDT-TTF molecule, which are rather intensive due to resonance conditions of their excitation [9, 21]. The energy of these bands is close to the expected energy of the gap and therefore those bands might be sensitive to the formation of a gap.

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The aim of our study was to measure the low-energy resonant Raman scattering data in single crystals of $(\text{BEDT-TTF})_2\text{I}_3$ below and above T_c in order to obtain information whether a formation of a gap occurs.

Experimental

Raman measurements on single crystals were made in a 90° scattering configuration using several lines of an argon-ion laser (Coherent Innova 90). Since the Raman scattering on the I_3^- -anions in the organic superconductors $(\text{BEDT-TTF})_2\text{I}_3$ has a resonant character [9], with a maximum for $\lambda=488$ nm, the majority of our studies have been performed for an excitation with laser light of this wave-length. The maximum intensity of the symmetric stretching mode of I_3^- , at about 120 cm^{-1} served as an indication of a proper laser beam adjustment and polarization. The intensity of the band at 120 cm^{-1} was maintained at a constant level and was controlled during the temperature measurements. The laser beam was filtered with a monochromator and an additional interference filter in order to suppress plasma lines. A SPEX 1404 double monochromator with a spectral resolution of 0.14 cm^{-1} was used to disperse the scattered radiation. The power of the laser beam was maintained at about 25 mW and not completely focused in order to prevent sample damages. For some crystals the spectra were studied for lower or higher laser powers. The focusing of the light was also adapted to the peculiarities of the sample surface. Sometimes the best spectra of samples with distinctly nonhomogeneous surfaces were measured with strongly focused light. The spectra were investigated with different slit widths, but no larger slits than $300\text{ }\mu\text{m}$ were used, which guarantees a resolution better than 1 cm^{-1} . The Raman shifts between 6 cm^{-1} and about 150 cm^{-1} have been investigated for temperatures from about 50 K down to 1.5 K.

α - and β - $(\text{BEDT-TTF})_2\text{I}_3$ crystals were grown from a THF solution by electrochemical methods as described earlier [1]. The single crystals with highly reflecting surfaces were selected for Raman measurements as well as for preparing the α_t - $(\text{BEDT-TTF})_2\text{I}_3$ phase. For this purpose α - $(\text{BEDT-TTF})_2\text{I}_3$ crystals were annealed in air for 1–6 d at temperatures between 75 and 95 °C. We observed that α -phase crystals tempered at 75 °C during 1–3 d kept their shapes much better than those tempered at higher temperatures. However, an attentive analysis of the Raman spectra of those crystals in the region of the stretching and bending modes of I_3^- indicated an incomplete transformation into the α_t -phase. On the other hand tempering at 75 °C during about 6 d caused considerable degradation of the crystal surface. A microscopic examination of the surface revealed numerous and large areas of completely degraded salt (orange spots of neutral donor BEDT-TTF). Besides, numerous cracks and breaks were observed. The surface of so tempered α_t - $(\text{BEDT-TTF})_2\text{I}_3$ samples was nonhomogeneous, mat and strongly dispersive. Our attempts to remove the degraded surface layer by a THF-bath did not lead to improve the crystal surface. Crystals of

α - $(\text{BEDT-TTF})_2\text{I}_3$ tempered at 95 °C for times shorter or equal to one day were most suitable for Raman measurements. Their surface, in spite of corrugation, was reflective and suitable for the studies.

The penetration depth of the laser light estimated from absorption coefficient was calculated from the spectra of single crystals of $(\text{BEDT-TTF})_2\text{I}_3$ [22] and is about 1000 nm. This low value explains the sensitivity of the Raman spectra to the surface quality of the samples.

Our remarks on the quality of the α_t - $(\text{BEDT-TTF})_2\text{I}_3$ surface layer were confirmed by electrical conductivity measurements performed for samples tempered at 75 °C as well as 95 °C. Both tempering procedures lead to a transformation of the α -phase into the α_t -phase in the bulk; it is seen as a transition to the superconducting state at about 8 K. A small remainder of the $M-I$ phase transition at 135 K in the α -phase can still be seen in both cases. Nevertheless, some contact resistance instabilities and nonregularities were observed above the $M-I$ phase transition temperature for the sample tempered at 75 °C during a few days. In this region the resistivity of the contacts is comparable to the resistivity of the sample. Some random changes at the contacts between the surface layer and the bulk of the crystal are responsible for this instabilities. Such an effect is not observable for the samples tempered shortly at 95 °C. This means that the surface of the crystals tempered at 95 °C is also transformed into the α_t -phase and therefore those crystals are relatively homogeneous and non-decomposed at the surface.

Results

The Raman spectra of the α - and α_t - $(\text{BEDT-TTF})_2\text{I}_3$ phases for an excitation of $\lambda=488.0$ nm at $T=1.5$ K are shown in Fig. 1. These spectra are similar to those reported by Swietlik et al. [9, 11]. However, the spectrum of α_t - $(\text{BEDT-TTF})_2\text{I}_3$ (Fig. 1c) is a little bit different. In the good crystals of α_t -phase we observed only weak and broad bands at 31.5 cm^{-1} and 38.5 cm^{-1} . The first one is surely a remainder of a phonon libration observed for the α -phase as well as for the α_t -phase above the phase transition temperature. It may indicate a non-total transformation into the superconducting state of the surface of the sample. It is also possible that on the surface of our α_t -samples were still small areas of α -phase. The spectrum of a partially transformed α - $(\text{BEDT-TTF})_2\text{I}_3$ crystal is shown in Fig. 1b and it seems to advocate the last interpretation. In principle the band at 38.5 cm^{-1} would coincide with a plasma line of the argon ion laser working at 488 nm. However, the spectra for the α_t -phase for an excitation wave length at $\lambda=501.7$ nm as well as 514.5 nm show the appearance of the same weak band at 38.5 cm^{-1} . The coincidence with plasma lines is excluded since the nearest plasma lines in these cases are shifted more than 15 cm^{-1} from the phonon band.

In addition a plasma line would be much narrower. An clear band was also observed at $T>T_c$ (Fig. 2).

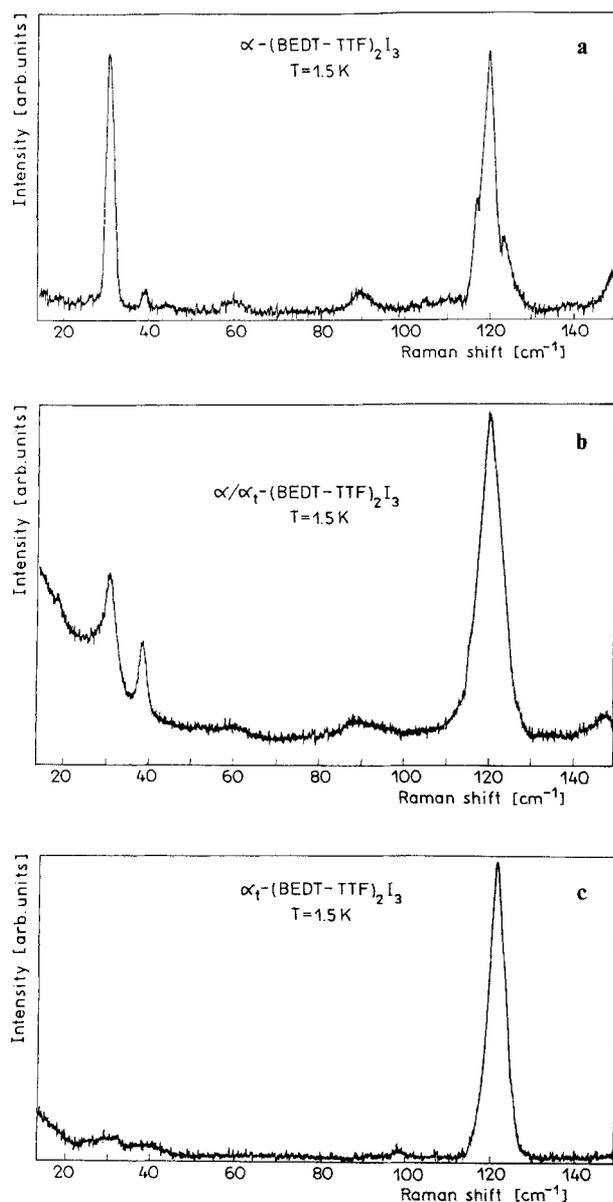


Fig. 1a-c. Low-energetic part of the resonant Raman spectra at $T=1.5$ K. **a** α -(BEDT-TTF) $_2I_3$, **b** α/α_r -(BEDT-TTF) $_2I_3$ and **c** α_r -(BEDT-TTF) $_2I_3$. α/α_r means non-totally transformed α -(BEDT-TTF) $_2I_3$ into α_r -(BEDT-TTF) $_2I_3$.

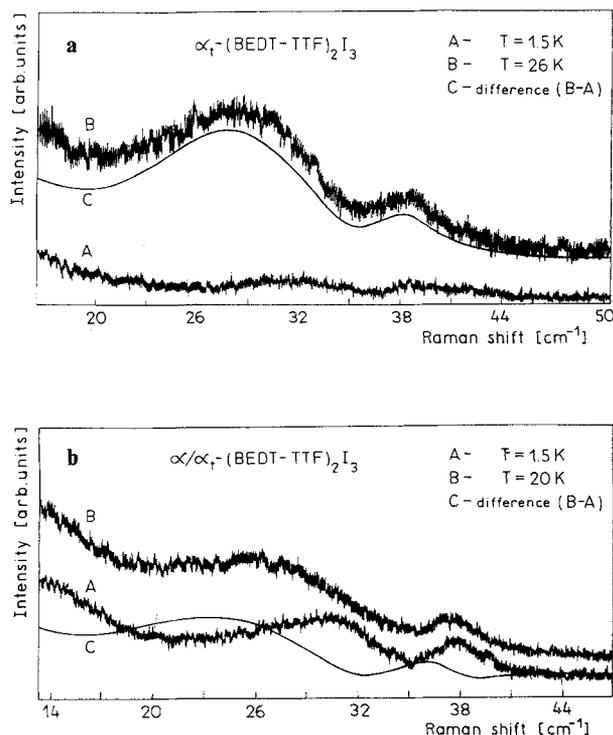


Fig. 2. Resonant Raman spectra of **a** α_r -(BEDT-TTF) $_2I_3$ and **b** α/α_r -(BEDT-TTF) $_2I_3$ in the region of the libration of the BEDT-TTF molecules at temperatures below and above T_c .

The linewidth $\Delta\omega$ of the symmetric stretching mode of I_3^- for α_r -(BEDT-TTF) $_2I_3$, at 120.5 cm^{-1} is 4.5 cm^{-1} and is a little bit larger than the strongest band of the analogue triplet band observed for the α -phase. The spectrum for the non-totally transformed α -phase crystals (Fig. 1b) shows the main features of both α - and α_r -phases. The band at 120 cm^{-1} in this case is considerably broadened ($\Delta\omega=7$ cm^{-1}) in comparison to the line of 120.5 cm^{-1} for α_r -(BEDT-TTF) $_2I_3$. The observed resonance Raman frequencies for α -, α_r - and non-totally transformed α -(BEDT-TTF) $_2I_3$ (in the following we will call those crystals α/α_r -(BEDT-TTF) $_2I_3$), are collected in Table 1. The spectra of the β - and β_H -phases are similar to the spectra shown in [9] and [11].

Table 1. Resonant Raman frequencies (cm^{-1}) for α -(BEDT-TTF) $_2I_3$, α/α_r -(BEDT-TTF) $_2I_3$ and α_r -(BEDT-TTF) $_2I_3$ observed below 150 cm^{-1} at $T=1.5$ K, excited by light of a wavelength of $\lambda=488.0$ nm

α -(BEDT-TTF) $_2I_3$	α/α_r -(BEDT-TTF) $_2I_3$	α_r -(BEDT-TTF) $_2I_3$
30 vs, $\Delta\omega=3$ cm^{-1}	30 m	31.5 vw, $\Delta\omega=5.3$ cm^{-1}
38.5 w	38 m	38.5 vw
45 vw		
59 w	59 vw	
89 m	89 w	
103.5 vw		95 w
116 m		
119 vs, $\Delta\omega<3.5$ cm^{-1}	120 s, $\Delta\omega=7$ cm^{-1}	120.5 s, $\Delta\omega=4.5$ cm^{-1}
123 m		
136 vw		
147.5 m	146.5 m	149.5 m

Intensity: vs – very strong, s – strong, m – medium, w – weak and vw – very weak

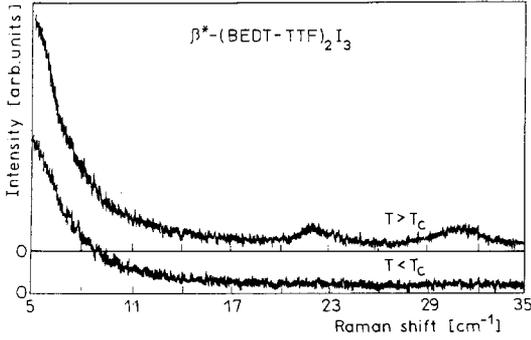


Fig. 3. Resonant Raman spectra of β_H -(BEDT-TTF) $_2$ I_3 at temperatures below and above T_c

Figure 2 shows the low energetic parts (below 50 cm^{-1}) of the resonant Raman spectra of the α/α_r -phases of (BEDT-TTF) $_2$ I_3 at 1.5 K ($T < T_c = 8 \text{ K}$) and at $T > T_c$. A relatively strong increase in intensity of both bands at 31.5 cm^{-1} and 38.5 cm^{-1} as well as an increase of the background scattering is observed in the normal (non-superconducting) phase of α_r -(BEDT-TTF) $_2$ I_3 . Beside this observation a considerable softening of the low-frequency band is seen (Fig. 2a). Above the phase transition in crystals of α/α_r -(BEDT-TTF) $_2$ I_3 a distinct broadening and shifting of the band at about 30 cm^{-1} is observed; some increase of the background scattering is seen as well (Fig. 2b). It is necessary to add that a further increase of the temperature up to about 60 K i.e. $T = 7.5 T_c$ does not change the spectra perceptibly. The spectra of control samples of α -(BEDT-TTF) $_2$ I_3 (which do not become superconducting) at $T = 1.5 \text{ K}$ and $10 \text{ K} < T < 60 \text{ K}$ did not undergo any changes.

Our Raman investigations on crystals of β -(BEDT-TTF) $_2$ I_3 confirmed a transformation of this material into the β_H -phase under illumination with laser light. The transformation induced by the laser light appears as a typical evolution of the split mode ν_1 of the I_3 -anions in β -(BEDT-TTF) $_2$ I_3 , similar as described in [9]. The low-energetic part of the resonance Raman spectra of β_H -(BEDT-TTF) $_2$ I_3 (Fig. 3) contains two very weak and broad bands at about $22\text{--}24 \text{ cm}^{-1}$ and $30\text{--}32 \text{ cm}^{-1}$. The intensity of the bands was comparable to the noise level for totally transformed β_H -samples, at 1.5 K. Above the phase transition temperature ($T_c = 8 \text{ K}$) an appearance of the bands at 22.5 cm^{-1} and 30.5 cm^{-1} was observed. It should be emphasized that the above mentioned bands as well as the split band at 109 cm^{-1} and 126 cm^{-1} [9] show only a small dependence on the light polarization in contrast to the intensities of the bands for the α - and α/α_r -phases which strongly depend on the polarization of the laser light.

The comparison of the low-energy resonant Raman scattering spectra of α_r -(BEDT-TTF) $_2$ I_3 (Fig. 2a) for temperatures below (spectrum A) and above (spectrum B) the phase transition temperature T_c reveals relatively large changes. The spectra of β_H -(BEDT-TTF) $_2$ I_3 (Fig. 3) show the same tendency as those of

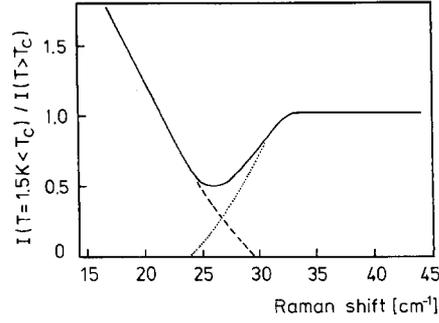


Fig. 4. Experimental electronic Raman scattering of α_r -(BEDT-TTF) $_2$ I_3 at $T = 1.5 \text{ K}$ normalized to scattering at $T > T_c$

α_r -(BEDT-TTF) $_2$ I_3 , but the phonon modes are shifted to somewhat smaller energies. The situation is more complicated for the α/α_r -(BEDT-TTF) $_2$ I_3 sample; it is a mixture on the surface of the sample of α_r -phase and non-transformed α -phase. Thus the bands at about 30 cm^{-1} and 38 cm^{-1} (Fig. 2b) observed at $T = 1.5 \text{ K}$ should be assigned to librations of the BEDT-TTF molecules of α -(BEDT-TTF) $_2$ I_3 . A small shift of the mode frequencies (about 1 cm^{-1}) in comparison to single crystals of α -(BEDT-TF) $_2$ I_3 is caused probably by defects and stresses induced by the annealing procedure of the crystals. At $T > T_c$ a distinct broadening and shifting of the phonon band at 30 cm^{-1} is observed (curve B in Fig. 2b). Assuming that the background at $T > T_c$ is approximated by the spectrum at $T = 1.5 \text{ K}$ we get a spectrum of the α/α_r -crystal transformed into the superconducting state as a difference between spectra B and A (Fig. 2b, line C).

Figure 4 shows the experimental electronic part of the Raman scattering of α_r -(BEDT-TTF) $_2$ I_3 at $T = 1.5 \text{ K} < T_c$ normalized to the scattering at $T > T_c$. It should be noticed that this scattering decreases below 33 cm^{-1} but starts to increase again strongly below 25 cm^{-1} .

Discussion

In our experiments we have observed a softening and weakening of the low frequency optical phonons at about 30 cm^{-1} in the superconducting state of α_r - and β_H -(BEDT-TTF) $_2$ I_3 .

A similar weakening of a low frequency "phonon" mode in the superconducting state was observed by Sooryakumar and Klein in NbSe $_2$ [23], using Raman spectroscopy. The "phonon" is in fact a CDW mode at a frequency of about 30 cm^{-1} . The weakening of the Raman line of this mode, as the temperature is lowered below T_c , is associated with the building-up of another mode at about 17 cm^{-1} , i.e. the superconducting gap energy 2Δ . This mode is an amplitude-mode of the gap parameter, i.e. is associated with a spatial modulation of the amplitude of the superconducting gap: $\Delta(R) = \Delta_0 + \delta\Delta \cos(q \cdot R)$, where q is the wave vector of the

amplitude mode. This mode is a Higgs mode, with a finite frequency as $q \rightarrow 0$, given by 2Δ in an “ideal” superconductor [24]. The sum of the intensities of the Raman lines due to the amplitude mode and the “phonon”, was found to be approximately constant up to 9 K ($T_c \approx 7$ K). Thus, the intensity of the amplitude mode is taken away from the “phonon”.

This phenomenon was interpreted theoretically by Balseiro and Falicov [25]. They considered the self-energy $\Pi(q, \omega)$ of a phonon, coupled with the amplitude mode in the superconducting state. This coupling should, in principle, shift the frequencies of both the phonon and the amplitude mode, pushing them apart, as well as reduce the Raman amplitude of the phonon mode. For the case of NbSe₂, they estimate the electron-“phonon” coupling constant of $\lambda = 2g^2\rho_0/h\omega_0 = 0.24$ and because of this small value, the reduction of the amplitude and frequency shifts are only about 10%.

The amplitude mode exists only for small values of q , $q < \xi^{-1}$, where ξ is the coherence length. Thus, only phonons with small q should be affected by the mixing with these modes. Note, that when the phonon and the superconducting amplitude mode mix, each one is partly “phonon” and partly a “superconducting gap” mode.

Littlewood and Varma [26] showed that the coupling between the “phonon” and amplitude mode depends not only on the electron phonon coupling constant λ , but also on another coupling constant α related to the depression of T_c by the CDW. Estimating α , they accounted for the decrease in intensity of the “phonon” Raman line by 10%, and the intensity and position of the amplitude mode, as observed experimentally.

Zwicknagl and Zeyher [27] showed that in principle, the mode at 17 cm^{-1} may be a CDW mode (rather than a superconducting amplitude mode), the role of superconductivity being just to reduce dissipations and thus prevent this mode from being excessively broadened.

In α_r - and β -(BEDT-TTF)₂ I₃ we have a situation in which the low frequency phonon mode is a real optical phonon (rather than a CDW mode) of frequency $\approx 30 \text{ cm}^{-1}$. Therefore, its coupling with the electrons is expected to be much stronger. The observed phonons at about 30 cm^{-1} and 39 cm^{-1} are probably librations of the BEDT-TTF-molecules, which are optical modes, i.e. $\omega(q)$ is finite as $q \rightarrow 0$. Such modes have a strong *quadratic* interaction with the electrons in linear chain compounds [28], but interact *linearly* with the electrons in the two-dimensional BEDT-TTF salts [29], and the interaction is expected to be very strong as well. Tunneling measurements indicate that essentially all the electron phonon coupling is with these phonons [30]; therefore, in order to account for the observed $T_c \approx 8$ K, λ must be close to 2. Therefore, both the shift of the phonons and the reduction of their amplitudes, must be much larger than in NbSe₂, and the phonon lines should practically disappear in the superconducting state, as found in our experiments.

However, here we are faced with the dilemma, where does the amplitude of the phonon Raman line go to? In the Balseiro and Falicov (BF) theory [25], the amplitude goes to the amplitude mode at 2Δ . For $T_c = 8$ K and assuming a BCS type superconductor $2\Delta_{\text{BCS}}$

$\approx 2.5 \text{ meV} = 20 \text{ cm}^{-1}$. Our experimental data do not show any change in the Raman scattering there, or in any other part of the investigated region.

More recent tunneling measurements on α_r -(BEDT-TTF)₂ I₃ [30] show large, very sharp peaks in two regions, namely $0.7 \text{ meV} \pm 6 \text{ cm}^{-1} (2\delta^{(0)})$, and $10 \text{ meV} \pm 80 \text{ cm}^{-1} (2\delta^{(1)})$ (and in addition, a second harmonic at 20 meV).

The “conventional” interpretation would associate $\delta^{(1)} \approx 40 \text{ cm}^{-1}$ with the superconducting gap which thus would be about four times larger than the expected BCS gap. However, we prefer to associate $\delta^{(1)}$ with the phonon frequency ω_{ph} , or with $\omega_{\text{ph}} + \Delta_{\text{BCS}}$; i.e. we consider this structure as a “giant” McMillan-Rowell peak [31, 32]. It is observed at $2(\omega_{\text{ph}} + \Delta_{\text{BCS}})$ because there are 2 superconducting-normal ($s-n$) junctions in series in this experiment [30].

We suggested that the structure near 6 cm^{-1} is the superconducting gap (mixed with the phonon), i.e. the smallest excitation energy in the system [30]. Because of its low energy, it is denoted “zero bias anomaly” and we suggested that it is analogous to the structure observed in YBaCuO at 4 meV [33]. This suggestion is supported by the following observations on another BEDT-TTF radical salt, namely κ -(BEDT-TTF)₂ Cu(NCS)₂, where the situation seems to be very similar to α_r - and β -(BEDT-TTF)₂ I₃.

a) Infrared absorption measurements by Kornelson et al. [34] on this salt ($T_c = 10.4$ K) show that there is *no change* around $20\text{--}25 \text{ cm}^{-1}$ in the superconducting state, i.e. there is (apparently) no superconducting gap there. In contrast, surface impedance measurements by Holzer et al. [35] around 3 cm^{-1} show a *large* change in the surface impedance in the superconducting state, indicating that the gap must exceed this energy. A superconducting gap of about $6\text{--}8 \text{ cm}^{-1}$ reconciles these apparently conflicting observations.

b) Measurements of the temperature dependence of the London penetration depth show a power-law dependence, rather than the expected BCS $\exp(-2\Delta/k_B T)$ dependence [36] (it should be mentioned that in contrast to the power-law dependence found in [36] the group of Grüner finds a BCS-like behaviour in the same compound [35]). If the lowest excitation energy is indeed 3–4 times smaller than the BCS-gap, such a power-law dependence in the investigated temperature range is to be expected.

If there is a strong coupling between an optical phonon at $30\text{--}39 \text{ cm}^{-1}$ and a superconducting amplitude mode, then by the BF-theory the amplitude mode should be pushed down, possibly to 6 cm^{-1} , with a transfer of Raman intensity from the phonon mode to the superconducting amplitude mode. In fact, in the ratio of the Raman scattering intensities below and above T_c (see Fig. 4) an increase in scattering intensity is seen at low frequencies (below 20 cm^{-1}) at temperatures below T_c . Unfortunately, at these very low energies (6 cm^{-1}) the Raman scattering is overshadowed by strong Rayleigh-scattering, so that the 6 cm^{-1} mode cannot be observed at present in a Raman experiment.

Effects of this type were investigated intensively in YBaCuO. There a zero bias anomaly was observed as well, but the phonon Raman lines shift only by as much as 1.5% in the superconducting state [17–20]. These shifts are much smaller than expected from BF-theory. This small effect is accounted for theoretically by Zeyher and Zwicknagl [37], employing the Eliashberg strong coupling theory. They find that for an Einstein spectrum with $\omega_{\text{ph}} \approx 2\Delta$ and $\lambda = 2.9$ the expected phonon shift is 600% (obviously the first order theory does not apply to such large shifts). Since there are 5Cu–O stretching modes coupled with each electron, the shift of each mode is 120%. Postulating sample inhomogeneities and strong elastic scattering of the electrons and in particular, strong admixture with many other phonon modes, they claim that the maximum theoretical shift is just 5%. The observed maximum shift is 1.5%. In particular, for fully symmetric modes, and $q \rightarrow 0$, the shift is small due to the large Coulomb effects.

This leaves us with the dilemma why are the effects of superconductivity on the phonon relatively strong in α_{r} - and β_{H} -(BEDT-TTF)₂I₃, while they are weak in YBaCuO. At the present stage, we can only speculate that this is associated with the (approximate) Einstein spectrum found in the BEDT-TTF salts, in contrast with the many modes in YBaCuO, and with the small coherence length $\xi_{\parallel} = 15$ Å in YBaCuO; thus $\xi_{\parallel}/a \approx 4$ [38]. In α_{r} - and β_{H} -(BEDT-TTF)₂I₃ the coherence length is much larger ($\xi_{\parallel} \approx 100$ –150 Å). The BF-theory cannot be expected to apply when the coherence length is of the order of a lattice constant a ; indeed, in this case the superconducting amplitude modes extend well into the Brillouin-zone, and neutron-diffraction experiments on YBaCuO [39] indicate that phonons over half the Brillouin zone are affected by the coupling with the amplitude modes. In α_{r} - and β -(BEDT-TTF)₂I₃ because of the larger coherence length, a theory in the spirit of the BF-theory (appropriately extended to strong coupling) should apply, and account for much larger effects on $q \approx 0$ phonons. This large coherence length may perhaps be due to less elastic scattering by defects, i.e. a more perfect crystal; this is in line with the calculations of Zeyher and Zwicknagl [37] also, it is possible that the symmetry of the phonon is much lower (the space group of the crystals of α_{r} - and β_{H} -(BEDT-TTF)₂I₃ is $P\bar{1}$), thus Coulomb effects do not suppress the shift for the $q \rightarrow 0$ modes, and/or the Coulomb effects in these BEDT-TTF salts may be weaker than in YBaCuO.

Conclusions

At the present stage, we suggest tentatively, that based on the Balseiro-Falicov-model, the superconducting amplitude mode interacts strongly with the 30–39 cm⁻¹ optical phonons and thus is pushed down, possibly to 6 cm⁻¹ (thus yielding the zero bias anomaly [ZBA]). In this way the origin of the (as yet unaccounted for) ZBA observed in tunneling experiments can be understood. Also, it is possible that part of the amplitude of this mode is shifted up, enhancing the McMillan-Rowell

peak, and thus accounting for the abnormally strong intensity of this structure. More detailed measurements, down to frequencies of ≈ 6 cm⁻¹ and below, as well as temperature and magnetic field dependences are obviously needed to test this conjecture.

The strong effects observed in α_{r} - and β_{H} -(BEDT-TTF)₂I₃ contrast with much weaker effects observed in YBaCuO. We are not yet able to account definitively for this difference.

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References

- Bender, K., Hennig, I., Schweitzer, D., Dietz, K., Endres, H., Keller, H.J.: *Mol. Cryst. Liq. Cryst.* **108**, 359 (1984)
- Yagubskii, E.B., Shegolev, I.F., Laukhin, V.N., Kononovich, P.A., Kartsovnik, M.V., Zvarykina, A.V., Buravov, L.I.: *Pis'ma Zh. Eksp. Teor. Fiz.* **39**, 12 (1984)
- Williams, J.M., Emge, T.J., Wang, H.H., Beno, M.A., Copps, P.T., Hall, L.N., Carlson, K.D., Crabtree, G.W.: *Inorg. Chem.* **23**, 2558 (1984)
- Schwenk, H., Gross, F., Heidmann, C.P., Andres, K., Schweitzer, D., Keller, H.J.: *Mol. Cryst. Liq. Cryst.* **119**, 329 (1985)
- Schwenk, H., Heidmann, C.P., Gross, F., Hess, E., Andres, K., Schweitzer, D., Keller, H.J.: *Phys. Rev.* **B31**, 3138 (1985)
- Laukhin, V.N., Kostyuchenko, E.E., Sushko, Yu.V., Schegolev, I.F., Yagubskii, E.B.: *Pis'ma Zh. Eksp. Teor. Fiz.* **41**, 68 (1985)/*JETP Lett.* **41**, 81 (1985)
- Murata, K., Tokumoto, M., Anzai, H., Bando, H., Saito, G., Jajimura, K., Ishiguro, T.: *J. Phys. Soc. Jpn.* **54**, 1236 (1985)
- Creuzet, F., Creuzet, G., Jerome, D., Schweitzer, D., Keller, H.J.: *J. Phys. (Paris) Lett.* **46**, L-1079 (1985)
- Swietlik, R., Schweitzer, D., Keller, H.J.: *Phys. Rev.* **B36**, 6881 (1987)
- Baram, G.O., Buravov, L.I., Dgtariev, L.C., Kozlov, M.E., Laukhin, V.N., Laukhina, E.E., Orischenko, V.G., Pokhodnia, K.I., Scheinkman, M.K., Shibaeva, R.P., Yagubskii, E.B.: *Pis'ma Zh. Eksp. Teor. Fiz.* **44**, 293 (1986)/*JETP Lett.* **44**, 376 (1986)
- Schweitzer, D., Bele, P., Brunner, H., Gogu, E., Haerberlen, U., Hennig, I., Klutz, T., Swietlik, R., Keller, H.J.: *Z. Phys. B – Condensed Matter* **67**, 489 (1987)
- Abrikosov, A.A., Falkovskii, L.A.: *Zh. Eksp. Teor. Fiz.* **40**, 262 (1961)/*Sov. Phys.-JETP* **13**, 179 (1961)
- Maksimov, A.A., Tartakovskii, I.I., Timofeev, V.B.: *Pis'ma Zh. Eksp. Teor. Fiz.* **50**, 44 (1989)/*JETP Lett.* **50**, 51 (1989)
- Hackl, R., Glaser, W., Muller, P., Einzel, D., Andres, K.: *Phys. Rev.* **B38**, 7133 (1988)
- Cooper, S.L., Klein, M.V., Pazol, B.G., Rice, J.P., Ginsberg, D.M.: *Phys. Rev.* **B37**, 5920 (1988)
- Cooper, S.L., Slakey, F., Klein, M.V., Rice, J.P., Bukowski, E.D., Ginsberg, D.M.: *Phys. Rev.* **B38**, 11934 (1988)
- Ruf, T., Thomsen, C., Lius, R., Cardona, M.: *Phys. Rev.* **B38**, 11985 (1988)
- Friedl, B., Thomsen, C., Cardona, M.: *Phys. Rev. Lett.* **65**, 915 (1990)
- Thomsen, C., Cardona, M., Gegenheimer, B., Liu, R., Simon, A.: *Phys. Rev.* **B37**, 9860 (1988)
- Friedl, B., Thomsen, C., Habermeier, H.-U., Cardona, M.: *Solid State Commun.* **78**, 291 (1991)
- Sugai, S., Saito, G.: *Solid State Commun.* **58**, 759 (1986)
- Sugano, T., Yamada, K., Saito, G., Kinoshita, M.: *Solid State Commun.* **55**, 137 (1985)

23. Sooryakumar, R., Klein, M.: Phys. Rev. Lett. **45**, 660 (1980)
24. Nambu, Y.: In: From symmetries to strings: forty years of rochester conferences. A. Das (ed.). Singapore: World Scientific 1990
25. Balseiro, C.A., Falicov, L.M.: Phys. Rev. Lett. **45**, 662 (1980)
26. Littlewood, P.B., Varma, C.M.: Phys. Rev. B **26**, 4883 (1982)
27. Zwicknagl, G., Zeyher, R.: In: Superconductivity of *d*- and *f*-band metals. Buckel, G.W., Weber, W. (eds.). p 549, Kernforschungszentrum Karlsruhe Press 1992
28. Gutfreund, H., Hartzstein, C., Weger, M.: Solid State Commun. **36**, 545 (1980)
29. Nowack, A., Weger, M., Schweitzer, D., Keller, H.J.: Solid State Commun. **60**, 199 (1986); Weger, M., Bender, K., Klutz, T., Schweitzer, D., Gross, F., Heidmann, C.P., Probst, Ch., Andres, K.: Synth. Metals **25**, 49 (1988)
30. Weger, M., Nowack, A., Schweitzer, D.: Synth. Metals **41-43**, 1885 (1991)
31. McMillan, W.L., Rowell, J.M.: In: Superconductivity. Parks, R.D. (ed.) New York: Marcel Dekker 1969
32. Weger, M., Wehrhahn, R.F.: In: Electronic structure and mechanisms for high temperature superconductivity. Ashkenazi, J. (ed.). New York: Plenum Press 1992
33. Gurvitch, M., Valles, J.M., Cucolo, A.M., Dynes, R.C., Garno, J.P., Schneemeyer, D.F., Waszak, J.V.: Phys. Rev. Lett. **63**, 1008 (1989)
34. Kornelsen, K., Eldrige, J.E., Wang, H.H., Williams, J.M.: Phys. Rev. B **44**, 5235 (1991)
35. Holczer, K., Klein, O., Grüner, G., Yamochi, H., Wudl, F.: In: Organic superconductivity. Kresin, V.Z., Little, W.L. (eds.). London: Plenum Press 1990
36. Takahashi, T., Kanoda, K., Akiba, K., Sakao, K., Watabe, M., Suzuki, K.: Synth. Metals **41-43**, 2005 (1991)
37. Zeyher, R., Zwicknagl, G.: Z. Phys. B – Condensed Matter **78**, 175 (1990)
38. Deutscher, G., Müller, K.A.: Phys. Rev. Lett. **39**, 1745 (1987)
39. Reichardt, W.: Privat communication (N. Pyka, et al.: to be published)