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Resonance Raman investigations of the symmetric stretching mode of I_3^- anions in α and β phases of di-bis(ethylenedithio)tetrathiafulvalene tri-iodide

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The resonance Raman spectra of I_3^- anions in the organic superconductor β-(BEDT-TTF)$_2$I$_3$ [BEDT-TTF represents bis(ethylenedithio)tetrathiafulvalene] were studied and discussed in comparison with the nonsuperconducting phase of α-(BEDT-TTF)$_2$I$_3$. In both modifications at low temperature a splitting of the Raman mode assigned to the symmetric stretching mode of the I_3^- anions was discovered. The splitting of this mode in the β-(BEDT-TTF)$_2$I$_3$ crystals is related to the commensurate superstructure developed below 125 K in contradiction to the α phase where the splitting is related to a crystal-field effect. It is shown that an electronic excitation of the β-phase crystals by laser light can induce a structural transformation at least in a thin layer of the surface. This transformation is observed by a disappearance of the splitting of the symmetric stretching mode. The structural change can be related to a transformation from the commensurate superstructure with a superconducting transition temperature $T_c = 1.3$ K into a more ordered and symmetric structure which becomes superconducting at $T_c = 8.1$ K.

I. INTRODUCTION

Intensive studies of the charge-transfer salts yielded by the organic donor bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) have been initiated by the discovery of superconductivity in (BEDT-TTF)$_4$(ReO)$_4$)$_2$ at about 2 K for an isotropic pressure above 4 (kbar).[1] The consequence of these studies was the discovery of ambient-pressure superconductivity in the systems (BEDT-TTF)$_2X$, where $X = I_3^-$, IBrI$^-$, and IAuI$^-$.[2-9]

(BEDT-TTF)$_2$I$_3$ crystallizes in two modifications, the α and β phase. Under ambient pressure the α-(BEDT-TTF)$_2$I$_3$ undergoes a metal-insulator phase transition at 135 K,[5,10] whereas β-(BEDT-TTF)$_2$I$_3$ preserves the metallic properties down to low temperatures and becomes superconducting for $T_c \approx 1.3$ K.[2-5] An isotropic pressure of greater than 12 kbar suppresses the metal-insulator transition in α-(BEDT-TTF)$_2$I$_3$ but no sign of superconductivity could be observed.[5] On the other hand, under a pressure of $p \sim 1$ kbar the superconductivity in β-(BEDT-TTF)$_2$I$_3$ can be raised to 7.5 K as was shown first by workers in the USSR (Ref. 11) and Japan.[12] These two groups have also claimed the stabilization of superconductivity around 7 K at ambient pressure either after temperature cycling[13] or after the release of a high pressure at ambient temperature,[14] but no volume superconductivity could be found. Finally the volume superconductivity in β-(BEDT-TTF)$_2$I$_3$ was obtained at ambient pressure and a $T_c = 8.1$ K after a particular pressure-temperature cycling procedure.[15,16] In consideration of the surprising superconducting behavior of β-(BEDT-TTF)$_2$I$_3$ it was assumed that two kinds of superconducting states exist in this salt with critical temperatures of around 8 and 1.3 K,[17] or that a number of superconducting transitions occur.[18] The coexistence of two structurally different states of β-(BEDT-TTF)$_2$I$_3$ was also suggested.[15,16]

Since the superconductivity in the organic materials is sensitive to any kind of disorder or structural changes several investigations of the structure of both phases at different temperatures have been performed. The structure of the α phase was investigated at room temperature[10] as well as below the metal-insulator phase transition at 135 K.[19,20] In the case of the β phase the situation is more complicated. Below 195 K at ambient pressure in β-(BEDT-TTF)$_2$I$_3$ there exists an incommensurate structural modulation (the triiodide anions and BEDT-TTF molecules displace sinusoidally from their average position in the unit cell[21-23]) and the origin of this modulation is connected with an anion-cation interaction.[23] According to the papers[21-23] this incommensurate structural modulation persists down to at least 8 K. In contrast recently it was shown[19] that below 125 K—at this temperature a phase transition was already observed in the thermopower data[24]—a commensurate superstructure with a unit cell volume of about three times as large as at room temperature exists. The basic structural change below 125 K with respect to the room temperature structure lies in a pronounced distortion of the tri-iodide chains and especially in a change of the linear and symmetric I_3^- anions at room temperature into nonlinear (angle ~175°) and asymmetric I_3^- anions. Therefore it was assumed[19] that the symmetric linear structure of the I_3 anions at room temperature is stabilized down to low temperatures by the special pressure-temperature cycling procedure[15,16] and this symmetric structure results in the high-T_c superconducting transition at about 8 K. In fact, recently this assumption could be proved and supported by neutron-diffraction experiments[25,26] and it was shown that no incommensurate modulated structure at 4.5 K exists,[26] indicating a higher degree of ordering of this high-T_c structure with respect to the low-T_c state.

The experimental evidence presented above shows several crystallographic changes in the β-phase crystals and shows that slight structural changes can significantly influence the superconducting transition in organic materials. Therefore it seems very important to study this problem more carefully by different techniques. Resonance Raman spectra are very sensitive to small shifts and alternations of molecular electronic levels caused by changes of intermolecular forces which are connected with the temperature variations or phase transitions.

The Raman spectra of iodine complexes exhibit unusually strong resonance lines from polyiodide ions. In this paper we present resonance Raman studies of α- and β-(BEDT-TTF)$_2$I$_3$ as a function of the temperature and the frequency of the exciting light. We have discovered that the Raman band assigned to the symmetric stretching mode of the I_3^- anions exhibits splittings for both modifications. In the α-(BEDT-TTF)$_2$I$_3$ the splitting is not dependent on the temperature and the power of exciting laser light and the splitting is related to a crystal field effect. On the other hand, for β-(BEDT-TTF)$_2$I$_3$ crystals the splitting of this band is both temperature and excitation dependent. It will be shown that this splitting is related to the phase transition at 125 K and that by illumination of the crystal with laser light the low-T_c superconducting structure ($T_c \sim 1.3$ K) can be transformed into the higher-ordered high-T_c superconducting structure ($T_c \sim 8$ K).

Recently a paper was also published on the resonance Raman spectra of the systems α- and β-(BEDT-TTF)$_2X_3$, where $X = I_3^-$ and BrIBr$^-$.[27] The spectra of the α-(BEDT-TTF)$_2$I$_3$ from Ref. 27 are in good agreement with our results, however, our experiments were performed with a higher resolution and the splitting of the symmetric stretching mode of I_3^- anion was discovered. On the other hand, for the β phase crystals the measurements in Ref. 27 were performed with an overly high power of exciting light and therefore the splitting of the I_3^- mode could not be observed and the structural transformation induced by the light was not seen.

II. EXPERIMENTAL AND RESULTS

The single crystals of α- and β-(BEDT-TTF)$_2$I$_3$ were prepared by the standard electrochemical method.[10] During the electrocrystallization process both modifications grow simultaneously at the anode, but it is easy to distinguish them under the microscope as well by the ESR techniques.[24]

The resonance Raman spectra were taken at 90° scattering for a wide range of temperatures using several different lines of an argon-ion laser (Coherent Innova 90). The scattering was investigated from the best developed crystal surfaces [i.e., from the surface (001) for both modifications]. The exciting light was polarized parallel to the [100] direction in α-(BEDT-TTF)$_2$I$_3$ and to the [110] direction in β-(BEDT-TTF)$_2$I$_3$ (i.e., parallel to the polyiodide chains). For perpendicular polarization of the light the intensity of the bands was between 10–50 times smaller. The laser beam was focused on the surface of the crystal. The typical power of the laser beam was maintained below 10 mW. For some crystals a power dependence of the spectra was studied for laser powers up to 50 mW. The spectra were investigated with different slit widths (resolution 0.9–2.5 cm^{-1}).

The Raman spectra of α-(BEDT-TTF)$_2$I$_3$ for an excitation of $\lambda = 4880$ Å are shown in Fig. 1. They are similar to those reported in Ref. 27. However, at low temperatures, instead of one line related to the symmetrical stretching mode of I_3^- near 120 cm^{-1}, we observed three lines very close to each other at 117, 121, and 123 cm^{-1} (see Fig. 2 at 15 K). When the temperature increases the splitting disappears continuously as a result of thermal broadening, without any distinct change of the relative intensities of the structure (Fig. 2); above about 100 K the splitting is nearly not seen. The phase transition in α-(BEDT-TTF)$_2$I$_3$ at about $T = 135$ K has no distinct influence on the Raman spectra. The strong line at about 30 cm^{-1} in α-(BEDT-TTF)$_2$I$_3$ exhibits no splitting even for the best resolution. Apart from the features described in Ref. 27 we have found some additional very weak bands at about 45, 102, and 135 cm^{-1} for $T = 55$ K (Fig. 1 and Table I).

The Raman investigations of β-(BEDT-TTF)$_2$I$_3$ crystals gave rather surprising results (Figs. 3 and 4). We have found that the band assigned to the symmetrical stretching mode of I_3^- of about 120 cm^{-1} is split into

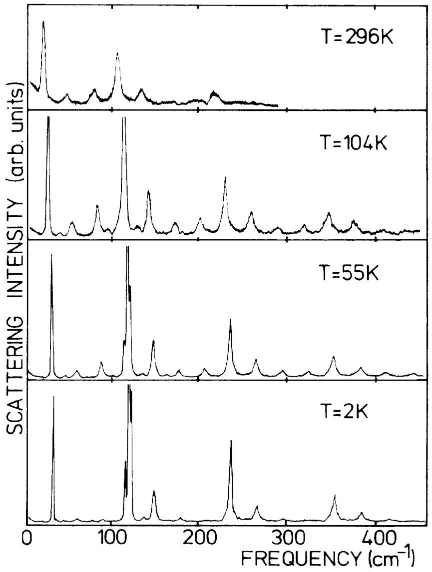

FIG. 1. Raman spectra of α-(BEDT-TTF)$_2$I$_3$ single crystals for different temperatures ($\lambda = 4880$ Å, $P = 10$ mW).

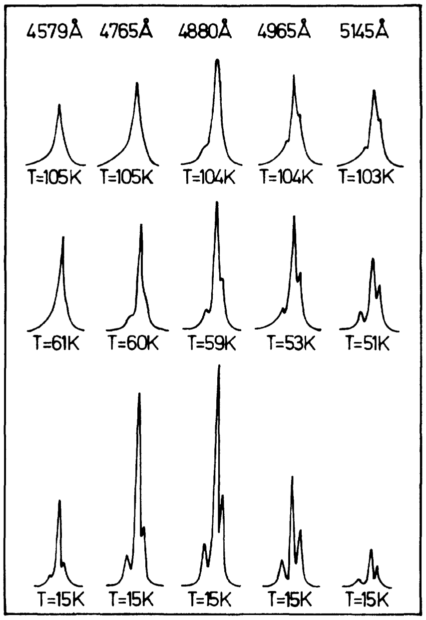

FIG. 2. Temperature dependence of the symmetric stretching mode ν_1 of I_3^- in α-(BEDT-TTF)$_3$I$_3$ for different excitations ($P = 10$ mW).

two or three lines (109, 120, and 126 cm^{-1}) at low temperatures. The splitting was stable for some crystals even during thermal cycling (Fig. 3), whereas for other crystals the splitting disappeared during the measurements and the spectra were nearly the same as those reported in Ref. 27 (Fig. 4). Above 125 K the spectra were the same for both kinds of β-(BEDT-TTF)$_2$I$_3$ crystals and only minor changes due to the temperature were observed. It should be emphasized that the splitting of the band at 120 cm^{-1} at temperatures below 125 K was observed for each β-(BEDT-TTF)$_2$I$_3$ crystal during the first measurement for a laser power below 10 mW. We compared the spectra of fresh grown crystals and the spectra of older crystals; moreover we polished the surface of the crystal and cleaned it by solvent. In every case the result was similar.

This phenomenon was carefully investigated as a function of temperature, frequency, and the power of the exciting laser light. The relative intensities of the lower-frequency component at about 109 cm^{-1} in comparison with the higher-frequency components (at about 120 and 126 cm^{-1}) were different for different β(BEDT-TTF)$_2$I$_3$ crystals and for some crystals the band at about 126 cm^{-1} was not clearly observed (Fig. 5). For four crystals the split band at 109 cm^{-1} disappeared when the ex-

TABLE I. Observed resonance Raman frequencies (cm^{-1}) for α-(BEDT-TTF)$_2$I$_3$ and β-(BEDT-TTF)$_2$I$_3$ crystals below 400 cm^{-1} (excitation $\lambda = 4880$ Å).

α-(BEDT-TTF)$_2$I$_3$ $T = 55$ K	β-(BEDT-TTF)$_2$I$_3$[a] $T = 55$ K	β-(BEDT-TTF)$_2$I$_3$[b] $T = 85$ K	Assignment[c]
	27	27	ν_4
30	30	30	
	37	38	
45			ν_3
59	56	53	$\nu_5, \nu_1 - \nu_5$
87	90	91	$\nu_1 - \nu_4$
102			
115			ν_1
118	109	121	
121	122		
135			
148	147	149	$\nu_1 + \nu_4$
166			ν_2
178	175	179	$\nu_1 + \nu_5$, $2\nu_1 - \nu_5$
208	218	214	$2\nu_1 - \nu_4$
237	237	240	$2\nu_1$
266	254	258	$2\nu_1 + \nu_4$
295			$2\nu_1 + \nu_5$, $3\nu_1 - \nu_5$
325	322		$3\nu_1 - \nu_5$
354	347	359	$3\nu_1$
384	362		$3\nu_1 + \nu_4$

[a] β-(BEDT-TTF)$_2$I$_3$—crystals for which a full irreversible transition by light would not be performed.

[b] β-(BEDT-TTF)$_2$I$_3$—crystals for which a full irreversible transformation by light was performed.

[c] The modes of I_3^-: ν_1-symmetric stretching, ν_2-asymmetric stretching, ν_3-bending, ν_4-libration, ν_5-libration.

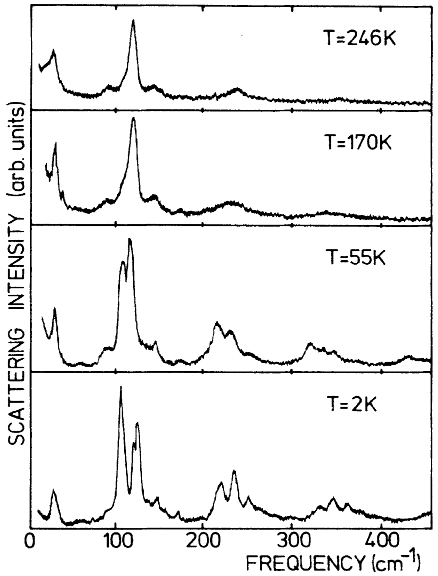

FIG. 3. Temperature dependence of the Raman spectra of β-(BEDT-TTF)$_2$I$_3$ crystals exhibiting stable splitting of the symmetric stretching mode ν_1 of I$_3^-$ ($\lambda=4880$ Å, $P=10$ mW).

citing power was increased (Figs. 6 and 7). The disappeared band at 109 cm^{-1} could be again observed after a temperature cycling when the upper temperature was higher than 125 K but the intensity ratio between the components of split band I(120 cm^{-1})/I(109 cm^{-1}) was usually different. For five other crystals the split band at 109 cm^{-1} was clearly observed even for the highest used laser power (~ 50 mW) but the intensity ratio I(120 cm^{-1})/I(109 cm^{-1}) did grow with the exciting laser power (Fig. 8).

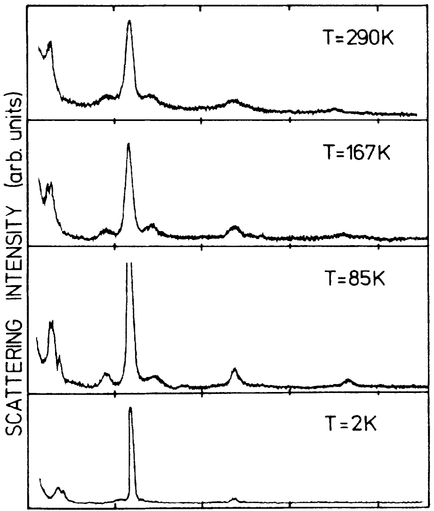

FIG. 4. Temperature dependence of the Raman spectra of β-(BEDT-TTF)$_2$I$_3$ crystals for which the splitting of the symmetric stretching mode ν_1 disappeared during the illumination by laser light ($\lambda=4880$ Å, $P=10$ mW).

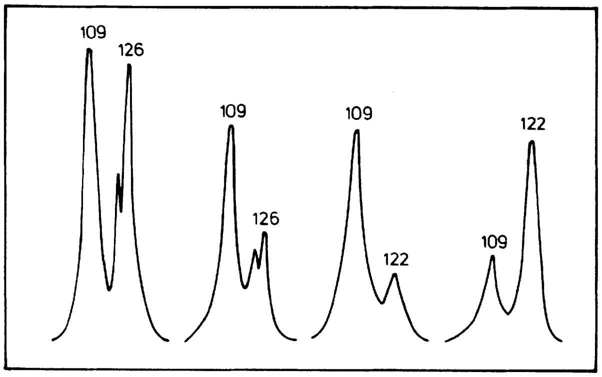

FIG. 5. Split band assigned to the symmetric stretching mode ν_1 of I$_3^-$ anions for different β-(BEDT-TTF)$_2$I$_3$ crystals ($T=2$ K, $\lambda=4880$ Å, $P=10$ mW).

The Raman spectra of the crystals where the splitting was always seen were studied as a function of the temperature and the frequency of the exciting light for a constant laser power maintained below 10 mW (Fig. 9). With increasing the frequency of the exciting light the intensity of the band at 109 cm^{-1} decreases. A similar behavior is found when the temperature increases. Simultaneously with the decrease of the band at 109 cm^{-1} the intensity of the higher frequency line at 122 cm^{-1} increases. The two bands of higher frequency (120 and 126 cm^{-1}) are separated only for the lowest temperatures while for higher temperatures a joint band at about 122 cm^{-1} was seen. The band of 109 cm^{-1} disappears for temperatures above 125 K and only one band at about 122 cm^{-1} was observed. The incommensurate structural modulation observed below $T=195$ K (Refs. 21–23) in β-(BEDT-TTF)$_2$I$_3$ crystals had no distinct influence on the Raman-spectra in agreement with the data published in Ref. 27.

It should be emphasized that the above mentioned results for β-(BEDT-TTF)$_2$I$_3$ are completely different in comparison with the results for α-(BEDT-TTF)$_2$I$_3$. For α-(BEDT-TTF)$_2$I$_3$, the intensity ratio of the split bands related to the symmetrical stretching mode of I$_3^-$ anion are not distinctly dependent on the power, the frequency of the exciting light and the temperature (compare Figs. 2 and 9). Moreover, in α-(BEDT-TTF)$_2$I$_3$ the disappearance of the splitting due to the exciting light power was

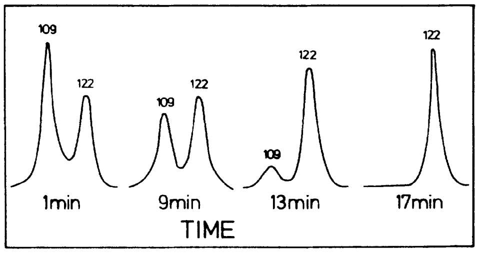

FIG. 6. Typical time dependence of the split mode ν_1 of I$_3^-$ anions for β-(BEDT-TTF)$_2$I$_3$ crystals which exhibit the irreversible transformation by laser light ($T=20$ K, $\lambda=5145$ Å, $P=15$ mW).

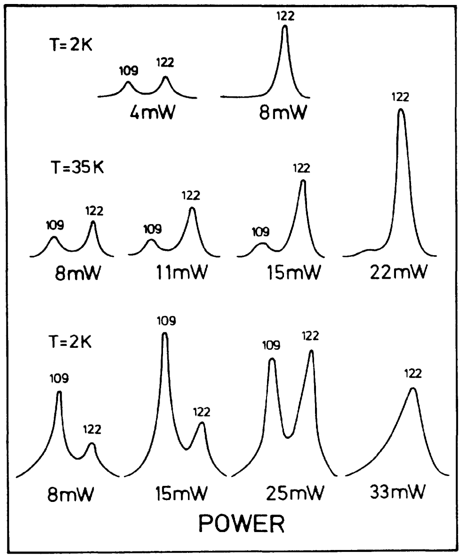

FIG. 7. Typical power dependence of the split mode ν_1 of I_3^- anions for different β-(BEDT-TTF)$_2$I$_3$ crystals which exhibit the irreversible transformation by laser light ($\lambda = 5145$ Å).

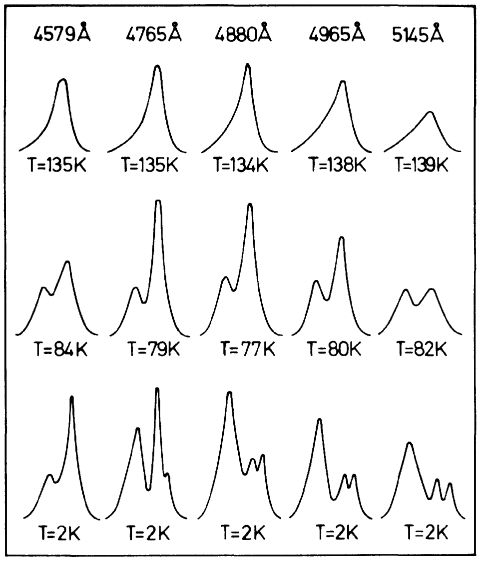

FIG. 9. Typical evolution of the split mode ν_1 of I_3^- anions in β-(BEDT-TTF)$_2$I$_3$ crystals for which full irreversible transformation by light could not be performed, as a function of temperature and the exciting wavelength ($P = 10$ mW).

never observed and the spilt bands were very similar for different crystals.

III. DISCUSSION

The linear, symmetrical I_3^- anion has three fundamental modes of vibration: the symmetric stretching mode ν_1 is Raman active and infrared nonactive, whereas the asymmetric stretching mode of ν_2 and bending mode ν_3 are infrared active only. However, the crystal forces can cause the distortion of the I_3^- anion and each mode of vibration can show both infrared and Raman activity.

The polyiodide systems exhibit unusually strong resonance Raman scattering for the stretching mode ν_1 with high intensity overtone progression (e.g., it is well seen in Figs. 1, 3, and 4). The resonance Raman spectra of such systems were studied both experimentally[28–32] and theoretically.[32,33] From these studies it results that the I_3^- anion is often deformed so that apart from the normal mode $\nu_1 = 103-120$ cm^{-1} forbidden modes can be sometimes seen in Raman spectra [the asymmetric stretching mode at $\nu_2 = 143-162$ cm^{-1} (Refs. 27, 31, and 32) and the bending mode at $\nu_3 \sim 55$ cm^{-1} (Ref. 31)]. The theoretical studies show that the fundamental geometry of the I_3^- anion is linear and symmetric but in the simulated crystalline environment the optimized structure is asymmetric and bent.[33] Nevertheless, both for symmetric and for asymmetric structures the deviation from linearity is always very small. It was also postulated that a linear, symmetric I_3^- anion cannot exist for a bond length above a critical estimated value of about 2.92 Å.[33,34] Nevertheless, in the case of α-(BEDT-TTF)$_2$I$_3$ the bond lengths in the linear symmetric I_3^- anion are equal to 2.937 Å, while for the β-(BEDT-TTF)$_2$I$_3$ these bond lengths are 2.904 Å at room temperature. From the calculations of the force constants of the fundamental modes results that the bonds of the I_3^- anion are very weak and that the central atom in the I_3^- anion is very loosely bound to the equilibrium position[28] (its position can be easily affected by weak forces).

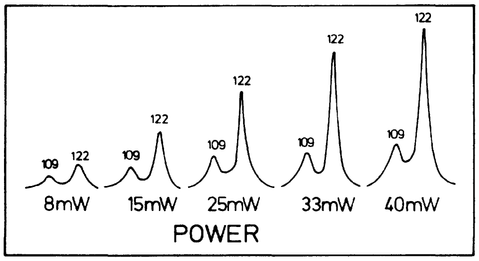

FIG. 8. Typical power dependence of the split mode ν_1 of I_3^- anions for β-(BEDT-TTF)$_2$I$_3$ crystals for which a full irreversible transformation by light could not be performed ($T = 20$ K, $\lambda = 5145$ Å).

In α-(BEDT-TTF)$_2$I$_3$ the I_3^- anions are arranged in zigzag chains which interleave the BEDT-TTF sheets.[10] Both in the high and the low temperature phase the ions are linear and symmetric.[19] The phase transition has very little influence on the crystal structure of α-(BEDT-TTF)$_2$I$_3$.[19,20] The interionic contacts along the chains are shorter than the sum of the van der Waals radii. There is also a significant interaction between the I_3^- anion and the BEDT-TTF molecules; each terminal atom of an I_3^- anion has contact distances with H atoms of BEDT-TTF molecules, which are very short in comparison to the sum of the van der Waals radii.[19,20]

These interactions are responsible for the observed splitting of the symmetric stretching mode ν_1 of the I_3^- anions in the α-(BEDT-TTF)$_2$I$_3$ crystals. The structure and the interactions do not change significantly as the temperature is growing, therefore there are only minor changes for the splitting of the bands.

The crystal structure of β-(BEDT-TTF)$_2$I$_3$ was investigated at room temperature[6] as well as at 100 K well below a phase transition at 125 K.[19] At room temperature the I_3^- anions are linear and symmetric. The interactions between adjacent I_3^- anions are not so strong as in α-(BEDT-TTF)$_2$I$_3$ since the distances are nearly equal to the sum of the van der Waals radii of the two iodine ions. On the other hand there exist also significant interactions between the anions and the cations (between H and I) both at room and low temperatures.[35,36] From the appearance of the superstructure in β-(BEDT-TTF)$_2$I$_3$ below 125 K two or three different Raman lines belonging to the ν_1 mode were expected—and as experimentally found (Fig. 5)—due to the three different I_3^- anions in each unit cell.[19] The I_3^- anions are relatively long in comparison with other anions used in the synthesis of the superconductors β-(BEDT-TTF)$_2X$ [$X = I_3^-$ (10.1 Å), IAuI$^-$ (9.4 Å), BrIBr$^-$ (9.3 Å)].[37] In the crystals of β-(BEDT-TTF)$_2$IAuI (Ref. 38) and β-(BEDT-TTF)$_2$BrIBr (Ref. 39), a distortion of the anions and a phase transition similar to that in β-(BEDT-TTF)$_2$I$_3$ at 125 K is not observed. Therefore only one resonance Raman line was expected in β-(BEDT-TTF)$_2$IAuI and only one line assigned to the symmetrical stretching mode of IAuI$^-$ was observed in this salt even for high resolution,[40] in contrast to the β-(BEDT-TTF)$_2$I$_3$ crystals. Therefore we relate the existence of the three resonance Raman lines at 109, 120, and 126 cm^{-1} (see Fig. 5) to the commensurate superstructure in β-(BEDT-TTF)$_2$I$_3$ as observed by x-ray studies at 100 K.[19]

The change of the resonance Raman spectra at low temperature with time at a constant power of 15 mW (Fig. 6) and the change of the spectra with an increase of the laser power (Fig. 7) can be only interpreted by a change of the superstructure into a structure in which the I_3^- anions are linear and symmetric as in the room-temperature structure. This must be concluded from the fact that for a high laser power (Fig. 7), or after a longer time of irradiation with laser light (Fig. 6) only one resonance Raman line at 122 cm^{-1} can be observed at the same frequency as for the symmetric I_3^- anions at a temperature above 125 K. This single line at 122 cm^{-1} is also found after decreasing the exciting laser power below 5 mW showing that the structure is stable at low temperature, as long as the temperature does not exceed 125 K. As soon as the temperature becomes larger than 125 K, in the next cooling down cycle of the crystal again three resonance Raman lines are observed, showing that because of the phase transition at 125 K (Refs. 16, 19, 24, 41, and 42) the asymmetric, nonlinear superstructure is created again.

The change of the superstructure by the exciting light may be understood in the following way. It is known that the symmetric high-temperature structure of β-(BEDT-TTF)$_2$I$_3$ and the asymmetric superstructure below 125 K are thermodynamically very close to each other since an isotropic pressure of only about 0.25–0.4 kbar (Refs. 41 and 42) is able to suppress the phase transition at 125 K, as well as the incommensurate modulated structure below 195 K. Even a release of the pressure at a temperature of about 100 K still stabilizes the symmetric structure resulting in superconductivity at 8.1 K.[16,41,42] In the resonance Raman-experiment, the I_3^- anions and possibly also the donor cations are excited into the first excited singlet state. During the radiationless desactivation of this excited state by internal conversion and vibronic relaxation, the I_3^- anion may fall down to the vibronic levels of the ground state S_0 in such a way that it reaches either the symmetric or asymmetric configuration with respect to the two possible structures. When the intensity of the exciting light increases the probability that the asymmetric anions do convert into the symmetric configuration is higher because we can assume that the symmetric structure is thermodynamically a little more favorable (otherwise the crystals would not grow at room temperature in this structure). In addition, we conclude from ^{1}H-NMR relaxation measurements[43] that the phase transition at 125 K is forced by a statistical freeze of the therminal ethylene groups on one side of the BEDT-TTF molecules in the stacks and the strong cation-anion interaction reported by Emge *et al.*[35] Furthermore, the temperature-pressure cycling experiments[15,16] and the neutron diffraction studies in the high-T_c β phase[26] have shown that a weak pressure of only about 1 kbar is sufficient to have an ordering of all therminal ethylene groups of the BEDT-TTF molecules resulting in symmetric and linear I_3^- anions in this phase. Therefore, we assume that the symmetric structure is thermodynamically more favorable.

At higher light intensities it might even happen that the structural change into the symmetric form undergoes in a larger part of the crystal. This might be concluded from the fact that with high laser powers ($\sim$50 mW) at low temperatures [with the exception of a few cases (Fig. 8)], only one line at 120–122 cm^{-1} is observed (see also Ref. 19). However, for the few exceptions (Fig. 8) the ratio between the two lines at 122 cm^{-1} and at 109 cm^{-1} grows when the light intensity increases showing that the symmetric structure is more favorable. It should be emphasized here that the changes of the resonance Raman lines induced by the light are dependent on the individual β-(BEDT-TTF)$_2$I$_3$ crystal and even these changes are different in the same crystal after several thermal cycles. This fact is not understood in the moment.

We conclude from our results that—similar as in the experiments where particular pressure-temperature cycling procedures lead to the superconductivity phase at 8.1 K (Refs. 15 and 16)—the excitation of the β-(BEDT-TTF)$_2$I$_3$ crystals (at low temperature) by laser light also leads to the high-temperature superconducting state with the higher ordered structure. Very recently the crystal structure of the β-(BEDT-TTF)$_2$I$_3$ in the high-T_c metastable superconducting phase was studied.[25,26] The result of these investigations are that the high-T_c phase is completely ordered in agreement with our conclusion.

Nevertheless, at the moment it is not clear to us if the transformation into the high-T_c superconducting state by light is a surface effect (due to the fact that the light is absorbed in a thin surface layer) or whether it is possible to convert the whole crystal into this state by irradiation, e.g., of infrared light and exciting only vibrational modes. Further experiments are necessary and are under progress.

The comparison of the β-(BEDT-TTF)$_2$I$_3$ data with the results for α-(BEDT-TTF)$_2$I$_3$ supports the above considerations. In the α-(BEDT-TTF)$_2$I$_3$ the I_3^- anions are linear and symmetric for the whole temperature range and a crystal change similar to the appearance of the superstructure in β-(BEDT-TTF)$_2$I$_3$ is not observed. The reason for the existence of the splitting of the symmetrical stretching mode in α-(BEDT-TTF)$_2$I$_3$ is not a superstructure as in β-(BEDT-TTF)$_2$I$_3$ but a crystal-field effect. Therefore the relative intensities of the components of the split mode in α-(BEDT-TTF)$_2$I$_3$ do not exhibit a dependence on the power, the frequency of the exciting light or the temperature since none of these reasons can induce changes of the polyiodine chains in this salt.

In Ref. 27, the dominant peaks in the α-(BEDT-TTF)$_2$I$_3$ spectrum were described as the composition of two modes: the librational mode of I_3^- (at about 30 cm^{-1}) and the symmetric stretching mode of I_3^- (at about 118 cm^{-1}). The other peaks in α-(BEDT-TTF)$_2$I$_3$ are assigned to the harmonics of the symmetric stretching mode ν_1, or the process of creation of one or more phonons and simultaneous creation (or annihilation) of one phonon related to the librational mode of I_3^-. Other bands in the spectrum were not interpreted. In our opinion the mode at about 59 cm^{-1} in α-(BEDT-TTF)$_2$I$_3$ spectrum is another lattice mode of I_3^- anion and it also creates combination bands with the symmetric stretching mode ν_1, whereas the weak bands at about 45 and 166 cm^{-1} can be assigned to the bending and asymmetric stretching mode of I_3^- anion, respectively. The assignment similar as that for α-(BEDT-TTF)$_2$I$_3$ was also made for β-(BEDT-TTF)$_2$I$_3$.[27] Similarly we suggest that the band at about 56 cm^{-1} in the β-(BEDT-TTF)$_2$I$_3$ spectrum is a lattice mode of the I_3^- anion (Table I).

In Ref. 27, a splitting of the Raman band assigned to the ν_1 mode of the I_3^- anions in β-(BEDT-TTF)$_2$I$_3$ at low temperature was not observed. Our experiments show that with the relatively high laser power of about 50 mW used in the experiment in Ref. 27 one cannot find such a splitting due to the change of the crystal into the high-T_c state.

IV. CONCLUSIONS

The resonance Raman spectra of α-(BEDT-TTF)$_2$I$_3$ and β-(BEDT-TTF)$_2$I$_3$ were studied and compared. In both modifications we discovered a splitting of the Raman band attributed to the symmetric stretching mode of the I_3^- anions at lower temperatures. In α-(BEDT-TTF)$_2$I$_3$ the splitting can be related to a crystal field effect and in β-(BEDT-TTF)$_2$I$_3$ the splitting is caused by a commensurate superstructure developed below 125 K. In contradiction to α-(BEDT-TTF)$_2$I$_3$ in the β-(BEDT-TTF)$_2$I$_3$ crystals the light can induce an irreversible change of the structure and the split band disappeared as long as the crystal temperature is kept below 125 K. To our knowledge this is the first observation of such a light-sensitive change of a crystal structure for an organic conductor, and might also explain the discrepancies of the structural investigations by x-ray and neutron diffraction at lower temperatures between several workers.[19,25,35]

The crystals of β-(BEDT-TTF)$_2$I$_3$ exhibit two kinds of superconducting transitions at ambient pressure at 1.3 and 8 K. In the discussion of this phenomena it was suggested that two crystallographically different states coexist. From annealing experiments[16] it results that both phases are energetically close to each other. The disappearance of the split band of the vibrational mode of the I_3^- anions at around 120 cm^{-1} due to illumination by laser light can be related to a transition between two different states of β-(BEDT-TTF)$_2$I$_3$, at least at the surface. As a result of this transformation the polyiodide chains become symmetric and ordered. Moreover, we know that the high-T_c superconducting state is completely ordered.[26] That is why we conclude that an excitation by light can induce a transition from the low-T_c into the high-T_c superconducting state in β-(BEDT-TTF)$_2$I$_3$

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