Raman-Studies of the Organic Superconductor β-(BEDT-TTF)$_2$IAuI

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The resonance Raman spectra of $(IAuI)^-$-anions in the organic superconductor β-(BEDT-TTF)$_2$IAuI as well as in the electrolyte salt n-Bu_4AuI_2 are investigated. In contrast to β-(BEDT-TTF)$_2I_3$ in the crystals of β-(BEDT-TTF)$_2$IAuI at low temperature only one Raman line at 120 cm^{-1} corresponding to the symmetrical stretching mode of the $(IAuI)^-$-anion is observed. No distinct change in the Raman spectra is observed at the superconducting transition.

Introduction

The superconductivity in organic materials is very sensitive against slight structural changes and disorder. Even very small changes can seriously influence the superconducting transition. In the organic charge transfer-salt β-(BEDT-TTF)$_2I_3$ [BEDT-TTF = bis-(ethylenedithio)tetrathiofulvalene] below 195 K exists an incommensurate modulation [1] and below 125 K a commensurate superstructure with a pronounced distortion of the I_3^--anions [2]. Under ambient pressure the superconducting transition temperature T_c is 1.3 K [3] but after a particular pressure-temperature cycling procedure superconductivity can be stabilized at ambient pressure even at $T_c = 8.1$ K [4]. A recent neutron diffraction study has shown that the high-T_c superconducting phase of β-(BEDT-TTF)$_2I_3$ is completely ordered [5] showing that during the pressure-temperature cycling procedure the distortion of the I_3^--anions in β-(BEDT-TTF)$_2I_3$ is suppressed resulting in an increase of T_c. The I_3^--anions and other polyhalide ions used in organic superconductors are sensitive to distortions and slight changes in the crystal. The Raman-spectra of the polyhalide ions exhibit unsually strong resonance lines. On the other hand, resonance Raman (RR)-scattering is very sensitive to small distortions and changes of intermolecular forces as demostrated for the I_3^--anions in β-(BEDT-TTF)$_2I_3$ [6]. In [6] the distortions of the I_3^--anions and the structural changes were investigated on the basis of RR-studies of the symmetrical stretching mode of the I_3^--anions.

In this letter we report on RR-investigations of the organic superconductor β-(BEDT-TTF)$_2$IAuI. The superconductivity in β-(BEDT-TTF)$_2$IAuI$_2$-crystals is observed below $T_c = 4-5$ K [7–10], and superconductivity is a volume property [9]. In contradiction to the geometry of the I_3^--anions in β-(BEDT-TTF)$_2I_3$ below 125 K the $(IAuI)^-$-anions in β-(BEDT-DDT)$_2$IAuI are linear and symmetric in the whole temperature range below 300 K [7]. The structure of β-(BEDT-TTF)$_2$IAuI is completely ordered. However, during the electrochemical process the $(IAuI)^-$ can decompose and "impurities" obtained in this way might partially replace $(IAuI)^-$-anions in the crystal lattice [10]. As a consequence the onset temperature for superconductivity varies over a broad temperature range. In this paper we report the Raman-spectra of β-(BEDT-TTF)$_2$IAuI-crystals below and above the temperature of the superconducting transition. Since n-Bu_4AuI_2 is used as electrolyte salt in the electrocrystallization of β-(BEDT-TTF)$_2$IAuI the spectra of this compound were also studied.

The linear, symmetrical ion $(I-Au-I)^-$ has three fundamental modes of vibration: the symmetric stretching mode ν_1, the asymmetric stretching mode ν_2 and a bending mode ν_3. Only the stretching mode ν_1 is Raman-active, however intermolecular inter-

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actions in the solid state can break the symmetry and all three modes might exhibit Raman-activity.

Experimental

The single crystals of β-(BEDT-TTF)$_2$IAuI were grown by electrochemical methods in the presence of n-Bu$_4$NAuI$_2$ as a supporting electrolyte similarly as described for the analog I_3^--compound [11]. The RR-spectra of β-(BEDT-TTF)$_2$IAuI single crystals were measured with a 90° scattering geometry as a function of temperature using three different lines of an argon-ion laser (4579, 4880 and 5145 Å). The beam was focussed on the surface of the crystal and the laser power was below 10 mW. The crystals of n-Bu$_4$NAuI$_2$ were powdered and compressed with KBr in a ratio 1 : 5.

Results and Discussion

The RR-spectrum of n-BuNAuI$_2$ dispersed in a KBr-pellet for $T = 14$ K and an excitation-wavelength $\lambda = 4579$ Å is shown in Figure 1. The spectra were not essentially dependent on the temperature and the frequency of the exciting light. The observed peak frequencies at 14 K are 31, 36, 91, 113*, 124* and 154 cm^{-1} ± 2 cm^{-1} (* indicates the strong lines); moreover some overtones are seen. Similar Raman-results were obtained for polycrystalline samples and for a sample solved in tetrahydrofurane. The strong doublet (113 and 124 cm^{-1}) (Fig. 1) can be assigned to the symmetrical stretching mode of the (IAuI)$^-$-anion and the splitting of this mode is due to crystal forces in the n-Bu$_4$NAuI$_2$-crystal. Our spectral results and proposed assignments disagree with [12], where a band at 157 cm^{-1} was the strongest and was assigned to the symmetric stretching mode of the (IAuI)$^-$-anion. However, the frequency of the symmetrical stretching mode for (IAuI)$^-$ and for I_3^- (120 cm^{-1}) should be close to each other since the structure of these anions is similar and the Au-atom is located in the middle. Moreover, the correctness of our results and proposed assignment is also supported by the results obtained from the β-(BEDT-TTF)$_2$IAuI-crystals presented below.

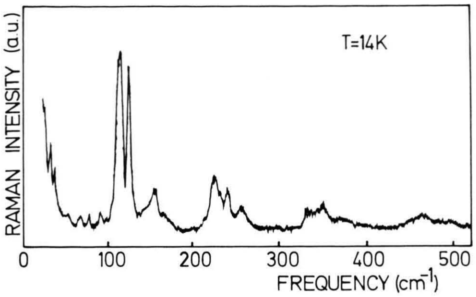

Fig. 1. The Raman spectrum of n-Bu$_4$NAuI$_2$ crystals dispersed in a KBr pellet (weight concentration $c = 20\%$, excitation $\lambda =$ 4579 Å).

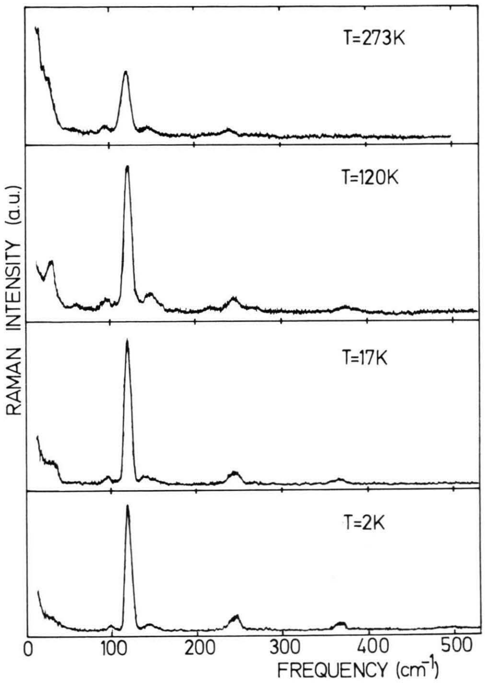

Fig. 2. The temperature dependence of the low energetic part of the resonance Raman spectra of β-(BEDT-TTF)$_2$IAuI single crystals (excitation $\lambda = 4579$ Å).

The low energetic part of the RR-spectra of β-(BEDT-TTF)$_2$IAuI single crystals for different temperatures is shown in Fig. 2 (excitation wavelength $\lambda = 4579$ Å). Similar results were obtained for excitations with light of $\lambda = 4880$ Å and $\lambda = 5145$ Å but the intensity of the lines was weaker. The stronger Raman-scattering for an excitation with light of the wavelength of $\lambda = 4579$ Å is due to the fact that this blue light is closer to the electronic absorption peak of the (IAuI)$^-$-anion in the crystals. The RR-bands are observed at about 30, 60, 90, 120*, 150 and 175 cm^{-1} (± 2 cm^{-1}) at a temperature of 120 K (* indicates the strongest line).

The band at 120 cm^{-1} can be assigned to the symmetrical stretching mode ν_1 of the (IAuI)$^-$-anions; some overtones of this mode are also seen. The band at 30 cm^{-1} corresponds to a librational phonon of the (IAuI)$^-$-anions. The bands around 90 and 150 cm^{-1} can be related to the process of creation or annihilation of a symmetric stretching vibration and simultaneous creation of one phonon related to the librational mode (30 cm^{-1}) of (IAuI)$^-$. This interpretation is similar to that described in [13] for (BEDT-TTF)$_2$X, where $X = I_3^-$ and IBr_2^-. The band around 60 cm^{-1} can be assigned to another lattice mode which also creates the combination band with the symmetric stretching mode ν_1 (175 cm^{-1}). The band around 150 cm^{-1} could be related to the asymmetric stretching mode of (IAuI)$^-$-anion, but this mode is very weak. The transition to the superconducting state has no distinct influence on the Raman-spectra as is seen from the comparison of the spectra for $T = 2$ K and $T = 17$ K (Figure 2). The band related to the mode ν_1 is not split even for the best resolution as it was observed for β-(BEDT-TTF)$_2$I$_3$ [6]. This means that no distortion of the IAuI-anions exists, showing that the chains of (IAuI)$^-$-anions are regular and every (IAuI)$^-$-anion has the same geometry in the metallic as well as in the superconducting state. A disorder due to "impurities" produced during the electrochemical process by decomposition of (IAuI)$^-$-ions has negligible influence on the Raman-results since the "impurity"-concentration is small. These "impurities" have an influence on the collective electronic phenomena whereas local phenomena influence the Raman-spectra.

In conclusion, we have performed resonance Raman-studies of the organic superconductor β-(BEDT-TTF)$_2$IAuI above and below the superconducting transition temperature. The investigations have shown that the (IAuI)$^-$-anions are symmetric and linear in the whole temperature range 1.3–300 K in contrast to the I$_3$-anions in β-(BEDT-TTF)$_2$I$_3$ and that no structural change exists below the temperature of the transition to the superconducting state.

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