RESONANT RAMAN SCATTERING FROM SUPERCONDUCTING GAP EXCITATIONS IN SINGLE CRYSTALS OF $(\text{BEDT-TTF})_2\text{I}_3$

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ABSTRACT

A study of low-energetic resonant Raman scattering of α_t - and β_H -(BEDT-TTF)₂I₃ superconductors was performed. The softening and weakening of the low frequency optical phonons at about 30 cm⁻¹ in the superconducting state of both α_t - and β_H -phases were observed below T_c.

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. These 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 Falkovskii [1] paid attention that the presence of an energy gap in the electronic energy spectrum of superconductors leads to the absence of absorption (at T = 0 K) 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 from the Raman scattering spectra is based exactly on this idea. Beside this observation a softening of some of the Raman-active modes at T_c in the crystals of RBa₂Cu₃O_{7-δ} (R is a rare earth) was noticed [e.g.2]. This fact was interpreted by the existence of the energy gap above the mode frequency.

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(BEDT-TTF) $_2$ I $_3$ is an unlc system for Raman scattering investigations of the superconducting gap. Several phases with rather high T_c exist inside this family which are suitable for Raman measurements. First of all, it is the α_t -phase with a $T_c = 8-8.5$ K which can be produced from the α -phase by tempering at temperatures higher than 75° C [3,4], and the β_H -phase ($T_c = 8$ K) which appears on the surface of β -phase crystals due to irradiation with a laser [5]. Maybe the most important feature for Raman investigations of this system is the existence of several low energetic phonon bands assigned to I $_3^-$ -anion librations, which are rather intensive due to resonance conditions of their excitation [5]. 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 the gap.

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

EXPERIMENTAL

Raman measurements on single crystals were made in a 90° scattering configuration using several lines of an argon-ion laser. Since the Raman scattering on the I $_3^-$ -anions in the organic superconductors (BEDT-TTF) $_2$ I $_3$ has a resonant character [5], with a maximum for $\lambda = 488$ nm, the majority of our studies have been performed for an excitation with laser light of this wavelength. 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 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 -(BEDT-TTF) $_2$ I $_3$ crystals were grown from a THF solution by electrochemical methods as described earlier [6]. The single crystals with highly reflecting surfaces were selected for Raman measurements as well as for preparing the α_t -(BEDT-TTF) $_2$ I $_3$ phase. For this purpose α -(BEDT-TTF) $_2$ I $_3$ crystals were tempered in air for 1-6 days at temperatures between 75° and 95° C. We observed that α -phase crystals tempered at 75° C during 1-3 days 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 days 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 -(BEDT-TTF) $_2$ 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 -(BEDT-TTF) $_2$ 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 of (BEDT-TTF) $_2$ I $_3$ is about 1000 nm. This low value explains the sensitivity of the Raman scattering spectra to the surface quality of the samples. Our remarks on the quality of the α_t -(BEDT-TTF) $_2$ I $_3$ surface layer were confirmed by electrical conductivity measurements performed for samples tempered at 75° C as well as 95° C.

RESULTS

The Raman spectra of the α - and α_t -(BEDT-TTF) $_2$ I $_3$ phases for an excitation of $\lambda = 488$ nm at $T = 1.5$ K are shown in Fig.1. These spectra are similar to

Fig.1. Low-energetic part of the resonant Raman spectra at $T = 1.5$ K of: a) α -(BEDT-TTF) $_2$ I $_3$ and b) α_t -(BEDT-TTF) $_2$ I $_3$.

those reported by Świetlik et al. [4,5]. However, the spectrum of α_t -(BEDT-TTF) $_2$ I $_3$ (Fig.1b) is a little bit different. In the good crystals of α_t -phase we observed only very 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 -(BEDT-TTF) $_2$ I $_3$ crystal 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 of 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 adequate band was also observed at $T > T_c$ (Fig.2).

Fig.2 Resonant Raman spectra of α_t -(BEDT-TTF) $_2$ I $_3$ in the region of libration of the I $_3^-$ -anions at temperatures below and above T_c .

Figure 2 shows the low energetic parts of the resonant Raman spectra of the α_t -(BEDT-TTF) $_2$ I $_3$ at 1.5 K ($T < T_c = 8$ K) and at $T > T_c$. A relative 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_t -(BEDT-TTF) $_2$ I $_3$. Beside this observation a considerable softening of the low-frequency band is seen. 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 $T = 1.5$ K and $10 \text{ K} < T < 60$ 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 Ref.5. The low-energetic part of the resonance Raman spectra of β_H -(BEDT-TTF) $_2$ I $_3$ 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 ($T_c = 8$ 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} show only a small dependence on the light polarization; in contrast to the intensities of the bands for the α -phase which strongly depend on the polarization of the laser light.

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_t - 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 $_2$ [7], 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 , called the "amplitude mode". 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 ($T_c \approx 7\text{ K}$). Thus, the intensity of the amplitude mode is taken away from the "phonon". This phenomenon was interpreted theoretically by Balseiro and Falicov [8]. 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 amplitude of the phonon mode. For the case of NbSe $_2$, they estimate the electron-"phonon" coupling constant of $\lambda = 2g^2\rho_0/\hbar\omega_0 = 0.24$ and because of this small value, the reduction of the amplitude and frequency shifts are only about 10 %.

Zeyher and Zwicky [9] extended this theory to strong coupling and found that for $\lambda = 2.9$ the phonon shift amounts up to 600 % for a single phonon coupled with the electrons. In YBaCuO there are many phonon modes, therefore the shift of each mode is much smaller, and experimentally amounts to 1.5 % [e.g. 2].

In α_t - and β_H -(BEDT-TTF) $_2$ I $_3$ we expect $\lambda \approx 2$ and just one or two phonon modes (at 30 and 39 cm^{-1}) strongly coupled with the electrons. Thus, the shift of each line, as well as the transfer of intensity to the amplitude mode should be large. Recent tunneling measurements of α_t -(BEDT-TTF) $_2$ I $_3$ [10] show large, very sharp peaks in two regions, namely $0.7\text{ meV} = 6\text{ cm}^{-1}(2\delta^{(0)})$, and $10\text{ meV} = 80\text{ cm}^{-1}(2\delta^{(1)})$ (and in addition a second harmonic at 20 meV). We suggest tentatively that these two peaks are neither pure "phonons" nor pure "gap" structures, but admixtures, being partly "phonon" and partly "gap", in the spirit of the Balseiro-Falicov theory [8] and our results obtained here by the Raman scattering match into this picture.

Fig.3. Experimental Raman scattering of α_t -(BEDT-TTF) $_2$ I $_3$ at $T = 1.5$ K normalized to scattering at $T > T_c$.

In fact, in the ratio of the Raman scattering intensities below and above T_c (see Fig.3) 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.

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