



RESONANT RAMAN SCATTERING ON SINGLE CRYSTALS OF (BEDT-TTF)₂Cu(NCS)₂

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Resonant Raman spectra of the organic superconductor (BEDT-TTF)₂Cu(NCS)₂ have been measured at 1.3 K as well as at 120 K. The Raman data do not show a superconducting gap opening in the investigated two dimensional superconducting system. The vibrational modes found in the Raman spectra are discussed and assigned. Possible mechanisms for resonance conditions in such two-dimensional organic superconducting systems are proposed.

INTRODUCTION

The discovery of superconductivity in radical salts of bis (ethylene dithio) tetrathiafulvalene (BEDT-TTF) under pressure and at ambient pressure¹⁻⁶ has initiated an intensive study of the structural and physical properties of this class of two-dimensional (2-D) organic metals.

Among these (BEDT-TTF) based radical salts, the (BEDT-TTF)₂ Cu(NCS)₂ is, until now, the ambient pressure organic superconductor with the highest critical temperature $T_c = 10.4$ K⁵. In addition, the (BEDT-TTF)₂ Cu(NCS)₂ shows a nearly isotropic electrical dc conductivity as well as the optical one in the *bc* plane⁷. For the optical conductivity this behaviour is different with respect to other 2-D radical salts, for example in the β -(BEDT-TTF)₂I₃ the optical conductivity is quite anisotropic^{8,9}.

Another peculiarity of the (BEDT-TTF)₂ Cu(NCS)₂ is the structure. The space group is lowered from P2₁/c to P2₁ with respect to parent compounds⁵. The two dimensional behaviour is due to conducting sheets of dimerized BEDT-TTF molecules which are separated by non-conducting anion layers. In the BEDT-TTF sheets the dimers are nearly orthogonally arranged with respect to each other^{5,10} and the dimers do not form the usual face to face piling along the stacking axis. The latter property increases the 2-D character of the molecular network and sup-

presses the Fermi surface instability¹¹. The investigation of molecular vibrations is useful and can provide knowledge on the structure and on electron molecular vibrations which are due to charge oscillation between the dimerized molecules coupled with the totally symmetric intramolecular modes¹²⁻¹⁵. For this reason, Raman scattering studies are important in order to account for totally symmetric vibrations. In addition, Raman spectroscopy can take advantage of resonant effects. In fact, when resonant conditions are fulfilled, not only selected molecular vibrations are observed, we also obtain information about the coupling of the carriers with those molecular vibrations, as well as information on the electronic manifold involved in resonance conditions. The (BEDT-TTF)₂ Cu(NCS)₂⁵ was discovered nearly two years ago, but no Raman data has been published in the literature. In this paper we report on the Raman spectrum of single crystals of (BEDT-TTF)₂ Cu(NCS)₂, at 1.3 K, that means in the superconducting state and at 120 K that means well above the superconducting transition temperature.

EXPERIMENTAL

High quality single crystals of (BEDT-TTF)₂ Cu(NCS)₂ have been obtained by electrochemical preparation^{6,16}. The largest crystals obtained in this way (10x2x0.1 mm) have been selected and oriented in a patchwork of about 10 mm². The Raman spectra

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were performed by different lines (514.5 nm, 488.0 nm, 476.5 nm) of an argon-ion laser (Coherent Innova 90) in a 90° scattering configuration.

The laser beam was filtered in a monochromator and with a proper interference filter in order to suppress the plasma lines. The power of the laser beam was maintained below 10 mW and not completely focused in order to prevent sample damages. Ten spectra were accumulated with a resolution of the monochromator of about 3 cm^{-1} in order to achieve an acceptable signal to noise ratio, and the Raman shift between 40 cm^{-1} and 3500 cm^{-1} has been investigated. The results were confirmed on several different crystals of $(\text{BEDT-TTF})_2\text{Cu}(\text{NCS})_2$. The Raman spectrum of the Cu-SCN powder was performed with a resolution of the monochromator of 0.6 cm^{-1} , at 296 K, and with a laser beam power of 20 mW.

RESULTS AND DISCUSSION

Fig. 1 shows the Raman spectra of a single crystal of $(\text{BEDT-TTF})_2\text{Cu}(\text{NCS})_2$ with the laser beam polarized parallel and perpendicular to the long axis of the $(\text{BEDT-TTF})_2$. The scattering was investigated from the (100) crystal surface which is the larger developed plane in the electrochemical synthesis. The dimers of $(\text{BEDT-TTF})_2$ molecules stack nearly perpendicularly with their molecular long axis predominantly parallel oriented along the c direction¹⁰. The $\text{Cu}(\text{NCS})_2$ counter anions build a sheet where the copper coordinates with one sulfur atom and two nitrogen atoms forming a coordination polymer¹⁰. Polarized reflectance data⁷ and I.R. absorption measurements¹⁵ confirm the existence of two different CN stretching vibrations with higher intensity along the c axis. The Raman spectrum of $(\text{BEDT-TTF})_2\text{Cu}(\text{NCS})_2$ at 1.3 K (Fig. 1) consists of a few

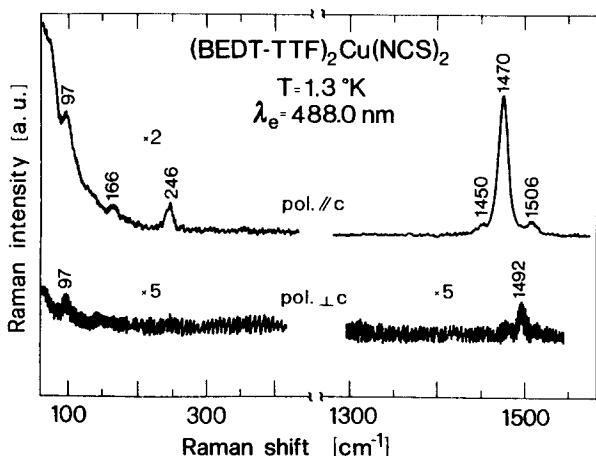


Fig.1: Resonant Raman scattering on a single crystal of $(\text{BEDT-TTF})_2\text{Cu}(\text{NCS})_2$. The laser beam is polarized parallel (upper trace) and perpendicular (lower trace) to the major axis of the BEDT-TTF molecules.

bands of very low intensity. The most intensive one is at 1470 cm^{-1} with a laser polarization along the major axis of the BEDT-TTF molecules. When the laser light is polarized perpendicular to the c -axis a weak band appears at 1492 cm^{-1} (see Fig. 2). In this case the band at 1470 cm^{-1} disappears totally. At 45° , with respect to the major axis of the BEDT-TTF molecules, the intensity of the 1470 cm^{-1} band is nearly half. We assign the 1470 cm^{-1} band to the $a_g\text{ C=C}$ stretching vibration of the central carbons and the 1492 cm^{-1} band to the $a_g\text{ C=C}$ stretching vibration of the rings. In the neutral BEDT-TTF molecule the totally symmetric vibrations of the central and ring C=C bands were found at 1552 cm^{-1} and 1494 cm^{-1} respectively^{17,14}. The large shift in frequency of the central C=C stretching means that the transition from neutral BEDT-TTF to the charged cation in the $(\text{BEDT-TTF})_2\text{Cu}(\text{NCS})_2$ is accompanied by an increase of the central length of the C=C double bond, that means an increase of negative charge in the

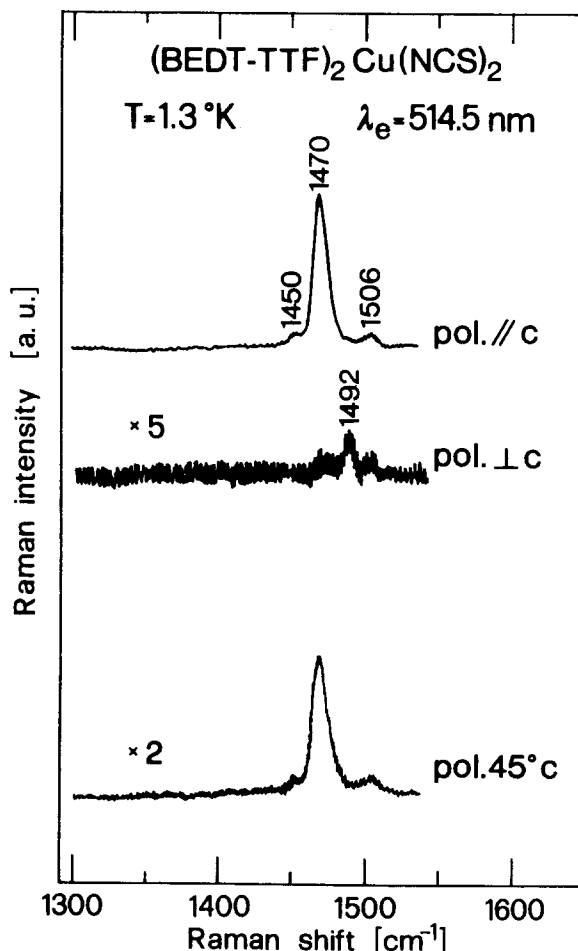


Fig.2: Resonant Raman Scattering on a single crystal of $(\text{BEDT-TTF})_2\text{Cu}(\text{NCS})_2$ in the C=C stretching frequency range with different laser beam polarizations.

central carbon atoms. This is not the case for the ring C=C bond where the frequency shift is only 2 cm^{-1} . The high relative intensity of the 1470 cm^{-1} band, nearly 10 times higher with respect to the other Raman bands, suggests that this vibration is strongly coupled with the electronic transition at 20000 cm^{-1} (see Fig. 3). This electronic transition is probably a bonding-antibonding one¹⁸, and is mainly located on the rigid and planar TTF fragment of the BEDT-TTF molecules. We would like to stress the fact that we carried out the Raman spectrum at 1.3 K (sample in pumped liquid helium), i.e. in the superconducting regime of the $(\text{BEDT-TTF})_2\text{Cu}(\text{NCS})_2$ single crystal. Two other weak bands at 1450 cm^{-1} and 1506 cm^{-1} are clearly visible. These are certainly related to C=C vibrations as we can see from I.R. and Raman investigation on deuterated samples of neutral BEDT-TTF and the β phase of $(\text{BEDT-TTF})\text{I}_3$ ^{17,19}. In particular the authors in Ref.17 found a band at 1511 cm^{-1} in the Raman spectrum of the neutral BEDT-TTF and they assigned it to an antisymmetric b_{1u} vibration of the ring C=C band which is Raman allowed by departure from molecular symmetry. In our data we can see the 1506 cm^{-1} band as well, in the spectrum with the polarization perpendicular to the c -axis (see Fig. 2). The partial polarization of the 1506 cm^{-1} band may support the previous assignment as well as the strong-

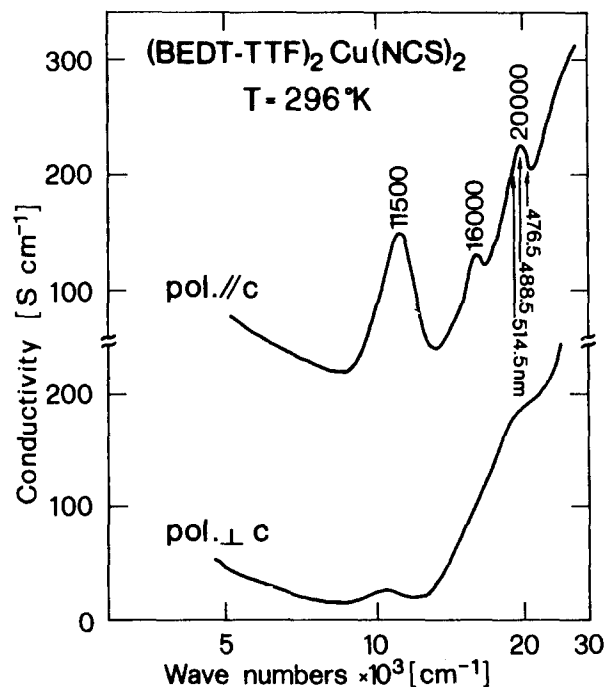


Fig.3: Optical conductivity spectra of a single crystal of $(\text{BEDT-TTF})_2\text{Cu}(\text{NCS})_2$. The polarization of the laser beam is taken parallel (upper trace) and perpendicular (lower trace) to the major axis of BEDT-TTF molecules. The arrows show the laser frequencies used in the Raman measurements.

ly asymmetric environment surrounding the BEDT-TTF molecules¹⁰.

In addition, very weak features were detected at 774 cm^{-1} (b_{1u} C-S stretching¹⁷) and 1037 cm^{-1} (C-C-H bending totally symmetric vibration¹⁴) but not shown here due to the very poor signal to noise ratio. In the lower part of the spectrum three modes have been found (see Fig. 1). The best resolved and most intensive one is the 246 cm^{-1} band. The authors in Ref.19 report on the Raman spectrum of $(\text{BEDT-TTF})\text{Br}$ powder. Working at room temperature with the 514.5 nm exciting line they found a weak band at 256 cm^{-1} and they attribute it to a b_{2u} mode which becomes Raman active¹⁹. If we extend this assignment to our band at 246 cm^{-1} (see Fig. 1) we have to explain the relative high intensity of such antisymmetric mode in

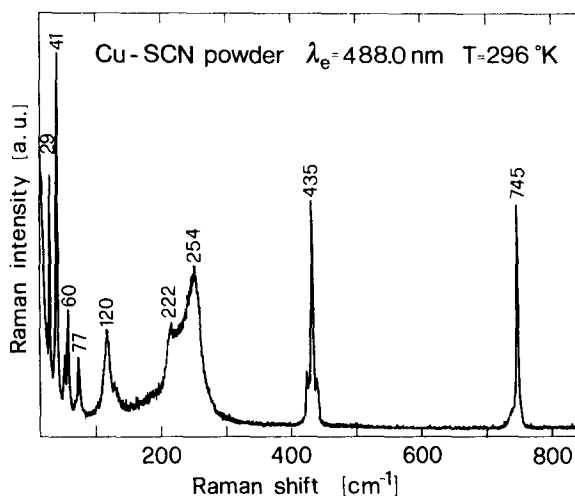


Fig.4: Raman Scattering on Cu-SCN powder. The Cu-SCN is a starting compound for the electrochemical synthesis of the $(\text{BEDT-TTF})_2\text{Cu}(\text{NCS})_2$ crystals.

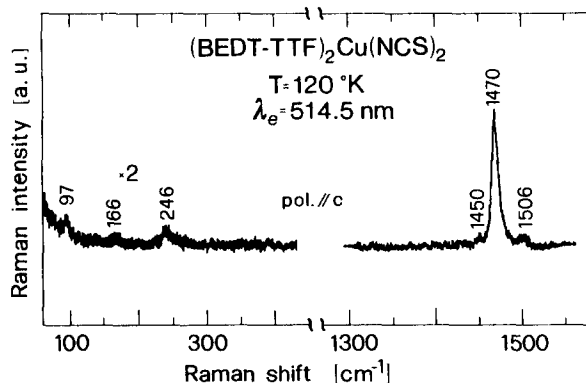


Fig.5: Resonant Raman Scattering at 120K on a single crystal of $(\text{BEDT-TTF})_2\text{Cu}(\text{NCS})_2$. The polarization of the laser beam is taken parallel to the major axis of the BEDT-TTF molecules

resonance Raman scattering conditions. A mechanism for antisymmetric vibrational scattering is the vibronic mixing of excited electronic states by vibrational modes. These modes gain Raman intensity via the Herzberg-Teller term. The Herzberg-Teller term may become dominant in resonance Raman scattering when a partially allowed transition is vibronically coupled to a nearby strongly allowed one^{20,21}. If this is the case the 246 cm⁻¹ band as well as the 1506 cm⁻¹ band are particularly active in the vibronic mixing. We also cannot exclude that the 246 cm⁻¹ band may be a totally symmetric vibration of the Cu-NCS group²³. In the Raman spectrum of the Cu-SCN powder (see Fig. 4) a broad band at 254 cm⁻¹ is seen, but presently we cannot assign this band.

The band at 166 cm⁻¹ (see Fig. 1) is assigned to a totally symmetric skeleton vibration along the major axis of the BEDT-TTF molecules. A similar weak band was found at 169 cm⁻¹ in (BEDT-TTF) Br and assigned to an a_g mode by the authors in Ref. 19. The band at 97 cm⁻¹ with the laser polarization along the c-axis and with the laser polarized perpendicular to the c-axis (see Fig. 1) could be a lattice vibration. Antiresonance conditions, and de-enhancement of Raman intensity could account for the low intensity

²². Nevertheless, the strong absorption in the region of the used laser wavelength of the (BEDT-TTF)₂ Cu(NCS)₂ (see Fig. 3) is certainly a reason for covering the Raman scattering intensity.

Fig. 5 shows the Raman spectrum at 120 K with the laser beam polarized along the major axis of the BEDT-TTF molecules. The frequency positions of the peaks are still the same as in the spectrum at 1.3 K. This means that, in our experimental conditions, (resolution 3 cm⁻¹), the Raman data do not show any evidence of the superconducting gap opening. Further theoretical and experimental investigations are necessary in order to account for the behaviour of the (BEDT-TTF)₂ Cu(NCS)₂. In particular from the point of view of Raman spectroscopy it would be very interesting to investigate the Raman scattering in resonance with the 11500 cm⁻¹ and 16000 cm⁻¹ intramolecular electronic excitations (see Fig. 3).

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