

## RAMAN INVESTIGATIONS ON SINGLE CRYSTALS AND POLYCRYSTALLINE PRESSED SAMPLES OF ORGANIC SUPERCONDUCTORS

R. ZAMBONI<sup>1</sup> and D. SCHWEITZER

Max-Planck-Institut für Medizinische Forschung, AG Molekülkristalle, Heidelberg, FRG

H. J. KELLER

Anorganisch-Chemisches Institut, Universität Heidelberg, FRG

### INTRODUCTION

The investigation of molecular vibrations is a powerful tool, which can increase our knowledge on structures and on electron molecular vibrations, which are due to charge oscillation between dimerized molecules, coupled with totally symmetric intramolecular modes<sup>(1-3)</sup>. Raman scattering studies account for totally symmetric vibrations. In addition, Raman spectroscopy can take advantage of resonant effects. In fact, when resonant conditions are fulfilled, selected molecular vibrations are obtained, as well as information on the electronic manifold involved in the resonance process.

In this paper, we report on Raman investigations of polycrystalline pressed materials of superconducting tempered  $\alpha$ -(BEDT-TTF)<sub>2</sub>I<sub>3</sub>, called, in the following,  $\alpha_t$ -(BEDT-TTF)<sub>2</sub>I<sub>3</sub>, and on untempered  $\alpha$ -(BEDT-TTF)<sub>2</sub>I<sub>3</sub>.

Furthermore we report on the polarized resonant Raman scattering in the superconducting regime of (BEDT-TTF)<sub>2</sub>Cu(NCS)<sub>2</sub> single crystals.

### EXPERIMENTAL

$\alpha$ -(BEDT-TTF)<sub>2</sub>I<sub>3</sub> crystals were grown in a THF-solution by electrochemical methods, as previously reported<sup>(4)</sup>. The samples for Raman investigations have been prepared by grinding single crystals, and by applying a pressure of 10<sup>4</sup> kg/cm<sup>2</sup> to the powder. The superconducting  $\alpha_t$ -(BEDT-TTF)<sub>2</sub>I<sub>3</sub><sup>(5)</sup> samples were obtained, by tempering the pressed  $\alpha$ -samples at 75 °C for several days.

Single crystals of (BEDT-TTF)<sub>2</sub>Cu(NCS)<sub>2</sub> have been obtained by electrochemical preparation<sup>(6)</sup>. The largest crystals obtained in this way (10x2x0.1 mm) have been selected and oriented in a patchwork of about 10 mm<sup>2</sup>. The Raman spectra have been carried out with the lines of an Ar<sup>+</sup> ion laser (Coherent Innova 90) in a 90° scattering configuration. The laser beam was filtered with a monochromator, and a proper interference filter, in order to prevent plasma lines.

The laser power was maintained below 10 mw in focused conditions for pressed pellets of  $\alpha_t$ -(BEDT-TTF)<sub>2</sub>I<sub>3</sub> and  $\alpha$ -(BEDT-TTF)<sub>2</sub>I<sub>3</sub>, but not completely focused on single crystals of (BEDT-TTF)<sub>2</sub>Cu(NCS)<sub>2</sub>, in order to avoid sample damage. For (BEDT-TTF)<sub>2</sub>I<sub>3</sub> materials, the conditions of a single Raman scan, with a resolution of the double monochromator of 0.5 cm<sup>-1</sup>, were sufficient for a good signal-to-noise ratio. For the (BEDT-TTF)<sub>2</sub>Cu(NCS)<sub>2</sub> ten spectra were accumulated, with a resolution of the monochromator of about 3 cm<sup>-1</sup>, in order to achieve an acceptable signal-to-noise ratio, and the Raman shift between 40 cm<sup>-1</sup> and 3500 cm<sup>-1</sup> has been investigated.

<sup>1</sup> On leave from Istituto di Spettroscopia Molecolare del C.N.R., Bologna, Italy

## RESULTS AND DISCUSSION

### The $(\text{BEDT-TTF})_2\text{Cu}(\text{NCS})_2$ single crystal.

The  $(\text{BEDT-TTF})_2\text{Cu}(\text{NCS})_2$  is up to now the ambient pressure organic superconductor with the highest critical temperature<sup>(7,8)</sup> ( $T_c = 10.4$  K).

In addition, this compound shows a nearly isotropic electrical and optical conductivity in the  $bc$  plane, and a very distinctive structure. The latter consists in a bidimensional sheet of dimerized (BEDT-TTF) molecules where one dimer is nearly orthogonal to the neighbouring ones<sup>(7)</sup>, and they do not form the usual face-to-face piling along the stacking axis. The  $\text{Cu}(\text{NCS})_2$  counter anion builds a sheet, where the copper coordinates with a sulfur atom and two nitrogen ones, to form a coordination polymer<sup>(7,10)</sup>.

Fig. 1 shows the polarized Raman scattering at 1.3K from the (100) crystal surface, with the laser beam polarized along the  $c$  axis, which is the long molecular axis of the  $(\text{BEDT-TTF})$ <sup>(7)</sup>.

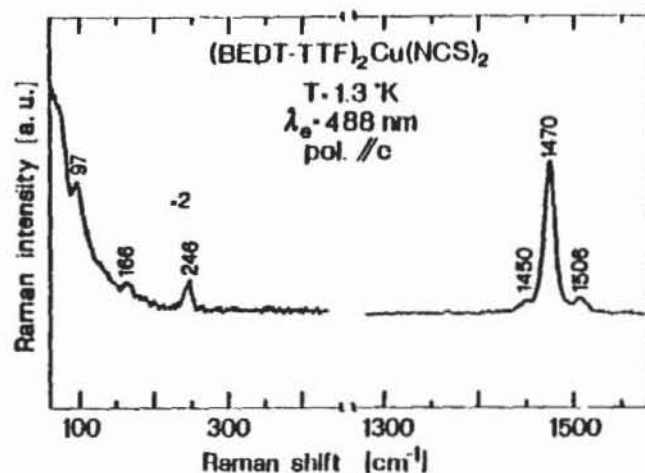


Fig. 1 Resonant Raman Scattering on single crystals of  $(\text{BEDT-TTF})_2\text{Cu}(\text{NCS})_2$ . The laser beam is polarized along the major axis of the  $(\text{BEDT-TTF})$  molecules.

The spectrum consists of a few bands of very low intensity. The most intense one is at  $1470 \text{ cm}^{-1}$ . In fig. 2 we show details of this range, varying the polarization of the laser beam.

As we can see, the  $1470 \text{ cm}^{-1}$  band totally disappears, and a band at  $1492 \text{ cm}^{-1}$  appears, when the beam polarization rotates perpendicular to the long molecular axis of the  $(\text{BEDT-TTF})$ . We can assign the  $1470 \text{ cm}^{-1}$  band to the totally symmetric  $\text{C}=\text{C}$  stretching vibration of the central carbons, and the  $1492 \text{ cm}^{-1}$  band to the  $\text{C}=\text{C}$  symmetric stretching vibration of the ring.

Note the consistency of the Raman data as a function of beam polarization; in fact, at  $45^\circ$  with respect to the major axis of the  $(\text{BEDT-TTF})$  the intensity of the  $1470 \text{ cm}^{-1}$  is nearly one half.

The relatively high intensity of the band at  $1470 \text{ cm}^{-1}$  is due to a strong coupling of this vibration to the electronic transition at  $20000 \text{ cm}^{-1}$  (see Fig. 3) because, in this resonance Raman experiment we excite at about  $20500 \text{ cm}^{-1}$  ( $488 \text{ nm}$ ). This electronic transition is probably a bonding-antibonding one, which is mainly localized on the rigid and planar TTF fragment of the  $(\text{BEDT-TTF})$  molecule. The weak bands, at  $1450 \text{ cm}^{-1}$  and  $1506 \text{ cm}^{-1}$ , are certainly connected with  $\text{C}=\text{C}$  vibrations, as results from IR and Raman scattering on deuterated samples of  $(\text{BEDT-TTF})$  neutral molecules and  $\alpha$ - $(\text{BEDT-TTF})_2\text{I}_3$  crystals<sup>(10-12)</sup>.

The authors in ref. (11) found a band at  $1511 \text{ cm}^{-1}$  in the Raman spectrum of the neutral  $(\text{BEDT-TTF})$ , and assigned this band to an antisymmetric  $b_{1u}$  vibration of the ring  $\text{C}=\text{C}$  stretching, which is allowed in Raman by departure from molecular symmetry. In our data, we found a band at  $1506 \text{ cm}^{-1}$  in both beam polarizations. This finding could support the previous assignment, as well as the strong asymmetric environment surrounding of the  $\text{BEDT-TTF}$  molecules<sup>(7)</sup>.

In addition, we found very weak features at  $774\text{ cm}^{-1}$  ( $b_{1u}$  C-S stretching<sup>(11)</sup>) and  $1037\text{ cm}^{-1}$  (C-C-H bending totally symmetric vibration<sup>(3)</sup>). The signal-to-noise ratio of these bands is very poor. The most resolved and intense band, in the lower part of the spectrum, is the one at  $246\text{ cm}^{-1}$ . Authors<sup>(12)</sup> reported on Raman scattering at room temperature with the  $514.5\text{ nm}$  line, on (BEDT-TTF) Br powder, and they found a weak band at  $256\text{ cm}^{-1}$ , which was attributed to a  $b_{2u}$  mode that became Raman-active.

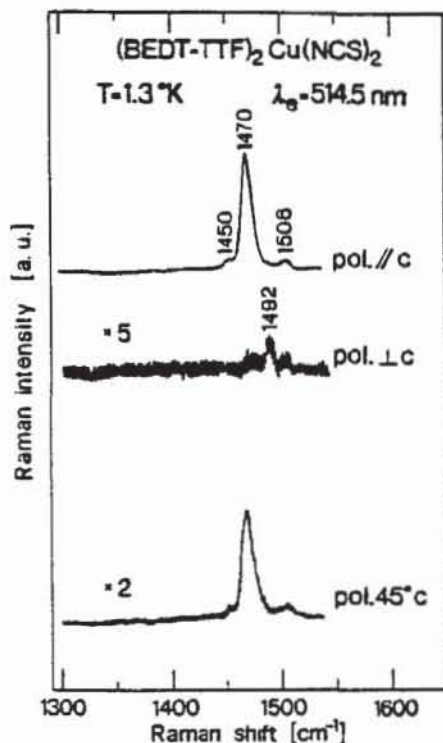


Fig. 2. Resonant Raman Scattering on a single crystal of  $(\text{BEDT-TTF})_2\text{Cu}(\text{NCS})_2$  in the C=C stretching frequency range with different laser beam polarization.

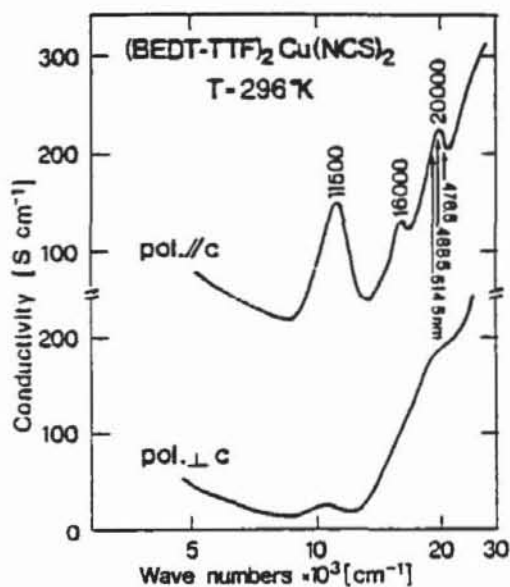


Fig. 3. Optical conductivity of a single crystal of  $(\text{BEDT-TTF})_2\text{Cu}(\text{NCS})_2$ . The polarization is taken parallel and perpendicular to the major axis of (BEDT-TTF) molecules.

In order to extend this attribution to our polarized  $246\text{ cm}^{-1}$  band (see fig. 1) we would have to explain the relative high intensity of an antisymmetric mode in resonance Raman scattering conditions. Antisymmetric vibrational scattering may be activated by a mixing of excited electronic states with vibrational modes. These modes can gain Raman intensity via a Herzberg-Teller term, which can become dominant in resonance with a partially allowed transition, vibronically coupled to a nearby strongly allowed one<sup>(13,14)</sup>. If this is the case, the  $246\text{ cm}^{-1}$  and the  $1506\text{ cm}^{-1}$  bands are particularly active in the vibronic mixing. The band at  $166\text{ cm}^{-1}$  (see fig. 1) is assigned to a totally symmetric skeleton vibration<sup>(12)</sup> along the major axis of the BEDT-TTF molecules. The  $97\text{ cm}^{-1}$  band could be a lattice mode.

Nevertheless, the Raman scattering intensity of this material is very low. Antiresonance conditions, and de-enhancement of Raman intensity could account for this low intensity<sup>(15)</sup> but, as we can see in fig. 3, the strong absorption of the  $(\text{BEDT-TTF})_2\text{Cu}(\text{NCS})_2$  is certainly a reason for covering the Raman scattering intensity. In addition we cannot exclude a totally symmetric Cu-NCS vibration for the  $246\text{ cm}^{-1}$  band<sup>(16)</sup>.

#### $\alpha_1$ - $(\text{BEDT-TTF})_2\text{I}_3$ and $\alpha_2$ - $(\text{BEDT-TTF})_2\text{I}_3$ polycrystalline pressed materials.

The superconductivity in organic materials is very sensitive to any kind of disorder, or structural changes. Recently resonant Raman spectra on single crystals of  $\alpha_1$ - and  $\alpha_2$ -phases of  $(\text{BEDT-TTF})_2\text{I}_3$  have been reported<sup>(17-19)</sup>. Resonance conditions with the  $\sigma_g \rightarrow \sigma_u$  electronic transition of the  $\text{I}_3^-$  anion are fulfilled with the usual lines of the  $\text{Ar}^+$ -ion laser, and a typical resonant Franck-Condon-like Raman scattering has been recorded<sup>(18,19)</sup>.

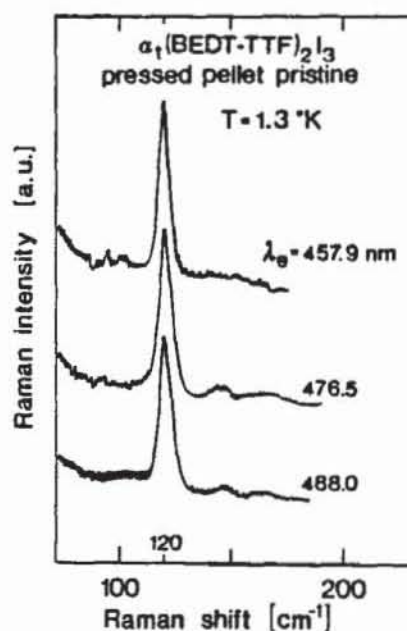


Fig. 4. Resonant Raman Scattering on the tempered polycrystalline pressed pellet of  $\alpha_1$ - $(\text{BEDT-TTF})_2\text{I}_3$  with different laser frequencies.

In particular, the most intense vibrational mode, coupled with the  $\sigma_g \rightarrow \sigma_u$  electronic transition, is the symmetric stretching vibration of the  $\text{I}_3^-$ . Nevertheless, the recent discovery of bulk superconductivity at ambient pressure in polycrystalline pressed samples<sup>(5)</sup> stimulates the Raman investigation on polycrystalline pressed materials.

Fig. 4 shows the Raman scattering at 1.3K on pressed pellets of  $\alpha_1$ - $(\text{BEDT-TTF})_2\text{I}_3$ , prepared as reported in the experimental section. The intense mode at  $120\text{ cm}^{-1}$  is assigned to the linear  $\text{I}_3^-$  sym-

metric stretching. It remains structureless, and in the same frequency position, varying the laser frequency and the sample temperature up to room temperature.

Fig. 5a shows the Raman scattering at 1.3K on pressed pellets of non superconducting  $\alpha$ -(BEDT-TTF) $_2$ I $_3$ . The I $_3^-$  stretching vibration shows a peak at 110 cm $^{-1}$  and a shoulder at 120 cm $^{-1}$ ; when working with the 514.5 nm line. The shoulder at 120 cm $^{-1}$  becomes dominant by varying the laser frequency from 514.5 nm to 413.5 nm. A similar behaviour is obtained by working with the laser frequency at 514.5 nm, and varying the sample temperature (see fig. 5b). This splitting observed here is, probably, due to a partial departure from linearity of the I $_3^-$  anion, which causes a splitting of the symmetric mode <sup>(18)</sup>. The drastic change in relative intensity between the two modes varying the laser frequency, as well as changing the sample temperature, is due to the tuning inside the electronic manifold of the I $_3^-$  anion.

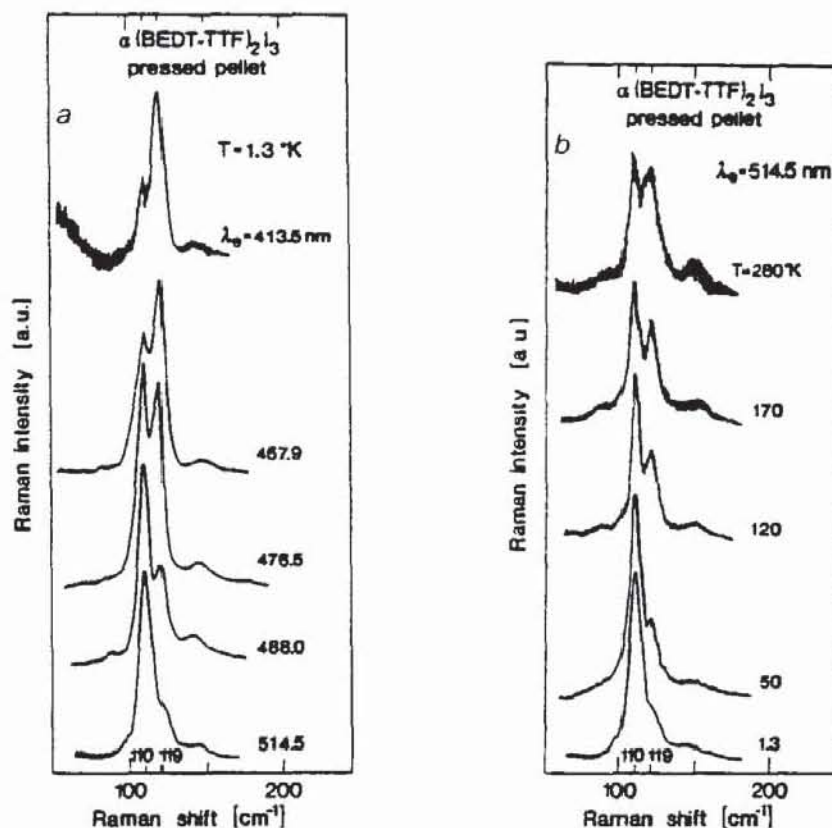


Fig. 5 a) Resonant Raman Scattering on the untempered polycrystalline pressed pellet of  $\alpha$ -(BEDT-TTF) $_2$ I $_3$  with different laser frequencies at 1.3K

b) Resonant Raman Scattering on the untempered polycrystalline pressed pellet of  $\alpha$ -(BEDT-TTF) $_2$ I $_3$  at a fixed laser frequency, varying the sample temperature.

If this is the case, in the  $\alpha$ -phase of (BEDT-TTF) $_2$ I $_3$  the superconductivity could be correlated with the linearity of I $_3^-$  anion, that means with the order in the system. In fact, in the superconducting  $\alpha$ -(BEDT-TTF) $_2$ I $_3$ , the I $_3^-$  shows only one, symmetric stretching mode (see fig. 4). Nevertheless, the grinding and pressure process, during the preparation of the pellets, could cause strains in the material, and different atomic charge distributions resulting in non-linear and asymmetric anions.

In fig. 6 the Raman spectrum of a  $\alpha$ -(BEDT-TTF) $_2$ I $_3$  sample shows such a splitting of the I $_3^-$  anion. In this case, the surface of the tempered pellet has been polished with a razor blade. The appearance of the splitting of I $_3^-$  anion means that the pressure, applied on the surface of the pellet by the razor blade, is sufficient to recreate the conditions of the untempered material, as well as to destroy the superconducting transition <sup>(5)</sup>.

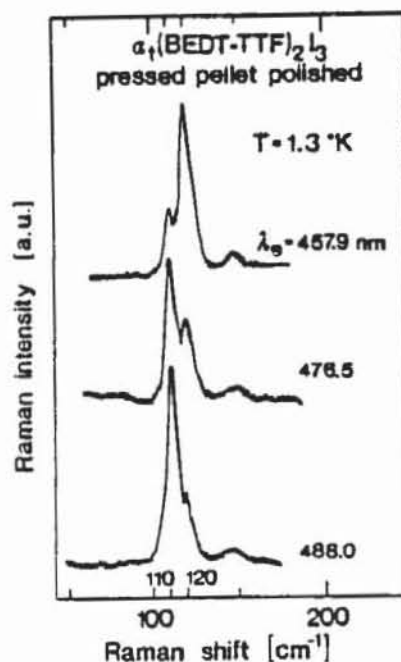


Fig. 6. Resonant Raman Scattering on the tempered pressed pellet of  $\alpha$ -(BEDT-TTF) $_2$ I $_3$  with different laser frequencies at 1.3K. The surface of the pellet was polished with a razor blade.

#### ACKNOWLEDGMENTS

We thank profs. C. Taliani, R. Tubino and dr. G. Ruani for useful discussions. We gratefully acknowledge the financial support of the European Economic Community (contract ST2J-0315-C)

#### REFERENCES

1. M. J. Rice, *Phys. Rev. Lett.*, 37:36 (1976).
2. M. J. Rice, N. O. Lipari and S. Strassler, *Phys. Rev. Lett.*, 39:1359 (1977).
3. M. Meneghetti, R. Bozio and C. Pecile, *J. de Physique*, 47:1377 (1986).
4. K. Bender, I. Henning, D. Schweitzer, K. Dietz, H. Endres and H. J. Keller, *Mol. Cryst. Liq. Cryst.*, 108:359 (1984).
5. D. Schweitzer, S. Gärtner, H. Grimm, E. Gogu and H. J. Keller, *Sol. St. Comm.*, 69:843 (1989).
6. D. Schweitzer, K. Polychroniadis, T. Klutz, H. J. Keller, I. Henning, I. Heinen, U. Haerberlen, E. Gogu and S. Gärtner, *Synth. Met.*, 27:A465 (1988).
7. H. Urayama, H. Yamuchi, G. Saito, S. Sato, A. Kawamoto, J. Tanaka, T. Mori, Y. Maruyama and H. Inokuchi, *Chem. Lett.*, 463 (1988).
8. S. Gärtner, E. Gogu, I. Heinen, H. J. Keller, T. Klutz and D. Schweitzer, *Sol. St. Comm.* 65:1531 (1988)
9. T. Sugano, H. Hayashi, H. Takenouchi, K. Nishikida, H. Urayama, H. Yamochi, G. Saito and M. Kinoshita, *Phys. Rev.*, B37:9100 (1988).
10. R. Zamboni, D. Schweitzer, H. J. Keller and C. Taliani, *Z. Naturforsch.*, 44a:429 (1989).
11. M. E. Kozlov, K. I. Pokhodnjia and A. A. Yurchenko, *Spectrochim. Acta*, 43A:323 (1987).
12. M. E. Kozlov, K. I. Pokhodnjia and A. A. Yurchenko, *Spectrochim. Acta*, in press.
13. T. G. Spiro and P. Stein, *Ann. Rev. Phys. Chem.*, 28:501 (1977).
14. A. R. Gregory, W. H. Henneker, W. Siebrand and M. Z. Zgierski, *J. Chem. Phys.*, 63:5475 (1975).
15. T. Stein, V. Miskowski, W. H. Woodruff, J. P. Griffin, K. G. Weiner, B. P. Gaber and T. G. Spiro, *J. Chem. Phys.*, 64:215 (1976).
16. Y. M. Bosworth, R. J. H. Clark and P. C. Turtle, *J.C.S. Dalton*, 2027 (1975).
17. D. Schweitzer, E. Gogu, I. Henning, T. Klutz and H. J. Keller, *Ber. Bunsenges. Phys. Chem.*, 91:890 (1987).
18. R. Swietlik, D. Schweitzer and H. J. Keller, *Phys. Rev.*, B36:6881 (1987).
19. S. Sugai and G. Saito, *Sol. St. Comm.*, 58:759 (1986).