

THE INFRARED OPTICAL PROPERTIES OF THE  $\alpha$ -PHASE ORGANIC SUPERCONDUCTOR,  $\alpha - (BEDT - TTF)_2(NH_4)Hg(NCS)_4$

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ABSTRACT

The title compound is the only known organic superconductor ( $T_c = 0.8$  K) with an  $\alpha$ -phase crystal structure, in which the conducting plane contains single *BEDT-TTF* molecules with alternating orientation, rather than the pairs of molecules found in the higher  $T_c$   $\kappa$ -phase compounds. We have measured the polarized reflectivity of protonated and deuterated  $(BEDT-TTF)_2(NH_4)Hg(NCS)_4$ , from  $80\text{ cm}^{-1}$  to  $8000\text{ cm}^{-1}$ , at temperatures between 6.5 K and 300 K. The overall shape of these spectra are discussed. The optical conductivity obtained after a Kramers-Kronig analysis shows no maximum in the mid-infrared as known from the compounds of the  $\kappa$ -phase due to the lack of dimerization of the *BEDT-TTF* molecules. This causes an accentuation of the far-infrared intraband conductivity. The vibrational features are assigned and discussed.

INTRODUCTION

Even if the first popular *BEDT-TTF* (*bis*-(ethylenedithio) tetrathiafulvalene) radical ion salt was  $\alpha - (BEDT - TTF)_2I_3$  [1], no superconductivity in an  $\alpha$ -phase crystal of this family was found. Various efforts to observe ambient pressure superconductivity in an  $\alpha$ -phase *BEDT-TTF* salt like  $\alpha - (BEDT - TTF)_2I_3$  or related components  $\alpha - (BEDT - TTF)_2AuI_2$  have failed: Doping of  $\alpha - (BEDT - TTF)_2I_3$  with iodine does not cause a partial suppression of the metal-insulator transition at 135 K and superconducting behaviour at  $T \leq 3$  K as reported [2], but only gives a slight rise of the high-frequency conductivity in the insulating phase after extreme doping of several hours [3]. Tempering of  $\alpha - (BEDT - TTF)_2I_3$  at  $75^\circ\text{C}$  for several days leads to a superconducting crystal ( $T_c = 8$  K), but the structure has changed to  $\alpha_1$ , which is similar to the  $\beta$ -phase, both crystallographically and in its physical behaviour [4].

The relatively high transition temperatures of  $\kappa - (BEDT - TTF)_2Cu(NCS)_2$  ( $T_c = 10.4$  K),  $(BEDT - TTF)_2Cu[N(CN)_2]Br$  ( $T_c = 11.6$  K) and  $(BEDT - TTF)_2Cu[N(CN)_2]Cl$  ( $T_c = 12.8$  K) have been obtained by increasing the size of the polymeric anion acceptors. Similarly, by extending the two component system to a three-component system (donor; anion + cation = acceptor), the first ambient-pressure superconductor in the  $\alpha$ -modification was found,  $\alpha - (BEDT - TTF)_2(NH_4)Hg(NCS)_4$  with  $T_c = 0.8$  K [5, 6, 7].  $(BEDT - TTF)_2(NH_4)Hg(NCS)_4$  crystallizes with the flat face parallel to the highly-conducting *ab*-plane. The *BEDT-TTF* molecules form stacks of two kinds along the *a* direction [5, 6]. The material has a very high metallic conductivity, rising from between  $100$  and  $400\ (\Omega\text{cm})^{-1}$  at room temperature to a value 100 times greater at  $4.3$  K [7].

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## EXPERIMENTAL

Using a Bruker IFS 113V Fourier spectrometer [8] the absolute reflectivity from a deuterated  $\alpha$ -(BEDT-TTF)<sub>2</sub>(NH<sub>4</sub>)Hg(NCS)<sub>4</sub> crystal was measured from 80 cm<sup>-1</sup> (300 K) and 250 cm<sup>-1</sup> ( $T < 300$  K) to 8000 cm<sup>-1</sup>. The spectra were recorded at 300 K, 200 K, 100 K, 50 K and 6.5 K

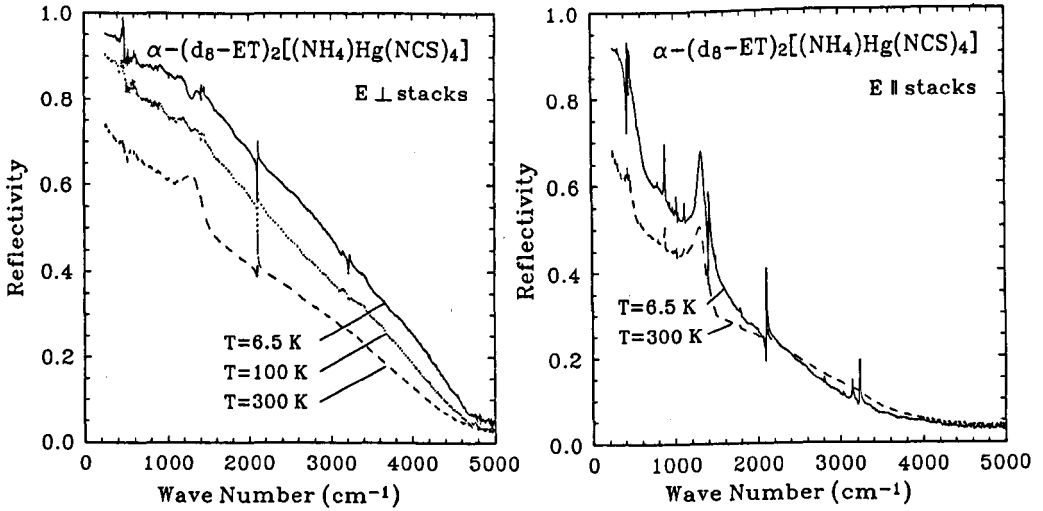


Figure 1: The reflectivity of deuterated  $(BEDT-TTF)_2(NH_4)Hg(NCS)_4$  at different temperatures for  $\vec{E} \parallel b$  and  $\vec{E} \parallel a$

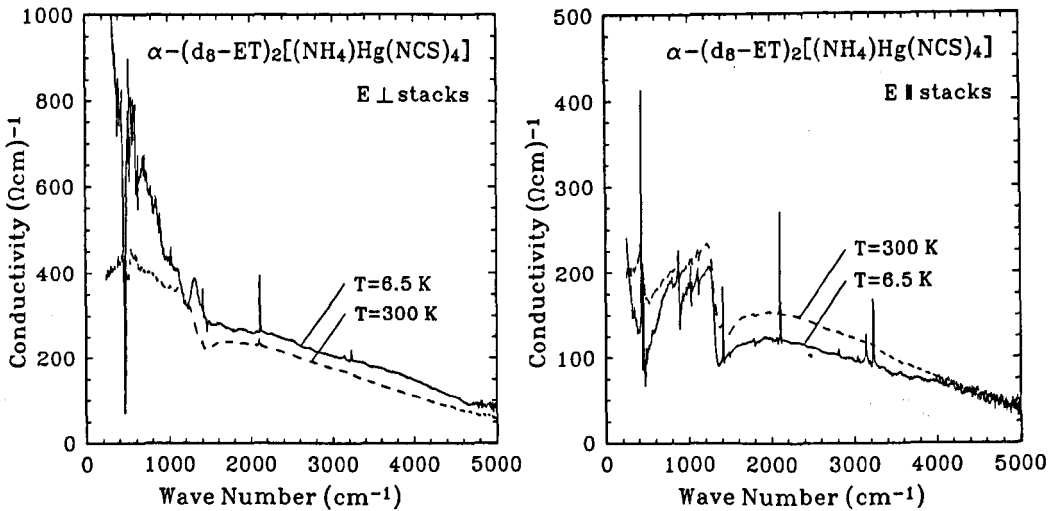


Figure 2: The conductivity of deuterated  $(BEDT-TTF)_2(NH_4)Hg(NCS)_4$  at two different temperatures for  $\vec{E} \parallel b$  and  $\vec{E} \parallel a$

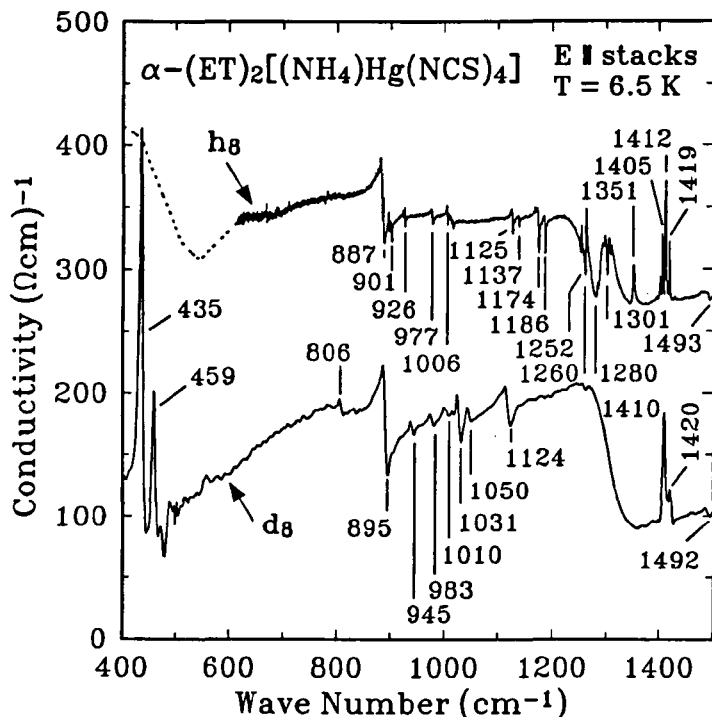


Figure 3: An expanded portion of the low-temperature conductivity spectrum of the protonated compound (upper trace, which has been displaced by  $200 (\Omega\text{cm})^{-1}$  for clarity) and of the deuterated compound (lower trace, corresponding to the ordinate scale). The upper trace below  $600 \text{ cm}^{-1}$  was very noisy due to the small crystal size. The resolution is  $0.5 \text{ cm}^{-1}$  ( $h_8$ ) and  $1.0 \text{ cm}^{-1}$  ( $d_8$ ).

for both polarization, parallel to the molecular stacks and perpendicular to the stacks. The spectra of the protonated sample were used only for vibrational assignments. Details of the experimental technique have been previously published [9, 10, 11].

## RESULTS AND DISCUSSION

Figure 1 shows the reflectivity up to  $5000 \text{ cm}^{-1}$  for  $\vec{E} \parallel b$  (perpendicular to the stacks) and  $\vec{E} \parallel a$  at the indicated temperatures. The conductivity obtained after a Kramer-Kronig analysis is displayed in Figure 2. In agreement with the spectra reported for  $\alpha\text{-(BEDT-TTF)}_2\text{I}_3$  [12] the conductivity perpendicular to the BEDT-TTF molecular stacks is greater than that parallel to the stacks. The overall shapes of the conductivity differ from those of  $\alpha\text{-(BEDT-TTF)}_2\text{I}_3$  mainly because of the much higher d.c. conductivity to which our infrared conductivities extrapolate. In our studies [9, 10, 13, 14] of the infrared optical properties of the three  $\kappa$ -phase superconductors  $(\text{BEDT-TTF})_2\text{Cu}(\text{NCS})_2$ ,  $(\text{BEDT-TTF})_2\text{Cu}[\text{N}(\text{CN})_2\text{Cl}]$  and  $(\text{BEDT-TTF})_2\text{Cu}[\text{N}(\text{CN})_2\text{Br}]$  a broad peak was observed in the mid-infrared near  $2200 \text{ cm}^{-1}$  for one polarization and between  $3000$  and  $4000 \text{ cm}^{-1}$  for the other. It was correlated with vertical interband transitions between occupied and unoccupied bands throughout the Brillouin zone. No such maximum is seen in Fig. 2.

Referring to calculations performed by Tajima et al. [15, 16, 17], the strength of the interband transitions which correlate with the mid-infrared conductivity depends strongly on the dimerization of the BEDT-TTF molecules. It would appear, therefore, that the accentuation of the far-infrared interband conductivity follows from the sum rule and is at the expense of the interband conductivity which has decreased due to the lack of dimers in the  $\vec{E}$  perpendicular to the stacks polarization.

The low-temperature,  $E$ -perpendicular-to-the-stacks conductivity can be fitted to two functions, namely a Drude response in the far-infrared ( $\omega_p = 7000 \text{ cm}^{-1}$  and  $\gamma = 700 \text{ cm}^{-1}$ ), combined with a heavily-damped oscillator to represent the broad mid-infrared strength [11]. With this value of  $\omega_p$  and assuming 2 holes from 4  $BEDT-TTF$  molecules per unit cell ( $V = 2008 \text{ \AA}^3$ ), one obtains an effective mass of  $1.8 m_e$ , which is in good agreement with magnetic measurements ( $2.1 m_e$ ) [18].

Figure 3 shows the detailed high-resolution vibrational spectra between  $400 \text{ cm}^{-1}$  and  $1500 \text{ cm}^{-1}$  of both the protonated and the deuterated compounds for  $\vec{E} \parallel a$ . A list of the vibrational assignments is published elsewhere [11]. The phonon feature which dominates the spectra of most  $BEDT-TTF$  salts is the vibrationally-activated, totally-symmetric  $\nu_3(a_g)$  internal mode of the  $BEDT-TTF$  radical cation involving the central  $C = C$  bond. In Fig. 3, however, this mode has become a broad shoulder extending from  $1200 \text{ cm}^{-1}$  to  $1350 \text{ cm}^{-1}$ , which is clearly a result of the absence of strong dimers in the  $\alpha$ -phase. On the other hand, the strongest feature, at  $435 \text{ cm}^{-1}$  in the deuterated spectrum of Fig. 3, along with the  $459 \text{ cm}^{-1}$  companion, is still either  $\nu_9(a_g)$  and/or  $\nu_{10}(a_g)$ . They occur at the same frequency as in the  $\kappa$ -phase compounds [9, 10, 13].

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