

INVESTIGATION OF α - AND β -(BEDT-TTF)₂I₃ BY ELECTRON ENERGY-LOSS SPECTROSCOPY

N. NÜCKER and J. FINK

Kernforschungszentrum Karlsruhe, Institut für Nukleare Festkörperphysik, P.O.B. 3640,
D-7500 Karlsruhe, Federal Republic of Germany

D. SCHWEITZER

Max-Planck-Institut für Med. Forschung, Abteilung für Molekulare Physik, Jahnstr. 29,
D-6900 Heidelberg, Federal Republic of Germany

H.J. KELLER

Anorganisch-Chemisches Institut der Universität Heidelberg, Im Neuenheimer Feld 270,
D-6900 Heidelberg, Federal Republic of Germany

The anisotropic electronic structure of the α - and β -phase of (BEDT-TTF)₂I₃ was investigated by electron energy-loss spectroscopy.

1. INTRODUCTION

Recently, molecular metals based on the donor bisethylenedithio-tetrafulvalene (BEDT-TTF) have attracted considerable interest because of the quasi-two-dimensional properties and the ambient-pressure superconductivity. In particular, for the β -phase of (BEDT-TTF)₂I₃ superconducting transition temperatures up to 8.1 K were reported³. The electronic structure of (BEDT-TTF)₂I₃ has been studied by several optical studies.³⁻⁶ In this contribution we have investigated the anisotropic electronic structure of the α - and β -phase of (BEDT-TTF)₂I₃ by electron energy-loss spectroscopy (EELS)

2. EXPERIMENTAL

Single crystals of α - and β -(BEDT-TTF)₂I₃ have been prepared by electrochemical methods⁷. For EELS, thin films having a thickness of about 1000 Å were cut by an ultramicrotome from the crystals and mounted on electron microscopy grids. Transmission EELS spectra were taken with a 170-keV spectrometer.⁸

3. RESULTS AND DISCUSSION

3.1 Valence band excitations

In Fig. 1 we show loss spectra of α - and β -(BEDT-TTF)₂I₃ for momentum transfer \vec{q} in the a-b plane parallel and perpendicular to the stack axis. For comparison we also show a loss spectrum of a thin film composed of BEDT-TTF. For all spectra a momentum transfer $q=0.1 \text{ \AA}^{-1}$ was chosen which is small compared with the dimension of the Brillouin-zone. Therefore, these measurements can be directly compared with optical data. Pure BEDT-TTF has a gap of about 2.8 eV and molecular orbital transitions at 3.2, 4 and 5.6 eV. The same transitions occur in the α - and in the β -phase of (BEDT-TTF)₂I₃. The reason for the different intensities of these transitions is the different direction of \vec{q} relative to the orientation of the BEDT-TTF molecules. Maxima below 2.8 eV are caused by the charge extraction from the highest occupied π band. Well pronounced plasmons appear near 0.6 eV parallel to the stacks, while perpendicular to the chains, broader peaks appear near 0.3 eV. The latter peaks can hardly be resolved with our best energy resolution of 0.08 eV from

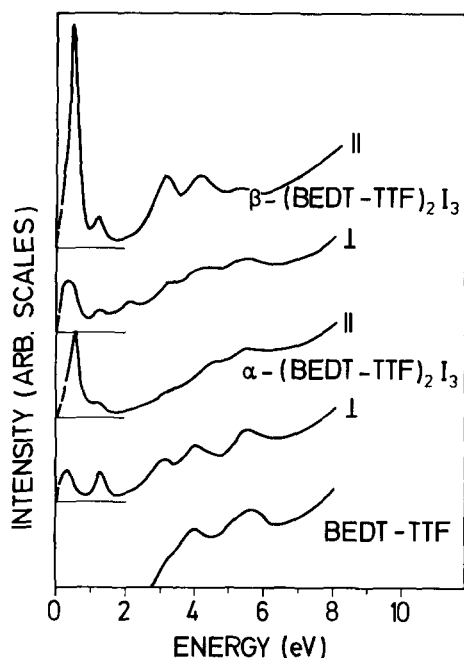


FIGURE 1

Electron energy-loss spectra of α - and β - $(\text{BEDT-TTF})_2\text{I}_3$ parallel and perpendicular to the stack axis and of unoriented BEDT-TTF

the quasi-elastic intensity at zero energy. These maxima in the loss function correspond to the plasma edges observed in the infrared reflectance data.³⁻⁶ Additional maxima appear near 1.2 eV and at 2.2 eV (for β - $(\text{BEDT-TTF})_2\text{I}_3$ perpendicular to the stack axis). In most of the previous optical studies, the low energy part was analyzed by a Drude model. In the framework of this model the first maximum in the loss function is assigned to a free-carrier plasmon. More information on the nature of this maximum can be obtained from momentum dependent measurements. The q -dependence of the plasmon for β - $(\text{BEDT-TTF})_2\text{I}_3$ parallel to the stack axis is shown in Fig. 2. For a free-carrier plasmon a dispersion is expected which is *quadratic* in q .

In the experiment, a *linear* dispersion is observed for $q \lesssim 0.3 \text{ \AA}^{-1}$. Moreover, the nega-

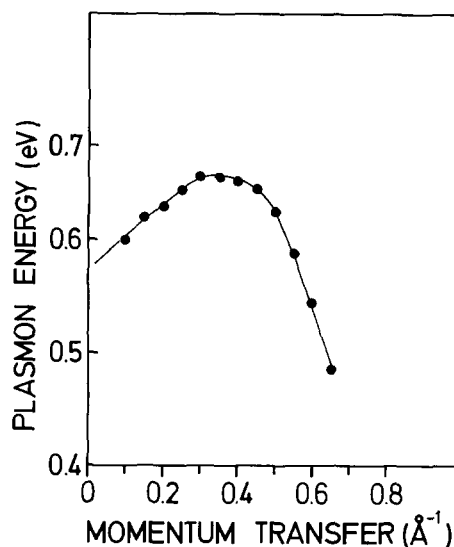


FIGURE 2

Dispersion of the π -plasmon of β - $(\text{BEDT-TTF})_2\text{I}_3$ with \vec{q} parallel to the stack axis.

tive dispersion of the π plasmon above $q > 0.4 \text{ \AA}^{-1}$ is inconsistent with an interpretation of this maximum by a free-carrier plasmon. Therefore, we think, that the plasmon is caused not by intraband transitions but by interband transitions. This interband transition is coupled with intraband transitions, giving rise to a zero crossing in ϵ_1 just below the oscillator and causing therefore the maximum in the loss-function $\text{Im}(-1/\epsilon)$. A similar non-Drude like explanation was already given for reflectance data by Tajima et al.⁴ According to the band structure calculations by Mori et al.⁹ the π -band is splitted into two bands since the unit cell contains two BEDT-TTF molecules. For $q=0$, the interband transition occurs dominantly from the lower band to the unoccupied part of the half filled higher band around the Fermi surface. With increasing q , i.e., going to non-vertical transition, parts of the upper band near the Γ point can be reached which are higher in energy. Thus a positive dispersion

should occur which is observed in the experiment. At momentum transfers larger than the Fermi wave vector $k_F \sim 0.35 \text{ \AA}^{-1}$, again parts of the upper band are reached by the interband transitions which are lower in energy. This is again in agreement with experiment. In a first approximation the dispersion shown in Fig. 2 reflects the band structure of the unoccupied part of the upper band. The width of this unoccupied part of the band can then be derived to be about 0.1 eV.

3.2 Core-level excitations

In Fig. 3 we show first measurements on carbon K edges which should in principle give information on the density of unoccupied

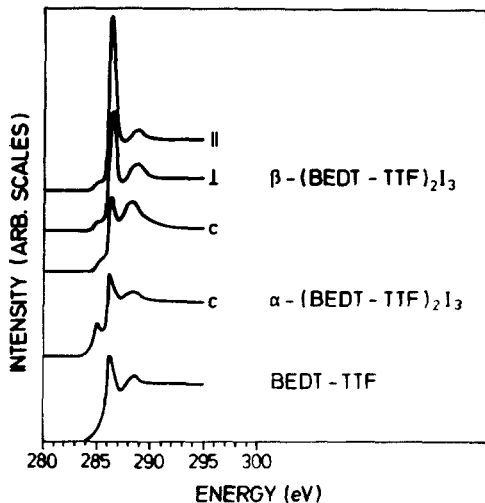


FIGURE 3
Carbon K edges of BEDT-TTF crystals. ||, ⊥ and c denotes q parallel to the stack axis, perpendicular to the stack axis in the a-b plane and perpendicular to the a-b plane, respectively.

states. Maxima appear at 285, 286 and 288.5 eV. From EELS measurements on other conjugated molecules and polymers we know, that the line near 285 eV can be assigned to a π^* orbital associated to a C-C bond. From the orientation dependence of the transition in β -(BEDT-TTF) $_2$ I $_3$, we conclude that the transition near 286 eV can be assigned to a π^* orbital associated to a C-S bond. Probably, transitions at higher energies correspond to transitions into unoccupied σ^* levels.

REFERENCES

1. E.B. Yagubskii, J.F. Shchegolev, V.N. Laukhin, P.A. Kononovich, M.V. Kartsovnik, A.V. Zvarykina, and L.I. Buravov, *Pis'ma Zh. Eksp. Teor. Fiz.*, 39 (1984) 12 [*JEPT Lett.* 39 (1984) 12]
2. F. Creuzet, G. Creuzet, J. Jérôme, D. Schweitzer, and H.J. Keller, *J. Physique Lett.*, 46 (1985) L-1079
3. B. Koch, H.P. Geserich, W. Ruppel, D. Schweitzer, K.H. Dietz, and H.J. Keller, *Mol. Cryst. Liq. Cryst.*, 119 (1985) 343
4. H. Tajima, K. Yakushi, H. Kuroda, and G. Saito, *Solid State Commun.*, 56 (1985) 159
5. M.G. Kaplunov, E.B. Yagubskii, L.P. Rosenberg, and Yu.G. Borodko, *phys. stat. sol. (a)*, 89 (1985) 509
6. C.S. Jacobsen, J.M. Williams, and Hau H. Wang, *Solid State Commun.* 54 (1985) 937
7. K. Bender, I. Hennig, D. Schweitzer, K. Dietz, H. Endres, and H.J. Keller, *Mol. Cryst. Liq. Cryst.* 108 (1984) 359
8. J. Fink, *Z. Phys. B*, 61 (1985) 463
9. T. Mori, A. Kobayashi, Y. Sasaki, H. Kobayashi, G. Saito, H. Inokuchi, *Chem. Letters* (1984) 957.