THE ELECTRICAL ANISOTROPY OF THE ORGANIC METALS $(BEDT-TTF)_3(ClO_4)_2$ AND $\alpha-(BEDT-TTF)_3(NO_3)_2$*

B. KOCH, H.P. GESERICH and W. RUPPEL

Institut für angewandte Physik, Universität Karlsruhe (F.R.G.)

D. SCHWEITZER

Max-Planck-Institut für medizinische Forschung, Heidelberg (F.R.G.)

H.J. KELLER

Anorganisch-Chemisches Institut, Universität Heidelberg (F.R.G.)

ABSTRACT

We report on the polarized reflectance spectra of the two-dimensional organic metals $(BEDT-TTF)_3(ClO_4)_2$ and $\alpha-(BEDT-TTF)_3(NO_3)_2$ in the energy range between 0.01 and 5 eV. In contrast to the results obtained on other conducting BEDT-TTF salts, these compounds show high metallic reflectance values at room temperature down to lower energies. In particular, the ClO_4-salts can be well described by a two-dimensional Lorentz-Drude model. On the basis of this model the transport parameters along the principal axes are evaluated for both compounds.

INTRODUCTION

From the several papers on the optical properties of highly conducting BEDT-TTF radical salts published so far [1-9], the metallic character of these compounds does not clearly emerge. Particularly, the hitherto reported reflectance spectra at room temperature and the resulting spectral distributions of the conductivity functions reveal drastic deviations from the free carrier absorption. Rather, broad absorption bands were found in the infrared region, indicating that the optical properties in this spectral region are mainly determined by molecular vibrations and interband transitions.

It is the aim of the present paper to search for two-dimensional organic compounds which show a clearly metallic behaviour of the

optical properties, as normally found in inorganic metallic compounds and in one-dimensional organic metals.

CRYSTALLOGRAPHIC AND ELECTRICAL DATA

Like other BEDT-TTF-salts, the investigated crystals consist of an alternating sequence of conducting layers of organic donor molecules and insulating layers of inorganic acceptor molecules. $(BEDT-TTF)_3(ClO_4)_2$ crystallizes in a triclinic lattice with $Z = 1$, whereas $\alpha-(BEDT-TTF)_3(NO_3)_2$ has a monoclinic unit cell, containing two formula units [10-13]. The plane of metallic conduction in the (ClO_4)-salt is parallel to the (001)-plane, and in the (NO_3)-salt parallel to the (010)-plane. The axis of the molecular stacks coincides in the (ClO_4)-salts with the $[1\bar{1}0]$ direction and lies in the (NO_3)-salt along the [100]-direction. The crystallographic data of both compounds are given in Table 1 and Table 2.

TABLE 1

Crystallographic data[a] of $(BEDT-TTF)_3(ClO_4)_2$

	a	b	c	α	β	τ	V
		(Å)					(Å)^3
(ClO_4)	7.613	9.498	16.463	95.91	87.17	90.84	1182

[a]from reference [10,12].

TABLE 2

Crystallographic data[a] of $(BEDT-TTF)_3(NO_3)_2$

	a	b	c	β	V
		(Å)			(Å)^3
$(NO_3)_2$	5.890	31.125	12.915	103.73	2300

[a]from reference [11,13].

Electrical measurements have shown that the (ClO_4)-compound undergoes a sharp metal semiconductor transition at 170 K [11], whereas the $(NO_3)_2$-compound remains metallic down to a few K [10].

OPTICAL RESULTS AND DISCUSSION

The polarized reflectance spectra were measured on the metallic planes. In the low-energy region between 0.01 and 0.05 eV a Fourier transform spectrometer, and at higher energies between 0.05 and 6 eV a single beam spectrometer, both adapted to tiny crystals, were used.
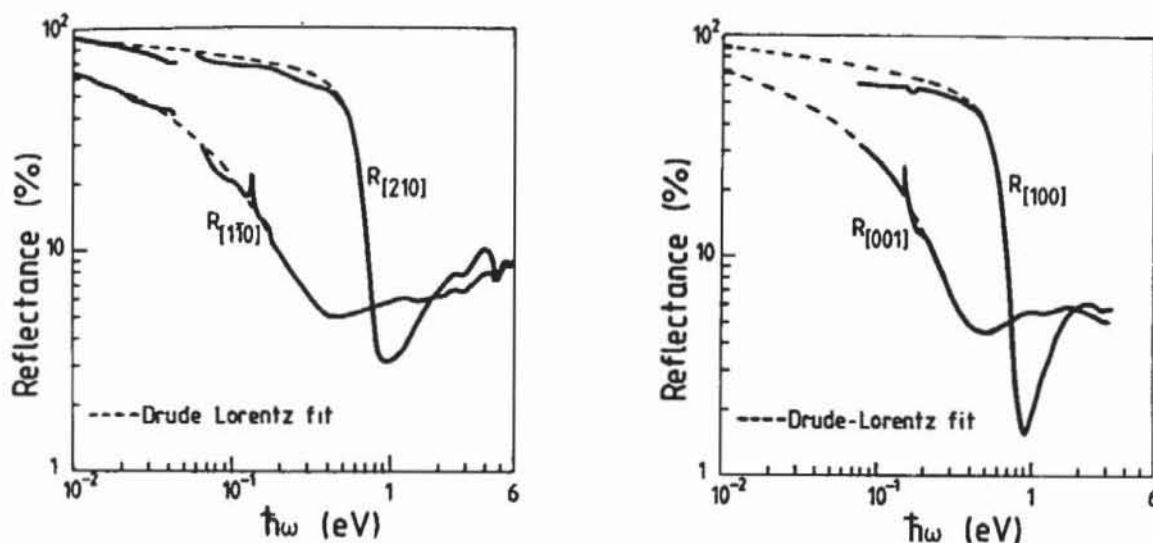
Fig.1. (left hand) and Fig.2 (right hand). Polarized reflectance spectra of $(BEDT-TTF)_3(ClO_4)_2$, (001)-plane, and of $(BEDT-TTF)_3(NO_3)_2$, (010)-plane. [210], [1̄10], [100], and [001] indicate the polarization direction.

The principle axes of the optical conductivity were determined carefully by taking the reflectance spectra using stepwise rotation of the polarizer. In Figs.1 and 2 the reflectance spectra, exhibiting the highest optical anisotropy, are plotted. As a common feature both compounds show a two-dimensional Drude-like behaviour at room temperature, manifesting itself not only in pronounced plasma edges but also in a monotonous increase of the reflectivity towards low energies.

In the (ClO_4)-salt this metallic reflectivity was demonstrated down to a photon energy of 0.01 eV. As shown in Fig.1, the reflectance spectra of this compound could be fitted by a two-dimensional Drude-Lorentz model. Also for the (NO_3)-salts, this model leads to a fairly good approximation of the experimental curves (Fig.2). The values of the transport parameters obtained from these fits are compiled in Table 3, and the resulting conductivity functions are shown in Figs.3 to 6. It can be seen that the direction of highest electrical conduction in the (ClO_4)-salt is perpendicular to the stack axis, showing that the best overlap between the organic molecules is side by side. This in good agreement with the results of band-structure calculations [11]. In contrast to these calculations, metallic behaviour is observed as well for the direction along the stack axis. Because of the high anisotropy of the effective mass, the Fermi surfaces of $(BEDT-TTF)_3(ClO_4)_2$ are, however, possibly not closed.

In the (NO_3)-salt the electrical anisotropy is opposite to the result obtained for the (ClO_4)-salt. The direction of the highest

TABLE 3

Drude parameters of $(BEDT-TTF)_3(ClO_4)_2$ and $(BEDT-TTF)_3(NO_3)_2$

		N $(10^{21}/cm^3)$	$h\omega_p$ (eV)	τ $(10^{-15}s)$	σ_{opt}	σ_{el}[a] $(\Omega^{-1}cm^{-1})$	m^*/m
(ClO_4)	[210]	1.69	.87	2.68	900	60-80	1.44
	[1$\bar{1}$0]		.35	1.29	60	20	10.6
(NO_3)	[100]	1.74	.73	2.40	650	100-800	1.81
	[001]		.35	1.60	45		17.8

[a] from reference [2.5]
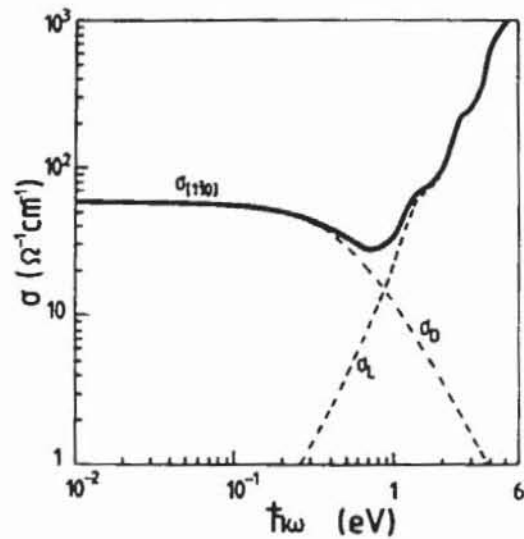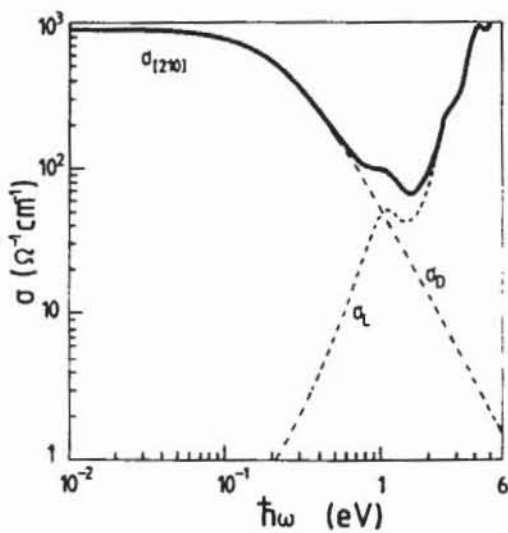
Fig.3 (left hand) and Fig.4 (right hand). Conductivity functions of $(BEDT-TTF)_3(ClO_4)_2$ obtained from Lorentz-Drude fit.
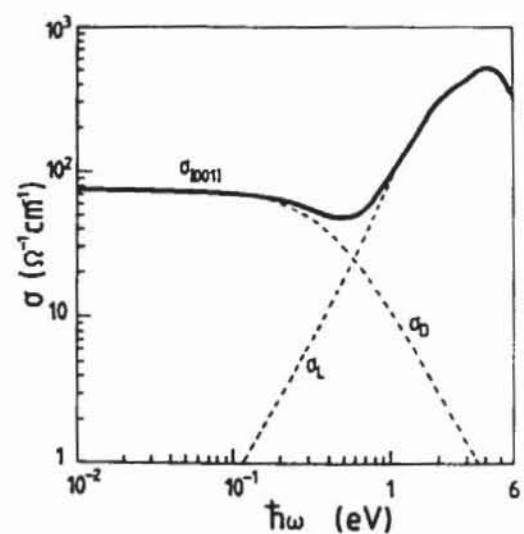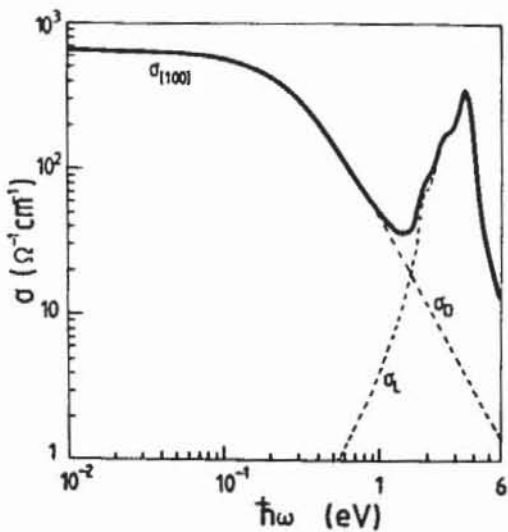
Fig.5 (left hand) and Fig.6 (right hand). Conductivity functions of $(BEDT-TTF)_3(NO_3)_2$ obtained from Lorentz-Drude fit.

electrical conductivity lies along the stack axis. The anisotropy of the effective mass $m^*_\perp/m^*_\parallel$ is about 10, a value somewhat higher than for the (ClO_4)-salt.

On both compounds preliminary investigations of the reflectivity at low temperature were performed. Within the energy range between 0.05 and 6 eV we could not detect the formation of an energy gap in the (ClO_4)-salt below the phase transition. This indicates that this gap has a value of at maximum about 0.05 eV. This upper limit is close to the value of 0.07 eV, determined from the activation energy of the dc-conductivity at low temperature [11]. It follows that the low temperature effects in both compounds consist within the investigated energy range mainly in steeper plasma edges.

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