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by

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Anisotropic behaviour of the electron energy loss spectra is discussed in terms of the oriented gas model. These measurements are compared with electron energy loss spectra in the vapour phase and normal incidence VUV-reflectivity from the (ab) plane for 2 directions of polarization. The VUV measurements were made at DESY using synchrotron radiation.

The main electronic excitations in the anthracene molecule up to the energy of 6 eV are $\pi - \pi^*$ - excitations of symmetry type $^1A_{1g} - {}^1B_{1u}$ (allowed for light polarized along the short axis M) and $^1A_{1g} - {}^1B_{2u}$ (allowed for light polarized along the long axis L) (References in[1]). Figure 1 shows the energy loss spectrum of 30 keV-electrons in anthracene vapour with a resolution in energy of 0.6 eV. The losses at 3.45 and 5.24 eV are due to the $^1A_{1g} - {}^1B_{1u}$ and $^1A_{1g} - {}^1B_{2u}$ transitions. The loss at 7.0 eV corresponds to a broad maximum in the optical absorption of anthracene vapour[2].

Anthracene crystallizes in the monoclinic spacegroup C_{2h}^5 and has 2 crystallographically equivalent molecules per unit cell[3]. (Figure 2). Its dielectric tensor with respect to the axis $\underline{a}$, $\underline{b}$, $\underline{c}'$ is of the form

$$\underline{\underline{\varepsilon}} = \begin{pmatrix} \varepsilon_{aa} & 0 & \varepsilon_{ac'} \\ 0 & \varepsilon_{bb} & 0 \\ \varepsilon_{ac'} & 0 & \varepsilon_{cc'} \end{pmatrix}$$

Each component of the tensor is a complex function of the frequency ω. For electrons of some tens of keV energy, the probability $P(\omega,k)$ for an energy loss $\hbar\omega$ and a momentum transfer $\hbar k$ to the bulk of the material is[4,5]

$$P(\omega,\underline{k}) \propto \mathrm{Im}\left(\frac{1}{\underline{k}\underline{\underline{\varepsilon}}\underline{k}}\right) \qquad (1)$$

The experimental method of evaluating $\underline{k}$ is described in[6] and[7] and the experimental techniques employed in our energy loss measurements are described in[1] and[7]. Figures 3a, b, c show the averaged energy loss spectra

of 30 keV electrons in anthracene single crystals (see also[8,7,9]). The cones show the direction (and the accuracy with which it can be given) of the momentum transfer $\hbar k$ with respect to the crystal axes. (The widths of the cones correspond to the half width $\pm 1.5 \cdot 10^{-4}$ rad of the angular spread of the electron beam accepted by the analyzer.) Due to the experimental conditions, this direction is changing slightly with energy loss.

In the oriented gas model of the organic solid state molecular excitations give rise to excitons in the crystal. The transition moments of the molecular excitations are added or subtracted geometrically in such a way as to obey the symmetry restrictions imposed by the lattice[10]. Applying this model to antrhacene and neglecting configuration interactions and Davydov splitting[10] every molecular transition results in a $A_g - B_u$ exciton in the (ac)-plane and a $A_g - A_u$ exciton in b-direction[10]. The normalized transition moments of the different A_u and B_u excitons from the molecular $\pi - \pi^*$ excitations B_{1u}, B_{2u} and the molecular $\pi - \sigma^*$ or $\sigma - \pi^*$ excitations B_{3u} are given in figures 3a, b, c.

In agreement with this model, the $^1B_u(^1B_{1u})$ and $^1A_u(^1B_{1u})$ excitons are seen in spectra 3a and 3b respectively, near 3.5 eV, but not in spectrum 3c. In Fig. 4 the experimental peak height of the $^1B_u(^1B_{2u})$ exciton near 6 eV is shown as a function of k within the ac-plane. The peak height has been normalized with respect to the height of the loss at 20 to 23 eV. (Normalization to the no loss peak (not displayed) was impossible, because the thickness of the anthracene foil changes slowly during the investigation because of evaporation.) It is clearly seen, that the intensity has its maximum in the direction predicted by the oriented gas model and its minimum perpendicular to this direction.

Figure 5 shows the reflectivity from the (ab)-plane of anthracene single crystals at room temperature for the electric vector of the incident radiation parallel to $\underline{a}$ and $\underline{b}$. The angle of incidence was 15°. The light source was the synchrotron radiation of DESY[11,12]. The crystals were oriented by a polarimetric method. Because of the combined effect of the grating efficiency and the sensitivity of the photodetector (open photomultiplier type Bendix M 306) the possible influence of the fluorescence radiation[13] was excluded. No time effect due to the slow evaporation from the anthracene crystal was observed. The absolute errors in the reflectivity may amount to ±15 %. In the energy range 12 - 17 eV, the reflectivities for both directions of polarization agree within 5 % with values taken with the help of a line source by Gotchev and Steinmann[14]. The maximum of the reflectivity near 17 eV agrees approximately with the electron energy loss in the vapor at 16.3 eV and the maximum of reflectance of graphite[15] and polycristalline tetracene at 17.2 eV[16]. The peak value for this maximum is remarkably large, comparable to that of graphite[15]. Apparently it results from $\sigma - \pi^*$ excitations of the molecule polarized perpendicular to the plane of the molecule ($^1A_{1g} - {}^1B_{3u}$). This interpretation is supported by the qualitative agreement of the ratio of the reflectivity of this main peak at 17 eV for $\underline{E} \parallel \underline{a}$ and $\underline{E} \parallel \underline{b}$ with what one would expect from the oriented gas model.

Theoretically, the normal incidence reflectivity from the (ab)-plane is

$$R_a = \left| \frac{1 - (\underline{a}_o \, \underline{\underline{\varepsilon}}^{-1} \, \underline{a}_o)^{1/2}}{1 + (\underline{a}_o \, \underline{\underline{\varepsilon}}^{-1} \, \underline{a}_o)^{1/2}} \right|^2 \qquad \underline{a}_o = \underline{a}/|\underline{a}| \qquad (2a)$$

for the electric vector of the incident radiation in the direction of the lattice vector $\underline{a}$ and

$$R_b = \left| \frac{1 - (\underline{b}_o \underline{\underline{\varepsilon}} \underline{b}_o)^{-1/2}}{1 + (\underline{b}_o \underline{\underline{\varepsilon}} \underline{b}_o)^{-1/2}} \right|^2 \qquad \underline{b}_o = \underline{b}/|\underline{b}| \qquad (2b)$$

in the direction of the lattice vector $\underline{b}$.

Comparison of (2a, 2b) and (1) shows, that only for the polarization direction $\underline{b}$ can the spectral dependence of $P(\omega,k)$ and R be described (like in an isotropic material) by the same dielectric constant ($\underline{bo}\ \underline{\underline{\varepsilon}}\ \underline{bo}$).

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Figure Captions

Fig. 1 Energy loss spectrum of 30 keV electrons in anthracene vapour, resolution 0.6 eV.

Fig. 2 Projection of the anthracene unit cell onto the (ac) and (ab) plane.

Fig. 3a, b, c, Energy loss spectra of 30 keV electrons in anthracene single crystals for the directions of momentum transfer as shown by the cones.

Fig. 4 Polar diagramm of the normalized intensity of the peak height of the energy loss near 6 eV for different directions of momentum transfer in the (ac) plane.

Fig. 5 Normal incidence reflectivities from the (ab) plane for polarization parallel a and b.

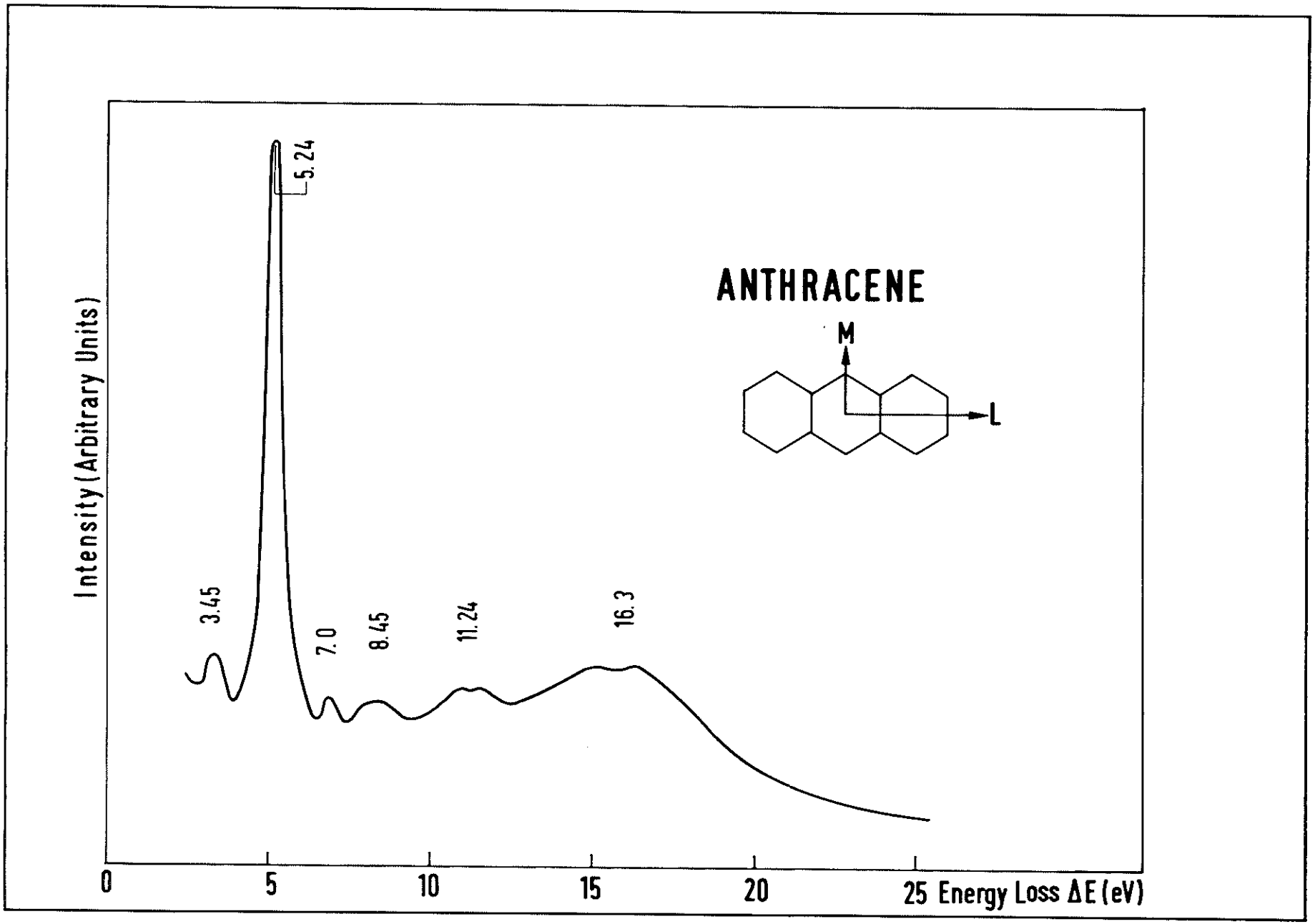
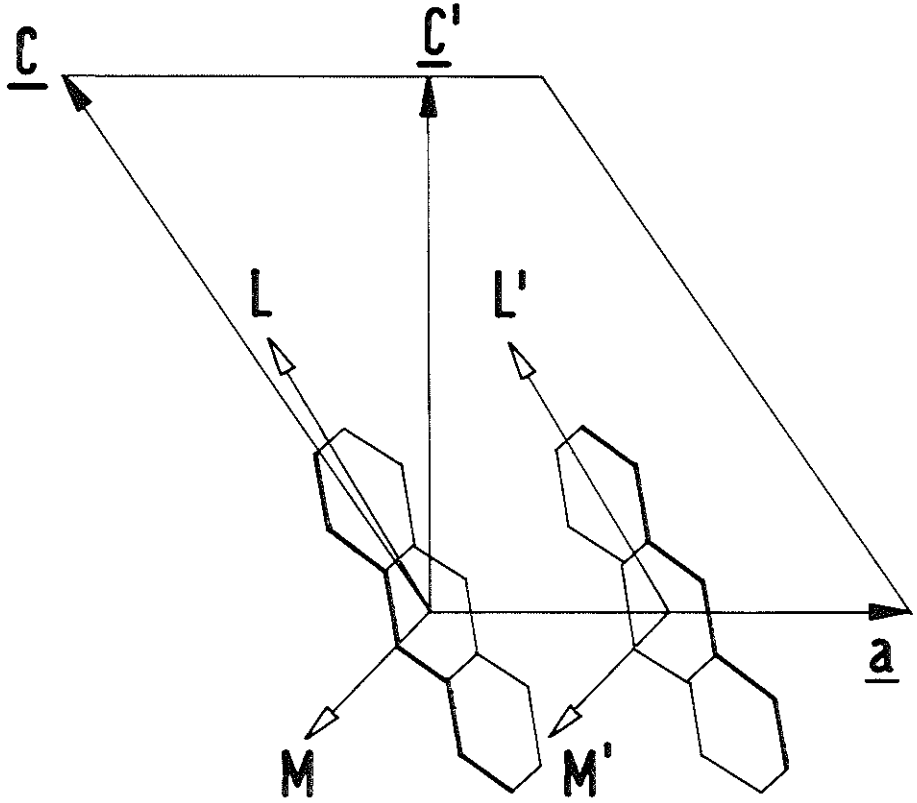

ANTHRACENE
M
L
Intensity (Arbitrary Units)
5.24
3.45
7.0
8.45
11.24
16.3
0
5
10
15
20
25 Energy Loss ΔE (eV)

Fig. 1



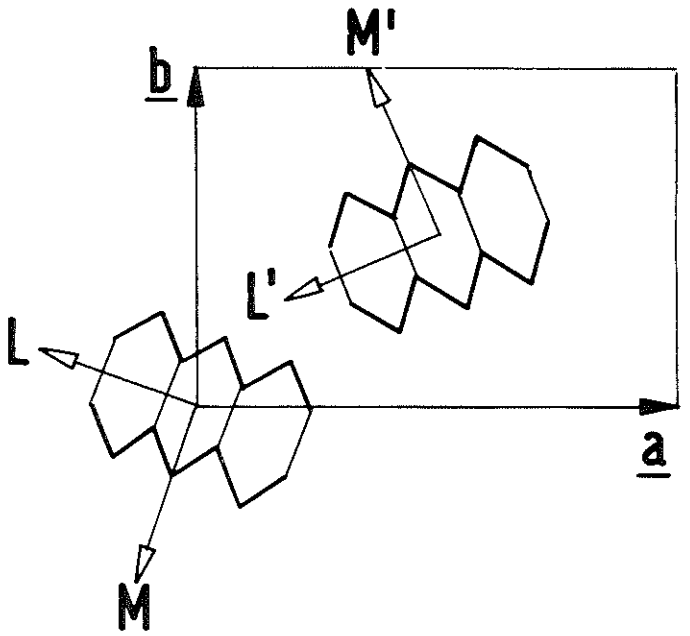


Fig. 2

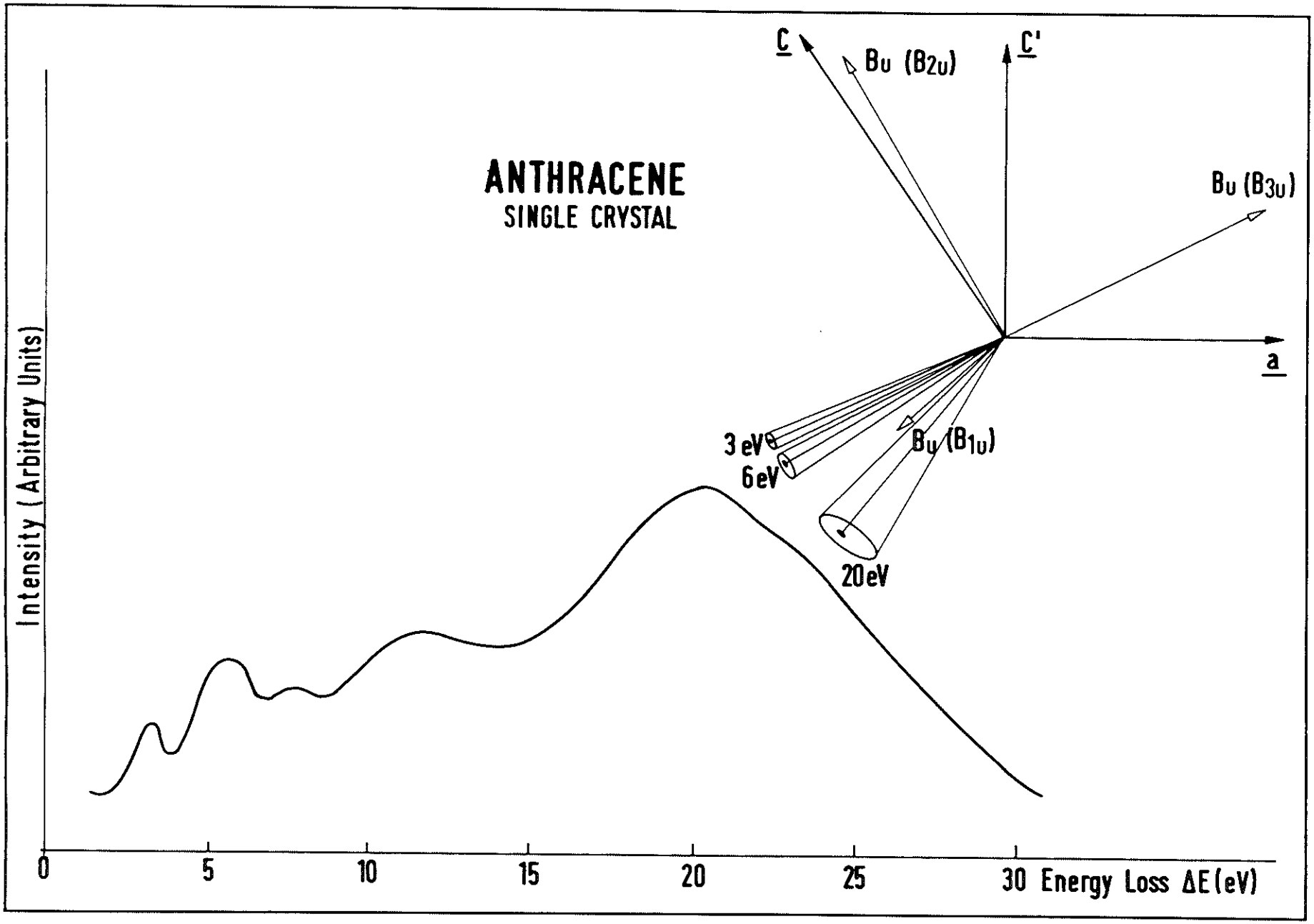

ANTHRACENE
SINGLE CRYSTAL
C
C'
Bu (B2u)
Bu (B3u)
a
3 eV
6 eV
Bu (B1u)
20 eV
Intensity (Arbitrary Units)
0
5
10
15
20
25
30 Energy Loss ΔE (eV)

Fig. 3a

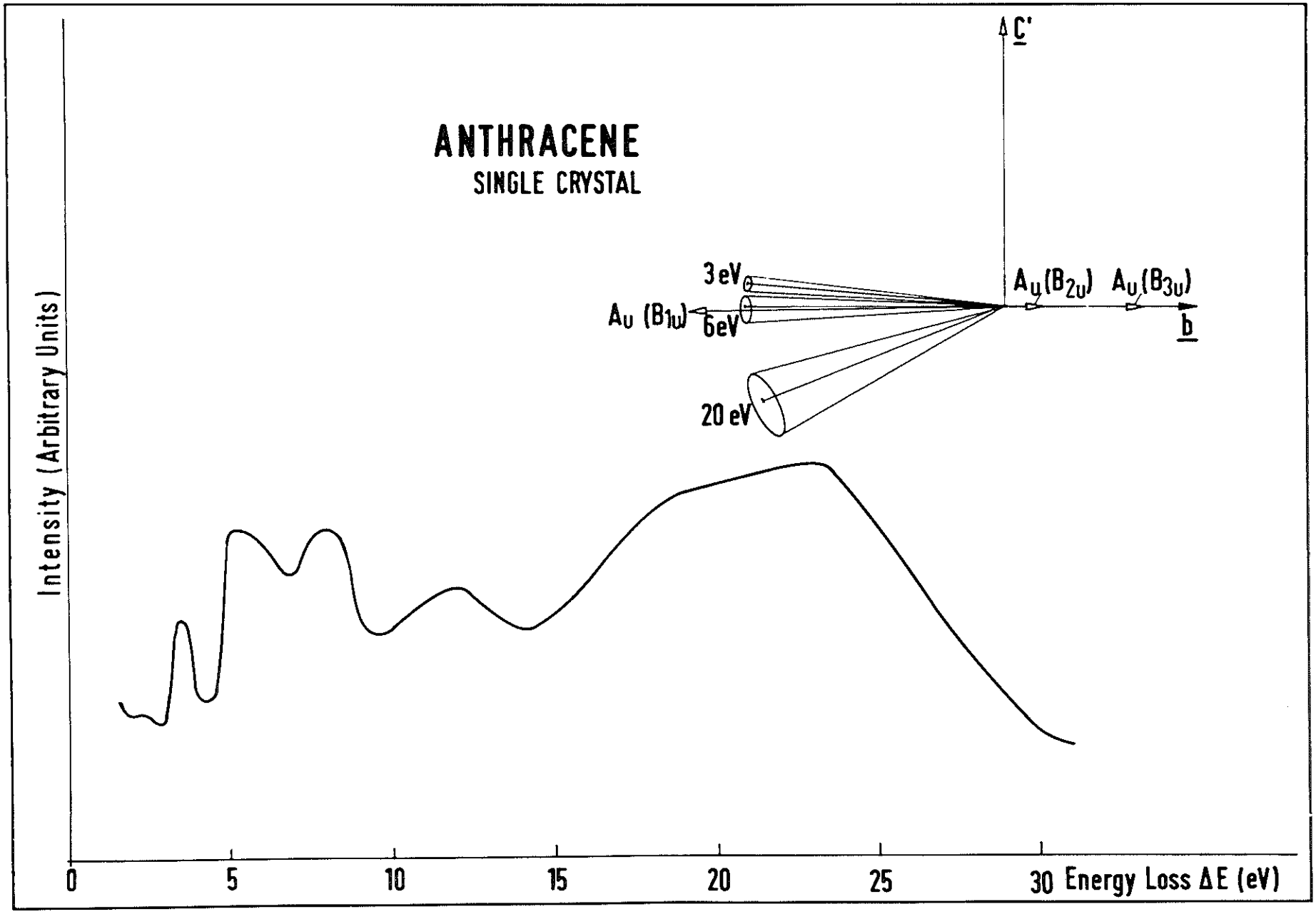

ANTHRACENE
SINGLE CRYSTAL
c'
3 eV
6 eV
20 eV
$A_u(B_{1u})$
$A_u(B_{2u})$
$A_u(B_{3u})$
b
Intensity (Arbitrary Units)
0
5
10
15
20
25
30
Energy Loss ΔE (eV)

Fig. 3b

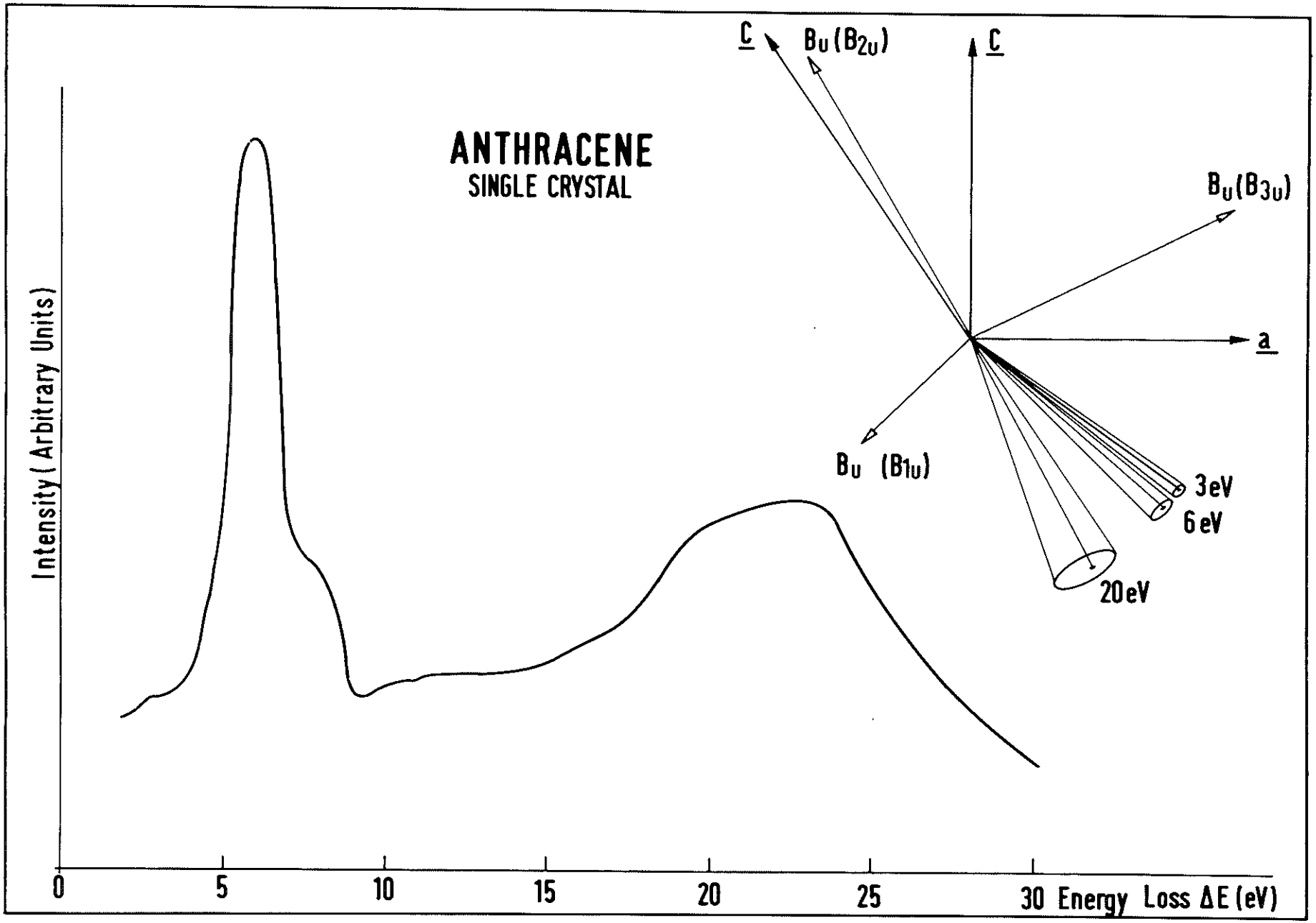

ANTHRACENE
SINGLE CRYSTAL
Intensity (Arbitrary Units)
C
Bu (B2u)
C
Bu(B3u)
a
Bu (B1u)
3eV
6eV
20eV
0
5
10
15
20
25
30 Energy Loss ΔE (eV)

Fig. 3c

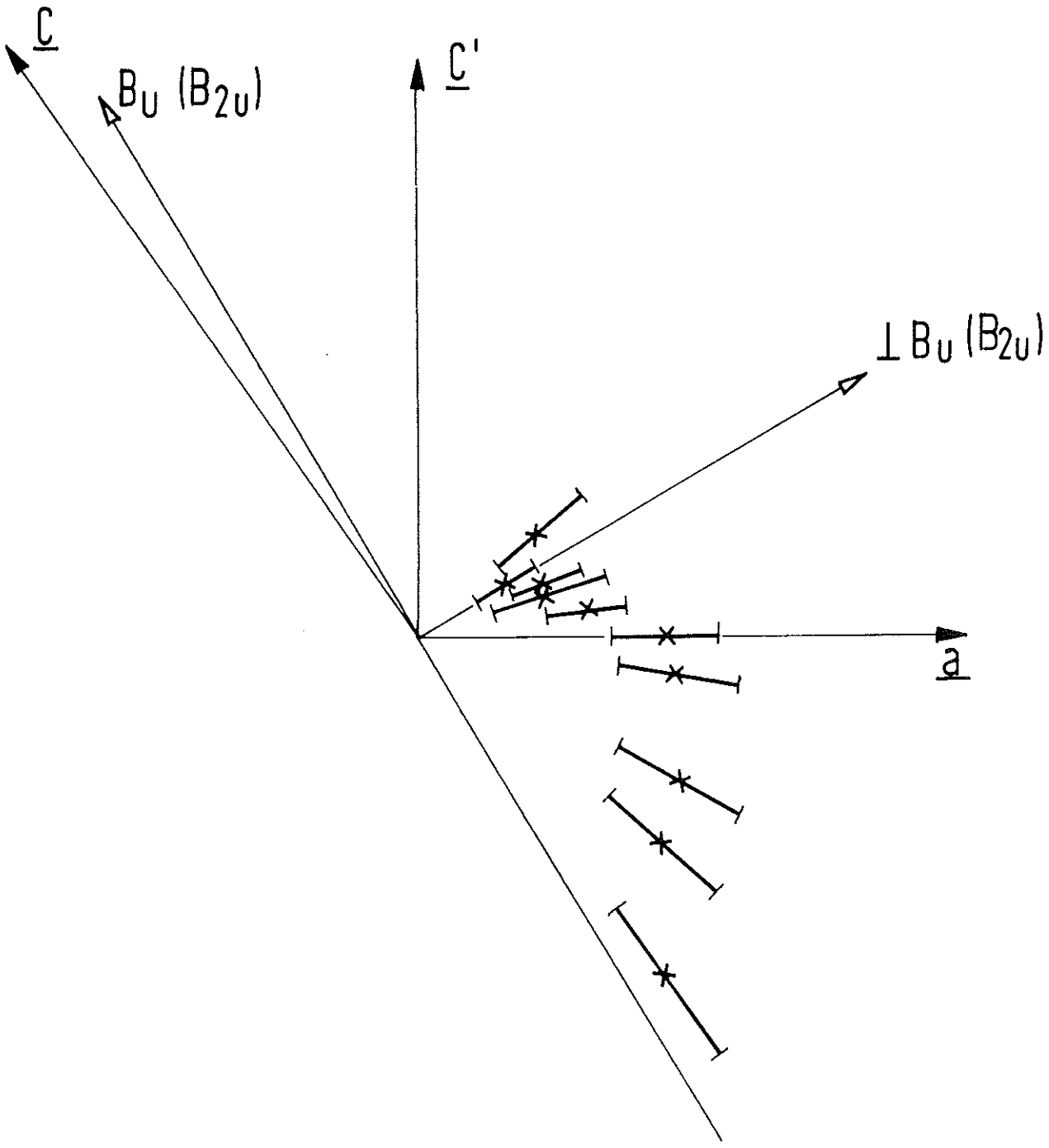


Fig. 4

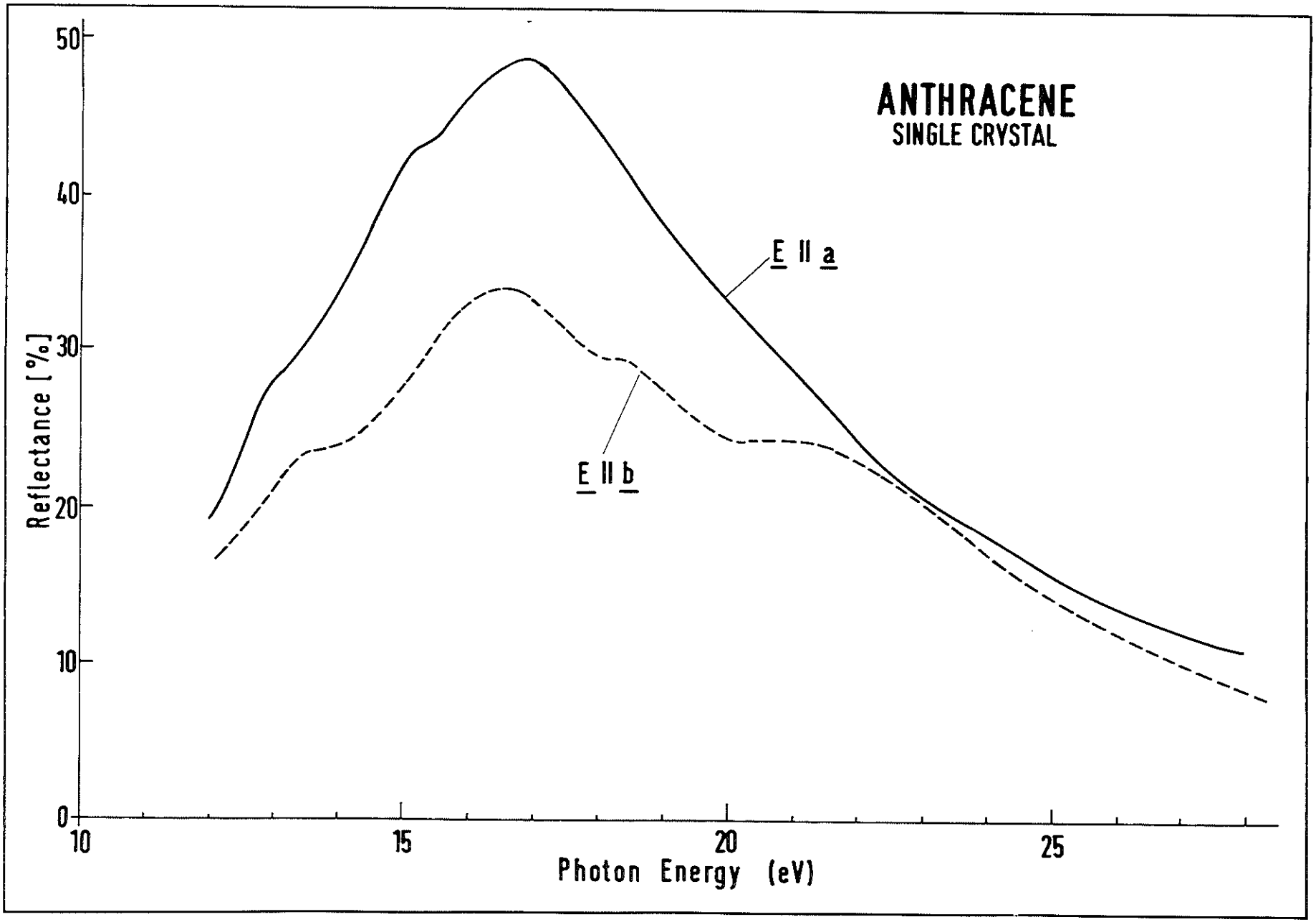

ANTHRACENE
SINGLE CRYSTAL
E II a
E II b
Reflectance [%]
Photon Energy (eV)
0
10
20
30
40
50
10
15
20
25

Fig. 5