Interner Bericht
DESY F41-71/1
May 1971

ANISOTROPY OF THE DIELECTRIC CONSTANTS OF TRIGONAL SELENIUM AND TELLURIUM BETWEEN 3 eV AND 30 eV

by

R. Klucker, E. E. Koch, and T. Tuomi

ANISOTROPY OF THE DIELECTRIC CONSTANTS OF TRIGONAL SELENIUM AND TELLURIUM BETWEEN 3 eV AND 30 eV[≠]

R. Klucker[+], E.E. Koch[+], and T. Tuomi[±]

Deutsches Elektronen-Synchrotron DESY, Hamburg, Germany

[≠] to be presented at the Europhysics Conference on the Physics of Selenium and Tellurium at Pont-à-Mousson, France, 16 May to 19 May 1971

[+] Sektion Physik der Universität München, München, Germany

[±] Alexander von Humboldt Foundation Fellow on leave from the Helsinki University of Technology

INTRODUCTION

Measurements of reflectance spectra of trigonal Se and Te single crystals with linearly polarized light, whose electric field vector lies perpendicular and parallel to the optical axis, yield the anisotropy of the optical constants. Due to the lack of suitable polarizers for shorter wavelengths and light source problems, these measurements have been limited to excitation energies smaller than 12 eV. The use of the synchrotron as a light source with its intense continuous radiation and its high degree of polarization allows such measurements to be extended into the XUV region. Thus, the whole energy range can be studied where excitations of the 6 outermost electrons, $4s^2\ 4p^4$ for Se and $5s^2\ 5p^4$ for Te, are expected to occur.

EXPERIMENTS

We have used the synchrotron radiation of DESY [1]. In our experiments, which covered an energy range from 3 to 30 eV, advantage was taken of a monochromator with its dispersion plane perpendicular to the plane of the synchrotron [2]. Figure 1 gives a sketch of the arrangement consisting of pre-mirror, normal incidence monochromator, and reflectometer attached to the exit slit of the monochromator. The pre-mirror reflects the light emitted from the electrons to the monochromator. The electric field vector of the synchrotron radiation is lying perpendicular to the plane of the drawing. Since the plane of incidence of the pre-mirror as well as that of the grating are perpendicular to the electric field vector E of the synchrotron radiation, this arrangement produces an even higher degree of polarization as compared to that of the incident synchrotron radiation. The degree of polarization $(I_\perp - I_\parallel)/I_\perp + I_\parallel$ was better than 0.98. Sample and

detector could be rotated independently. This allowed spectra to be taken at various angles of incidence. Moreover, the sample and the detector could be rotated around the optical axis, which makes it possible to take spectra with light polarized parallel and perpendicular to the c-axis of the crystals.

The measurements were performed with different crystals grown from the melt and from the vapour phase, the c-axis of the crystals lying parallel to the surface. The crystals were freshly cleaved before measuring. The direction of the c-axis within the surface was determined by optical inspection as well as by X-ray diffraction.

In contrast to the relative spectral shape the absolute value of the reflectance was not determined with great accuracy since the reflected intensity I_r and the incident intensity I_o were not measured simulataneously. We, therefore, normalized our measurements at low energies to spectra taken by Henrion [3] and Leiga [4] for Se and Tutihasi et al. [5] for Te. At high energies we checked our data against reflectance values for discrete photon energies using conventional techniques [6].

RESULTS

In Fig. 2 the reflectance spectra of Se and Te for an angle of incidence of 15^{o} are presented. Below 3 eV measurements of Henrion [3] and Tutihasi et al. [5] are included, as well as our extrapolation to 0 eV. The reflectance values at 0 eV were calculated from the dielectric constant ε for small energies taken from Gobrecht et al. [7] for Se and Geick et al. [8] for Te. Our spectra were taken with the electric field vector E parallel to the c-axis of the crystal ($E \parallel c$) with E lying perpendicular to the plane of incidence. Spectra with $E \perp c$ were obtained with E parallel to the plane of incidence.

For both substances and both directions of polarization we observed in the range from 0 to 6 eV the prominent anisotropic reflectance maximum followed by a sharp decrease of the reflectivity followed by a range of strong anisotropic behaviour up to approximately 11 eV. Up to this energy our measurements agree fairly well with earlier results [3-5]. At higher energies the spectra show two broad maxima at around 14 eV for both directions of polarization, followed by a smooth decrease of the reflectance. The energies for the peaks observed in reflection are listed in Table I.

In order to obtain the complex dielectric constant $\hat{\varepsilon}(E) = \varepsilon_1(E)+i\cdot\varepsilon_2(E)$ a Kramers-Kronig transformation was applied to the reflectivity spectra R(E) of Fig. 2 for both directions of polarization. A computer programme yielded $\varepsilon_1, \varepsilon_2$, and the energy loss function $|\mathrm{Im}\ 1/\hat{\varepsilon}|$. It was capable of dealing with reflectance data taken at non-normal incidence and with the E vector parallel and perpendicular to the plane of incidence [9]. Figure 3 gives our ε_2-curves for both substances for $E \parallel c$ and $E \perp c$.

For Se both our extrapolation at high energies used for the Kramers-Kronig analysis and its accuracy were checked against measurements of the reflectance at different angles of incidence, which independently yielded ε_1 and ε_2 and derived quantities at fixed photon energies. Both methods yielded ε_1 and ε_2 values in satisfactory agreement.

In Fig. 4 the energy loss functions are shown. The peaks at lower energies are due to optical excitations whereas the large maxima at 19.0 eV for $E \parallel c$ and 20.5 eV for $E \perp c$ for Se and at 17.0 and 17.5 eV for Te are due to the plasma frequency ω_p. These experimental values are in good agreement

with those calculated using the well-known plasma formula $\omega_p = \left(\frac{4\pi Ne^2}{m}\right)^{1/2}$, which yields 17.4 eV for Se and 15.6 eV for Te. Of course, the simple plasma model does not take into account the anisotropy which is manifested in the experimental results.

DISCUSSION

We are now going to discuss our results for Se according to the bandscheme calculated by Sandrock [10] and which is partly shown in Fig. 5. The spectral features in the range from 0 to 6 eV are due to excitations of electrons from the upper part of the valence band to the lower part of the conduction band, as already extensively discussed in the literature. At 6 eV a deep minimum is observed for both directions of polarization. This has been explained by Sandrock [10,11]. According to his pseudopotential calculations at this energy the transitions from the upper valence to the lower conduction band triplet are exhausted.

Above 6 eV two contributions to the ε_2-spectra are considered by Sandrock. The first one starting at about 6 eV is due to transitions from the lower valence to the lower conduction band triplet. The transitions from the upper valence to the upper conduction band triplet, which form the second contribution, start at about 7 eV. The strong anisotropy observed at 7.3 eV is due to the onset of these transitions. However, this peak at 7.3 eV for $E \parallel c$ is not associated with any particular symmetry point in the Brilloin zone.

The transitions from the lowest subband of the lower valence band to the lowest conduction band start at about 9 eV. At this photon energy the

selection rule is reversed so that the ε_2-spectrum for E $\parallel$ c becomes smaller than that for E $\perp$ c. The transitions of the above contributions extending up to 12 eV are the highest taken into account by Sandrock. According to his band model, one would expect the next higher transitions to occur in the energy region from 12 to 18 eV. They would be due to transitions from the lower valence to the upper conduction band triplet. As the new results of this work show there is still a relatively large contribution to the ε_2-spectrum in this high energy region. Its maximum is located at about 12.3 eV for both directions of polarization.

Sandrock [10] gives the eigenvalues at symmetry points for three more valence bands below the lower valence band triplet. Transitions from these bands, not included in Fig. 5, should occur in the energy range from 16 to 25 eV. For both directions of polarization we observe weak reflectance peaks at about 16.5 eV which may be associated to such transitions. The next higher transitions in Se are those from the 3d core level to the conduction band which do not "switch on" until about 55 eV.

For Te the spectra have been discussed by Maschke [12] for the low energy range. We hope that an extensive bandscheme will also allow for discussions on the transitions at higher energies.

ACKNOWLEDGMENTS

Thanks are due to P. Bammes, Dr. G. Weiser, and Prof. T. Stubb for providing us with single crystals. For valuable discussions we would like to thank Dr. M. Skibowski and Prof. W. Steinmann.

REFERENCES

1 R.P. Godwin in: Springer Tracts in Modern Physics, Vol. 51, ed. G. Höhler (Springer, Berlin, 1969)

2 E.E. Koch and M. Skibowski, Chem.Phys. Letters, ... (1971)

3 W. Henrion, phys.stat.sol. 22, K33 (1967)

4 A.G. Leiga, J.Opt.Soc.Am. 58, 880 (1968)

5 S. Tutihasi, G.G. Roberts, R.C. Keezer, and R.E. Drews, Phys.Rev. 177, 1143 (1969)

6 W. thank B. Gotchev for his help in this measurements.

7 H. Gobrecht and A. Tausend, Z. Physik 161, 205 (1961)
In this reference the following values are given: $\varepsilon_1^{\parallel} = 13.3$, $\varepsilon_1^{\perp} = 8.0$.

8 R. Geick, P. Grosse, and W. Richter, in W.C. Cooper ed., Proceedings of the International Symposium, Montreal, 1967 (pergamon Press, Inc., New York 1969), p. 309.
In this reference the following values are given: $\varepsilon_{1_\infty}^{\parallel} = 36$, $\varepsilon_{1_\infty}^{\perp} = 23$.

9 R. Klucker, unpublished

10 R. Sandrock, Phys.Rev. 169, 642 (1968)

11 R. Sandrock, phys.stat.sol. (b) 43, 199 (1971)

12 K. Maschke, Verhandl. DPG (VI) 6, 726 (1971)

Table I

Energy position (in eV) of the most prominent structures of the 15° reflectance spectra for Se and Te single crystals for both directions of polarization. Shoulders are denoted by sh. Values below 3 eV are taken from Refs. [3,5].

Se		Te	
$E \parallel c$	$E \perp c$	$E \parallel c$	$E \perp c$
2.0	1.9	1.0	1.0
3.1	3.1 sh	1.4	
4.0	3.9	2.4	2.4
4.9 sh	4.8 sh	2.9	
6.7 sh	6.8 sh	3.4 sh	3.6 sh
7.5	7.4 sh	5.4 sh	
8.6 sh		7.4	
9.1	8.9	8.0 sh	8.0
10.4 sh	10.5	9.5	9.2
13.0	13.5	11.2 sh	10.9 sh
16.2	16.4	12.9	13.2
		16.3	15.9
			16.6

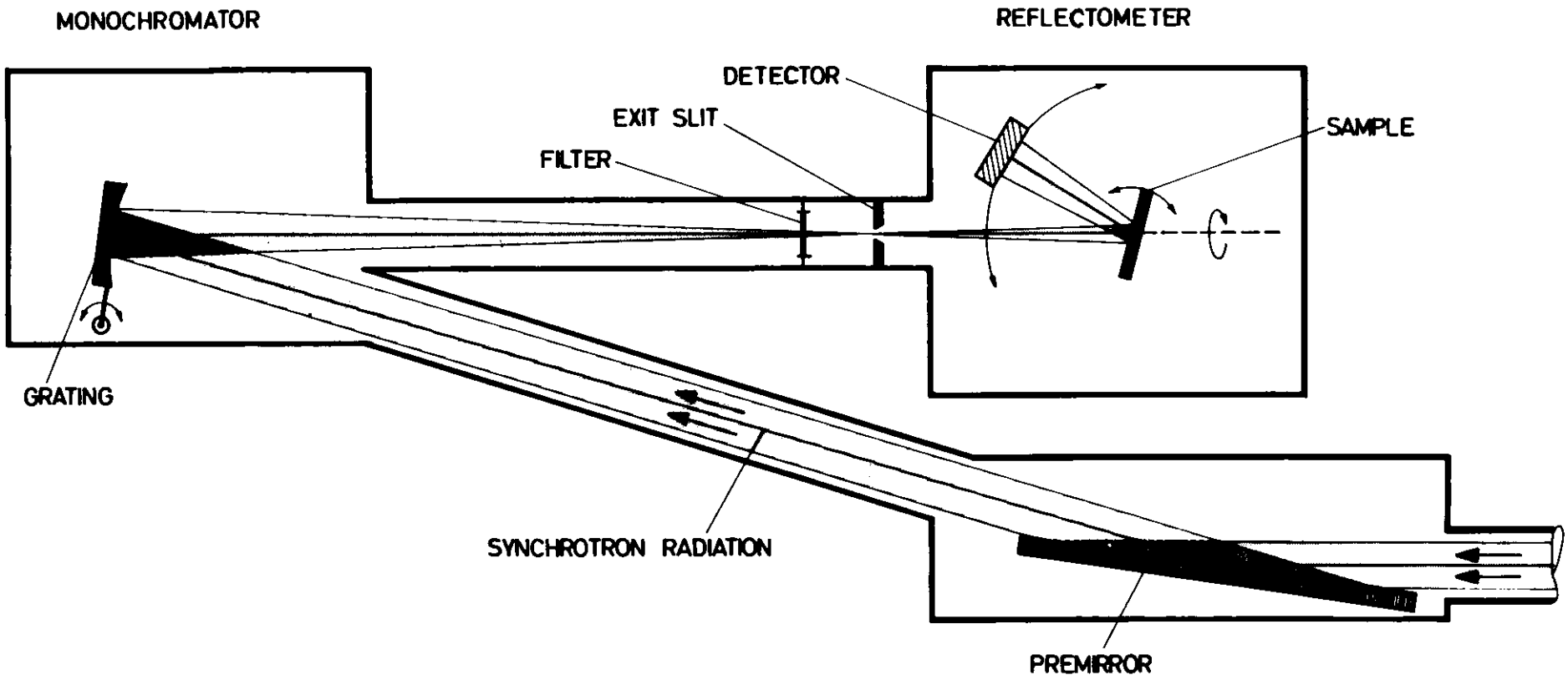

FIGURE 1: Experimental arrangement

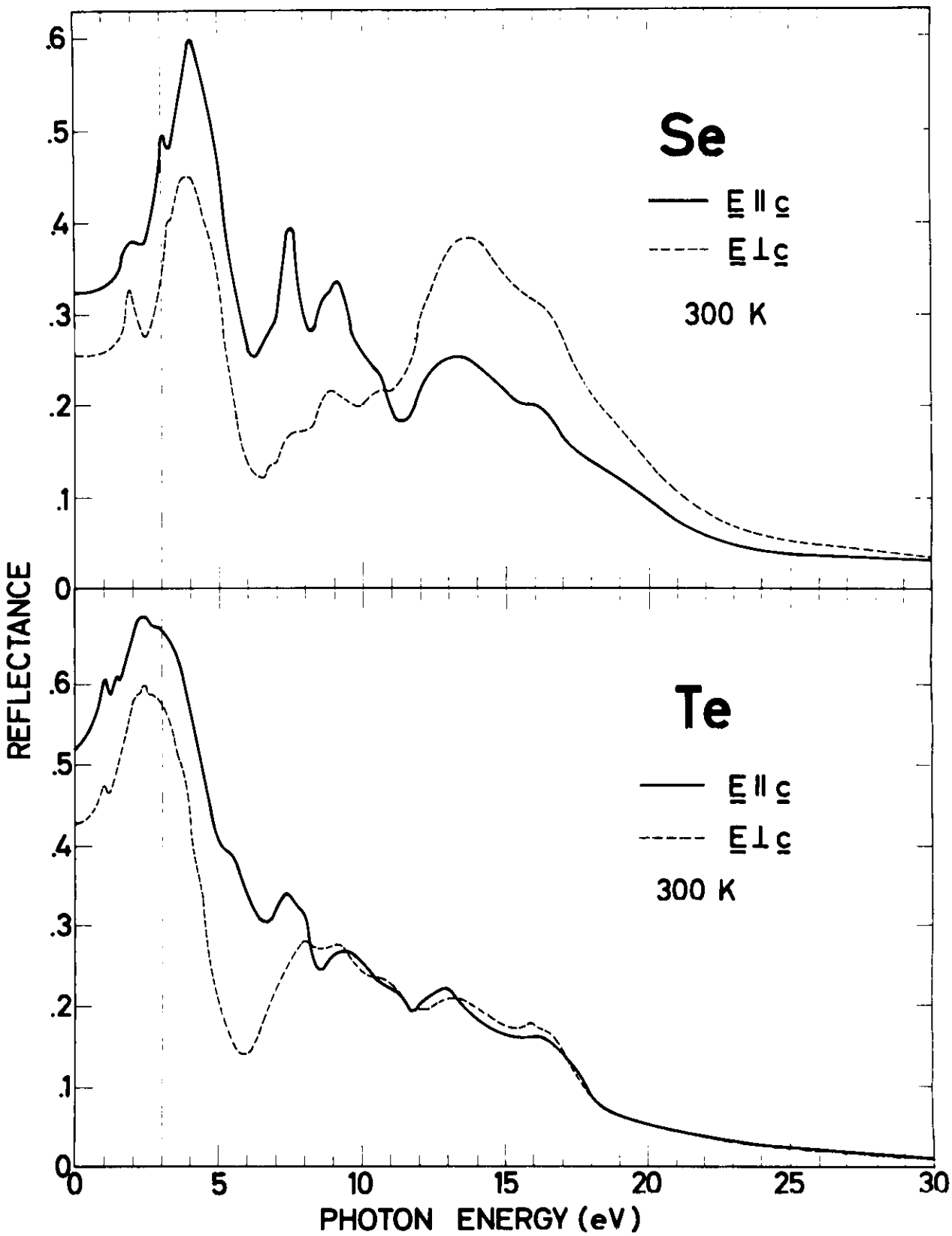

FIGURE 2: Reflectance at 15° angle of incidence. Below 3 eV measurements of refs. (3) and (5) are included.

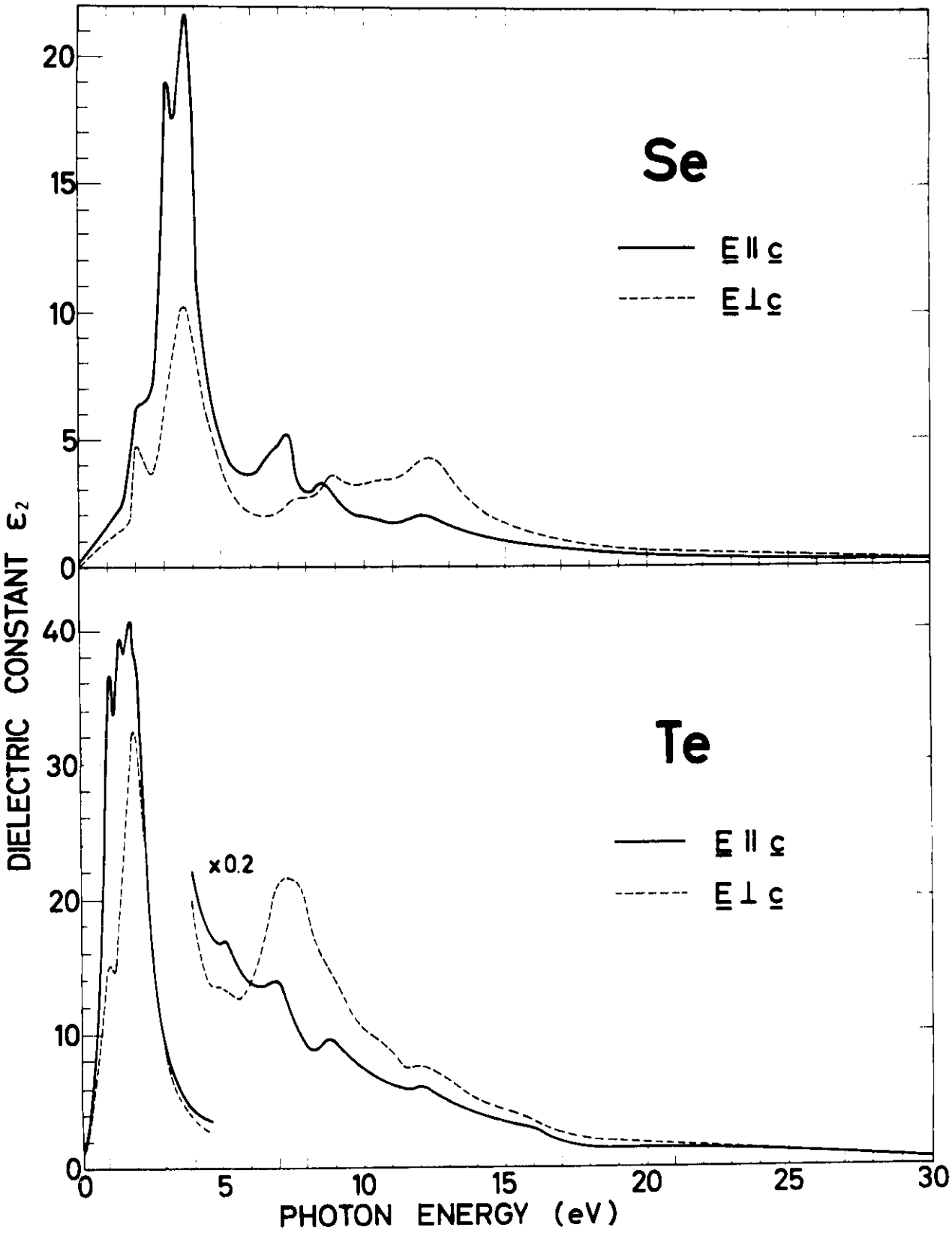

FIGURE 3: Dielectric constant ε_2

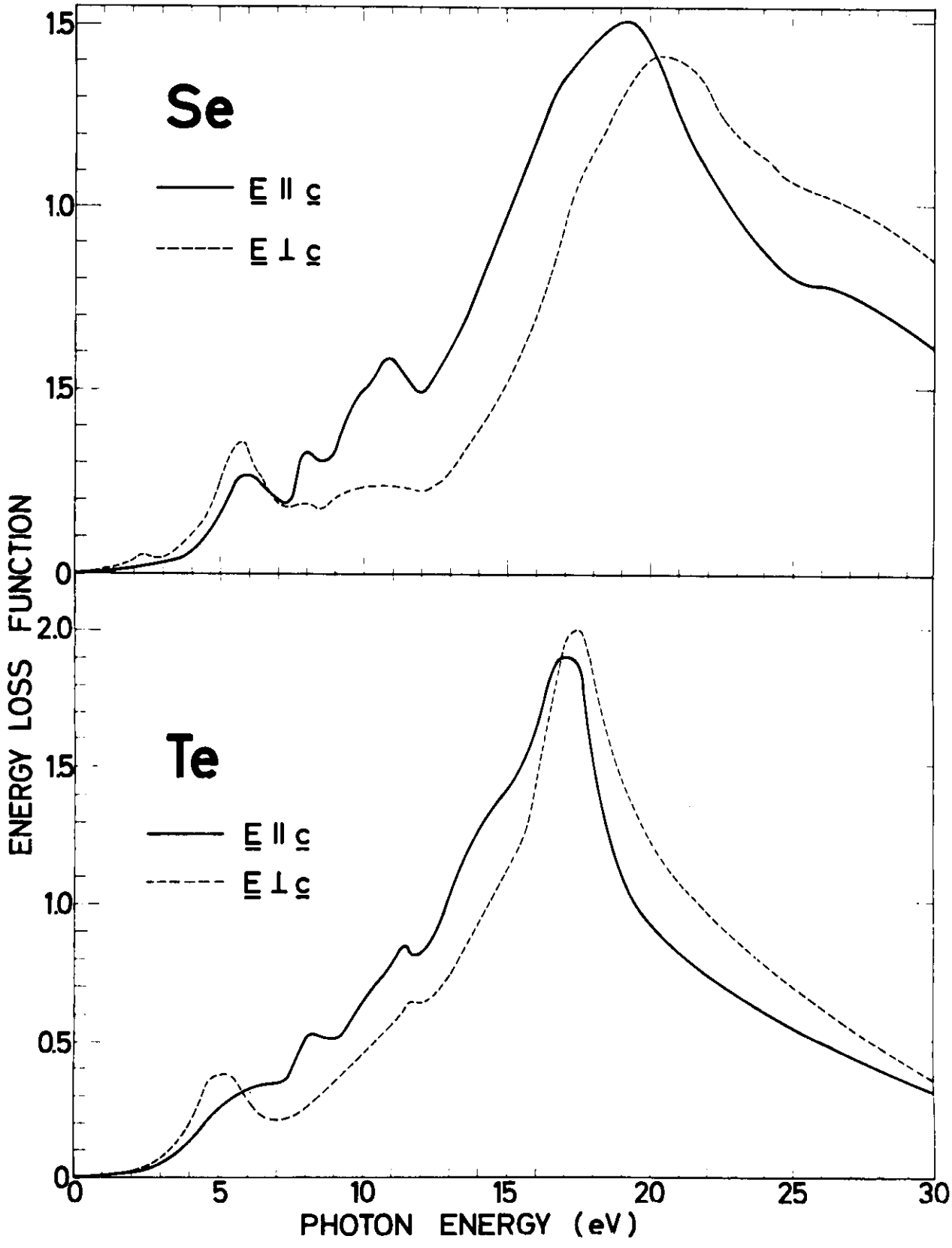

FIGURE 4: Energy loss function $\left|\mathrm{Im}(1/\hat{\varepsilon})\right|$

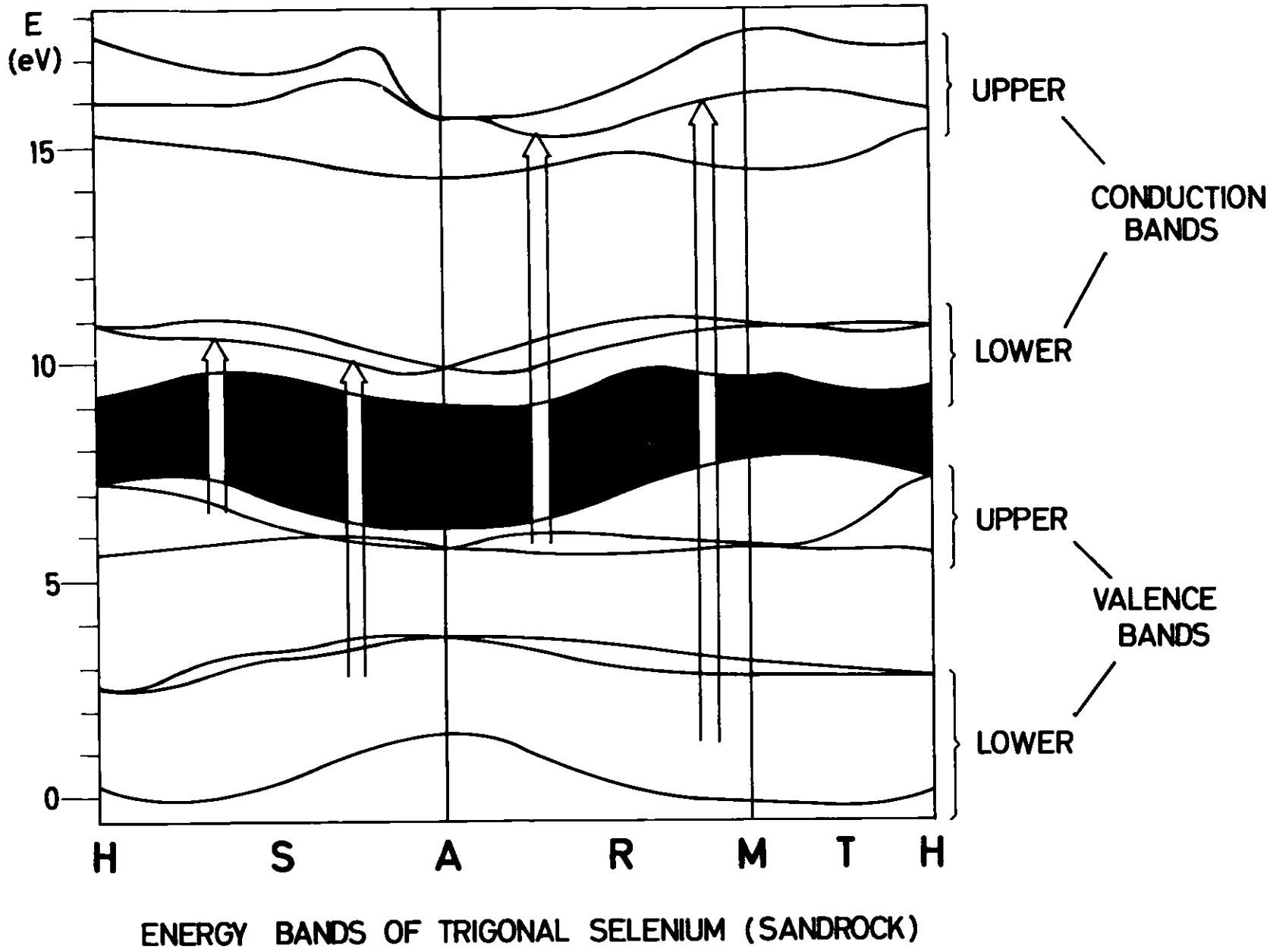

FIGURE 5: Energy bands of trigonal Se
(Taken from reference (10)).