DEUTSCHES ELEKTRONEN-SYNCHROTRON DESY

DESY SR-73/1
January 1973

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Photoemission from the Valence Bands of Solid Rare Gases[≠]

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The photoelectric yield of thin films of solid Ar, Kr, and Xe has been studied between 10 and 32 eV using synchrotron radiation. The exciton series is associated with weak photoemission caused by decay of excitons. Above the band gap, however, an intensive broad maximum followed by a distinct minimum is observed. Only weak spectral structure is superimposed. The gross spectral features of the yield in this energy range can be interpreted in terms of electron-electron scattering.

[≠] Work supported by the Deutsche Forschungsgemeinschaft

The optical properties of solid rare gases have recently been investigated extensively by reflection[1-4] and absorption[5-7] spectroscopy, but only one experiment on the photoemission of solid rare gases has been reported so far. Some years ago O'Brien and Teegarden[8] have measured the photoelectric yield of solid Xe and Kr for photon energies below the LiF-cut-off (12 eV). Because of the limited energy range they were essentially only able to investigate the region of excitons. In this paper we report the first results on the photoyield of solid Ar, Kr and Xe between 10 and 32 eV. They were obtained using synchrotron radiation. The experiment covers the entire range where optical valence band spectra show characteristic structure due to either a spin orbit split exciton series converging to the band gap or interband transitions at higher energies, presumably modified by Coulomb interaction[9,10].

The yield measurements were performed by means of a normal incidence monochromator in connection with the synchrotron radiation of the Deutsches Elektronen-Synchrotron DESY (7.5 GeV)[11]. The wavelength resolution was about 2 Å (i.e. ≈30 meV at 15 eV) over the whole energy range under investigation. The experiment was carried out at a pressure in the low 10^{-9} Torr range in an ultrahigh vacuum system attached to the monochromator. The samples were thin films of rare gases which were evaporated on a gold-coated quartz crystal mounted onto a liquid He cryostat cooled down to 30 K. Temperature effects and annealing were not studied systematically. The film thickness could not be measured. Evaporation was usually stopped when the photocurrent at the photon energy of the yield maximum no longer changed. An accelerating voltage of 200 V between the emitter and the collector ensured saturation of the photocurrent from these films. When the film thickness was further increased changes of the spectrum were observed presumably due to space charge effects. The

highest photocurrents measured were of the order of 10^{-11} A. In order to determine a relative photoyield per incident photon the spectrum of the photocurrent was divided by the relative spectral distribution of the light intensity measured at the exit slit of the monochromator with a Na-salicylate coated multiplier. An absolute value for the yield was estimated by also measuring the photocurrent of the gold coated substrate before evaporation of the rare gas film and comparing it with the result for the Au yield obtained by Cairns and Samson[12].

Figure 1 shows the yield spectrum of Ar together with previous optical results. The ε_2-spectrum has been derived from the reflection spectrum by Kramers-Kronig analysis[13]. Between 12 and 14 eV a relatively low yield is observed which, however, exhibits a fine structure related to the spin orbit split exciton series. In the optical spectrum this series is the most remarkable structure while in the yield it is only weak. Starting at 13.3 eV there is a strong increase of the yield by about one order of magnitude within about 3 eV. A broad maximum is found around 20 eV associated with an absolute yield of about 0.5. This figure is based on the assumption that the yield of gold is only about 0.1 according to Ref. 12. The maximum is followed by a distinct minimum located at about twice the band gap energy. Superimposed on the broad maximum some weak spectral structures are found. Only in a few cases they can be directly associated with structure found in the optical spectra. There is definitely no close similarity concerning spectral structure between the yield and the optical spectra of valence band excitations as has been observed for excitations from core levels of other materials[14-15]. Some of the weak structures on the broad maximum, which are certainly not due to the gold substrate, vanishes even more and more with increasing thickness of the solid rare gas film.

The gross features of the yield of solid Kr and Xe (Fig. 2) are very similar to that of solid Ar, if one takes into consideration the decrease of the energy gap E_g between valence and conduction band from solid Ar (14.2 eV), Kr (11.6 eV) to Xe (9.3 eV). The main difference between the Kr and Xe spectra as compared to Ar is a steeper slope on the high energy side of the first maximum, a more pronounced minimum and second maximum and the fact that the minimum occurs at photon energies $E > 2\ E_g$.

The experimental results can be interpreted as follows:
The photon energies 13.3 eV for Ar, 11.9 eV for Kr and 10.0 eV for Xe, where the yield begins to rise steeply, are tentatively ascribed to the threshold energy E_g+E_A (see Fig. 3). The value for Xe is not very accurate since measurements at and below 10 eV were hampered due to low intensity and low yield. By subtracting the band gap energies, one obtains for the electron affinity E_A, - 0.9 eV, 0.3 eV and 0.7 eV for Ar, Kr and Xe respectively. The negative value for Ar does not agree with a value derived from spectroscopical data[7].

The excitons below the threshold energy cannot directly contribute to photoemission. A decay of excitons by ionization of defect or impurity states with weakly bound electrons is presumably responsible for the photoemission in this spectral range[8]. Although the yield is only about 10 % of the maximum, it is higher than the corresponding effect in alkali halides[17,18] which may indicate a higher concentration of defects or impurities in our samples.

The intensive yield maximum is caused by electrons excited into the conduction band with final energies above the vacuum level. The magnitude of the absolute yield suggests that for photon energies close to the position of the yield maximum all excited electrons with a momentum component towards the surface will

escape from the sample. Inelastic electron-electron scattering cannot occur in perfect crystals up to photon energies as high as the sum of band gap energy and the first exciton energy. In this range the resulting escape depth L(E) for electrons is expected to be much larger than the attenuation length of the light $\mu^{-1}(E)$, where μ is the absorption coefficient. The increase of the yield above the threshold can be explained by an increasing number of contributing initial and final states and in terms of an escape function A(E) which describes the penetration of the electron through the surface barrier.

Large escape depths are also consistent with the experimental fact that no remarkable fine structure is found in the yield spectra where the optical spectra exhibit characteristic structure associated with transitions to final energies above the vacuum level (see Fig. 1). The spectral dependence of the yield per incident photon Y_i on the escape depth of the photoelectrons and on the attenuation length of the photons with energy E may be approximated by[19]

$$Y_i(E) = A(E)\left(1-R(E)\right)\mu(E)\left(\mu(E)+L^{-1}(E)\right)^{-1} \qquad (1)$$

where R denotes the reflectivity of the sample. Since $R(E)<0.1$ above the band gap for all solid rare gases[13], $1-R \approx 1$, and the yield does not depend on μ, if and only if $L >> \mu^{-1}$. In Ar, for instance, the escape depth at the yield maximum at 20 eV will be much larger than 250 Å, the approximate value for μ^{-1} calculated from the optical constants at this energy. The yield per incident photon shown in Figs. 2 and 3 will not differ very much from the yield per absorbed photon $Y_a = Y_i\ (1-R)^{-1}$ in this range.

At the photon energy $E_1 = E_g+E_x$ the excited electron has enough energy to excite an exciton and electron scattering, therefore, will set in. If there are electronic defects or impurities in the sample inelastic scattering is

possible already at lower energies. The result of electron→exciton scattering is an exciton and an electron at the bottom of the conduction band, none of which can directly escape into the vacuum for positive electron affinity. The yield should, therefore, be reduced above this energy. The yield spectra indeed show a marked increase in slope at this energy. The fact that the yield does not drop to zero can be explained by the energy dependence of the cross section for inelastic scattering and by the finite width E_B of the valence band (see Fig. 3).

As the photon energy is increased, the primary electron can excite a valence electron to the bottom of the conduction band at $E = 2\,E_g$. Finally, at $E > 2(E_g+E_a)$ both electrons may have enough energy to escape into the vacuum and the yield will begin to rise again. If one would, therefore, assign the minimum of the yield located at 28.4 eV for Ar, 24.4 eV for Kr and 21.0 eV for Xe to $2(E_g+E_A)$ one would obtain electron affinities of 0.0 eV, 0.6 eV and 1.2 eV for Ar, Kr and Xe respectively. These values are larger than those derived above from the threshold energies. The finite width of the valence band will probably cause a shift of the minimum towards higher photon energies because a decrease of the yield due to a delayed onset of scattering for electrons from deeper regions of the valence band will overlap with the increase associated with scattered electrons already being able to escape. Although the two sets of electron affinities do not agree quantitatively, they show the same trend: Ar has the lowest and Xe the highest electron affinity.

We would like to thank U. Nielsen and V. Saile for technical support and B. Raz for discussions.

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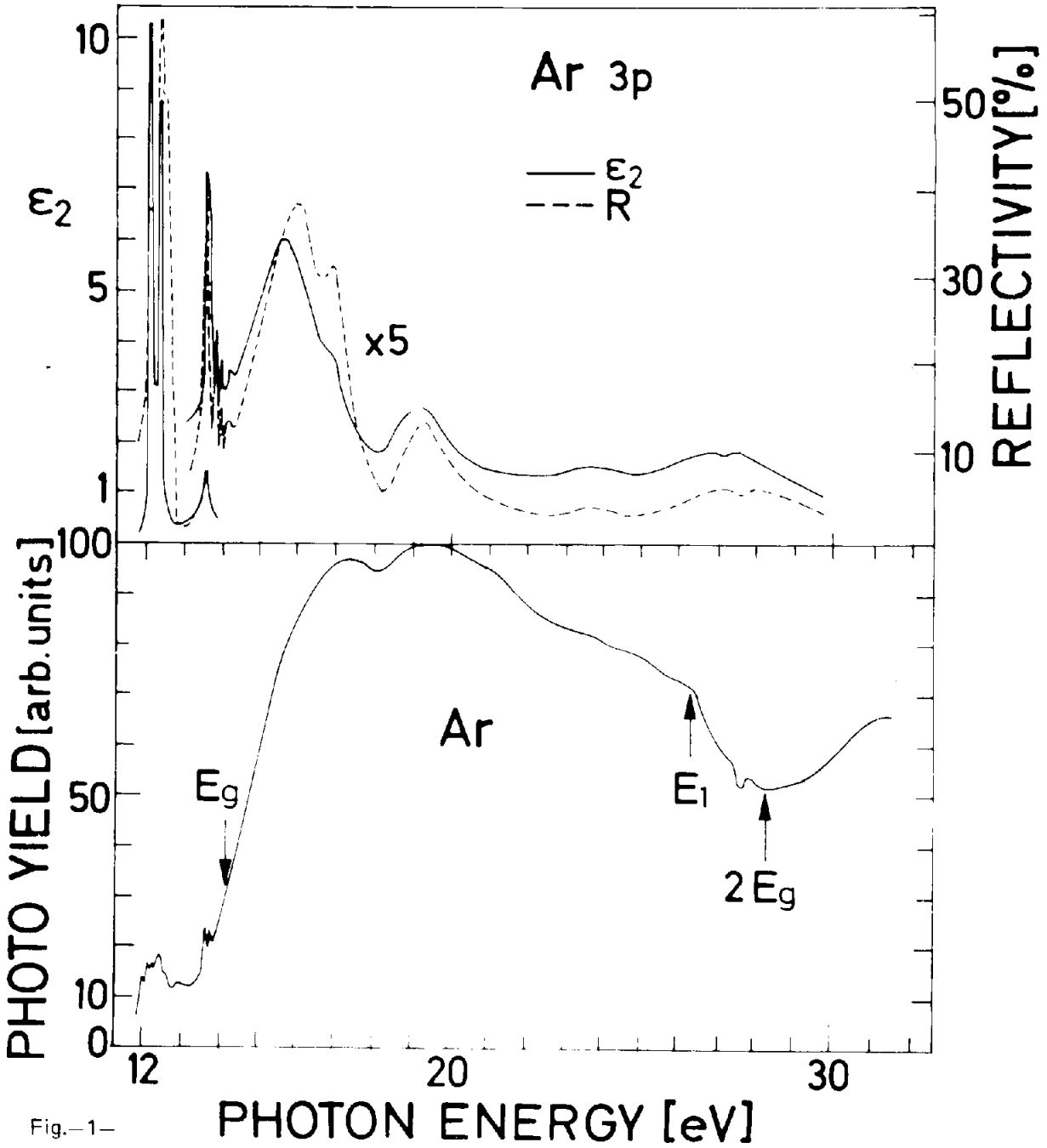
Figure Captions

Fig. 1 Upper half: reflection and ε_2-spectrum in the range of the 3p valence band excitation of solid Ar showing the exciton series and transitions at higher energies.

Lower half: relative photoyield per incident photon for solid Ar. The vertical bars mark the positions of the band gap E_g, $2\,E_g$ and the sum of the band gap and the energy of the first exciton $E_1 = E_g + E_x$. The maximum yield at 19.5 eV is estimated as 0.5 electrons per photon.

Fig. 2 The relative photoyield per incident photon for solid Kr and Xe. The vertical bars mark the positions of the band gap E_g, $2\,E_g$ and the sum of the band gap and the energy of the first exciton $E_1 = E_g + E_x$. The maximum yields are estimated as 0.6 and 0.5 electrons per photon for Kr and Xe respectively.

Fig. 3 Simplified scheme of energy levels relevant in photoemission from solid rare gases. V = top of the valence band, C = bottom of the conduction band, VL = vacuum level, Ex = excitonic levels, D = defect or impurity levels, E_g = gap energy, E_B = width of valence band, E_A = electron affinity, E = photon energy.


Ar 3p
ε2
R
x5
ε2
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5
1
50
30
10
100
50
10
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Eg
E1
2Eg
12
20
30
PHOTON ENERGY [eV]

Fig.—1—

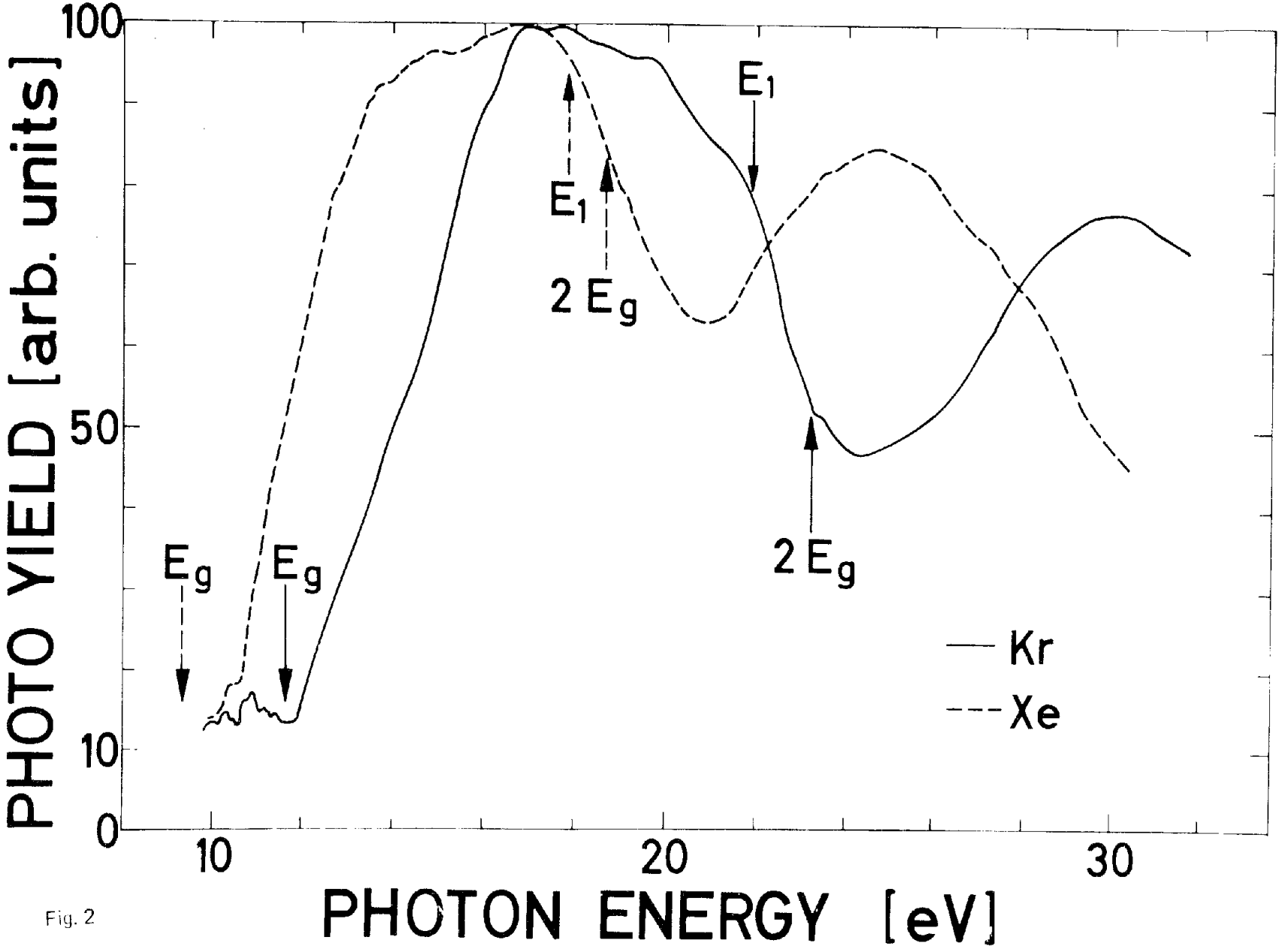
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Fig. 2

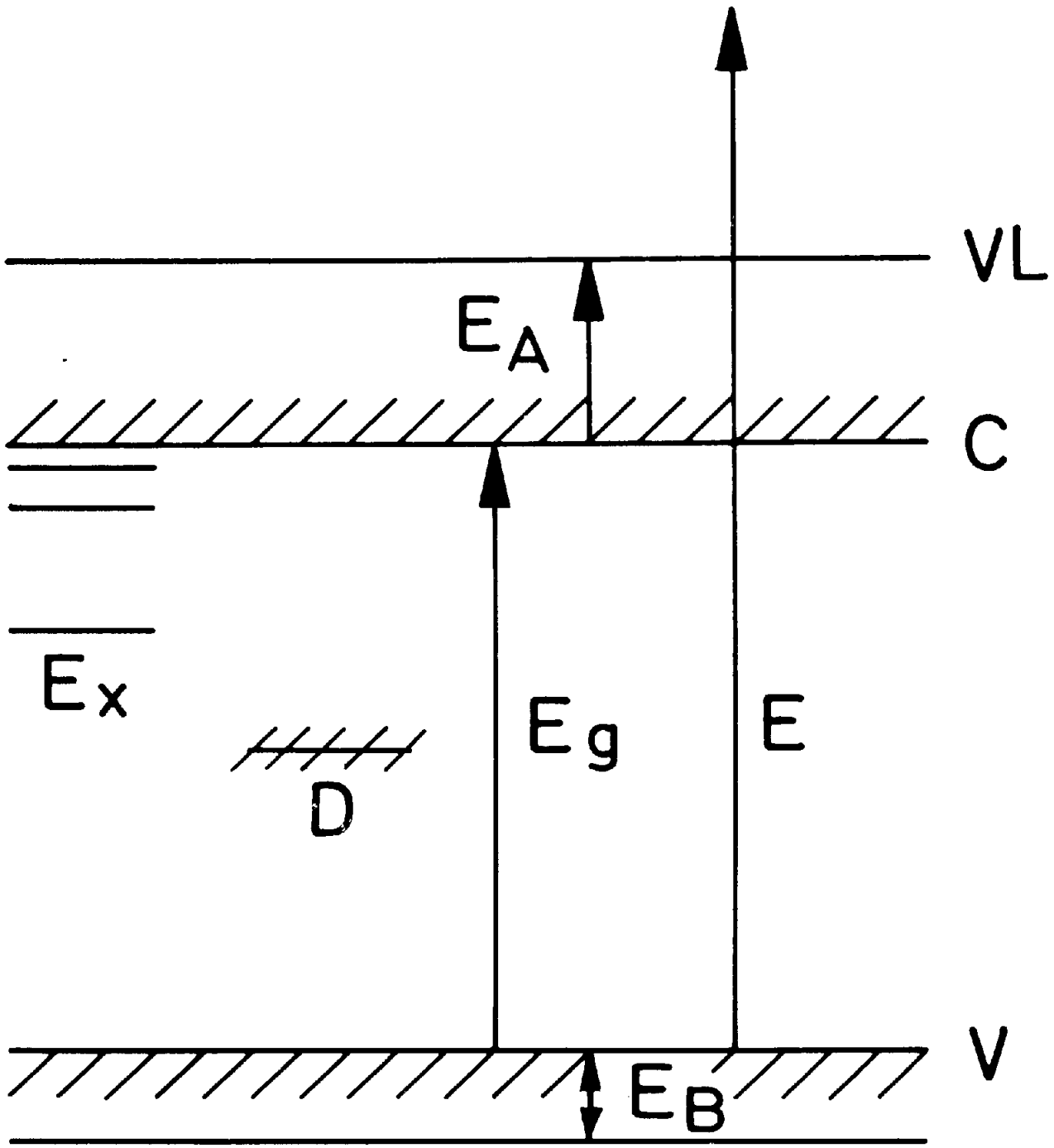

Fig. 3