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Influence of Electron-Electron Scattering on the Luminescence Quantum Efficiency in Solid Argon*

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The quantum efficiency of the intrinsic luminescence of solid Ar has been investigated for excitation energies between 15 eV and 55 eV. The spectral dependence of the quantum efficiency yields a stepwise increase with increasing excitation energies. The threshold energies for the steps closely correspond to the sum of the gap energy and multiples of the energy of the n = 1 exciton. The results are discussed in the framework of electron-electron scattering and give evidence that excitation of free electronic polaron complexes occurs in solid rare gases at higher excitation energies.

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In semiconductors and insulators, the energy loss rate of photoelectrons with sufficient excess energy, ΔE (measured from the bottom of the conduction band), is manily determined by electron-phonon and electron-electron scattering. In semiconductors[1], electron-phonon scattering is dominant for ΔE around and even somewhat above E_g (energy of the band gap). Electron-electron scattering gets only important for photoelectrons with $\Delta E \gg E_g$.

In insulators, due to the large value of E_g, electron-electron scattering may be already dominant for photoelectrons with $\Delta E \approx E_g$. In the case of f.c.c. solid rare gases we have the following special situation:

- The energy loss rate due to electron-phonon scattering is relatively small because optical phonons are absent and because acoustical phonon energies are very small ($\approx$ 5 meV[2]).
- The probability for electron-electron scattering should not be restricted seriously by momentum conservation arguments because the valence bands are very flat.

Therefore, solid rare gases are expected to be well-suited for the investigation of electron-electron scattering. Up to now, this process has been studied by photoelectron emission spectroscopy in solid Ar, Kr, and Xe[3]. The scattering length, L, of photoelectrons was obtained as a function of E[4]. L is very large (several houndred Å) for electrons with $\Delta E < E_{ex}$ (energy of the n = 1 exciton) and decreases rapidly to values below 10 Å for $\Delta E \gtrsim E_g$.

For some alkali halides[5,6] it was shown that photoluminescence can be influenced drastically by electron-electron scattering which leads to prominent structures in the excitation spectra. These structures are found at excitation energies corresponding to multiples of E_g.

In this paper, the influence of electron-electron scattering on the quantum efficiency, η, of photoluminescence of pure solid Ar is reported using the method of luminescence excitation spectroscopy. Ar layers (thickness ≈ 6500 Å) were condensed on a cooled substrate (temperature ≈ 5 K) in an UHV sample chamber (pressure $< 10^{-9}$ Torr). They were excited by monochromatic light (15 eV to 55 eV, band pass ≈ 1 Å). As light source, we used the electron storage ring, DORIS, Hamburg.
The luminescence light was analyzed by a second monochromator. The set up is similar to the one described in reference 7. In our samples only the intrinsic Ar luminescence band at $9.7 \sim 9.8$ eV showed up[8]. The intensity of this band was measured as a function of photon energy of exciting light and normalized to the excitation intensity (excitation spectrum). The excitation intensity was measured via conversion of the vacuum ultraviolet light to the visible by a sodium salicylate phosphor. Because the reflectivity of Ar is very small in the range of photon energy under consideration in this paper, the excitation spectra directly display $\eta(\hbar\omega)$ = (number of Ar luminescence photons)/(number of absorbed photons of energy $\hbar\omega$) in relative units.

In Fig. 1 typical results are presented. The most interesting feature of this curve is the stepwise increase of η towards higher excitation energies. The onset energies, E_m, of the steps are indicated in Fig. 1 by arrows and listed in table 1. At the present stage, no conclusions concerning the absolute increase of η around the steps m = 1,2,.. are possible for the following reasons :

(i) Solid rare gas luminescence is influenced by surface quenching[7], η being severely reduced if penetration depth of light is small. Between 15 eV and 55 eV, the penetration depth of light in solid Ar is increasing with increasing photon energy. This may contribute substantially to the general increase of the curve displayed in Fig. 1.

(ii) Due to the spectral distribution of the exciting light, the absolute values of the measured curve between the low energy part and the high energy part may be consistent only within ± 30%. The short range consistency is expected to be better than ±5%.

(iii) Measuring the intensity of exciting light it was assumed that the quantum efficiency of sodium salicylate is independent of excitation energy. For energies > 40 eV the quantum efficiency of sodium salicylate seems to decrease[10]. This decrease would influence the absolute value of our results for excitation energies > 40 eV but not change the qualitative behaviour.

The increase of η can be understood in the following way:
A photoelectron with $\Delta E \approx E_g$ (corresponding to an excitation energy $2\ E_g$) can be scattered inelastically at a valence electron and produce one additional electron-hole pair or exciton. The photoelectron itself is scattered hereby to a lower state in the conduction band or even to an excitonic state. In this way, finally two excitations are present per one absorbed photon.

For $\Delta E \approx 2\ E_g$ (corresponding to excitation energies $3\ E_g$) via electron-electron scattering three excitations can be obtained per absorbed photon etc.

From our measurements we can clearly deduce the character of the final (scattered) states at the threshold of the scattering process (either excitons or electron-hole pairs).

For this purpose, in table 1 the measured values of E_m are compared with threshold energies of some possible combinations of scattered states: two excitons, one exciton and one electron-hole pair, two electron-hole pairs etc. These thresholds are also indicated in Fig. 1. E_m closely corresponds to $E_g+m\cdot E_{ex}$. Therefore the scattered states at threshold must preferably be one electron-hole pair and m excitons.

Step m = 1 may be discussed in more detail. In Fig. 2, it is compared with the energy dependence of the scattering length for photoelectrons taken from reference 4. An excellent agreement between the increase of luminescence and the decrease of L (indicating an increase of scattering probability) is found. The small structures around 28 eV are connected to excitations of the Ar 3s core levels[11] and are beyond the scope of this paper. The broad maxima at 29.5 eV and 33.5 eV are probably caused by different quantum-efficiencies of the scattered states. Model calculations for the proof of this interpretation are carried out now.

Up to now, the influence of electron-electron scattering on luminescence was discussed in a temporary model with three steps (Fig. 3a):

(i) Initial excitation of an electron-hole pair.

(ii) The electron moves around the crystal.

(iii) The electron is scattered inelastically at a valence electron.

This interpretation may be problematic, if the scattering length for the photoelectrons is comparable to the lattice constant. In this case, the scattering process may take place at the initially excited atom itself.

In this case, an alternative interpretation of our data is possible in the framework of "electronic polaron complex" excitation, discussed by Devreese et al[12]. In Fig. 3b, the final (scattered) states of an optical transition to an excited state of the electronic polaron complex are scetched. They consist of an electron and a hole, both surrounded ("dressed") by an electronic polarization cloud, and an additional exciton. This exciton is a real quantum of the (exciton) boson field which couples to excess charges in insulators forming the electronic polaron (for details see reference 12).

From point of view of luminescence, the creation of electronic polaron complexes must lead to an enhancement of η because the final (scattered) states consist of an exciton + an electron-hole pair. Two different types of electronic polaron complexes are possible: in the bound complex the dressed electron is coupled to the dressed hole via Coulomb interaction; in the free complex, this Coulomb interaction is neglected. In the case of alkali halides the cross-sections for excitation of both complexes has been given in reference 12. The threshold for the free complex (E_g+E_{ex}) as well as its maximum ($E_g+1.2\ E_{ex}$) are predicted explicitely, whereas the cross-section for the bound complex is only an estimate. The cross-sections in solid rare gases should be very similar to the published ones for alkali halides[13], because the electronic polaron coupling constant is of the same size in both cases ($\alpha \approx .5$). In Fig. 2 the cross-sections for both complexes are scetched in analogy to the results in alkali halides[12]. The bound complex can be ruled out by comparison with our measurement because at its excitation energy there is no increase of photoluminescence. The free complex, however, corresponds very well to the increase of luminescence quantum efficiency.

The steps m = 2,3.. may be tentatively ascribed to electronic polaron complexes with m = 2,3.. emitted excitons in the final state. However, theoretical calculations of the cross-sections for such many body effects are necessary to confirm this interpretation.

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Figure Captions

Fig. 1 Excitation spectrum of the intrinsic Ar Luminescence band.

Fig. 2 Comparison of the excitation spectrum of the intrinsic Ar luminescence band with the spectral dependence of the scattering length for photoelectrons, the estimated cross-section for the bound (- - -) and free (▨) electronic polaron complex.

Fig. 3 Schematic representation of (a) electron-electron scattering of photoelectrons and (b) creation of electronic polaron complexes as shown in reference 12.

Caption of Table 1

Comparison of measured threshold energies, E_m, for the steps, m, in the excitation spectrum of the intrinsic Ar luminescence, with calculated threshold energies for electron-electron scattering into different final states. The values of the band gap, E_g, of solid Ar and of the energy of the n = 1 exciton, E_{ex}, have been taken from reference 9.

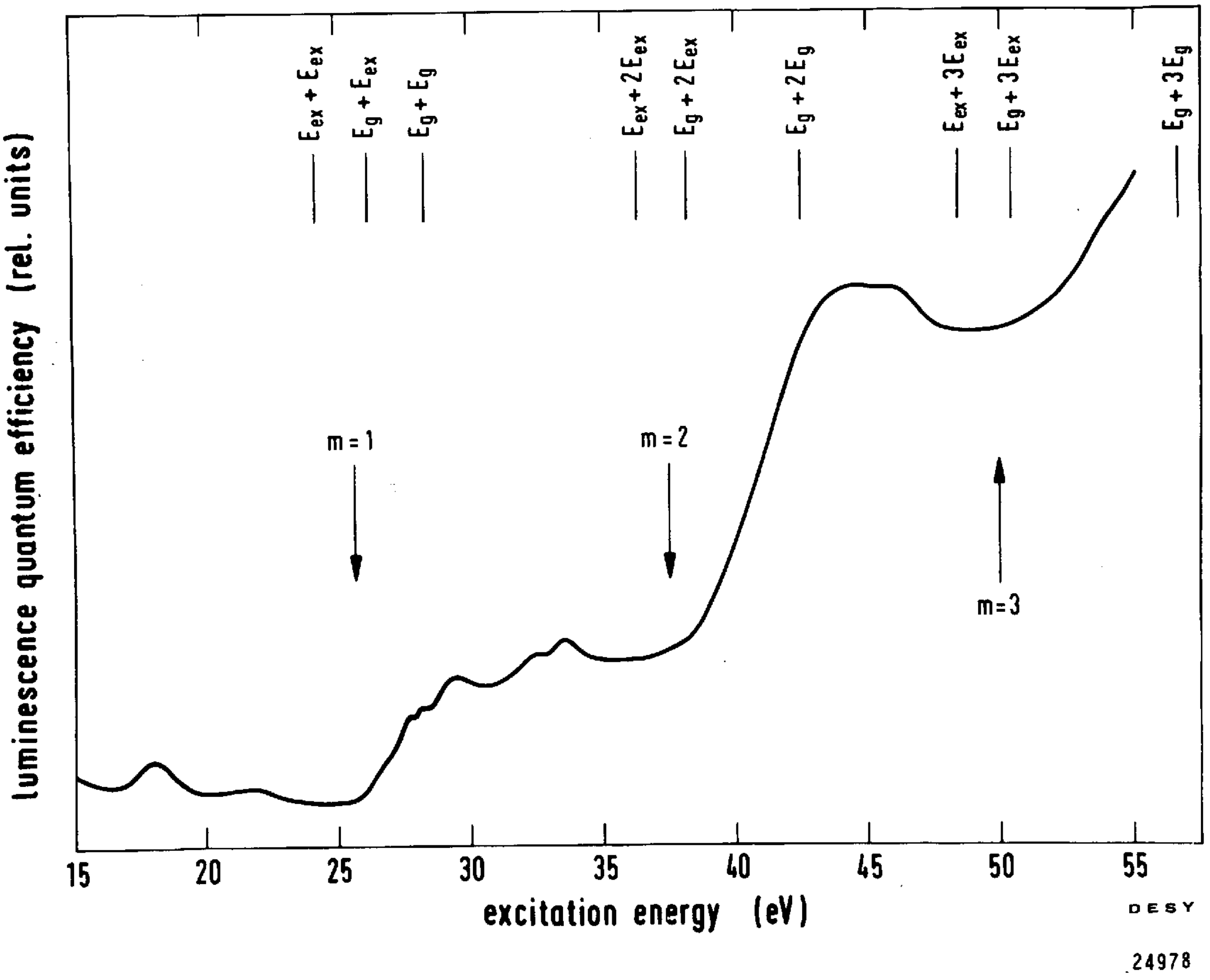
luminescence quantum efficiency (rel. units)
excitation energy (eV)
15
20
25
30
35
40
45
50
55
$E_{ex} + E_{ex}$
$E_g + E_{ex}$
$E_g + E_g$
$E_{ex} + 2E_{ex}$
$E_g + 2E_{ex}$
$E_g + 2E_g$
$E_{ex} + 3E_{ex}$
$E_g + 3E_{ex}$
$E_g + 3E_g$
m = 1
m = 2
m = 3
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Fig. 1

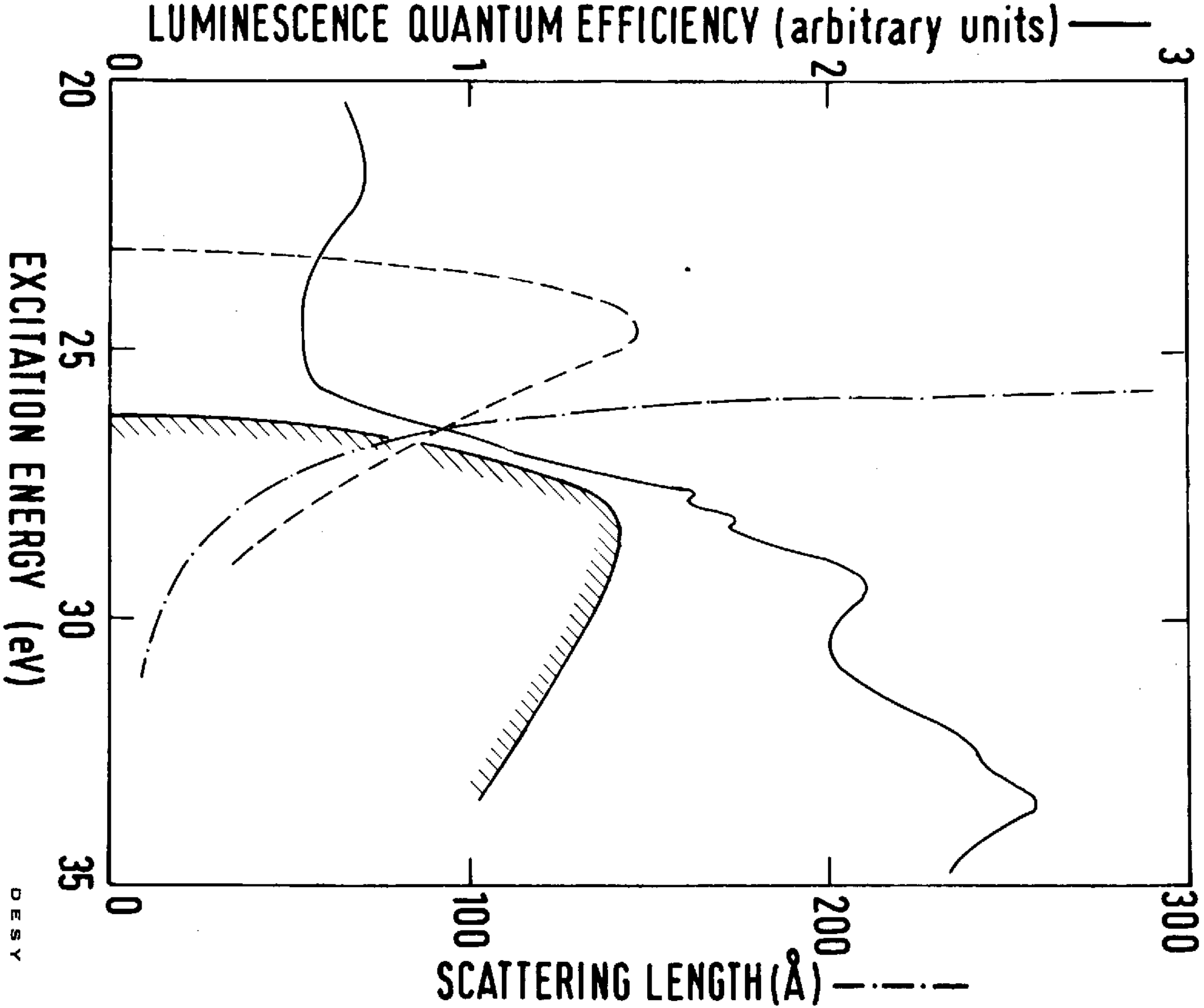
LUMINESCENCE QUANTUM EFFICIENCY (arbitrary units) ——
0
1
2
3
20
25
30
35
EXCITATION ENERGY (eV)
0
100
200
300
SCATTERING LENGTH (Å) —·—·—

Fig. 2

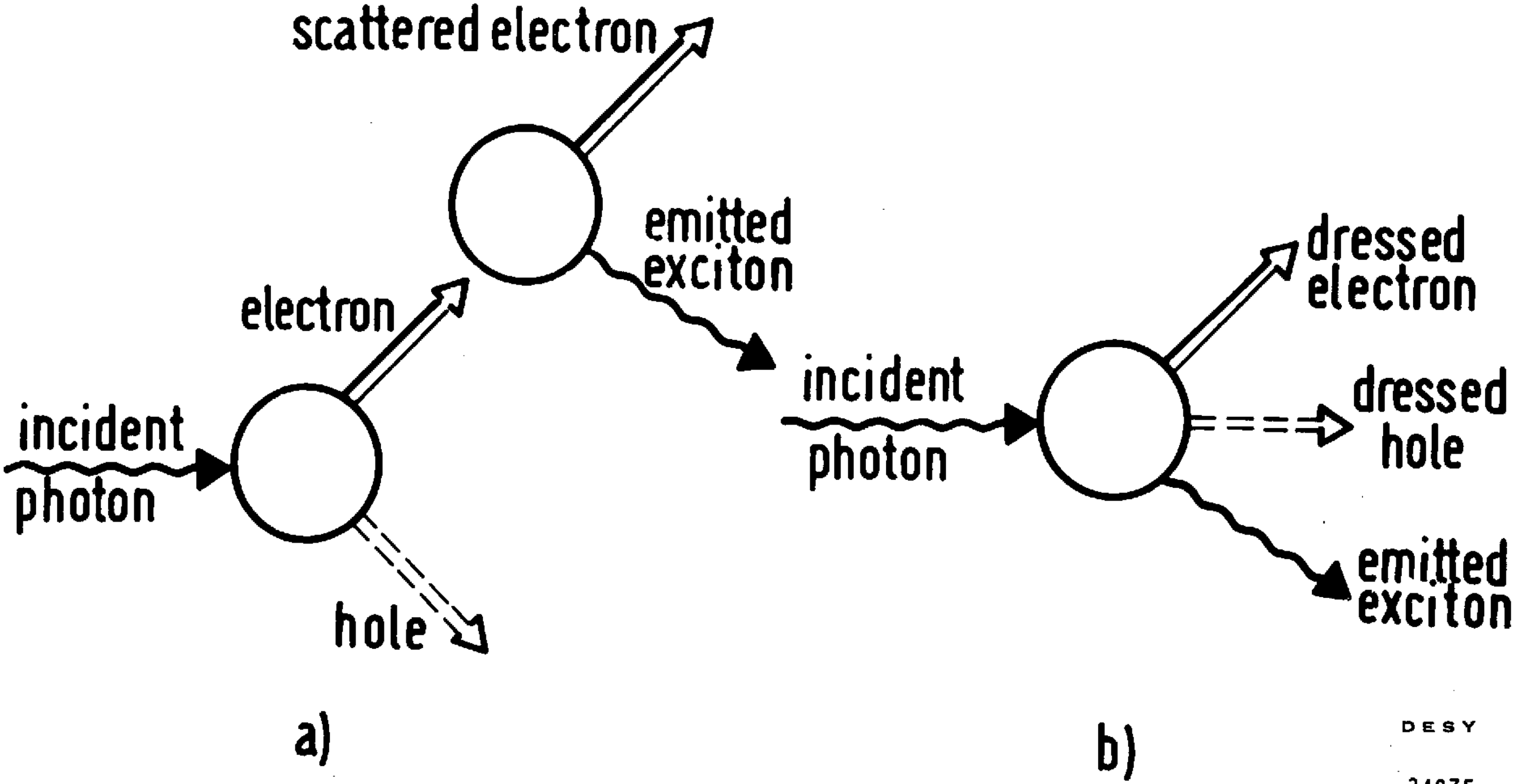

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Fig. 3

m	E_m (eV)	$E_{ex} + m \cdot E_{ex}$ (eV)	$E_g + m \cdot E_{ex}$ (eV)	$E_g + m \cdot E_g$ (eV)
1	25.5 ± 0.5	24.2	26.2	28.3
2	37.5 ± 1	36.3	38.3	42.5
3	50 ± 2	48.4	50.4	56.6

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Table 1