

Investigations on Diffuse Reflectance Spectra of V_2O_5 Powder

BÉLA KARVALY and IMRE HEVESI

Institute of Experimental Physics, József Attila University, Szeged, Hungary

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On the base of Schuster-Kubelka-Munk's theory, quantitative relations between the bulk absorption and diffuse reflectance spectra of undiluted and diluted semiconductor powder samples are established in the region of the long-wave tail of the absorption edge. Investigations in the long-wave region of the diffuse reflectance spectra of V_2O_5 , based on these relations, led to the result that in contradiction with earlier observations on single crystals^{7, 22, 27}, allowed direct optical transitions between valence band and conduction band do not seem to be excluded. Quantitative optical activation energies are obtained from diffuse reflectance spectra.

Introduction

The band gap width is one of the most important parameters of semiconductors. Though its value, apart from rare exceptions^{1, 2}, cannot be theoretically predicted, there exist, however, several experimental methods which yield the value with moderate accuracy. Most of these methods require relatively complicated equipments and the use of single crystals^{3, 4, 5}.

On the basis of qualitative considerations and experimental evidences, FOCHS⁶ suggested the use of diffuse reflectance spectra of powdered semiconductors for determining the band gap width and the long-wave limit of the absorption spectra of semiconductor materials. His results on powdered samples of Se, Si, Ge and CdS proved to be in good agreement with the results obtained using other methods. HEVESI^{7, 8} compared the values of the activation energy determined on V_2O_5 single crystals using FOCHS' method with diffuse reflectance measurements on powdered samples, and found satisfactory agreement. TANDON and GUPTA's investigations on Cu_2O and other samples^{9, 10} gave a

less satisfactory agreement as the earlier investigations mentioned above.

The modifications of the above method, suggested in the present paper, permit to find theoretical connections between the shape of the long-wave tail of the absorption edge and the shape of the diffuse reflectance spectra. On the basis of our measurements on powdered V_2O_5 samples, it may be expected that it will be possible to obtain further informations about the long-wave part of the absorption spectrum from its connections with the diffuse reflectance spectrum.

Theoretical Considerations

Several theories about the correlation between absorption spectra diffuse reflectance spectra of powdered solids are known^{11–17}. These theories (and the respective models) are apparently independent from each other, but it can be shown that there exist close connections between them¹⁸. Numerous investigations concerning the range of applicability of the different models were made, but the results published hitherto want further theoretical elaboration and experimental control^{13, 14, 17, 19, 20}.

Reprints request to Dr. BÉLA KARVALY, Institute of Experimental Physics, József Attila University, Szeged, Dóm tér 9. Hungary.

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In view of the fact that most of the extensive experimental work performed was concerned with SCHUSTER-KUBELKA-MUNK's theory¹⁹, the quantitative considerations of the present paper are also founded on this theory.

Let us consider a homodisperse, isotropically scattering, not too strongly absorbing powder sample of "infinite" thickness. Then, if the particle size is sufficiently (but not excessively) great compared with the wavelength of the incident radiation, the diffuse reflectance R_∞ of the sufficiently thick ("infinite") sample can be expressed with the optical parameters of the sample as follows¹⁹:

$$f(R_\infty) \equiv \frac{(1-R_\infty)^2}{2 R_\infty} = \frac{K^*}{s}, \quad (1)$$

where K^* is the so-called effective absorption coefficient of the sample proportional to (but not identical with) the true absorption coefficient K of the powder material, and s the so-called scattering coefficient independent from, or only slightly dependent on wavelength.

As it is well known²¹, the shape of the long-wave side of the absorption spectra of solids, expressed as a function of photon energy, differs according to whether the transition determined by the symmetry of the electron wavefunctions is allowed or forbidden. For allowed transitions

$$K_a \propto \frac{[h\nu - E_g]^{1/2}}{h\nu}, \quad (2)$$

whereas for forbidden transitions

$$K_f \propto \frac{[h\nu - E_g]^{3/2}}{h\nu}. \quad (3)$$

If K_a and K_f are not too great, then it follows from (1), using (2) and (3), that

$$[f(R_\infty) h\nu]^2 \propto (h\nu - E_g), \quad (4)$$

and

$$[f(R_\infty) h\nu]^{2/3} \propto (h\nu - E_g), \quad (5)$$

i. e. the intercepts of the straight lines determined by Eq. (4) in case of allowed transitions and by Eq. (5) in case of forbidden transitions will give the value of the band gap E_g .

However, in the region of the long-wave tail (and especially in its initial part) the low values of R_∞

may lead to significant inaccuracies in the measurements and consequently to uncertainties of the spectral dependence of R_∞ , which may influence the results of calculations. Therefore, it seems expedient to embed the semiconductor powder in a powder, colourless (without selective reflectance in the range of measurements) and not reacting chemically with the semiconductor (e. g. MgO, BaSO₄, TiO₂ etc.) and to measure the diffuse reflectance R_∞^* of the "diluted" sample.

It has been shown¹⁹ that, in this case, Eq. (1) can be written as

$$f(R_\infty^*) \approx \frac{\varepsilon c}{s}, \quad (6)$$

and so relations analogous to Eqs. (4) and (5) will hold for the diluted samples (here c means the concentration of the absorbing component in the diluted sample, ε its extinction coefficient at the quantum energy in question and s the scattering coefficient of the mixed sample).

Measurements and Results

For experimental checking of the relations mentioned above and the method suggested, it seemed desirable to choose as model a material the optical and semiconductor parameters of which had been determined and controlled with known accuracy. Therefore our experiments were performed with V₂O₅, studied in detail by HEVESI (for his researches on V₂O₅ single crystals see^{7, 22, 23}).

A double beam grating spectrophotometer Type OPTICA MILANO CF 4 DR with a reflectance attachment consisting of an ULBRICHT's sphere of 15 cm diameter was used for measuring the diffuse reflectance spectra. The linear dispersion of the monochromator unit was 1.6 nm/mm, the band width of the beam issuing from the monochromator did not exceed 0.6 nm in the range of measurements. The samples were put in sample holders 3 mm deep (to be considered practically as of infinite thickness).

A MgO layer, 1 mm thick, freshly smoked on a compressed MgO layer of 2 mm thickness, was used as reference standard; its reflectance was taken as corresponding to the mean of values found in literature^{24, 25, 26}. BaSO₄ powder of high purity was used for diluting the V₂O₅ powder. The concentration of V₂O₅ in the samples was 100, 10, 1 and 0.1 percent, respectively. To obtain sufficient homogeneity and

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reproducibility, the samples were mixed in a braying mortar till the changes in reflectance on further mixing did not exceed the inherent uncertainty of measurements.

Diffuse reflectance spectra of the pure and diluted V_2O_5 samples are shown in Fig. 1.

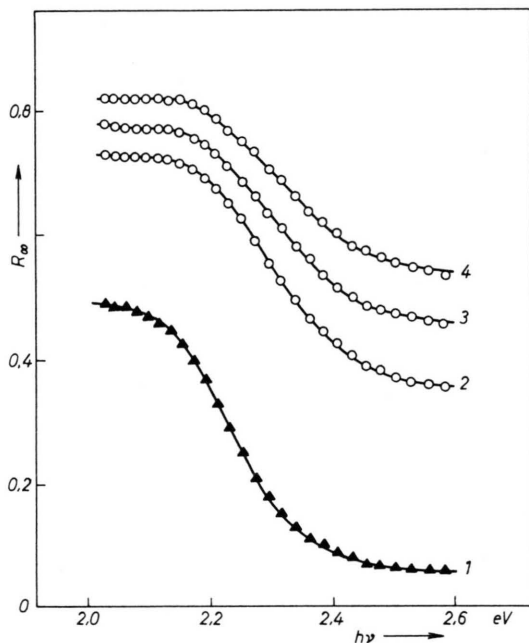


Fig. 1.

Discussion

As can be seen from Fig. 1, with decreasing concentration the reflectance spectra are shifted towards higher reflectance, which is more favourable for the measurements; at the same time they appear somewhat reduced along the ordinates. The dilution offers the advantage of higher accuracy of measurements; on the other hand it secures the elimination of the regular reflection superposed on the diffuse reflectance spectrum, which would be particularly disturbing in the spectral ranges of higher absorption and therefore of less reflectance.

This means that the influence of the long-wave tail on the diffuse reflectance spectra in diluted samples is presumably more correctly rendered by the shape of the diffuse reflectance spectra, than in the case of pure (undiluted) samples, especially in the critical range of the absorption edge.

It is evident from the derivation of Eqs. (4) and (5) and their analogon obtained using Eq. (6) that the scattering factors s connected with the particle

size of the powder sample is included in the proportionality factor omitted in the course of derivation. Therefore, in reasonable ranges of particle size and in spectral regions where the scattering coefficient is only slightly influenced by the wavelength or quantum energy, the results obtained with this method should be independent from particle size and dilution.

The functions $\lg f(R_\infty)$, calculated from the results shown in Fig. 1 using the relations Eqs. (1) and (6), are plotted in Fig. 2. As can be seen, in

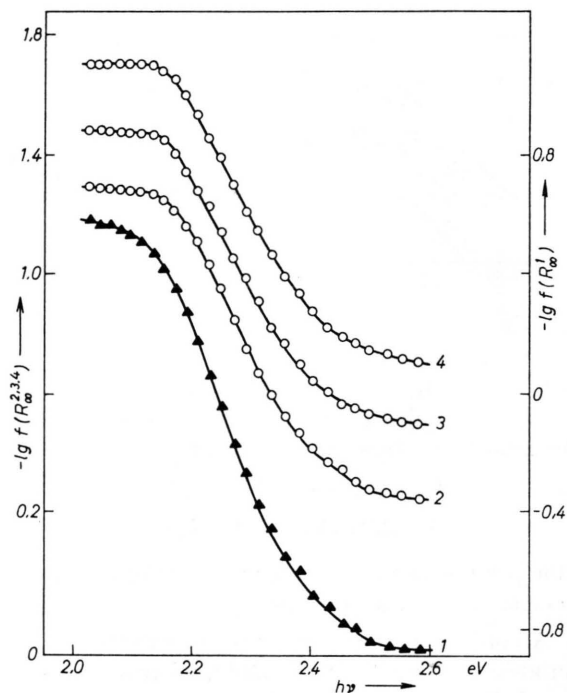


Fig. 2.

the energy range of interest, the functions $\lg f(R_\infty^*)$ for different dilutions can be brought into very good coincidence by parallel shifting in direction of the ordinates. This shows that in the range of absorption considered Eq. (6) holds, i.e. our basic suppositions are fulfilled. The curves of Eq. (4) for allowed direct optical transitions in case of undiluted samples, and those corresponding to the analogous equation

$$[f(R_\infty^*) h\nu]^2 \propto (h\nu - E_g) \quad (7)$$

valid for diluted samples are plotted in Fig. 3 (R_∞^* is the diffuse reflectance of the diluted powder sample). The parts of the curves corresponding to higher quantum energies can be represented by

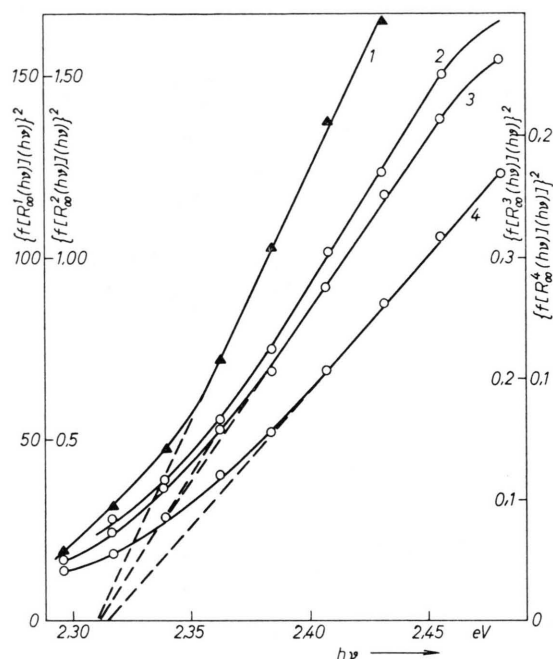


Fig. 3.

straight lines; extrapolating for zero energy, the band gap width E_g can be determined. In our case the following values were obtained:

$$\begin{aligned} E_g^{100} &= 2.31 \text{ eV}, & E_g^{10} &= 2.31 \text{ eV}, \\ E_g^1 &= 2.31 \text{ eV}, & E_g^{0,1} &= 2.32 \text{ eV} \end{aligned}$$

(the percentage of the V_2O_5 contained in the sample is denoted by the superscripts).

According to measurements of KENNY, KANEWURF and WHITEMORE²⁷ and of BODÓ and HEVESI^{7, 22} on single crystals the band gap width shows slight anisotropy and is different in the directions parallel (\parallel) with and perpendicular (\perp) to the c axis of the crystal:

	KENNY et al.	HEVESI
E_g^{\parallel}	2.34 eV	2.30 eV
E_g^{\perp}	2.36 eV	2.32 eV.

The method suggested above evidently gives only mean values of the band gap width. A comparison of our results with those obtained by KENNY et al. and HEVESI shows very good agreement, independently from the concentration of the samples. This proves the usefulness of the method.

²⁷ N. KENNY, C. R. KANEWURF, and D. H. WHITEMORE, J. Phys. Chem. Solids **27**, 1237 [1966].

Fig. 4 contains curves based on the supposition of forbidden direct electron transitions calculated using Eq. (5) for undiluted samples and the analogous relation,

$$[f(R_{\infty}^* h\nu)^{2/3} \propto (h\nu - E_g) \quad (8)$$

for diluted samples. Each curve shows slight inflections, therefore it is difficult to find an unequivocally fitting straight line. The intercepts of

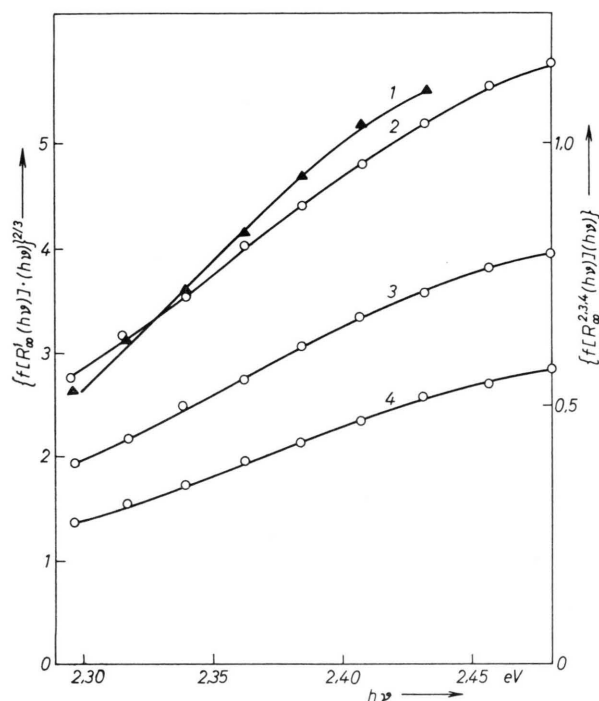


Fig. 4.

the straight lines fitted to the ranges which can be taken as approximately linear show rather high deviations and are not in accordance, even approximately, with the results obtained with single crystals.

Comparing with what has been said in connection with Figs. 3 and 4, the supposition of forbidden direct electron transitions (i.e. the validity of the "3/2-law") seems not to be confirmed by the diffuse reflectance measurements. The possibility of allowed direct transitions does not seem to be excluded. This is in contradiction with the results of KENNY et al.²⁷ and HEVESI^{7, 22} for single crystals, according to which a mechanism corresponding to forbidden direct optical transitions can be inferred on the basis of the analysis of the absorption edge; although, as point-

ed out by KENNY et al., the absorption coefficient plotted according to both the "1/2-law" and "3/2-law" give curves in which well defined linear sections can be found. Thus it seems difficult to decide about the mechanism of the optical transitions on the basis of results obtained with single crystals. At the same time, the data for the band gap width quoted from the papers of KENNY et al. and HEVESI were obtained with the supposition of forbidden direct transitions. The results of transmission measurements on thin single crystals in the region of the long-wave tail of the absorption edge are relatively inexact due to the comparatively high transmission values. Therefore, the true mechanism cannot be unequivocally secured. Further investigations seem necessary to throw more light on this contradictory situation.

Studying the long-wave tail of the absorption edge of some solids, the absorption coefficient K was found to present an exponential dependence on energy and on inverse temperature in a certain range of these parameters (URBACH's rule). According to the measurements of BODÓ and HEVESI²² on V₂O₅ single crystals the relation

$$K = K_0 \exp(\beta h \nu / k T) \quad (9)$$

holds, where K_0 means a constant, k is BOLTZMANN's constant, T the absolute temperature and β a constant about 1/2. Accordingly, it is to be expected

that, on the basis of Eqs. (1) and (6), in a certain spectral range in the region of the long-wave tail, the following two relations will be fulfilled:

$$\lg f(R_\infty) \propto \beta h \nu / k T, \quad (10)$$

$$\lg f(R_\infty^*) \propto \beta h \nu / k T, \quad (11)$$

i. e. $\lg f(R_\infty)$ should be a linear function of the quantum energy $h \nu$. As can be seen in Fig. 2, this linearity is well fulfilled in the quantum energy range from 2.2 eV to 2.34 eV; this confirms the validity of URBACH's rule (from the energetic point of view). From Eqs. (10) and (11) also the value of parameters β can be determined, namely

$$\beta = k T \frac{\Delta \lg f(R_\infty)}{\Delta (h \nu)} = k T \frac{\Delta \lg f(R_\infty^*)}{\Delta (h \nu)}. \quad (12)$$

For the slope of the linear section a value of about 0,24 was obtained, independently from concentration, against 0,47–0,52 given for single crystals^{7, 22, 27}. For the time being there are not sufficient experimental and theoretical results to understand this deviation. We should like to point at our earlier experimental results²⁰ according to which in case of powder samples consisting of particles of small optical thickness, the function $f(R_\infty)$ is not a linear function of the quotient (K^*/S) , as supposed in Schuster-Kubelka-Munk's theory.

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