VALIDITY OF URBACH'S RULE FOR THE ABSORPTION EDGE OF V_2O_5

By

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The transmission of V_2O_5 single crystals was measured and the absorption was calculated in a wavelenght range corresponding to the long wave tail of the absorption edge, at temperatures between 90 and 670 °K. The results were analysed in terms of Urbach's rule and the respective parameters were estimated. It could be stated that Urbach's rule is reasonably well fulfilled for temperatures higher than 390 °K. The estimated values of the parameters are in good accordance with the band gaps and absorption constants calculated from the short wavelenght part of the absorption edge.

1. *Introduction*

The character of the absorption edge of V_2O_5 single crystals has been the object of several investigations [1—7]. According to the results of these analyses, it seems plausible that the absorption edge is connected with direct forbidden transitions from the valence band to the conduction band. On the base of this supposition, the band gap E_g was calculated with the formula $K^{2/3} \sim (\hbar\omega - E_g)$, where K is the absorption constant and $\hbar\omega$ the photon energy. These results were confirmed by the values obtained from diffuse reflexion of V_2O_5 powder [3].

It has to be remarked, however, that contrary to the transitions in single crystals, investigations on the reflexion spectra of V_2O_5 powders of different particle size seem to support the supposition of direct allowed transitions [4].

Further information concerning the character of interactions of light with the crystals studied and the type of transitions can be obtained from the long wave tail of the absorption edge. At lower photon energies, the shape of the absorption edge is different from that corresponding to the potence law quoted above. In the investigations of [1] and [2] it was found that the long wave tail of V_2O_5 single crystals shows an exponential dependence on the photon energy and on the inverse of the absolute temperature, respectively, and obeys Urbach's rule expressed by the relation

$$K = K_0 e^{-\sigma \frac{E_0 - \hbar\omega}{k\Theta}}; \tag{1}$$

σ, E_0 and K_0 are constant or weakly temperature dependent; σ is a parameter of order unity, the dependence of wich on temperature can be expressed by the formula

$$\sigma = \sigma_0 \frac{2k\Theta}{\hbar\omega_p} \tanh \frac{\hbar\omega_p}{2k\Theta}, \tag{2}$$

where σ_0 is a constant and $\hbar\omega_p$ is the phonon energy.

Urbach's rule was found to hold for several insulators and semiconductors; however, no satisfactory and generally valid theoretical explanation of the rule could be given up to now. Therefore it appears justified to collect further experimental material on a broader basis, besides trying to find adequate theoretical models.

The aim of the present paper is to account on measurements concerning the validity of Urbach's rule in a wider temperature range and to estimate the values of the parameters in Eq. (1).

2. *Experimental method*

For determining the absorption contants in the wavelength range corresponding to the long wave tail of the absorption edge, V_2O_5 single crystal plates of different thicknesses were used. In this spectral range and with the thicknesses employed, interference could not be observed and we could calculate with the relation $T=(1-R)^2e^{-Kd}$ where, T is the transmission, R the reflectivity and d the thickness of the plate. The methods of growing the single crystals and preparing the samples, as well as the devices used for transmission measurements are described in a previons paper [8] of one of the authors. The transmission of the crystal plates cut in the (010) plane was measured with two different conditions of polarization ($\mathbf{E}\|c$, and $\mathbf{E}\perp c$ *i.e.* $\mathbf{E}\|a$). The temperature of the crystal was varied from 90 to 670 °K. For producing low temperatures, a cryostat cooled with liquid nitrogen was used. At temperatures exceeding 570 °K, the temperature radiation of the samples was taken into account. Inhomogeneities of the samples were eliminated by taking the average of measurements made on numerous samples. The accuracy of the measurements of transmission and of sample thickness exceeds that permitted by the errors caused by inhomogeneities of the samples.

3. *Results*

Using samples of suitable thickness, it was possible to measure the temperature dependence in the spectral range corresponding to the long wavelength tail of the absorption edge. Figs. 1 and 2 show the wavelength dependence of the transmission at different temperatures Θ for two crystal plates of different thickness under the conditions of polarization mentioned above. The values of K were calculated by comparing the transmissions of similar pairs of plate thicknesses, according to the relation given for the connection between transmission and absorption in Section 2. The curves $T^{\|}(\Theta)$ and $T^{\perp}(\Theta)$, illustrating the temperature dependence of transmission for different wavelengths, were calculated from similar pairs of curves (see Figs. 3

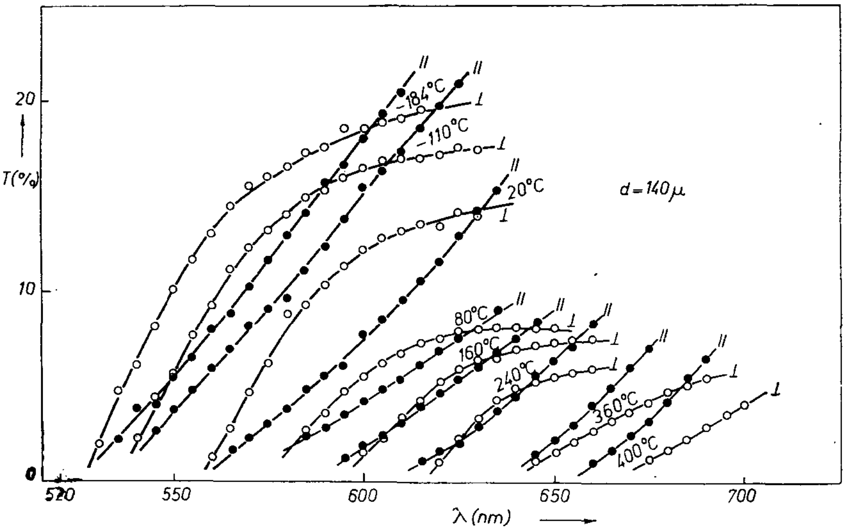

Fig. 1. Dependence on wavelength of the transmission of V_2O_5 single crystals of 140 μ thickness at different temperatures, for ∥ and ⊥ polarization

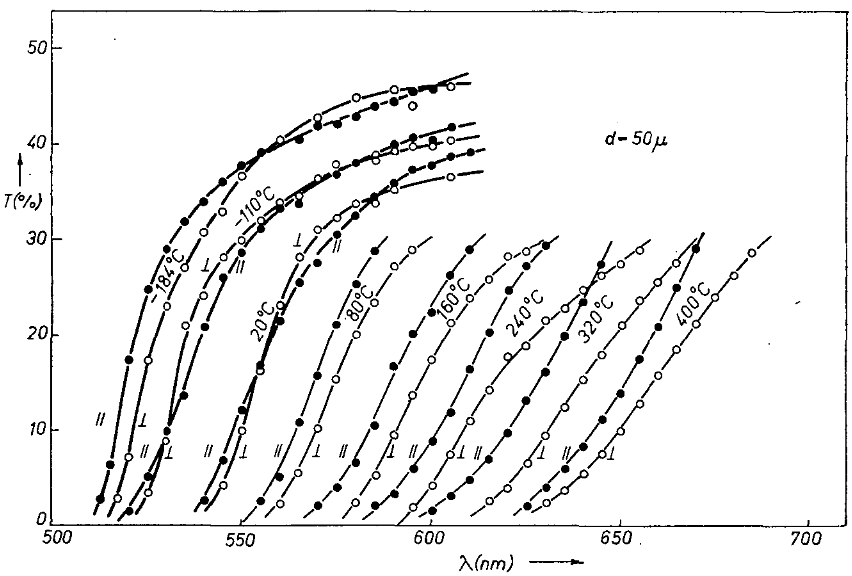

Fig. 2. Dependence on wavelength of the transmission of V_2O_5 single crystals of 50 μ thickness at different temperatures, for ∥ and ⊥ polarization

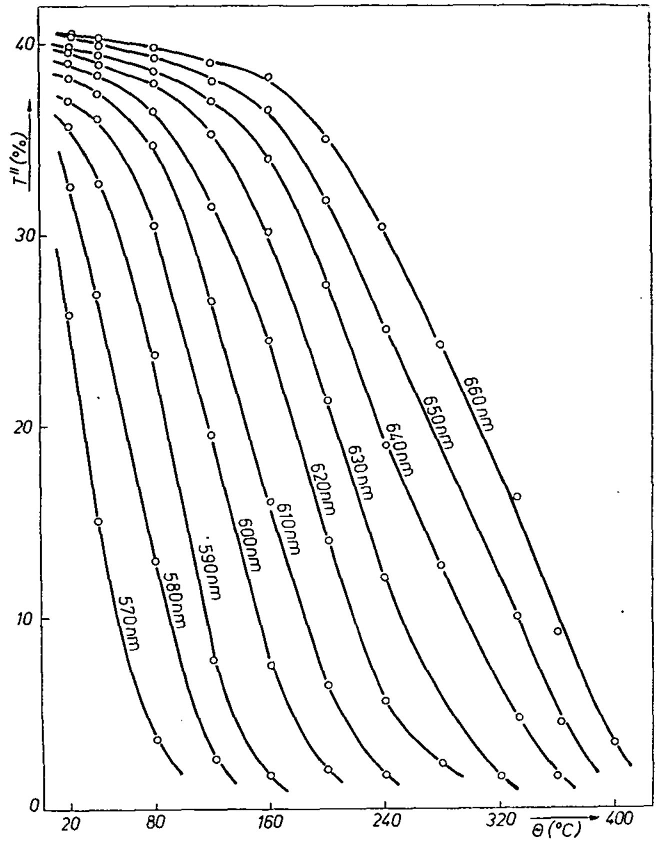

Fig. 3. Dependence on temperature of the transmission at different wavelengths for ∥ polarization

and 4). The values of $T(\Theta)$ were determined from the temperature dependence of the refractive index n (through the relation $T_0=(1-R)^2$), of the sample thicknes d, and of the absorption constant K:

$$\frac{dT}{d\Theta}=\frac{\partial T_0}{\partial\Theta}e^{-Kd}-T\frac{\partial d}{\partial\Theta}K-T\frac{\partial K}{\partial\Theta}d. \tag{3}$$

Supposing that the contribution of the first and second terms of the equation is less important, and the dependence of the absorption coefficient on photon energy and on the inverse of Θ is exponential, a linear dependence of K on $\frac{\Theta^2}{T}\cdot\frac{dT}{d\Theta}$ should result. The validity of this supposition is shown by Figs. 5 and 6, where the linear

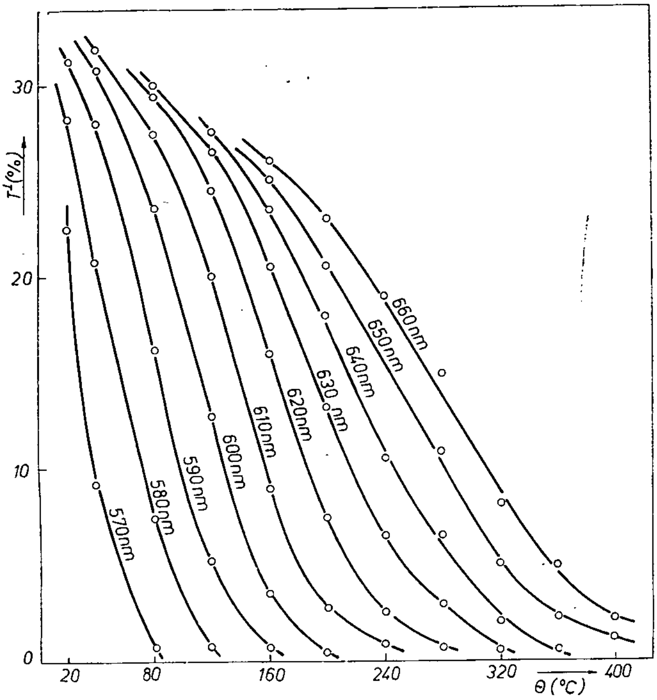

Fig. 4. Dependence on temperature of the transmission at different wavelengths for ⊥ polarization

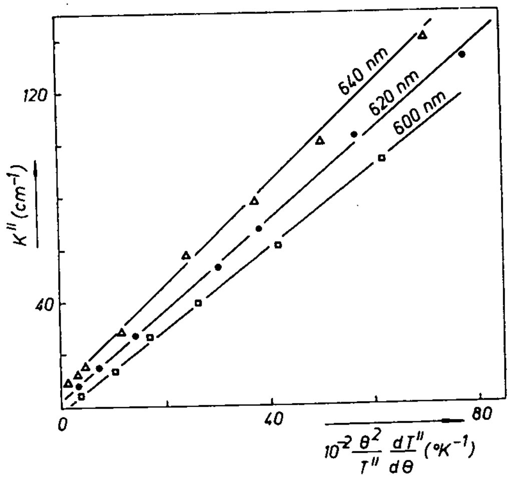

Fig. 5. Dependence of $K^{\parallel}$ on $\frac{\Theta^2}{T^{\parallel}}\frac{dT^{\parallel}}{d\Theta}$ for three different wavelengths

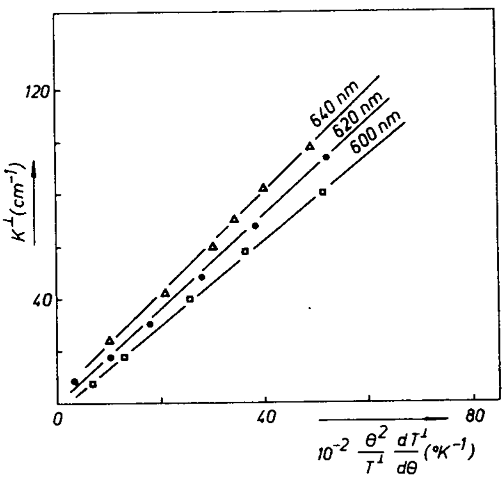

Fig. 6. Dependence of $K^{\perp}$ on $\frac{\Theta^2}{T^{\perp}}\frac{dT^{\perp}}{d\Theta}$ for three different wavelengths

character of the curves and the slopes increasing with wavelength support our supposition.

In Fig. 7, curves of $\ln K$ *vs.* $h\nu$ are shown for several temperatures. In the range of photon energies shown in the figures, the curves are of linear character and their

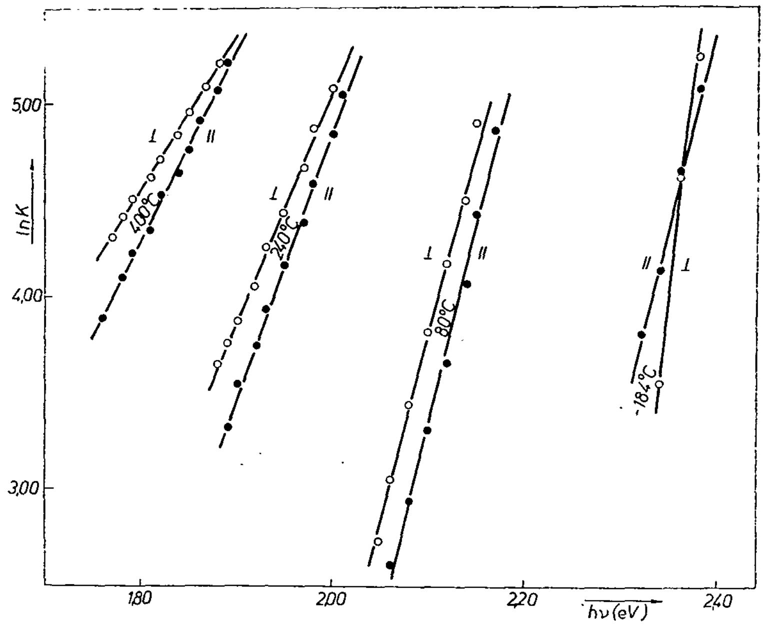

Fig. 7. Dependence of $\ln K$ on photon energy at different temperatures for ∥ and ⊥ polarization

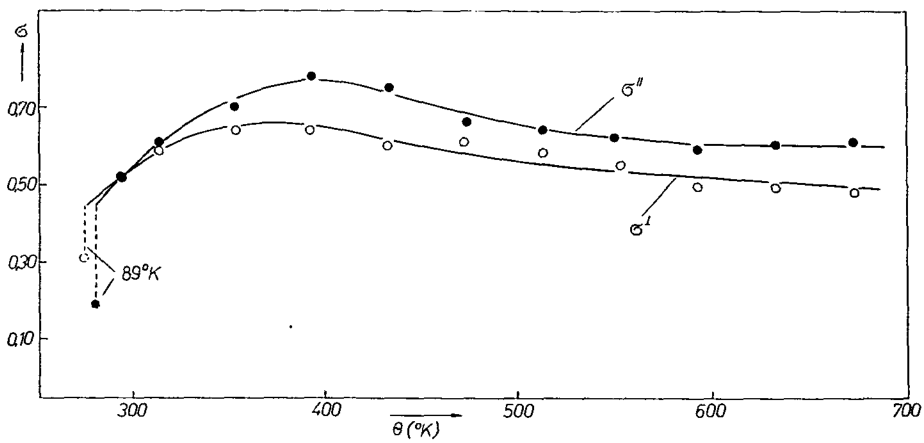

Fig. 8. Temperature dependence of $\sigma^{\parallel}$ and $\sigma^{\perp}$

slopes decrease with increasing temperature. The curves of $\sigma^{\parallel}(\Theta)$ and $\sigma^{\perp}(\Theta)$ calculated from these slopes are presented in Fig. 8. It can be seen that up to about 390 °K, the values of σ change with the temperature; at higher temperatures, both $\sigma^{\parallel}$ and $\sigma^{\perp}$ become constant. For deep temperatures, only the values corresponding to 89 °K, marked in the figure, were calculated. Some calculated values of σ are listed in Table I.

Table I

Values of the Parameters in Urbach's Rule for ∥ and ⊥ Polarization

Θ (°K)	σ		E_0 (eV)		K_0 (cm^{-1})		$\hbar\omega_p$ (meV)	
	∥	⊥	∥	⊥	∥	⊥	∥	⊥
89	0.19	0.31						
313	0.61	0.59						
393	0.78	0.64	2.49	2.54	$1.3\cdot10^5$	$2.3\cdot10^5$	49	47
513	0.64	0.58						
633	0.60	0.49						

In Figs. 9 and 10 the values of $h\nu$ and Θ pertaining to the same values of the absorption coefficient are shown. Values of E_0 and K_0 estimated from these curves are also given in Table I. The values of $E_0^{\parallel}$ and $E_0^{\perp}$ extrapolated from the straight portions of the curves pertaining to the same absorption coefficient (2.54 ev and

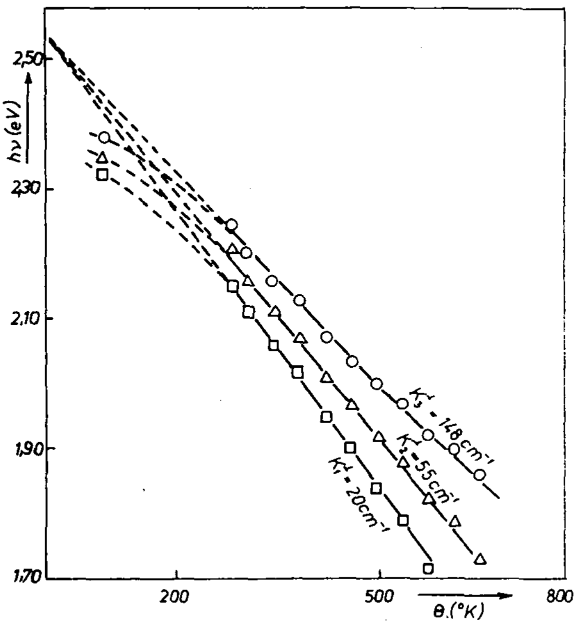

Fig. 9.
Values of $h\nu$ and Θ pertaining to the same values of $K^{\perp}$

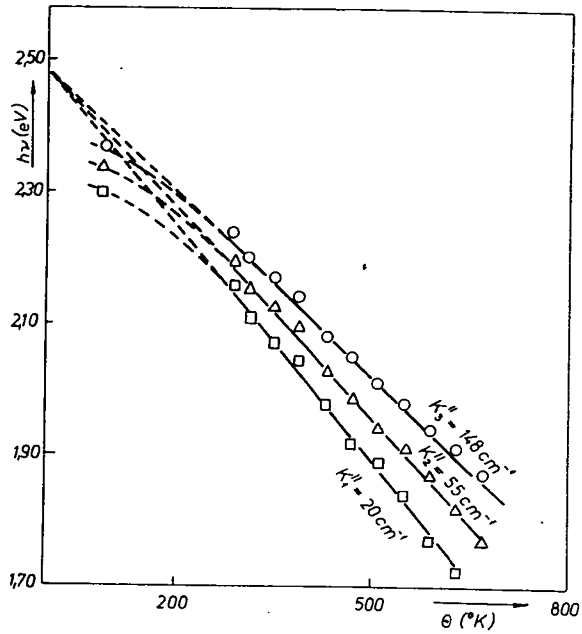

Fig. 10. Values of $h\nu$ and Θ pertaining to the same values of $K^{\parallel}$

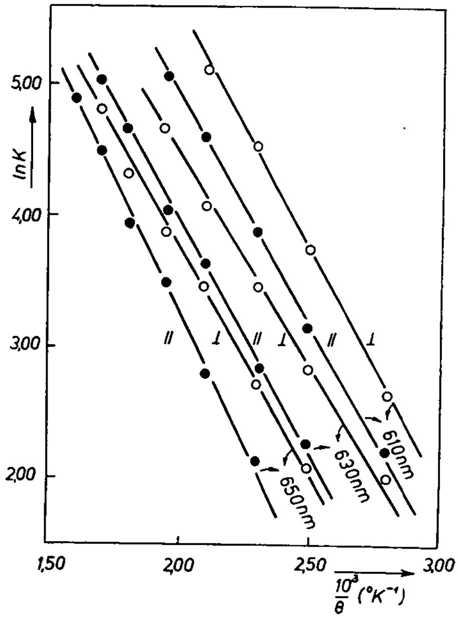

Fig. 11. Dependence of ln$K$ on $\frac{1}{\Theta}$
at the same wavelengths for ∥ and ⊥ polarization

2.49 eV, respectively, see Table I) are in good agreement with the band gaps at room temperature calculated supposing forbidden direct transitions. The calculated average values of $K_0^{\parallel}$ and $K_0^{\perp}$ ($1.3 \cdot 10^5\,\mathrm{cm}^{-1}$ and $2.3 \cdot 10^5\,\mathrm{cm}^{-1}$, see Table I) are consistent with those pertaining to regions of higher energy of the absorption edge. It can be stated that the estimations of the parameters in Urbach's rule fit well to results of other optical measurements published in literature.

The values of $\ln K$ are plotted *vs.* $1/\Theta$ in Fig. 11. It can be seen that the plots are straight and their slope for the same type of polarization in nearly the same.

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К ПРОВЕРКЕ ПРАВИЛА УБРАХА У КРАЯ ПОГЛОЩЕНИЯ V_2O_5

Н. Т. Кванг и И. Хевеши

Измерено пропускание и вычислено поглощение монокристалла V_2O_5 в области длин волн, соответствующей длинноволновой стороне края поглощения в интервале температур от 90 °K до 670 °K. Результаты были анализированы на основе правила Убраха, и были оценены соответствующие параметры. Установлено, что при температурах выше 390 °K хорошо выполняется правило Убраха. Оцененные значения параметров находятся в хорошем согласии с полученными данными по измерению ширины зон и коэффициента поглощения в коротковолновой части края поглощения.