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SELECTIVE ELECTRON EMISSION FROM F-CENTERS IN CsCl

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Résumé. — Les émissions photoélectrique et thermoélectrique ont été appliquées pour étudier les aspects du dégagement des électrons à partir des centres F dans CsCl. La courbe de photoémission coïncide parfaitement avec la bande d'absorption F. La sélectivité spectrale indique que la photoabsorption a lieu seulement à l'état excité du centre F tandis que la délocalisation et l'éjection d'électrons à partir de la surface sont effectuées par énergie thermique. Le blanchissement de la bande d'absorption F et la trempe de l'émission photoélectronique correspondante sont accrus par ionisation thermique des centres F. Un pic d'émission thermique spécifique est observé à 360 K, dû aussi aux centres F. L'énergie d'activation thermique correspondante est égale à 0,95 eV et le facteur de fréquence à 10^{12} s^{-1} . La différence avec l'énergie d'activation optique ($\approx 2,3 \text{ eV}$) est expliquée par le principe de Franck-Condon.

Abstract. — Photoelectron and thermal electron emission have been applied to investigate the features of electron release from F-centers in CsCl. The photoemission curve perfectly coincides with the F-absorption band. The spectral selectivity indicates photoabsorption to the excited state of the F-center only whereas the delocalization and ejection of electrons from the surface is effected by thermal energy. Bleaching of the F-absorption band and quenching of the corresponding photoelectron emission is enhanced by thermal ionization of the F-centers. A specific thermal emission peak at 360 K is observed which also can be ascribed to F-centers. The corresponding thermal activation energy is computed to be 0.95 eV with an effective frequency factor of 10^{12} s^{-1} . The difference to the optical activation energy ($\approx 2.3 \text{ eV}$) is explained by the Franck-Condon principle.

1. Introduction. — Recent reactivation of early investigations of electron emission from CsCl [1] covers the stationary electron ejection from valence states [2] as well as the decaying emission from localized F-center states [3], [4]. Special applications of electron storage in CsCl F-centers have been proposed for image storage devices [5]. After photon impact the F-electrons are generally emitted in a nonselective process [6]. An additional selective photoemission coincident with the optical absorption band is observable at materials with a sufficiently small electron affinity. By thermal stimulation following photoresonance absorption, F-electrons are released from the excited state into the conduction band and then ejected from the surface thermally [7]. This kind of photothermal emission is the subject of this paper with special regard to the influence of increasing temperature. Moreover, thermal stimulation causes a specific dark emission depending on pre-illumination in the F-band and permitting the determination of the activation energy of the thermal ionization of F-centers in CsCl in comparison with the optical activation energy.

2. Experimental. — The polycrystalline samples were prepared by cold-pressing disks of 10 mm diameter and 1 mm thickness from CsCl powder material (Merck, suprapur). By plastic deformation this pro-

cedure introduces a large amount of anion vacancies [8]. We observed that the electron emission of the pressed samples was much higher than that of the powders used for pressing. To avoid charging we added inactive graphite powder excepting those samples we used for optical absorption measurements.

F-centers were formed at room temperature by X-ray exposure using voltages between 7 and 15 kV. The electron emission was detected by means of a methane flow counter; the complete experimental equipment has been already described elsewhere [9]. Linear heating of the sample was performed by a constant rate of 0.7 K s^{-1} . The temperature was measured at the surface of the sample by means of a differential method [10].

3. Results and discussion. — **3.1 OPTICAL ABSORPTION AND SELECTIVE PHOTOELECTRON EMISSION.** — Starting the experiments we first reproduced the well known F-absorption band of CsCl. The absorption peak is located at 605 nm, figure 1a. By increasing the temperature from 300 K to 340 K the peak is shifted to 620 nm and the half-width increases evidently. In comparison, figure 1b demonstrates the spectral distribution of the selective photoelectron emission which nearly perfectly coincides with the F-absorption band. Peak location, temperature-induced peak shift and F-band broadening are

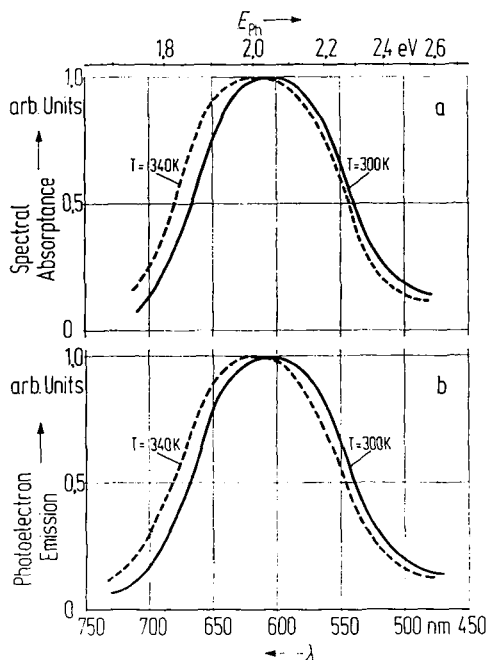


FIG. 1. — Spectral distribution of absorbance a) and photoelectron emission b) at 300 K and 340 K.

common features and indicate the identical F-center origin of both effects. Structures that have been found in CsCl absorption spectra at low temperatures [11] and in recent photoemission studies [5], could not be resolved in our measurements.

The congruence of the experimental curves in figure 1a and 1b means that the ordinary nonselective photoelectric effect which we found to be increasing in the short wavelength region (not drawn in Fig. 1, see [9]) is present in the F-band region as a background emission only. In comparison to the electron transitions from the ground to the first excited state of the F-center, the complicated thermal emission is a process of secondary importance. On the other hand, thermal ionization after optical excitation leads to the decay of F-centers (optical bleaching). This effect is only small at optical irradiances usually applied.

Much more effective is the ionization of F-centers by thermal energy (thermal bleaching). With the optical absorbance at the 605 nm absorption peak as a measure for the F-center concentration, figure 2 shows the F-center decay at a constant heating rate of 0.7 K s^{-1} . At 450 K nearly all F-centers initially present are bleached.

3.2 TEMPERATURE DEPENDENCE OF PHOTOELECTRON EMISSION. — Considering optical transitions, the photoelectron emission curve under the conditions given above should be similar to the thermally bleached optical absorption curve of figure 2. Actually, the thermal decay of the photoelectron emission rate, given in figure 3, is superimposed by 3 peaks which become prominent if the optical irradiance is reduced. Even without any illumination an electron emission

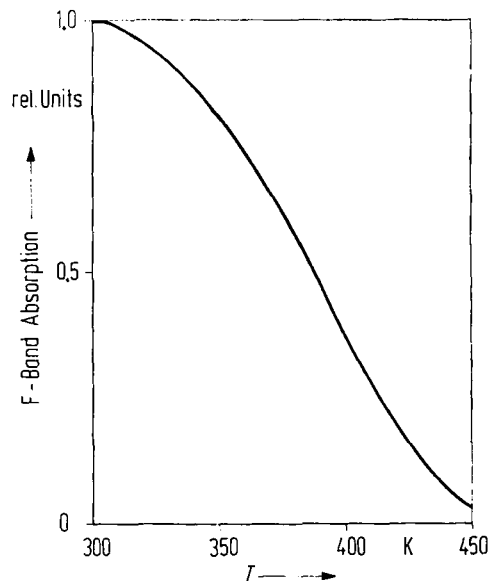


FIG. 2. — Temperature dependence of the F-center induced absorption at 605 nm, normalized to the initial absorption. Heating rate 0.7 K s^{-1} .

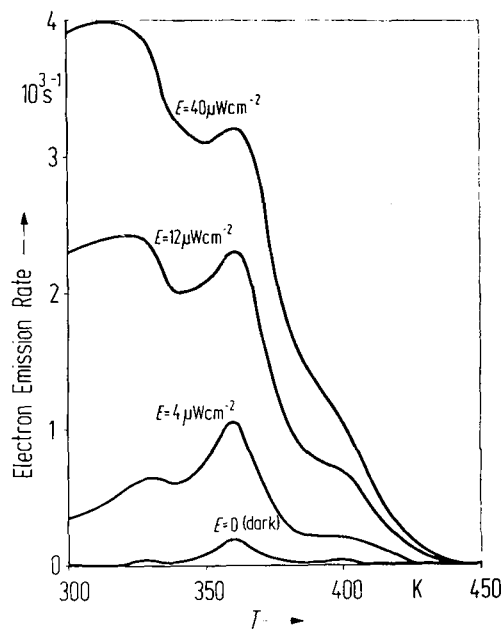


FIG. 3. — Photoelectron emission at 605 nm as a function of increasing temperature. Heating rate 0.7 K s^{-1} . Parameter E = optical irradiance.

is measurable. The position of the main peak at 360 K and of the two satellite peaks at 330 K and 400 K are independent of the illumination conditions. The existence of a thermally stimulated dark emission indicates the thermal release of F-electrons from the ground state. Under illumination this process is parallel to the thermal release from the optically excited state.

As can be seen from figure 3 the total electron emission evidently is not a simple additive superposition of thermal dark emission from the F-center

ground state and photothermal emission via the F-center excited state. Illumination strongly increases the 330 K satellite peak and moderately increases the 360 K main peak, whereas no change is caused at the 400 K satellite peak. We cannot present a convincing explanation of this experimental fact. Similar results have been obtained from experiments with simultaneous optical and thermal stimulation on NaCl and have been explained by physico-chemical reactions on the illuminated surface [12], [13].

3.3 THERMAL ELECTRON EMISSION AFTER PRE-ILLUMINATION. — Assuming the 360 K main peak of thermal emission to be due to F-centers, the following experiments on optical bleaching by pre-illumination in the F-band region also indicate changes of surface contaminations which seem to be connected with the 330 K and 400 K satellite peaks. Excessive pre-illumination on the short wavelength side of the F-band at 540 nm decreases the main peak definitely and the 400 K satellite peak totally, see figure 4. Pre-illumination in the F-band center at 605 nm causes a similar effect, decreasing the 330 K satellite peak additionally.

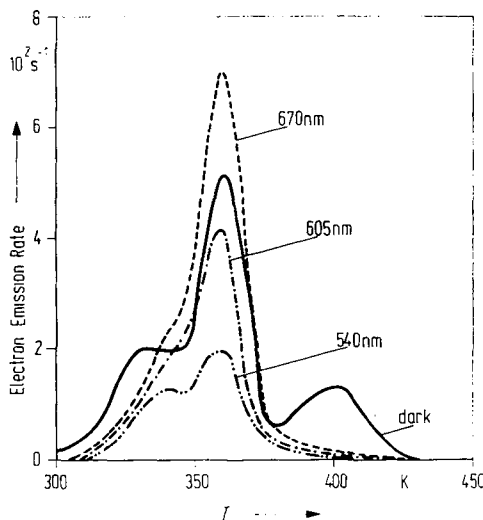


FIG. 4. — Thermal electron emission curves (heating rate 0.7 K s^{-1}). Solid line (« dark ») : After X-ray exposure. Dashed lines : Pre-illumination at different wavelengths (radiant energy 0.3 W.s.cm^{-2}) between X-ray exposure and heating.

Optical bleaching on the long wavelength side of the F-band at 670 nm obviously causes another effect since the main peak is increased in comparison with the dark emission curve (solid curve in Fig. 4), whereas both satellite peaks are decreased strongly. We interpret this observation by photodesorption of surface contaminations which lowers the electron affinity of the surface, and thus increases the thermal emission from F-centers which are not yet bleached by the previous illumination.

3.4 ACTIVATION ENERGIES. — The electrons are believed to be emitted from the surface of the crystal

by a thermionic process after reaching the conduction band [14]. In the case of small or even negative electron affinities as discussed for CsCl [2] the electron emission rate is nearly proportional to the rate of thermal electron release from the F-center ground state into the conduction band [15]. Therefore, the latter process is displayed by thermal electron emission curves as shown in figure 4. From the usual kinetics of the thermal electron release the activation energy ϵ_{therm} of F-centers can be evaluated by analyzing these curves.

For this purpose we applied the method of Balarin and Zetzsche [16]. Plotting $\ln(-\ln C(T))$ versus the reciprocal temperature (with $C(T) = c(T)/c(T_0)$, $c(T_0) =$ initial center concentration at T_0) results in a straight line in that temperature region where the emission peak does not overlap with other peaks. ϵ_{therm} is then calculated from the slope of the function

$$\frac{d \ln(-\ln C(T))}{d 1/T} \cong \frac{\epsilon_{\text{therm}}}{k}$$

($k =$ Boltzmann factor).

A typical computer plot, see figure 5, analyzing the thermal electron emission given in the solid curve of figure 4, exhibits a linear part in the temperature region of the 360 K main peak. The deviations from

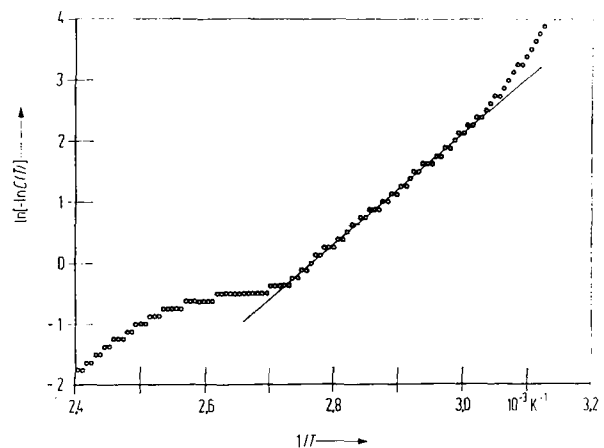


FIG. 5. — Analysis of a thermal electron emission curve (Fig. 4, solid curve) after the method of Balarin and Zetzsche [16].

the straight line on both sides are caused by the satellite peaks. The slope of the linear part yields a thermal activation energy of $\epsilon_{\text{therm}} = 0.95 \text{ eV}$ for the electron release from F-centers which has been coordinated to the 360 K main peak. Further, assuming simple kinetics and considering peak temperature and activation energy an effective frequency factor for the thermal electron release of 10^{12} s^{-1} is calculated. This value is in the right order of effective frequencies of thermal relaxation processes.

The F-band peak at 605 nm yields an energy of 2.05 eV for the optical electron transition to the

excited state at room temperature. By extrapolation to the higher photon energy value at $T = 0$ and adding the energetic gap of about 0.2 eV between the excited state and the conduction band we roughly estimate the optical activation energy to be 2.3 eV. The difference to the thermal activation energy of 0.95 eV is explained by the Franck-Condon principle. Using the simple model of the F-center existing in a homo-

geneous dielectric continuum we get a Franck-Condon ratio of 2.4 by dividing the optical and the thermal activation energy, and a ratio of 2.7 by dividing the static and the optical dielectric constant which are 7.2 and 2.7 [17] respectively. These results fairly agree with the old statement of Mott and Gurney [18] that the thermal activation energy should be in the order of half the optical activation energy.

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