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Photoelectric Yield of the Potassium Halides in the Photon Energy Range 10 to 35 eV

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The spectra of the relative photoelectric yield of thin films of all potassium halides have been measured with the synchrotron radiation of DESY. The spectra exhibit two broad maxima at about 12 to 18 and 25 eV which are discussed in terms of electron-electron scattering. Superimposed is a fine structure which generally corresponds to the optical spectra and is interpreted as excitonic and interband transitions from the valence band and K^+3p core level.

Introduction

The optical properties of the potassium halides in the photon energy range above 12 eV have recently been investigated by reflection (1-7), absorption (8-10), and electron energy loss (12-13) measurements. The spectra exhibit a rich structure which is attributed to excitations from the valence band (19-22) and from the K^+3p core level. The latter begin at about 20 eV with the prominent Γ-X-exciton doublet.

Previous photoyield studies of the potassium halides in this energy range have generally been restricted to a few discrete wavelengths. Only Duckett and Metzger (8, 11) used a continuous light source up to 21 eV. They found some correlation between photoyield and absorption below 20 eV, a structure due to K^+3p excitations, however, is not clearly exhibited in their yield curves. For KF they observed only the Γ exciton, for KI the exciton doublet was not resolved, while for KCl and KBr no structure occured at corresponding energies.

We have, therefore, measured the relative photoelectric yield of all potassium halides up to 35 eV with improved resolution, thus aiming at comparing the yield spectra with the optical data in order to gain additional information for the interpretation of both of them.

Experimental

The synchrotron radiation of the Deutsches Elektronen-Synchrotron (15) in Hamburg provided a continuous spectrum. The normal incidence monochromator (16) and the ultra high vacuum sample chamber (17) used have been described elsewhere. The samples were films evaporated in situ onto gold coated optical flats. The experiments were made at a pressure of 2×10^{-8} Torr which for a few seconds during the evaporation rose to 1×10^{-7} Torr. The film thickness ranged from 1500-3000 Å. The samples were mounted in the center of a gold coated spherical collector. The measurements were made at normal incidence with a wavelength resolution of 2 Å.

The photocurrent saturated at a collector voltage of 2-4 V, depending on the type of halide. For the yield measurements a collector voltage of +15 V was applied. The photocurrents ranged from 10^{-13} to 10^{-11} amps. The spectral distribution of the incident intensity was determined by a sodium-salicylate coated photomultiplier.

In situ preparation of the samples was important since venting of the system after evaporation and even more evaporation in a separate vacuum system and subsequent transfer to the sample chamber caused considerable changes in the yield curves. The spectra (Fig. 1) were measured immediately after evaporation; the time needed to run one spectrum was about 3 minutes. No changes were noticed when the measurement was repeated after five hours, provided the samples were kept at 2×10^{-8} Torr.

Results

The spectra of the relative photoyield are shown in Fig. 1 together with the most recent data for the imaginary part of the dielectric constant, as obtained from reflection measurements on single crystals (4, 7).

The data present the yield per incident photon Y_i. The spectra of the yield per absorbed photon $Y_a=Y_i/(1-R)$ do not differ appreciably from the ones shown, since the reflectivity R in this spectral range is rather low (3 % on an average, never exceeding 10 %). The fine structure in the reflection spectra generally corresponds to that of the yield spectra, so that the effect of this correction is just a slight increase of the peak height.

The overall feature of the yield spectrum is the same for all potassium halides. A broad range of high yield in the low energy part is followed by a pronounced minimum between 15 and 22 eV depending on the halide, after which the yield rises again and reaches values which are considerably higher (up to a factor of two) than the low energy maximum. Towards higher photon energy, a steplike decrease of the yield occurs again, which is most pronounced in KI. The absolute yield was not determined in our experiment. The quantum efficiency has, however, previously been published in the low energy range (8). If one assumes that the yield of our samples is the same in this range, one can calculate the maximum yield in the high energy range and finds about 1.0 for KF, 1.5 for KCl, 1.7 for KBr, and 1.2 for KI, which are the highest yield values ever reported.

A comparison with the optical data shows a rather good peak to peak correspondence for the fine structure. The resolution of the peaks in the yield spectra is comparable to that in the optical ones (4, 7). The splitting (o.2 eV) of the first exciton peak Γ at 20 eV in KI is clearly resolved in the yield curve, while in the optical data it is only indicated by a shoulder (7). There is one obvious violation of the correspondence between optical and photoelectric spectra: the pronounced peak in the ε_2-curve of KI at 15 eV is completely absent in the yield curve.

Discussion

a) electron-electron scattering effects

The high photoelectric yield for low photon energies and the subsequent minimum has been extensively discussed (8, 11, 18).

The high yield can be explained by the absence of inelastic electron-electron scattering at low energies for materials with a large band gap. For photon energies $E_p < 2\,E_g$ (E_g = gap energy) the excited valence electron can not excite a second one across the gap. At $E_p = 2\,E_g$, where scattering becomes possible (arrow (1) in Fig. 1), one would expect a decrease of the yield. It should remain low until E_p is high enough for one of the photoelectrons to retain an energy above the vacuum level. The threshold for this process should occur at $E_p = 2\,E_g + E_a$ (E_a = electron affinity). A second threshold should be found at $E_p = 2\,E_g + 2\,E_a$, which is the minimum energy at which both electrons may be emitted. As E_p is increased this process becomes more and more probable. This explains why the high energy maximum in the yield is up to twice as high as the low energy maximum. The process is not a double excitation in which one photon excites two electrons directly but rather an effect of electron-electron scattering which produces two electrons neither of which can scatter again. The explanation is supported by measurements of the energy distribution of the photoelectrons, where we found for all potassium halides a decrease of the number of high energy electrons at photon energies just exceeding $2\,E_g$ (14).

One expects the yield minimum to be at $E_p = 2\,E_g + E_a$ which provides a possibility to determine E_a. This has already been suggested by Metzger (8) who, however, seemed to expect the minimum to be at $2\,E_g + 2\,E_a$. Evaluation of the experimental data as compared to Metzger's data is presented in Table I. The values for E_a are not expected to be very accurate.

The threshold for double scattering should occur at $E_p = 3E_g$. The effect, however, ought to be much less pronounced, since in contrast to the situation $E_p = 2E_g$, the multiple scattering is only one of several possible scattering events. In accordance with this picture we do not observe any decrease of the yield at $3\,E_g$ and $4\,E_g$.

An other scattering process may result from interaction of the excited electrons with the core K^+3p electrons. This process may occur at $E_p \geq 2E_g + E_{vc}$, where E_{vc} is the energetic difference between the top of the valence band and the K^+3p core level (cf. Table I). A similar decrease in the yield spectra as that at $E_p = 2E_g$ is expected at this photon energy. Our experimental data suggest the occurence of such a process, at least for KBr and KI. The arrows $\underline{2}$ in Fig. 1 indicate the corresponding photon energies.

b) fine structure of the yield spectra

The spectral behaviour found for ε_2 is generally reproduced in the photoyield. Consequently the yield structure is attributed to excitations from the valence band and from the K^+3p core level, beginning at about 20 eV with the Γ-X-exciton

doublet, Fig. 1. A similar yield-absorption correspondence has recently been observed on NaCl for Na^+2p excitations above 30 eV (23). The Γ exciton of KI consists of two peaks associated with spin orbit splitting of the K^+3p core level (7).

The close correspondence between yield and ε_2 is somewhat surprising in cases where the excitation should lead to final states below the vacuum level, as for instance in the case of excitations of Γ excitons. The pronounced structure can then be explained by a recombination or Auger process in which the exciton energy is imparted wholly or partially to a valence electron.

In the yield of KF two maxima are observed at 10.2 and 12.3 eV. They seem to be associated with Γ- and X-excitons from the valence band (4). The first maximum is quite analogous to the yield maximum of KI at 5.6 eV observed by Apker and Taft (26) which was explained by ionization of F-centers by excitons. Such ionization of defects may also contribute to the yield structure at the core exciton energy.

The main discrepancy between optical and photoemission spectra, the 15 eV-peak in the ε_2-spectra of KI may be due to a double excitation (24, 25) of two electrons by one photon. This explanation, however, as well as the identification of the rest of the fine structure not discussed here, cannot be deduced from the yield spectra with certainty. Measurements of the energy distribution of the photoelectrons are necessary to clarify this point.

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Figure caption

Fig. 1 The relative photoelectric yield (full line) of KF, KCl, KBr, and KI together with the yield obtained by Metzger (8) (dot-dash line) and recent data of ε_2 (dashed line) obtained from reflectance measurements on single crystals of KF (4) and the other potassium halides (7). The arrows indicate the threshold energies for electron-electron scattering, ①: $2\,E_g$, ②: $2\,E_g+E_{vc}$; cf. Table I. The K^+3p exciton doublet is noted by Γ and X.

Table I Threshold energies for electron-electron scattering and electron affinity

	KF	KCl	KBr	KI
E_m	21.5	18.2	16.5	14.6
E_m'	> 20.0	18.3	16.1	14.0
$2E_g$	20.6 (4)	17.0 (27)	15.0 (28) 14.6 (29)	12.6 (28, 29)
$E_a = E_m - 2E_g$	0.9	1.2-1.6	1.5-1.9	2.0
E_a'	-	0.65	0.27	0.80
E_{vc}	10.1 (4)	12.4 (7)	13.3 (7)	14.6 (7)
$2E_g + E_{vc}$	30.7	29.0-29.4	27.9-28.3	27.0-27.2

E_m: experimental minimum of the yield (this work)
E_m': experimental minimum of the yield (Metzger (8))
$2E_g$: double gap energy, arrow (1) in Fig. 2
$E_a = E_m - 2E_g$: estimated electron affinity (this work)
E_a': electron affinity (Metzger (8))
E_{vc}: energy difference $\Gamma_{15}(3/2)$ (valence band) and $\Gamma_{15}(K^+3p)$
$2E_g + E_{vc}$: arrow (2) in Fig. 2

Table II Position of the yield maxima including interpretation

KF		KCl		KBr		KI	
10.2	max. $\Gamma_{15} \rightarrow \Gamma_1$	12.8	max. $\Gamma_{15} \rightarrow \Gamma_{25}'$	13.4	max.	12.0	max.
12.3	max. $\Gamma_{15} \rightarrow X_3$	13.7	shoulder	16.1	shoulder	13.5	shoulder
		17.5	max.	18.4	shoulder	16.3	shoulder
14.4	shoulder $\Gamma_{15} \rightarrow \Gamma_{25}'$	19.2	shoulder	19.95	max. $K^+3p \rightarrow \Gamma_1$	18.7	shoulder
17.2	max	20.2	max. $K^+3p \rightarrow \Gamma_1$	21.5	max. $K^+3p \rightarrow X_3$	19.87±0.03	max. $\Gamma_8^- \rightarrow \Gamma_1$
18.9	max.	21.5	max. $K^+3p \rightarrow X_3$	22.5	shoulder	20.05±0.05	max. $\Gamma_6^- \rightarrow \Gamma_1$
19.9	max. $K^+3p \rightarrow \Gamma_1$	23.1	max.	25.6	max. $\Gamma_{15}(K^+3p) \rightarrow \Gamma_{25}'$	20.86±0.04	max. $K^+3p \rightarrow X_3$
21.35	shoulder	25.6	max. $\Gamma_{15}(K^+3p) \rightarrow \Gamma_{25}'$	28.2	shoulder	23.9	shoulder
22.0	max. $K^+3p \rightarrow X_3$	28.6	shoulder	30.8	max.	25.25	max. $\Gamma_{15}(K^+3p) \rightarrow \Gamma_{25}'$
23.4	weak shoulder	31.1	shoulder	31.6	shoulder weak	26.1...26.8	broad max.
25.1	max. $\Gamma_{15}(K^+3p) \rightarrow \Gamma_{25}'$			33.0	shoulder	29.65	weak max.
26.6	max.					32.5	max.
29.2	shoulder						

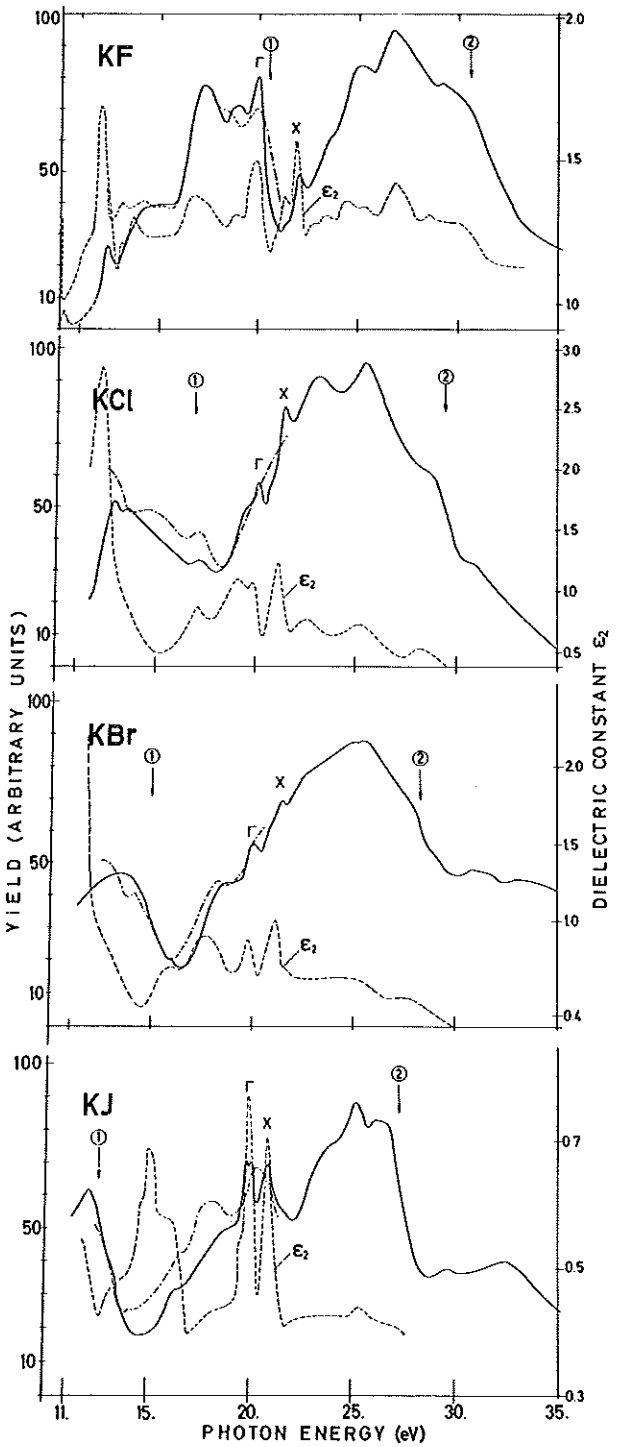
KF
KCl
KBr
KJ
Γ
X
ε2
①
②
YIELD (ARBITRARY UNITS)
DIELECTRIC CONSTANT ε2
PHOTON ENERGY (eV)
11.
15.
20.
25.
30.
35.

Fig. 1