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Fine Structure of the Extreme Ultraviolet Spectra of the Potassium Halide Crystals at 10° K[++]

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The reflection spectra of KCl, KBr, and KI single crystals and of a KF film evaporated in situ have been measured at about 10° K for photon energies between 10 and 30 eV using the continuous spectrum of synchrotron radiation. Many new spectral features have been observed in the range of the high energy valence band transitions between 10 and 20 eV. Due to spin orbit interaction of the K^+3p level the Γ-K^+3p core exciton at about 20 eV is split into two lines with an energy separation of about 0.2 eV for all halides. A shoulder between the Γ and X core exciton indicates either the onset of interband transitions from the K^+3p level or an unresolved Wannier series. The observed fine structure and a comparison with the conduction band density of states in the case of KI support the excitonic nature of the K^+3p doublet.

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During the last decade the valence band transitions of the potassium halides as well as of other alkali halides have extensively been studied for photon energies below 10 eV[1,2]. The experimental results were successfully interpreted in terms of excitons and interband transitions, although there is some doubt in several cases whether the given assignments are unequivocal. Very recently new interesting features, such as higher members of a Wannier series[3] and side bands due to phonon emission[4], have been observed in the reflection spectra of alkali halides at low temperature in this energy range.

Because of light source problems investigations of the optical spectra above 10 eV, where the high energy valence band transitions and core level excitations occur, remained imperfect for a long time. The improvement of light sources for extreme ultraviolet radiation, particularly the use of the continuous and intensive spectrum of synchrotron radiation, has initiated careful work in this energy range a few years ago. In the 10 - 30 eV range reflection[5-8], transmission[9] and photoemission[10] experiments have been performed on the potassium halides at room temperature only. Besides high energy valence band transitions a characteristic doublet at about 20 eV was found in all these experiments suggesting the existence of a Γ and X core exciton from the potassium 3p-level[6-10].

In this work the first measurements of the reflection spectra of potassium halides for the 10 - 30 eV range at 10^{o} K are reported. The remarkable fine structure observed over the entire range may help to clarify which levels and mechanisms are involved in the electronic transitions from the valence band and from the K^{+}3p-level.

The synchrotron radiation of DESY[11] has been used as a light source. Monochromatic light with a spectral half-width of 2 Å (0.06 eV at 20 eV) was provided over the whole energy range by a normal incidence monochromator in a modified Wadsworth mounting[12]. The wavelength calibration was accurate within 2 Å. The single crystals of KCl, KBr and KI were freshly cleaved before they were mounted into a He-cryostat which was attached to an ultra-high vacuum sample chamber[13]. The KF-films were evaporated in situ onto a KBr single crystal. Chamber and cryostat were baked for four hours at 150° C, so that a pressure in the 10^{-9} Torr range could be obtained before cooling the cryostat with liquid He. The reflected light was detected by an open magnetic multiplier. Contamination of the surfaces during cooling was so low that the recorded spectra remained stable within 10 % for one hour.

Figure 1 represents the reflection spectra of KCl, KBr and KI single crystals as well as of a KF film evaporated in situ. The reflectivity I/I_o is given in arbitrary units, since the reflected intensity I and the incident intensity I_o were not measured simultaneously. The spectral behaviour of I_o, however, is well known. The features observed at low temperature are compared to the results at room temperature in Table 1.

The low temperature spectra show a much greater variety than the room temperature data[8], except for the KF film. The Γ-X-exciton doublet at about 20 eV due to K^+3p level excitation shows remarkable fine structure for all the halides. The Γ exciton is clearly split into two lines which are separated by about 6 Å (0.2 eV). This value indicates that spin orbit splitting of the K^+3p level is responsible for this feature. The spin orbit splitting of the 3p-level of the free K^+ ion is of the same magnitude (0,26 eV).[14] The splitting was already indicated at room temperature in the case of KI as a shoulder in the

reflection spectrum[8] and a weak double maximum in the photoyield[10]. A corresponding splitting has been observed in electron energy loss spectra of KBr at low temperature[15].

Between the Γ-doublet and the X exciton a marked shoulder appears for all potassium halides. It is responsible for the slight asymmetry observed for the X exciton at room temperature. This shoulder can be interpreted as the K^+3p interband transition edge (a M_o-type singularity) or an unresolved Wannier exciton series converging to the K^+3p edge. If the shoulder represents the edge one can roughly estimate the binding energy B of the Γ exciton. One obtains $B \sim 1.3$, 0.7, 0.8 and 0.5 eV for the sequence KF to KI. If the shoulder represents the n=2 member of a Wannier series one obtains, together with the Γ exciton (n=1), values for B which are by 4/3 larger using the well known Wannier formula $E_n = E_o - Bn^{-2}$. The above calculated values for the binding energy should not be considered to be very accurate, since the position of the shoulder can hardly be located with an error smaller than 0.2 eV.

The X exciton is only sharpened during cooling. No spin orbit splitting is observed. Due to energetic degeneracy with conduction band states a smaller lifetime of the X exciton as compared to the Γ exciton is expected. Crystal field splitting of the K^+3p level at X could be another reason for the fact that the X exciton does not show substructure under the given experimental conditions.

The details of the described fine structure and its development during cooling are demonstrated in Fig. 2 for KCl as an example. While the Γ exciton is shifted to somewhat higher energies the X exciton remains unshifted within

1 Å. The peak intensity of the latter exciton, however, increases more rapidly. The prominent maximum at the low energy side of the Γ exciton still contributes a high reflectivity background at the position of the Γ doublet. This maximum is attributed to valence band transitions. For KBr and KI the valence band contribution at Γ is much smaller (cf. Fig. 1) so that in these cases the spin orbit splitting of the Γ exciton can be observed more clearly. It is interesting to notice that at the low energy side of the spectrum in Fig. 2 two weak shoulders appear.

For energies above the X exciton the reflection maxima which are caused by exciton formation or interband transitions are only slightly changed by cooling. In the case of KCl, for example, the maxima are shifted by $\sim$0.5 eV to higher energies while their shape remains approximately the same. In two cases the broad and asymmetric nature of peaks at room temperature can be understood as a superposition of two transitions: The structure (slope-like) at 22 eV in KBr[8] has changed into a shoulder at low temperature. The asymmetry of the X exciton in KI at 21 eV[8] is caused by an underlying shoulder (21.7 eV) observed at low temperature.

It has recently been attempted to explain the spectral structure found for KI at the onset of the I^-4d core absorption around 52 eV without exciton effects by simply adding two conduction band density of states which were shifted and statistically weighted against each other due to the spin orbit interaction of the I^-4d level[16]. The conduction band density of states used in this procedure is characterized by two maxima separated by about 2 eV. The sharper maximum at lower energies shows a half-width of the order of 1 eV. The experimental half-width for the Γ and X-K^+3p exciton in KI is much smaller, about 0.5 eV, and the energy separation of the exciton lines is only 1 eV. We, therefore, conclude that the K^+3p doublet at 20 eV cannot be ex-

plained by interband transitions.

Between 10 and 20 eV, where high energy valence band transitions determine the spectrum, striking new features are observed (Fig. 1). The variety of new peaks and shoulders increases from KF to KI similar to the results for the low energy valence band transitions below 10 eV at low temperature.[1] While the KF thin film spectrum remained essentially unchanged the spectrum of a KI singly crystal showed the largest number ob new features after cooling. A greater complexity of a spectrum seems to be correlated with a larger spin orbit splitting of the valence band (1.2, 0.5, 0.2, 0.05 eV for the halide ions in the sequence KI to KF[1,17,18]).

Since KF has the largest band gap ($\sim$ 11 eV), our measurements cover the entire range of valence band transitions in this case. Figure 1 shows that almost all the characteristic transitions recently observed in the reflection spectrum of a KF single crystal[7] can also be studied in the reflection spectrum of thin films. The prominent peaks at 9.9 and 12.3 eV are attributed to Γ_1 and X_3 excitons associated with the F^- 2p valence band. The Γ exciton is expected to be weakly split by 0.05 eV due to spin orbit splitting of the valence band.[1] Neither in our reflection spectrum at 10^o K nor in the reflection spectrum of single crystals at room temperature[3,7] could a significant splitting be observed. A joint density of states calculation has recently been performed by which one is able to understand the gross behaviour of the KF spectrum between 13 and 18 eV as being due to interband transitions.[19]

Inspite of the good over-all-agreement there are some obvious differences between the reflection spectra of a thin film and a single crystal of KF[7]:

1. The Γ exciton of a thin film at 9.9 eV is located by 0.35 eV higher than that of a single crystal[3,7], while reflection and absorption measurements[1] on thin films yield the same position. 2. We have not observed a double shoulder between the Γ and X exciton. 3. The structures at 13.4 and 14.2 eV are inverted in intensity and an extra shoulder appeared at 15.3 eV. 4. An additional shoulder was observed on the low energy side of the Γ-K^+3p-exciton which we attribute to the spin orbit splitting of the K^+3p-level. 5. No distinct maximum could be found between the Γ and X core exciton. 6. No double structure was detected for the maxima at 23.5 and 25 eV.

By comparing the experimental spectra and the conduction band structure[17-20] we suggest that the strong absorption band centered at about 11, 12, 13 and 17 eV (for KI to KF) is attributed to transitions to the lowest conduction band originating from Γ_1, the bottom of the conduction band. The weaker band at about 13.5, 16, 17.5 and 19 eV (for KI to KF) and the strong band at about 15.5, 18 and 19 eV (for KI to KCl) are tentatively ascribed to higher bands originating from points with Γ'_{25} and Γ_{12} symmetry, for example. The shifts of the two lower bands to higher energies from KI to KF is consistent with the atomic picture in which transitions from p-like valence band states to final states with mainly K^+4s (Γ_1) and K^+3d (Γ'_{25}, Γ_{12}) character are important. The latter conduction band states are assumed not to have shifted very much in energy with respect to the bottom of the conduction band (Γ_1) when the halogen ion is exchanged. Therefore, the absorption bands should shift to higher energies by approximately the same amount by which the band gap increases from KI to KF. In the case of KF the third strong band (which is expected at about 21 - 22 eV) is apparently missing. This could be explained by the fact that no 2d level exists for

fluorine. Final states with mainly halide d-character may cause the third strong band for the other potassium halides. The fine structure of every absorption band is suggested to reflect partly the substructure, spin orbit and crystal field splitting of the valence band. For KI the energy separation of two adjacent maxima is between 0.5 and 1 eV. This value decreases from KI to KF corresponding to the decreasing width of the valence band.

It is clear that accurate assignment of the observed structures below 30 eV to interband or excitonic transitions can only be made when reliable calculations of the joint density of states together with matrix elements are performed. Density of states calculations have recently become available for KF[19], KCl[20] and KI[16]. None of these, however, can account for details of the optical spectra so far. It is hoped that the observed fine structure in the 10 - 20 eV range will soon be understood by improved calculations which will also include high energy parts of the conduction band.

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KF	KCl		KBr		KI		
RT / 10° K	RT	10° K	RT	10° K	RT	10° K	general assignments
9.87	12.8	12.9	11.8	11.8	11.1	11.4	high energy valence band excitations
11.0	≈13.8 s	14.0		≈12.3 s	≈11.8 s	≈11.9 s	
12.3		≈14.8 s		≈12.8 s		12.5	
		≈15.5 s	≈13.2 s	13.2	13.5	13.4	
13.4						13.9	
≈14.2 s	17.35	17.5		≈15.5 s		≈14.4 s	
≈15.3 s		≈18.9 s	16.1	16.2		14.9	
		≈19.4 s			15.3	15.4	
17.0	19.5	19.7		≈17.4 s	16.35	16.3	
17.7			18.25	18.0		≈16.5 s	
≈18.9 s				18.5		17.4	
					≈18.5 s	≈18.7 s	
≈19.7 s	20.1	20.1	19.93	19.78	20.0 s	20.06 s	Γ (K^+3p) j=3/2
20.0		20.3		19.95	20.2	20.26	Γ (K^+3p) j=1/2
≈21.0		≈20.8 s		≈20.6 s		≈20.6 s	
22.1	21.4	21.5	21.3	21.3	21.2	21.1	X (K^+3p)
23.3	22.7	23.3	≈22.5 s	≈22.1 s		≈21.7 s	further K^+3p-excitations with a high energy valence band background
	≈23.6 s				23.8	≈23.6	
			25.9	25.5	25.3	25.2	
25.2	25.8	26.1	28.3	28.4	27.4	27.1	
27.0	28.7	29.0			29.6	29.9	
≈29.1 s	≈29.9 s						
30.8							

Table 1: Positions of the reflection maxima between 10 and 30 eV for room temperature (RT) and 10° K. s denotes spectral shoulders.

Figure Captions

Fig. 1 Reflection spectra I/I_o of the potassium halides for 15° angle of incidence at 10° K. New features appearing at low temperature are marked by vertical bars.

Fig. 2 Fine structure at the onset of K^+3p-core excitation for KCl. Solid line: 10° K, dashed line: room temperature. The curves represent the reflected intensity spectra $I(\lambda)$ without division by the incident intensity $I_o(\lambda)$. I_o is approximately independent of the wavelength in this range.

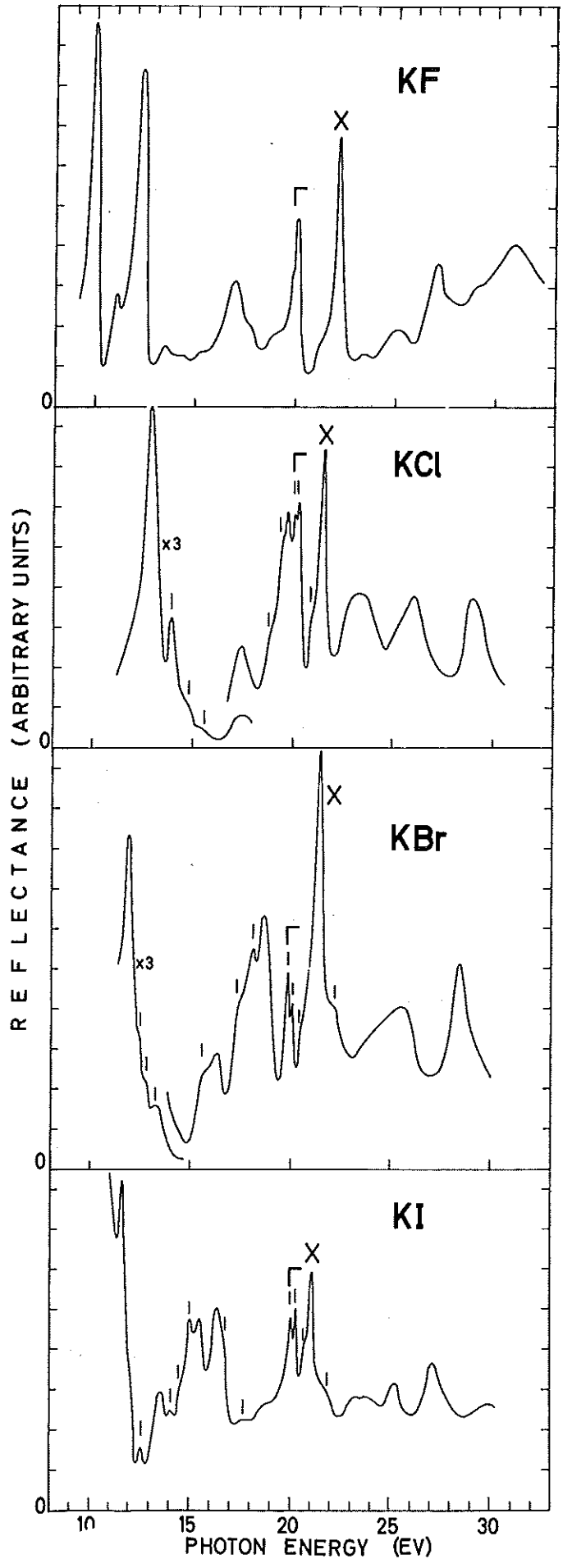
KF
X
Γ
0
KCl
X
Γ
x3
0
KBr
X
Γ
x3
0
KI
X
Γ
0
REFLECTANCE (ARBITRARY UNITS)
10
15
20
25
30
PHOTON ENERGY (EV)

Fig. 1

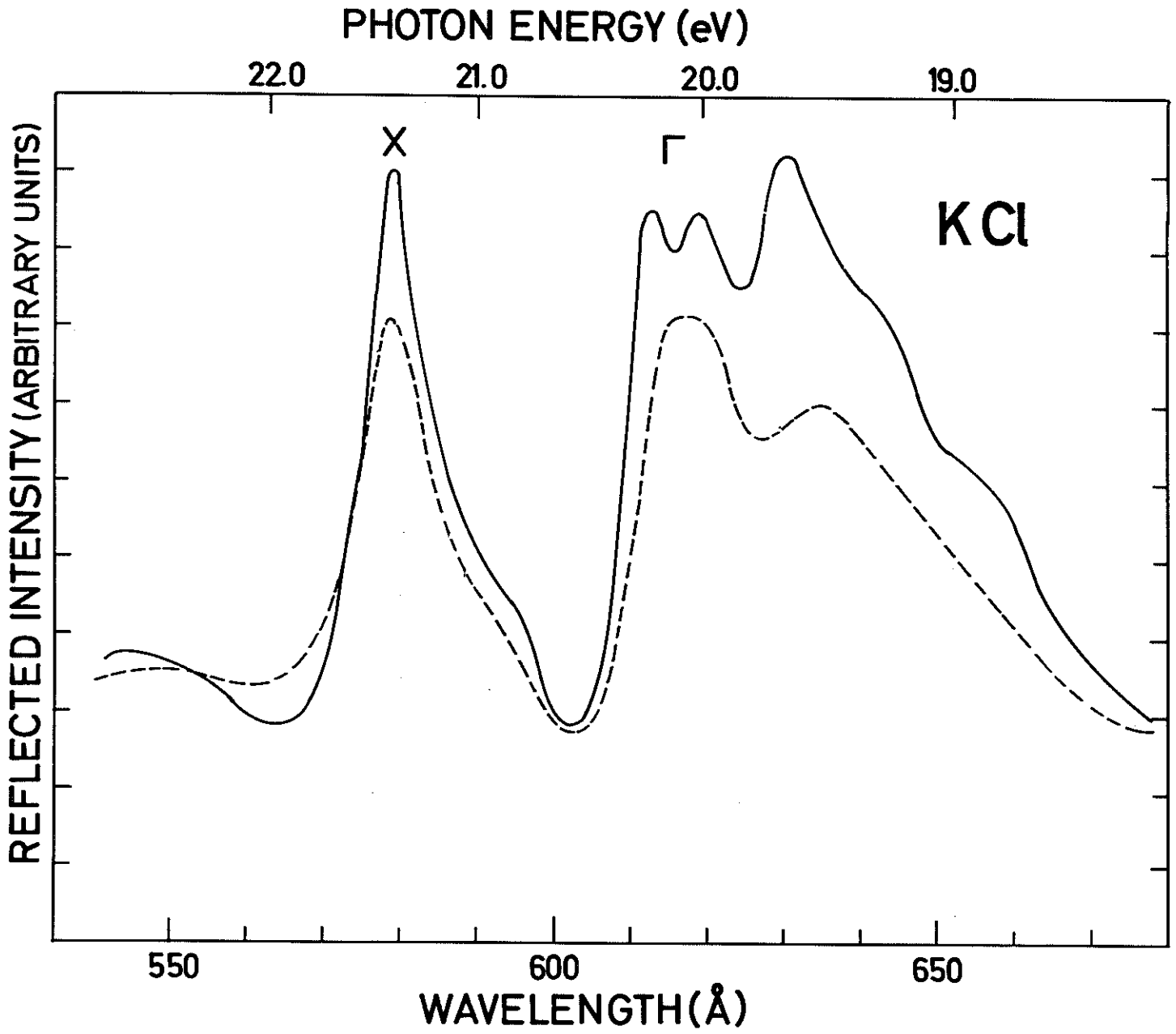
PHOTON ENERGY (eV)
22.0
21.0
20.0
19.0
X
Γ
KCl
REFLECTED INTENSITY (ARBITRARY UNITS)
550
600
650
WAVELENGTH (Å)

Fig. 2