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Photoemission from Solid Rare Gases: Electron Energy Distributions  
from the Valence Bands\*

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Abstract

Photoelectron energy distributions for solid Ne, Ar, Kr and Xe have been measured for  $8 \text{ eV} \leq h\nu \leq 30 \text{ eV}$  by use of synchrotron radiation. From these we obtained the total width and structure of the valence bands. Our data demonstrate that almost all available band structure calculations fail to predict quantitatively other features than the spin orbit splitting. Photoelectron energy distributions for Xe in Ar and Xe in Ne support this viewpoint.

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The electronic structure of solid rare gases and solid rare gas mixtures has attracted much interest, due to their key role for a better understanding of weakly bound van der Waals crystals. We report in this letter the first photoelectron energy distribution measurements on solid rare gases. They provide detailed information about the structure of the valence and conduction bands, beyond what has been known from absorption, reflection<sup>1</sup> and photoyield studies<sup>2, 3</sup>.

For all the solid rare gases several narrow absorption bands, associated with the low lying excitations of the Ne 2p, Ar 3p, Kr 4p and Xe 5p valence electrons have been observed in the optical measurements. They have been successfully interpreted in terms of exciton series converging at the bottom of the conduction band<sup>4</sup>. From these studies together with photoyield measurements the gap energies and electron affinities have been derived (see e.g. Ref. 2, 3). Almost no information has been obtained experimentally on the actual structure of the valence and conduction bands, although a number of band structures has been calculated for all solid rare gases by various methods<sup>4-17</sup>. Therefore specific experiments seemed desirable to improve the present knowledge about the band structure, and in particular, to clarify the discrepancies between the various calculations.

Our measurements of the photoelectron energy distributions (EDC's) profited to a large extent from the possibility to use the broadband vacuum ultraviolet (VUV) radiation of a synchrotron source. Varying the excitation energy continuously between 8 and 30 eV we have studied the structure of the valence bands, the influence of the conduction bands on the EDC's as well as electron-electron scattering processes. Details, including results for electron escape depths will be reported elsewhere<sup>18</sup>.

General aspects of the techniques employed in our experiments are well documented in the literature. The system for combined photoemission and reflection measurements at liquid He temperature has already been described<sup>19</sup>. The DESY synchrotron serves as a light source. The apparatus consists of a normal incidence monochromator for the choice of the excitation energy and an UHV-experimental chamber (base pressure  $4 \cdot 10^{-11}$  Torr) with a He-flow crystat, reflectometer and an electron spectrometer. The photoelectron energy analyzer, a combination of electrostatic lenses and a retarding grid, was mounted normal to the sample surface (angle of acceptance  $3^\circ$ ). Counting rates of 1000 counts/sec with a resolution of 200 meV are typical. Charging of the samples, one of the

major problems in photoemission of insulators, was minimized by measuring EDC's from thin films. They were prepared by in situ condensation of the rare gases onto a cooled gold substrate. The film thickness was determined by monitoring the change of the reflectance during evaporation. It was typically between 20 and 100 Å.

In Fig. 1 the EDC's (counting rate versus initial state energy) are shown for Ne, Ar, Kr and Xe for several exciting photon energies well below the onset of electron-electron scattering. In this energy range the influence of the electron transport on the EDC's can be neglected because of the large electron escape length (e.g. > 1000 Å for Ar)<sup>18</sup>. The zero count line for each individual curve is shifted upwards proportional to the exciting photon energy. Zero of the binding energy coincides with the top of the valence bands.

The results shown in Fig. 1 contain a large amount of information:

First we note, that from the EDC's the position of the vacuum level  $E_V$  can be obtained unambiguously. These values together with the gap energies  $E_G$  determined from absorption and reflection measurements<sup>1</sup> result in values for the electron affinities  $E_A = E_V - E_G$ . They have been compiled in Table 1. The results corroborate the values obtained from earlier photoelectron yield measurements<sup>2,3,20</sup>. In particular they confirm the negative electron affinity for Ar,  $E_A(\text{Ar}) = -0.4$  eV. For Ne a very large negative value of  $E_A(\text{Ne}) = -1.4$  eV is found, confirming the negative value predicted from theoretical estimates<sup>21,22</sup> and expected from the experimental trend in the  $E_A$  values for the other rare gases. Previous yield measurements for Ne could give only a lower limit for  $|E_A|$ <sup>3</sup>. By comparing the  $E_V$  values determined in the present experiment with the  $E_V$  values obtained in band structure calculations one has a further criterion, in addition to the  $E_G$  values, for the reliability of the various band structure calculations<sup>18</sup>.

Secondly we note that the width  $W$  of the EDC's, once the photon energy is sufficient to excite electrons from the whole valence band (23 eV for Ne, 17 eV for Ar, 15 eV for Kr and 14 eV for Xe) increases systematically from Ne to Xe in accord with the expectations from the increasing atomic spin orbit splitting  $SO$  (Table I). However, the experimentally determined width, which stays constant with increasing excitation energy, exceeds the value one would expect naively from the spin orbit splitting of the upper and lower valence bands and the total width obtained for the valence bands in almost all band structure calculations (see Table 1).

Thirdly we note, that for Xe a typical EDC curve has three maxima. Due to the smaller spin orbit splitting and smaller total band width these maxima are partly overlapping in Kr, Ar and Ne. For Kr two maxima and a shoulder, for Ar at least two maxima and for Ne an asymmetric maximum are observed. In order to explain these features we refer to the calculated band structure.

For Xe the measured EDC's can be compared to EDC's calculated by Rössler<sup>23</sup> from the band structure as obtained earlier using the Korringa-Kohn-Rostoker (KKR) method<sup>6</sup>. The energy distribution  $N(E, \hbar\omega)$  for direct transitions was obtained by

$$N(E, \hbar\omega) \propto \sum_{\underline{k}} \sum_{C,V} \delta [E_C(\underline{k}) - E_V(\underline{k}) - \hbar\omega] \delta [E_C(\underline{k}) - E]$$

thus assuming constant matrix elements (for the  $\underline{k}$ -Summation over the Brillouin Zone (BZ) see Ref<sup>7</sup>). Comparison is made in Fig. 2 between the calculated and experimental EDC for  $\hbar\omega = 13.78$  eV incident photon energy. Both experiment and calculation show a very similar shape. In particular three distinct maxima are obtained. The maxima A and B are associated with excitations from the upper valence bands ( $j = 3/2$ ) split by the crystal field. The peak C is attributed to the lower valence band ( $j = 1/2$ ). The main contributions to these maxima come from flat regions near the BZ boundary. The experiment gives a larger peak separation AB and AC, than the calculation. This difference is not caused by a different spin-orbit splitting at the center of the BZ but rather due to a stronger bending of the bands towards the BZ boundary than that calculated (see Table 1).

In support of this viewpoint and in order to show that the differences are not caused by secondary processes such as electron phonon scattering we have obtained EDC's from Xe in Ar and Xe in Ne (see Fig. 2). They show that the spin orbit splitting of the  $n=1$  exciton bands at the  $\Gamma$  point of pure Xe and that from Xe in Ar or Xe in Ne environment agrees well with the calculation. Since possible scattering mechanisms are similar for pure Xe and Xe in Ar and Xe in Ne, and since we measure for Xe atoms isolated in a rare gas matrix the expected spin orbit splitting, we conclude, that the valence band width for Xe is actually significantly larger (3 eV) than calculated (1.8 eV)<sup>6</sup>. At the  $\Gamma$  point the separation between the upper and lower valence band is about 1.3 eV. It follows that the effect of k-dispersion of the lower ( $j=1/2$ ) valence band is about 1.7 eV as determined by our experiment, rather than 0.5 eV obtained in the band structure calculations<sup>5,6</sup>.

For Kr two relativistic band structure calculations are available<sup>6,10</sup>. They both result in a total band width considerable smaller than that observed (2.3 eV). The nonrelativistic bands calculated by Lipari<sup>9</sup> have a total width of 2.8 eV. If one additionally takes into account the spin orbit splitting, the discrepancy with the observed value would be even worse. The nonrelativistic calculations by Kunz and Mickish<sup>8</sup>, with a band width of 1.6 eV, match the experimental value closely, provided the spin orbit splitting is added. This simple procedure may, however, be too crude<sup>10</sup>.

For Ar the spin orbit coupling effects are minor. This leads to a fair agreement of the values calculated by Kunz and Mickish<sup>8</sup> and Dagens and Perrot<sup>11</sup> with the experiment. The other available calculations are worse (see Table 1).

For Ne the measured total width of 1.3 eV exceeds all calculated values considerably. Although in this case the experimental value might be influenced by charging, we can put a lower limit for the total width, being 1.0 eV. This value is still 30% larger than the value calculated most recently by Euwema et al.<sup>12</sup>, which comes nearest to the experimental result.

Strong changes of the shape and relative intensities occur in the EDC's for different exciting photon energies. They are determined mainly by the conduction bands. Using the parameters for the valence bands as deduced from our experiments one can obtain from these changes estimates for the structure of the density of states in the conduction bands. Thus we would locate the first maximum of the density of states, corresponding to flat regions of the lowest conduction band, at 1.1 - 1.9 eV for Xe, 1.6 - 2.1 eV for Kr and 2.5 - 3.5 eV for Ar above the bottom of the conduction band. From modified calculations for the EDC's, considering realistic valence bands one can extract more detailed information about the structure of the conduction bands, which is difficult to get otherwise. Such calculations are in progress<sup>23</sup>.

At energies equal to the sum of the gap energy and the first exciton energy the onset of electron-electron scattering is observed (not shown in Fig.1). These energies are 17.8 eV for Xe, 21.9 eV for Kr and 26.3 eV for Ar. The cross section for this process has been studied in detail for Kr and Ar and will be discussed elsewhere<sup>18</sup>.

We would like to thank A.B.Kunz and U.Rössler for helpful discussions and for making available to us unpublished calculated EDC's. A detailed comparison of our results with these and other calculations is in preparation<sup>18</sup>.

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Table 1

		Ne	Ar	Kr	Xe
$E_G^{\text{exp}}$	(a)	21.7	14.2	11.6	9.3
$E_V^{\text{exp}}$	(b)	20.3	13.8	11.9	9.8
$E_A^{\text{exp}}$	(b)	-1.4	-0.4	0.3	0.5
$E_A^{\text{calc.}}$	(c)	-0.6	0.3	0.62	0.39
$SO^{\text{exp}}(\text{gas})$	(a)	0.14	0.22	0.67	1.31
$SO^{\text{exp}}(\text{solid})$	(a)	<0.1	0.2	0.64	1.3
$SO^{\text{calc.}}(\text{solid})$	(d)	-	0.2	0.7	1.37
$W_{VB}^{\text{exp}}$	(b)	1.3	1.7	2.3	3.0
$W_{VB}^{\text{calc.}}$	(e)	0.4	1.0	1.6	1.8
	(f)	0.4	1.3	1.6	-
	(g)	0.65	(h)2.3	(i)1.5	(j)1.7
	(k)	0.5	(k)1.2		
			(l)2.6	(l)2.8	
			(m,n)0.6		

Table 1

Parameters for the band structure of solid rare gases as obtained by experiment (exp) and calculation (calc.). All energies are in eV.  $E_G$  band gap energy,  $E_V$  vacuum level,  $E_A$  electron affinity,  $SO$  spin orbit splitting,  $W_{VB}$  total width of the valence bands.

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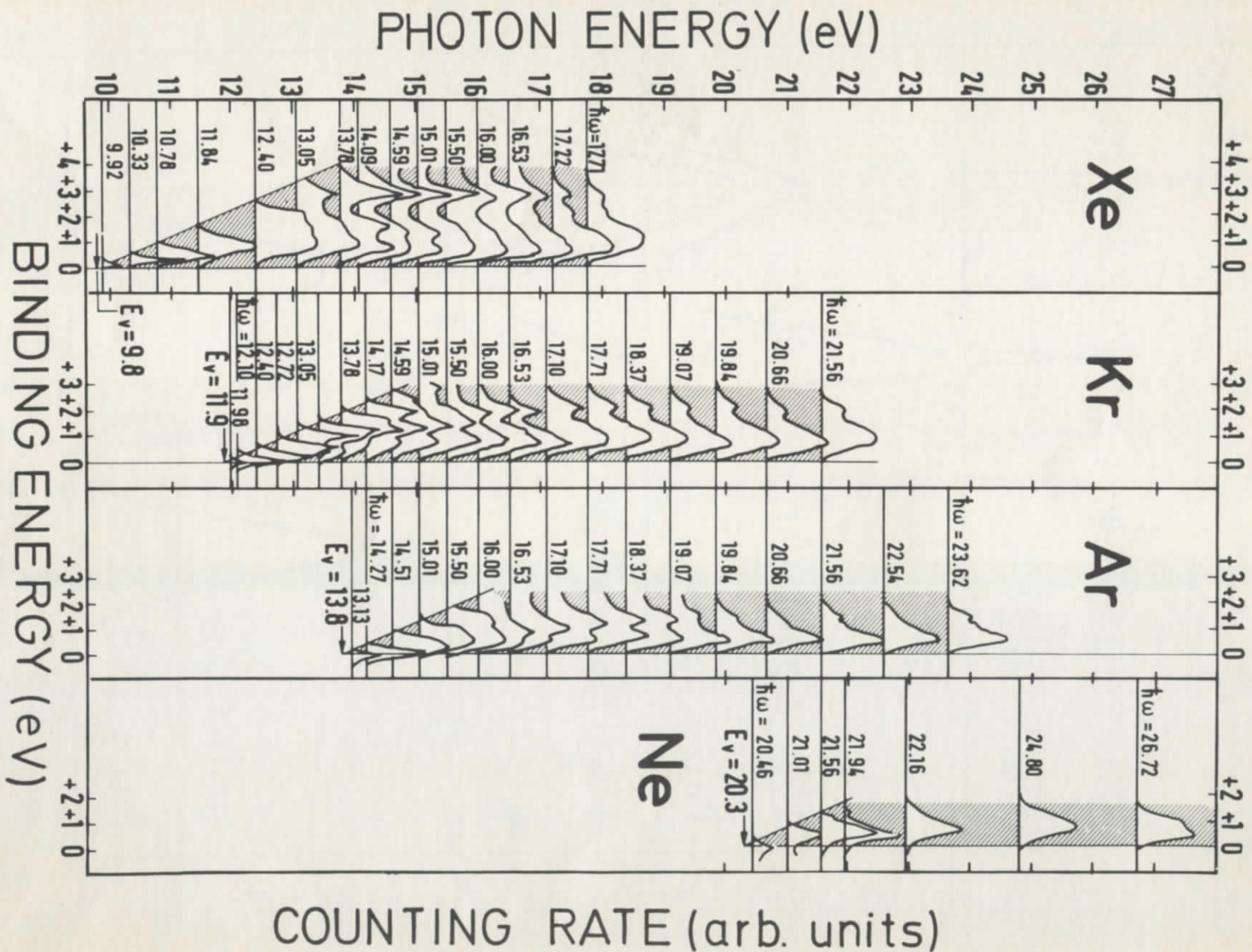
## Figure Captions

Fig. 1 Photoelectron energy distribution curves for solid Ne, Ar, Kr and Xe for various energies of the exciting photons below the onset of electron-electron scattering. Maximum counting rates have been normalized except near threshold.

Fig. 2 bottom:  
Photoelectron energy distribution curve for solid Xe for  $\hbar\omega = 13.78$  eV, the solid curve shows the experimental results, the hatched area shows the result of a calculation by Rössler<sup>23</sup>.

middle:  
Photoelectron energy distribution curve for 1% Xe in Ar and 1% Xe in Ne ( $\hbar\omega = 12.5$  eV and 17.6 eV). The structureless background due to electrons from the gold substrate has been subtracted.

top:  
Photoelectron spectrum of gaseous Xe<sup>24</sup>.



COUNTING RATES (ARB. UNITS)

