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Abstract

We present a comparison of recent experimental data and recent theoretical calculations of the photoelectron energy distribution curves for solid argon and krypton. These comparisons are significant in that they support the idea that the valence states of the solid rare gases are band like and of non-negligible width (Ar is about 1.5 eV wide and Kr is about 2 eV wide). Furthermore, in order to obtain reasonable agreement between theory and experiment, the calculations needed were selfconsistent Hartree-Fock in nature and were corrected for both long range correlation effects (polarization) and short range effects (relaxation).

Zusammenfassung

Es werden experimentell bestimmte Energieverteilungskurven für Photoelektronen mit berechneten Energieverteilungskurven für festes Argon and Krypton verglichen. Diese Gegenüberstellung unterstützt die Annahme, daß die Valenzzustände der festen Edelgase Bandcharakter haben, wobei die Bänder eine nicht zu vernachlässigende Breite haben. (etwa 1.5 eV für Ar und etwa 2 eV für Kr). Um eine brauchbare Übereinstimmung zwischen Theorie und Experiment zu erzielen, wurden selbstkonsistente Hartree-Fock Rechnungen zugrunde gelegt. Dabei mußten sowohl lang reichweitige Korrelationseffekte (Polarisation) als auch kurz reichweitige Effekte (Relaxation) als Korrekturen berücksichtigt werden.

In the past several years a large amount of photoelectron emission data on semiconductors, metals or ionic insulators has become available. These data have been instrumental in testing the validity of various band structure calculations.[1] Due to severe experimental difficulties it is only in recent months that photelectron emission data (EDC's) for the solid rare gases have become available.[2,3] The solid rare gases are important in that they are prototype insulators and have been widely studied for that reason. Substantial amount of experimental work on the valence- and inner shell reflection and absorption spectra using the DESY synchrotron radiation source has established some close correlations between the absorption spectra of the atomic rare gases and the solid rare gases.[4] However, recently Flynn and Layton[5] have also demonstrated that the solid rare gas absorption spectrum is similar to that for the diatomic gas molecule.

On the other hand there have been substantial efforts to calculate the band properties of the solid rare gases for the past 15 years or so. The theoretical group at the University of Rochester has provided non-self-consistent calculations for solid Ar, Kr and Xe using a Slater exchange approximation.[6] More recently, Rössler has also provided Slater exchange calculations which are relativistic for solid Ne, Ar, Kr and Xe.[7] This is also a non-self-consistent calculation. There has been an alternate approach employed, which is based upon the Hartree-Fock approximation. Lipari and Fowler have given calculations for solid Ar which include polarization corrections[8] and Lipari has given a Hartree-Fock calculation for Kr.[9] Dagens and Perrot have provided calculations for solid Ne and Ar.[10] All these calculations are non-self-consistent. More recently Kunz and Mickish[11] have performed self-consistent calculations for Ne, Ar, and Kr. These calculations include polarization corrections but not relaxation corrections.

There is a clear difference between the Slater-exchange calculations and those based upon Hartree-Fock. This is the valence bands in the Slater limit are substantially narrower than in the correlation corrected Hartree-Fock limit. It has been seen experimentally that the measured width favors the Hartree-Fock results.[2,3] In this letter we attempt a detailed comparison of theoretical and experimental EDC's for solid Ar and Kr. We begin with the theoretical calculation of Kunz and Mickish[11] and we recognize it is deficient in that we neglect relaxation corrections to the energy bands. These corrections are calculated using the model given by Mickish, Kunz, and Collins.[12] Having obtained the corrected energy bands one may proceed to compute the theoretical EDC's. In doing this we make several approximations. We follow the recent note of Kunz[13] and assume the excited electron untergoes only elastic scattering. By this we mean that in our calculation, the electron excited to the conduction band does not either gain or lose energy by interaction with phonons, excitons, plasmons etc. before it emerges from the crystal but simply scatters from conduction state to conduction state elastically. We note that the phonon energies in rare gas solids are small in comparison with the resolution of both the calculation and the experiment. Plasmons would perhaps cause satellite structure to appear. Further we neglect $\vec{k}$ conservation selection rules, being aware of the problems involved with this assumption.[14] Finally we employ a constant transition matrix element in this calculation. Making these assumptions the calculation of the theoretical EDC's proceeds as one does in any optical absorption calculation. Rössler has previously computed similar EDC's based upon the Slater approximation and they may be seen for comparison in Ref.2. The calculated EDC's (number of emitted electrons as a function of the kinetic energy of the electrons) in our model are shown here as a function of incident photon energy in Fig.1 for all energies calculated.

The relevant experimental EDC's may be obtained from Ref.3 which in fact also includes results for Ne and Xe. These data are obtained using the DESY Synchrotron as a broad band source of radiation. The apparatus consists of a normal incidence monochromator and an UHV-experimental chamber (base pressure 4×10^{-11} torr) with a He-flow cryostat, 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 is 3°). The counting rates are typically 1000 counts/sec with a resolution of 200 meV. Charging of the samples, one of the major problems in photoemission of insulators was minimized by measuring EDC's from very thin films (typically 20-100 $\mathring{A}$ thick). The experimental resolution given allows for uncertainties due to charging. Fig.2 shows a detailed comparison of theoretical and experimental EDC's for Ar and Kr. The experimental data for Ar is limited to photon energies of less than 26.3 eV and of 21.9 eV for Kr due to strong electron-electron scattering for energies greater than these values. At these energies equal to the gap energy plus the exciton energy one has the onset of strong electron-electron inelastic scattering. Thus the EDC's as measured no longer reflect the true convolution of valence and conduction band density of states.

In the case of solid Ar a reasonable level of agreement between theory and experiment is achieved. This is not true in Kr. We argue that the errors in Kr reflect the absence of relativistic corrections in the Kr valence band calculation. Here the principal correction is to split the Kr valence bands into two spin orbit components the upper having twice as many states as the lower and the separation of these two bands at the zone center is about 0.6 eV. Thus our present calculations should not reflect the splitting which is present in the experiment. If this absence of a second valence band split off below the upper band by about 0.6 eV is taken into account, the agreement of theory

and experiment for Kr seems reasonable, at least with respect to the overall band widths.

We thank M. Skibowski and W. Steinmann for their interest in and support of this work and for stimulating discussions. Thanks are also due to U. Rössler for making available to us unpublished calculated EDC's and for helpful discussions.

References

[1] See e.g. W. Pong and J. A. Smith; Phys. Rev. B7, 5410 (1973); Phys. Rev. B9, 2674 (1974) and references given in Ref. 14.

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[4] For a recent review see B. Sonntag, in Rare Gas Solids, edited by M. K. Klein and J. A. Venables, Academie Press, New York, in press.

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[13] A. B. Kunz; J. Phys. C (Solid State) 7, L231 (1974)

[14] See e.g. the discussion by D. E. Eastman, in Vacuum Ultraviolet Radiation Physics edited by E. E. Koch, R. Haensel and C. Kunz, Pergamon-Vieweg, 1974, p.417.

Figure Captions

Fig.1: Calculated EDC's for solid argon and krypton for various incident photon energies. Zero of the energy scale coincides with the vacuum level.

Fig.2: Comparison between calculated (solid curves) and measured EDC's (dashed curves) for solid krypton and argon for various incident photon energies below the onset of electron-electron scattering. Zero of the energy scale coincides with the vacuum level.

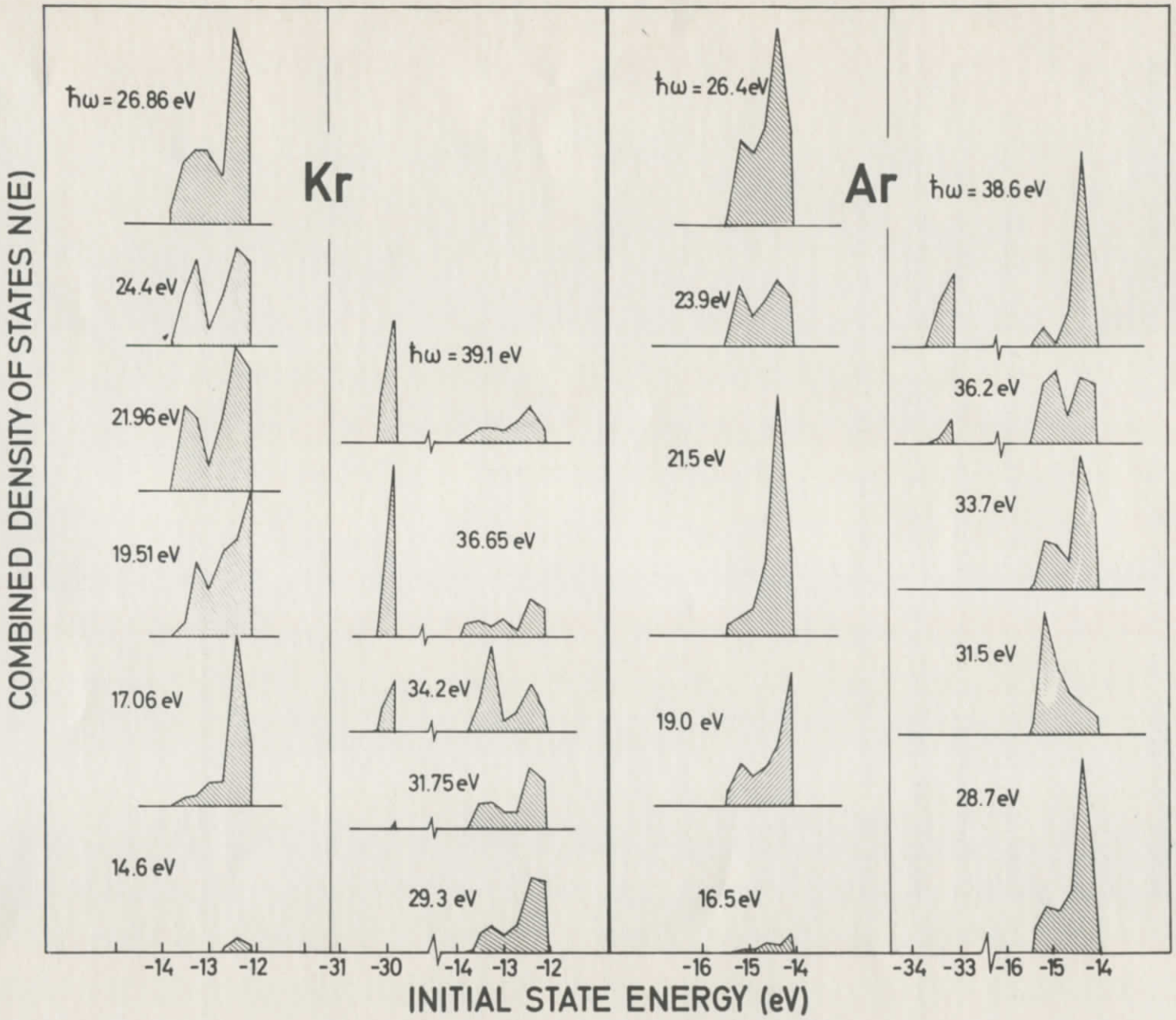
Kr
Ar
ħω = 26.86 eV
24.4 eV
21.96 eV
19.51 eV
17.06 eV
14.6 eV
ħω = 39.1 eV
36.65 eV
34.2 eV
31.75 eV
29.3 eV
ħω = 26.4 eV
23.9 eV
21.5 eV
19.0 eV
16.5 eV
ħω = 38.6 eV
36.2 eV
33.7 eV
31.5 eV
28.7 eV
COMBINED DENSITY OF STATES N(E)
-14 -13 -12
-31 -30 -14 -13 -12
-16 -15 -14
-34 -33 -16 -15 -14
INITIAL STATE ENERGY (eV)

FIG. 1

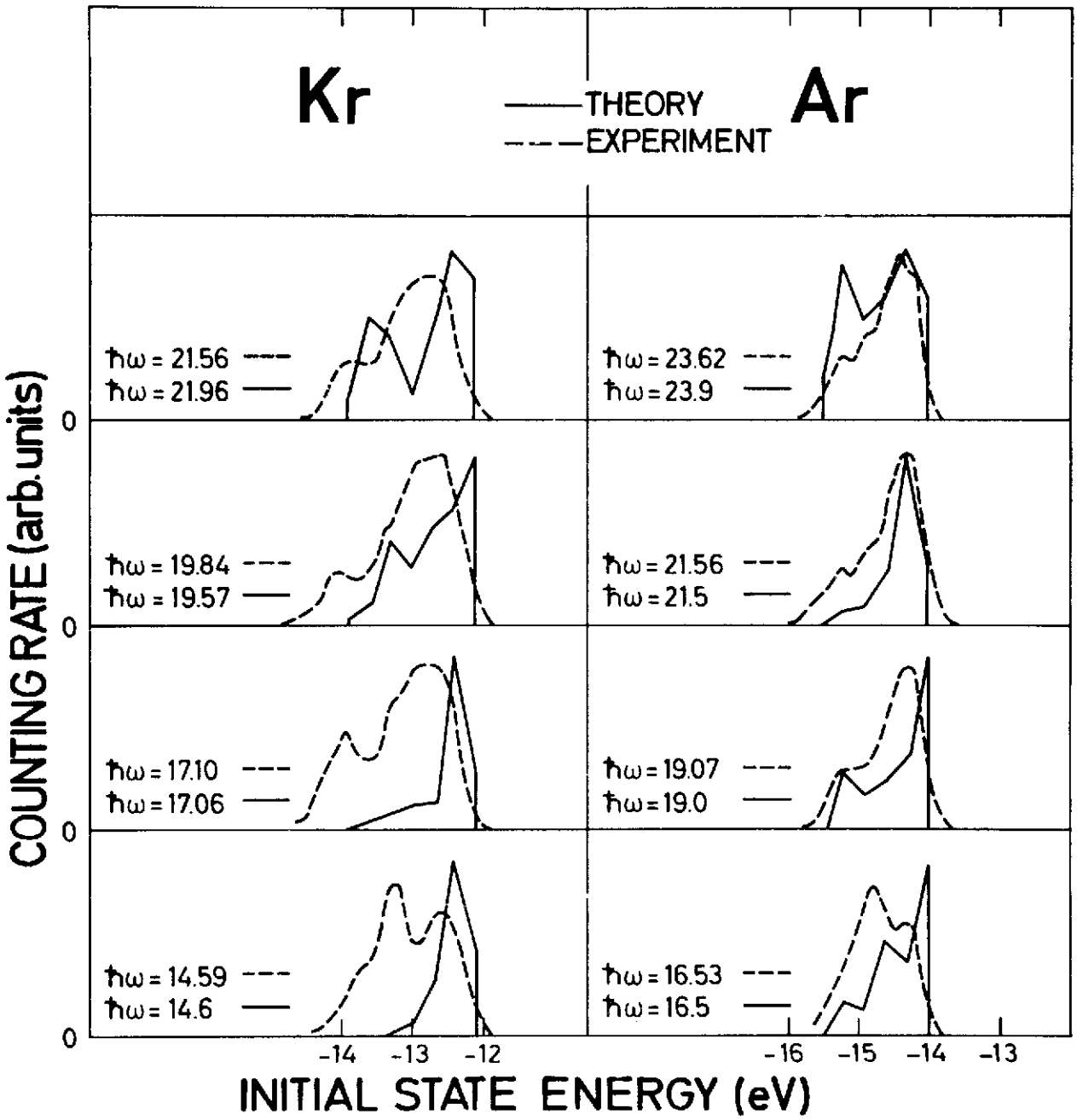
Kr
THEORY
EXPERIMENT
Ar
ħω = 21.56
ħω = 21.96
ħω = 23.62
ħω = 23.9
ħω = 19.84
ħω = 19.57
ħω = 21.56
ħω = 21.5
ħω = 17.10
ħω = 17.06
ħω = 19.07
ħω = 19.0
ħω = 14.59
ħω = 14.6
ħω = 16.53
ħω = 16.5
COUNTING RATE (arb.units)
0
0
0
0
-14
-13
-12
-16
-15
-14
-13
INITIAL STATE ENERGY (eV)

FIG.2