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"Free" Electrons and Excitons in Fluid Krypton

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Abstract

The electronic band structure of fluid krypton was studied by means of photoconductivity excitation spectra and VUV reflectivity spectra. The photoconduction threshold found at 11.55±0.05eV for liquid krypton near its triple point indicates the onset of transitions from the uppermost valence band to the lowest conduction band.

The evolution of the electron band structure was investigated by following the evolution of excitonic states with increasing density. The excitons were shown to be entities different from broadened and shifted atomic/molecular states.

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The very high electron mobility in the liquid phase of the heavier rare gases [1,2] has been interpreted as due to a conduction mechanism similar to that prevailing in a crystalline insulator. In particular, electronic conduction is supposed to occur in a conduction band formed by the overlap of atomic (n+1)s levels, n denoting the principal quantum number of the uppermost filled p-shell, provided bound electrons are raised into this normally empty band. The existence of such a conduction band has been clearly demonstrated both in liquid xenon and in the dense gas by the study of the evolution of excitonic bands [3,4] and by photoconductivity excitation spectra [5,6]. The photoresponse of fluid xenon has been recently investigated in detail, emphasizing the changes that occur with increasing fluid density [7].

Because of the high vapour pressure of the liquid rare gases, photo-effects in these substances have to be studied in closed cells. Therefore the LiF absorption edge (≈11.8eV at room temperature and ≈12.5eV at 77°K) sets an upper photon energy limit for such investigation in the vacuum ultraviolet. In this letter we report the determination of the band gap in liquid krypton by means of photoconductivity excitation spectra and present VUV reflection spectra demonstrating the evolution of exciton bands in this system.

In the experimental arrangement for photoconductivity excitation spectra a stainless steel sample cell equipped with a LiF front window was used. The two electrodes (shaped as intertwinned combs) were prepared by gold sputtering on the inner surface of the window. The cell was positioned within a vacuum kryostat; it was pumped together with the gas handling system by a turbomolecular pump. Baking and helium purging preceded each filling of the cell. The Honormi system [8] at Hasylab provided monochromated synchrotron radiation from the Doris storage ring at DESY. The optical reflectance measurements were performed in Saint Etienne; the experimental details were described elsewhere [9].

Fig. 1 represent the photocurrent (normalized to the number of incident photons as function of photon energy) for liquid krypton at 121^oK, $n=1.72x10^{22}$ atoms/cm^3. It is seen that below about 11.3eV there is very little photoresponse. Extrapolating the linear part of the subsequent rise to the background level one obtains a photoconduction threshold energy E_{pc}=11.55eV. This value is correct probably within ±0.05eV; the steep rise of the LiF absorption and its temperature dependence are the main factors determining the accuracy.

It is of interest to compare this result on E_{pc} of liquid krypton with determinations of the band gap E_G in the solid. For the latter system, E_G was found by extrapolating the Wannier exciton series to $n=\infty$. E_G=11.61eV was calculated in this manner, using transmission data [10] obtained at about 10^oK. Direct determination of E_G in the solid by a two-photon photoemission technique [11] was in excellent accord with this value. Thus the difference in photon energy between E_G of the low-temperature solid and E_{pc} of the triple-point liquid is 0.06eV. For xenon [6], the same difference is 0.09eV.

Reflection spectra of fluid krypton yield independent information on the energy band structure [12]. Figure 2 presents such spectra at three densities. The low - energy

peak (≈10eV) corresponds to the n=1 ($\Gamma 3/2$) exciton level in the solid and it is also related to the first atomic resonance line in the gas (10.032eV). It is seen in Fig. 2a that the reflection peak around 10eV is composed of two adjoining peaks: the one at higher energy corresponds to the broadened and shifted atomic/molecular line while the lower one is due to the exciton. With increasing density (Fig. 2b) the excitonic peak increases strongly; finally in 2c the presence of the "atomic" transition is indicated only by the considerable breadth (≈0.4eV) of the combined peak. In contrast, the peak at 10.7eV does not change in shape though increases in height when the density increases. We infer that this peak is the n'=1($\Gamma \frac{1}{2}$) exciton band that had evolved from the corresponding atomic state already at densities lower than those presented in the figure.

These results show that exciton bands are entities different from broadened and shifted atomic/molecular lines: their appearance is dependent on the evolution of electron energy bands. Quantitative support for this statement were presented for the case of fluid xenon [3,4].

The exciton bands in fluid krypton and fluid xenon behave very similarly.[3,4] In both systems, the n'=1 exciton band forms at considerably lower densities than the n=1 exciton band. In both systems there is no appreciable shift between the position of the n'=1 exciton and that of the corresponding atomic/molecular state, while there is a clear shift between the n=1 exciton and its atomic/molecular "parent". For both systems the n=1 $\Gamma(3/2)$ exciton band is red-shifted with respect to the atomic/molecular parent line.

A detailed report on the evolution of the exciton bands in fluid krypton will be published in the near future[13].

The results demonstrate that fluid krypton, like fluid xenon, is a very simple non-crystalline photoconductor and also a prototype for liquids with Van der Waals forces between the molecules. In spite of the disorder of the fluid state, there is no indication for electron localization. The evolution of the exciton state and the position of the photoconduction edge clearly point to the existence of electron energy bands similar to those in the solid.

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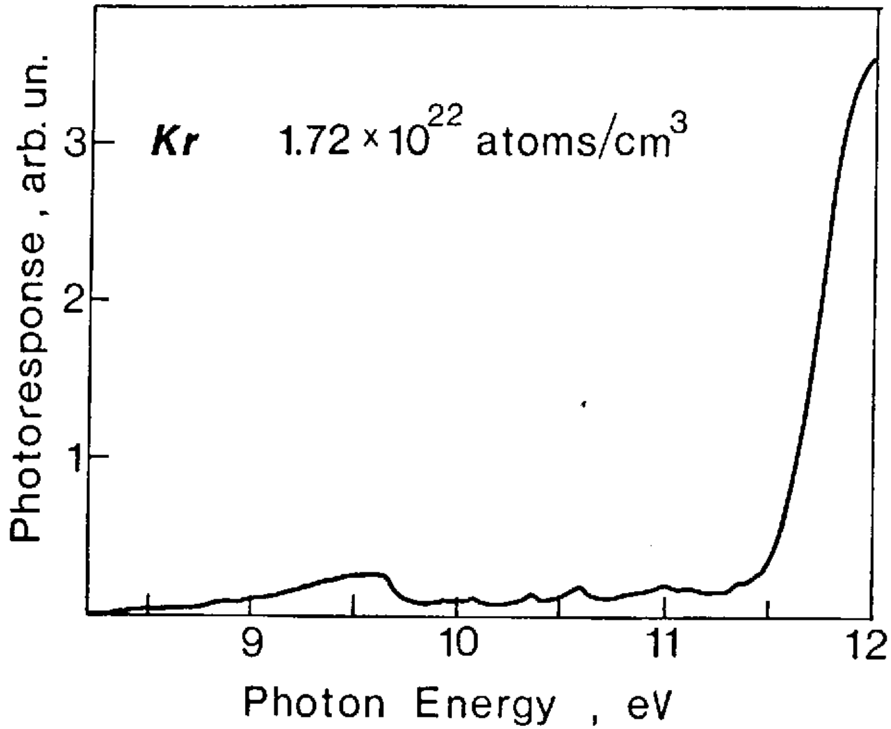
Figure Captions

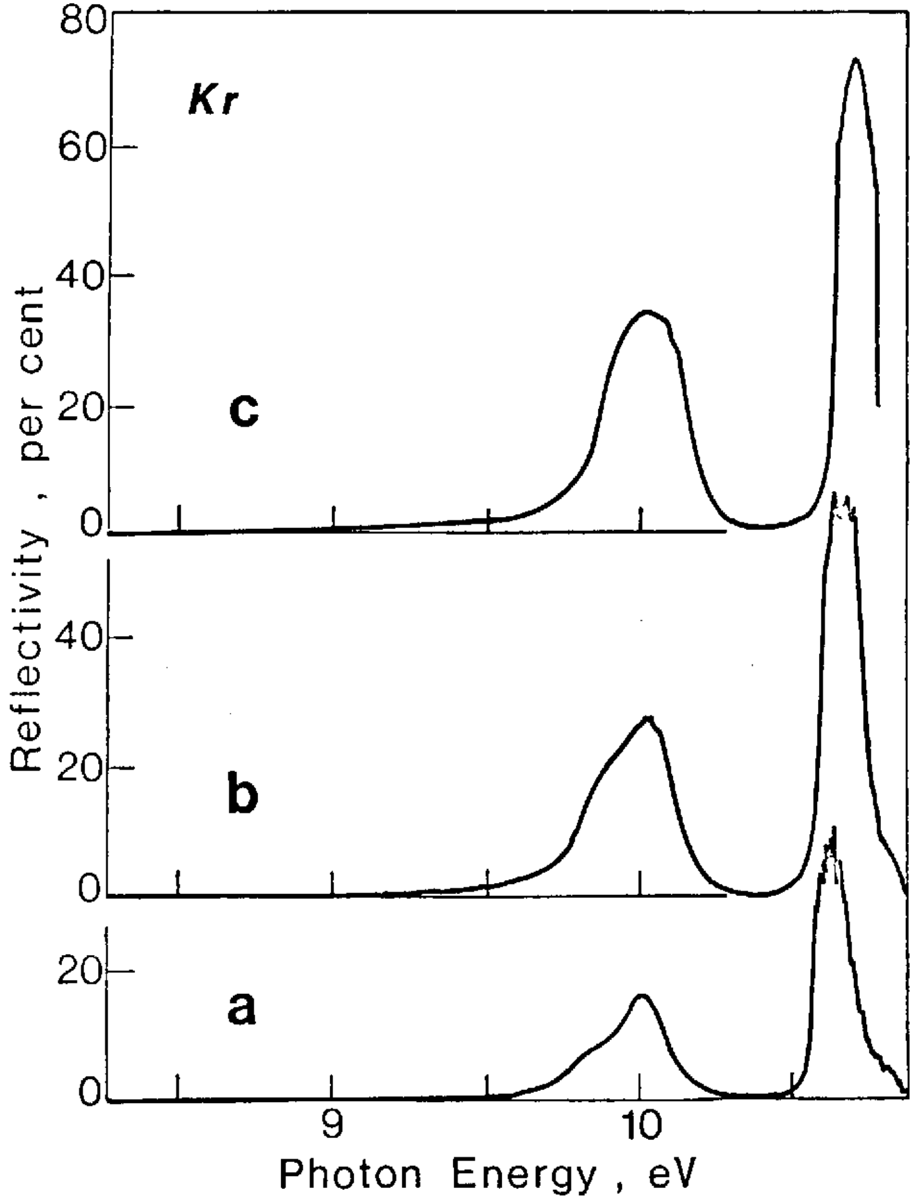
Figure 1 Photocurrent normalized to equal number of photons transmitted by the LiF window as a function of photon energy. Liquid krypton at 121°K, $n=1.72\times10^{22}$ atoms/cm^3. The critical temperature of Kr is $T_c=209.4$°K, the critical density $n_c=6.52\times10^{21}$ atoms/cm^3.

Figure 2 The reflectivity of the Kr/MgF_2 interface as a function of the energy of the incident photons. The krypton temperatures (in °K) and densities (in units of 10^{22}atoms/cm^3) were as follows: a) 180.9, 1.375; b) 150.0, 1.585; c) 122.2, 1.741.



Photoresponse , arb. un.
Kr
1.72 × 10^22 atoms/cm^3
3
2
1
9
10
11
12
Photon Energy , eV

Fig. 1



Kr
Reflectivity , per cent
80
60
40
20
0
c
b
a
9
10
Photon Energy , eV

Fig. 2