Photoelectric Determination of V_0-Values in Solid Rare Gases

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Electronic conduction state energies V_0 were measured by photoelectric effect for solid xenon ($V_0 = -0.57 \pm 0.05$ eV, 160 K), solid krypton ($V_0 = -0.40 \pm 0.05$ eV, 114 K), and solid argon ($V_0 = -0.0 \pm 0.05$ eV, 82 K). A novel photo cell was employed which eliminated some of the problems encountered in photoelectric work with rare gas solids.

Introduction

Photoemission of electrons or holes from a metal electrode into an insulator is a method for obtaining information on the electronic energy levels in the material. Liquids as well as solids have been investigated by this technique [1 – 8]. The experiment consists in the measurement of photoemission currents from a metal electrode in a vacuum or in contact with the insulator. Usually a shift V_0 in the work function Φ occurs which is given by

$$V_0 = \Phi_{\text{sol}} - \Phi_{\text{vac}} . \qquad (1)$$

Positive V_0-values indicate that energy is necessary to bring an electron from the vacuum into the solid, negative values indicate that energy is released. V_0 can also be identified as the energy of the bottom of the conduction band.

While this experiment yields reliable data for liquified rare gases [8 – 10] application to solid rare gases is troubled by difficulties due to problems of the electrode-solid interface. Only scattered remarks on this problem can be found in the literature [11]. Another method which is based on the observation of excited states avoids these problems [12]. It relies, however, on the correct identification and interpretation of the observed optical phenomena.

It seemed to be interesting to study the photoeffect in solid rare gases since it allows the injection of unipolar currents and the metal-rare gas solid interface should be a model system for other metal-insulator interfaces.

Experimental

The experimental apparatus for the observation of the photo effect consisted of a high pressure xenon lamp, a monochromator and a photomultiplier for monitoring the light intensity [6, 8]. The schematic of the photo cell, which was placed in a commercial cryostat, is shown in Figure 1. With respect to photo cells used by other authors [6, 13] two new features were incorporated in the construction.

Firstly, since the rare gas solids were prepared as a polycrystalline film, which attenuates the incident light by scattering, the photo cathode was formed by a semitransparent gold layer deposited on a quartz plate. The gold layer had a thickness of 70 to 90 Å and exhibited a transmission of 30 to 50 per cent. Monochromatic light was falling through the quartz plate on the gold layer and photo electrons were injected into the electrode gap. The vacuum work function of these layer electrodes was determined to be between 3.9 eV and 4.3 eV. There

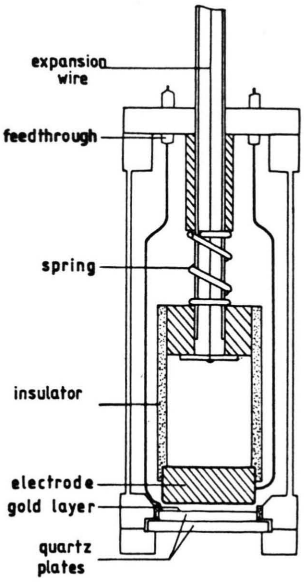

Fig. 1. Schematic of photocell.

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seemed to exist a correlation between thickness and workfunction with the thinner layers giving the lower work function. The vacuum photocurrent density exhibited a maximum value at around 255 nm (Band width 10 nm) with typical values of 200 pA/cm^2 decreasing to around 1 pA/cm^2 at 300 nm. Typical spectral dependencies of the photo emission currents obtained for three layers of different thickness are shown in Figure 2. The yield increases with decreasing thickness. Siomos et al. [14] found a maximum emission from a gold layer of 25 Å.

The vacuum photocurrents saturated for voltages above 100 V at an electrode separation of approximately 1 mm. Above 500 V a slight increase with voltage was observed, which may be caused by secondary ion emission at the anode.

Secondly, since the rare gases show a considerable contraction upon transition from the liquid to the solid state, it was necessary to ensure good contact of the sample with the electrodes. While the photo cathode was fixed at the bottom of the cell the anode could be moved axially. The anode assembly was held at a certain position by the simultaneous action of the compression spring and the suspension wire which was fixed at the end of a 90 cm long glass tube. The electrode separation was usually adjusted to 1 mm. The cell was then filled with liquefied rare gas. After solidification good electrode contact could be maintained by elongating the suspension wire by passage of a heating current through the wire. This way the anode could follow the contracting sample.

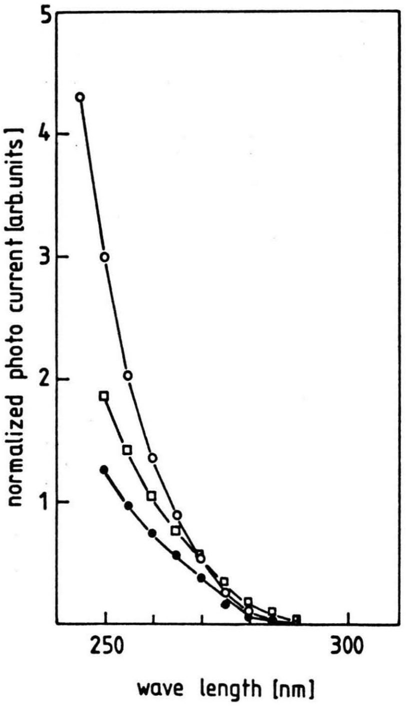

Fig. 2. Wave length dependence of the vacuum photo current for gold layers of different thickness at 295 K. ○ 57 Å, □ 80 Å, ● 124 Å.

Special attention must be paid to the purification of the rare gas before condensation. The main impurities found in commercial grade rare gases are oxygen, water and nitrogen. In the present experiments tank gases from Messer Griesheim GmbH were passed through a titanium sponge maintained at 850 K and through a column of activated chromium on silica gel (also available commercially as Oxisorb from Messer Griesheim GmbH). The gas was then condensed in the evacuated cell. Measurements of the photo current as a function of the photon energy were carried-out for the liquid as well as for the solid. While measurements with the liquid are not so sensitive with respect to electronegative impurities, insufficient removal leads to quickly decaying photocurrents in the solid samples. Photoelectrons are converted into immobile negative ions and a space charge layer is generated near the photo cathode which inhibits further injection. Dark current densities in the liquid or solid samples usually were of the order of 0.1 pA/cm^2 with 500 V applied voltage and 1 mm electrode separation.

Results

Fowler plots of the normalized photo currents in liquid and solid Ar, Kr and Xe are shown in Figure 3. The vacuum response of the particular gold layers used in the experiments is also shown for comparison. From the intercept with the x-axis the work functions Φ_{vac}, Φ_{liq}, Φ_{sol} are obtained.

Work functions were also calculated by comparing the normalized photo current data with the universal Fowler-curve by making use of a computer programm which had been applied in previous liquid work [13]. There was no systematic deviation between the values obtained by the two methods. The mean values measured are given in Table 1. An interesting Fowler-plot observed in a sample of solid krypton is shown in Figure 4. In this experiment the photo cathode seemed to have been in partial

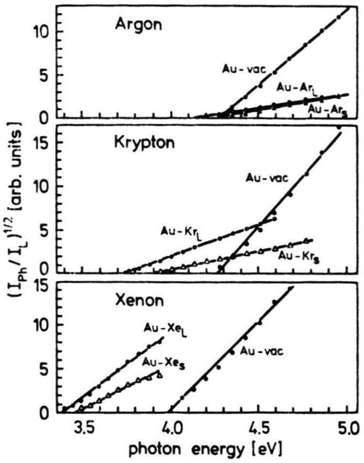

Fig. 3. Normalized photo currents (Fowler-plot) in solid and liquefied rare gases; temperatures given in Table 1.

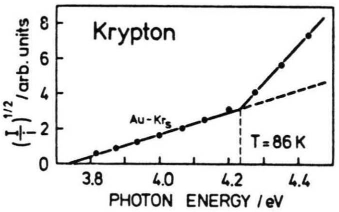

Fig. 4. Fowler-plot for injection in solid krypton with only partial contact of metal and solid.

contact only with the solid. The steep rise of the photo current at higher photon energies is then caused by injection in vacuum.

Discussion

Condensed rare gases exhibit an electron conduction level which for the liquids is below the vacuum level (negative V_0-values) while a shift of V_0 towards the vacuum level ($V_0(\text{vac}) \equiv 0$ eV) is observed upon solidification. The energy V_0 is determined by the balance of repulsive and attractive interactions of the injected electron with the bound electrons of the rare gas atoms. Repulsion is a strongly varying function of the distance between the atoms, and since the solids exhibit a greater density as compared to the liquid, V_0 shifts towards the vacuum level. A similar behavior was found in solid and liquid hydrocarbons [15 – 17].

This shift is also predicted by the Wigner-Seitz theory [12] if a constant scattering length $\tilde{a}$ is assumed for each rare gas. Best agreement is obtained with $\tilde{a}(\text{Ar}) = 0.936$ Å, $\tilde{a}(\text{Kr}) = 1.047$ Å, and $\tilde{a}(\text{Xe}) = 1.261$ Å.

Table 1. V_0-Values of condensed rare gases.

Substance	T(K)	Phase	V_0(eV)	Reference
Argon	85	l	– 0.10 ± 0.05	this work
	84	l	– 0.20 ± 0.03	8
	85	l	– 0.33	10
	82	s	0.0 ± 0.05	this work
		s	0.06 ± 0.2	11
	6	s	0.3 ± 0.1	12
Krypton	118	l	– 0.52 ± 0.05	this work
	123	l	– 0.45 ± 0.05	8
	114	s	– 0.40 ± 0.05	this work
		s	– 0.30 ± 0.1	11
	20	s	– 0.25 ± 0.1	12
Xenon	162	l	– 0.66 ± 0.05	this work
	161	l	– 0.67 ± 0.05	8
	160	s	– 0.57 ± 0.05	this work
	60	s	– 0.59 ± 0.05	11
	40	s	– 0.46 ± 0.05	12

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