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Note on the External Photoelectric Effect of Semi-Conductors

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An analysis of the effect of contact potentials on photoelectric measurements with semi-conductors is made, which indicates a new method of determining the width of the forbidden energy interval for electrons in a semi-conductor. A possible application to precision determination of h/e by the photoelectric effect is indicated.

THE usual textbook and lecture account of Einstein's photoelectric equation does not state the case very carefully in regard to the effect of contact potentials on the actual experimental arrangements. The situation is correctly presented in Hughes and DuBridge, *Photoelectric Phenomena*, p. 22, where attention is called to some anomalous results obtained with copper oxide in Millikan's early work, which Millikan described as "spurious" contact potential differences. The point of this note is to show that these "spurious" contact potential differences have a natural explanation in terms of current theories of semi-conductors and that accurate measurement of them can give information of importance for our knowledge of semi-conductors.

For the reader's convenience, the argument concerning the stopping potentials for photoelectrons will be repeated here in its usual form. Fig. 1 shows the experimental setup with light of frequency ν falling on the photoelectrically sensitive plate A, and potential V adjustable until none of the electrons emitted from A are able to reach the collector C. Then V is said to be the stopping potential for this combination of electrodes and this frequency of light. Of course, as is well known from the recent careful researches of DuBridge, Houston, and others,[1] there is no sharply defined value of V at which the current abruptly cuts off, but rather it tails off as an exponential function of Ve/kT. This is as good as a sharp cut-off if we ignore quantities of the order kT (1/40 electron volt at room temperature) which will be done in the first part of the discussion.

Figure 2 is a schematic energy level diagram showing the potential energy of an electron when in A, in C, and in the space between. The curve, potential energy, labeled U, rises abruptly by 10 or 20 electron volts in a distance of 10^{-8} cm or so at the surface of each conductor and is approximately constant over the macroscopic distance of separation of the two conductors. For each conductor there is drawn in Fig. 2 a horizontal line at the level corresponding to the thermodynamic potential per electron, $u-Ts+pv$, of the electrons in that conductor. If the two conductors are allowed to come into thermodynamic equilibrium by mutual exchange of charges, they will take up total charges that will set up a field such that the thermodynamic potential of the electrons in each metal is the same. However, if they only exchange charges rapidly through the agency of an external source of electromotive force located between them as at V in Fig. 1, then a quasi-equilibrium state is set up in which the thermodynamic potentials of the electrons in the two conductors are related as in Fig. 2.

In the theory of thermionic emission, it is shown that the thermionic work function is equal to the difference between potential energy of an electron just outside the emitter and the thermodynamic potential per electron of an electron inside the emitter, so K_A and K_C are the respective work functions in Fig. 2. In considering the

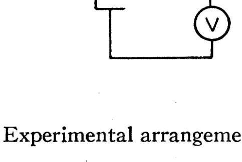

FIG. 1. Experimental arrangement.

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[1] DuBridge, *New Theories of the Photo-electric Effect*, Actualités scientifiques et industrielles, 268 (Herman et Cie., Paris, 1935): Houston, Phys. Rev. **52**, 1047 (1937).

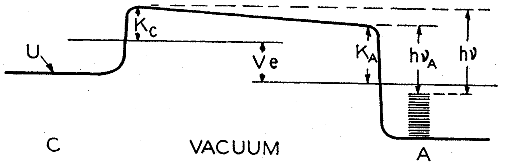

FIG. 2. Schematic energy level diagram.

photoelectric emission of electrons from A, the usual Einstein relation is used, which says that in the direct act of absorption of a quantum of light, all the energy $h\nu$ of that quantum is directly given to the single electron, which makes a transition in the absorption act. This means that the most energetic electrons emitted have an energy $h\nu$ greater than that of the most energetic electrons in the emitter that are able to absorb light. Ignoring quantities of the order kT we may say that the most energetic electrons in A are those whose energy is $h\nu_A$ less than the potential energy of a free electron at rest just outside of A. Then if V has been so adjusted that it just stops the fastest electrons from reaching the collector C, we shall have a situation in which the level that is $h\nu$ above the limiting energy of electrons in A will be equal to the energy of an electron at rest just outside of C, that is, calling this stopping potential V_A,

$$eV_A+K_C=(K_A-h\nu_A)+h\nu. \tag{1}$$

If arrangements are made to substitute an emitter B in place of A without disturbing the properties of C, then for its stopping potential V_B, the analogous equation holds

$$eV_B+K_C=(K_B-h\nu_B)+h\nu. \tag{2}$$

Suppose we measure V_A and V_B for the same light frequency. Subtracting the two equations, we have

$$e(V_A-V_B)=(K_A-h\nu_A)-(K_B-h\nu_B), \tag{3}$$

which gives, on the right, the theoretical interpretation of the experimentally observed quantity on the left.

The experiments[2] of Millikan and also of Kadesch and Hennings show that when various metals are used for the different emitters A, B, the quantity V_A-V_B is zero. From this we conclude that the difference $(K_A-h\nu_A)$ is the same for all metals tested which is quite in accord with modern theory of metals. In the modern theory[3] the thermodynamic potential appears in the Fermi distribution function factor

$$(e^{(E-K_A)/kT}+1)^{-1},$$

which gives the probability of occupation of an allowed state by an electron if the allowed state is of energy E. This factor changes rapidly from unity down to zero over a region of the width kT at the place where $E=K_A$. Hence the theory predicts that $(K_A-h\nu_A)$ is the same for all metals and is actually equal to zero. The stopping potential measurements verify the first part of this statement and are consistent with the second.

However, the experiments of Millikan showed that when one of the pair of emitters was a metal, say B, and the other, say A, is copper oxide, a semi-conductor, then V_A-V_B is not zero, but is of the order of one volt. This effect was described by Millikan by saying that copper oxide showed a *spurious* contact potential difference as contrasted with the *true* contact potential difference shown by metals. Attempts have been made to find an origin of the spurious contact potential difference in terms of grease films, etc.

It is clear that the origin of the so-called spurious potential difference is an intrinsic property of the semi-conductor itself. If B is a metal, then $K_B-h\nu_B$ is actually zero and the experimentally measured quantity (V_A-V_B) is a direct measure of the quantity $(K_A-h\nu_A)$ for the semi-conductor. This interpretation is also in accord with the modern theories of semi-conductors as developed principally by A. H. Wilson[4] and presented in Fowler's *Statistical Mechanics*. In a semi-conductor, it will be recalled, we have a band of allowed energy states which at absolute zero is completely filled. Above it is a forbidden range of energy, then one or more bands of allowed levels which are normally not occupied. In the case of an im-

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[2] Millikan, Phys. Rev. **7**, 18, 355 (1916); **18**, 236 (1921); Kadesch and Hennings, Phys. Rev. **8**, 221 (1916).

[3] See for example, Sommerfeld and Bethe, *Handbuch der Physik*, Vol. 24/2 (Springer, Berlin, 1933), p. 342, or Fowler, *Statistical Mechanics* (Cambridge University Press, 1936), Chap. XI.

[4] A. H. Wilson, Proc. Roy. Soc. **A133**, 458 (1931); **A134**, 277 (1932).

purity semi-conductor, there are some extra levels associated with wave functions localized around the impurities or lattice imperfections in a manner that has often been discussed in the literature of semi-conduction. At any finite temperature there will be a very few electrons thermally excited into the upper band with a corresponding small deficiency of electrons from the otherwise filled band. The thermodynamic potential K_A has to take up such a value that the number of electrons thermally excited to the "empty" band is equal to the number missing from the "filled" band. Under simple, plausible assumptions, this makes K_A have a value at the center of the interval between the "filled" and "empty" bands. (See Fig. 3.) This neglects impurity levels and supposes the effective mass of electrons in each band to be the same. If these conditions are not fulfilled, then K_A will not be exactly in the middle of the forbidden interval, but in any case its location can be calculated in terms of basic features of the band structure and the location and number of impurity levels.

As to photoemission from the semi-conductor, the electrons of highest energy will result from the absorption of a quantum $h\nu$ by the very few electrons in the "empty" band. But these will be so few in number that it may be expected that they will have escaped detection in experiments where no special effort was made to find them. Then the highest energy electrons which appear in abundance will be those which come from the top of the "filled" band. Hence $(K_A - h\nu_A)$ will theoretically be not zero, and will in fact, be equal to one-half the width of the forbidden energy range in the simpler cases. This is the interpretation which is offered for Millikan's observations on copper oxide.

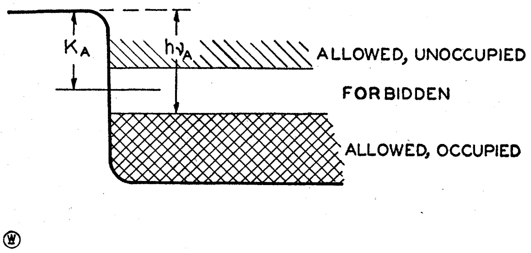

FIG. 3. Energy level diagram for semi-conductor.

The width of the forbidden energy range also plays a role in the temperature dependence of the bulk conductivity of the semi-conductor on Wilson's theory. While the existing data do not permit of any precision test of whether the photoelectric effect and the temperature dependence of conductivity give the same results, still both methods are in agreement for copper oxide in giving about two volts for the width of the forbidden range.[5]

Another interesting consequence of these ideas was pointed out to me by Dr. W. H. Wells, in a conversation at these Laboratories. He notes that the sharpness of cut-off of the photoelectron current with gradual increase of the retarding potential V ought to be much sharper in the case of a semi-conductor than in the case of a metal. This fact is of considerable interest in itself in view of the large amount of work that has gone into studying the details of the cut-off for metals.[1] It also seems to have an important bearing on experiments such as those of Houston and his associates[6] who are making precision determinations of h/e by measuring the change of stopping potential with change of light frequency. Difficulty of exact definition of what is meant by stopping potential is one of the most troublesome features of such experiments, and it seems that the difficulty would be obviated by using a semi-conductor instead of a metal as the photoemitter.

It appears, therefore, that the ideas here presented should provide a useful new approach to the study of semi-conductors and afford a means of unraveling the hitherto chaotic field of photoemission by compounds. They also suggest an improved way of determining h/e from the photoelectric effect. Experiments from the point of view of application to semi-conductors are being planned in these Laboratories.

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[5] Gudden, Ergebn. d. exakt. Naturwiss. **13**, 223 (1934).

[6] Overhage, Phys. Rev. **52**, 1039 (1937). Also unpublished work reported by Houston at a colloquium during the Physics of Metals summer session of the University of Pittsburgh, 1938.