(*a*) the absorption lines are much narrower than would be predicted by dipolar coupling considerations alone, and (*b*) for orientations of the crystal at which there should be separate lines for Cu*I* and Cu*II*, only one line is observed. The second effect depends upon exchange coupling of the type of Cu*I*–Cu*II* while the first depends upon any of the types, Cu*I*–Cu*I*, Cu*II*–Cu*II*, or Cu*I*–Cu*II*. Neither of these effects is noted in $CuK_2(SO_4)_2\cdot 6H_2O$.

The difference in the magnitudes of the crystalline electric field splittings in the two salts is not related to exchange coupling, but is rather an indication that the octahedral water-oxygen complex is of smaller dimensions in the single salt.

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The Work Function of Lithium

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Because they approximate their free electron models so closely, lithium and sodium are of exceptional importance in studies of the theory of the work function. For the purpose of supplementing theoretical calculations on these metals, a thorough experimental investigation of the work function of lithium has been carried out and the results, in combination with the calculations of Wigner and Bardeen, used to estimate the contribution of the surface double layer term to this work function.

As in previous studies of this series, the work function was determined by measurement of the contact difference of potential of lithium with respect to a barium reference surface of known work function. The measured surfaces of both lithium and barium were prepared by condensation of their vapors on glass targets after each of the metals had been subjected to fractional and multiple distillation in the measuring tube itself. The time interval between deposition and measurement of the films was of the order of 30 seconds. The observed contact difference of potential is 0.03±0.02 ev, lithium electro-positive to barium. This result assigns the value 2.49±0.02 ev to the work function of lithium. The effect of gaseous contaminants is to lower the work function.

The volume and surface double layer terms which determine the work function of lithium are of the order of 2.2 and 0.3 ev, respectively, a result which supports the conclusion that the surface double layer makes a relatively small contribution to the work functions of the alkali metals.

A PROBLEM of major significance in work function theory and in surface physics generally is that of separating and evaluating individually the volume and surface terms which determine the external work function of a metal. Wigner and Bardeen[1] and Bardeen[2] have obtained equations of the form:

$$\phi=\phi_v+\phi_s=\phi_v+4\pi eP_n,$$

where ϕ is the external work function which is measured experimentally. ϕ_v is the volume contribution to the work function and ϕ_s the contribution of the surface double layer. ϕ_v is determined entirely by the bulk properties of the lattice and may be defined as the work done in removing an electron from a hypothetical neutral lattice in which P_n, the surface dipole moment per unit area, is zero. ϕ_s contains all of the surface sensitive part of the work function, e.g., the dependence of ϕ on the crystal orientation of the surface. Neither ϕ_v nor ϕ_s can be measured independently. Wigner and Bardeen[1] made rough calculations of ϕ_v for the free electron models of the alkali metals and by comparing their results with experimental values for ϕ reached the conclusion that ϕ_s is small, i.e., of the order of a few decivolts, for these metals. Bardeen[2] carried out a more complete evaluation of ϕ_v and also an explicit calculation of ϕ_s for sodium obtaining a calculated value for the work function which could be compared with the results of experimental measurements. These procedures evidently put a heavy burden on the experimental data. Examination of published work[3] reveals a divergence in ϕ values, especially in the values for lithium, which is considerably larger than the probable magnitude of the double layer term which is to be evaluated and, in the case of lithium, no determination in which the experimental conditions now known to be essential were realized. The major objective in the present work was a thorough experimental study of lithium, a metal which approximates its free electron model quite exactly and

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[1] E. Wigner and J. Bardeen, Phys. Rev. **48**, 84 (1935).

[2] John Bardeen, Phys. Rev. **49**, 653 (1936). See Frederick Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), pp. 395–400.

[3] A. L. Hughes and L. A. DuBridge, *Photoelectric Phenomena* (McGraw-Hill Book Company, Inc., New York, 1932), p. 75.

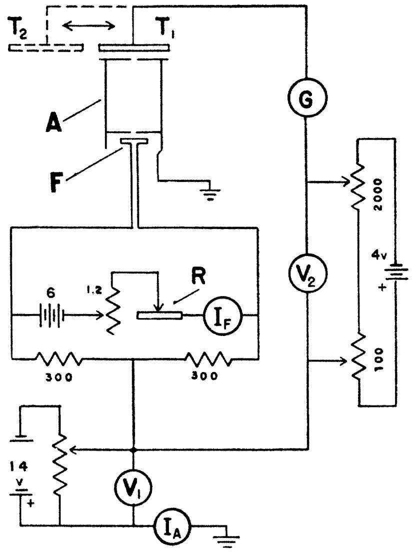

FIG. 1. Circuit for measuring contact difference of potential between metal-on-glass films T_1 and T_2. The gun AF projects a constant intensity, constant energy (order of 10 ev) electron beam monitored by voltmeter V_1 and microammeter I_A. The target current-retarding potential characteristic is measured by voltmeter V_2 (0–3-v reading to 0.005 v) and galvanometer G with Ayrton shunt, not shown. I_F is 0–10 ammeter and R is 3-mm×100-cm nichrome wire sliding in a mercury well. Filament battery: six 6-v accumulators in parallel; other batteries small accumulators. All resistances in ohms.

is well adapted to the methods of work function measurement in use in this laboratory.

EXPERIMENTAL METHOD

The experimental method, described in detail in previous reports of this series,[4] may be summarized briefly as follows. (1) The work function of the "unknown" metal under investigation is determined by measurement of its contact difference of potential with respect to a barium surface of known work function. (2) Specimens of the unknown and reference metals, of the highest available chemical purity but containing absorbed and adsorbed gases, are outgassed by repeated fusion while the measuring tube is undergoing baking and high frequency treatment on the pumps. (3) The tube is sealed off, repetitive fusion and solidification of the metal charges continued, and both metals fractionally distilled. A middle fraction of one of the metals is finally condensed on a movable glass target. (4) Immediately after the deposition of a fresh metal film upon it, the target is moved to the "measuring position" in front of an electron gun which supplies a constant energy, constant intensity beam, and the retarding potential required to establish a given reference current is determined. This reference current is selected to be near the middle of the straight line portion of the current-potential characteristic. (5) Step four is repeated for a succession of films of the first metal and the reproducibility of the potential setting for this metal thus determined for a large number (order of ten to fifteen) of different films. (6) Steps four and five are repeated for the second metal of the pair. The contact difference of potential between the two metals is then given directly by the difference between the potential settings, i.e., by the parallel shift of the characteristic with change of surface. The work functions of barium reference surfaces prepared by this method have been found[4] to be extraordinarily reproducible and constant.

EXPERIMENTAL PROCEDURES

The tubes used in the present work were similar to those employed in our earlier measurements on zinc[5] except that circular trays spun from 10-mil tantalum foil, 6-mm deep×25-mm diameter, are now being used on the "first vaporizers." The outgassing schedule was similar to that for zinc but with the following modifications. (1) The barium was premelted in vacuum on a separate pumping system before it was introduced into the measuring tube. After the premelted barium was placed in the measuring tube and before seal-off, it was held for 48 hours or more at a temperature just below that at which vaporization was detectable and was then melted down at least ten times on the first vaporizer. This relatively drastic preliminary treatment was adopted because of the fact that the commercial barium now available, in contra-distinction to the Osram material used in our earlier work, is not premelted and contains considerable quantities of absorbed gases. (2) In outgassing the lithium charge, use was made of the fact that vaporization of lithium is extremely slow at temperatures just above its melting point. The metal was held in the molten state for at least 30 hours before seal-off and showed no detectable release of gas on subsequent fusions. (3) The final baking of the tube after introduction of the metal charges was carried out at 120°C.

The lithium was of the highest purity available commercially. The impurities present in significant amount were sodium and potassium. Since the contact potential method measures the average work function of a surface and the work functions of the alkali metals differ only slightly from one another, errors due to traces of these contaminants in the final films must have been negligible. The same remark applies to the traces of strontium and calcium which are the significant metallic impurities in barium. Both the lithium and barium

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[4] Paul A. Anderson, Phys. Rev. **59**, 1034 (1941); **57**, 122 (1940), and earlier reports cited therein.

[5] See reference 4, 1940 paper, Fig. 1.

charges were large enough to fill the first vaporizer pans to the brim after the initial fusions.

After sealing off the tube, fusions of the lithium and barium charges were continued until a fusion produced no appreciable change in the emission of the gun filament.[6] After flashing the second vaporizers to remove the discarded fractions of barium and lithium, the measuring schedule was carried out as previously described.[4] Since lithium films deposited directly on pyrex glass have a tendency to blister, barium was deposited first on both targets and the potential setting for each of a succession of barium films taken as the film was formed. A series of lithium films was then laid down on one of the barium coated targets and the potential setting for each lithium film taken immediately after its deposition. In this way, contact potential differences were obtained from the barium and lithium potential settings for a given target and also for lithium films on one target and a renewable barium surface on the other target. When an electropositive metal is deposited on an electronegative metal such as silver, it is easy to determine from the potential settings for a series of films the point at which the substrate metal is so completely covered that it ceases to have any influence on the work function of the surface. Since the work functions of lithium and barium are very nearly equal, this criterion of complete coverage could not be used in the present work and care was taken to deposit a relatively thick film of lithium before each measurement. Films which are "thick" in this sense are, of course, so thin that the middle fractions of the barium and lithium charges were sufficient for the preparation of a far larger number of films than was necessary for establishing reproducibility of the potential settings. In general, ten to fifteen individual films of each of the metals were measured in each tube. The improved circuit now being used in our measurements is shown in Fig. 1. It has the advantage that the target current is insensitive to small variations in the anode potential on the gun.

THE WORK FUNCTION OF LITHIUM

The first tube to be measured did not clean up well[7] but showed that the contact difference of potential Li-Ba would probably turn out to be less than 0.1 v. In this tube, freshly deposited lithium films always showed a progressive drift toward lower work function on aging, a result which is of significance in appraising the effects of gaseous contaminants on the work function of lithium. The second and third tubes behaved very satisfactorily. Potential settings for both barium and lithium were reproducible to 0.02 v or better and were constant to 0.02 v from 30 seconds after deposition through periods as long as 72 hours after deposition. These measurements give 0.03 ±0.02 v for the contact difference of potential of lithium with respect to barium, lithium electropositive to barium. In combination with the value 2.52 ev for the work function of barium, this result assigns a work function value of 2.49±0.02 ev to lithium.

THE SURFACE DOUBLE LAYER IN LITHIUM

In the work of Wigner and Bardeen,[1] the work functions of the free electron models of the alkali metals were estimated with explicit neglect of the double layer terms. The value of ϕ_v thus obtained for free-electron lithium was 2.19 ev. For the experimental value of the work function of lithium, Wigner and Bardeen selected 2.28 ev taken from unpublished measurements by Olpin. The double layer term for lithium thus turned out to be very small, of the order of one decivolt. Our value for the work function of lithium when combined with Wigner and Bardeen's rough evaluation of ϕ_v raises the double layer term of lithium to 0.3 ev, a value which is still small with respect to the volume term. For free-electron sodium, Bardeen,[2] in more exact computations which included estimation of the effect of correlation forces on the surface charge density and an explicit calculation of the double layer moment, obtained 2.35 ev for the work function ϕ and 0.4 ev for the contribution of the surface double layer. The effect of substituting a crystal of sodium for the free electron model is to reduce the double layer term by an amount which is determined by the orientation of the crystal face under consideration. There seems, then, to be enough evidence at present to warrant the conclusion that the volume term is dominant and the surface double layer term relatively unimportant in determining the work functions of the monovalent metals. More exact evaluation of the individual terms which determine the work functions of these metals will evidently require the most complete theoretical calculations which are practicable and also good experimental measurements of the work functions of crystal faces of known orientation.

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[6] When, as in this work, a tungsten filament is operated at a temperature which is not high enough to remove adsorbed gases instantly, a sudden increase in residual gas pressure raises the work function and lowers the emission of the filament.

[7] This behavior, which eliminates about half of the tubes used in work of this kind, is apparently due to extremely slow leaks through or around the tungsten wires of the presses.