ture T. The first factor $(\epsilon_b-\epsilon_a)/T$ is the entropy increase for each quantum so transformed, and the second factor $Nc(p_a-p_b)$ is the net number of quanta absorbed per unit time.

In conclusion we may say that the viewpoint of irreversible thermodynamics and the principle of minimum entropy production provide additional insight into the nature of the Overhauser nuclear polarization effect.

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Work Function of Cadmium*

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The contact difference of potential Cd-Ba is measured by the electron beam and Kelvin methods. These measurements agree within the limits of reproducibility of either method alone and yield a work function value of 4.08±0.02 ev for the work function of cadmium films deposited on tantalum. The barium surfaces, formed by redistillation following fractional distillation, show their characteristic constancy and reproducibility to ±0.01 ev. Cadmium retains some gas after exhaustive multiple distillation. Measurements taken immediately after deposition of a Cd film and during its aging show (1) that freshly deposited Cd films are generally contaminated with gas which distills with the metal; (2) that the adsorbed gas is removed progressively by getter clean-up with an attendant rise in work function totalling 0.10 ev in extreme cases, and (3) that the work function thus established is constant and reproducible to 0.03 ev or better. Comparison of these measurements with our earlier work on zinc leads to the conclusion that a cadmium surface in equilibrium with the residual gas of a well-gettered tube contains so little adsorbed gas that its final work function can probably be accepted as characteristic of the clean metal.

THIS report describes further results in a program in which the external work functions of the pure metals are determined by measurement of their contact differences of potential with respect to a reference metal of known work function, barium. Earlier work in this laboratory[1] has shown that the work functions of zinc surfaces prepared by distillation of the outgassed metal in sealed-off, barium gettered tubes are highly reproducible and constant over long periods of time. Objective evidence for the absence of gaseous contamination was obtained by making the time interval between deposition and measurement of the surfaces short with respect to the time required for deposition of a monolayer of adsorbed gas. A series of similar measurements was carried out on cadmium in 1941 but was not reported at that time. A second series of measurements by a Kelvin technique[2] was completed recently. The results of the two series agree well and taken together constitute a reasonably thorough study of this metal. Since the experimental procedures follow closely those previously described,[1,2] only the variations in technique made necessary by the peculiarities of cadmium are emphasized here. The cadmium employed in these measurements was kindly supplied to me by the New Jersey Zinc Company with an analysis showing a total impurity content of less than 0.001 percent.

ELECTRON BEAM MEASUREMENTS

The high vapor pressure of cadmium at and below its melting point precludes satisfactory outgassing by the method of repetitive fusion commonly used in our work. A second troublesome property of cadmium is its extraordinarily low critical condensation temperature on glass; at room temperature surface migration is so pronounced that agglomeration of the condensate into isolated islands generally occurs. To meet these conditions, tubes of the type used in the measurements on zinc were modified as follows. (1) The multiple distilling arrangement shown in Fig. 1 was substituted for the "first and second vaporizers" of the zinc tubes, and (2) the targets on which the films were formed and measured were 10-mil tantalum foil disks; a 60-mil tungsten post and 60-mil tantalum crossbar replaced the glass target mount of the zinc tubes.

Before charging with cadmium and zinc, the tube was subjected to our standardized outgassing schedule.[1] After charging, the baking temperature was limited to 120°C to avoid vaporization of cadmium. While the tube was on the pumps, fusions of the barium and complete distillations of the cadmium were carried out alternately through ten complete cycles. After seal-off the fusions and distillations were continued until the

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[1] P. A. Anderson, Phys. Rev. **57**, 122 (1940).
[2] P. A. Anderson, Phys. Rev. **88**, 655 (1952).

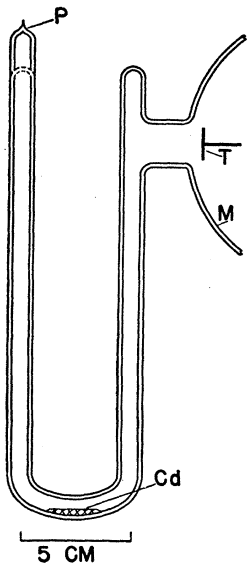

FIG. 1. Outgassing-dispensing tube for cadmium. The metal is distilled repetitively between the outer and inner walls by tubular heaters (not shown) while the condensing surface is cooled by CO_2-acetone. Both inner and outer walls are heated to dispense vapor to target T of measuring tube M. P=loading port for Cd.

electron emission test[3] showed that the evolution of gas during the heating of the metals had been reduced to a low level. A cadmium film was then laid down on one of the targets and its current-potential characteristic determined in the usual manner.[1] A succession of fresh films was then formed and measured to establish the reproducibility of the potential setting for cadmium. This procedure was then repeated for a series of barium films laid down over the cadmium. The entire schedule was then repeated for the second target.

Initial readings on the newly deposited cadmium films were reproducible to ± 0.06 volt, a reproducibility markedly inferior to that obtained for zinc.[1] On aging, the films showed a small and limited, but definite, drift toward higher work function. This drift totalled 0.10 volt in extreme cases and was largest for the films which showed the lowest initial work functions. The potential readings obtained after drifting ceased were reproducible to ± 0.03 v or better and gave a value of 1.55 ± 0.03 for the contact difference of potential Cd-Ba. The work function assigned to cadmium by these measurements is therefore $1.55+2.52=4.07$ ev. The behavior of cadmium on aging is probably due to the fact that when cadmium is distilled the gases contained in it vaporize with it; outgassing is attained only through differentiation between the condensation efficiencies of metal and gas and is never complete. On aging however, the gas which remains on the cadmium surface is removed progressively by the barium getter and the work function finally attained is that of the clean surface. This interpretation is consistent with our findings for zinc[1] which, like cadmium, has a low affinity for the residual gases present in a barium-gettered tube.

[3] P. A. Anderson, Phys. Rev. **75**, 1207 (1949).

KELVIN MEASUREMENTS

The tube employed in the Kelvin measurements on Cd-Ba was similar to those used for Ag-Ba,[2] but had no provision for electron beam measurements. The outgassing procedures followed the plan outlined in the aforementioned, but the preliminary distillations of cadmium were omitted with a view to testing the conclusion, reached in the earlier measurements, that exhaustive outgassing of the cadmium should be unnecessary if gas adsorbed on a cadmium surface during its deposition is subsequently removed by the barium getter. The barium and cadmium films were formed as in the Ag-Ba studies.[2] Eight sets of measurements on different pairs of Cd-Ba surfaces, in which each set included measurements taken immediately after deposition of the films and during their aging, were carried out during a 14-day period. The first set showed the effects of pronounced gas evolution from the first cadmium distillations, and abnormally low contact potentials. All measurements thereafter fell within the limits 1.55 ± 0.03 volts. As the measurements progressed, reproducibility improved and drift decreased. In the last two sets of measurements, which covered deposition-measurement intervals ranging from a few minutes to 24 hours, all readings fell within the limits 1.55–1.57 volts. The value 1.56 ± 0.01 volts is taken as representing the Kelvin measurements. Since sealed-off, barium gettered tubes always show a progressive lowering of residual gas pressure under the conditions obtaining in these experiments, the Kelvin results lend further support to the desorption mechanism discussed above. It now seems clear that zinc, cadmium, and silver belong to a class of metals which, when in equilibrium with the residual gas of a well-gettered tube, contain so little adsorbed gas that the measured work functions can be accepted as characteristic of the clean metals. Excellent reproducibility and constancy in the work function of cadmium can be expected under conditions which are easily obtained in sealed-off tubes.

Our value of 4.08 ± 0.02 ev for the work function of cadmium is very close to Bomke's[4] photoelectrically determined value (4.07 ev) and is in good agreement with the photoelectric measurements of Suhrmann and Pietrzyk[5] (4.10 ev). Other values have been reported by Klein and Lange[6] (4.00 ev), Schulze[7] (3.68 ev) and Lukirsky and Prilezaev[8] (3.75 ev).

[4] H. Bomke, Ann. Physik **10**, 579 (1931).
[5] R. Suhrmann and J. Pietrzyk, Z. Physik **122**, 600 (1944).
[6] O. Klein and E. Lange, Z. Elektrochem. **44**, 542 (1938).
[7] R. Schulze, Z. Physik **92**, 212 (1934).
[8] P. Lukirsky and S. Prilezaev, Z. Physik **49**, 236 (1928).