

large changes in some of the coefficients, will invalidate most of that comparison. We shall not attempt at this time, however, to make an alternative comparison with experiment. There are two ways in which this comparison can be made. First, the observed Curie temperature permits an evaluation of q^2/a , and the temperature dependence of the dielectric constant gives us $(3b_1+2b_2)/a^2$. We have already considered the resulting values of these constants, and have shown them to be of reasonable order of magnitude. To check them better we should have to have an elaborate study of the structure of the crystal from the standpoint of atomic theory, in order to be able to compute the interionic forces. Devonshire has given such a theory in a rather elementary way, but the writer believes that a more elaborate treatment would be necessary before the results could have great pretensions to accuracy. On the other hand, the behavior of the polarization below the Curie point gives information about the coefficients of the fourth-power terms (and sixth-power terms, which Devonshire also has to introduce),

but modified by the contributions resulting from the elastic strain. If the elastic and piezoelectric constants of single crystals were known accurately enough, we could evaluate these modifications, and then we should be able to find the b 's independently from the fourth-order terms, as well as from the second-order terms, and hence have a valuable internal check of the theory. Unfortunately, these elastic and piezoelectric constants are not known sufficiently well. It is to be hoped that future experiments will supply this missing information. In the meantime, it can be said that there does not seem to be anything about the present form of the theory which does not have a good chance of agreeing with experiment, when better experimental data are available.

The writer is greatly indebted to his colleague Professor A. von Hippel for stimulating his interest in the problem, and for useful discussions; and to Drs. W. Shockley and P. W. Anderson of the Bell Telephone Laboratories, for valuable exchange of information regarding the work on the subject of those Laboratories.

Evaporation of Zinc and Zinc Oxide under Electron Bombardment

FRANCIS E. DART*

Cornell University, Ithaca, New York

(Received January 16, 1950)

By use of a mass spectrographic method, the rate of evaporation of zinc and zinc oxide is measured as a function of temperature both with and without electron bombardment of the surface being evaporated. In the case of zinc metal no increase of evaporation could be detected as resulting from bombardment whereas a definite increase was observed in the evaporation of zinc oxide. The enhancement of the evaporation rate of zinc oxide increases slowly at first and then rapidly with increasing temperature.

1. INTRODUCTION

THE experimental investigation of many solid state phenomena would be much simplified if a sensitive method of microanalysis were available for measuring the chemical constitution of solids containing impurities in very small concentration. Especially would this be the case if the method were capable of analyzing the constituents of solid surfaces, for many surface phenomena such as thermionic emission, secondary electron emission, photoelectric emission, etc., are very sensitive to the atomic or molecular constitution of the surface in question. The mass spectrometer is an instrument which would be very well suited to such analysis if means could be found to remove atoms or molecules from the surface and subsequently identify them in the spectrometer.

There is evidence that under electron bombardment atoms or ions may be removed from solids. Baldock¹

found that calcium ions are obtained from calcium metal when it is bombarded with electrons. Jacobs² found oxygen compounds to be removed by electron bombardment from anodes coated with thin layers, and Sproule³ found evidence that electron bombardment of heated triple oxide surfaces removed barium, strontium and calcium atoms. The experiments reported below were undertaken to study this phenomenon in greater detail in order to see whether electrons of themselves can cause dissociation of atoms from a surface or whether this comes about only by virtue of the heating produced by the electrons. A beam of electrons was directed against a target whose temperature could be controlled. The relative number of atoms leaving its surface was detected with a mass spectrometer and compared with the number leaving by thermal evaporation alone.

* Now at University of Oregon, Eugene, Oregon.

¹ R. Baldock, Ph.D. Thesis, Cornell University, Ithaca, New York.

² H. Jacobs, *Phys. Rev.* **69**, 692 (1946).

³ R. L. Sproule, RCA Laboratories Report.

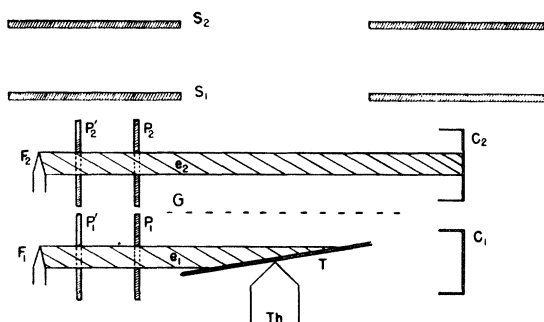


FIG. 1. Cross section of the source end of the spectrometer showing the arrangement of parts. Section taken parallel to the magnetic field.

2. EXPERIMENTAL METHOD

At the source end of the mass spectrometer two electron beams were used, one of which was directly in front of the slit and acted as the ionizing beam while the other was used to bombard the target. The geometrical arrangement of the source end of the spectrometer is shown in Fig. 1. The material to be bombarded was evaporated onto the tantalum strip T mounted so that electrons in the beam e_1 would strike it obliquely. The tantalum strip could be heated by passing a current through it. Its temperature was measured by means of the thermocouple Th made of 0.0025 in. copper and "Advance" wires spot welded to its mid-point. Because of end cooling and the very slight cooling due to the thermocouple wires the temperature of the strip was not uniform, but there was a region of about two thirds of the length of the strip the temperature of which was nearly uniform and could be determined to within about 0.5°C .

Atoms leaving the target passed through the coarse grid G and into the electron beam e_2 where some of them were ionized and subsequently accelerated toward the slits S_1 and S_2 (here shown lengthwise) by electric fields maintained between G and S_1 and S_1 and S_2 , respectively. The grid G insures the complete independence of the two beams so that e_1 could be varied at will while the number of electrons per second in e_2 was kept always constant and their energy was adjusted to give maximum ionization cross section. This grid also served to prevent ions originating in e_1 or at the target from reaching the slits.

Since the space between the target and slits is within the magnetic field of the spectrometer, the ions will travel in a curve as they are accelerated toward S_1 . Because of this curved path it is uncertain just what direction the accelerating field should have in order that ions will encounter a maximum aperture at S_1 and S_2 . Grids on each side of the electron beams and parallel to the plane of Fig. 1 were introduced in order to adjust the direction of the accelerating field and thereby focus ions into the slits. These grids increased the efficiency of ion collection by more than a thousandfold. The

mass spectrometer itself was of the conventional Dempster⁴ type using a 180° deflection. Ion currents were amplified in a cathode follower circuit similar to that described by Richter⁵ and read on a sensitive galvanometer. Currents of the order of 10^{-14} amp. could be detected readily.

3. RESULTS

A. Zinc

With the target strip coated with metallic zinc and the spectrometer set on the Zn^{64} peak, ion currents were recorded as a function of target temperature with only the beam e_2 in operation, no bombarding electrons being present. The results are plotted in Fig. 2 where the solid line represents the mean of six series of measurements and the dashed line is extrapolated from values given in the literature^{6,7} for the temperature range 250° to 490°C . These curves are not expected to coincide as absolute measurements were not made here. The data follow a straight line as expected but the slope, 8440, is about 21 percent greater than that given in the literature (the maximum variation among the six sets of measurements was 1.5 percent). This discrepancy might be accounted for by the absence of equilibrium conditions in the present apparatus if it were also assumed that the reflection of zinc atoms from the metal walls is a function of their velocity. The extra-

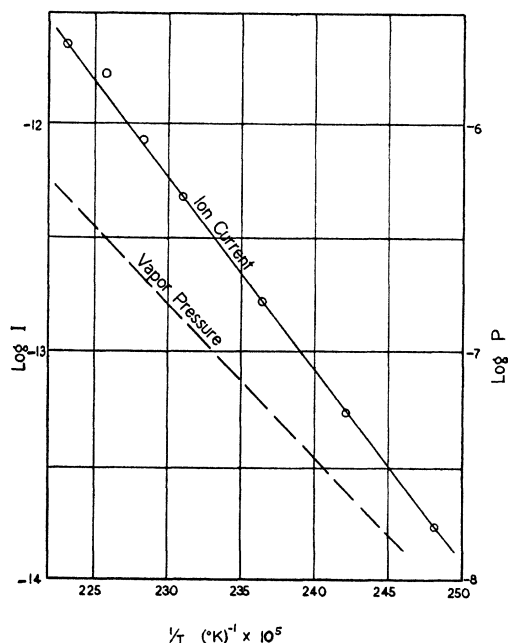


FIG. 2. Logarithms of ion currents (solid line) and vapor pressure (dashed line) plotted against reciprocal absolute temperature. Both curves represent data from metallic zinc.

⁴ Dempster, *Phys. Rev.* **11**, 316 (1918).

⁵ W. Richter, *Electronics*, **16**, No. 11, 112 (1943).

⁶ International Critical Tables **3**, 205.

⁷ Edgerton, *Phil. Mag.* **33**, 33 (1917).

polation mentioned above may also be in error, as Edgerton⁷ finds evidence for a curved line. It was not possible to extend the measurements into the temperature range covered by Edgerton's results due to the very rapid evaporation of the zinc at higher temperatures.

Data were next taken with the target strip under constant bombardment by 1.2 ma of electrons with energies which were varied in succeeding series of measurements from 200 to 1000 ev. The temperature of the target was controlled during bombardment by varying the current in the tantalum strip. The results are shown in Fig. 3 where the solid curve is an evaporation curve without bombardment and the circles represent data taken with bombardment. In no instance

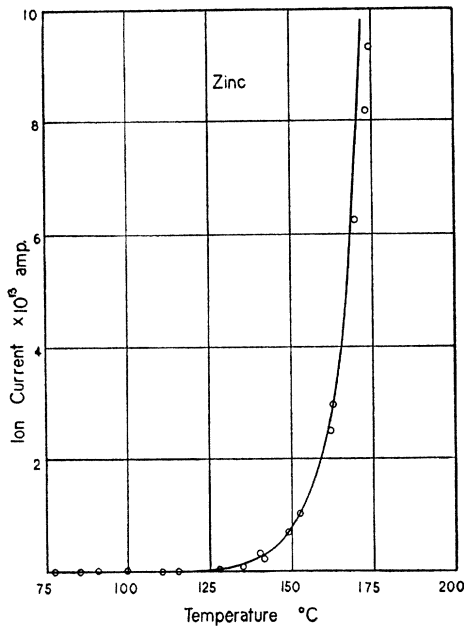


FIG. 3. Ion current vs. temperature for a metallic zinc target. The solid line represents data taken without bombardment of the target while the circles represent data taken with bombardment by 1.2 ma of 400 volt electrons.

was any enhancement of the rate of evaporation detected as a result of the electron bombardment.

B. Zinc Oxide

When the target was coated with zinc oxide and heated, ion peaks were detected with the mass spectrometer both at mass 64, corresponding to Zn, and at mass 80, corresponding to ZnO, as was expected. Because the Zn⁶⁴ peak was the larger and in order to avoid any possibility of varying background contamination, the evaporation of the zinc oxide was followed by measuring the Zn⁶⁴ ions produced. The experiments were repeated exactly as with zinc metal both with and without the bombarding beam. In this case the data show a definite increase of evaporation due to bombardment, that is,

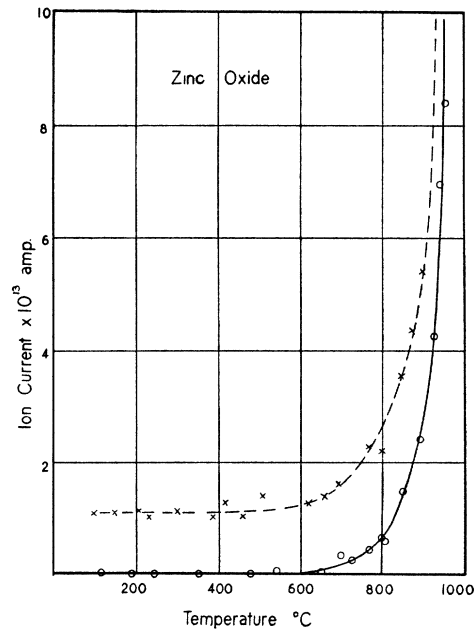


FIG. 4. Ion current vs. temperature for a zinc oxide target. The solid curve represents data taken without bombardment while the dashed curve represents data taken with the target bombarded by 400 microamperes of 400 volt electrons.

more atoms of zinc were removed under bombardment than would have evaporated due to temperature alone. Figure 4 shows data taken with a 400 μ a beam of electrons with energies of 400 ev striking the target. The solid curve is that taken with no bombardment while the dashed curve was taken with the electron beam striking the zinc oxide. The number of additional atoms removed as a result of electron bombardment increases slowly with increased temperature at low temperatures and almost exponentially at higher temperatures. This is shown in Fig. 5 where the increase of ion current due to bombardment is plotted against target temperature.

4. DISCUSSION

It is difficult to explain the increase in evaporation of ZnO under bombardment as a purely thermal effect. Considerable care was exercised to obtain a uniform distribution of the beam over the central two thirds of the target strip, and the layer of zinc oxide was so thin (about 0.045 mm) that the total power delivered by the beam would be sufficient to maintain average temperature differences across it of less than 2°C. In order to account for the observed data on the basis of local heating in the zinc oxide coating, temperatures 500°C or more above those of the target as a whole would need to be assumed. On the other hand, local heating of 10° or 15° C would have produced a measurable increase in the case of metallic zinc where no increase was observed.

In order that an atom may dissociate from the surface of a solid it must gain enough energy to allow a transition to one of the stable states of a single atom, i.e. of

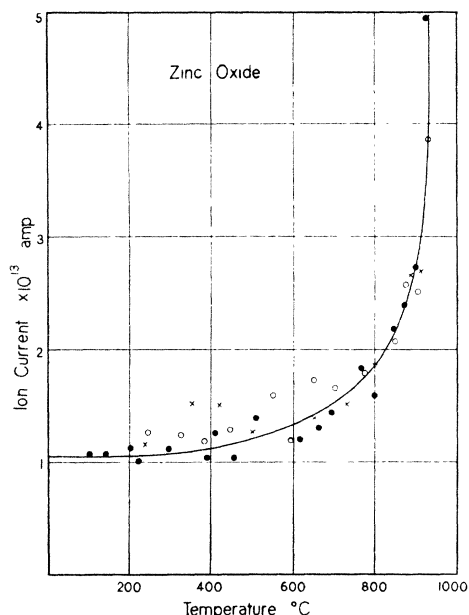


FIG. 5. The increase of Zn^{64} ion current caused by bombarding a zinc oxide target with $400\mu a$ of 400 v electrons vs. the temperature of the target. The open circles, solid circles, and crosses represent respectively three different sets of data all taken under the same conditions.

an atom of the element in the gaseous phase. The bombarding electrons carried more than enough energy to make such a transition possible. However, there are

other processes which may cause the excited atom to lose its energy before it can dissociate. The dissociation time will depend both upon the force of repulsion between the excited atom and its neighbors and upon its vibrational energy, the latter being a function of the temperature. If the de-excitation time due to the transfer of energy to an electron of the solid, or to an exciton state or due to radiative transitions is very much smaller than the dissociation time, then the probability of dissociation will be very small. This appears likely in the case of zinc metal.

It is not unreasonable to suppose, however, that the transfer of energy from an atom of the surface to the lattice or electrons of the solid will take place with more difficulty in the case of an insulator. If the de-excitation time is very much greater than the time for dissociation, almost all excited surface atoms will leave the solid, and the dissociation rate should be independent of the temperature, but if the two processes are strongly competing, a temperature dependence of the sort observed in Fig. 5 might result. The foregoing considerations may then provide a qualitative explanation for the observed behavior of both zinc and zinc oxide.

ACKNOWLEDGMENT

The author wishes to acknowledge his indebtedness to Professor L. P. Smith who proposed this investigation and offered many helpful suggestions and to Professor H. F. Newhall for many valuable discussions during the course of the work.