The Pennsylvania State University

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Field Ion Microscopy of Beryllium

A thesis in

Physics

by

John Panitz

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Approved:

12-2-66 — E. W. Müller

Research Professor of Physics
Thesis Advisor

12/2/66 — D. H. Rank

Head of the Department of Physics

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I. INTRODUCTION

The field ion microscope has proven to be a powerful tool for the investigation of metal surfaces. With a theoretical resolution of about two angstroms, it provides visual information concerning lattice structure which is unobtainable from any other source. Since its conception in 1951 by Müller, it has been used to obtain both qualitative and quantitative information about numerous metal surfaces. Most investigations have been restricted, however, to the study of refractory metals with atomic weights much greater than those of the two imaging gases most frequently used: Helium with an atomic weight of 4 amu, and neon with an atomic weight of 20 amu.

Beryllium metal, the subject of this investigation, is unique in that its small atomic weight of 9 amu makes it the lightest metal studied thus far. This special property of beryllium may affect its imaging in the field ion microscope for the following reason: Atoms of the imaging gas, upon colliding with the surface of the metal under examination must transfer their large kinetic energy due to dipole attraction, $1/2\ \alpha F^2$, to the lattice of the specimen in order to provide the sufficiently small tangential velocity component needed for realizing the highest possible resolution. The fraction of the energy transferred in such a collision depends upon the masses of the metal surface, and impinging

gas atoms. With a metal such as tungsten whose mass is approximately 45 times that of helium the energy lost in each collision is small, whereas with beryllium whose mass is about twice that of helium the energy transferred per collision is quite high. One can define a thermal accommodation coefficient $\frac{\Delta E}{E} = \frac{4mM}{(m + M)^2}$ as a measure of the fraction of energy transferred per collision; where m is the mass of the gas atom and M that of the metal atom.

After colliding with the metal surface the imaging gas atom rebounds, only to collide again with the surface a short time later and loose a fraction of its kinetic energy. After many such "hops" the gas atom dwells increasingly longer in a zone, some four angstroms above a metal surface atom, where the probability for its ionization is quite high. It ionizes, and the resulting ion is accelerated in a straight line by the high electric field to the fluorescent screen, its collision with which is recorded by a scintillation of the phosphor. Since the ionization of the imaging gas atoms occurs over all "protruding" metal surface atoms, an image of the metal surface is formed on the fluorescent screen.

The brightness of this image depends upon the number of ions hitting the screen per unit time and this in turn depends upon the number of imaging gas atoms which are ionized per unit time. The number of imaging gas atoms ionized per unit time depend upon the number present, per unit

time, at the critical height above the metal surface. This in turn depends upon the amount of energy which an impinging gas atom transfers to a metal surface atom in each collision. That is, it depends upon the thermal accommodation coefficient of the imaging gas-metal surface system. One would expect, therefore, a beryllium surface imaged in helium to give a brighter image than a tungsten surface imaged under the same gas supply conditions[1,2].

In addition to the improved thermal accommodation coefficient, resulting from the small mass of the beryllium atom, the small lattice constant of beryllium, only 2.28 angstroms, provides a resolution test for the microscope.

It is the purpose of this study to develop the techniques necessary to obtain useful field-ion micrographs of beryllium so that the lattice structure of the metal and the effects resulting from its small mass may be studied in greater detail at a future date.

II. APPARATUS

A field ion microscope based on designs by Müller and suitable for the examination of beryllium surfaces is shown in Figure 1. The complete system as shown consists of a microscope body with cold finger assembly, a titanium getter, and a vacuum system with provision for adding suitable imaging gases.

Microscope Body and Cold Finger

The specimen to be examined is carefully electropolished to a fine point which is spot welded to a loop of 8 mil molybdenum wire. The loop is inserted into tungsten springs which are sealed into the base of the Pyrex cold finger. These springs allow the specimen to be connected to an external thirty-thousand volt power supply while, at the same time, cooling the specimen by conduction from the cryogenic liquid placed in the cold finger during operation of the microscope.

A 2S alloy aluminum cone, approximately 45 mils thick and containing an orifice through which the specimen projects, surrounds the lower portion of the cold finger. A retaining ring, to which a tungsten spring is spot welded, is slipped over the cone in such a way as to make electrical contact with the conductively-coated glass wall of the microscope when the cold finger is inserted into it. The cone, cooled by conduction from the liquid in the cold

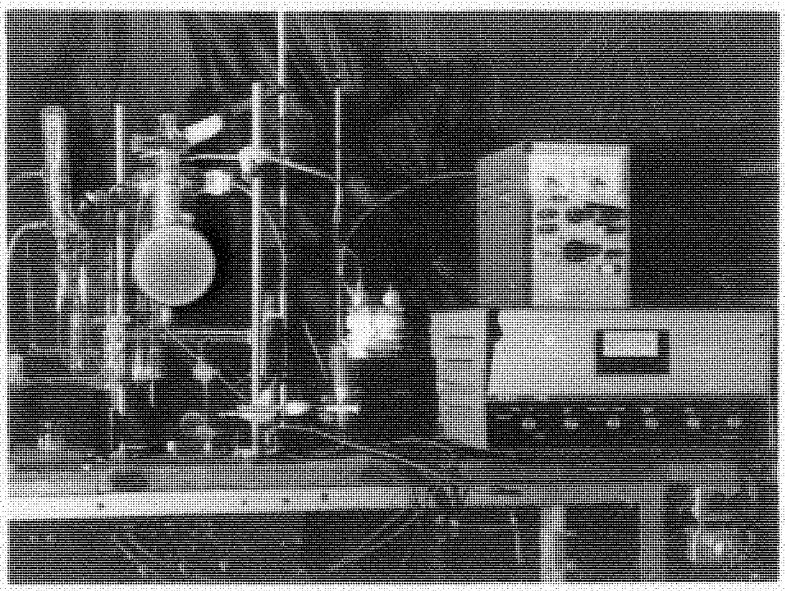

Figure 1. A Field-Ion Microscope (Front View).

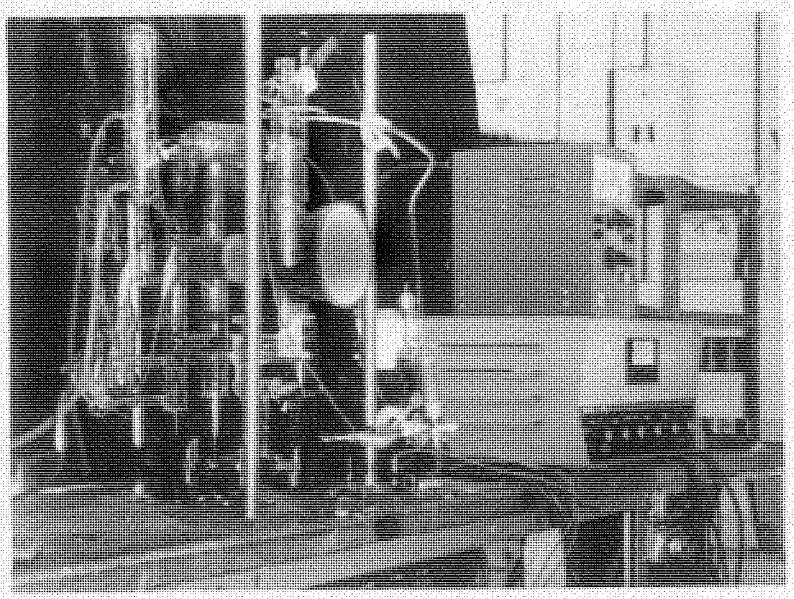

Figure 1. A Field-Ion Microscope (Side View).

finger, has been shown by Müller[3] to increase image intensity by as much as 300 %. Figures 2 and 3 show the base of the cold finger assembly in detail.

During operation the cold finger assembly is inserted into the microscope body, and oriented so that the specimen faces a silver doped zinc-orthosilicate screen dusted onto the face plate of the microscope.

Titanium Getter

The microscope is provided with a titanium getter to obtain the low ultimate pressures required for successful operation. It consists of 8 mil titanium wire loosely wound on a 6 mil tungsten wire support. The assembly, in vacuum, is heated by passing an electric current through the wires. By carefully controlling the current, the titanium wire can be made to melt and wet the tungsten. Once this condition is achieved the getter is ready for operation.

During operation a current is passed through the tungsten until titanium is evaporated onto the surrounding liquid-nitrogen cooled glass wall, and a corresponding decrease in system pressure is noted. This "flashing" of the getter is usually repeated two or three times to achieve the lowest possible pressure.

Vacuum System

The microscope is connected to a mechanical pump through a foreline valve, and to a Pyrex-glass, two-stage, mercury

Figure 2. Cold Finger Assembly: Tip Mounting Detail.

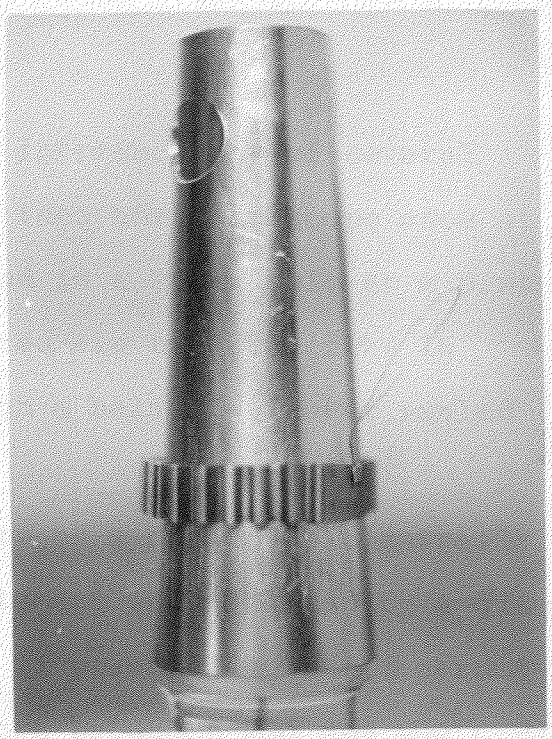

Figure 3. Cold Finger Assembly: Aluminum Cone and Tungsten Spring.

diffusion pump through a high vacuum valve. Two liquid nitrogen cooled cold traps are situated, in series, between the diffusion pump and high vacuum valve to prevent mercury vapor from entering and contaminating the microscope. A schematic diagram of the complete glass vacuum system is shown in Figure 4.

Gas Handling System

Provision has been made to introduce any of several gases or a combination of gases into the microscope once it has been evacuated. Neon, stored in a Pyrex bulb at a pressure of 0.3 mm Hg, can be admitted via two stopcocks in series. Helium can enter through a helium diffuser sealed to the microscope.

The helium diffuser consists of a quartz bulb spirally wound with a Nichrome heating element and enclosed by a glass jacket through which helium gas is passed. As the Nichrome element is heated at a temperature betweeen 400 and 600^{o}C the quartz will become permeable to the helium which will pass through the jacket and into the vacuum system. The flow rate is determined by the temperature of the quartz bulb which is controlled by the power input to the Nichrome element.

Hydrogen is made available by heating a hydrogen impregnated zirconium foil suspended in the system by means of tungsten electrodes sealed through the Pyrex. Zirconium

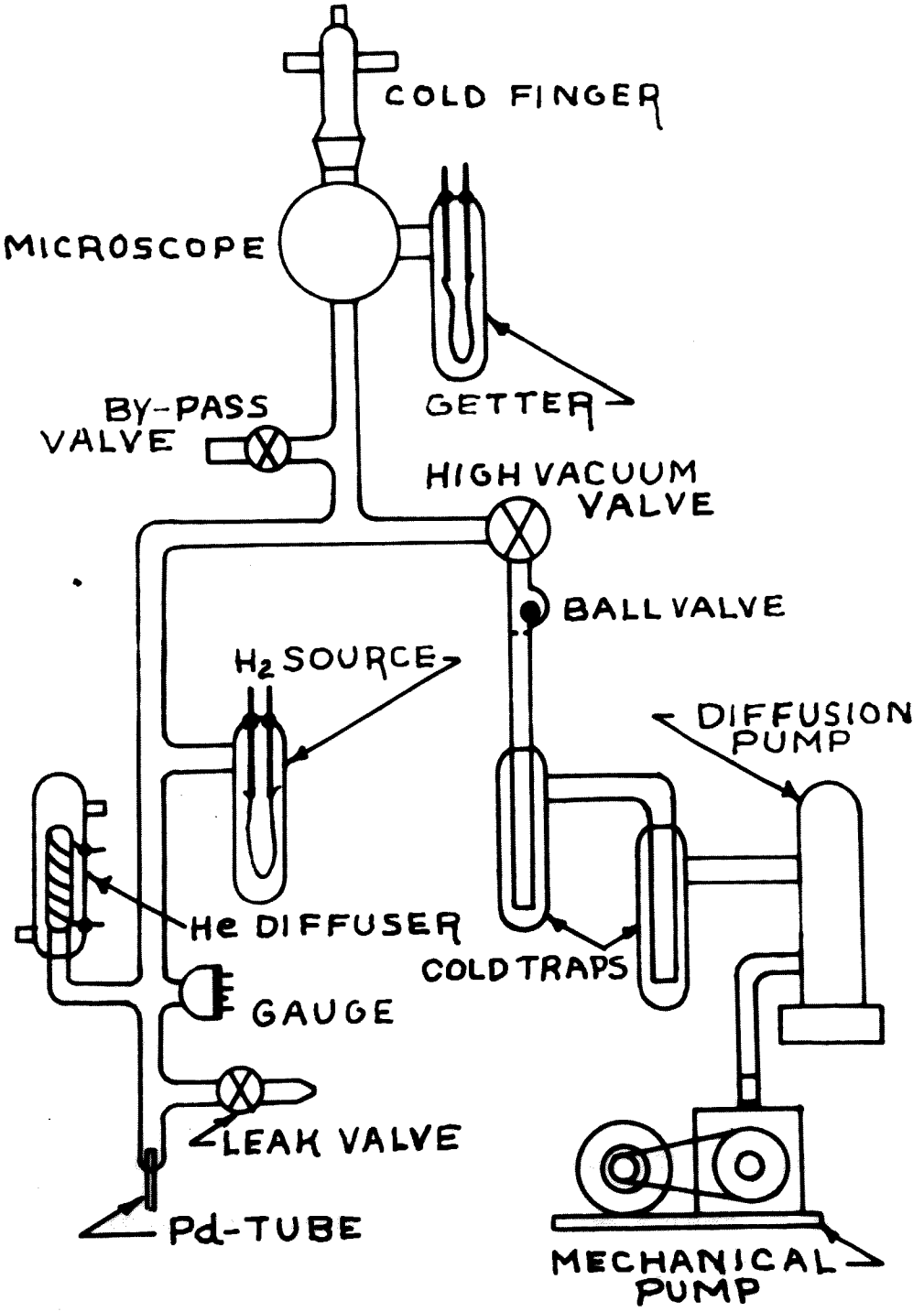

Figure 4. The Vacuum System.

foil if heated to approximately 400°C in the presence of hydrogen will absorb a large quantity of the gas, only to release it upon reheating above 500°C.

The foil is initially impregnated by heating to 400°C in situ at a pressure of 10 Torr of hydrogen. This hydrogen is admitted through a closed palladium tube sealed into the system. When heated in an alcohol flame the palladium tube will become permeable to the hydrogen in the flame allowing it to pass into the vacuum system.

Photographic Equipment

Provision has been made for recording the beryllium images directly from the screen with a modified Argus 35-mm camera, or through an external image intensifier. The latter device allows for either 35-mm still photography or motion pictures; both have been used successfully in this study.

In order to record the beryllium images directly from the microscope screen a 35-mm Argus camera was fitted with a F:0.87, 72-mm focal length, Super Farron lens providing a 4 to 1 reduction of the field of view. The optical system allows the four inch diameter microscope screen to be recorded on 35-mm film with little cropping of the image. A suitable mount providing adjustment in three mutually perpendicular planes holds the camera in rigid orientation with respect to the microscope screen. Since the depth of focus

of the lens is of the order of 1/2 mm, extreme care must be exercised in aligning the film plane parallel to the microscope screen.

Kodak spectroscopic film type 103AG is used to record the field-ion images. The spectral response of this film matches, quite closely, that of the fluorescent screen. Typical exposure times with beryllium images are of the order of a fraction of one to three minutes with this film, depending upon the applied voltage, imaging gas, and the radius of the tip.

Provision has also been made to record the images with an RCA type C70021A image intensifier tube having a gain of approximately 10,000. Such an increase in intensity permits the recording of unstable or transient beryllium images with exposure times of the order of 1/30 to 1/8 of a second.

The image is recorded on Tri-X film using a modified Cannon 35-mm camera. Alternately, a Pathe Super-16 motion picture camera has been used to record the beryllium images. Both 4 to 1 and 2 to 1 reductions of the size of the image may be affected with either camera by using suitable, interchangeable lenses. Complete details concerning the image intensifier used in this work are given in references 4 and 5.

III. EXPERIMENTAL PROCEDURE

Preparation of the Samples

1) Materials Used:

The beryllium wire used in this work was obtained from the Brush Beryllium Company. Samples included both "impure" and zone-refined wire. The impure wire, 0.00477 inches in diameter, was supplied with an analysis showing the following impurity concentrations:

2.0 % BeO	420 ppm C
250 ppm Fe	60 ppm Cr
85 ppm Ni	55 ppm S

The zone-refined wire, 0.00407 inches in diameter, contained 300 ppm of iron as the largest impurity.

All of the beryllium wire was cleaned prior to use by soaking in concentrated nitric acid for 24 hours to remove any deposits resulting from the manufacturing process. As supplied, the wire appeared "blackish" to the unaided eye. After cleaning, the silvery grey luster of beryllium metal was apparent.

2) The Annealing Process:

A small, ultra-high vacuum, ion-pumped, bakeable metal system was used to anneal specimens of impure and zone refined wire. In practice, a sample of wire was spot-welded across a pair of stainless steel rods which were clamped to

copper rods passing out of the system through a ceramic header. The header, welded to a stainless steel flange, was bolted to a mating flange on the test chamber.

A liquid nitrogen cooled, molecular sieve trap was used to evacuate the test chamber to better than 1 micron, after which the trap was isolated from the test chamber and a small Vac-Ion pump, connected directly to the test chamber, was started. After bakeout for 24 hours at 400°C the vacuum was better than 10^{-9} mm Hg.

Several samples of beryllium wire were heated, under vacuum, in this system to determine an optimum annealing temperature; all temperature measurements being made with a Leeds and Northrop optical pyrometer. Visual observation of the samples indicated that annealing for prolonged periods at temperatures in excess of 900°C greatly hastened wire burn out. 850°C seemed to be the best annealing temperature, so all samples of annealed wire used in this investigation were heated at this temperature at pressures between 10^{-7} and 10^{-9} mm Hg for approximately 24 hours.

3) Electropolishing Techniques:

Several formulas, as found in the literature for electropolishing Be wire, were investigated. They included:

a) Conc. H_3PO_4 at 30-50 v.p.c.[6]

b) 100 ml $HClO_4$[7]

350 ml C_2H_5OH

100 ml Butyl Cellosolve

(at -60^oC and 3-4 Vac)

c) 20 cc Ethylene Glycol Monobutyl Ether[8]

2 cc concentrated HNO_3

0.4 cc concentrated H_2SO_4

0.4 cc concentrated HCl

(at 40-50 Vac)

All of the above were found to be unsatisfactory for obtaining the desired tip shape. Because the chemical properties of beryllium are not unlike those of aluminum[9], it was decided to investigate a non-electrolytic aluminum polish used in this laboratory for some time. The polish, consisting of concentrated potassium hydroxide heated to just below its boiling point, proved most successful when used in conjunction with the zone refined wire. The impure wire did not etch satisfactorily in this, or any other etch which was tried. When polishing was attempted it rapidly assumed an extremely rough surface showing pronounced, local etching which did not allow for a successful tip shape.

The highly localized attack of the impure wire by the polishes used was probably due to preferential etching of the beryllium oxide impurity which was present in high concentration. For this reason all experiments were conducted with only annealed or unannealed zone-refined wire. Optical

microphotographs of some of the polished tips made from this wire and used successfully in this work are shown in Figure 5.

Operation of the Microscope

A specimen is prepared and spot welded to a molybdenum loop which is inserted into the base of the cold finger. The aluminum cone and tungsten spring are positioned on the cold finger and the whole assembly is inserted into the microscope body.

The microscope is connected to the mechanical pump through the foreline valve and evacuated until a pressure of approximately 10 microns is obtained. The foreline valve is then closed and the high vacuum valve opened connecting the microscope and getter, through the liquid nitrogen cold traps, to the diffusion pump (see Figure 4).

The system is pumped out until a pressure of approximately 1×10^{-6} Torr is reached, as indicated by an NRC type 753 ionization gauge. At this pressure the titanium getter is flashed resulting in a pressure decrease of approximately one order of magnitude. The high vacuum valve is closed, isolating the microscope and getter from the vacuum system, and the getter is flashed once again.

At this point a small amount of liquid nitrogen is carefully added to the cold finger to precool it before adding liquid hydrogen, the cryogenic coolant used in these

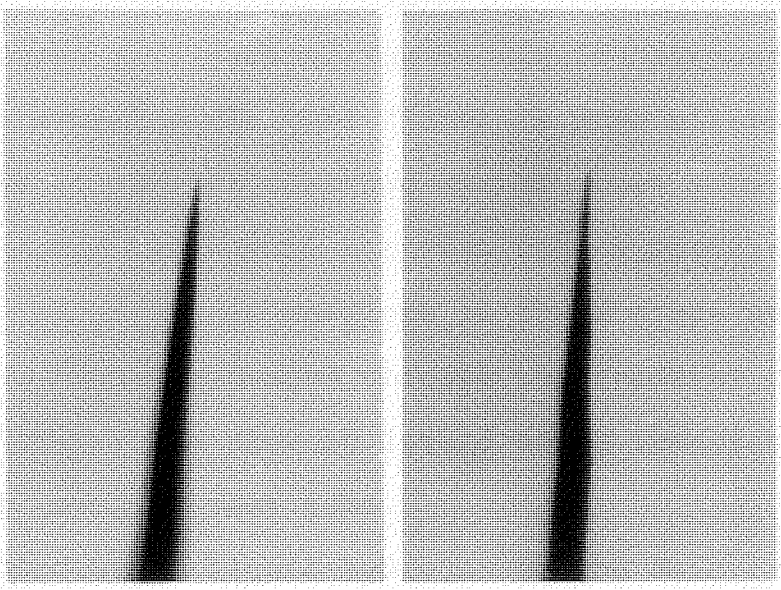

Figure 5. Optical Microscope Photographs of Chemically Polished Beryllium Tips.

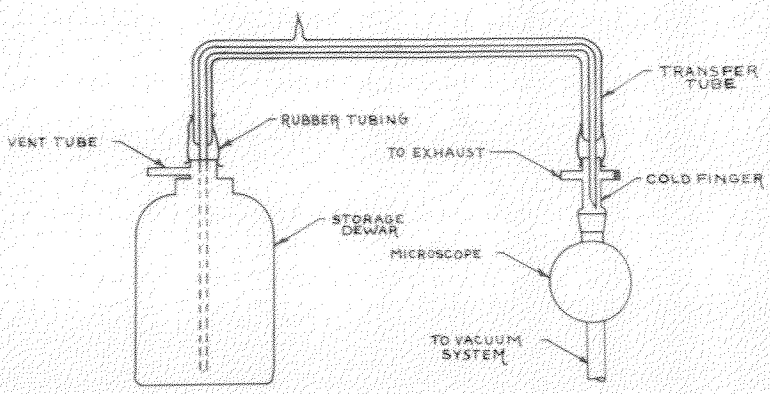

Figure 6. The Liquid-Hydrogen Transfer System.

experiments. Because of the explosive nature of hydrogen-oxygen mixtures all transferring of liquid hydrogen from the storage Dewar to the cold finger is accomplished by means of the closed transferring system shown schematically in Figure 6. By closing the vent tube a positive pressure of hydrogen gas develops in the storage Dewar which forces liquid hydrogen through the transfer tube into the cold finger. The flow of liquid stops immediately upon opening the hydrogen vent tube.

The addition of liquid hydrogen to the cold finger results in a further decrease of the system pressure to approximately 4×10^{-8} Torr. At this point the microscope is ready for operation once a suitable imaging gas has been added.

IV. EXPERIMENTAL RESULTS

The beryllium specimens examined in the field-ion microscope consisted of both annealed, and non-annealed zone refined wire imaged in neon, helium, or a neon-helium mixture. All of the helium images observed were only marginally stable for direct photography while the neon and neon-helium images, because of their significantly lower intensity as compared with the helium images[10], could not be photographed directly.

Reasonably successful direct photographs imaged in helium and showing atomic detail have been made by Müller[11], previously, and are shown in Figure 7. The extreme contrast of the images is characteristic of beryllium surfaces imaged in pure helium, and neon-helium mixtures containing a predominance of helium. Because of the difficulty in obtaining stable images for direct photography, all of the other photographs included in this work were taken through the image intensifier described earlier. A crystallographic map of beryllium's hexagonal-close-packed structure is shown in Figure 8.

Figure 9 is representative of a non-annealed zone refined beryllium tip imaged in neon at 18 kV. One notes the apparent lack of order on the $21\bar{3}0$ and $3\bar{1}\bar{2}0$ planes. Such a feature was characteristic of all the images resulting from non-annealed tips using neon as an imaging gas. One might

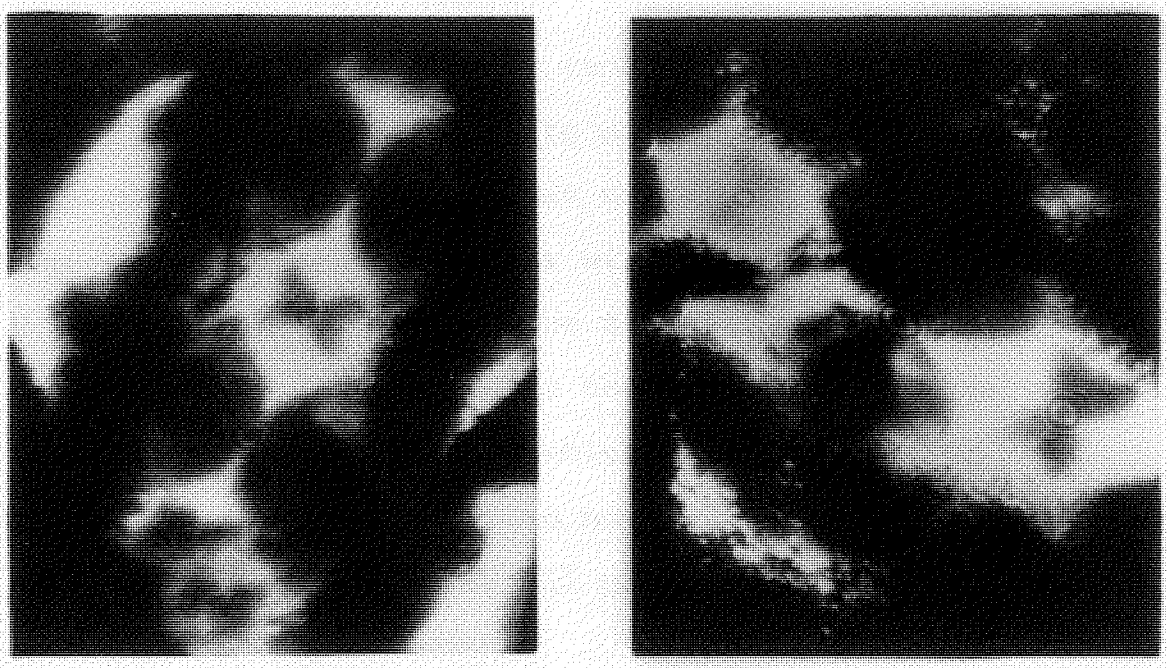

Figure 7. Direct Photographs of Beryllium as taken by Professor E. W. Müller (1965).

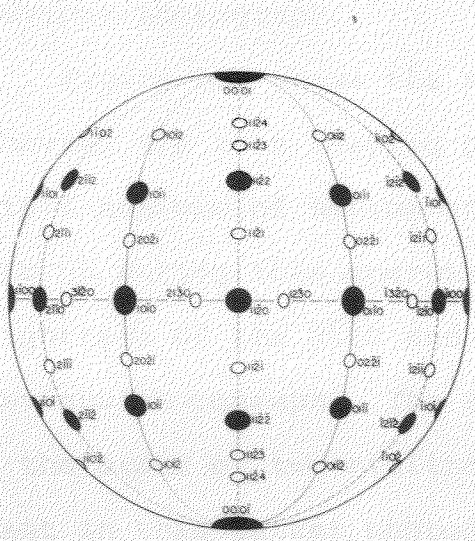

Figure 8. A Crystallographic Map for Hexagonal-Close-Packed Crystals.

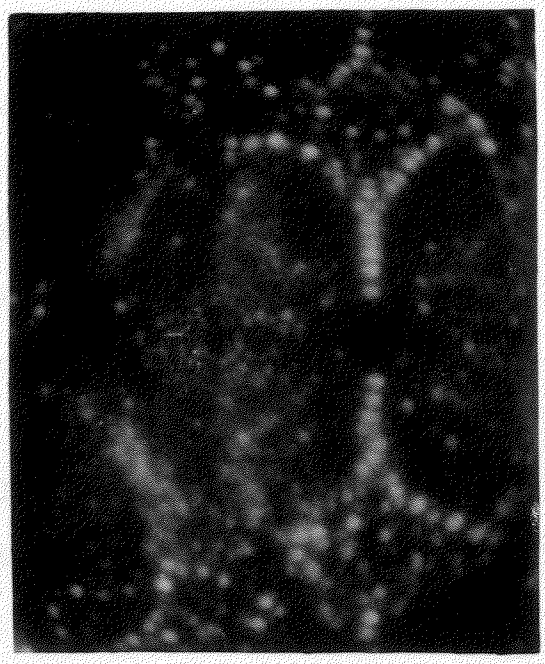

Figure 9. A Non-Annealed Beryllium Tip.

expect the disorder to arise from collision damage due to the 18 kV neon atoms impinging on these planes, especially since neon's mass is more than twice that of beryllium. However, as later photographs will show, the annealed tips imaged in neon do not show the disorder of these planes and one is led, therefore, to the conclusion that perhaps it is the annealing process which leads to order in the latter case. One should also note in this photograph the reasonably well developed $20\bar{2}\bar{1}$ plane which will be seen, again, in later photographs.

Figure 10a shows a field ion image of an annealed beryllium tip imaged in neon at 15 kV. Note the partial ordering on the $3\bar{1}\bar{2}0$ and $21\bar{3}0$ planes not apparent in the previous photograph.

Figure 10b shows the same tip imaged at 16 kV after removing the neon imaging gas, and replacing it with a 1 to 1 mixture of helium and neon; the high voltage was left on during this operation. Note the great increase in brightness of the $3\bar{1}\bar{2}0$ and $21\bar{3}0$ planes as compared to the previous photograph. The system pressure in both cases was of the order of two millitorr. The sharp increase in contrast in this latter photograph is due to the addition of the helium imaging gas.

Figure 10c shows the same tip, but the system pressure has been reduced to one millitorr, and a new lens substituted so that a magnified image of the region surrounding

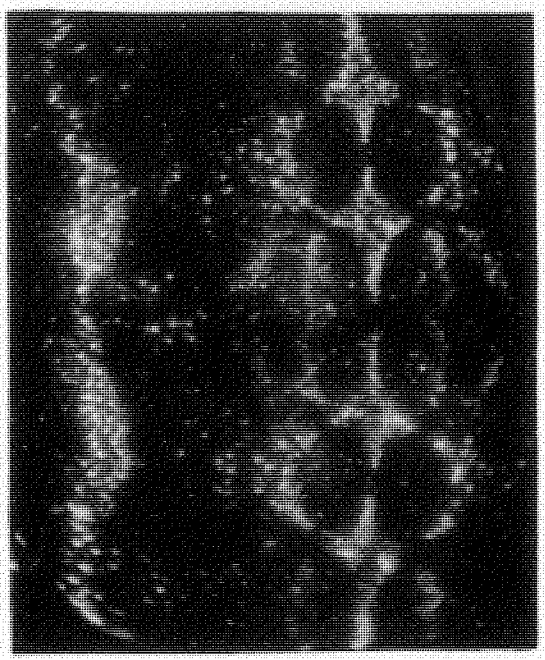

Figure 10a. An Annealed $10\bar{1}0$ Oriented Tip Imaged in Neon with a 4:1 Lens.

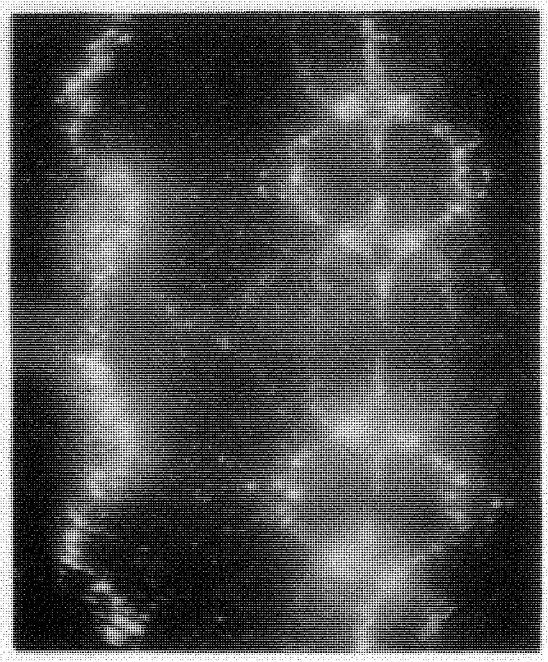

Figure 10b. The Same Tip as in Figure 10a but Imaged in 1:1 Ne-He using a 4:1 Lens.

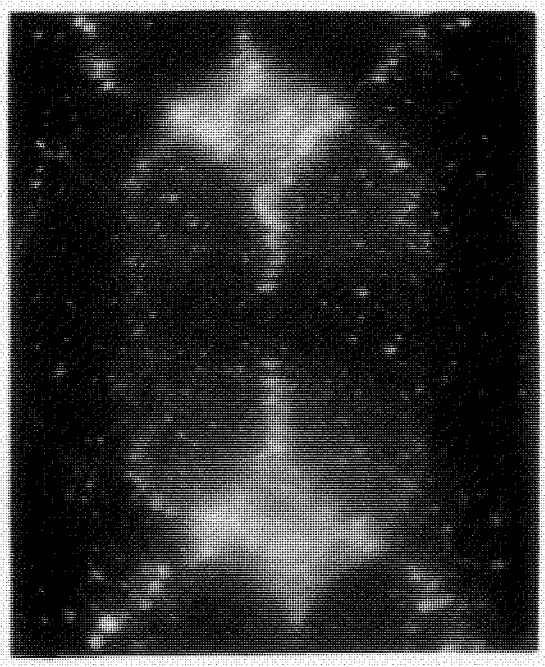

Figure 10c. The Same Tip as in Figure 10b at a Reduced Imaging Gas Pressure using a 2:1 Lens.

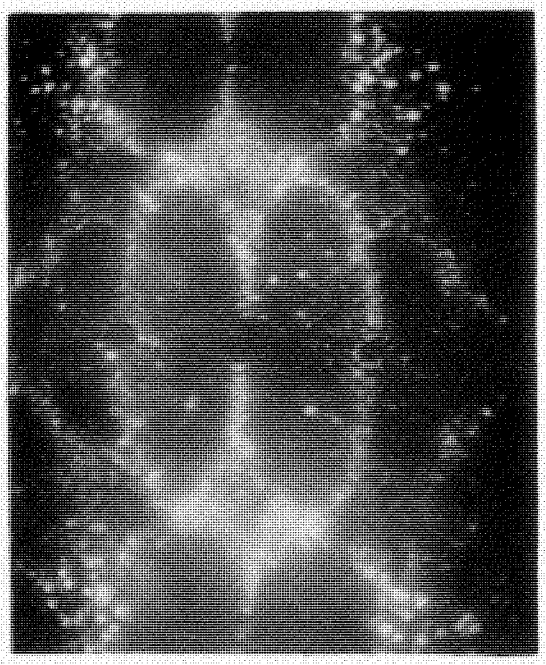

Figure 10d. The Same Tip as in Figure 10c after Continued Field Evaporation.

the $10\bar{1}0$ plane could be obtained. In this photograph the detail on the $3\bar{1}\bar{2}0$ and $21\bar{3}0$ planes is immediately apparent. The photograph was taken at 16.75 kV.

Figure 10d shows the same tip imaged in neon at 25kV after continued field evaporation. The $3\bar{1}\bar{2}0$ and $21\bar{3}0$ planes as well as the $20\bar{2}\bar{1}$ and $20\bar{2}1$ planes have developed and show atomic detail. Because of the relatively large tip radii used it was not possible to resolve the close-packed atom chains of 2.28 angstrom spacing crossing the $[\bar{2}110]$ zone line, and therefore the proposed resolution test of the microscope could not be made.

Figure 11a and 11b show the results of attempting to evaporate beryllium onto a rhodium substrate. Unfortunately, the experiment is inconclusive because it was not performed in situ. That is, the evaporation was carried out in another system, and the tip was exposed to air before imaging. The atoms shown on the rhodium substrate may well be, then, impurities resulting from the preparation of the specimen. The photographs are included only for the sake of completeness.

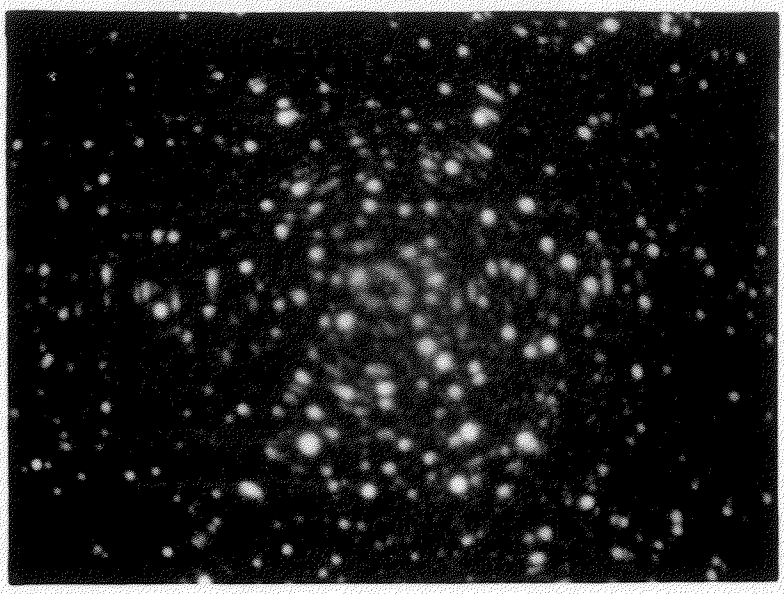

Figure 11a. Beryllium Evaporated onto Rhodium.

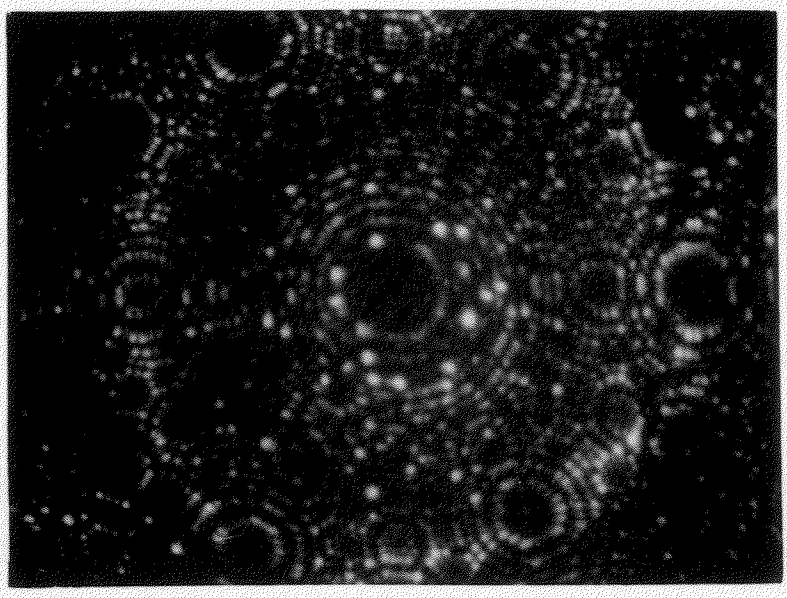

Figure 11b. The Same Tip as in Figure 11a after Field Evaporation.

V. SUMMARY AND CONCLUSIONS

Statement of the Problem

The field ion microscope image properties of beryllium are of interest for two main reasons: the small lattice constant of 2.28 $\mathring{A}$ provides a resolution test of the microscope, and the low atomic lass suggests a better thermal accommodation of the imaging gas, so that a reduced imaging field can be expected. It was the purpose of this work to develop the techniques necessary to obtain successful field ion micrographs of beryllium for use in future research.

Results and Conclusions

This investigation has shown that acceptable field ion micrographs of beryllium can be obtained. Zone refined wire is preferable since the high impurity concentration in the "impure" wire tested led to localized, preferential etching of the specimen and hence poor tip geometry. A polish suitable for preparing beryllium specimens has been found, and consists of concentrated potassium hydroxide heated to just below its boiling temperature. The specimens, previously cleaned by soaking in concentrated nitric acid for 24 hours, are polished to the desired shape by a series of quick dips in the recommended solution. The resulting tips are imaged most successfully in the field ion microscope using a 1 to 1 mixture of helium and neon respectively at a total pressure of 1.5 millitorr. Under such conditions the use of

some form of image intensification is mandatory because of the rapidly progressing field evaporation at an acceptable imaging field.

Suggestions for Future Research

It is hoped that in the near future the proposed difference in image brightness between beryllium and a metal of greater mass but similar crystal structure, perhaps ruthenium or rhenium, will be examined. In order to demonstrate the effect of the thermal accommodation coefficient on image intensity, the electric field strength at the ruthenium and beryllium surfaces must be the same. Practically, this means that the geometry of the metal specimens under examination must be identical. Producing identical specimens is almost impossible. It would seem, therefore, that another solution is needed.

Such a solution is presented by the possibility of evaporating beryllium metal in situ so as to partially coat a substrate having a similar crystal structure but a greater mass. The evaporated beryllium would not appreciably change the radius of the substrate and hence the electric field strength over the entire tip would remain practically constant. The difference in mass of the beryllium and substrate would reflect itself in the variations in brightness of the resulting image; the portion of the image due to beryllium appearing brighter than

that of the substrate because of the improved thermal accommodation with the imaging gas in the former case.

In addition, one might investigate the feasibility of growing epitaxial layers of beryllium on a suitable substrate using a technique similar to that described by Melmed[12] for the nucleation and growth of copper on tungsten from the vapor phase.

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