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ANISOTROPIC VAPORIZATION RATES OF OPPOSITE FACES OF ZINC OXIDE SINGLE CRYSTALS

Robert J. Galluzzo and Alan W. Searcy

Inorganic Materials Research Division, Lawrence Radiation Laboratory, and Department of Materials Science and Engineering, College of Engineering, University of California, Berkeley, California

ABSTRACT

The rates of vaporization of opposite basal faces of zinc oxide have been measured as functions of temperature. The rates differed by about a factor of 4. The average apparent enthalpies of vaporization for the reaction $ZnO(s) \rightarrow Zn(g) + 1/2\ O_2(g)$ for the two faces were measured to be: zinc-rich (0001) face, 134.6 kcal/mole; oxygen-rich $(000\bar{1})$ face, 140.8 kcal/mole, compared to 110.5 kcal/mole for the equilibrium reaction.

The apparent entropies for the reaction were for the (0001) face, 49.9 eu and for the $(000\bar{1})$ face, 49.2 eu. These entropies, to within expected limits of error, are equal to each other and to the entropy of the equilibrium reaction at the same temperature, 48.0 eu. The results are consistent with expectations if desorption is rate limiting. The theoretical arguments that justify this conclusion are reviewed.

I. INTRODUCTION

It has been known for some time that opposite crystallographic faces of crystals that have anisotropic arrangements of constituent atoms show different etching behavior and different rates of decomposition (1-3). Until recently, however, the rates of vaporization of the opposite faces of the only solid of anisotropic packing for which congruent vaporization had been studied, cadmium sulfide, were believed to be indistinguishable (4,5). Zinc oxide was then found, however, to vaporize about three times as fast from the zinc-rich (0001) face as from the oxygen-rich $(000\bar{1})$ face (6-8). And when cadmium sulfide (8) was studied in a lower temperature range than that of the pioneering study (4), where a different mechanism probably governs the reaction, the opposite basal faces showed different vaporization rates. The temperature dependence of vaporization from these opposite faces was established for cadmium sulfide, but remains unclear for zinc oxide because of apparent interactions with a container material when zinc oxide was studied as a function of temperature (6).

Reliable determinations of temperature dependences of evaporation rates provides particularly important information for models describing the vaporization process (9-10), so additional measurements of temperature dependences of vaporization for anisotropic materials are of value.

For oxide materials the theoretical interest of vaporization data is complemented by an exceptional practical interest. Oxides are important structural materials for use at high temperature and their usability is partly determined by their vaporization rates. The present work is designed to measure (0001) and $(000\bar{1})$ face vaporization for zinc oxide as a function of temperature.

II. EXPERIMENTAL

The 3 M Company supplied the sliced and polished crystals of zinc oxide (11). The crystals were grown as hexagonal needles and cut with a diamond saw to expose basal slices of 1 mm thick by 8 mm diameter. The wafers were lightly polished with 600 grit SiC papers which left traces of Si on the surface of the crystal. Several crystals were ordered in an unpolished condition. No differences in the vaporization characteristics were observed between polished and unpolished crystals.

Observations by Mariano and Hanneman (12) were used as a basis for determining the crystallographic polarity of the wafers. Mariano and Hanneman showed that the asymmetric nature of the crystal structure, along the c-axis, produces slightly different X-ray scattering factors for opposite orientations. They developed an etching technique that gave surface morphologies which could be correlated with X-ray data.

The samples were etched with 20 vol% HNO_3 for 20 min. The zinc-rich (0001) face developed hexagonal pits and the oxygen-rich $(000\bar{1})$ face developed rough "hillocks." Etched surfaces of the prismatic face provided unambiguous identification of the polarity of the ZnO crystal because the apex of the large etch pits points towards the zinc-rich surface (12). Care was taken to expose to free surface vaporization only the surface of the crystal that was not etched. This was especially important in the vaporization of the oxygen-rich $(000\bar{1})$ surface, which is attacked more rapidly than the zinc-rich surface by the nitric acid solution.

Free surface vaporization rates were measured by the torsion-Langmuir method, and equilibrium pressures were measured by the torsion-

effusion method (13). The torsion cells were constructed of 99.5% alumina encased in a molybdenum cell holder. The cell holder was of a "dumbbell" shape to reduce its weight. The cells were designed so that they could be used interchangeably for torsion-effusion and torsion-Langmuir studies. The cell assembly was suspended from a 1.5 mil tungsten torsion fiber. The torsion constant of the wire was measured before any of the runs were made and checked repeatedly to insure that it remained constant.

Care was taken to avoid leakage from the cells in a direction that would add to the moment. The orifice caps were thinned to the desired thickness, and the cells were heated with zinc oxide inside but without orifices. No deflection was found in the temperature range of interest. The force corrections for the effect of the orifice on the effusion measurements were of the order of .58 for the .08 cm diameter orifice and .44 for the .15 cm diameter orifice. The orifice corrections for the torsion-Langmuir study averaged .68 for the .40 cm orifice, but because the evaporation coefficient is low, the condensation coefficient of molecules returned to the surface after presumably deactivating collisions with the wall should also be low (10). It was assumed that no correction for the free surface vaporization measurements (13,16) was required.

The apparatus was calibrated with zinc oxide for which the equilibrium vapor pressure is well known (14,15). Vaporization occurs by the congruent reaction

$$ZnO(s) = Zn(g) + 1/2\ O_2(g) \qquad (1)$$

Temperatures were measured with a platinum/platinum-10% rhodium thermocouple inserted into a dummy cell of molybdenum of roughly the same weight as the cell assembly. Temperature profiles were run previous to the vaporization studies. Two thermocouples, one in contact with the cell assembly and the other inserted in the dummy cell, were moved up and down the furnace. A region about 5 cm long was found in which the temperature was constant to 1.5°C. All thermocouples were calibrated using the melting point of copper as a reference point.

III. RESULTS

The torsion effusion results as shown in Fig. 1 showed an orifice area dependence. Extrapolation to zero orifice by means of the Whitman-Motzfeld equation (17,18) puts the experimental plot of pressure above the accepted thermochemical data by a factor of about two.

Torsion Langmuir measurements for the zinc-rich (0001) face were more reproducible than for the oxygen-rich ($000\bar{1}$) face. As seen in Fig. 2, two independent runs for the zinc-rich face lead to consistent results with little experimental scatter. Oxygen-face pressures tended to increase with time. The reason for the difference between faces can be seen by comparing profiles. Figure 3 is a photograph of a crystal after vaporization from the zinc-rich (0001) surface. The cross sectional view shows vaporization took place with little undercutting of the orifice cap. The white arrows in the photograph show the size and position of the orifice. The area of vaporization remained substantially constant throughout the run.

On the oxygen-rich $(000\bar{1})$ face, as can be seen from the cross sectional view of Fig. 4, there is much undercutting. In fact, there was some vaporization from the whole crystal face. Again the white arrows show the size and position of the orifice on the crystal. Clearly the effective area of vaporization of this oxygen face is ill-defined and increasing with time.

A run was made in which the effective area of vaporization of an oxygen face was determined more accurately. The crystal was held in the furnace at approximately the temperature range of interest until its rate of vaporization had become constant, a process that required about 1 hour for each face. The crystal was removed from the furnace and the diameter of its thermally etched surface was measured to be .44 cm, compared to the 0.40 cm diam defined by the collimator. The crystal was again heated but in order to minimize the change in effective area of vaporization, only a few points were taken to establish the temperature dependence. The run was completed in 2-1/2 hours. The diameter of the vaporized surface after this period was .46 cm. For the calculation of the pressures from the deflections, the average diameter (.45 cm) was used.

For the zinc-rich (0001) face the total pressure is given as a function of temperature by

$$\log P = 8.084 - 2.025 \times 10^4 \ (1/T)$$

and for the oxygen-rich face by

$$\log P = 8.079 - 2.119 \times 10^4 \ (1/T).$$

Least squares analysis of the data yield raw values of the apparent enthalpy and apparent entropy of vaporization. These quantities were calculated for each face exactly as though equilibrium pressures were being measured for reaction 1. For the zinc-rich face the data yielded $\Delta H^* = 139.0$ kcal and $\Delta S^* = 53.34$ eu over the temperature range 1400-1537°K. For the oxygen-rich face at 1460-1550°K the values are $\Delta H^* = 145.5$ kcal and $\Delta S^* = 53.59$ eu.

This method of calculation implies the tentative assumption that desorption is rate determining (10). If, for example, the formation of activated zinc oxide molecules in a self adsorbed surface layer is assumed to be rate limiting, the calculated apparent enthalpy of activation would be about 2/3 that calculated by the assumption used (10).

As mentioned previously, the equilibrium pressures calculated from the effusion data by means of the Whitman-Motzfeld equation (17,18) were higher than calculated from the thermochemical data. Since Anthrop and Searcy (15) and Hoenig (19) obtained agreement with the thermochemical data in more detailed studies of zinc oxide effusion the difference between the extrapolation in the present study and the calculated value probably represents a systematic error inherent in the present experiments. The free surface data should be adjusted to correct for this systematic error. The enthalpy from the extrapolated curve was about 2 kcal higher than the accepted enthalpy. Free surface apparent enthalpies were corrected by multiplying them by the ratio of the slope of the thermochemical data to the slope of the extrapolated data. Pressures of free surface studies were corrected by multiplying them by the ratio of pressures calculated from the thermochemical data to measured pressures at the midpoint

of the free surface temperature range.

The corrected apparent enthalpies and entropies for reaction 1 are then for the zinc-rich face, $\Delta H^* = 134.6$ kcal and $\Delta S^* = 49.9$ eu, and for the oxygen-rich face $\Delta H^* = 140.8$ kcal and $\Delta S^* = 49.2$ eu. These values can be compared to the enthalpy and entropy of the equilibrium reaction (14,15), $\Delta H = 110.75$ kcal and $\Delta S = 48.0$ eu. For the zinc-rich (0001) face, the evaporation coefficients are .0086 at 1428°K, and .0122 at 1515°K. For the oxygen-rich $(000\bar{1})$ face, the evaporation coefficients are .0019 at 1428°K, and .0029 at 1515°K.

IV. DISCUSSION

The rates of vaporization of single crystals have usually been assumed to be controlled by reactions that occur on specific surface sites (20) or by the advancement of ledges across the exposed surface planes (21). However, those vaporization reactions that occur at the maximum possible rates consistent with the given vapor pressures, that is, with unit vaporization coefficients α_v, must necessarily be limited by the rate of desorption from the self-adsorption layer (10). If desorption is rate determining, the apparent enthalpy of the vaporization reactions must equal or exceed the equilibrium enthalpy and the apparent entropy should be approximately equal to the entropy of the equilibrium process (10).

Leonard and Searcy (8) found apparent entropies for the cadmium-rich (0001) face vaporization of cadmium sulfide that are near the entropy of the equilibrium reaction. The present study yields apparent entropies of vaporization for both (0001) and $(000\bar{1})$ faces of zinc oxide that are also within expected experimental error of the entropy of the equilibrium reaction.

These apparent entropies are all calculated on the assumptions (a) that the appropriate frequency factor for the rate determining step is $(2\pi MkT)^{-1/2}$ for each desorbing species with concentrations expressed as partial pressures (this factor is the factor from gas phase kinetics that relates pressure to flux at a plane), and (b) that surface roughness should be neglected in assigning the area of vaporization. The assumed frequency factor is appropriate only if desorption rather than a step prior to final desorption is rate limiting, but is chosen because it provides a good basis for comparison of the free surface vaporization data to equilibrium pressure data and, therefore, for analysis of whether or not desorption is the probable rate limiting process. The analysis will now be described, and then the appropriateness or inappropriateness of a surface roughness correction will be discussed.

An appropriate expression for the flux $J\hat{s}$ expressed in moles per cm^2 per sec. of molecules undergoing an elementary surface reaction step is one of the general form (22) $J_s = \kappa\nu[C^*]$ where κ is the transmission coefficient, a constant often assumed to be 1 or 0.5, ν is the frequency with which molecules of the activated complex vibrate in the reaction coordinate, and $[C^*]$ is the concentration of the activated complex for the surface step in moles per cm^2.

When desorption is viewed in terms of activated complex theory, it is apparent that the activated complex is the particle with just the energy necessary to escape from the surface (10) or, more exactly, is the weakly bonded "giant molecule" that consists of the particle just escaping from the field of attraction of the condensed phase plus the condensed phase. For the special, but important, case of substances that

vaporize with unit vaporization coefficients, the activated complex can be viewed as consisting of the solid plus the escaping vapor molecules. With the concentration of vapor molecules expressed in pressure units, the proportionality factor from gas kinetic theory that relates the pressure of the escaping vapor to its flux is $(2\pi MkT)^{-1/2}$. This factor assumes a Boltzman distribution of kinetic energies. Very limited experimental data for substances that vaporize with vaporization coefficients smaller than unity indicate that this same frequency factor is valid for the desorption step in such reactions (23,24). We expect the factor to be generally applicable for desorption because a Boltzman distribution means that the escaping molecules have an equilibrium distribution of kinetic energies--an expected situation if the energy for formation of the activated complexes is provided by the thermal energy supplied to the surface.

Considering first simple vaporization of a single kind of particle, the flux desorbing, J_d can be expressed as

$$J_d = (2\pi MkT)^{-1/2} P^* \tag{2}$$

where P^* is the pressure that the vaporizing molecules would exert on a surface placed above the vaporizing surface. But if the activated complex is at equilibrium with the bulk condensed phase, as it would be if desorption is rate limiting, the free energy of formation of the activated complexes at the pressure P^* is zero. Then

$$P^*/P^{*o} = \exp(\Delta S^*/R) \exp(-\Delta H^*/RT) \tag{3}$$

where P^{*o} is the pressure of the activated complex in its standard state, k Boltzman's constant, and ΔS^* and ΔH^* are the standard molar entropy and standard molar enthalpy of formation of the activated complex from the bulk condensed phase. Substituting (3) in (2)

$$J = (2\pi MkT)^{-1/2} P^{*o} \exp(\Delta S^*/R) \exp(-\Delta H^*/RT) \qquad (4)$$

(In equations of ref. 10, the factor $(2\pi MRT)^{-1/2}$ was incorrectly written where $(2\pi MkT)^{-1/2}P^o$ or $(2\pi MkT)^{-1/2} P^{*o}$ should have been written. However, the numerical calculations of that paper employed the correct conversion factors.)

Equation (2) has a form similar to that of the Langmuir equation,

$$J = \alpha_v (2\pi MkT)^{-1/2} P^o \exp(\Delta S^o/R) \exp(-\Delta H^o/RT) \qquad (5)$$

where P^o is the standard pressure of the equilibrium vapor and ΔS^o and ΔH^o are the standard entropy and enthalpy of vaporization. Comparison of Eqs. (4) and (5) shows that when $\alpha_v = 1$, (a) the activated complex is identical to the equilibrium reaction product, (b) $\Delta S^* = \Delta S^o$, and (c) $\Delta H^* = \Delta H^o$.

When more than one kind of particle is produced in a vaporization reaction, expressions like Eqs. (4) and (5) are required to describe vaporization of each, and the entropies and enthalpies are partial quantities. For comparison of free surface vaporization rate data for zinc oxide with equilibrium data we can write

$$J_{Zn} \times J_{O_2}^{1/2} = \tag{6}$$

$$(2\pi M_{Zn}kT)^{-1/2}(2\pi M_{O_2}kT)^{-1/4}\left(P_{Zn}^{*o}\right)\left(P_{O_2}^{*o}\right)^{1/2}\exp(\Delta S^*/RT)\exp(-\Delta H^*/RT)$$

Equation (6) departs from the usual conventions for writing rate equations in two respects. Ordinarily the rate of reaction (1) would be expressed in terms of a single flux--usually the flux of zinc oxide molecules that react. Furthermore, the rate equation would customarily be written for whole molecules, while Eq. (6) is written for a fractional mole of oxygen. Departure from the usual convention is justified by our objective, which is to compare apparent standard activation entropies and enthalpies that are calculated from the rate data with standard entropies and enthalpies of the equilibrium reaction. To facilitate the comparison we have chosen to transform the kinetic data into a form that parallels the usual thermodynamic expression rather than the equally valid approach, to express the thermodynamic data in a form that parallels a conventional expression in reaction kinetics.

Suppose that a step prior to desorption is rate limiting, perhaps, for example, the electron transfer reaction $Zn^+(ads) + O^-(ads) = Zn(ads) + O(ads)$. Then equilibrium concentrations would be maintained during vaporization in vacuum only for particles formed as products of steps up to the rate determining step, and for the activated complex in that step. For the electron transfer the activated complex might be a

ZnO^*(ads) molecule, and the expression equivalent to (6) would be

$$J_{ZnO} = \kappa\nu[ZnO^{*o}] \exp(\Delta S_a^*/RT) \exp(-\Delta H_a^*/RT) \quad (7)$$

where ΔS_a^* and ΔH_a^* are the difference in standard entropy and enthalpy of a mole of the ZnO^*(ads) activated complexes and a mole of bulk ZnO and $[ZnO^{*o}]$ is the concentration of the activated complex in its standard state. For convenient comparison with the entropy and enthalpy of the equilibrium reaction and the expected activation entropy and enthalpy if desorption were rate limiting, Eq. (7) can be raised to the 3/2 power:

$$J_{ZnO}^{3/2} = (\kappa\nu)^{3/2} [ZnO^{*o}]^{3/2} \exp(3\Delta S_a^*/2R) \exp(-3\Delta H_a^*/2RT) \quad (8)$$

The Langmuir equation gives for the relationship between the maximum possible fluxes $J_{M(Zn)}$ and $J_{M(O_2)}$ and the standard enthalpy and entropy of reaction (1)

$$J_{M(Zn)} \times J_{M(O_2)} =$$

$$(2\pi M_{Zn}kT)^{-1/2}(2\pi M_{O_2}kT)^{-1/4}(P_{Zn}^o)(P_{O_2}^o)^{1/2} \exp(\Delta S^o/R)\exp(-\Delta H^o/RT) \quad (9)$$

Comparison of Eqs. (6) and (9) leads to the general conclusion stated at the beginning of this discussion section--for desorption to be rate limitive ΔH^* calculated on the assumption that Eq. (6) is correct

must equal or exceed ΔH^o in Eq. (9), otherwise sufficient energy to produce vapor particles of the given formula is not supplied. And ΔS^* must be approximately equal to ΔS^o as can be seen when the entropy difference between the activated complex for a desorption step and bulk zinc oxide is estimated.

For the vaporization of the zinc oxide, the particles that desorb are known to be zinc atoms and oxygen molecules. If desorption is rate limiting, excess free energy of excitation might be carried off by excited zinc atoms or excited oxygen molecules or might be left at the surface. But regardless of which of these alternatives or combination of them is correct, the entropy content of the activated particles should be little different from that of the corresponding particles in their equilibrium reaction.

For example, if all the oxygen molecules desorbed in their lowest excited state, the $^1\Delta_g$ state, rather than predominantly in their $^3\Sigma_g^-$ ground state the activation enthalpy would necessarily exceed the enthalpy of the equilibrium reaction by at least the energy difference between the singlet and triplet state (25) (the difference could be more if excess rotational or vibrational energy were present), that is by about 22.6 kcal per mole of O_2 or 11.3 kcal for reaction 1. But the activation entropy would to a first approximation differ from that of the equilibrium reaction only by the difference in the contribution to the entropy of the multiplicity of the two states, that is by $-R \ln 3 = -2.2$ eu per mole of O_2 or -1 eu for reaction 1.

The product

$$(\kappa\nu)^{3/2}\,[ZnO^{*o}]^{3/2}\,\exp\,(3\Delta S^{*}/2R)$$

or any similar product expressions for formation of other possible surface activated complexes from bulk zinc oxide could fortuitously be approximately equal to

$$[(2\pi kT)^{-3/4}(M_{Zn})^{-1/2}(M_{O_2})^{-1/4}\left(P^{o}_{Zn}\right)\left(P^{o}_{O_2}\right)^{1/2}\exp\,(\Delta S^{o}/R)]$$

but such a coincidence for both zinc oxide basal faces, which have very different surface structures (8) seems unlikely. The near agreement between the calculated apparent activation entropies and the entropy of equilibrium reaction, therefore, is circumstantial evidence, but not of course proof, that desorption limits the rate of vaporization of both basal surfaces of zinc oxide.

The conclusion that desorption is probably rate limiting is important background information for deciding whether the total or projected surface area should be used in calculating apparent entropies from the experimental data. While surface roughness or porosity has been shown not to increase the flux from a solid that has unit condensation coefficient (26), if the condensation coefficiention is very low the vaporization flux is increased in nearly direct proportion to increases in total surface area (27). We expect that the most probable value of the condensation coefficient of an equilibrium vapor is the value of the vaporization coefficient for the same experimental conditions (10).

Since the vaporization coefficient for zinc oxide is low, of the order of 10^{-2} in our experimental range, it would at first thought seem that the total rather than projected area should be used in our calculations.

But if the enthalpy of activation for vaporization is higher than the enthalpy of the equilibrium reaction because the vapor molecules leave the surface in activated states, these molecules may still be activated when they collide with projections of the roughened surface. And while the expected condensation coefficient for a stoichiometric equilibrium beam of zinc atoms and oxygen molecules on a zinc oxide surface is 10^{-2}, for excited molecules the condensation coefficient should be unity. These excited molecules experience no activation free energy barrier for condensation. If the excess excitation free energy is retained by the surface rather than one of the vaporizing particles, on the other hand, these particles would only rarely encounter an activated portion of surface when colliding with a projection and would have low condensation coefficients.

We think that the most probable reason for the low vaporization coefficient of zinc oxide is that the oxygen molecules vaporize largely in the $^1\Delta_g$ or in higher excited states. A 45 minute half-life has been estimated for spontaneous emission of O_2 molecules in the $^1\Delta_g$ state (28). We think, therefore, that the effective condensation coefficient of the vapor from the zinc oxide surface on surface projections is likely to be unity, and have consequently used the projected surface areas for our calculations.

Fortunately, the total surface areas estimated from scanning electron microscope examination of zinc oxide surfaces (8), are only about a

factor of 2 greater than the projected area. If we are mistaken in assuming an effective condensation coefficient of unity on surface projections, the apparent entropies of activation that we have reported should be reduced by about R ln $2x2^{1/2}$ = 2 eu. The lower values are slightly closer to the entropy of the equilibrium reaction than the values that are calculated using the projected area, but both are within probable experimental error of that value.

A desorption-limited vaporization mechanism is compatible with the exerpimental evidence that Somorjai and co-workers found with cadmium sulfide that the vaporization is catalyzed by light (29) and is inhibited by a flux of sulfur (4) that impinges on the surface. Desorption rates would be expected to be a function of the ratio of metal to non-metal atoms in the self-adsorbed layer. The equilibrium ratio of metal to non-metal atoms in the self-adsorption layer may sometimes be very different from the ratio in the crystal lattice, and impingement of atoms from the vapor would almost certainly influence the ratio. In semiconductors the ratio is probably influenced by light quanta of energy sufficient to excite electrons across the band gap.

On the other hand, the fact that vaporization rates on opposite zinc oxide faces are similar seems inconsistent with a mechanism such as that proposed by Hirth and Munir for cadmium-rich face vaporization (30) of cadmium sulfide. Their mechanism assumes that the spacing between crystal ledges plays a critical role in determining the extent to which the measured vaporization rate falls below the maximum possible rate. Leonard and Searcy (8) have shown that opposite basal faces of both zinc oxide and cadmium sulfide have very different structures. These different

structures imply dissimilar ledge spacings. If the ledge concentration is critical in fixing the vaporization rate, great dissimilarity in vaporization behavior might be expected, and while the observed rates of vaporization are different, the differences amount to a factor of 4 for zinc oxide and less than a factor of 2 for cadmium sulfide (8) in the temperature ranges for which surface structures have been observed.

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FIGURE CAPTIONS

Fig. 1. Equilibrium pressure of zinc oxide.

Fig. 2. Langmuir pressures of zinc oxide single crystals.

Fig. 3. (0001) face after vaporization.

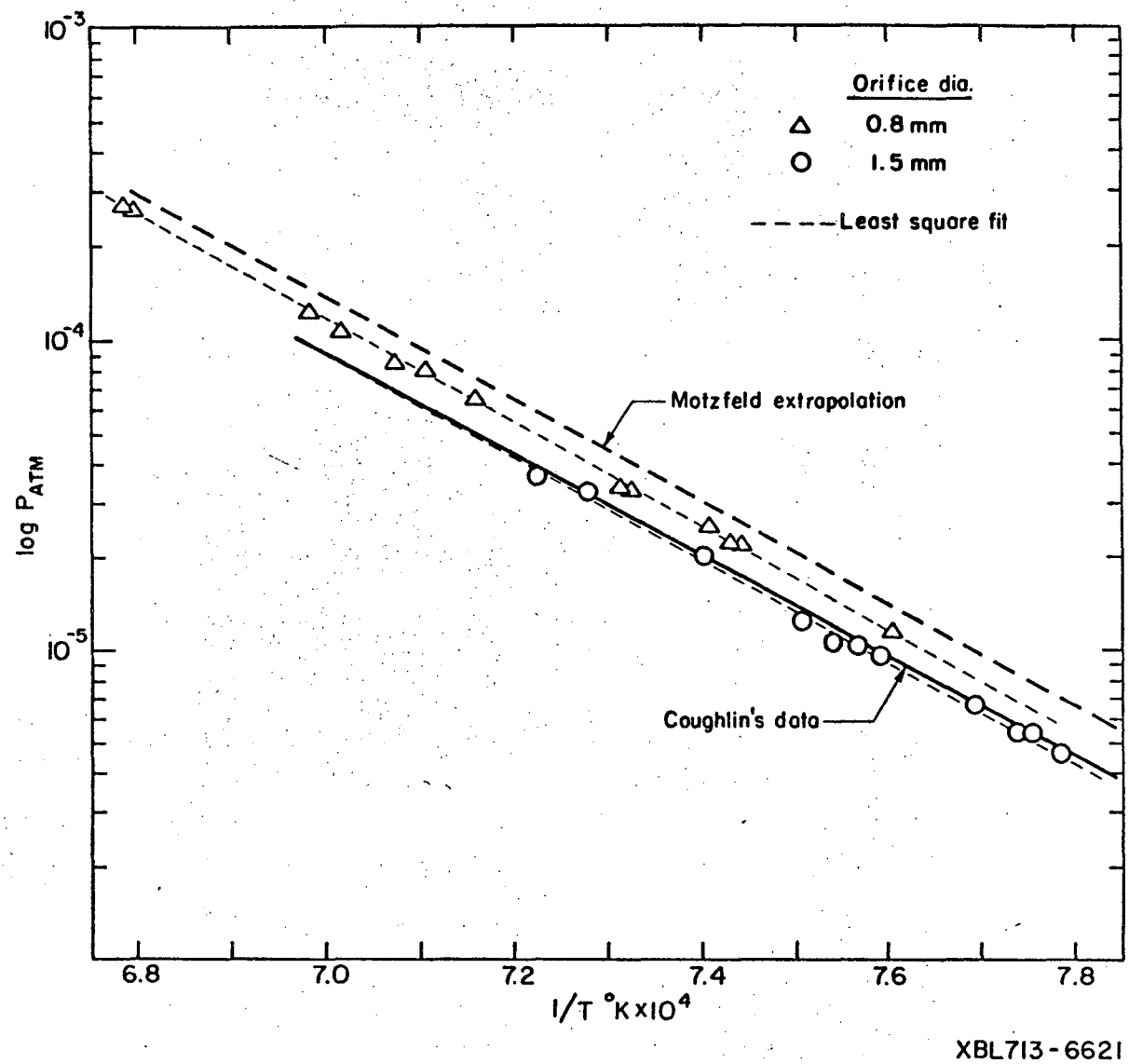
(a) Top view

(b) Cross sectional view

Fig. 4. $(000\bar{1})$ face after vaporization.

(a) Top view

(b) Cross sectional view



XBL713-6621

Fig. 1

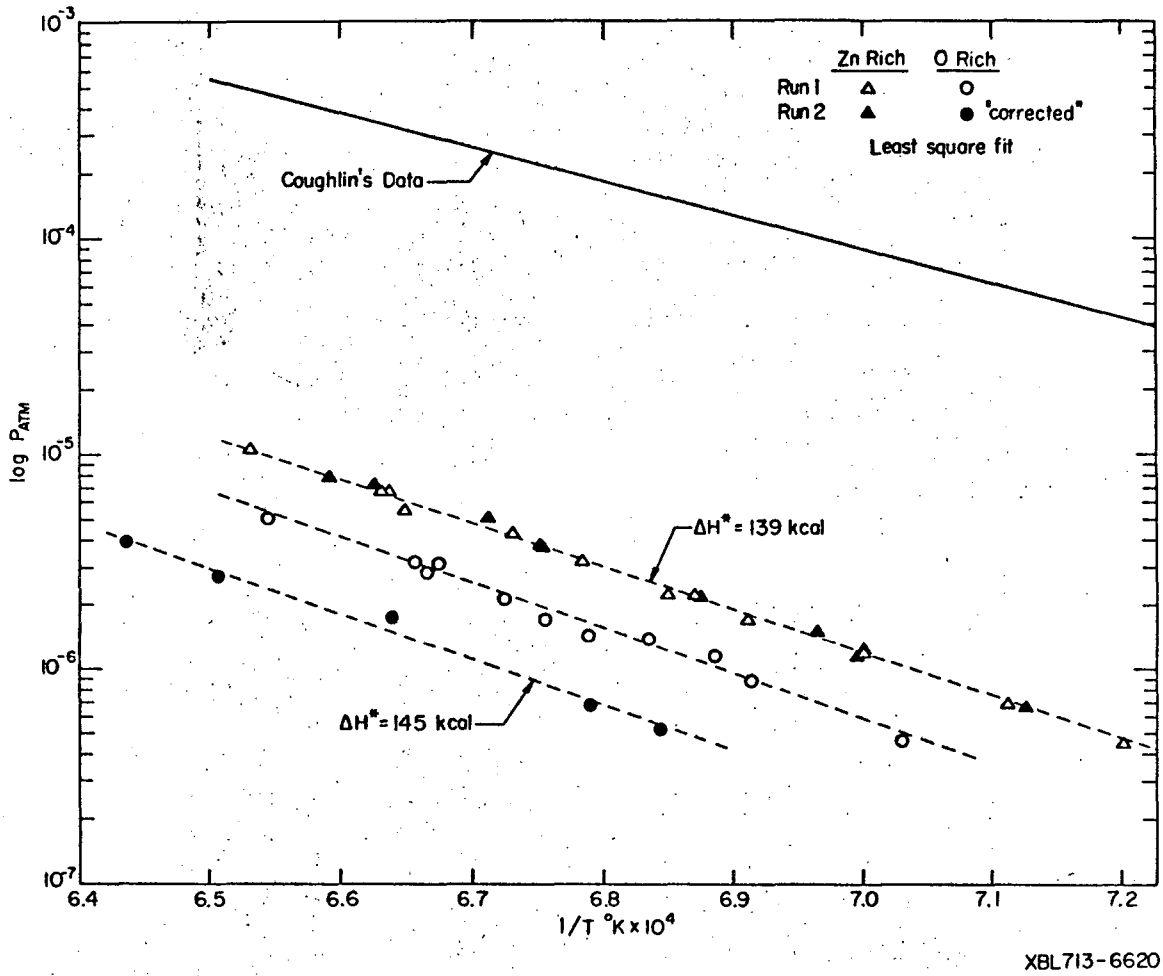
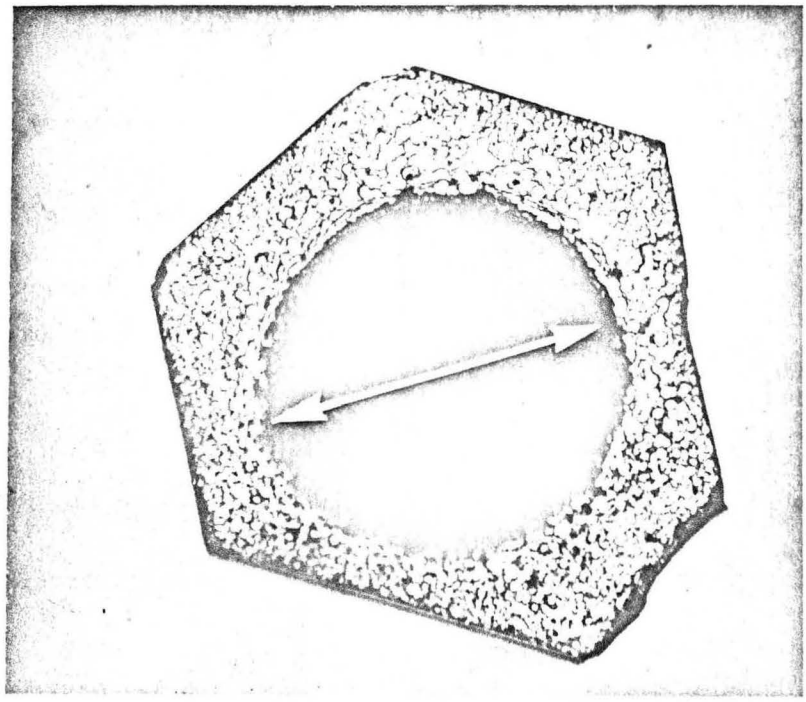
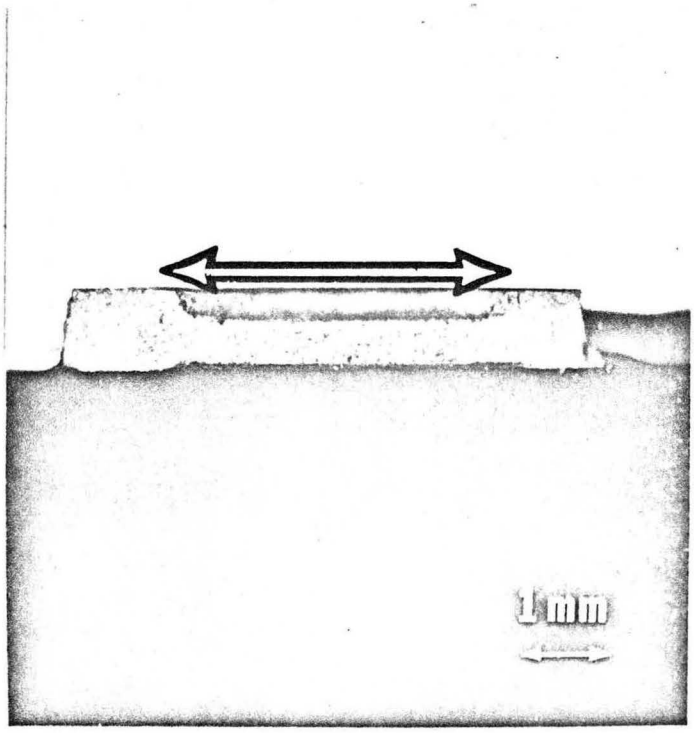

Zn Rich
O Rich
Run 1
Run 2
"corrected"
Least square fit
Coughlin's Data
ΔH* = 139 kcal
ΔH* = 145 kcal
log P_ATM
1/T °K x 10^4
XBL713-6620

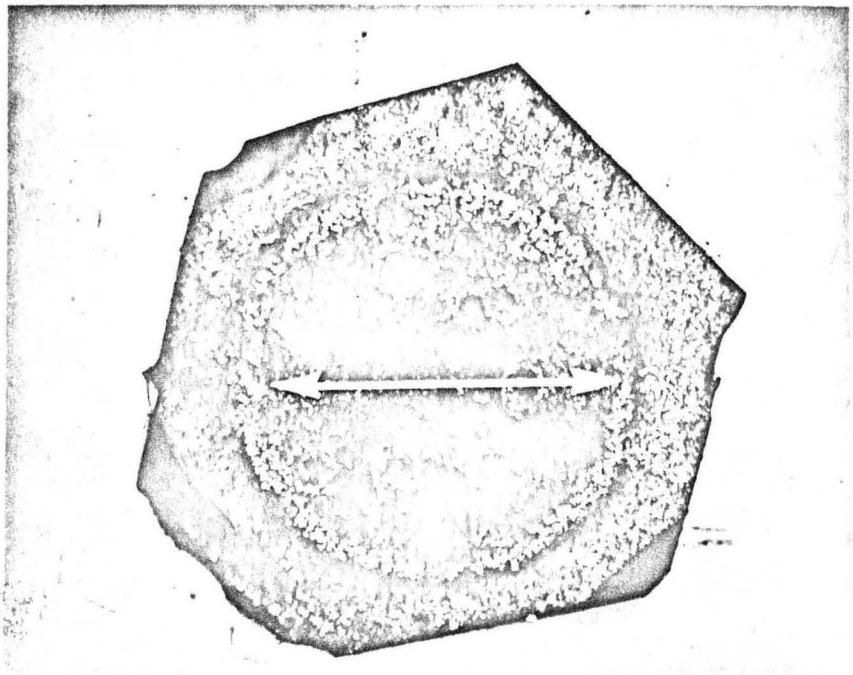
Fig. 2

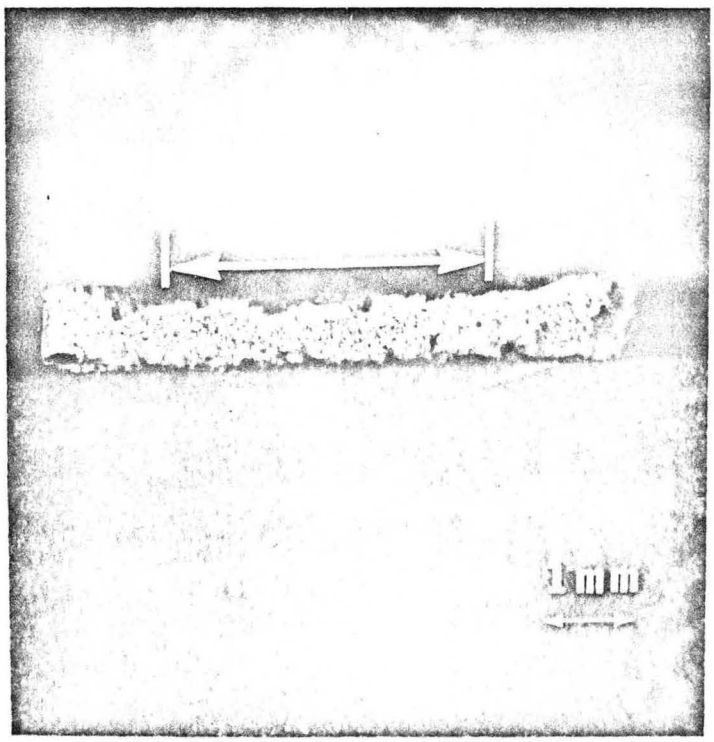




XBB 713-845

Fig. 3





XBB 713-844

Fig. 4

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TECHNICAL INFORMATION DIVISION
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720