THE THEORETICAL ANALYSIS OF STACKING FAULT ENERGIES IN METALS
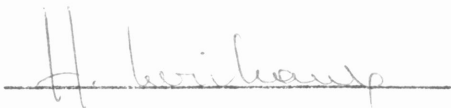
by

GENE CAMMACK

NUCLEAR ENGINEERING

Submitted in Partial Fulfillment of the Requirements of the

University Undergraduate Fellows Program

1976 - 1977

Approved by:

Dr. H. R. LERIBAUX

May 1977

ABSTRACT

The second order pseudopotential theory is applied to the calculation of stacking fault energies for the noble metals and their alloy systems with tin and zinc. The theory fails to simulate the known experimental values and the failure is linked to the failure of the characteristic shape function, which is inherent to the calculations.

ACKNOWLEDGEMENTS

I wish to express my gratitude to Dr. H.R. Leribaux, who suggested this topic and worked with me throughout the research. Also, I wish to thank the Nuclear Engineering Class of 77 and my professors at Texas A&M for indulging my many questions prompted by this research.

DEDICATED

To Sharon, for three years of waiting.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

INTRODUCTION

While a singularly perfect crystal may be aesthetically inter-
esting, it is important to ralize that almost all the unique
properties of a solid material arise from imperfections in the
crystal structure. Furthermore, the study of defects in materials
is a tool for the testing of the predictions of crystalline theory.
One relatively simple defect, and one that is well suited to simple
analysis, is that of the stacking faults. Second order pseudopoten-
tial theory has been applied with some success to the calculation of
stacking fault energies in simple metals. However, when the theory
has been applied to copper,[7] it has failed to obtain the experimental
results. This paper examines the application of the theory to other
noble metals, namely to silver and gold. Of particular attention
is the variation of the stacking fault energy with the electron to
atom ratio, Z. This alloving situtation is the area where the
descrepancy has been most apparent.

THEORY

A. Stacking Faults and Crystal Structure

Two types of important, metallic crystals, hexagonal close-packed and face centered cubic, consist of planes of hexagons with one plane located in the valley sites of the adjacent planes. The arrangement of atoms into a hexagonal plane leaves six valley sites. (See Figure I) Three of these sites constitute the placement of the next plane of atoms. For example, in Figure I, if the atom centers of the original plane are designated as A, then the atom centers of the next atomic plane can be located with its atom centers on either the B locations or on the C locations. Therefore, two different orientations of the planes exist. In one orientation, the first plane is designated A, the second plane, B, and the third layer occupies the C lattice sites. This sequence is called A-B-C stacking and is characteristic of the face centered cubic structure. (F C C) (See Figure II) The second possible orientation of the planes occurs when the third plane of atoms is located directly above the first layer in the lattice site designated A. This type of stacking sequence is found in hexagonal close-packed structures. (H C P) (See Figure II)

A stacking fault then, occurs whenever one of the planes in a normal space lattice shifts, causing an irregularity in the stacking sequence. In the FCC type structure there are three distinct forms of the stacking fault: the intrinsic fault, the extrinsic fault, and the twin, or mirror fault. (See Figure III) The

-2-

intrinsic fault involves the removing of a plane, or partial plane

of atoms from the lattice. The extrinsic fault is an added plane

of atoms inserted into the lattice structure. The twin fault is

a bit more complicated, involving a shift of an entire subcrystal,

from the A-B-C-A-B-C sequence of the normal lattice, to an A-B-C-B-

A-C-B. On either side of the fault line is a perfect subcrystal of

the proper stacking sequence.
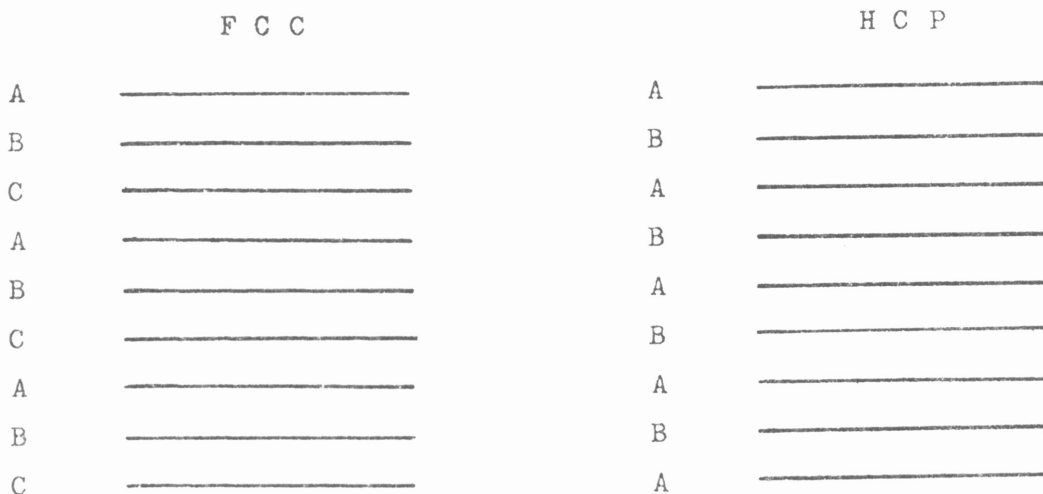
B. Energy Relationships

In examining the energy relationships of metallic structures,

it is important to keep in mind some basic facts about the atomic

nature of metals. Unlike covalent or ionic bonding structures,

FIGURE I: Schematic Representation of Lattice Planes
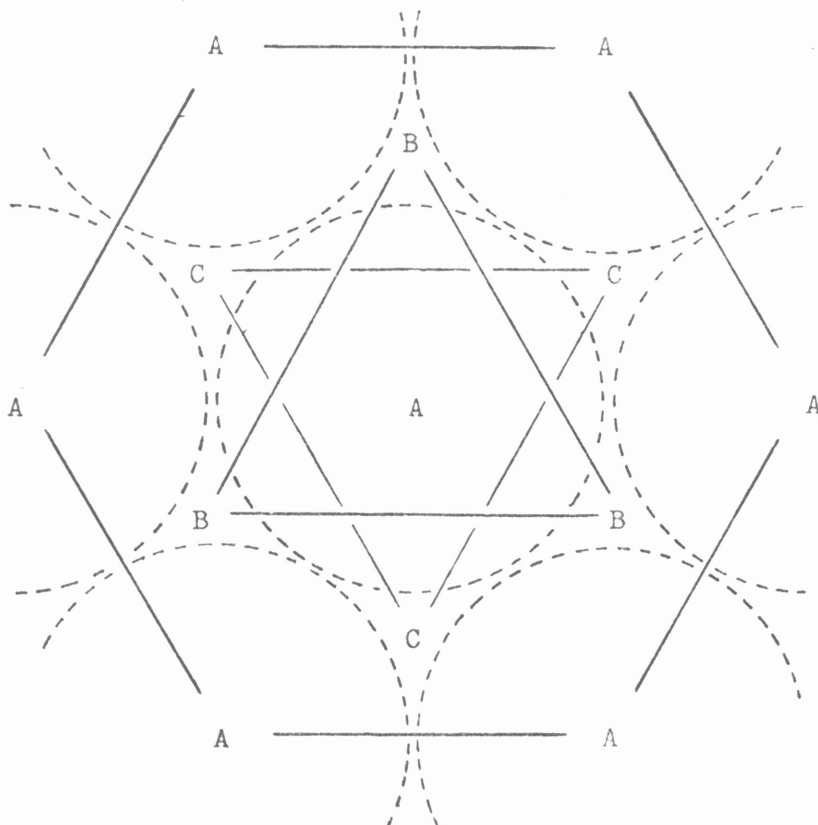
metals have a free electron gas--that is, the outer, valence electrons are free to move throughout the lattice. Most metals have rather low ionization energies reflecting low electron affinities. Covalent bonds between metal atoms, then, do not lead to energetically favorable bonding states. Contrary to this logic however, metals form very strong and stable structures. The key to the stability of the metallic bond is found in the relatively free nature of the electron gas. Consider for simplicity, two ions with a single electron between them. (See Figure IV) The potential energy of each ion due to the electron, consists of two components: a coulombic, attractive energy between the positive ion and the negative electron, and a repulsive energy due to the interactions of the free electron with the core electrons of the ion. This repulsive energy is due partly to the coulombic force

FIGURE II: Stacking Sequences

	F C C			H C P	
A	————————		A	————————	
B	————————		B	————————	
C	————————		A	————————	
A	————————		B	————————	
B	————————		A	————————	
C	————————		B	————————	
A	————————		A	————————	
B	————————		B	————————	
C	————————		A	————————	

```
              INTRINSIC                           EXTRINSIC
   faulted              normal          faulted              normal

      A    _____    A                A    _____    A

      B    _____    B                B    _____    B

      C    _____    C                C    _____    C

                  |___    A                B    _____|    B

      B    _____    B                A    _____    A

      C    _____    C                B    _____    B

      A    _____    A                C    _____    C


                         TWIN FAULT

              A    _____    A

              B    _____    B

              C    ═══════════    C

              B    _____    B

              A    _____    A

              C    _____    C

              B    _____    B
```
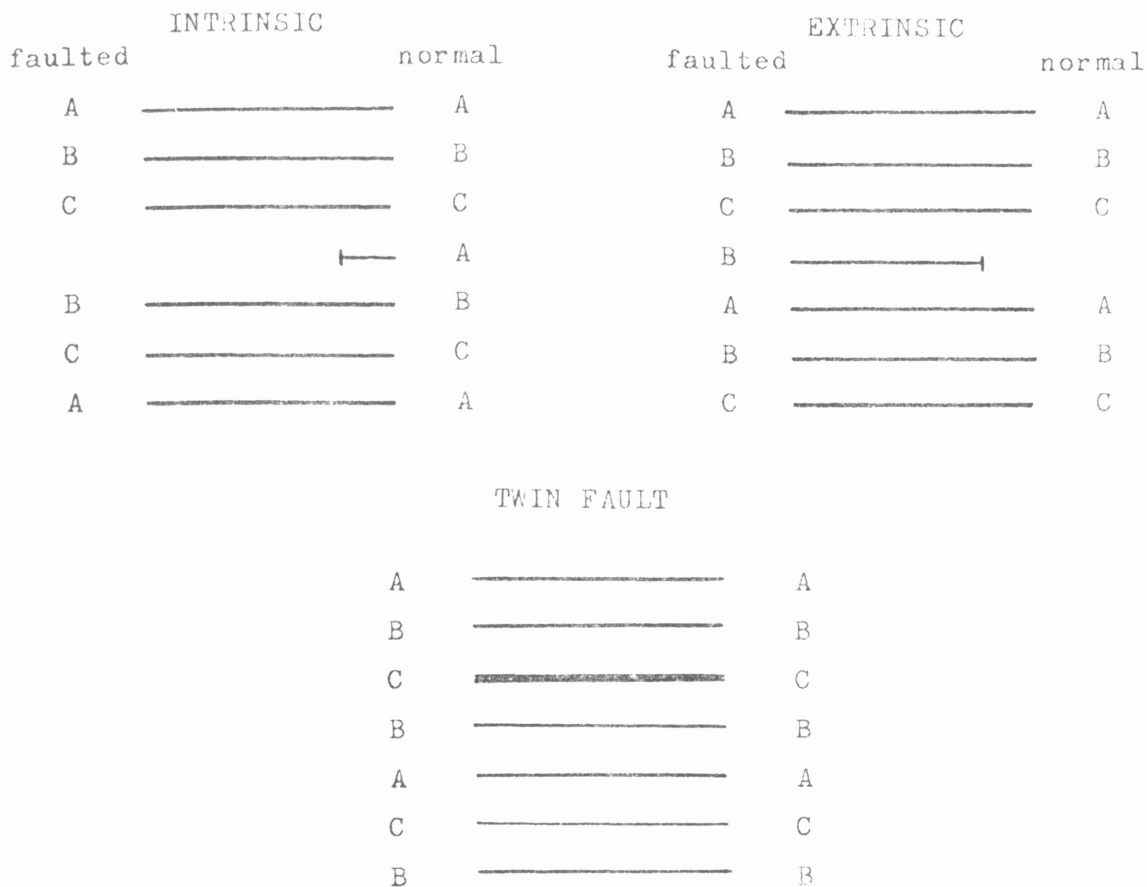
FIGURE III: Types Of Stacking Faults

between like charges, but at short range, the Pauli Exclusion

Principle becomes dominant.   The Pauli Exclusion Principle states

that two electrons can never occupy the same quantum state.   If

then, the energy of the electron is plotted vrs. the distance from

the ion, as in Figure V, it can be seen that the negative, attrac-

tive energy component follows Coulombs law of electrostatics and

is just $-Z-e^2/r$. [1]   The repulsive force arises quickly at the radius

of the atom, and causes spike increases in the energy, one for each

core electron shell.   The net result of these two contributions is

slightly attractive and therefore the electron gas, that is, the

sharing of free electrons by several atoms, results in a significant
favorable energy contribution to the stability of the crystal.

C. Pseudopotential Theory

In order to calculate the stacking fault energies of a crystal, it
is necessary to examine these energy relations in light of more
recent developments from quantum theory. While the ion cores
account for about 15% of the volume of the crystal, the free elec-
trons are extremely transparent both to the cores and to other free
electrons. Basically, there are two explainations of this behavior.
First, wave theory holds that waves are free to propagate in an
orderly, periodic array. Thus, the free electron waves avoid
interaction with the ion cores. The second explaination is that
the Pauli Exclusion Principle innibits the interaction of free
electrons with themselves.

The free electron model, however, fails to explain some very

FIGURE IV: Electron Energy Contributions
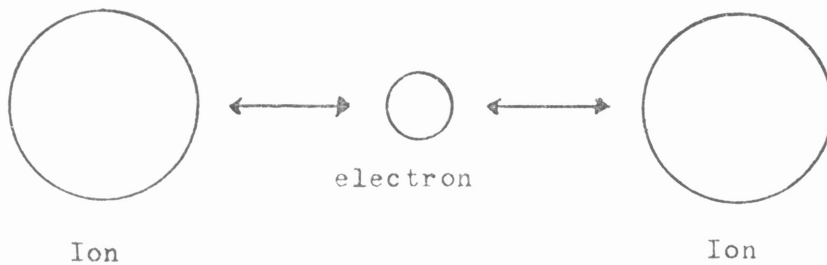
$$U_t = U_e + U_i$$

repulsive   attractive

important characteristics of crystals. When the wave number, k, is plotted against energy, ϵ, the plot is continuous to infinity. (See Figure VIa) However, in a lattice structure, Bragg reflection of the electron wave occurs and energy values for which the wave equation is insoluble arise. This causes band gaps to occur in the quantum structure. (See Figure VIb) Small band gaps, as are found in metals, result from a weak scattering potential.[2] This, however, does not imply that the actual atomic potential is weak, but rather just that the scattering potential is weak. It is convienent, then, to replace the actual potential by an effective potential which results in the same scattering power.[2] This is the pseudopotential.

FIGURE V: Electron Energy vs. Radius

(After Mahan)[3]

$$U_{attraction} = \frac{-Ze^2}{r}$$
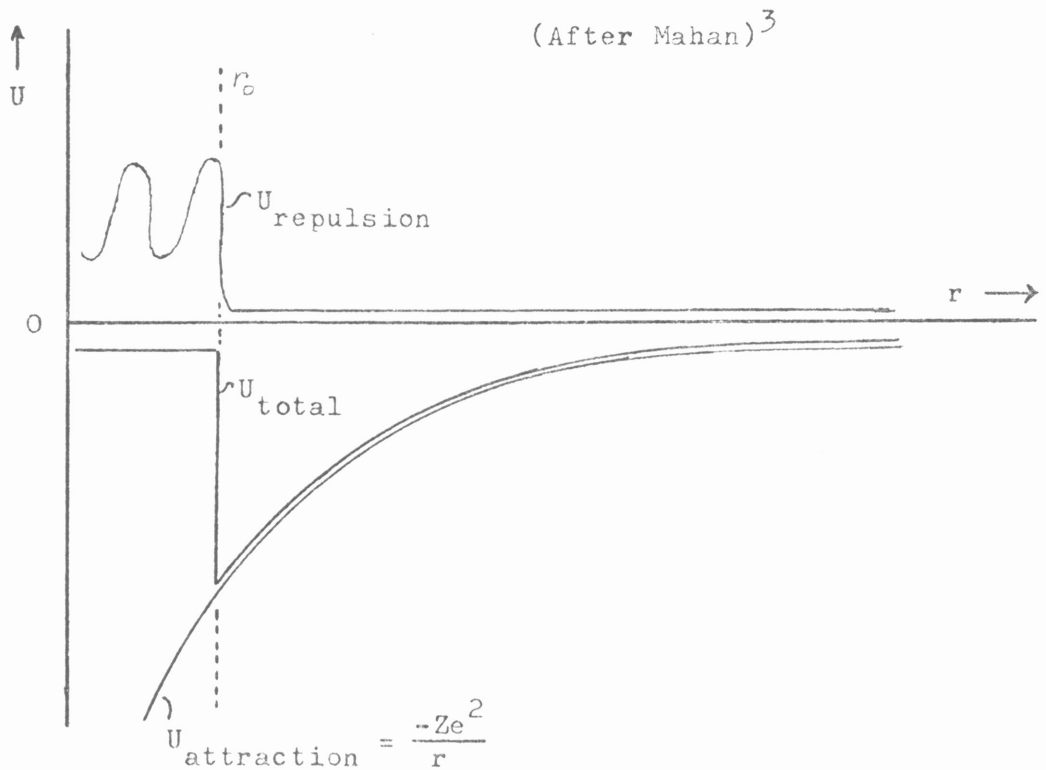
The Fourier transform of the pseudopotential into q space is equal
to one half the magnitude of the band gap.[2] If the pseudopotential
is just a measure of the scattering potential of the ion, then it
may be considered as just the average of the spiked, repulsive
energy within the boundries of r_o in Figure V.

    While the pseudopotential accounts for electron-ion interactions,
the relationship between the electrons themselves are considered via
a correction factor. Known as a screening function, G, it is a
dielectric function which describes the response of the electron
gas to the perturbation caused by the ion cores.[4]

FIGURE VI: Band Structure of Metal Crystals
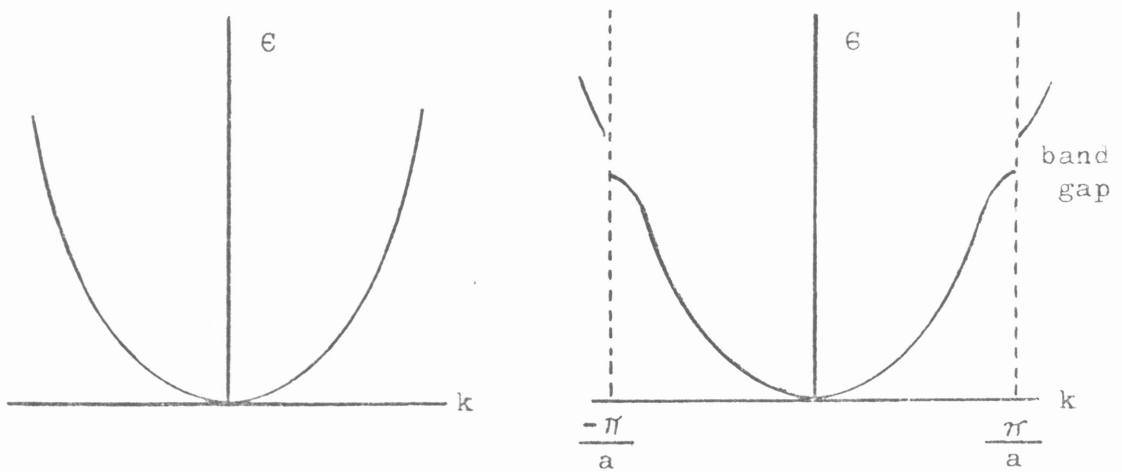
a) Completely Free Electron   b) Nearly Free Electrons

FORMULATION

A. The Calculational Model

Two mathematical models have been proposed to calculate stack-
fault energies; a q-space formulation and an asyptotic, real-space
formulation. Both models assume that the stacking fault energy, γ ,
can be expressed as a sum of the interactions of neighboring planes
of atoms, or:

$$\gamma = a \sum_{n=2}^{\infty} N(n) \psi(nh) \tag{1}$$

where: $\psi(nh)$ = A characteristic function designating the
interaction between planes. Depends on the
planer spacing ,h, and the plane number,n.

$N(n)$ = A weighting function for each plane.

a = A constant for a given alloy and composition.

The q-space formulation uses an entirely numerical characteristic
function calculated from the Fourier transformed—q-space—consider-
ations.[5] The asymptotic model is based on real space planer inter-
actions rather than numerical functions.[6] According to the
Blandin-Friedel-Saada[6] formulation, the planer interactions can be
expressed as sinusoidal functions of the distance between the plane
in question and the actual fault plane. This theory is known as
the asymptotic theory because it further assumes that for n=2 and
greater, the function has reached its asymptotic value.

The series function is dependent upon the valance electrons per
atom ratio, Z, and includes the weighting function, N(n). For

intrinsic faults and for $Z > Z_c = 1.14$, Leribaux[7] gives the function as:

$$\phi = \sum_{n=1}^{\infty} \frac{\sin(3n\theta)}{3n} - \frac{\sin(3n-1)\theta}{(3n-1)} \qquad (2)$$

$$\text{where:} \; \theta = 5.67(Z^{2/3} - Z_c^{2/3})^{1/2} \qquad (3)$$

Since sinusoidal series such as equation 2 are difficult to evaluate, Blandin et al[6] use an analytical calculation:

$$\phi = \frac{\sqrt{3}}{6} \left[\beta(\theta + \frac{4}{3}) - \beta(\theta + \frac{2}{3}) \right] + \frac{1}{2} f(\theta) \qquad (4)$$

$$\text{where:} \; \beta(\theta) = \sum_{n=1}^{\infty} \frac{\cos(\theta)}{n} = -\log 2 \left| \sin(\theta/2) \right| \qquad (5)$$

$$\text{and:} \; f(\theta) = -\theta \qquad 0 < \theta < \frac{2\pi}{3} \qquad (6)$$
$$= (\pi - \theta) \qquad \frac{2\pi}{3} < \theta < \frac{4\pi}{3}$$
$$= (2\pi - \theta) \qquad \frac{4\pi}{3} < 0 < 2\pi$$

The 'a' coefficient for intrinsic faults is the pseudopotential calculation of the energy of an atomic plane, and is given as:[7]

$$a = \frac{\alpha k_F^2}{(2\pi)^3 Z^2} \left[1 - (Z_c/Z)^{2/3} \right]^{1/2} \qquad (7)$$

where: k_F = wave number of the Fermi Surface.

$$\alpha = \frac{72\pi^3 Z^2 \; W(2k_f)^2}{\left[2\pi k_F - G(2k_F) \right]^2} \qquad (8)$$

-10-

$W(2k_F)$ is the screened pseudopotential form factor.

$G(2k_F)$ is the self consistent screening function that accounts for the effects of the electron-electron interaction of the electron gas.

Using the free electron metal model[7]:

$$k_F \approx (3\pi^2 \frac{Z}{\Omega})^{(1/3)} \qquad (9)$$

where: Ω = the average atomic volume of the alloy.

Thus, for $Z > Z_c$, the intrinsic stacking fault energy can be calculated as:

$$\gamma_i = a\, \phi \qquad (10)$$

where ϕ is from equation (3) and 'a' is from equation (6).

For the case where $Z < Z_c$ a little different calculation is used. The stacking fault energy is:

$$\gamma_i = a'\, \phi' \qquad (11)$$

where: $a' = \frac{\alpha k_F^2}{(2\pi)^3 Z^2}((Z_c/Z)-1)^{\frac{1}{2}} \qquad (12)$

$$\phi' = \frac{-e^{-2\theta}}{(2)^2} + \frac{e^{-3\theta}}{(3)^2} + \frac{-e^{5\theta}}{(5)^2} + \frac{e^{-6\theta}}{(6)^2} \qquad (13)$$

$$\theta = 5.67(Z_c^{(2/3)} - Z^{(2/3)})^{1/2} \tag{14}$$

and where the other values are defined as before.

B. Input Data

The actual calculations were conducted using the computer program listed in Appendix I. The screening function used was for a typical monovalent metal[7,6] and was 0.60. The values of $W(2k)$ and Ω are from Moriarty[8] or *Heine*[19] as summarized in Table 1. Both the pseudopotentials and the atomic volumes used were weighted by the relative concentrations of the alloy, using the following formulas:

$$W(2k) = C_B W_B(2k_F) + (1-C_B)W_A(2k_F) \tag{15}$$

$$\Omega = C_B \Omega_B + (1-C_B) \Omega_A$$

where: C_B = concentration of the base metal.

$W_B(2k_F)$ = pseudopotential of base metal.

$W_A(2k_F)$ = pseudopotential of alloying element.

Ω_B = atomic volume of base metal.

Ω_A = atomic volume of alloying element.

TABLE 1

KNOWN INPUT INFORMATION

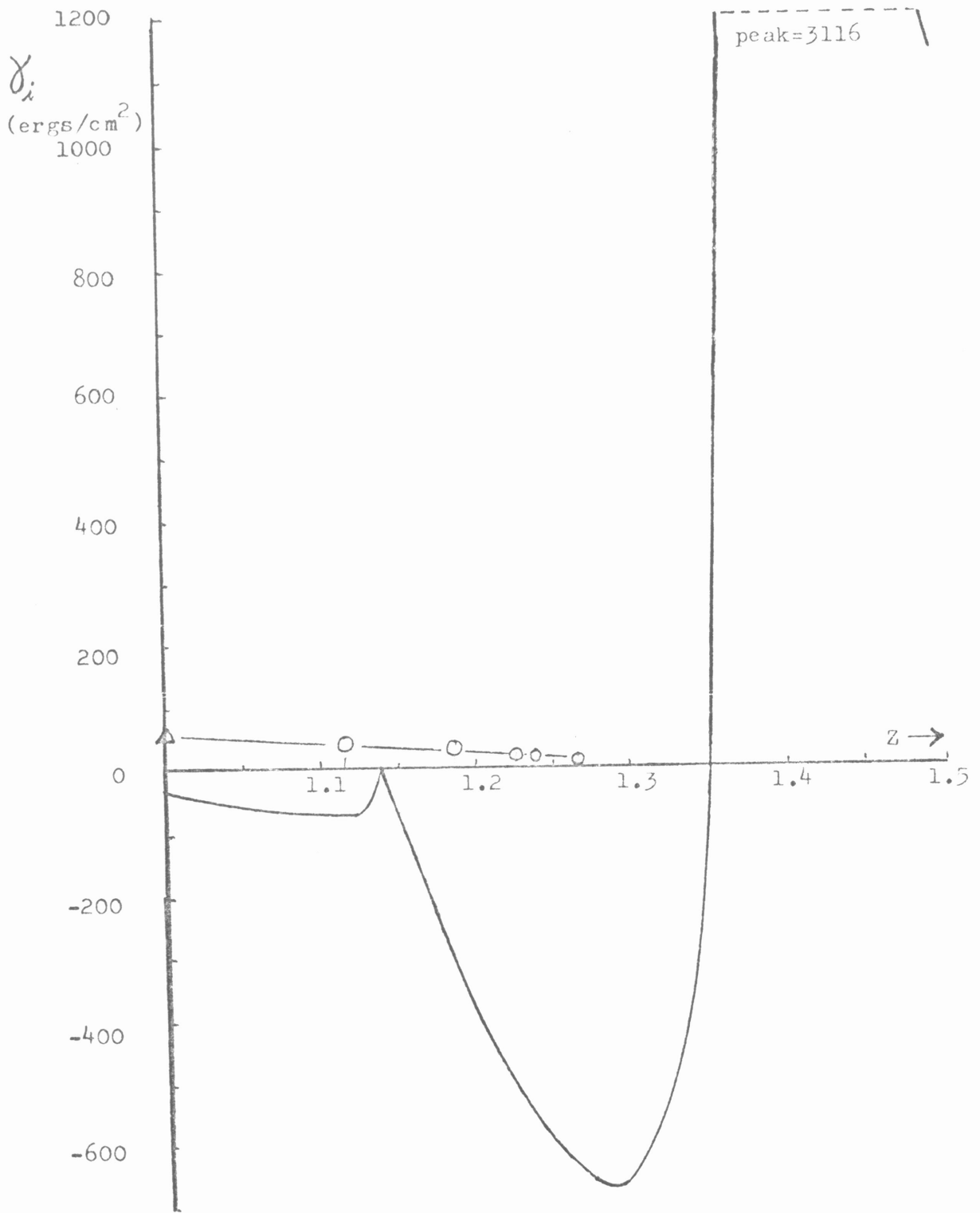| METAL	PSEUDOPOTENTIAL	ATOMIC VOLUME	VALENCE
Copper[+]	0.1246	79.68	1
Gold[+]	0.10415	114.4	1
Silver[+]	0.07495	115.1	1
Zinc[*]	0.04	102.65	2
Tin[*]	0.025	230.73	4

[+]From Moriarty[8]

[*]From Heine[19]

RESULTS

The stacking fault energies for seven alloy systems were
calculated, namely: Copper-Zinc, Copper-Tin, Gold-Zinc, Gold-Tin
Silver-Zinc, Silver-Tin, and Aluminum-Zinc. The results are shown
in Figures VII-XII, and Figure XIV. The aluminum-zinc curve is
shown to show the ability of second order theory to predict the
stacking fault energy of simple metals and in this respect it does
quite well. The calculated fault energies in all the curves, are
plotted from the formulas developed earlier, (Blandin et 'al)[6] and
are compared to experimental results. The experimental numbers
come from the sources indicated on the figures as they were reviewed
by Gallagher.[9] No experimental values were available for the gold-
alloy systems or for the aluminum-zinc system. Table 2 summarizes
the experimental and calculated values in the case of the pure
metal. The experimental information consists of the best values
from Gallagher.[9]

TABLE 2

STACKING FAULT ENERGIES OF PURE METALS

METAL	CALCULATED	EXPERIMENTAL
Copper	-31.72	55
Gold	-23.06	50
Silver	-11.95	21.7
Aluminum	251.04	200

-14-

FIGURE VII: Stacking Fault Energy of Copper-Tin Alloys

γ_i
(ergs/cm^2)

1000

800

600

400

200

peak=
1615

0

1.1   1.2   1.3   1.4   1.5

Z

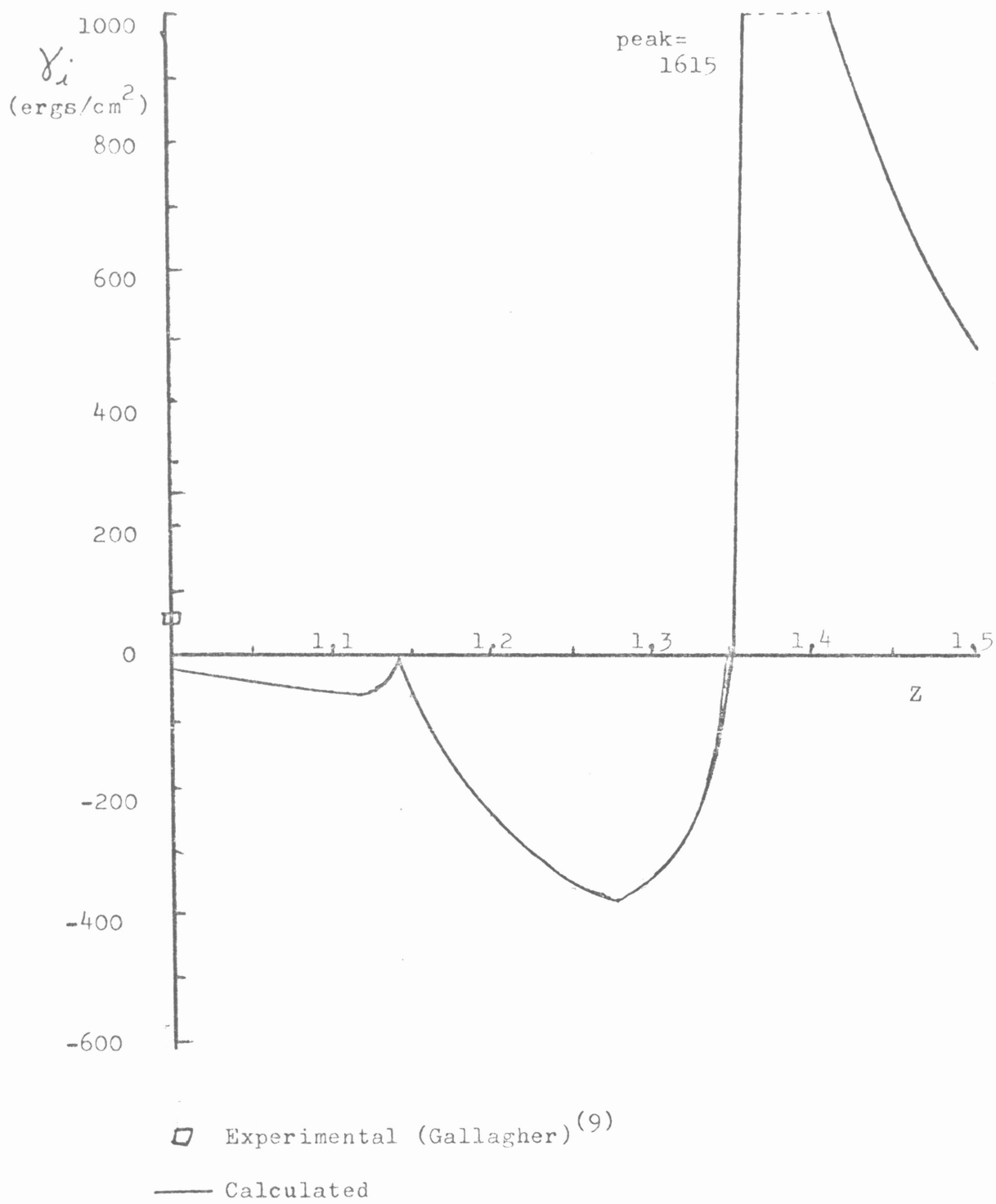-200

-400

-600

▱ Experimental (Gallagher)[9]

——— Calculated

FIGURE VIII: Stacking Fault Energy of Gold-Zinc Alloys

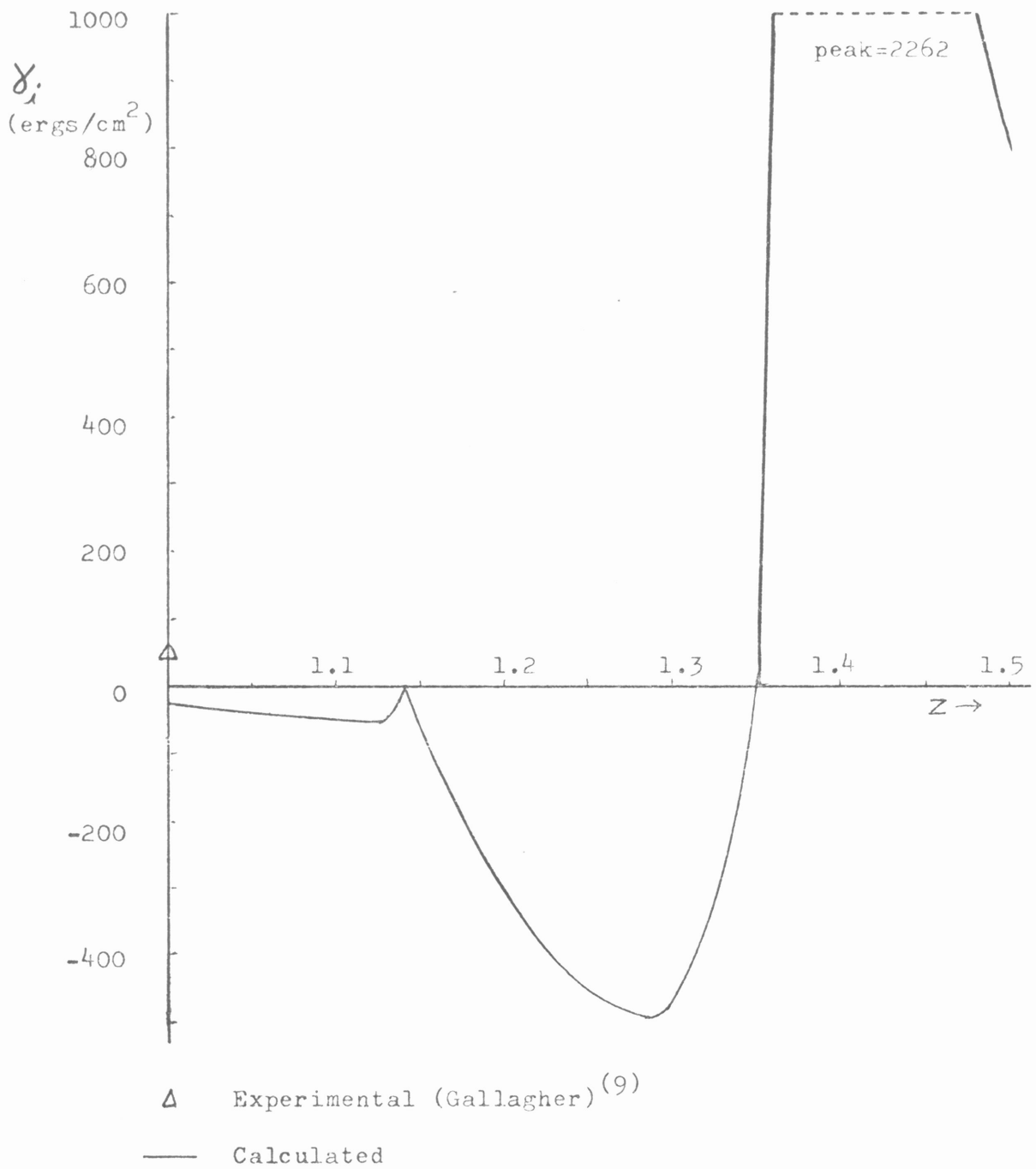FIGURE IX: Stacking Fault Energy of Gold-Tin Alloys

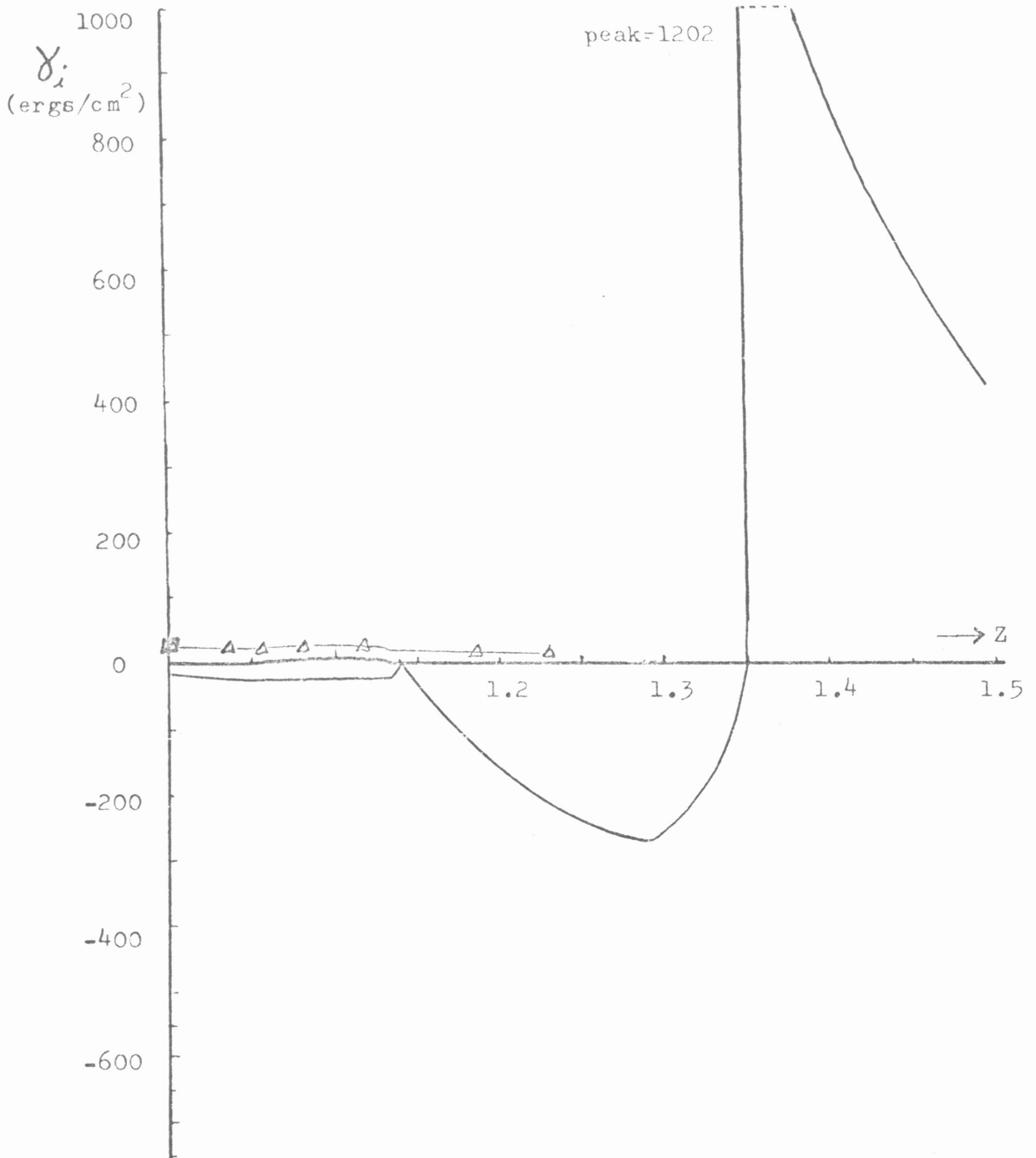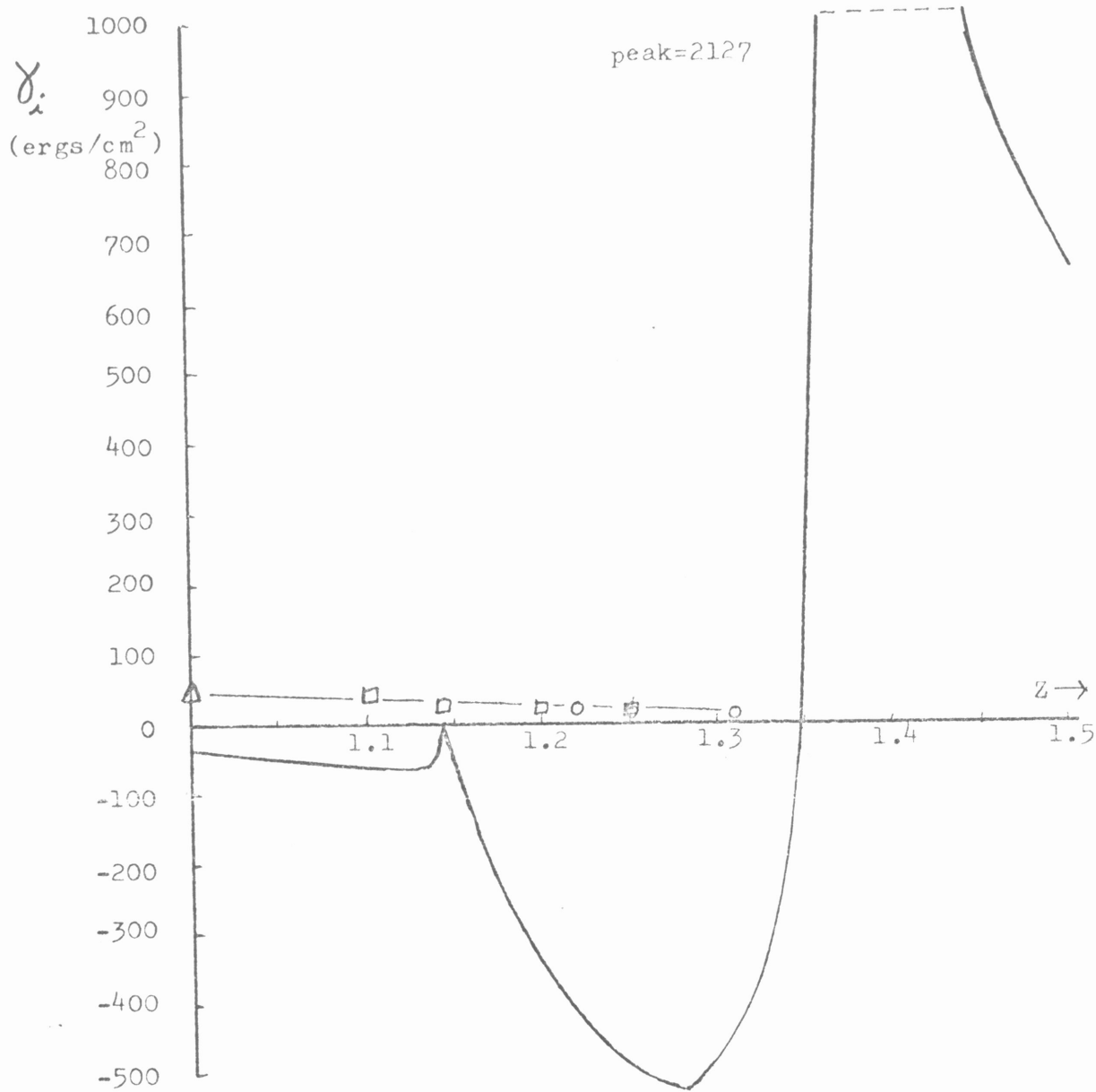FIGURE X: Stacking Fault Energy of Silver-Zinc Alloys

FIGURE XI: Stacking Fault Energy of Silver-Tin Alloys

— ▢ — Experimental (Gallagher)[9]

— △ — Experimental (Ruff and Ives)[13]

———— Calculated

peak=2127

—△— Experimental (Gallagher)[9]

—□— Experimental (Howie and Swann)[10]

——— Calculated

—O— Experimental (Gallagher and Ku)[11]
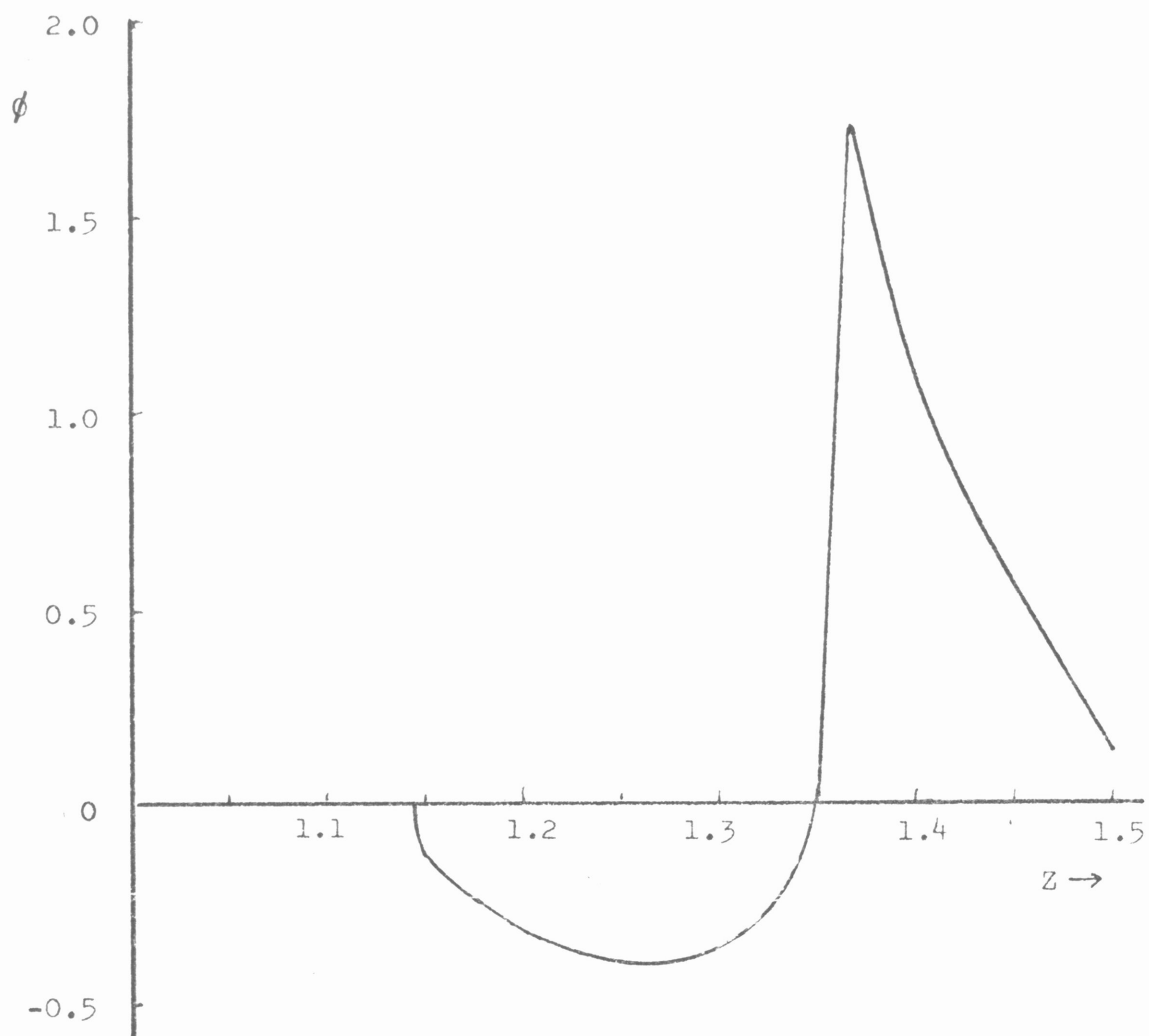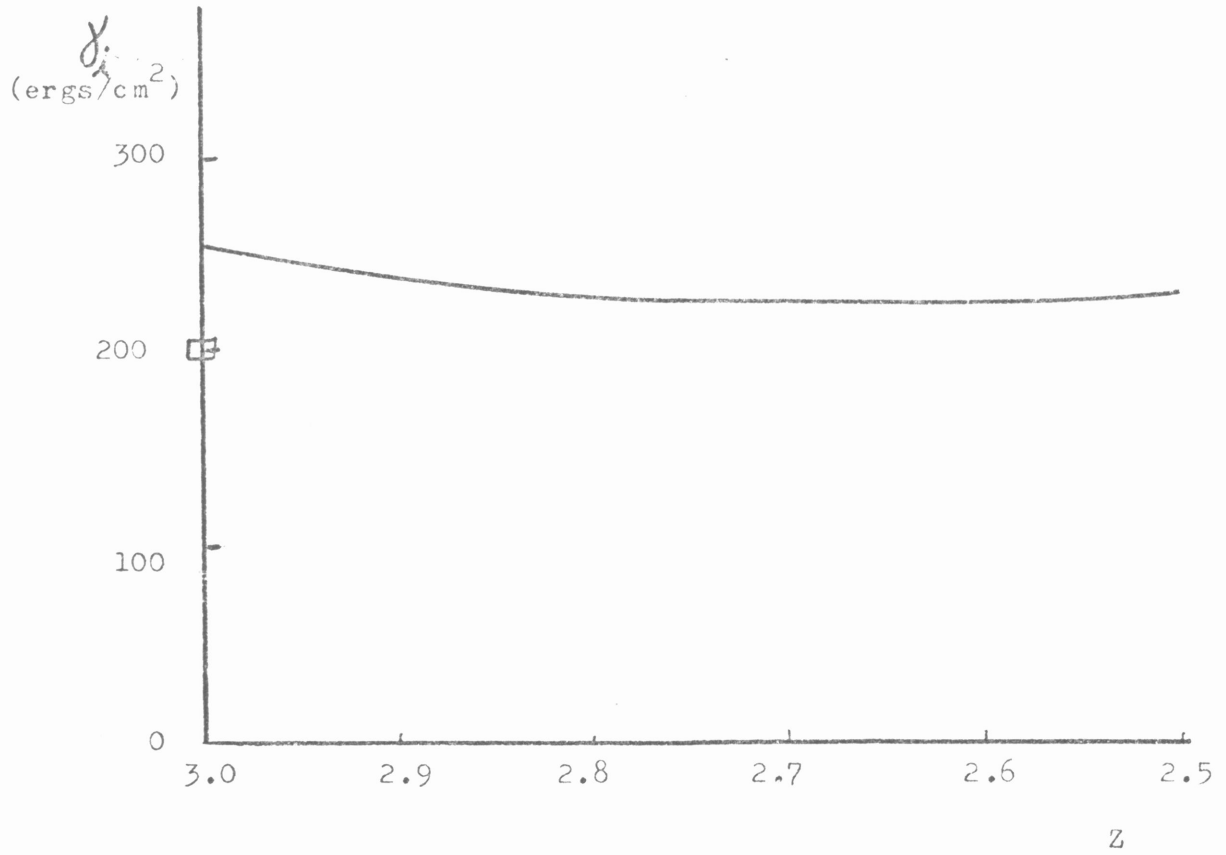
FIGURE XII Stacking Fault Energy of Copper-Zinc Alloys

FIGURE XIII: Characteristic Shape Function For Noble Metals

FIGURE XIV: Stacking Fault Energy in Aluminum-Zinc Alloys

A. Pure Metals

Blandin et 'al[6] have suggested that the problems of treating the
noble metals by pseudopotential theory might be solved by simply
reversing the sign of the coefficient α, in equation (8). Applying
this device to the values in Table 2, the agreement is close, with
the calculated values being a bit lower than the experimental.
However, the trends of the stacking fault energies within the
noble metals are similar in the calculated and experimental values
if the sign reversal is adopted.

B. Material Constant

The alloy systems however, provide the test of the model and
here the results are completely hopeless. All three noble metals
exhibited very similar curves (Figures VI - XII) indicating a strong
family resemblence. Furthermore, the curve for Copper-Zinc, (Figure
XII) shows the same results as found by Leribaux[7]. The differences
in the calculated energy is mainly one of magnitude rather than
shape. The Copper systems show the largest amplitude followed by
Gold and then Silver. The magnitude of the energy is determined by
value of 'a' or 'a'' in equations 9 and 10. Furthermore, if the
curves for silver and gold, two metals with similar atomic volumes,
are compared, it is easily seen that the pseudopotential is the
controlling factor in determining the amplitude of the curves. It
is interesting to note that the ordering of magnitude with respect
to amplitude on the calculated curves, is the same as the order of

the experimental values of Table 2. Since this magnitude is based on the pseudopotential, it is likely that the pseudopotential concept could be used to explain differences in the stacking fault energy of alloys.

C. Characteristic Shape Functions

It is the general shape of the curves however, that is the most distressing problem. The theory predicts that the shape function of equation 10, $\emptyset$, will determine the general trend of the curves. As can be seen by comparing the shape function plot (Figure XIII) with the other curves, the shape is indeed dominated by $\emptyset$. Further-more, a kink exists in all the curves at $Z = Z_c = 1.14$ as noted by Leribaux[7]. This kink is inherent in the calculations and fails to appear anywhere in the experimental curves.

D. Conclusions

Therefore, it would seem that the second order pseudopotnetial theory as presented here fails not only for copper as suggested by Leribaux[7], but for noble metals in general. Also, while changing the sign of the α constant (equation 7) may produce results in fairly close agreement with the experimental values for the pure metals, it fails for the alloy systems. The curve shapes of the noble metal-alloy systems resembles in no way the experimental values and a mere reversal of sign is insignificant in eliminating the problem. Rather, the problem seems to be inherent in the calculation of the charateristic shape function.

REFERENCES

1. Halliday, D. and Resnick, R., Physics,(John Wiley and Sons, New York, 1974.)

2. Heine, V. and Weaire, D., Solid State Physics, 24, 249, (1970)

3. Mahan, B.H., University Chemistry, 2nd Ed., (Addison-Wesely, Reading, Mass., 1972).

4. Tosi, M.P., "Screening Functions", Interatomic Potentials and Simulation of Lattice Defects, Ed.:Gehlen, Beeler, Jaffee, Plenum Press, New York, 1972.

5. Beissner, R.E.. Phy. Rev. B, 8, 12, 5432 (1973)

6. Blandin, A., Friedel, J., and Saada, G., J. Physique, Suppl. C3, 128 (1966).

7. Leribaux, H.R., Phys. Stat. Sol., (a), 31, K27, (1975).

8. Moriarty, J.A., Phys. Rev. B, 6, 1239, (1792).

9. Gallagher, P.C.J., Metall. Trans., 1, 2429, (1970).

10. Howe, A. and Swann, P.R., Phil.Mag., 6, 1215, (1961).

11. Gallagher, P.C.J., and Ku, R.C., Ford Motor Co., Dearborn, Mich. unpublished research,(1967).

12. Köster, W., and Speidel, M.O., Z. Metallk., 55, 585, (1965).

13. Ruff, A.W., and Ives,L.K., National Bureau of Standards, Washington, D.C., unpublished research, (1969)

14. Kittel, C., Introduction to Solid State Physics., 3rd Ed., (John Wiley and Sons, New York, 1967).

15. Clark, D.S., and Varney, W.R., Physical Metallurgy for Engineers, 2nd Edition., (D. Van Nostrand, New York, 1952).

16. Guy, A.G. and Hren, J.J., Elements of Physical Metallurgy, 3rd Ed. (Addison-Wesely Publishing Company, Reading, Mass., 1974).

17. Seeger, A., Phil. Mag., 9, 887, (1964)

18. Hull, D., Introduction to Dislocations, 2nd Ed., (Perganon Press, Oxford, 1975).

19. Heine, and Cohen, Solid State Physics, 24, 550 (1970)

APPENDIX I

BASIC COMPUTER PROGRAM FOR CALCULATING STACKING FAULT ENERGIES


```
10 REM A CALCULATION OF STACKING FAULT ENERGIES
20 REM TEXAS A&M UNIVERSITY UNDERGRADUATE FELLOWS PROGRAM
30 REM SPRING 1977
40 REM GENE CAMMACK--NUCLEAR ENGINEERING
50 REM
60 REM
70 REM
80 REM
90 REM K8=OUTPUT UNIT NUMBER
100 REM Z=ELECTRON/ATOM RATIO
110 REM M=CRITICAL Z
120 REM W1=PSEUDOPOTENTIAL OF BASE METAL
130 REM W2=PSEUDOPOTENTIAL OF ALLOYING ELEMENT
140 REM W3=PSEUDOPOTENTIAL AVERAGE FOR ALLOY
150 REM G=G(2K)=SELF CONSISTENT SCREENING FUNCTION
160 REM K=WAVE NUMBER
170 REM C=CONCENTRATION OF BASE METAL
180 REM P=PI
190 REM Q=ALPHA
200 REM A=SMALL A
210 REM R=SMALL GAMMA
220 REM B1=A-PRIME FOR Z<ZC
230 REM T=THETA FOR Z>ZC
240 REM S=THETA FOR Z<ZC
250 REM V=PHI FOR Z<ZC
260 REM O1=OMEGA=ATOMIC VOLUME OF THE BASE METAL
270 REM O2=OMEGA=ATOMIC VOLUME OF ALLOYING ELEMENT
280 REM O3=OMEGA=AVERAGE ATOMIC VOLUME OF THE ALLOY
290 REM J(Z)=STACKING FAULT ENERGY
300 REM
310 REM
320 REM ALL INPUT MUST BE IN ATOMIC UNITS
330 REM
340 REM
350 DISP "ENTER OUTPUT UNIT NUMBER";
360 INPUT K8
370 DISP "ENTER AT. VOL. OF BASE METAL";
380 INPUT O1
390 DISP "PSEUDOPOTENTIAL OF BASE METAL";
400 INPUT W1
410 DISP "ENTER VALENCE OF BASE METAL";
420 INPUT N1
430 DISP "ENTER AT. VOL. OF ALLOY ELEMENT";
440 INPUT O2
450 DISP "PSEUDOPOTENTIAL OF ALLOY";
```

```
460 INPUT W2
470 DISP "ENTER VALENCE OF Al1OY ELEMENT";
480 INPUT N2
490 DISP "ENTER G(2K)";
500 INPUT G
510 P=3.141592654
520 M=1.14
530 DIM J(100)
540 DIM V(6)
550 DIM M$(1)
560 DISP "ENTER BOUNDRIES OF Z, STEP";
570 INPUT E,D,H
580 FOR Z=E TO D STEP H
590 C=(Z-N2)/(N1-N2)
600 03=C*01+(1-C)*02
610 K=(3*P↑2 *Z/03)↑(1/3)
620 W3=C*W1+(1-C)*W2
630 Q=(72*P↑3*Z↑2*W3↑2)/((2*P*K-G)↑2)
640 IF Z <= M THEN 800
650 T=5.67*(Z↑(2/3)-M↑(2/3))↑0.5
660 A=(Q*K↑2)*((1-((M/Z)↑(2/3)))↑0.5)/((2*P)↑3*Z↑2)
670 IF T<(2*P/3) THEN 720
680 IF T< (4*P/3) THEN 700
690 IF T<(2*P) THEN 740
700 F=P-T
710 GO TO 760
720 F=-T
730 GO TO 760
740 F=(2*P)-T
750 B3=-LOG(2*(ABS(SIN((T+(4*P/3))/2))))
760 B2=-LOG(2*(ABS(SIN((T+(2*P/3))/2))))
770 R=(((3) 0.5)/6)*(B3-B2)+(0.5*F)
780 J(Z)=A*R
790 GO TO 880
800 B1=(Q*K↑2)*(((M/Z)↑(2/3)-1)↑0.5)/((2*P)↑3*Z↑2)
810 S=5.67*((M↑(2/3)-Z↑(2/3))↑0.5)
820 U=0
830 FOR N=2 TO 6
840 V(N)=B1*(EXP(-N*S))/(N 2)
850 NEXT N
860 U=-2*V(2)+3*V(3)-5*V(5)+6*V(6)
870 J(Z)=U
880 J(Z)=J(Z)*1556194.021
890 FOR N=0 TO Z STEP 0.1
900 IF Z=1+N THEN 930
910 NEXT N
920 GO TO 940
930 WRITE (K8,*)"//Z=";Z;GAMMA=";J(Z);"ERGS/SQ.CM"
940 NEXT Z
950 END
```