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A non-destructive method of determining the densities of edge and screw dislocations was developed. Using it, thermal elimination of dislocation was shown to be a binary and two stage process for both (a) cold-rolled and (b) metallographically polished specimens. The process involves the glide of dislocation dipoles rather than vacancy migration and climb. A method of extracting kinetic information from isochronal runs was developed and tested with isothermal runs. The strong effect of surface dislocations on reducing the diffusion of hydrogen and deuterium in iron single crystals was demonstrated.

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FINAL REPORT
ON
HYDROGEN PERMEATION AND
POSITRON ANNIHILATION STUDY
OF ALPHA-IRON SINGLE CRYSTALS



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INTRODUCTION

Since this final report has some historical flavor, the idea of measuring the occupation of hydrogen traps with positron annihilation came during a TMS meeting on hydrogen embrittlement and after the Principal Investigator had worked at BNL studying vacancies in NiO with positron annihilation - basically if a known trap for a positron was occupied by hydrogen, the positron would no longer be trapped or annihilated in it because of the similarity of charge. Thus positrons could give valuable information about traps.

This final report covers research carried out first at Northwestern University in the Materials Sciences Department where Yong-Ki Park obtained his Ph. D. He spent a summer at Brookhaven working with Drs. Kelvin Lynn and Louis Snead as well as with three of their collaborators, Prof. Innes McKenzie (Univ. of Guelph), A. Vehanen and B. Nielsen (Risø National Lab, Denmark). Subsequent positron research was conducted in the Physics Department of Michigan Technological University.

To put things into perspective, Prof. Doyama (Tokyo University) and Cotterill¹ stated, "There is not much of an opening of ions at the core of the dislocations. Therefore positrons probably do not annihilate at the normal sites of the core of the dislocations." The idea that there was insufficient room for a positron to be trapped at a dislocation was based on some approximate calculations carried out while they were associated with Argonne National Lab. In their opinion, positron might be trapped at a jog because "...it looked like a vacancy..." and vacancy trapping was already known. The latter in α -iron had a lifetime of ca. 175 psec. The mean lifetime which Yong-Ki Park found that summer was 165 psec and in some cases, 155 psec. It was Vehanen's surmise that the value of 165 came from a mixture of vacancies and dislocations with the latter being due to an

¹ M. Doyama and R. M. J. Cotterill, in *Proceedings of the 5th International Conference on Positron Annihilation, Japan 1979*, eds, R. R. Hasiguti and K. Fujiwara (Japan Inst. of Metals, Sendai) p.89

unspecified type of dislocation.

When Park returned from Brookhaven, working with single crystals supplied by Prof. Meshii at Northwestern, he found that under conditions of loading designed to produce screw dislocations in BCC iron, the lifetime was as low as 142 psec. With further careful work, he was able to identify separate positron lifetimes of edge and screw dislocations in single crystals of α -iron.

Prior to this time and specifically at the Arlington International Conference on Positron Annihilation in 1981 the Doyama-Cotterill opinion was still widely accepted and the positron group at Argonne National Lab published calculations² dealing with the thermal de-trapping of positrons from jogs in FCC aluminum. It was based on the idea that positrons would not be localized but rapidly move through dislocation cores as in *pipe diffusion*. No experimental evidence was provided.

In view of the controversy and in preparation for publication, the lifetimes in BCC iron were verified by Park³ with

- (i) 50 runs using 10 different specimens gave
114 \pm 2 picosecs for annihilation in the bulk
- (ii) 40 runs using 9 different specimens gave
142 \pm 5 picosecs for annihilation in screw
dislocations
- (iii) 65 runs using 7 different specimens gave
165 \pm 3 picosecs for annihilation in edge
dislocations

Positron lifetime results were then used to determine dislocation densities and the results were verified using transmission electron microscopy (TEM) and etch pit techniques on the same crystals. A few confirmatory experiments were made on

² L. C. Smedskjaer, M. Manninen and M. J. Fluss, *J. Phys. F*, 19 (1980) 2237.

³ Yong-Ki Park, *Thesis, Northwestern University, 1986.*

annealed and on twisted iron whiskers⁴.

Internal friction measurements (to show the effects of trapped hydrogen) were also made on annealed, cold-worked, and charged high-purity single-crystal iron specimens⁵. In fairness, a subsequent study by Hidalgo *et al.*⁶ using one deformed polycrystalline iron sample failed to separate several lifetimes. They strained aluminum samples in ways designed to produce one or more jogs and observed some differences. Hence they concluded that positrons were not trapped by dislocations but by jogs. However, they presented no further supporting evidence. They attributed the mobility to *pipe diffusion* of the hydrogen like species.. Waber⁷ has stated that various experts are not aware of any experimental evidence for pipe diffusion of interstitial atoms in iron or other BCC metals. *However, it could be argued that the present results only apply to BCC metals where pipe diffusion was not readily observed.*

Recently, Shirai *et al.*⁸ has measured the lifetimes of positrons in vacancies and in various forms of dislocation in carefully prepared Al, Au, Cu and a Cu alloy specimens. They find distinct lifetimes for each type of defect and the data fall on a general line when normalized. These authors take exception to the Doyama-Cotterill position. They believe that the positrons indeed are trapped in the dislocations and that annihilation occurs in the dislocation-core region. Their positron lifetimes are roughly

⁴ Niel Roth and James T. Waber, *Unpublished Results, Northwestern University, 1987.*

⁵ Yong-Ki Park, James T. Waber, M. Meshii, C. L. Snead, Jr, and C. G. Park, *Phys. Rev.*, **34 B** (1986) 823-836.

⁶ C. Hidalgo, S. Linderoth, G. Gonzales-Doncel and J. San Juan, *Proc. 8th Intl. Conf. on Positron Annihilation, Delft, 1989.* (World Scientific Publishers, Singapore, 1990) pp. 371-373.

⁷ James T. Waber, *Private Communication, (1988).*

⁸ Y. Shirai, K. Matsumoto, G. Kawaguchi and M Yamaguchi, *Proc. 9th Intl. Conf, Positron Annihilation, Szombathely 1991.* ed Cs. Szeles, (Materials Science Forum, Aedermannsdorf, Switzerland, 1992) in press.

proportional to the magnitude of the Burgers' vector. So the results of Hidalgo *et al.* are not supported.

While Hirth had estimated binding energies of hydrogen atoms to edge and to screw dislocations in his Campbell Lecture⁹, the development of a non-destructive method of determining dislocation concentrations afforded a new approach to identifying hydrogen traps and determining whether they were occupied. It also became possible to estimate the binding energy of a hydrogen atom in a dislocation from the measured diffusion coefficient, Park and Waber¹⁰ showed that after the specimens had been electrolytically charged with hydrogen, the trapping of positrons by edge dislocations was reduced by 20 percent and by about 40 percent in the case of screw dislocations. Trapping returned after holding a specimen for several hours in a vacuum desiccator.

The research then developed along two paths: one, was to study more about the behavior of dislocations and the other was to study the deposition and diffusion processes for hydrogen.

II. FURTHER POSITRON ANNIHILATION STUDIES

Waber and Jong-Lam Li, a Post-doctoral Fellow from the Korean Advanced Institute of Science and Technology, pursued this non-destructive method of determining edge and screw dislocation densities at Michigan Tech.

DISLOCATION MOTION

One of the important questions concerning dislocations is how they are removed during thermal annealing. It is clear that many of them can be annihilated during the recovery stage; more complex processes, namely recrystallization and grain growth occur at later stages and exhibit further effects. The text books all illustrate the disappearance of dislocations by the diffusion of vacancies to the extra half-plane on the slip plane where the former is "eaten away" by arriving vacancies and *climb* occurs to

⁹ J. Hirth, *Metall. Trans.*, A 11 (1980) 861-869.

¹⁰ Yong Ki Park with Prof. Waber, See references 3 and 5.

new slip planes. To "dissolve" a half plane would require vacancy concentrations in the vicinity of 10^{-6} molar. However, it was observed that the lifetime of 175 psec which is associated with vacancies in α -iron, was not a significant component of the measured lifetimes of cold-worked samples. While vacancies might be generated by dislocation interactions during deformation, few of them remained afterwards. Thus it was unlikely that after the production of vacancies by the interacting dislocations (the former were assumed to have diffused away to free surfaces), the process could be reversed and dislocations could be reduced in number. However, Park *et al.*¹¹ did not detect a significant number of vacancies either before or after annealing, although the method is inherently capable of detecting vacancies at this level.

The study of this fundamental metallurgical question was undertaken by Jong-Lam Lee and Waber using these positron annihilation techniques and deformed single crystals to prove Li's theory¹² of recovery processes - namely that a vacancy mechanism was not dominant in the thermal elimination of dislocations - but that recovery occurred by the annihilation of dislocation dipoles on glide planes. Two separate activation energies were determined both of which were much smaller than that for self-diffusion of iron atoms - a crucial component of the conventional vacancy-based theory. Screw dipoles had the smaller activation energy and in isochronal runs, they had virtually disappeared (at lower temperatures) before significant reduction of edge dipoles occurred.

Specifically, Lee, Waber and coworkers¹³ developed two kinetic expressions which relate the amount of change during each isochronal heating step to the overall kinetics and the activation energies. To verify the rates, several isothermal runs were made

¹¹ Park *et al.*, See References 5 and 3.

¹² J. C. M. Li, in *Recrystallization, Grain Growth and Texture*, (Amer. Soc. Metals, Metals Park, 1966) p. 45ff

¹³ Jong Lam Lee, James T. Waber, Yong-Ki Park and Jeff M. Th. de Hosson, *Mater. Sci. Eng.*, 81 (1986) 379-390

with the same crystals and rates were in good agreement with the isochronal data. These isothermal runs were important in establishing that the process was governed by a second order kinetic equation i.e., depended on the product of $\rho^+\rho^-$ and not on one of them alone, as would be the case with the vacancy diffusion mechanism.

Two major conclusions of this study were: (1) that at low strains, the dislocations exist primarily as dipoles and glide on common planes with low activation energy; the screw components are more mobile and have the lower activation energy, and (2) the excess density ρ_{ex} which is equal to $|\rho^+ - \rho^-|$ is a small fraction of the total density $(\rho^+ + \rho^-)$ or ρ_0 . As predicted by Li, the concentration of screw dislocations must become small before the edge components decrease significantly.

After reading a paper by Marcinkowski¹⁴ on surface dislocation dipoles, Waber realized that positrons could be used to determine their surface concentration. Lee and Waber¹⁵ undertook a study of the effect of metallographic polishing on the distribution of dislocations in sub-surface layers of iron single crystals i.e., the depth profile of edge and screw dislocations produced by mechanical polishing. This work has general importance since almost all of the samples used in a wide variety of experimental studies of surface phenomena are mechanically polished.

It was generally assumed that dislocations would readily diffuse to and escape at any free surface. Contrary to expectation, the dislocation densities were larger at the specimen surface. With normal polishing the dislocations penetrate into the first 50 microns of well annealed single crystals - even using 0.05 μm alumina slurries, the depth is 15-20 microns. As shown in Fig. 1, the dislocation density decreases logarithmically with depth. The thermal elimination of both edge and screw dislocations

14 R. J. Marcinkowski, *J. Mater. Sci.*, 19 (1984) 1296 ff

15 Jong Lam Lee and James T. Waber, *Metall. Trans.*, 21A (1990) 2037-2045

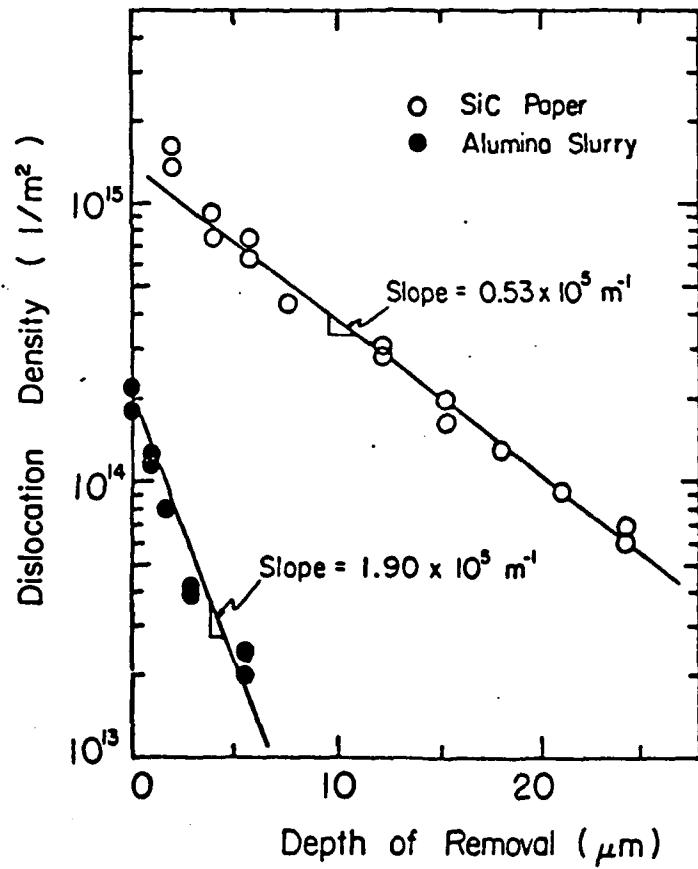


Fig. 1 Dislocation Profile in Polished Single Crystals of BCC Iron

components is comparable. One difference in procedure, is that his observations were made in the presence of the electron beam of the TEM microscope, whereas in the present work, the dissolved hydrogen was removed *in vacuo* at liquid nitrogen temperature after each step of isochronal hydrogen annealing but before each set of positron measurements was made.

Doping with amounts of nitrogen, insufficient to lead to nitride precipitation, reduced the glide of the dipoles. However, this study was complicated by the desorption of the nitrogen from the dislocation traps in the interesting temperature region and is being revised. To show the consistency of annealing behavior, one of the expressions developed for isochronal annealing is plotted in Fig. 2 versus a *modified time*. Data for isothermal and isochronal are presented in the left hand panel together with the behavior of the mechanically polished samples, In the right panel, the same isothermal and isochronal data are plotted with the data for nitrogen doped specimens. These four different types of runs fall on the same line.

HYDROGEN DEPOSITION AND DIFFUSION

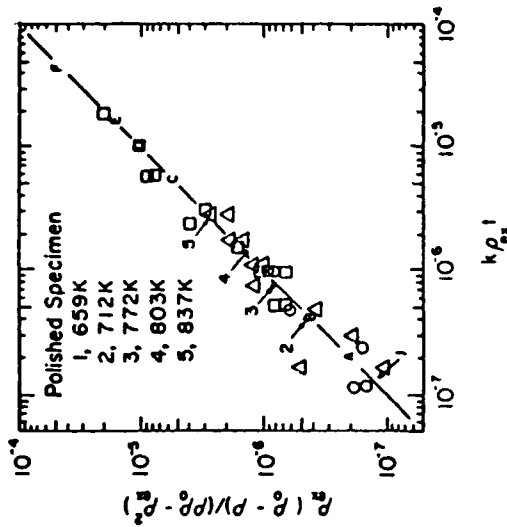
In the period of 1970 to 1982, a series of models for the diffusion of hydrogen in iron or steel containing saturable and/or unsaturable traps were developed. These range from McNabb & Forster¹⁹ to Iino²⁰. Without going into specific details of individual papers, the over-all situation can be summarized as follows :

- (i) different assumptions and different mathematical techniques were used
- (ii) authors concentrated on simple parameters such as time-lag or break-through times
- (iii) detailed comparisons between theoretical expressions and experimental charging curve data were scant

¹⁹ A. M. McNabb and P. K. Forster, Trans. Met. Soc. AIME, 227 (1963) 618-627.

²⁰ M. Iino, Acta Met., 30 (1982) 367-375.

CHANGES IN DISLOCATION DENSITY
FOR POLISHED AND FOR COLD-ROLLED SPECIMENS



Cold-rolled iron	Isochronal
○	A 416K
△	B 458K
□	C 618K
	D 657K
	E 696K
	F 769K

DISLOCATION CONTENT CHANGES IN PURE
AND NITROGEN DOPED IRON SINGLE CRYSTALS

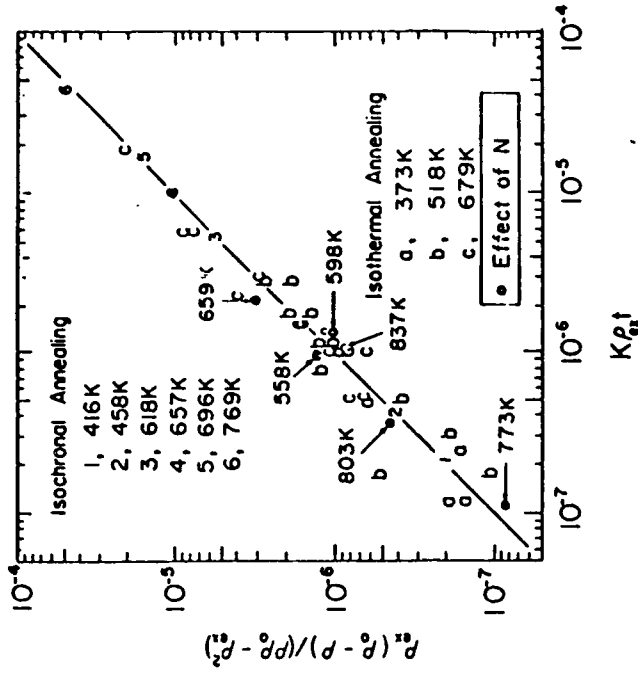


Fig. 2 Comparison of the Kinetics of Dislocation Annihilation in Four Different Kinds of Specimens

- (iv) little effort was made to identify the traps or to quantify them - impure metal and/or complex alloy samples were studied

Researchers from New Zealand²¹ analyzed a two-step process of deposition at cathodic potentials followed by a rapid reversal of the potential to "de-plate" the adsorbed hydrogen. They considered following model conditions:

I. SURFACE REACTION BOUNDARY CONDITIONS FOR HYDROGEN DEPOSITION

- Reasonable Models
- (A) Constant Surface Concentration
Potentiostatic
 - (B) Constant Surface Flux
Galvanostatic
 - (C) Flux Limited by Reactions
in Solution

They did some work with deformed polycrystalline iron specimens since they noted that experiments by Pumphrey²² in 1980 indicated that

- (i) Constant surface coverage of Hydrogen on steel was the preferable model - but-
- (ii) Sharp deviations from either models (A) or (B) occurred after short charging times
- (iii) Deviations were in the same sense whether the experiments were carried out in dilute H_2SO_4 or in NaOH

Pumphrey concluded that the effects were due to the fact that "...diffusion of hydrogen [atoms] were reduced one or two orders of magnitude by dislocations."

Pound and Wright²³, studied the ingress of H atoms into plane

²¹ R. M^CKibben, R. M. Sharp, D. A. Harrington, B. G. Pound and G. A. Wright, *Acta Met.*, 35 (1987) 253.

²² P. H. Pumphrey, *Scripta Met.*, 14 (1980) 695 -791.

²³ B. G. Pound, G. A. Wright and R. M. Sharp, *ibid* p. 263 ff

surfaces of zone-refined iron by this "double step" potentiostatic method. They observed diffusion control, rather than interface control, and the influence of eliminating dislocations by annealing, as predicted by Pumphrey. They found that trapping rate constant k was five times larger with the cold-rolled specimens than it was with their annealed specimens. They concluded that the traps were nearly irreversible. They used an unreasonably large trap diameter and found a much lower number of traps than the present authors.

Effect of Dislocations on the Diffusion of Hydrogen in Iron

In fairness, the Principal Investigator recently discovered that he had failed to reference fully earlier work on the effect of hydrogen in reducing positron annihilation from dislocations carried out by J. G. Byrne and his colleagues.²⁴

Replotting the diffusivities determined in Yong-Ki's thesis for iron single crystals deformed in three different ways, - (Waber and colleagues had used cold-rolled single crystal specimens, single crystals specimens bent in a mandrell at room temperature and single crystal specimens pulled in tension at 200° K) - the apparent D_0 values fall on a common curve, that is as shown in Fig. 3a. The measured diffusivity is inversely proportional to the dislocation density. While that may initially seem surprising, all the mathematical models predict that D_{app} should be related to the density of traps N_T by a divisor similar to

$$D_{app} = D_0 / (1 + a N_T)$$

If the second term in the parentheses is large compared to unity,

²⁴ F. Alex, T. D. Hadnagy, K. G. Lynn and J. G. Byrne, "Positron annihilation studies of hydrogen embrittlement" in *Proc. Intl. Conf. on Effect of Hydrogen on the Behavior of Materials, Jackson Hole Lodge, 1975*, eds A. W. Thompson and I. M. Bernstein. (AIME, New York, 1976) 642-650. In his discussion of a paper by R. Gopahengar, J. F. Wallace and R. A. Oriani, *Mater. Sci. Eng.*, **68** (1984-85)191-196 Byrne cites hydrogen/dislocation studies on nickel and copper. His comments appear in *Mater. Sci. Eng.*, **80** (1986) 221.

Apparent H Diffusivities
Replotted From Yong Ki
Park's Thesis

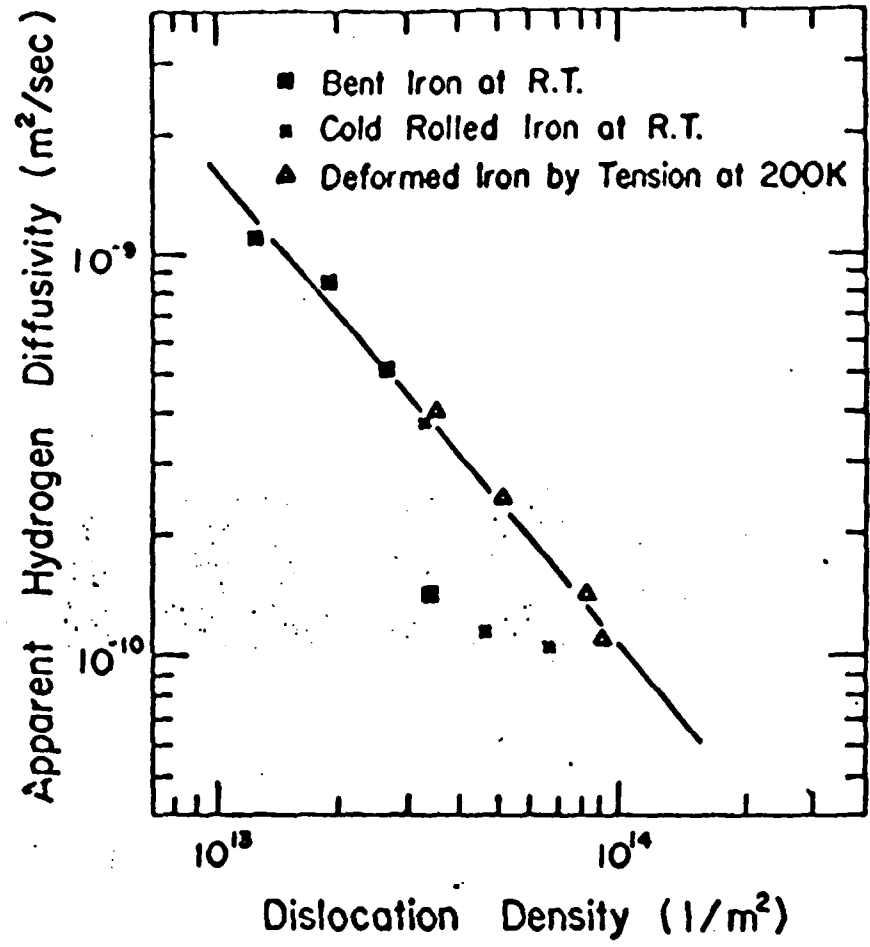
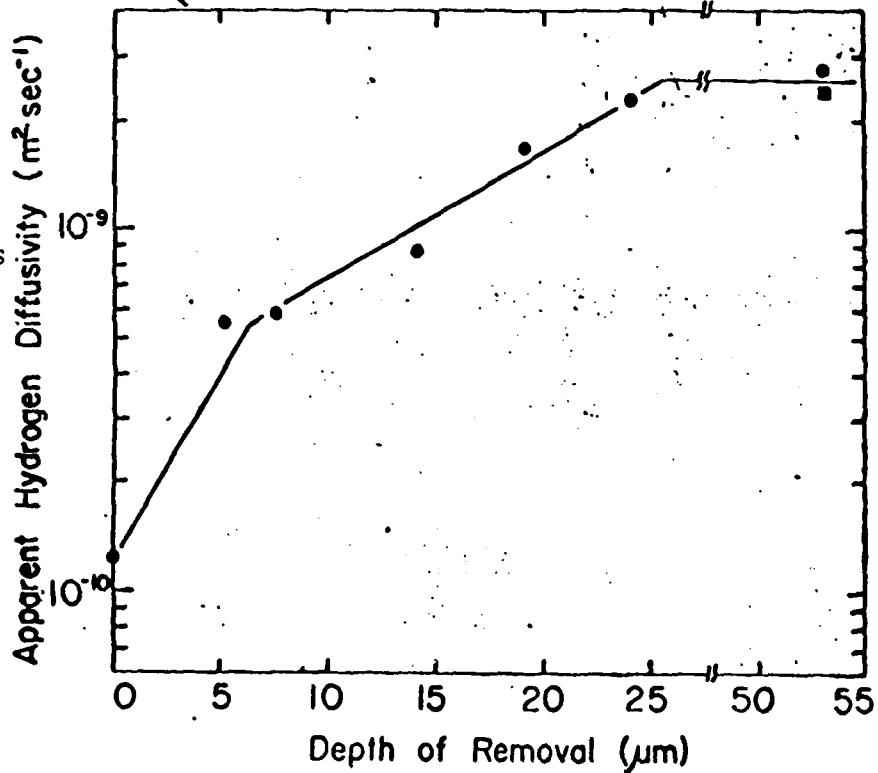


Fig. 3

Apparent H Diffusivities
Increased by Removal
of Surface Layers
Damaged by Polishing



the relation experimentally observed would be inverse.

The development of the non-destructive method of determining dislocation densities afforded the opportunity of readily verifying the relation experimentally.

Lee, Waber and Park²⁵ studied the rate of permeation in mechanically polished single crystals. It increased monotonically with the removal of dislocations in the disturbed zone. Dislocations in the first 50 microns of a specimen 950 microns thick reduced the diffusivity tenfold! Data are presented in Fig. 3b.

This is consistent with Pumphrey's conclusion about the importance of dislocations in the surface layers. This is not what one would expect if pipe diffusion were dominant. Note the dislocations are traps not conduits!

The famous Arrhenius plot of Alefeld and Vökl²⁶ is presented here as Fig. 4. It shows that the diffusivity of hydrogen in iron as measured by a number of authors falls very close to a single line for the data collected above roughly 300^o C. However, as the test temperature approached room temperature, there was considerable variability in D_0 . The diffusivity obtained with the present mechanically polished single crystal fell in the middle of the other reported data for room temperature. When roughly the first 50 microns of the surface were removed chemically, the resulting D_0 value increased by an order of magnitude and fell slightly above the Arrhenius line labelled D_2 . The hold-up of hydrogen isotopes in dislocation traps is evidenced by a graph in the next section.

²⁵ Jong Lam Lee, James T. Waber and Yong Ki Park, *Scripta Met.*, 20 (1989) 823-828.

²⁶ J. G. Alefeld and J. Vökl, "Hydrogen Diffusion in Metals" in *Hydrogen in Metals*, eds. A. S. Nowick and J. J. Burton (Springer Verlag, Berlin, (1983) p. 231.

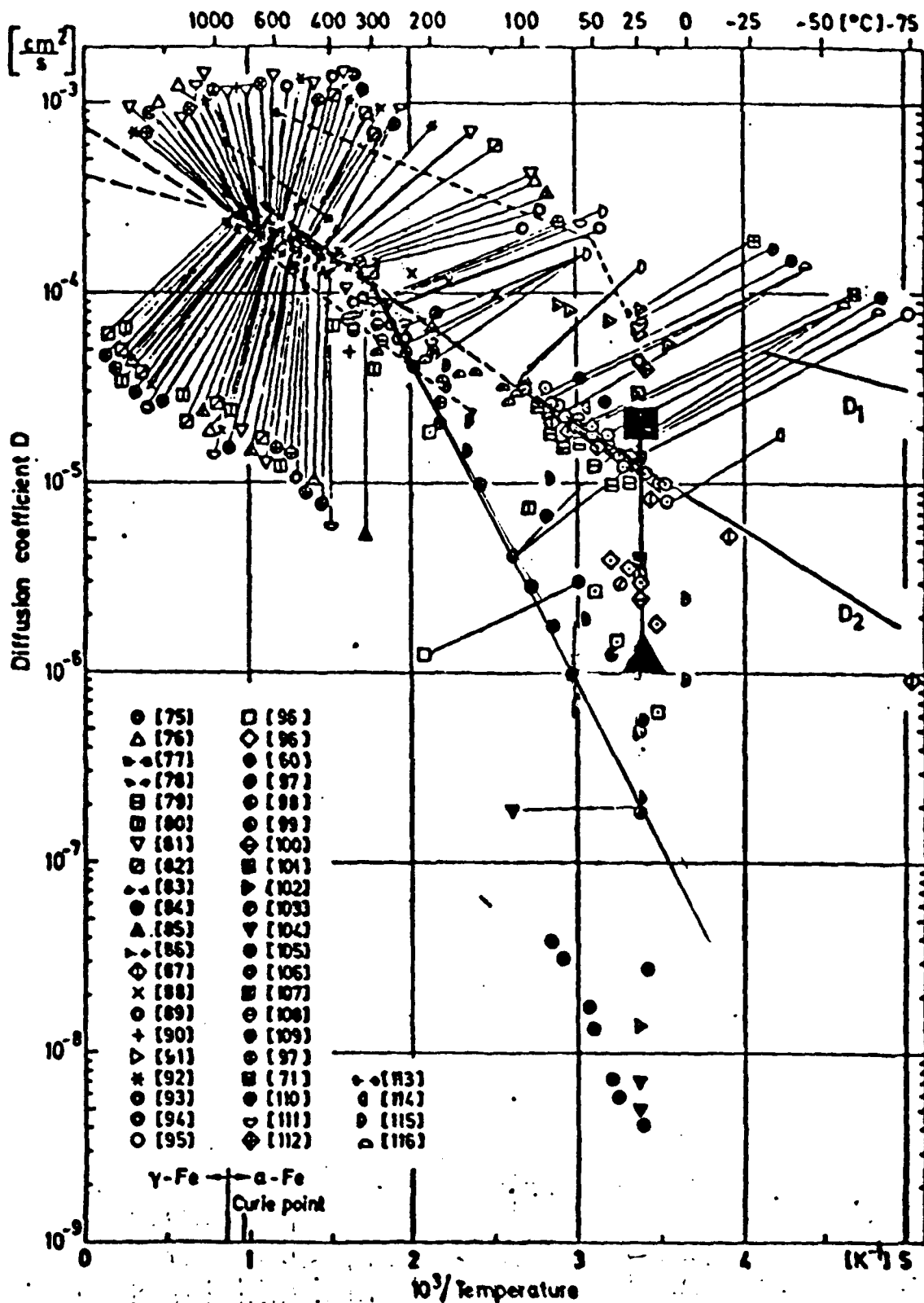


Fig. 4

Diffusion coefficient of Hydrogen in α -Fe (2).

■: hydrogen diffusivity in iron before mechanical polishing.

▲: hydrogen diffusivity in iron after mechanical polishing.

IV. RAPID ELECTROLYTIC CHARGE & DISCHARGE MOBILITY OF HYDROGEN AND DEUTERIUM

Shi and Waber²⁷ observed results similar to those of Pumphrey. - we found that the trapping constant k was increased by the presence of dislocations. Wright and coworkers used H_2S as a poison instead of As_2O_3 and both sets of researchers observed that the surface coverage became nearly complete as the overvoltage was sufficiently increased. However, Pound and Wright noted that the coverage is quite small in the absence of a poison.

Shi and Waber calculated the surface coverage and the total number of H or D atoms left in the solid after the cathodic potential was changed to anodic. Those atoms which diffused out were oxidized to hydrogen ions. Then the number of hydrogens remaining was related to the surface density of dislocations. Half of the residual atoms were assumed were to be trapped in the dislocations and the remainder were assumed to be in the bulk in interstitial positions. - this is a conservative estimate in view of the equilibrium constant. These data are summarized for the two isotopes in Fig. 5 for both annealed and cold rolled single crystals. Trapping in contrast to rapid diffusion along dislocation cores is consistent with these results.

IV. THEORETICAL STUDY OF THE TRAPPING OF HYDROGEN BY DISLOCATIONS

Min Yan, a graduate student at Michigan Tech, applied a modification of the Embedded Atom model²⁸ (EAM) to calculate the binding of a hydrogen atom in an interstitial site of α -iron. In general, these workers at Sandia National Lab had not carried out any calculation on BCC metals. Although the energy value for

²⁷ Xiaolin Shi, *Thesis at Michigan Tech, 1989*

²⁸ M. Baskes, C. F. Melius and W. D. Wilson, *Zeit. für Phys. Chem., Neue Folge*, 116 (1979) 289. See also *Proc. Effect of Hydrogen on the Behavior of Materials, Jackson Lake Lodge, Wy. 1980*

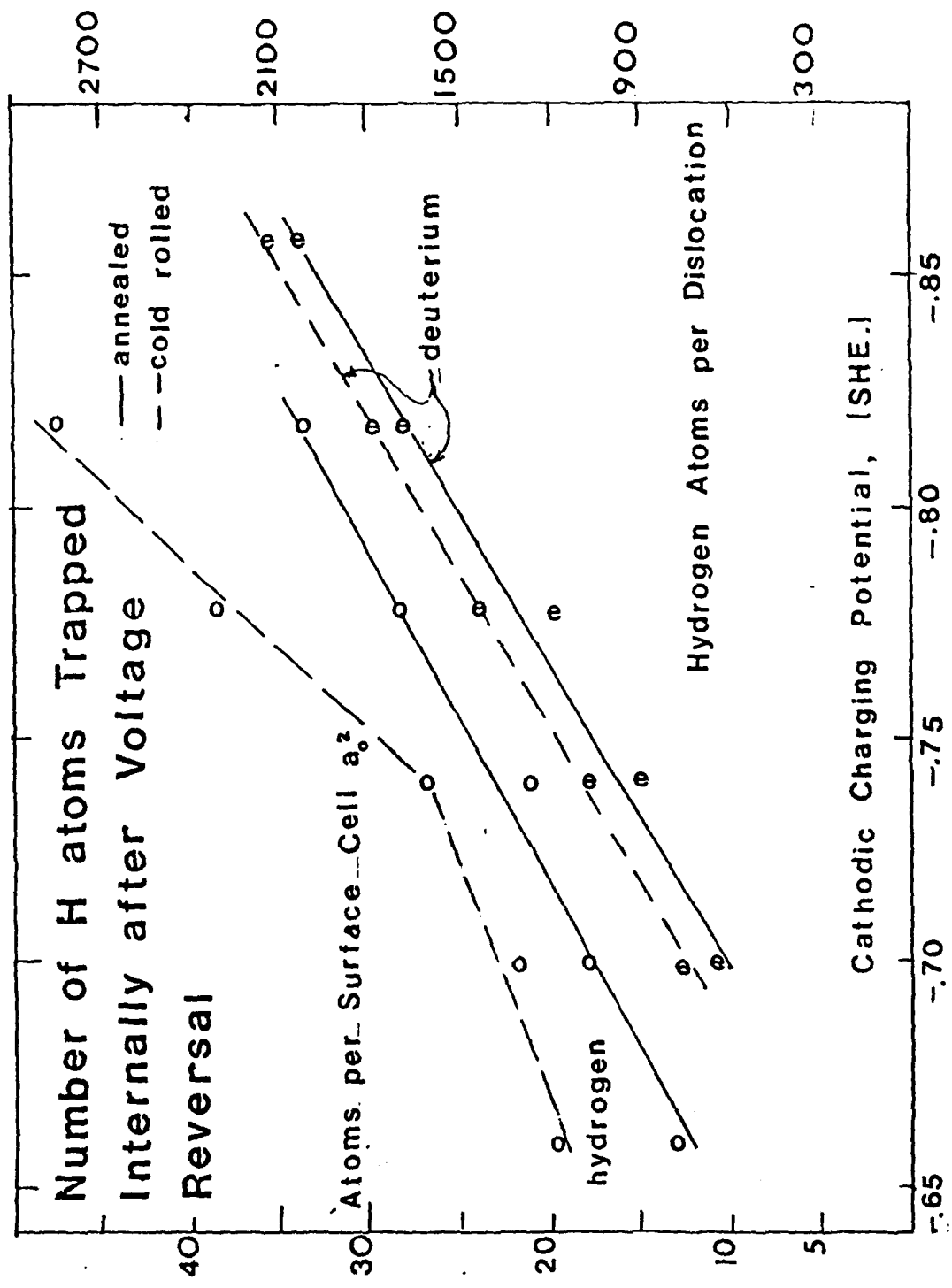


Fig. 5 Diffusion of Hydrogen and Deuterium to dislocation traps.

THE DISLOCATION CONFIGURATION

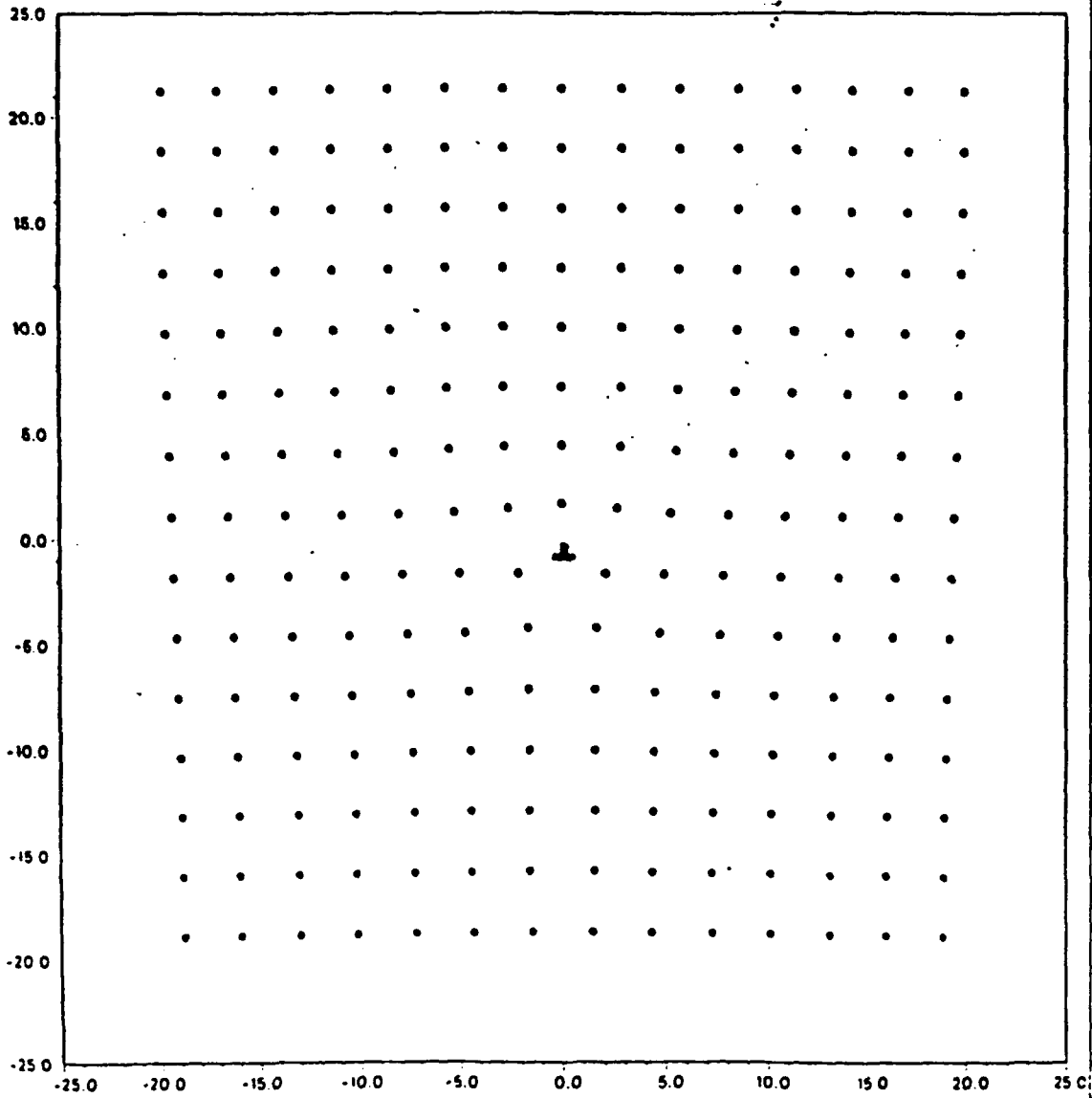


Fig. 6 Placed perpendicular to the Dislocation line. Cross marks the approximate location of the minimum energy of a Hydrogen Atom.

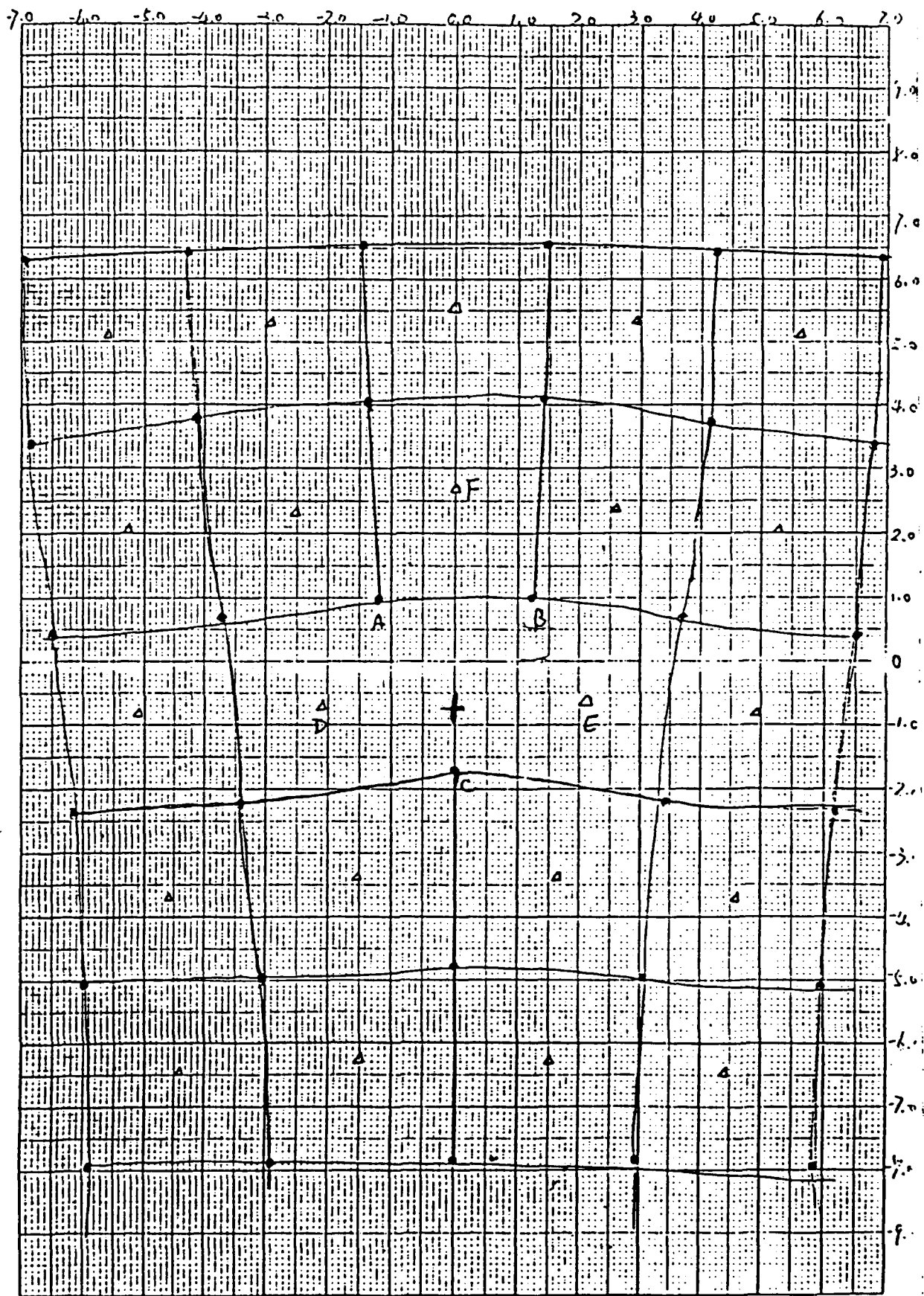
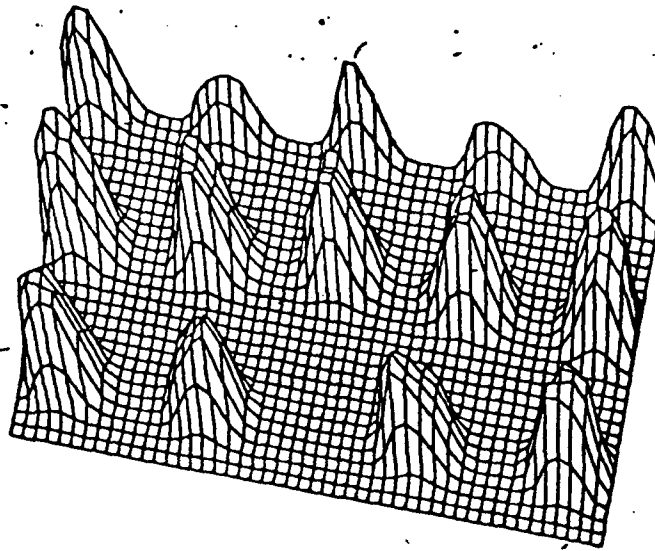


Fig. 6 A



Perspective View

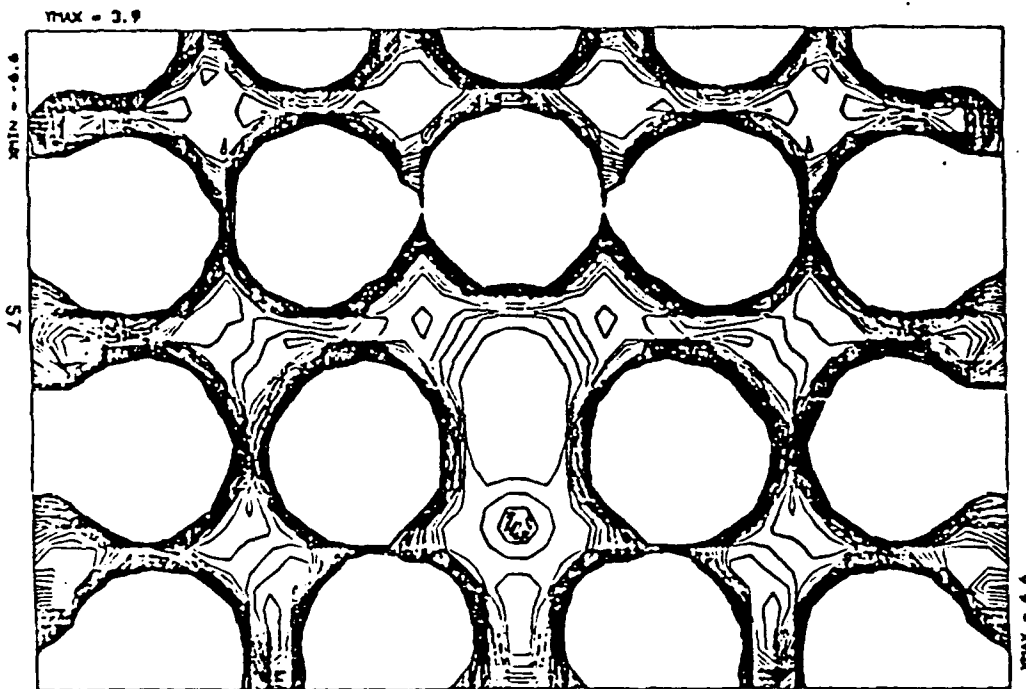


Fig. 7(a). Contour energy plot of hydrogen in region of gh shown in Fig. 4(b).

Fig. 7 Two Complementary Views of the Variation of the Potential of A Hydrogen Near the Core of A Dislocation in Iron Over the XY Plane

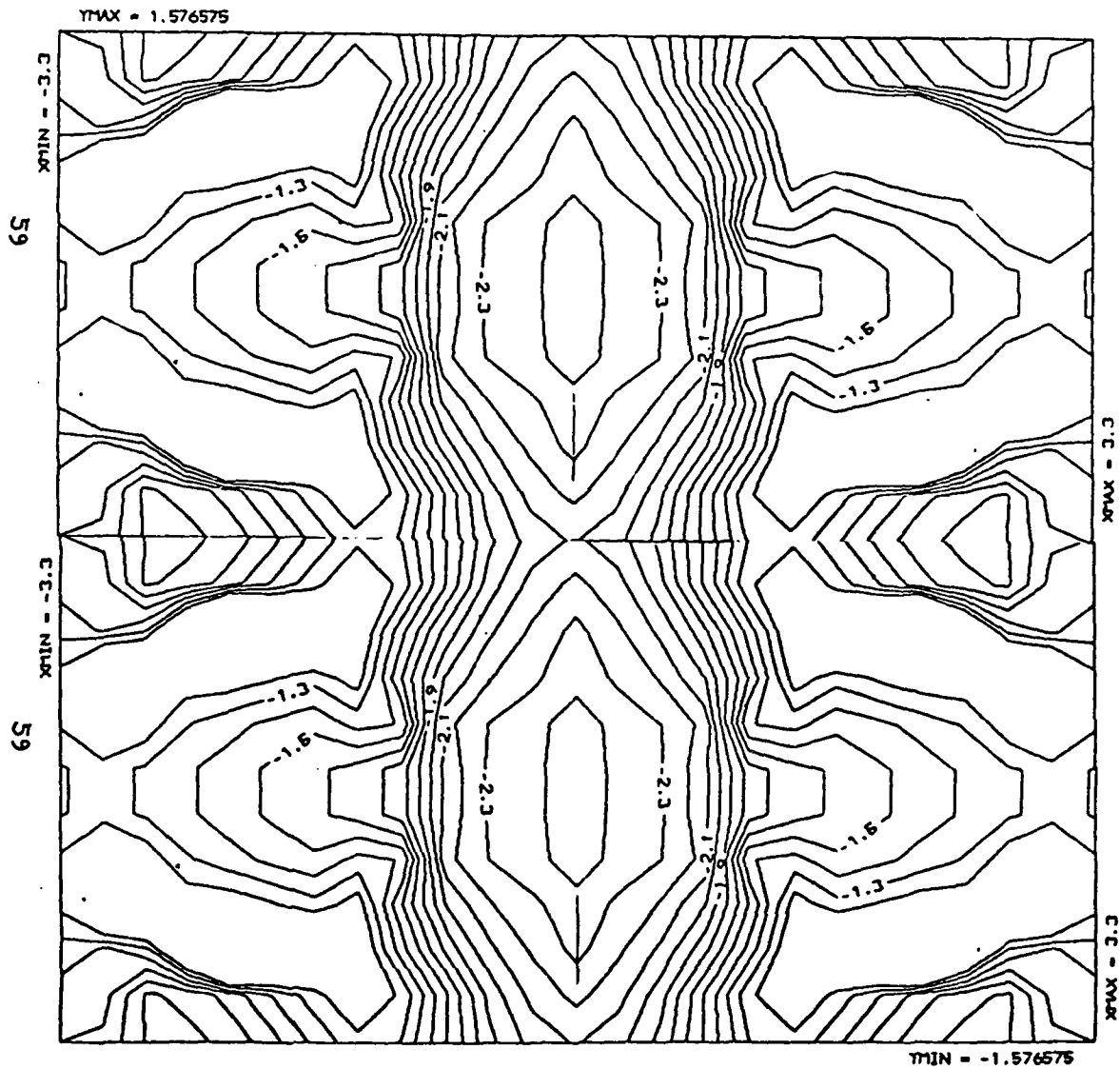


Fig. 8 The contour energy plot of hydrogen on the slip plane of dislocation.

THE POTENTIAL ENERGY OF H IN JOG

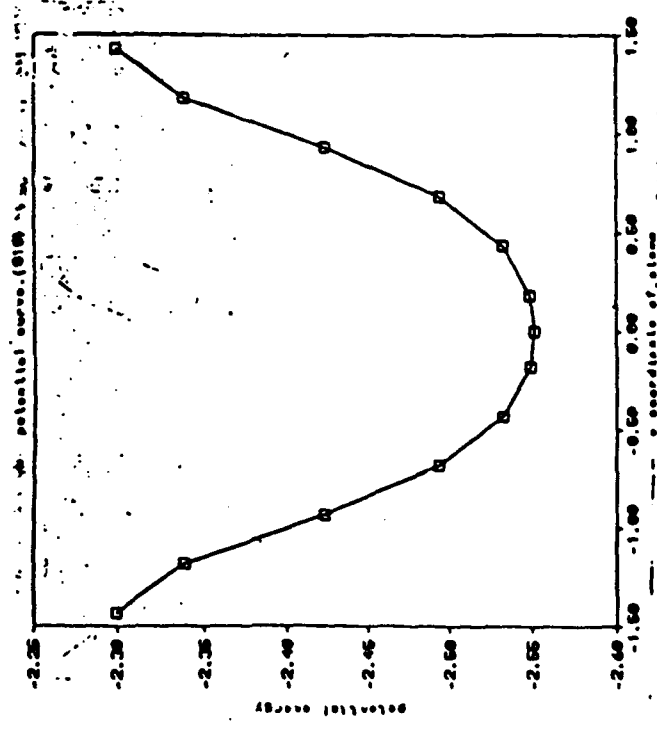
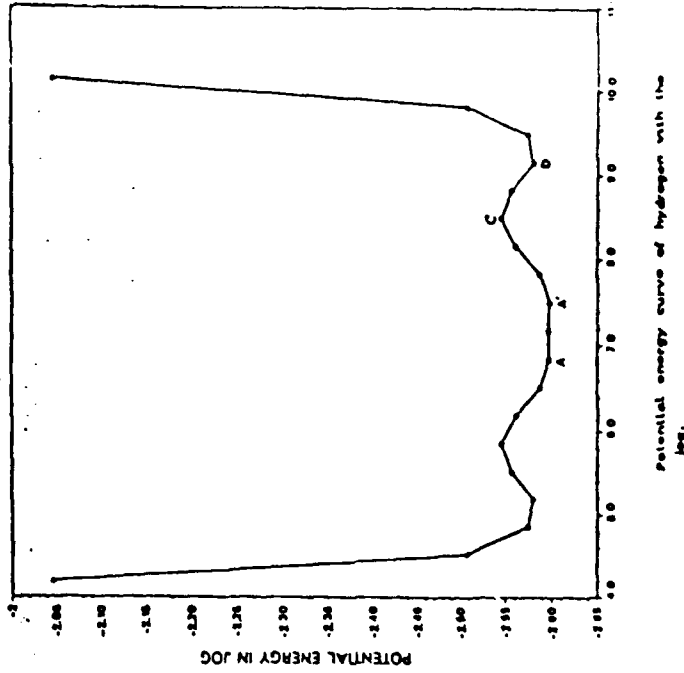


Fig. 9 Variation of the Potential for A Hydrogen Along The [010] Direction of A Dislocation
It is slightly deeper with a jog.

binding at an interstitial site was quite high it agreed well with a calculation made by another method.

The next step she took was to introduce a (100) edge dislocation into the lattice by movement of half planes with a common slip plane. The relaxation of the atoms in the vicinity of the core was done initially using the elastic strains of a continuum model of a dislocation. Then displacements due to the x and y contributions to the interatomic forces were calculated from the modified EAM. All the atoms were treated pairwise through several iterations. The region which was considered, extended to five lattice parameters from the core.

The displacements are indicated in Fig. 6 and the bending of the slip plane is evident. Isopotential energy lines for a hydrogen atom in the vicinity of the core are shown in two different versions in Fig. 7. The minimum for hydrogen is located just below the slip plane. The influence of the iron atom just behind the XY plane of the contour plot is not clearly revealed. The variation of the potential along the dislocation core within the additional half plane of the dislocation is shown in the Fig. 8. The indicated binding energy is 0.35 eV which is larger than the value Park deduced in his thesis²⁹, namely 37 kJoules for edge dislocations and 26 for screw dislocations. The latter value is in good agreement with the value Hirth³⁰ reported, namely 20-30 kJoules for screw dislocations. In the right hand panel, the potential is plotted for jog created by removing two atoms from the half plane. As noted in the legend, the calculated potential well is about 0.05 eV deeper when the jog is included.

Incomplete Study of Dislocations in FCC Metals

Eric Bylaska, an undergraduate, undertook a study of equivalent calculation for hydrogen in FCC palladium after completing an undergraduate thesis in Physics. However, it took much more coding to obtain a block containing a (111) [110]

²⁹ See Ref. 3.

³⁰ See Ref. 8.

dislocation and with a sufficient number of atoms than with the (100) [010] dislocation of iron. The direction of viewing the FCC palladium is along a $\langle 112 \rangle$ direction. The movement of the half planes to create an edge dislocation is indicated in the three portions of Fig. 10. Unfortunately the elastic displacements have not yet been computed.

POSITRON TRAPPING IN POLYMERS

Ronghai Wang³¹ studied the trapping of positrons in a series of epoxy resins. The initial purpose was to assess the thermal variation of the *free volume* of the polymers and the glass transition temperature. In addition, the effect of changes in the structure of the polymers on the free volume was also studied; specifically, changes in the functionality of the amino group and changes in the number of CH_2 in the side chains of the *curing agents* were made. N-methylation of the amino group is designated C2M0, C2M1, and C2M2; these symbols mean that 0, 1 and 2 methyls have been added to diamino-ethane. Thus the number of functional N-H bonds which can react with the epoxy groups was reduced. The symbols C3M0 and C4M0 signify that n-propyl diamine and n-butyl diamine were used as curing agents.

It was possible to measure the coefficient of expansion of the free volume over a range of temperatures. In the literature, it is postulated that the free volume is constant and possibly is even negligibly small, just below the glass transition temperature T_g . Using the lifetime of the so-called third or longest component of the lifetime spectrum τ_3 , it was found that the fractional free volume varied from 3.7 to 5.4 per cent at T_g for the five polymers and decreased to 2 to 3 per cent at -50°C . Contrary to the published assumptions, the free volume was not constant. When the data were extrapolated to absolute zero, the residual volume was -0.34 ± 0.58 percent. This indicates the inherent problem of extrapolating the data over a long range, i.e., more than 200° .

³¹ Rong-Hai Wang, *Thesis Michigan Tech* 1991

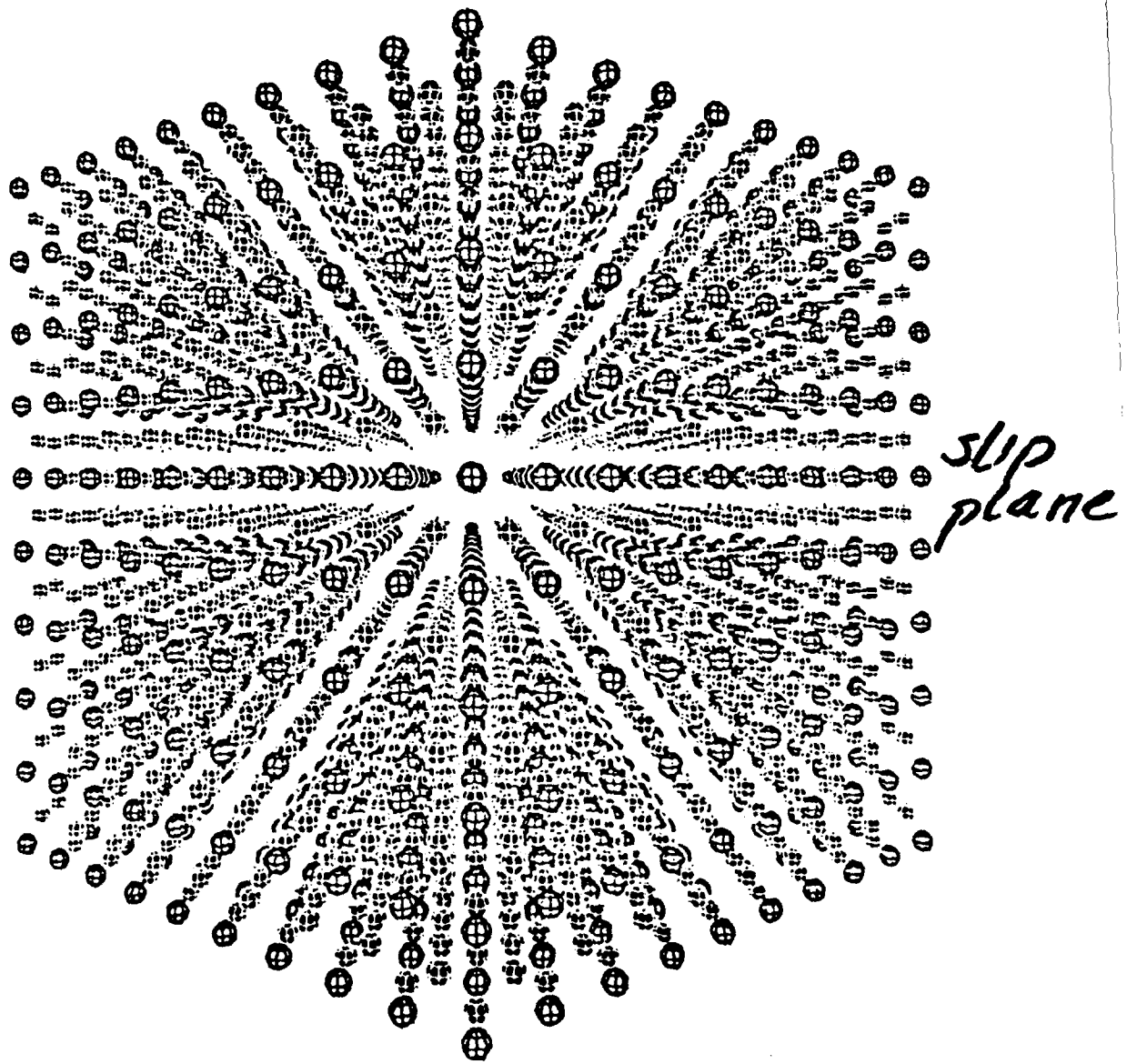


Fig. 10a FCC Lattice Viewed Along $[1\bar{1}2]$ Direction

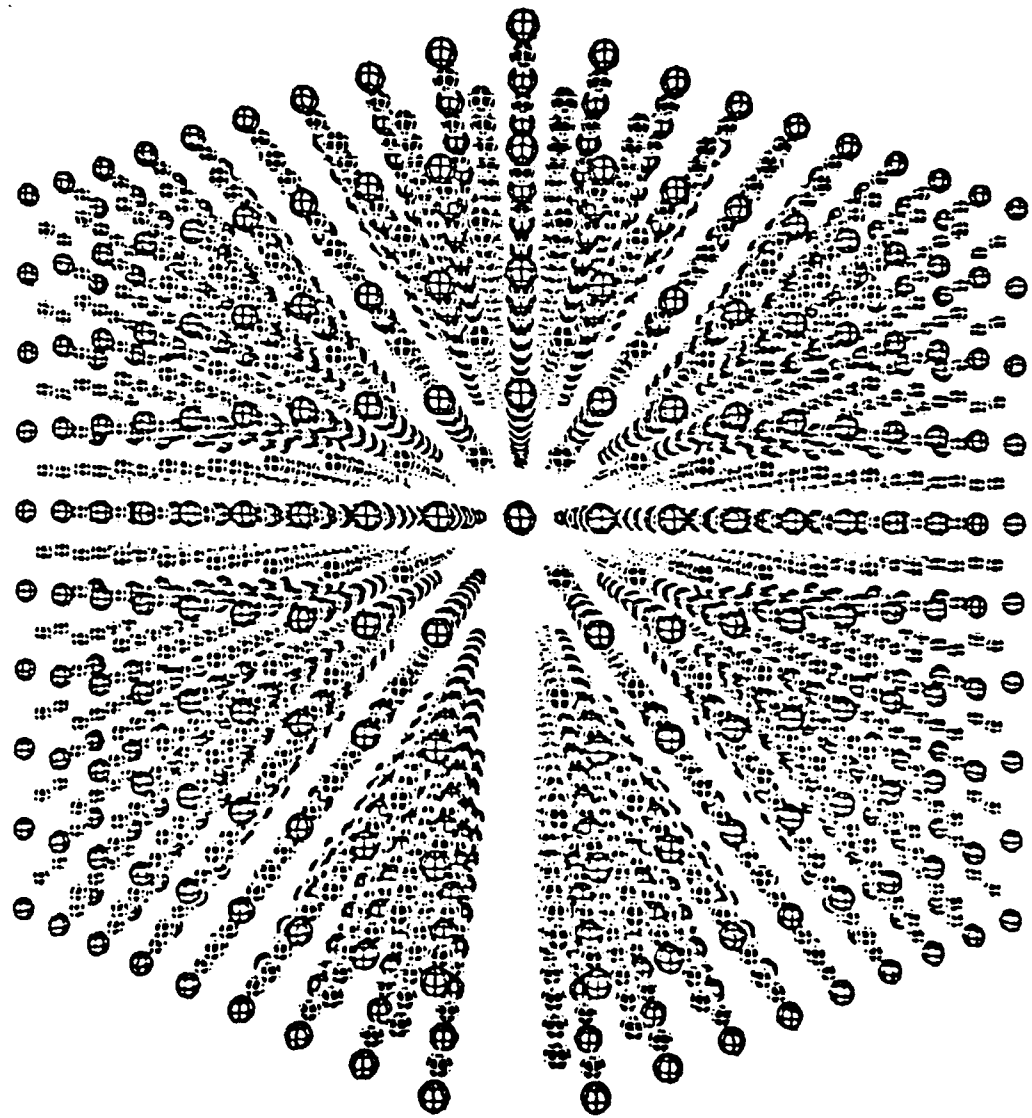


Fig. 10b Same, with two adjacent $\langle 110 \rangle$ planes removed

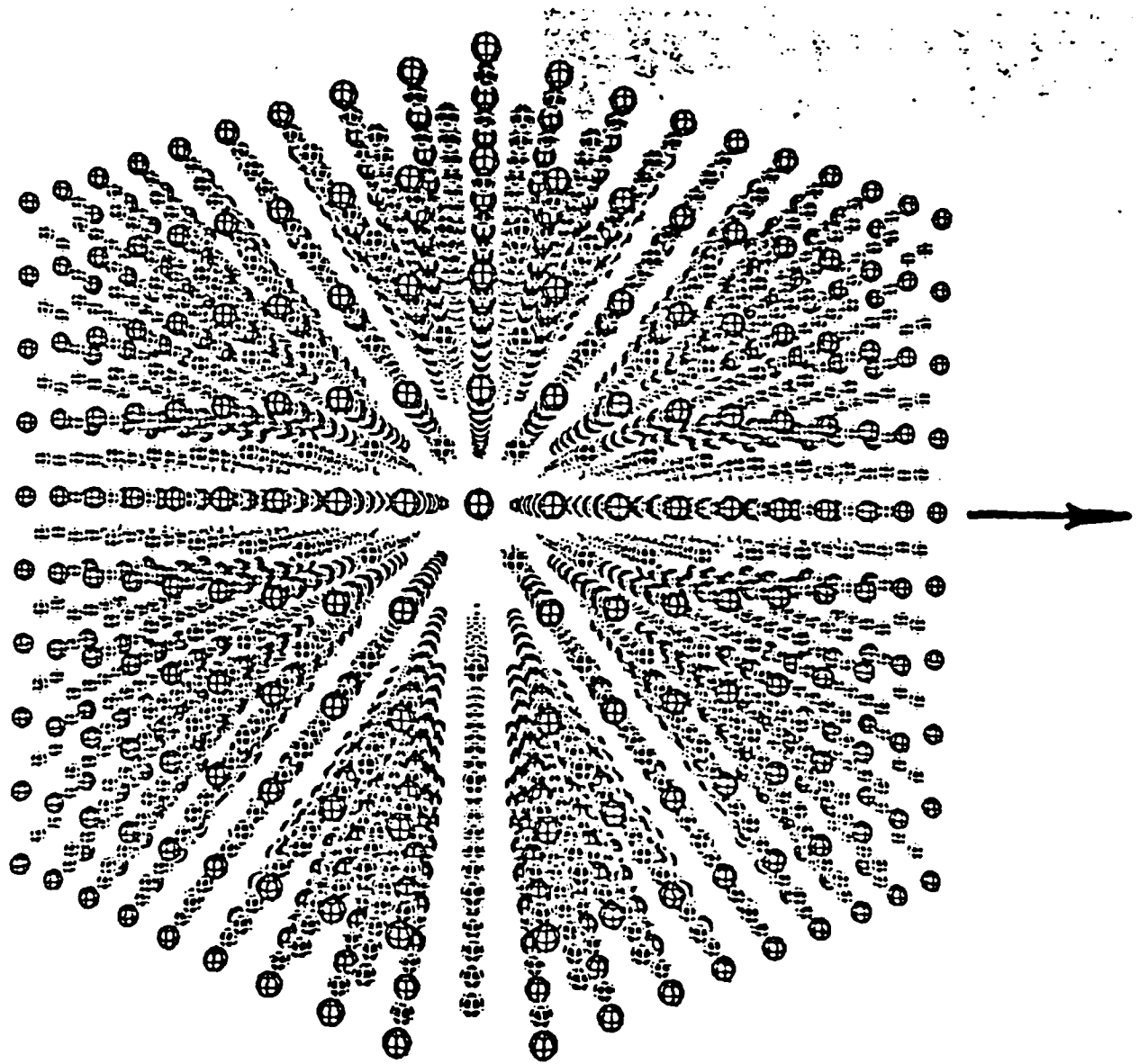


Fig. 10c Same, With One half-plane shifted by Burger's Vector, $\frac{a_0}{2} [111]$.

The free volume did increase significantly above T_g . While other researchers had used such a change in the slope of the positron lifetime curve to find T_g , no comparison with the thermal expansion of the solid as a whole was made nor was the free volume measured at such low temperatures. In addition, the thermal dilation of the occupied volume, i.e., the C-H chains themselves, was estimated by the increase in the second component τ_2 . Both of these lifetimes were converted into fractional free volumes from the products $\tau_2 I_2$ and $\tau_3 I_3$ (where I is the intensity or better, the fraction of the positrons annihilating in a specific manner) using an expression Nakanishi and Jeans³² had developed. As shown in the table below, the sum of the two volume increases was in good agreement with the thermal expansion coefficients measured in a torsional apparatus. Because of the possibility of the stylus distorting the heated sample, the value in the last column tends to be high, except for C2M2 which is only one of the five polymers to melt well above T_g . It is interesting that most of the dilation below T_g , in our experiments, comes from the free volume, and not from the occupied volume as previously assumed.

In view of this inaccuracy in measuring the dilation mechanically, there is good agreement between the measured values and those deduced from the positron lifetimes. One conclusion drawn is that the nature of the "joint" between the curing agent segments and the epoxy-molecule plays a minor role compared with the composition of the resin, i.e., the mixing ratio needed for complete reaction.

32 H. Nakanishi and Y. C. Jeans, in *Positrons and Positronium Chemistry*, (1988) pp. 159-162.

TABLE 1. COMPARISON OF THE THERMAL EXPANSION BEHAVIOR
OF THE FIVE EPOXY-RESINS

Below the Transition Temperature		
Symbol	Sum of 2 Alphas	Exper. Dilation
C2M0	16.35 x 10 ⁻⁵	17.5 x 10 ⁻⁵
C2M1	16.51	21.5
C2M2	17.53	20.1
-----	-----	-----
C3M0	18.19	18.3
C4M0	14.01	20.1
Above Transition Temperature		
C2M0	50.45	61.9
C2M1	59.0	55.3
C2M2	66.5	40.8
-----	-----	-----
C3M0	59.5	40.1
C4M0	42.1	40.8

GOAL AT THE TIME OF FUNDING:

USE POSITRONS TO SAMPLE WHETHER HYDROGEN TRAPS WERE OCCUPIED AND HOPEFULLY TO DETERMINE THEIR FRACTIONAL OCCUPATION.

IN ADDITION TO THIS BEING SUCCESSFULLY ACHIEVED, THE FOLLOWING RESULTS WERE OBTAINED:

1. A NON-DESTRUCTIVE METHOD OF DETERMINING THE CONCENTRATION OF EDGE AND SCREW DISLOCATIONS WAS DEVELOPED, AS DESCRIBED ABOVE,

2. A THEORY OF THE THERMAL REMOVAL OF DISLOCATIONS WAS VERIFIED. J. C. M. LI'S MECHANISM INVOLVES THE ANNIHILATION OF DISLOCATION-DIPOLES BY GLIDE. THIS IS IN CONTRAST TO THE PREVIOUSLY ACCEPTED VACANCY-DRIVEN DIFFUSION MECHANISM, HOWEVER, SINCE THE VACANCY CONCENTRATION COULD BE INDEPENDENTLY DETERMINED BY THE POSITRONS, IT WAS CLEAR THAT THERE WERE INSUFFICIENT NUMBERS OF VACANCIES TO DIFFUSE TO THE CORE OF DISLOCATIONS AND REMOVE THEM BY CLIMB.

3. MECHANISM OF DISLOCATION GENERATION YIELDS A BALANCED NUMBER OF POSITIVE AND NEGATIVE DISLOCATIONS TO FORM DIPOLES ON THE SAME PLANE - THAT IS, THE EXCESS OF ONE SIGN OVER THE OTHER IS ONLY A FEW PERCENT OF THE TOTAL. THIS WAS ALSO DEDUCED FROM THE ANNEALING STUDIES USING LI'S THEORY.

4. A METHOD WAS DEVELOPED FOR EXTRACTING ISOTHERMAL KINETIC ANALYSIS INFORMATION FROM ISOCHRONAL ANNEALING RUNS. A COMPARISON SHOWED GOOD AGREEMENT BETWEEN THE TWO METHODS. MAINLY USING ISOTHERMAL RUNS, IT WAS ESTABLISHED THAT THE RATE OF DISLOCATION ANNIHILATION WAS A SECOND ORDER REACTION AND DEPENDED ON THE CONCENTRATION OF BOTH OF THE DIPOLE COMPONENTS.

5. THE ACTIVATION ENERGY FOR SCREW DIPOLE MIGRATION WAS SMALLER THAN THAT FOR EDGE DIPOLE MIGRATION - AND BOTH WERE SMALLER THAN 178 KJOULES FOR VACANCY MIGRATION -SELF-DIFFUSION - IN ALPHA-IRON,

5. DISLOCATION PROFILE FORMED BY MECHANICAL POLISHING WAS ESTABLISHED - CONCENTRATION IS A DECREASING LOGARITHMIC FUNCTION OF DEPTH. RESULTS ARE CONSISTENT WITH THE STUDY OF DISLOCATION REMOVAL DURING CREEP IN BOTH BCC AND FCC METALS BY ARSENAULT AND COWORKERS.
[TWO ACTIVATION ENERGIES AND A DECREASING PROFILE]

6. DIRECT INFLUENCE OF DISLOCATIONS IN THE SURFACE LAYERS ON BULK PERMEATION OF HYDROGEN IN IRON WAS MEASURED. WHEN COUPLED WITH EFFECTS OF MECHANICAL POLISHING OF DIFFUSION SAMPLES, THIS OBSERVATION OFFERS A PARTIAL EXPLANATION OF THE LARGE VARIABILITY OF DIFFUSIVITY MEASUREMENTS BELOW 300° C. ABOVE 300 ALMOST OF THE EDGE AND SCREW DISLOCATION ANNEAL OUT DURING THE EXPERIMENT AND HENCE HAVE LITTLE EFFECT ON DIFFUSION..

7. MEASUREMENT OF THE DIFFUSIVITY OF DEUTERIUM AND HYDROGEN INDICATE A NON-CLASSICAL VALUE OF THE EFFECT OF ISOTOPIC SUBSTITUTION,

8. THEORETICAL COMPUTATION OF THE DIFFUSION ACTIVATION ENERGY AND ENERGY CONTOURS FOR HYDROGEN IN A DISLOCATION AND A JOG OF BCC IRON

9. POSITRON LIFETIME MEASUREMENTS ON A SERIES OF EPOXY RESINS CAST DOUBTS ABOUT THE PUBLISHED ASSUMPTIONS ABOUT THE BEHAVIOR OF THE FREE VOLUME BELOW THE GLASS TRANSITION TEMPERATURE. IT IS NEITHER SMALL NOR CONSTANT.

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HYDROGEN PERMEATION and POSITRON ANNIHILATION

STUDY of ALPHA IRON CRYSTALS¹

by

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Dislocation densities in deformed iron single crystals were determined by positron annihilation techniques. Electrochemical measurements of hydrogen diffusion were made on the same crystals. It was shown that apparent diffusivity D_0 was inversely proportional to the dislocation density - results cover three different modes of deformation. Mechanical polishing of annealed specimens with even fine abrasives introduced sufficient dislocations to reduce the diffusivity tenfold.

Cathodic deposition of hydrogen and of deuterium atoms followed by rapid removal by potential reversal was studied on similar crystals. Holdup of the hydrogen atoms in surface layers was increased by the dislocations. The effect was stronger with deuterium charging. Surface coverage was approximately 5 percent of the available sites.

¹

To be presented at the UM-ARO Workshop on Surface Science and Technology, Ann Arbor, MI on November 7-9, 1990.

Hartree-Fock Calculations
on N-Alkanes Adsorbed on Graphite²

by

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Scanning tunneling microscope study by McGonigal, *et al.* of simple aliphatic hydrocarbons on pyrolytic graphite shows highly ordered 2-D pattern of the adsorbed molecules. The zig-zag C-C chain is apparently slightly elongated to be commensurate with graphite cell spacing.

Unrestricted Hartree-Fock calculations were carried out with an optimized basis set of Huzinaga² for a graphite cluster as well as for several small alkanes. This set had been used to determine correctly the crystal structure of several normal alkanes C_nH_{2n+2} and change in crystal symmetry which occurs when n is either even or odd.³

The effect of superposing the alkane on the graphite surface was studied and the location varied to find a local energy minimum.

Reasons how the adsorbate enhances the tunneling current from specific graphite sites will be discussed.

1. G.C. McGonigal, R.H. Bernhardt, R.H. and D.J. Thompson, *App. Phys. Lett.* **57** (1) 1990, 28-30.
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²

To be presented at 10th International Conference on Scanning Tunneling Microscopy, Interlaken Switzerland, August, 1991.

FREE VOLUME CHANGES AND POSITRON

LIFETIMES IN EPOXY-DIAMINE POLYMERS

by

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Abstract

Five epoxy-cured diamine resins have been studied with positron annihilation techniques. The data were fitted by three lifetimes.

Principal attention was paid to the third and longer lifetime which is associated with ortho-positronium (O- Ps). Temperatures ranged from -50 to 150° to C. Changes in the volume - coefficient of expansion and the glass-transition temperature were determined. It was established that aging at temperatures for periods several times longer than a measurement required had no discernible effect on these parameters.

The correlation between the temperature variation of the free volume and that derived from WLF theory of viscosity was investigated.

To be presented at
First Pacific Rim Conference on
Advanced Materials and Processing

Hangzhou China
JUNE 1992

THE VIEWS, OPINIONS, AND/OR FINDINGS CONTAINED IN THIS REPORT ARE THOSE OF THE AUTHOR(S) AND SHOULD NOT BE CONSTRUED AS AN OFFICIAL DEPARTMENT OF THE ARMY POSITION, POLICY, OR DECISION, UNLESS SO DESIGNATED BY OTHER DOCUMENTATION.