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Crystal Geometry and Mechanisms of Phase Transformations
in Crystalline Solids*⁺

MASTER

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Italics:

a

Bold Face

B

Bold Face Vectors:

$\vec{r}$

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Corrections and changes in the manuscript, "Crystal Geometry and Mechanisms of Phase Transformations in Crystalline Solids", by D. S. Lieberman.

- Page 6 Line 4: Delete "steals"--replace with "steels"
- Page 7 Lines 1 and 2 should read: "The most important crystallographic or geometric features of a martensitic transformation, illustrated in part in Fig. 1, are:"
- Page 9 Line 12: Add "in" after "3 mm"
Line 13: Delete "long"--replace with "in length"
Line 13: Bridgman
- Page 11 Line 4: Delete "crystallographic"--replace with "crystal geometric"
- Page 12 Lines 10 and 11 should read: "smallest (and hence what appears to be energetically the most favorable) distortions, is established, as in Fig. 6-a. For the cubic to orthorhombic transformation in AuCd, these Bain distortions are"
- Page 17 Line 3: Delete "distribution"--replace with "distortion"
- Page 19 Line 4 should read: "is not simple parallelism, the distortions in both regions"
Line 5: Delete "subjected"
- Page 24 Line 22: Add "in" after "change"
- Page 26 Line 15: Delete "slip"--replace with "shear"
- Page 27 Line 10: Delete " $\vec{b}$ "--replace with " $\vec{d}$ "
- Page 29 Line 17: Delete " $\vec{n}_2(\vec{a}, \vec{c}_2)$ "--replace with " $\vec{n}_1(\vec{a}, \vec{c}_1)$ "
- Page 32 Line 8: Delete "orthogonal"--replace with "orthorhombic"
- Page 38 Line 10: Replace "Fig. 28" with "Fig. 27"
- Page 39 Line 12: Delete "be"--replace with "lie"
- Page 42 Line 1: Delete "theories have"--replace with "theory has"
- Page 49 Line 8: Insert word "generation" after "energy"
Line 24: Delete "U-at.% Mo"--replace with "in U ~ 4 at.% Mo"
- Page 55 Line 7 should read: "Thus, the effect of ($\underline{SH}$) as a pseudo matrix on $\underline{B}$ is"

Page 61 Line 7 should read: "...energy in the region of the interface..."
 Line 16: Delete "is"--replace with "are"
 Line 19: "...two parts: the energy of..."
 Line 20: Delete "interface"--replace with "interfacial region"

Page 63 Line 10: Delete " $\sin\phi_1$ "--replace with " $\sin\phi_1^{\frac{1}{2}}$ "

Page 65 Reference 2: Replace "to be published" with "Monograph #33, London (1969)"

Page 69 Reference 84 should read: "D. P. Dunne and J. S. Bowles, Acta Met. 17, 201 (1969)"
 Add Reference 84-a: J. S. Bowles and D. P. Dunne, ibid. 17, 677 (1969)

Page 74 Last line: 10.66° and 10.71° should not be included in parentheses.

Page 75 Line 3 should read: "... (after 60) "
 Line 13: Delete "PARAMARTENSOTE"--replace with "PARAMARTENSITE"

Page 76 Line 7: Delete "of"--replace with "for"

Page 77 Line 8: Delete "in 2-b"--replace with "at right"

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INTRODUCTION

That phase transformations are of increasing theoretical and technological importance to a large number of scientists and engineers of various persuasions is at least partly evidenced by the number of meetings and conferences devoted to this topic within the past eight months alone: (1) an "International Conference on the Metal to Nonmetal (Mott) Transition" in March 1968, in San Francisco; (2) the "International Symposium on the Mechanisms of Phase Transformations in Crystalline Solids," Manchester (England), in July; (3) the Solid State Studies in Ceramics Gordon Research Conference on "Phase Transformations" in Meriden (New Hampshire) in August and now; (4) this ASM Seminar on "Phase Transformations"; (5) the Physical Metallurgy Gordon Research Conference on interface motion at Crystal Inn (Washington) in July should properly be included here since a substantial fraction of the talks and discussions were on phase transformations. Although it would appear that the subject of phase transformations in solids is interdisciplinary to a degree exhibited by few other phenomena, miserable dictu, (1) was almost exclusively by and for physicists, (2), (4), and (5) were heavily dominated by metallurgists, and those at (3) who were not ceramists or crystallographers could be counted on one hand. The interested reader will (nevertheless) find this volume and the published proceedings of the other conferences*^(1,2) an excellent, timely source of comprehensive and

*Although the proceedings of Gordon Conferences are of course not published nor referenced as such, almost all of the material discussed has or will appear in print.

critical reviews, information on current theoretical and experimental activity and emphasis, and possibly suggestions of significant areas of future exploration.

Many of the papers at these conferences dealt with displacive first order martensitic transformations or with transitions which exhibit some of the features characterizing such transformations. These transitions fall into II-A in Table 1 which is here reproduced from the chapter on "Phase Transformations in the Solid State" in "Perspective in Materials Research."⁽³⁾ Although I would rephrase some of the material in II-A-2, and will do so below, this scheme--which is almost ten years old and arbitrary as any classification must be--is satisfactory for our purposes and includes almost all of the topics treated in this seminar with the possible exception of explicit reference to spinodal decomposition.

Part of the interest in martensitic transformations is due to the fact that they are frequently accompanied by an important change in some significant property such as the transformation on cooling to a ferromagnetic martensite of high hardness in iron base alloys; from paraelectric to ferroelectric in the titanates and related compounds; from semiconductor to metallic conductor in some oxides; to an ordered, antiferroelectric, or ferroelastic product in some intermetallic compounds. The transformation which occurs just above the superconducting temperature in V_3Si and perhaps other alloys may be of this type also.

In keeping with what is probably the main purposes of a seminar such as this, viz. to be tutorial and heuristic, a model will be evolved from an analysis of a particular transformation and the physical basis developed of the Wechsler-Lieberman-Read phenomenological theory which successfully

relates all of the salient crystallographic features in several very different systems exhibiting a remarkably wide range of kinetic and physical behavior. The emphasis will be on the essence of the theory rather than the details in accordance with my conviction as well as the spirit of the late Tom Read, as pointed out so fittingly in Morris Cohen's sensitive tribute. It will then be demonstrated how examination of a transformation with the generalized and often only qualitative arguments based on this descriptive theory can provide insight into the nature of the transition and an assessment of probabilities that certain mechanisms were or were not operative, particularly when the presence (or absence) of some critical property is taken into account. The importance of "shuffles" in some transformations as well as some thoughts on the dilatation parameter will be discussed and the direction of future research indicated.

THE DEVELOPMENT OF THE CRYSTALLOGRAPHIC THEORY OF MARTENSITIC TRANSFORMATIONS

Historical Perspective

The phenomenological theory of the crystal geometry of displacive transformations was developed simultaneously just fifteen years ago by Monroe Wechsler, Tom Read, and myself in the United States, and John Bowles and Jock Mackenzie in Australia . . . further support for Victor Hugo's assertion that "Nothing in this world is so powerful as an idea whose time has come." The stage had been set. Bain had suggested (1924)⁽⁴⁾ that the b.c.c. structure of iron can be produced from the f.c.c. by a contraction of about 17 pct in the direction of one of the austenite cube axes and an expansion of about 12 pct

in the plane perpendicular thereto; Kurdhumow and Sachs (1930)⁽⁵⁾, Nishiyama (1934)⁽⁶⁾, and Greninger and Troiano (1941, 1949)^(7,8) had proposed various shearing processes to account for different orientation relationships in several steels; the latter (even) suggested a two-shear mechanism--homogeneous shear on the "irrational" habit plane to produce the surface upheavals and a second "invisible" shear on $(112)_\alpha$ $[\bar{1}\bar{1}\bar{1}]_\alpha$, plus some minor adjustments. Cohen wrote in 1948⁽⁹⁾ ". . . the Greninger-Troiano mechanism is the only one proposed to date that attempts to account for the 'irrational' habit plane as well as the observed structure and lattice relationships."

It was also in 1948 that Jaswon and Wheeler⁽¹⁰⁾ introduced the application of matrix algebra to the analysis of the austenite-martensite transformation. Bowles in 1951⁽¹¹⁾ concluded that the surface relief effects he observed, similar to those in Fig. 1, must have been produced by a plane of zero average macroscopic distortion and Machlin and Cohen, in the same year,⁽¹²⁾ deduced from a scratch measurement determination of the transformation distortion matrix that the (259) habit plane in steels is undistorted and unrotated. Both of these works included an analysis based on Bowles' double strain (two shear) proposal.⁽¹¹⁾ Although all of the important crystallographic features of the transformation had been observed (or at least deduced), none of the attempts mentioned was successful in accounting for all of them in a self-consistent general manner; i.e., if the crystal structure change was correctly described, the habit plane and/or orientation relationship usually was not. Important contributions were also made by other workers but will not be discussed further here; the work prior to 1953 has been critically summarized by Cohen⁽⁹⁾ and Bowles and Barrett.⁽¹³⁾

Figure 1 illustrates the most important crystallographic or geometric features of a martensitic transformation:

(1) a shape deformation which results in upheavals on a polished reference surface of the parent indicating that, from a macroscopic point of view, the transformation consists of shear on an undistorted plane--the habit plane--and a possible volume change perpendicular thereto.

(2) the habit plane separating the parent and product, which is generally irrational; the set of direction cosines of its normal is characteristic of the material.

(3) a rather precise orientation relationship between principal directions and planes in the two phases on either side of the interface as revealed by x-ray analysis.

(4) evidence of a fine inhomogeneous structure (here found to be twins by x-rays and metallographic analysis) in the product phase (usually).

No attempt will be made here to review again how the terms "martensite" and "martensitic" for the product phase and transformation process respectively were generalized to so many systems (even when the product in no way resembles the hard ferromagnetic steel constituent) if they can be characterized by these geometric features (and perhaps others implied by them) since this has been done.⁽¹⁴⁻¹⁷⁾ Nor will the many elements, alloys, and other systems exhibiting this type of transition be listed since this has also been done, at least for metallic systems.^(2,18-21)

The Transformation in Near Equiatomic AuCd

Although the W-L-R theory was first presented and published⁽²²⁾ as applied to the austenite-martensite transformation in Fe-Ni-C alloys because of the widespread metallurgical interest in steels, it was actually developed to describe

the easily observed single interface transformation in an alloy of AuCd.⁽²³⁾ Tom Read had begun work on this system soon after returning to Columbia University, his alma mater, as Associate Professor of Metallurgy in 1948. Ölander,⁽²⁴⁾ in the early 30's, and Benedicks,⁽²⁵⁾ in the early 40's, had pointed out the remarkable "rubber-like" or 'ferroelastic' behavior of the product phase resulting from a first order martensitic transformation of the ordered CsCl phase of AuCd; Read and a research associate, Roger Chang, published a series of papers⁽²⁶⁻²⁸⁾ in the early 50's on this unusual phenomenon, the transformation, crystal structure, etc. Not only has this alloy furnished the prototype of an almost ideal martensitic transformation for the development of the crystal geometric theory as well as examples of very dramatic alterations in the transformation behavior with thermal history,⁽²⁹⁻³³⁾ but apparently an order of magnitude larger number of vacancies can be quenched-in from near the melting point than for pure metals^(34,35) and, further, the pioneering work on simultaneous radioactive self diffusion of both species in the same specimen was done on this alloy.⁽³⁶⁾

Figure 2B shows one reason that the transformations occurring in the rather narrow CsCl β phase field are so attractive for experimental work: the transitions take place in the easily accessible temperature range between room temperature and 100°C, and they are readily followed since the parent and product phases differ in electrical resistivity by ~20 pct. Alloys having compositions near 47.5 atomic pct Cd transform to the β' twinned orthorhombic phase at approximately 60° on cooling while alloys having near equiatomic compositions transform at 30°C to a β'' phase which also has a lower symmetry than the parent structure. Chang and Read⁽²⁶⁾ first reported that the

transformations go to completion and exhibit relatively narrow temperature hysteresis widths of $\sim 15^{\circ}\text{C}$. The transition region of a few degrees between the beginning and end of the β to β' transformation on cooling in the 47.5 atomic pct Cd alloy indicates that this reversible transformation occurs only with continuous temperature change; the behavior appears to be independent of the rate of varying the temperature in specimens of this composition.

This alloy is particularly well suited for the critical experiment to test the hypothesis that the interface habit plane is one of zero average distortion and the transformation an invariant plane strain (see below) since it can be transformed on cooling by the movement of a single interface which is clearly visible because of the dihedral angle between the single crystal parent and the twinned product phases, as shown in Fig. 3. A specimen 3mm diameter and 5-7 cm long was grown by a modified Bridgemen technique, polished on two surfaces in the high temperature parent single crystal region, and allowed to cool and partially transform by a single interface, as shown. It was then rather easy to determine all of the crystallographic features experimentally. The power to the heater could be adjusted so that the interface was fixed at some convenient position (since the transformation is not isothermal). The low temperature β' phase (to the right of interface in Fig. 3) possesses an orthorhombic unit cell but consists of stacks of fine twins with $(111)_{\beta'}$ twin planes as revealed by a stereographic analysis of the markings on two surfaces. By x-ray analysis, Chang⁽²⁷⁾ had determined the low temperature phase to consist of twin-related orthorhombic domains and reported the same twin plane. This observation demonstrates that the transformation results in an inhomogeneous product phase.

It was observed that the parent and product regions seemed to fit perfectly at the interface. High magnification photographs and interference fringe patterns of the region of the interface in Fig. 3 revealed that if there is any distortion, it is confined to a region within 10^{-2} mm at the interface. This interference study was made with a partially silvered optical flat and monochromatic light from a sodium arc which formed fringe systems and was an early example of an experimental technique which has become invaluable in examining the nature of the interface and the macroscopic distortion, as will be seen in the following article. Thus it was concluded that the interface plane is undistorted and unrotated when averaged over the twin-related low temperature domains. These two important observations, viz. that the product phase is inhomogeneous and that the interface plane is invariant, i.e. the transformation distortion is an invariant plane strain, are intimately related and form the basis of the W-L-R theory.

All of the crystallographic features of the transformation could thus be measured without difficulty. Heater and specimen were placed in a large double circle optical goniometer (which could be read to one minute of arc) and by the application of simple vector analysis to the normals to the two parent and product surfaces and subsequent Laue x-ray orientation, determination of the elements of the macroscopic shape distortion on the habit plane were obtained. The system of heater and crystal with its fixed interface was then positioned on a metallograph and the orientation of the interface plane determined relative to the parent cubic axis system. It was found to be irrational, as were the orientation relationships between principal directions and planes in the two phases as determined by putting the 'heater+specimen' in an x-ray

goniometer and taking Laue photographs of the two phases, translating the system between exposures and/or slightly altering the heater current and moving the interface a small distance so that the same region was observed in both phases. The fundamental irrational nature of the crystallographic features of the transformation was thus emphasized and their direction cosines relative to the cubic axis reported in contrast to most of the work before that time on martensitic transformations which had been reported in terms of the nearest rational planes or directions to those actually observed. The single interface transformation in AuCd exhibits all of the crystallographic features of the iron base alloys, but being free of shear and volume restraint to be expected when the martensite plate is imbedded in the austenite matrix, as in Fig. 1, is thus a much more attractive system to study and on which to develop and test the theory.

The Model of the Transformation and the Physics of the Theory

From a macroscopic point of view, the transformation distortion is an invariant plane strain. An invariant plane strain is just what the name implies, a strain or distortion which leaves at least one plane invariant. The simplest examples are shown in Fig. 4: simple shear where the plane on which shear takes place is not altered during the process, and simple extension or contraction, where the plane perpendicular to the direction of extension (or contraction, is unchanged. Clearly, the most general invariant plane strain is a combination of these two, as shown. As has been proven and discussed,^(22,23) the necessary and sufficient conditions that a plane be undistorted during a transformation is that one of the principal distortions be unity and the other two be respectively, greater and less than unity. This can be seen from an examination of Fig. 5. In a, even

if there is no distortion perpendicular to the plane of the figure, there are no planes containing vectors which are not altered in length, while in b, provided there is zero distortion perpendicular to the paper, there are two planes, which although rotated, contain vectors which are not changed in length during the transformation.

Now, from the x-ray analysis and lattice parameters of Chang⁽²⁸⁾ mentioned earlier, a reasonable lattice correspondence between cubic and orthohombic unit cells and a Bain distortion, which, apart from possible small shuffles, transforms the parent into the product within any small region with the smallest (and hence energetically the most favorable) distortions is established, as in Fig. 6-a. For the AuCd transformation, these Bain distortions are found to be

$$\eta_1 = \frac{b}{\sqrt{2}a_o} = \frac{4.7549\text{\AA}}{\sqrt{2} \times 3.3232\text{\AA}} = 1.0138$$

$$\eta_2 = \frac{c}{\sqrt{2}a_o} = \frac{4.8644\text{\AA}}{\sqrt{2} \times 3.3232\text{\AA}} = 1.0350$$

$$\eta_3 = \frac{a}{a_o} = \frac{3.1810\text{\AA}}{3.3232\text{\AA}} = 0.9491$$

From x-ray determination of the orientation relationships of the phases on either side of the interface and the lattice parameters, the transformation from the microscopic point of view in any small region is similar to the two dimensional analogue in Fig. 7.

The Bain distortion cannot in itself result in the observed undistorted habit plane since its components do not satisfy the theorem mentioned. Yet the measurable (as described above or from the bending of scratches on a polished surface) macroscopic shape deformation cannot produce the product lattice from the parent, as was pointed out for iron base alloys in 1949 by Greninger and Toriano⁽⁸⁾ who concluded that there must be an additional fine scale heterogeneous deformation which does not contribute further to the shape deformation. Furthermore, neither one of these could account for the orientation relationships between planes and directions on either side of the habit plane nor the orientation of the habit plane normal. This unsatisfactory state of affairs persisted in spite of a substantial amount of work (and publications) until 1953 when Read, Wechsler, and I published⁽²²⁾ our formulation of the theory which successfully relates and accounts for all of the crystallographic features. This was followed within a few months by Bowles and Mackenzie's⁽³⁷⁾ almost identical (but mathematically somewhat different) treatment--whereas the W-L-R method of analysis has no adjustable parameters, the B-M formulation does in the form of a uniform dilatation in the interface, which will be discussed below.

The essence of the theory can be described in a straightforward manner, although the mathematical representation of the operations involved (by matrices or manipulations on a stereographic net) may appear complicated to someone not working directly in the field. It is simply that if the macroscopic shape deformation is to be an invariant plane strain in accord with experiment, it must include not only the Bain distortion to describe the per se change in crystal structure but another strain or distortion which can adjust shape

without changing the crystal structure further. An example of such a lattice invariant shear is slip, as shown in the Fig. 8. Note that the shape is altered but not the lattice structure by slip. Another is simple twinning, which produces a mirror image of a structure while changing the shape. Either of these or a combination of both may effect the shape change without changing the lattice, as shown in Fig. 8.

Let us develop the model and theory with the lattice invariant shear twinning in the product, as shown in Fig. 3 for AuCd. Figure 6^A again shows the CsCl parent with a face centered tetragonal cell (still 'austenite' before transformation) indicated within it. The orthorhombic 'martensite' after transformation is shown next ~~to it~~^{6-b} and in Fig. 9-a. In some other region, the situation illustrated in Fig. 9-b could take place where the transformation is to a product cell oriented perpendicular to the first. Because of the cubic symmetry of the parent austenite, these two situations are completely equivalent; in principle the unique contraction axis to the martensite cell is equally probable along any of the three cubic directions and since b and c can be interchanged, there are six a priori equally probable Bain distortions.

Note that in Fig. 6 and 9-a all vectors in the ~~xy~~^{x-y} plane are increased in length due to the Bain distortion and vectors perpendicular to this plane are decreased while in 9-b, an adjacent region of the crystal, all vectors in the plane are lengthened and vectors perpendicular to this plane are shortened. That is, almost all vectors* are affected oppositely in the two regions. Thus,

*There is a locus of vectors (a cone with the cone axis the contraction axis) which are not changed in length at all which is actually made great use of in the mathematical analysis and graphical formulation of the theory, as will be seen, but the main points can be made without pursuing this further here.

if it were possible for the transformation to occur to alternating regions of volume fraction x of the product as in 9-a and $(1-x)$ of 9-b, then, for some value of x , the vectors in some plane(s) of the parent may, on the average, be unchanged in length by the transformation, i.e., their length changes will 'cancel out' over many alternating regions thus producing an invariant habit plane and minimizing the strain energy associated with fitting the two structures at the interface during the transformation, as shown in the Appendix. However, as thus far described, these product regions do not fit or match along their interface.

These two product cells are related by reflection in the mirror plane shown shaded in figures 9-a and 9-b; this may be more clearly seen by looking at the (exaggerated) two dimensional analogue sketched in Fig. 10. Here the square parent lattice in two different regions transforms to the two completely equivalent rectangles ABCD and A'B'C'D'. However, if these two rectangles are rotated toward each other so that C and C' coincide, then the two structures are twin related; the twin plane in the product (martensite) rectangular lattice comes from the mirror plane in the parent square lattice. Now there is no misfit along the twin boundary. It is, of course, not implied that a physical body rotation actually occurs, but that the transformation takes place in such a way that two adjacent regions are twin related.

This, then, is the assumption of what happens in our real three dimensional crystal, and becomes the essential postulate of the theory as a paraphrase of the statement above: In order to minimize the distortional energy associated with the interface, transformation takes place to alternate regions of volume fraction x of one orientation of the product and $(1-x)$ of its twin as in 9-b so that for some values of x , vectors or lines in some plane(s) in the original austenite are on the average unchanged in length by the transformation since their length

if it were possible for the transformation to occur to alternating regions of volume fraction x of the product as in 9-a and $(1-x)$ of 9-b, then, for some value of x , the vectors in some plane(s) of the parent may, on the average, be unchanged in length by the transformation, i.e., their length changes will 'cancel out' over many alternating regions thus producing an invariant habit plane and minimizing the interfacial strain energy associated with the transformation, as shown in the Appendix. However, as thus far described, these product regions would not fit together.

These two product cells are related by reflection in the mirror plane shown dotted in the figure; this may be more clearly seen by looking at the two dimensional analogue in sketched Fig. 10. Here the square parent lattice in two different regions transforms to the two completely equivalent rectangles ABCE and A'B'C'D'. However, if these two rectangles are rotated toward each other through the small angle ϕ so that C and C' coincide, then the two rectangular structures are twin related; the twin plane in the product (martensite) rectangular lattice comes from the mirror plane in the parent square lattice. Now there is no misfit along the twin boundary. It is, of course, not implied that a physical body rotation actually occurs, but that the transformation takes place in such a way that two adjacent regions are twin related.

This, then, is the assumption of what happens in our real three dimensional crystal, and becomes the essential postulate of the theory as a paraphrase of the statement above: In order to minimize the strain energy at the interface, transformation takes place to alternate regions of volume fraction x of one orientation of the product and $(1-x)$ of its twin as in 9-b so that for some values of x , vectors or lines in some plane(s) in the original austenite are on the average unchanged in length by the transformation since their length

changes will 'cancel out' over many alternating twin regions, as shown in Fig. 11. The orthorhombic martensite cells are shown in Fig. 12 rotated and twin related across a $(111)_\beta$ plane, which comes from a $(110)_\beta$ mirror plane (Figs. 6,12). The rotation required to insure that this undistorted plane is also unrotated (and hence an invariant plane, as observed) produces the irrational orientation relationships between principal planes and directions in the parent and product.

Again it must be emphasized that this is a phenomenological theory relating initial and final positions of lattice points and planes in the two structures and the salient crystallographic features; no physical significance is ascribed to mathematical sequential operations such as Bain distortion, twinning, and rotations. The problem can now be set up and solved according to the talents and taste of the investigator since it can be couched as a type of eigenvalue problem (and programmed for a computer) or solved graphically on a stereographic net. Since the interface plane is one of zero average distortion (and hence an invariant plane in accordance with experiment), there is no reason to expect it to be a rational plane in either phase, such as the planes bounding the sides of the unit cells or the mirror or twin planes mentioned earlier; indeed it is observed to be irrational in all cases and best denoted by the set of direction cosines of the normal to the plane.

At the time that this theory was proposed, unequivocal experimental evidence for the existence of martensite twins in steels did not exist. It was gratifying indeed that the electron microscope (Fig. 13) revealed them several years later--and precisely the type predicted. However, in that first paper,⁽²²⁾ it was shown how the theory could be formulated in a completely equivalent way with

the lattice invariant shear as slip rather than twinning (and hence even a combination of the two) since these two strains can effect the necessary shape adjustment to permit a plane of zero distribution or invariant plane strain to exist as shown in Fig. 8 and for martensite plates in retained austenite, in Fig. 14. In the slip case, the angle of shear α corresponds to x , the fraction of twinning, and depends, as x does, on the lattice parameters of the particular alloy and the plane and direction of the lattice invariant shear.

Methods of Calculation

All of the crystallographic features can be calculated from a knowledge of the lattice parameters of the two phases and a specification of the inhomogeneous shear (lattice invariant shear) alone. Although a detailed mathematical analysis would be inappropriate here, a brief introduction to the matrix algebra formulation and the graphical method will be presented for completeness to indicate how the operations are carried out to solve real problems and obtain numerical answers; the interested reader can then dig out the details in the literature. The graphical method will be treated here somewhat more thoroughly since it brings out with particular clarity the physical significance of the operations inherent in the theory and will be most useful in later sections.

The Matrix Algebra Formulation

The pure distortion associated with alternate regions in Figs. 9a and 9b can be represented in the $(\vec{i}', \vec{j}', \vec{k}')$ and $(\vec{k}'', \vec{j}'', \vec{i}'')$ axes systems respectively by the matrices

$$(1a) \quad \tilde{T}_1' = \begin{pmatrix} \eta_1 & 0 & 0 \\ 0 & \eta_2 & 0 \\ 0 & 0 & \eta_3 \end{pmatrix} \quad \text{and} \quad \tilde{T}_1'' = \begin{pmatrix} \eta_1 & 0 & 0 \\ 0 & \eta_3 & 0 \\ 0 & 0 & \eta_2 \end{pmatrix}$$

where the η 's are the Bain distortions defined above. These two matrices can then be expressed in the parent cubic ($\vec{i} \vec{j} \vec{k}$) axis system by the standard similarity transformation procedure which involves rotation matrices of 45 deg about the $\vec{k}$ and $\vec{j}$ axes respectively; the matrices for the cubic to orthorhombic transformation in AuCd become

$$(1b) \quad \tilde{T}_1 = \begin{pmatrix} \frac{\eta_1 + \eta_2}{2} & \frac{\eta_2 - \eta_1}{2} & 0 \\ \frac{\eta_2 - \eta_1}{2} & \frac{\eta_1 + \eta_2}{2} & 0 \\ 0 & 0 & \eta_3 \end{pmatrix} = \begin{pmatrix} 1.024 & 0.01063 & 0 \\ 0.01063 & 1.024 & 0 \\ 0 & 0 & 0.9491 \end{pmatrix}$$

$$(1c) \quad \text{and } \tilde{T}_2 = \begin{pmatrix} \frac{\eta_1 + \eta_2}{2} & 0 & \frac{\eta_2 - \eta_1}{2} \\ 0 & \eta_3 & 0 \\ \frac{\eta_2 - \eta_1}{2} & 0 & \frac{\eta_1 + \eta_2}{2} \end{pmatrix} = \begin{pmatrix} 1.024 & 0 & 0.01063 \\ 0 & 0.9491 & 0 \\ 0.01063 & 0 & 1.024 \end{pmatrix}.$$

However, since these two regions must be related as twins and not just by a mirror plane, and since their orientation relative to the cubic axis system (as given by the x-ray determined orientation relationships discussed above) is not simple parallelism, the distortions to which the two regions are subjected must be impure, i.e., they contain rotations. Therefore, $\tilde{M}_1$ and $\tilde{M}_2$, the matrices which describe what happens to vectors in the two regions as a result of transformations, can be written

$$(2) \quad \tilde{M}_1 = \phi_1 T_1 \text{ and } \tilde{M}_2 = \phi_2 T_2$$

where ϕ_1 and ϕ_2 describe the rotations of the principal axes of the pure distortions in regions 1 and 2 relative to an axis system fixed in the untransformed cubic.

In Fig. 110, it was shown how a vector in the interface is on the average undistorted by the transformation. Figure 15 shows the effect of the transformation on an arbitrary vector not in the habit plane. A scratch $\vec{r} = \overrightarrow{OV}$ that was originally a straight line in the cubic phase becomes the broken line $\overrightarrow{OA'B'C'}$. . . $\overrightarrow{U'V'}$. However, since the distortion averaged over the twin regions is to be considered, it is sufficient to treat the vector sum $\overrightarrow{OV} = \vec{r}' = \overrightarrow{OA'} + \overrightarrow{A'B'} + \overrightarrow{B'C'} + \dots + \overrightarrow{U'V'}$ as describing the transformed position of the vector $\vec{r}$. Thus,

$$(3) \quad \vec{r}' = (1-x)\tilde{M}_1\vec{r} + x\tilde{M}_2\vec{r} = [(1-x)\tilde{M}_1 + x\tilde{M}_2]\vec{r},$$

or

$$(3') \quad \vec{r}' = \tilde{E} \vec{r},$$

where

$$(4) \quad \tilde{E} = (1-x)\tilde{M}_1 + x\tilde{M}_2.$$

The crux of the matrix algebra method is that for vectors in the invariant habit plane

$$(5) \quad \tilde{E} \vec{r} = \vec{r}$$

i.e., the vectors remain unchanged. $\tilde{E}$ is called the "total distortion matrix." Equation (3) states that if $\vec{r}$ is a vector in the cubic phase, then as a result of the transformation $\vec{r}$ goes to $\vec{r}' = \tilde{E} \vec{r}$ where $\vec{r}$ and $\vec{r}'$ are expressed with respect to the cube edge directions in the as yet untransformed cubic phase. From Eq. (3),

$$(6) \quad \tilde{E} = (1-x)\tilde{\phi}_1\tilde{T}_1 + x\tilde{\phi}_2\tilde{T}_2$$

$\tilde{\phi}_1$ and $\tilde{\phi}_2$ cannot be determined from the development thus far, but the relative rotation $\tilde{\phi}$ can be obtained. This is done by imposing the condition that vectors $\tilde{OR}'$ and $\tilde{OS}'$ in Fig. 9 must coincide with $\tilde{OR}''$ and $\tilde{OS}''$, respectively, after transformation to insure the coherent twins shown in Fig. 12. This

means that the relative rotation must bring the plane $R'' OS''$ into coincidence with $R' OS'$. Both of these planes were the $(011)_{\beta_1}$ before transformation. The normals to these planes are easily determined from the vector product of two vectors in each plane (such as $\underline{OR'}$ and $\underline{OS'}$). The axis of rotation is obtained from the vector product of the two plane normals and the magnitude of the rotation from their scalar product. In this way, the rotation matrix $\underline{\phi}$ is calculated* to be:

$$(7) \quad \underline{\phi} = \begin{pmatrix} 0.9999 & -0.01034 & 0.009585 \\ 0.009585 & 0.9970 & 0.07618 \\ -0.01034 & -0.07608 & 0.9970 \end{pmatrix}$$

since $\underline{\phi}$ is the relative rotation between $\underline{\phi}_1$ and $\underline{\phi}_2$, and thus (6) may be written as

$$(8) \quad \underline{E} = \underline{\phi}_1 [(1-x)\underline{T}_1 + x\underline{\phi}\underline{T}_2].$$

Then $\underline{E}$ may be written as

$$(9) \quad \underline{E} = \underline{\phi}_1 \underline{F}(x)$$

where

$$(10) \quad \underline{F}(x) = (1-x)\underline{T}_1 + x\underline{\phi}\underline{T}_2$$

*The so called nonian form of $\underline{\phi}$ written here was calculated using Euler's theorem. (23)

The substitution of (1b), (1c), and (7) in (10) gives

$$(11) \quad \tilde{F} = \begin{pmatrix} 1.024 & 0.01063 - 0.02045x & 0.02045x \\ 0.01063 & 1.024 - 0.07814x & 0.07817x \\ 0 & -0.07221x & 0.9491 + 0.07221x \end{pmatrix}$$

Thus, we see that the total distortion matrix $\tilde{E}$ is a function of the relative twin fraction x , or the equivalent amount of the shear α , -- the thus far unknown rotation ϕ_1 is calculated at the end to insure that the habit plane is unrotated as well as undistorted, i.e., is invariant. Hence the determination of the invariant plane reduces to an eigenvalue problem; for vectors in the habit plane

$$(12) \quad \tilde{E}\vec{r} = \phi_1 \tilde{F}(x)\vec{r} = \vec{r}$$

with solutions (if they exist) only for certain values of x .

The problems are soluable by rather standard matrix methods which are explained in detail in the original papers^(22,23) and will not be given here. The relative amount of twins, the interface plane normal direction cosines, the magnitude and direction of the macroscopic shear of the invariant plane strain (shape deformation) shear, and the orientation relationships are all calculated with no adjustable parameters; the interested reader can pursue the details at his leisure.

The Graphical Method

Although graphical manipulations carried out on a stereographic projection cannot of course be as precise as the matrix algebra treatment delineated above (particularly when programmed for a computer), they do permit the physical significance of the operations and the relationships among the various crystallographic features to be visualized immediately. The method has been successfully applied by several workers to a wide variety of systems since we developed it within a year of announcing the matrix formulation. Tom Read reported it at the I.U. Cr. "Symposium on Martensite" in Paris in 1954⁽³⁸⁾ and I discussed it at the Inst. of Metals Symposium on "The Mechanism of Phase Transformations in Metals" in London in November 1955.⁽³⁹⁾ It was developed further in several papers;⁽⁴⁰⁻⁴²⁾ the presentation here follows the more elegant and shorter version developed in connection with solving the inverse problem of determining directly from observations of the crystallographic features the inhomogeneous deformation part of the transformation,⁽⁴¹⁾ which at the time had not been observed in steels, for example.

The operations of distortion, rotation, shear, etc. can be represented by matrices or by equivalent graphical operations and constructions on a stereographic net. As has previously been emphasized,^(22,23,40-42) the order of operations in 'decomposing' the total transformation distortion matrix is arbitrary. Thus, slip and/or twinning can be postulated (mathematically) to take place in the product phase after the Bain distortion or on the corresponding system in the parent preceding the Bain distortion. The latter is expressed as $\tilde{E} = \tilde{\Phi} \tilde{B} G(\alpha)$ where $\tilde{G}$ is the lattice invariant shear of amount α (equivalent to twinning of amount x), $\tilde{B}$ is the Bain distortion, and $\tilde{\Phi}$

again is the rotation required to make the habit plane unrotated as well as undistorted. Written in this order, the analysis is more tractable and convenient since the parent phase almost always has a higher symmetry than the product, and it is easier to express the shear (either as a matrix or as an operation on a stereographic net) in, for example, the cubic axis system than the tetragonal or orthorhombic; the solution is independent of the order and no physical significance is attached to it.

In order to facilitate understanding of the graphical method, it will be described as applied to a particular case: the cubic to tetragonal transformation in iron-base alloys. The loci of all vectors unchanged in length by the inhomogeneous deformation (slip and/or twinning) are two planes as shown in Fig. 16. K_1 is the shear plane and K_2 is a plane which makes an angle of $90^\circ \pm \alpha$ with the shear plane where α is the net angle of shear. The positions of the K_2 plane before and after shear (K_2') are shown in Fig. 16. The K_1 and K_2 planes divide all space into regions where the vectors are either increased or decreased in length by the shear. To illustrate the method, slip on the $(011)_A$ plane in the $[01\bar{1}]_A$ direction (equivalent to $(\bar{1}21)_M$ $[11\bar{1}]_M$ twinning as seen in Fig. 13) has been chosen and the positions of K_1 , K_2 , and K_2' are shown on the stereographic projection in Fig. 17 for an arbitrary amount of shear. As in Fig. 16, the dotted region contains all vectors which are increased in length due to the lattice invariant shear.

Figure 18 shows the Bain distortion which accounts for the per se change crystal structure from f.c.c. austenite to b.c.t. martensite within a small region. Note that this involves a contraction in the y direction and a uniform expansion in all directions in the plane perpendicular to this direction. This distortion is completely specified by two parameters:

$$\eta_1 = \frac{\sqrt{2a}}{a_0} \quad \text{and} \quad \eta_2 = \frac{c}{a_0}$$

where a_0 is the lattice parameter of the parent phase and a and c are the lattice parameters of the product phase. The Bain distortion can equally well be described by another set of parameters: the volume ratio of the two phases,

$$V = \frac{2a^2c}{a_0^3} \quad \text{and} \quad \frac{c}{a}$$

The locus of all vectors which are not changed in magnitude by the Bain distortion is a pair of right circular cones*--one for the vectors before transformation and one for these same vectors after transformation. The expressions for the semi-vertex angles of these two cones are obtained[†] by simple vector algebra or geometry and are here written in terms of the η_i values (although they could be written equally well in terms of V and c/a).

$$\tan \phi_i = \left(\frac{1-\eta_2^2}{\eta_1^2-1} \right)^{1/2} \quad \text{and} \quad \tan \phi_f = \frac{\eta_1}{\eta_2} \left(\frac{1-\eta_2^2}{\eta_1^2-1} \right)^{1/2}$$

These semi-vertex angles are shown in cross-section in Fig. 19. Here the data of Greninger and Troiano⁽⁸⁾ will be used:

*Elliptical cones for the cubic to orthorhombic transformation. (39, 40)

[†]See Appendix.

$$\underline{a}_0 = 3.592\text{\AA}$$

$$\underline{a} = 2.845\text{\AA}$$

$$c = 2.973\text{\AA}$$

For this case $\eta_1 = 1.1201$, $\eta_2 = 0.8277$, and the semi-vertex angles ϕ_1 and ϕ_f are respectively 48.0° and 56.4° . The Bain cones B_1 and B_f are shown in Fig. 20-- all vectors within B_1 are decreased in length owing to the Bain distortion-- the hatched regions in Figs. 19 and 20 contain all vectors decreased in length, while all vectors outside this cone are increased in length due to it.

The two undistorted planes K_1 and K_2' must intersect the cone B_1 for a solution to exist at all,* and whether this is true depends critically on the ratio of the lattice parameters of the two phases and on the slip system considered. The intersections of these planes with the cone B_1 determine four vectors which are not distorted by the Bain distortion nor by the shear, and are thus not distorted by the total transformation. Thus in Fig. 21 the unit vectors $\vec{a}$ and $\vec{b}$ on the net become $\vec{A}$ and $\vec{B}$ due to slip on the $(011)_A$ plane and (subsequently) $\vec{A}'$ and $\vec{B}'$ owing to the Bain distortion. Similarly $\vec{C}$ and $\vec{D}$ on K_2' must have come from $\vec{c}$ and $\vec{d}$ on K_2 during the shear distortion and become $\vec{C}'$ and $\vec{D}'$ owing to the bain distortion. $|\vec{a}| = |\vec{A}| = |\vec{A}'| = |\vec{b}| = |\vec{B}| = |\vec{B}'| = 1$. Taken in pairs, these four vectors $\vec{a}$, $\vec{b}$, $\vec{c}$, $\vec{d}$,

*If the problem were being studied in the reverse order, with shear following Bain distortion (see cubic to twinned orthorhombic transformation), ⁽⁴⁰⁾ K_1 and K_2 would have to intersect B_f for a solution to exist.

⁺The procedure for finding the motion of specific vectors due to shear is a straightforward one on the stereographic net, and is described in standard texts such as C. S. Barret and T. B. Massalski, Structure of Metals, 3rd edition (McGraw-Hill, 1966). See also Ref. 8, 41.

determine four possible planes in the parent phase which may be undistorted by the total transformation. The positions of $\vec{a}$ and $\vec{b}$ depend on the Bain distortion and on the slip plane being considered, while the positions of $\vec{c}$ and $\vec{d}$ will, in addition, depend on the amount of shear, α . For a plane determined by $\vec{a}$ and $\vec{d}$, for example, note that except for these vectors--which are unchanged in length both by shear and Bain distortion--all other vectors which lie on this plane in the dotted region between K_1 and K_2' planes are increased in length due to the shear but are sheared into the hatched region within the inner Bain cone where they are decreased in length by the Bain distortion; similarly the other remaining vectors in the plane determined by $\vec{a}$ and $\vec{b}$ are decreased in length due to slip and increased in length due to the Bain distortion. Thus all vectors on this plane are either unaltered in length by the total transformation distortion or changed oppositely by its components. The problem is to find the value(s) of the amount of shear α so that the changes of opposite sense exactly cancel for these vectors; the invariant habit plane(s) will then be determined.

Initially, some arbitrary third vector on the (possible) habit plane, such as the intersection of this plane and the $(010)_A$ plane, was examined as the shear angle α was varied in small increments and the value(s) of α leaving it unchanged in length obtained by trial or interpolation. The plane thus determined was then identified as an undistorted (habit) plane in accordance with the easily proven theorem⁽⁴⁰⁾ that "if three non-collinear vectors in a plane are unchanged in length by a transformation distortion, all vectors in that plane are undistorted, i.e., the plane is one of zero average distortion." A little thought led from this to the

statement:⁽⁴¹⁾ "If two (non-collinear) vectors in a plane are undistorted (unchanged in length) and the angle between them is unchanged, by a transformation, all vectors in that plane are undistorted (and all angles are unchanged) i.e., the plane is one of zero distortion." Since only angle measurements and rotations need now be made, this improved method avoids the considerable supplementary calculations and constructions inherent in the earlier versions which required the determination of length changes. Hence this method is much shorter and easier to use and will be presented here briefly.

Now the problem is to find that value of α for which the angle between $\vec{a}$ and $\vec{c}$ ($\angle \vec{a}, \vec{c}$) is equal to $\angle \vec{A}', \vec{C}'$ between the same two vectors after transformation. Then, in accordance with the theorem, the plane determined by $\vec{a}$ and $\vec{c}$ will be an undistorted plane in the original parent phase. Furthermore, the rotation necessary to make $\vec{A}'$ and $\vec{C}'$ coincide with $\vec{a}$ and $\vec{c}$ contributes to the final orientation relationship between the crystal axis systems in the parent and product phases. A second value of α will be found for which $\angle \vec{b}, \vec{c} = \angle \vec{B}', \vec{C}'$ and thus for which the plane determined by $\vec{b}$ and $\vec{c}$ is undistorted. There are only two values of α . One gives rise to planes $(\vec{a}, \vec{c})$ and $(\vec{b}, \vec{d})$ and the other to planes $(\vec{b}, \vec{c})$ and $(\vec{a}, \vec{d})$. The two values of shear in general give four distinct solutions. The degenerate case here, for which $(\vec{a}, \vec{c})$ and $(\vec{a}, \vec{d})$ are crystallographically equivalent to $(\vec{b}, \vec{d})$ and $(\vec{b}, \vec{c})$ respectively, simplifies the diagram considerably. The method is quite general; Christian,⁽⁴³⁾ for example, has discussed in detail how four solutions arise from the two values of shear, and the conditions under which they reduce to two, and in some cases even one.

Part of the method of calculation will be delineated here. The open circles on B_1 in Fig. 22 are the intersections in K_2' for several values of α and are labeled as points $\tilde{C}$. The corresponding points $\tilde{C}'$ on B_f lie along radii* through the points $\tilde{C}$. The corresponding points $\vec{c}$, solid circles, are obtained by reverse shear of the appropriate amount on the net. Thus the vectors $\vec{a}, \vec{b}, \vec{c}, \vec{d}$ go to $\tilde{A}, \tilde{B}, \tilde{C}, \tilde{D}$ by slip shear and to $\tilde{A}', \tilde{B}', \tilde{C}', \tilde{D}'$ by Bain distortion. The angles $\angle \vec{a}, \vec{c}$, $\angle \tilde{A}', \tilde{C}'$, $\angle \vec{b}, \vec{c}$ and $\angle \tilde{B}', \tilde{C}'$ are measured directly on the stereographic net for the various values of α and plotted against α on a graph. The symmetry of this illustrative problem makes it unnecessary to measure angles $\angle \vec{a}, \vec{d}$, $\angle \tilde{A}', \tilde{D}'$, $\angle \vec{b}, \vec{d}$ and $\angle \tilde{B}', \tilde{D}'$. The critical values α_1 and α_2 are read from the intersection of the curves of $\angle \vec{a}, \vec{c}$ and $\angle \tilde{A}', \tilde{C}'$, and $\angle \vec{b}, \vec{c}$, and $\angle \tilde{B}', \tilde{C}'$ respectively. It is now a simple matter to determine the interface planes in the parent phase. $\vec{c}, \tilde{C}, \tilde{C}'$ and $\vec{d}, \tilde{D}, \tilde{D}'$ corresponding to the two values of shear (as indicated by the subscripts) are shown in Fig. 23 along with $\vec{a}, \tilde{A}, \tilde{A}', \vec{b}, \tilde{B}$ and $\tilde{B}'$. The four undistorted planes determined by $(\vec{a}, \vec{c})$, $(\vec{b}, \vec{d})$, $(\vec{a}, \vec{d})$, and $(\vec{b}, \vec{c})$ are indicated by their normals--the subscripts on each $\vec{n}$ being arbitrary. Only the plane $\vec{n}_2(\vec{a}, \vec{c}_2)$ has been drawn.

The orientation relationships can also be found directly on the net, Fig. 23. $\tilde{A}'$ and $\tilde{C}'$ determine the position of the undistorted interface plane resulting from the transformation distortion as considered so far. However, the habit plane must not only be undistorted but unrotated as well. Hence the graphical

*There is a one-to-one correspondence between each point on B_1 and each point on B_f . In the orthorhombic case, (41) the points are not related along radii, but the relationship is still easily obtained.

treatment of the total transformation distortion must also include an operation to bring the habit plane as determined by A' and C' into coincidence with $\vec{n}$, i.e., an operation which makes A' lie on $\vec{a}$ and C' lie on $\vec{c}$. (Again it should be emphasized that no physical paths are implied by this sequence of mathematical steps--thus it is not implied that the atoms first slip, then move according to the Bain distortion, then rotate.. This treatment only considers the relationship between initial and final positions and proposes a convenient method of calculating these positions mathematically or graphically.) The axis and amount of rotation needed are determined by performing on the stereographic net the operations implicit in Euler's theorem. ⁽²³⁾ The 'orientation rotation' required to make A' and C' coincide with $\vec{a}$ and $\vec{c}$ also rotates all other vectors. In particular, the principal planes and directions--some of which have already been rotated by the Bain distortion--are rotated; the angular separation between them and the corresponding planes and directions in the original parent cubic lattice then constitute the orientation relationships.

The magnitude and direction of the macroscopic shape distortion can also be obtained graphically, but the operations will not be carried out here. Hence all of the crystallographic features, including the amount of shear α , can be determined by this method which brings out their irrational nature with particular clarity; the reader is referred to the original papers for the details. ⁽⁴⁰⁻⁴²⁾ It has been shown that the interface plane normal, obtained graphically ⁽⁴⁰⁾ using a 20 cm radius net, agrees within $1/2^\circ$ of arc with that calculated with the matrix algebra formulation of the theory, with similar results for the other geometric features. Since the experimental error is

generally somewhat larger than this possible discrepancy, even in the most favorable cases, the graphical formulation is more than adequate for calculating the crystallographic features and relationships of martensitic transformations for comparison with experiment. In the following sections, no particular mention will, in general, be made of the method of calculation, unless attention is to be drawn to it for some reason.

Comparison with Experiment

The comparison between the values of the crystallographic features calculated with the W-L-R theory and those observed or reported are shown in Table II for AuCd, InTl and an Fe base alloy; the habit plane comparison for the steel case is also shown on a standard stereographic triangle in Fig. 24. The InTl alloy was studied by Burkhart and Read⁽⁴⁴⁾ at the same time that the AuCd system was under investigation and was part of the general program on phase transformations under Tom's direction. In contrast to the earlier work of Bowles, Barrett, and Guttman⁽⁴⁵⁾ on this alloy, they used single crystals and were able to examine in detail a single interface transformation, as in the AuCd case. It will be seen that agreement between experimental and calculated results for these systems is rather good and gave us confidence that the basic ideas of the theory were valid and the approach reasonable.

That the theory works for InTl is perhaps not a proper test, since the transformation strains based on Guttman's⁽⁴⁶⁾ lattice parameters are extremely small. The AuCd and Fe alloys exemplify the extremes of morphology and something of the range of kinetic behavior exhibited by martensitic transformations. In an early review article, Kaufman and Cohen⁽⁴⁷⁾ compared these important differences in terms of the significance of nucleation in the iron base alloys

and growth of existing plates or domains in the systems like AuCd; Christian⁽¹⁷⁾ has also discussed these types. Figure 25 from the Kaufman-Cohen paper shows the comparison in the widths of the hysteresis loop for the two cases. The sizable discrepancies in the amount of under-cooling and super-heating required are directly associated with the magnitudes of the transformation strains involved as mentioned earlier: a contraction of 18-20% and a (perpendicular) expansion of ~ 12% in the cubic to tetragonal transformation in Fe alloys and a contraction of 5% and expansions of 3.5 and 1.3% in the cubic to orthogonal transformation in AuCd. The large shear and volume constraints and considerable strain energy involved in the former (compared with the latter) apparently inhibit the growth of plates and produce a nucleation controlled transformation to many small platelets which grow very little, while in the latter, the transformation goes to completion by the growth of only a few large domains of the product,^(23,26-28,47) or even, as we have seen, by the movement of a single interface. In the iron base alloys, the transformation may be very rapid (10^{-6} sec. for each event) while in the latter, minutes or hours may be required for transformation. This type of growth may only be slow on a macroscopic scale; it is possible that the interface moves through a small distance rapidly but then must stop to allow relaxation at the interface before it can move again.⁽²⁷⁾

The range of morphologies, rates, and behavior is so large and varied that kinetics, for example, is not a very fruitful criterion for martensitic transformations. Hence I feel that only the geometric and crystallographic features delineated above should be considered as distinguishing characteristics since the salient ones are exhibited by all martensitic transformations.

Further, the agreement between theory and experiment for iron base alloys exhibiting the (259) type habit warrants the conclusion that even in this transformation to a ferromagnetic product involving considerable shear and volume constraints, minimizing the strain energy at the interface must be the dominant factor since this is really the only energetic term considered in the simple phenomenological theories based on the invariant plane strain which accounts for all of the features in this type of transformation. Other systems will be discussed in the next section.

APPLICATION TO OTHER SYSTEMS AND CLASSIFICATION OF TRANSFORMATIONS

After the initial successes described above, the theory--either the W-L-R or the B-M formulation employing either the matrix algebra or graphical technique--was applied to many other iron base alloys and nonferrous systems; no attempt will be made here to reference all of these since they have been reviewed and summarized recently. (2,18) Wayman and his co-workers, in particular, have studied transformations in several iron base alloys; most of these have been reviewed. (2,16,17,18,48,49) In some cases, better fit with observations was obtained by including an isotropic dilatation in the interface rather than insisting that the habit plane be undistorted. This δ factor, which can be easily incorporated in both the W-L-R and B-M formulations, will be discussed below. Among the transformations analyzed by Bowles and Mackenzie, and others with varying degrees of success, are those occurring in Cu-Al, (50,51) Li, (52) and Ti and Ti alloys. (50,52) Recently DiDomenico and Wemple (53) successfully applied the W-L-R treatment to the paraelectric to ferroelectric transformation in semiconducting BaTiO_3 and KTN, to be discussed below.

There is general agreement that transformations discussed thus far are martensitic and the products martensite, although this was not always the case.⁽⁵⁴⁾ They are heterogeneous (being accompanied by the formation of new interfaces), there is a discontinuous change in the lattice constant during the transformation, and a change in symmetry of the lattice. In addition to the four fundamental crystallographic features characterizing martensitic transformations listed earlier, in these examples:

(5) the atoms move less than an interatomic distance, nearest neighbors are maintained, and any degree of order in the parent persists in the product during the transformation.

Rather than listing more transformations of this kind for which the applicability of the theory is not too surprising, it is more interesting to examine some transformations where (5) does not obtain and which have not, in general, been considered martensitic, but where the theory has been applied with remarkable successes.

The disordered cubic to twinned ordered orthorhombic transformation in AuCu (II) in the temperature range 380-400°C which occurs over a period of about 20 hours, clearly involves the relaxation of (5) since some sort of short range diffusion must take place; nearest neighbors are not maintained although atomic sites are, as pointed out by Christian.⁽¹⁷⁾ Yet the crystallographic features of the transformation shown in Fig. 26 were calculated by Smith and Bowles⁽⁵⁵⁾ using the B-M formulation and were in good agreement with the measured values. Apparently, the slow isothermal growth of α plates from β brass is controlled by the diffusion of zinc away from the transforming region which involves a further relaxation of (5) to permit such long range

diffusions. However, Garwood⁽⁵⁶⁾ recently analyzed the transformation with the graphical formulation of the W-L-R theory described here and found good agreement between predicted values of the crystallographic features and experimental results. Bowles and McG. Tegart⁽⁵⁷⁾ were the first to analyze a transformation which is obviously controlled by long range diffusion. They reported that the crystallographic features of the initial stage of the precipitation of b.c.c. CuBe from the f.c.c. alloys could be described by the B-M method. Srinivisan and Wayman^(58,59) suggested from their observations on an isothermal transformation in an FeCrC alloy that "lower bainite forms by a shear mechanism, not unlike martensite" while upper bainite forms by a different mechanism.

These transformations and others prompted me to propose⁽⁶⁰⁾ a classification system which differentiates according to the relaxation of condition (5) (with (1) - (4) satisfied), and which is summarized in Table III. I believe it is consistent with Cohen's comment made 20 years ago:⁽⁹⁾ "Since martensite is best defined not by what it is, but by how it forms, scientific emphasis must be placed on the reaction process rather than on the product itself. Consequently, it is not at all facetious to specify martensite as a structure that is produced by a martensitic reaction, provided, of course, that the nature of the transformation is then described." It also supports a suggestion made 16 years ago by Bowles and Barrett⁽¹³⁾ that "the martensitic mechanism may be operative in the early stages of some transformations (including some cases of precipitation from solid solution) that are ordinarily classed as nucleation and growth transformations."*

*This statement was made before the many discussions and reviews^(2,3,14,15) concerning the classification of transformations and the conclusion that since all transformations generally involve both nucleation and growth, the distinction between "martensitic" and "nucleation and growth" was not very fruitful and rather archaic, if not incorrect. Today the quote above would probably end: . . . "that involve long range diffusion and not just atom movement of less than an interatomic distance."

Transformations satisfying (5) are termed orthomartensitic. The categories of paramartensitic and quasimartensitic, chosen to convey the strong similarity to the 'classical' martensitic transformation, while relaxing (5) are useful for the present at least. A large number of transitions are not completely sharp but are at least partly diffuse or spread out with only a fraction of the transition first order or discontinuous in some easily measured parameter such as lattice constant. Thus there are cubic to tetragonal transformations in which, on heating from the low temperature tetragonal phase, the c/a ratio gradually goes from $1 + y$ to $1 + y/2$, say, as the transformation temperature is approached and then there is an abrupt discontinuous change in c/a to unity as one goes through this critical temperature, as indicated schematically in Fig. 28. Again, on cooling many systems one observes a softening of certain vibrational modes, as reflected in the profound change in the anisotropy constant,⁽⁶¹⁻⁶³⁾ which begins well above the transformation temperature as if in anticipation of the 'transformation.' Such "premonitory" effects, as Ubbelohde⁽⁶⁴⁾ has called them, must certainly be considered as part of the transformation if one is to really understand the mechanism involved even though we may focus attention on that (possibly small) part of the transformation which is discontinuous, and, perhaps, amenable to analysis by the crystallographic theories.

The oxidation of Ta to the sub-oxide TaO_y is a transformation which I first thought was quasimartensitic. This transformation from b.c.c. Ta to the finely twinned orthorhombic sub-oxide clearly involves long range diffusion of the oxygen atoms during growth and yet satisfies all the four crystallographic criteria listed earlier; it was studied and analyzed by Pawel et al.⁽⁶⁵⁾

(using the W-L-R theory as generalized by Wechsler and Otte⁽⁶⁶⁾ and more recently by Van Landuyt and Wayman⁽⁶⁷⁾). However, since these latter workers were able to retain and observe the 'austenite', i.e., b.c.c. TaO_y apparently of the same composition as the orthorhombic product martensite, then as pointed out by Altstetter and Wayman,⁽⁶⁸⁾ the diffusion of oxygen into the tantalum is no more a part of the transformation process than the diffusion of C (and/or Ni) into Fe is a part of the subsequent austenite-martensite transformation in steel. In the TaO_y , the temporal contiguity of the events of oxygen diffusion and structural transformation under the particular temperature and pressure condition of the experiment, in a sense, confused the issue, and, hence, this transformation perhaps should be considered as orthomartensitic and its product orthomartensite. I suspect other transformations should be re-examined from this point of view.

There is probably a continuum of transformation behavior depending on the degree of relaxation of (5) and it may not be easy (or even necessary) to distinguish between para and quasimartensitic reactions. However, the pseudomartensites must be carefully distinguished and separated. The martensite-like appearance of the product of a transformation, such as a banded surface indicating surface upheavals among twin related regions of the product, is no proof whatsoever that it was formed by a martensitic transformation--unless surface upheavals were observed between parent and product across an interface during transformation. Products of a transformation which is not martensitic (as defined by the characteristic crystallographic features) exhibiting this deceptive appearance I have termed pseudomartensite.

As I have already pointed out,⁽⁶⁰⁾ but repeat here for emphasis and completeness, systems may exhibit true martensitic behavior and a martensite product as well as pseudomartensite in the same alloy, depending on thermal history. The AuCu system is probably the most completely described system of this sort. The paramartensitic cubic to twinned orthorhombic transformation at 380-400°C occurring over a period of 24 hours has already been mentioned above. When, however, ordering occurs isothermally below 380°C or in a temperature gradient below this temperature, the transformation product is a twinned tetragonal structure but the transformation is not martensitic. No sharp interface exists between the two phases; rather, as shown in Fig. 28 from the work of Smith and Bowles,⁽⁵⁵⁾ there is a gradual increase in degree of order and tetragonality over an appreciable region. They⁽⁵⁵⁾ conclude that "for the conditions studied, the tetragonal phase does not form at the expense of the cubic phase by the advancement of a well-defined interface. The results are consistent with the view that the bands are mechanical twins which form after some degree of order and tetragonality has developed" presumably to relieve the stresses set up as c/a increases. When the transformation is complete, the surface of the crystal and the product are not inconsistent with their formation by a martensitic phase change, as is also true in other cases; hence the name pseudomartensite is appropriate for this product.

ON THE DILATATION OR IGNORANCE FACTOR, PHYSICAL PROPERTY CHANGES, AND THE MECHANISM OF TRANSFORMATION

In their original pronouncement, Bowles and Mackenzie⁽³⁷⁾ introduced an adjustable parameter, δ , representing a uniform dilatation in the interface

which could be varied so that the calculated quantities agreed better with the experimental observations for certain alloys. Since that time, and continuing to the present, there has been a considerable amount of time, effort, and publications^(69-73,49,52,16) dealing with this which, I believe, has generated more heat than light and merits little further serious discussion here. A glance at Figs. 21-23 will make it clear why Bowles and Mackenzie introduced this factor which says, in effect, that we don't know (and perhaps can never determine) the exact lattice parameters of the parent and product right at the interface and, hence, the distortions obtained from our x-ray determinations may be somewhat incorrect and not the ones which should be used. The location of (225) type habit observed in iron alloy of about 1% C, for example, is shown in Fig. 23. $[01\bar{1}]_A$ must be in this $(522)_A$ plane but so must $\vec{a}$, the intersection of the K_1 plane and the Bain cone--this can only be if $[01\bar{1}]_A$ and $\vec{a}$ coincide and thus if the semiapex angle of the Bain cone, ϕ_1 , is 45 deg. From the figure it can be seen that this is not the case--nor can it be for any of the lattice parameters of any iron alloy--using this pattern of inhomogeneity. However, if the η 's are varied so that the vertex angle ϕ_1 of the inner Bain cone is decreased, then it can be visualized from the figure that the cone will shrink and the intersection of the K_1 plane and the Bain cone, $\vec{a}$ -- which always lies on the habit plane -- will slide along the trace of this plane toward the right until it coincides with the $[01\bar{1}]_A$ direction. The habit plane will simultaneously move from the (259) type position to the (225) type along the line sketched. Note that any plane between $(952)_A$ and $(522)_A$ could be obtained by an arbitrary choice of δ ; a strain of ~2% ($\delta \approx 1.02$) is required for $(522)_A$. However, this effort failed to account for all of the crystallographic features. The subsequent suggestion^(71,74,75) that the dilatation may be anisotropic was not very fruitful nor were W-L-R approaches, using different

patterns of inhomogeneity.^(42,76-80) Lieberman and Bullough⁽⁸¹⁾ and Lieberman⁽⁸²⁾ were able to account for all of the features consistently without the use of a dilatation by incorporation into the W-L-R formulation the consequences of the fact that no $(225)_A$ type habit plane had ever been reported where the martensite plate was completely twinned. An example of the comparison between the L-B theory (which includes the W-L-R treatment as a limiting case) and experiment is shown in Fig. 29; the agreement is rather good. This theory 'results' in a distorted martensite cell which is not exactly tetragonal; this distortion is maximum for the $(225)_A$ type, zero for the W-L-R solution, and monotonically decreases for habit planes in between.⁽⁸³⁾

The experimental evidence for the conclusion that δ differs from unity--other than that at least some of the crystallographic features calculated using the existent phenomenological theories seem to be in better agreement with those observed in a particular transformation--is not unequivocal. It is based on the measured displacement of scratches on one surface used to obtain the macroscopic distortion, $\tilde{E}$, (as first done by Machlin and Cohen on three surfaces⁽¹²⁾), and then the existence of δ is inferred^(72,73) from the difference between $\det |\tilde{E}|$ and $\det |\tilde{B}|$; the only volume change permitted in the present theories comes from $\tilde{B}$ because the other operations--rotation, $\tilde{\Phi}$, and shear $\tilde{G}$,--have no volume change. As pointed out earlier,⁽⁸²⁾ the wide scatter in the direction of macroscopic shear calculated from the scratch displacements--as much as 24° for two planes whose normals differed by only $50'$ of arc⁽⁷³⁾--may be due to the fact that this feature is probably much more sensitive than the others to such factors as shear and volume restraints, details of the plate growth, and the orientation of the plate

relative to the surface being examined; conclusions from such measurement are rather tenuous. Recently, Dunne and Bowles⁽⁸⁴⁾ also discussed this and concluded from similar measurements on a similar alloy exhibiting the (225) type habit, that δ is not measurably different from 1; they have proposed a modification of the theory including some plastic accommodation to account for (225) habits. Bowles and co-workers are reportedly now working on more direct experiments to measure a dilatation; it would be very fitting if the same school which introduced this arbitrary factor would, 15 years later, be the one to demonstrate that it is not measurably different from unity.

In a way, it is tempting to elevate this ignorance factor δ to a role in this theory similar to the position that the effective mass plays on the electron behavior in solids. There the expression $\vec{F} = \underline{m}\vec{a} = q\vec{E}$ relates observables such as the charge q , the electric field acting on the charge $\vec{E}$, and the acceleration $\vec{a}$ through the inertial mass, $\underline{m}$. Since one cannot really determine the internal crystalline field, and, hence, the total field acting on the charge, one adjusts the mass to an "effective" mass so that the expressions are satisfied when the field is only the applied field, $\underline{m}^*\vec{a} = q\vec{E}_0$. Similarly, the original B-M proposal, couched in the W-L-R formulation, says that in the expression relating all of the crystallographic features, $\underline{E} = \phi \underline{B} \underline{G}$ where $\underline{B}$ is a function of η 's one should adjust the η_i to $\delta\eta_i$. It may be that the onus of understanding and explaining the discrepancy between theory and experiment is being improperly put on our ignorance of the 'correct' lattice constants in the interfacial region or of the correct (perhaps complex) lattice invariant shear system.

I suggest another attack. The phenomenological theories have heretofore generally ignored considerations other than minimum interfacial strain energy. Its application with reasonable success to such cases as the $(259)_A$ habit in iron base alloys, with its large transformation strains, a ferromagnetic product in a paramagnetic matrix, and appreciable volume and shear restraints suggests that at least in the initial stages of growth, these other effects are secondary as pointed out by Wechsler *et al.*⁽²²⁾ in commenting on the experimental scatter of habit planes reported in the same alloy. That other forces are probably operative in determining the mode of a transformation can sometimes be inferred from the discrepancy between the crystallographic features to be expected on the basis of the simple theory and those observed; something about the physics and mechanism of transformations can be learned from this.

The transformation from the high temperature paraelectric (cubic) phase to the ferroelectric (tetragonal) phase in semiconducting BaTiO_3 and $\text{KTa}_{0.65}\text{Nb}_{0.35}\text{O}_3$ (KTN), as reported by DiDomenico and Wemple,⁽⁵³⁾ is a striking example of the interrelationship among physical properties, crystal geometry, and mechanism. I have discussed it elsewhere,⁽⁶⁰⁾ but repeat it here because of its relevance.* That this transformation is first order martensitic is demonstrated for KTN in Fig. 30 from their paper. The explicit expressions for the direction cosines of the habit plane normal predicted by the W-L-R theory as published for the similar transformation in InTl ⁽⁴⁴⁾ (which involves

*Not only is this material germane to this paper, but it is especially appropriate that it be included in this volume since Tom Read, often in the forefront of speculative and exciting research, was in correspondence with DiDomenico and Wemple just before his terminal illness; their paper⁽⁵³⁾ reflects his contribution to their understanding and appreciation of phase transformations.

the same type of Bain distortion) were used to calculate the direction cosines of the habit plane. They were found to be in excellent agreement with the measured values--the predicted angles relative to cube axes being 90° , 49.7° , and 40.3° and the measured angles $89-90^\circ$, $50 \pm 1^\circ$, and $40 \pm 1^\circ$. Agreement is reported to be equally good for semiconducting BaTiO_3 .

Such agreement between theory and experiment is indeed gratifying, but more important for the understanding of mechanism is the fact that in insulating BaTiO_3 , preliminary observations indicate a habit plane close to $(110)_c$, approximately 5° from the irrational habit plane exhibited when the crystal is semiconducting. This significant difference, as the authors pointed out, is associated with the fact that in semiconducting crystals, the free charges present can neutralize the bound polarization charge inside the crystal, whereas in highly insulating crystals, the absence of free charges imposes restrictions on the paraelectric-ferroelectric boundary and the ferroelectric domain configuration. Thus the minimization of the strain energy at the interface and matching consideration can be the factor determining the nature of the transformation and interface boundary in semiconducting crystals but not in insulating crystals, where electrostatic and electrostrictive terms must be considered in the free energy and in the theory. The possibilities are exciting; research is now in progress and will be reported in due course. (86)

An assumed $\delta \neq 1$ or real errors in determining the lattice constants used to calculate the η 's, can, of course, result in a 'shift' of the habit plane as well as the other crystallographic features. The theory presumes that the distortions (η 's) are determined at the transformation temperature

and a common cause of error is the uncertainty in extrapolating the lattice parameters to the transformation temperature when the data were taken far from this temperature, as can be imagined from Fig. 28. Whether the effect is significant or not depends quite sensitively on the transformation strains. For the iron base alloys, the transformation strains $|\epsilon_t| \approx 0.20$ and the dilatation or 'uncertainty' in the η 's taken as ≈ 0.020 for $\delta \approx 1.020$ to shift the habit plane from (259) to (225). The 'dilatation shift' to shift the habit plane one degree is $\epsilon_\delta \approx \frac{2 \times 10^{-2}}{20^\circ} \sim 10^{-3}/^\circ$ and the ratio of this 'shift strain' to the transformation strain is $\frac{\epsilon_\delta}{\epsilon_t} \sim 5 \times 10^{-3}$.

Now, in KTN and BaTiO_3 , the transformation strains are quite small, $|\epsilon_t| \sim 5 \times 10^{-5}$, which is perhaps why the W-L-R theory works so well. From preliminary calculations,⁽⁸³⁾ the predicted habit plane shifts 5° for $\delta = 0.999994$. Thus, for this case, $\epsilon_\delta \sim \frac{5 \times 10^{-6}}{5^\circ} \sim 10^{-6}$. However, $\frac{\epsilon_\delta}{\epsilon_t} = 2 \times 10^{-2}$. Thus, whereas the habit plane shift effect differs by 10^3 in these two systems, the ratio of the 'shift strain' to the transformation strain differs by only a factor of 4, and, hence, for these two cases at least, we can write approximately $\epsilon_\delta \approx 10^{-2} \times \epsilon_t$. In the AuCd transformation, the average transformation strain is $|\epsilon_t| \sim 4 \times 10^{-2}$ and, thus, if this relation is general, one would expect $\epsilon_\delta = 4 \times 10^{-4}/^\circ$, i.e., a $\delta \approx 1 \pm 0.002$ should be required to shift the habit plane 5° .

There is unquestionably an intimate relationship among property changes, kinetics, morphology, crystal geometry, and the mechanism of transformation in phase changes, although it may not be obvious. Applying an external field or stress, quenching or changing the thermal history, or altering the conditions or state of the parent phase frequently affects the transformation profoundly.

It may be that the effect can be interpreted as some sort of δ , which may actually be associated with magnetostriction or electrostriction, but variation in the other parameters may alter the relationships among the crystallographic features differently from what a simple δ would. Thus, clues as to the nature of the mechanism may be provided if the transformation is observed under various conditions of stress, applied fields, etc., and examined within the framework of the phenomenological theory. A few examples of various types of effects, some of which have already been discussed, will be listed here.

In iron base alloys, M_s is raised by quenching in a magnetic field and may be raised or lowered by the application of a stress. The normal-to-superconducting transition is first order at finite H and T but becomes second order at $T = 0$ and $H = 0$. The CsCl-to-twinning orthorhombic transformation in $\text{Au}_{52.5}\text{Cd}_{47.5}$ (discussed above) which occurs at about 55°C on cooling is suppressed on rapid quench and a transformation at 25°C is observed⁽²⁹⁻³¹⁾ to a product having the same resistivity and apparently the same crystal structure as the β'' product of the 49 atomic pct. Cd alloy under normal cooling (see Fig. 2). Further, this transformation in quenched specimens can take place isothermally while the β to β' transformation has never been reported to occur except under continuous cooling. The isothermal disorder to order transformation in AuCu changes completely when the temperature is altered by a few degrees, as mentioned above. M_s is decreased in the martensitic transformation in β brass when the parent phase is irradiated with neutrons. As discussed above, the habit plane of the paraelectric to ferroelectric transformation in perovskite crystals is measurably different when the crystal is prepared as a semiconductor than when it is insulating. The twin plane in

the antiferromagnetic tetragonal product of a slowly cooled MnNi crystal is reported to be a crystallographically different plane than when a specimen is quenched, although the crystal structures appear to be identical.

The last example cited illustrates how--even when data and observations are incomplete--qualitative arguments based on the W-L-R phenomenological theory may provide some insight into the modes of transformation which could (or could not) have been operating in a specific system and may suggest the direction of further investigation. Since this was discussed briefly earlier⁽⁶⁰⁾ and will be treated in detail elsewhere,⁽⁸⁵⁾ it will only be summarized here. Two interesting transmission electron microscopy studies of the product phases in MnNi following transformation under two different sets of cooling conditions have been reported by Krasevec *et al.* The first⁽⁸⁹⁾ was on the order twins and antiphase boundaries in antiferromagnetic tetragonal NiMn formed when the bulk specimen was slowly cooled from the high temperature CsCl phase before thinning and the second⁽⁸⁸⁾ described the superstructure in an alloy apparently of the same composition quenched from the high temperature parent phase prior to thinning. The critical point for this discussion is that according to Krasevec *et al.*, although the crystal structures of the product phases are apparently the same*--f.c.t. with $c/a = 0.96$ --the twin planes are quite different: $\{110\}_t$ in the slow cooled case and $(111)_t$ in the quenched specimen.

*That the product crystal structure apparently is the same for such widely different heat treatments is not unique, as shown by the AuCd system described above where the same specimen seems to transform to the same product crystal structure under different conditions and with markedly different kinetics and morphology. Thus, it will be assumed here that this is indeed the case for NiMn since there is no reported evidence to the contrary.⁽⁸⁷⁻⁹⁰⁾

Using the graphical formulation of the W-L-R theory described, it can be shown that whereas the $(111)_t$ twinned f.c.t. structure was very likely produced by an orthomartensitic transformation from the CsCl phase on quenching; what appears to be the same f.c.t. structure twinned on $(011)_t$ produced as reported on slow cooling was probably not a result of the same type of transformation; the argument is briefly as follows.

The cone containing vectors which are undistorted due to the Bain distortion* is shown in Fig. 31 where we are looking down on the unique axis. Also shown are the normals and traces of the two shear planes $(112)_c$ and $(101)_c$ in the parent which, as can be seen from figures such as 6 for the AuCd case which also involves axes at 45 deg, become the $(011)_t$ and $(111)_t$ planes in the product phase for the slowly cooled and quenched specimens respectively. Since one of the conditions for the existence of an undistorted habit plane is that the plane of the lattice invariant shear part of the transformation distortion intersect the Bain cone, it will be seen from this figure that whereas the Bain cone intersects the $(101)_c$ plane, it apparently does not intersect the $(112)_c$ plane. Hence $(111)_t$ which comes from the former will be a permissible lattice invariant shear so that an undistorted habit plane may exist, while $(011)_t$ which comes from the latter will not, i.e., there will be no solution for $(011)_t$ twinning.

*The lattice parameters used to determine the Bain distortions and hence the vertex angles of the Bain cones, were the only ones available at the time and were not taken at the transformation temperature. Thus this analysis is at best qualitative and must be viewed as preliminary. However, a reasonable conjecture based on the behavior in other systems leads to the same proposal below and makes it even more plausible.

We are thus led to the proposal that the transformation in NiMn reported on quenching was orthomartensitic from the CsCl parent phase to a twinned $(111)_t$ product while the transformation described on slow cooling was not. If, (a), the composition of the alloy which was slowly cooled is identical to the one which was quenched, then it can be concluded that the $(011)_t$ twinned product is pseudomartensite and the transformation probably second order. If, (b), the composition is somewhat different, as recently suggested by Amelinckx,⁽⁹¹⁾ then ordering could be occurring, the sequence of structures different, and the situation similar to the AuCu system, as he points out.⁽⁹¹⁾ In that case, the twinned produce could be paramartensite or pseudomartensite as in the AuCu system described. Only possibility (a) has been considered so far-- (b) will be treated elsewhere.⁽⁸³⁾ In any event, the essence of the argument obtains, viz. an idea of the possible nature of the transformation can sometimes be deduced and fruitful directions for future work suggested from even limited or incomplete observations examined within the framework of the phenomenological theory.

THE IMPORTANCE OF "SHUFFLES" IN MARTENSITIC TRANSFORMATIONS

In some transformations, the Bain distortion obtained from a reasonable correspondence between the parent and product lattice does not 'transform' all of the atoms in the arbitrarily chosen cell of the parent into their corresponding positions in the product, and some inhomogeneous 'shuffles' within each product cell are required to account for all the atom positions. Bain's early suggestion of a distortion(sic 'lattice correspondence') for iron base alloys was discussed by Wechsler et al.⁽²³⁾ who pointed out that

it did indeed involve the smallest transformation strains of any correspondence distortion they could envisage at the time and, hence, was energetically the most favorable. Of course, in that system the correspondence is rather simple, and all atoms go to their proper positions in the product. In the actinides, however, this is by no means the case--the 'best' lattice correspondence is extremely difficult to determine, and 'shuffles' or adjustments must be applied to a majority of the atoms in some cases. They appear to be particularly prevalent in these materials which are so important in atomic energy and will be discussed briefly here.

Of these systems, uranium and its alloys has received the most experimental and theoretical attention; it has been discussed most recently by Bar-Or and Kimmel⁽⁹²⁾ and by Crocker and Ross.⁽⁹³⁾ The first analysis was by Lomer⁽⁹⁴⁾ in 1955 in his symposium paper following the report by Butcher and Rowe⁽⁹⁵⁾ of their experimental results on habit planes and orientation relationships in the $\beta \rightarrow \alpha$ transformation in U-1.4 at. pct. Cr. Before he determined a correspondence with reasonable small strains, Lomer had to examine 1600 distinct ways in which a β tetragonal cell containing 30 atoms could transform into $7 \frac{1}{2}$ α orthorhombic cells each containing 4 atoms--and even for this case, only one atom in 30 'went' to its proper position in the product by the Bain distortion alone! Crocker⁽⁹⁶⁾ incorporated Lomer's correspondence into the crystallographic theories, but the lack of experimental determination of the shear systems and the wide choice of possible lattice invariant shears militated against any definite conclusions about the validity of the analysis. Christian⁽⁹⁷⁾ analyzed the b.c.c. $\gamma \rightarrow \alpha$ transformation U-at. % Mo and Crocker and Ross⁽⁹³⁾ reported their analysis using a different correspondence due to

May⁽⁹⁸⁾ for this transformation. They⁽⁹³⁾ conclude that "the theories do not give real solutions for the crystallographic features." They further opine that the crystallographic theories as presently formulated are not suitable and suggest the development of a new, largely mechanistic, theory of martensitic crystallography produced by shears, something I hope can be discussed in a future seminar.

Although plutonium is very important as an energy source, its six allotropes, from b.c.c. ϵ stable above 490 dg. C. to simple monoclinic α stable below 110 deg. C, are extremely difficult to study experimentally and to analyze. The transformations exhibited by neptunium, although not simple, appear to be the easiest to analyze of the three systems. J. Rechtien and I reported⁽⁹⁹⁾ a preliminary examination of the crystal geometry of the b.c.c. γ to tetragonal β (4 atoms/unit cell) to orthorhombic α (8 atoms/unit cell) transformations in Np as the temperature is lowered. In the former transition, half the atoms shuffle in a plane perpendicular to a principal axis with two atoms moving in a direction 180 deg. to the other two. In the lower temperature transformation, there is further shuffling--still in the same plane, but now in several directions--by more of the atoms and doubling of the unit cell size together with a decrease in symmetry. Work is being continued on this system; further aspects of the $\alpha \rightarrow \beta$ transformation will be presented elsewhere.⁽¹⁰⁰⁾

In the process of studying the Np transformations and the models and transparent overlays constructed by Rechtien,⁽⁹⁹⁾ I reexamined the CsCl to orthorhombic transformation in AuCd discussed in some detail above. It would not be an unreasonable inference from Fig. 6, 9, and 12, that the structure of the twinned product is face centered orthorhombic. You will note,

however, that I have carefully refrained from stating what the actual structure is since in fact the orthorhombic cell is not face centered. Ölander⁽²⁴⁾ and Bystram and Almin,⁽¹⁰¹⁾ reported the following approximate atomic positions from x-ray measurements: two Cd atoms at 0,0,0, and 0, 5/8, 1/2, and two Au atoms at 1/2, 1/2, 0, and 1/2, 1/8, 1/2, for the variant in Fig. 32, which shows the transformation from CsCl to orthorhombic and now includes the 'shuffles' to produce these atomic positions. The orthorhombic coordinates (with suffix o) in Fig. 32 have been chosen to be similar to those of Toth and Sato.*⁽¹⁰²⁾ These authors and co-workers have written extensively on shear structures in alloys with long period stacking order.⁽¹⁰³⁻¹⁰⁵⁾ In particular, they state in their paper on the structure of martensites in AuCd alloys⁽¹⁰²⁾ that the β' phase first determined by Ölander⁽¹⁰⁶⁾ and since designated as the B19⁽¹⁰⁷⁾ or Ölander structure, is a transition form from a b.c.c. structure to a h.c.p. They add that for a transformation from the former to the latter, the close packed planes and close packed directions in the parent and product are respectively parallel. These observations will be commented on and developed further below.

The CsCl $(011)_c$ and $[11\bar{1}]_c$ (Fig. 32-a) are the close packed plane and direction in the parent which become the $(001)_o$ and $[110]_o$ in the product (Fig. 32-b), which are also close packed. As far as this plane is concerned, the Bain distortion is an extension of ~ 3.5 pct. in the $[01\bar{1}]_c \rightarrow [010]_o$ direction and a compression of ~ 5 pct. in the $[100]_c \rightarrow [100]_o$ direction.

*Apparently these authors use the designation of Bystrom and Almin⁽¹⁰¹⁾ for the cell edges; Chang⁽²⁸⁾ interchanges their $\underline{b}$ and $\underline{c}$ so that the lattice constants increased from $\underline{a}$ to $\underline{b}$ to $\underline{c}$; this convention has been followed here and in all references in AuCd work.

This can be visualized most easily by looking down on this plane, as in Fig. 33. An attractive way to view the distortion in this plane is to imagine that the parent cubic structure is pinned at 0 and to assume that the Au and Cd atoms 'touch' in the close packed directions in both the parent and product. From the lattice parameters at the transformation given earlier, $OA = \frac{1}{2}\sqrt{2} \underline{a}_0$ and $OA_0 = (\underline{a}^2 + \underline{c}^2)^{\frac{1}{2}}$ differ by $\approx 1\%$. If this small change is ignored for the present, the distortion consists of pulling outward along $[01\bar{1}]_c$ and allowing the four corners of the rectangle ABCD to simultaneously move inward along $[100]_c$. In this zeroth order approximation, $CA = DB$, they remain rigidly the same length, and pivot at 0. During this extension of about 3.5%, the angle $\theta_c = 2 \tan^{-1} 1/\sqrt{2} = 70^\circ 32'$ decreases to $\theta_0 = 2 \tan^{-1} \underline{a}/\underline{c} = 66^\circ 22'$ and $A_c B_c \rightarrow A_0 B_0$ with a decrease of about 5%, which is consistent with the behavior of tangents for angles of this size. Due to this Bain distortion, the atoms in the parent on the positions designated by dots (.) move in this plane to the positions of the full atoms, as shown. Meanwhile, in the plane below, the atoms on the parent dot positions move to the positions indicated by x's due to the Bain distortion alone (as can be seen from Fig. 32-b also). However, the 'shuffle' moves all of the atoms in this plane to the right by $1/8$ of the $\underline{c}$ length to the positions indicated by squares, as shown in Fig. 33-a.

The reason for this shuffle is apparent from Fig. 33-b. Here we have allowed the radii of the Cd and Au atoms to expand until they touch along the close packed directions, keeping the ratio $\underline{r}(\text{Au})/\underline{r}(\text{Cd}) = 49/51$, from the

literature values.* This 4% difference in the radii is indicated to scale in Fig. 33-b. If there were no difference in atomic radii and the structure were really h.c.p., the angle θ would = 60° and the atomic positions in the layer beneath would be at the '+'s, as marked; the positions of the atoms on this lattice would be given as two Cd atoms at 0,0,0, and 0, 1/2, 2/3, and two Au atoms 1/2, 1/2, 0, and 1/2, 1/2, 1/6, as pointed out earlier.[#] The actual positions of the atoms in the layer beneath--designated by the dots--which come from the Bained positions (x's) by glide shuffle of 1/8, differ from where they would be if all the radii were the same size and h.c.p. by $1/6 - 1/8 = 0.167 - 0.125 \approx 0.04$, a discrepancy the same as the difference in atomic radii and probably associated with it. Actually, even when the atoms are not the same size, a more hexagonal array with θ becoming closer to 60° and $\frac{A_o B_o}{OA_o}$ approaching unity can theoretically be achieved by further extension in the $[010]_o$ direction and contraction in $[100]_o$ until the Cd atoms touch in $[100]_o$. If this hypothetical condition is denoted o.c.p. (for orthorhombic close packed), then under these conditions $\theta_{o.c.p.} = 61^\circ 20'$ and $\frac{A_{ocp} B_{ocp}}{OA_{ocp}} = 1.02$. Table IV summarizes the comparison of the various structures with regard to packing, which will be treated in detail elsewhere. (83)

The shuffles do permit some understanding of why the low temperature phase is orthorhombic rather than tetragonal. This puzzled me because the symmetry of the parent phase, as shown in Fig. 32-a is high enough so that the distortion

*As summarized, for example, in Barrett and Massalski's Structure of Metals, 3rd edition, Table A-6.

[#]One of Toth and Sato's⁽¹⁰²⁾ atom positions for h.c.p. is stated⁽¹⁰²⁾ as 0, 5/6, 1/2, for this variant; this is incorrect, the 5/6 should be 2/3.

described thus far could equally well take place on the $(01\bar{1})_c$ plane, as a rotation of 90° around the $\vec{i}$ axis will show. However, once the shuffles are permitted, then the distance between the layers can be decreased relative to what they would be if the atoms were at the X position instead of at the dots, i.e., the alternate layers now 'fit' into the interstitial spaces. Although no physical sequence of steps is necessarily implied, one can picture the transformation as taking place by two simultaneous 'planer Bain distortions' similar to the one described above, one on the $(011)_c \rightarrow (001)_o$ plane as discussed and the other on the equivalent $(0\bar{1}1)_c \rightarrow (010)_o$. The result of this intermediate 'tetragonal Bain distortion' is a tetragonal cell with edges $\underline{a}'$, $\underline{c}'$, $\underline{c}'$ where $\underline{a}' \sim \underline{a}$ and $\underline{c}' \sim \underline{c}$; this combined distortion can be written as

$$\underline{B}' = \begin{pmatrix} \underline{a}'/\underline{a}_o & 0 & 0 \\ 0 & \underline{c}'/\sqrt{2}\underline{a}_o & 0 \\ 0 & 0 & \underline{c}'/\sqrt{2}\underline{a}_o \end{pmatrix}$$

However, the stacking shuffles on alternate planes of either $(011)_o$ or $(010)_o$ then permit the packing density to increase by decreasing the distance between these planes, as described above. The $\underline{c}'$ perpendicular to these planes thus decreases to $\underline{b}$ while minor adjustments, if any, take the other $\underline{c}'$ to $\underline{c}$ and $\underline{a}'$ to $\underline{a}$. This shuffle plus stacking collapse is an operation of lower symmetry than the tetragonal Bain distortion $\underline{B}'$ and the resulting structure is a specific orthorhombic cell.

It is interesting to note that the W-L-R treatment of the cubic to twinned orthorhombic transformation in AuCd, which seems to work quite satisfactorily, did not take into account in any way these shuffles explicitly.* In a sense, one could say that the combined effect on the per se change in unit cell or correspondence of the B' distortion plus shuffle, $(\underline{SH})$ is another distortion equivalent to $\underline{T}'$ Eq. (1-a) or $\underline{T}''$ Eq. (1-b) written for the variant in Fig. 32a and b and the axis system therein. Thus,

$$(\underline{SH})\underline{B}' = \underline{T}''' = \begin{pmatrix} \eta_1 & 0 & 0 \\ 0 & \eta_2 & 0 \\ 0 & 0 & \eta_3 \end{pmatrix}$$

in the $\hat{i}'''$, $\hat{j}'''$, $\hat{k}'''$ axis system in Fig. 32 where the η_i are as previously defined and employed. We are then back to our first discussion of the model of the transformation and the development of the W-L-R theory; when the shuffles are included in such figures as 6-b, 9, and 12, the twin relationship still obtains and the subsequent steps and description are valid and follow without change. The simple geometric considerations thus permit the irrationality of the habit plane to be accounted for as well as the irrational orientation relationships -- close packed planes and directions in the two phases are not parallel, as Toth and Sato have written, and the discrepancy between the relations observed and parallelism 'results' from the averaging process incorporated in the theory. In this case, at least, a model utilizing a correspondence and Bain distortion based on initial and final lattice constants,

*Chang first suggested⁽²⁸⁾ that "it is reasonable for purposes of simplification, to describe the orthorhombic cell as face centered" in his attempt to analyze the transformation in AuCd.

such as T'' , is sufficient--without further analysis into $(SH)B'$ --to describe all of the crystallographic features of the transformation satisfactorily. This may also be true for other cases, but apparently is not for the actinides. Christian has pointed out⁽¹⁸⁾ that in some cases, the need for atomic 'shuffles' may depend on the choice of lattice correspondence, i.e., the same structural change may be affected by either primitive or non-primitive corresponding cells and that 'shuffles' may be required by the latter but not by the former. Consideration of the transformation in AuCd as well as the actinides from this point of view will not be pursued further here, but will be treated elsewhere;⁽⁸³⁾ at this writing it seems doubtful if any correspondence can be found which will eliminate the need for 'shuffles' in the latter materials.

SUMMARY AND CONCLUSIONS

I have attempted to present the development of the phenomenological theory of the crystal geometry of martensitic transformations in such a way that the reader will understand and appreciate its physical essence, will be able to read with pleasure and profit the literature which employs or refers to it, and will himself be able to examine other transformations (perhaps such as those described in this volume) within its framework and apply it if appropriate in order to better understand mechanism. I have not dealt in any detail with the Bowles Mackenzie formulation nor compared the two approaches since this has been done^(15,43) to some extent. Nor have I mentioned one of the most important theoretical developments, viz. the Bullough-Bilby⁽¹⁰⁸⁾ surface dislocation approach (which is closely related to the matching method of Frank⁽⁷⁴⁾ and the prism matching of Bilby and Frank.⁽¹⁰⁹⁾ Algebraically the surface dislocation

method is identical to the earlier phenomenological theories but nevertheless does provide useful insight into the actual mechanism by which transformations occur. Thus, whereas the action of certain dislocation arrangements is implicit* in the specification of the lattice invariant shear (twinning and/or slip) in the W-L-R and B-M theories, Bullough and Bilby at the very outset specify the dislocation content of the interface in such a way that the habit plane shall be definitely glissile.

Although I regret the necessity of omitting several important topics, some of which I hope to treat elsewhere, I do not think any apology is necessary for the fact that this paper is not exhaustive. The reader will find almost everything of interest in phase transformations mentioned or treated in detail in this volume and the proceedings of the conferences referenced in the introduction. If one investigator merits a particular citation, it is Jack Christian who has authored or co-authored so many original contributions and critical review articles, as well as a monumental book in this area. I can think of no better point of departure for an appreciation of the present state of the art than his papers at the Scarborough⁽¹⁷⁾ and Manchester⁽¹⁶⁾ meetings; I hope the reader will find my paper⁽⁶⁰⁾ at the latter interesting and informative also.

*In the paper describing the simpler graphical method⁽⁴¹⁾ outlined here, I discussed how the problem could be "inverted" to determine the pattern of inhomogeneity--and thus obtain information about the dislocations--from observations of the crystallographic features such as the habit plane normal, orientation relationships, etc. I also said at that time "the possibility is inferred of putting certain arrays of dislocations into the metal or alloy before transformation, and thus predetermining the pattern of inhomogeneity and the transformation mechanism"; we are on our way to doing this in metallurgical practice.

Jock Mackenzie wrote⁽¹⁴⁾ in 1960 that the 'W-L-R & B-M' theory "had gained general acceptance because its predictions are in substantial agreement with experimental results in all cases where it has been applied" and this is more or less true today. However, he also pointed out at that time that "theory has advanced almost independently in two complimentary directions--thermodynamics and kinetics on the one hand and geometry and crystallography on the other; these theories have yet to be joined to form a coherent whole"--and I am afraid this statement is also true eight years later. The phenomenological theory as constituted thus far is descriptive and depends on the measured lattice parameters of the two phases through the correspondence--Bain distortion. It says nothing about the cause, mechanism, or nature of that distortion--just as Newton's laws say nothing explicit about the cause of the force or the details of its nature. Thus although the phenomenological theory satisfactorily describes or relates the crystallographical features of many transformations, even in cases in which its applicability is somewhat unexpected, and may even be helpful in sorting out possible modes of transformation, such things as 'shuffles' must be considered carefully and electrical, magnetic, electrostrictive, piezoelectric, etc. effects and property changes will have to be included if it is to make its maximum contribution to our understanding of phase transformations. The theoretical and experimental skills, talents, and experience of people of interests and background as widely different as the kinds of materials exhibiting such transformations should be brought to bear on a first principles understanding of mechanisms, such as is now being attempted.⁽¹¹⁰⁾

Morris Cohen, the late Tom Read, and others⁽³⁾ wrote almost 20 years ago in their contribution to "Perspectives in Materials Sciences" titled "Phase Transformations in the Solid State:"

The science of phase transformations should enable one to predict the time-temperature conditions under which a reaction will occur in a given system. In addition, it should be possible to foretell the nature of the transformation and to calculate its overall kinetics. In the final analysis, it should even be possible to describe in advance the ultimate morphology resulting from the transformation, and thereby control the structure-sensitive properties of materials. It goes without saying that the current science of phase transformations falls far short of achieving this goal. There is now strong need for carefully controlled experiments and realistic theories if we are to make substantial progress toward a deeper understanding of phase transformation. The main purpose of this report is to set the stage for such progress.

There has indeed been some progress; I hope that this paper (and this volume) contributes to further advances.

ACKNOWLEDGMENTS

I would like to acknowledge many helpful and stimulating discussions with colleagues and graduate students and the continued support of the U. S. Atomic Energy Commission. More importantly, to Morris Cohen's moving tribute and acknowledgment of our debt and that of the field of metallurgy to Tom Read for his incisive contribution to our understanding of the formation of martensite, I want to add my own. It is not uncommon for former students and co-workers of a scientist and teacher of Tom's caliber who is held in such esteem and affection to commemorate his 60th birthday by some event, such as a volume of contributed papers in his honor. Tom's untimely death at 52 deprived me of this privilege and honor. This paper, which I hope

reflects some of Tom's work and inspiration, will have to suffice as a small token of my debt to him as teacher, advisor, and co-worker. To have lived and worked with him and his intelligence, inventiveness, enthusiasm, humor, understanding, and empathy was a unique and unforgettable experience for which I shall always be grateful. With Tom's passing, I have lost a colleague and friend who cannot be replaced.

APPENDIX A (after Lieberman et al.)⁽²³⁾

It will be demonstrated from dimensional and order of magnitude considerations that homogeneous transformation and concomitant distortion at the interface plane involves a larger energy than inhomogeneous transformation to a set of twin related regions, say, with an interface plane of zero average distortion.

It is assumed that all other energy terms are independent of the mode of transformation except the strain energy at the interface; it is thus sufficient to minimize it to find the energetically most preferable mode. In Fig. 34(a) is shown the schematic appearance of a square cross section specimen if the transformation were homogeneous. The resultant distortion in the region containing the interface is indicated, and the strain energy would be of the order

$$W_a = \epsilon^2 Y l^2 l' , \quad (10)$$

where Y is Young's modulus, ϵ the strain, l the width of the specimen, and l' the order of l , according to Saint Venant's principle. The inhomogeneous transformation and the product twin-related domains is shown schematically in Fig. 34(b). Alternate strains at the interface are of opposite sign and thus the average strain vanishes, permitting a plane of zero average distortion to exist. The energy now consists of two parts: the energy at the interface and the twin boundary surface energy. Neglecting angular dependence, the energy is now of the form

$$W_b = \epsilon^2 \gamma \ell^2 \underline{h}' + \gamma \frac{\ell}{\underline{h}} \ell^2, \quad (11)$$

where $\underline{h}'$ is of order $\underline{h}$ and γ is the twin boundary surface energy. Letting $\underline{h}' = \underline{h}$ and differentiating W_b with respect to $\underline{h}$ yields the result that W_b will be a minimum when the interface strain energy is equal to the twin boundary energy and hence W_b can be written

$$W = 2\epsilon^3 \gamma \ell^2 \underline{h}. \quad (12)$$

Since $\ell \sim 3$ mm and $\underline{h} \sim 5 \times 10^{-3}$ mm, inhomogeneous transformation with a plane of zero average distortion is energetically the most favorable.

APPENDIX B DERIVATION OF THE SEMIVERTEX ANGLES IN FIGS. 19 AND 20

For the variant shown in Fig. 20, the Bain distortion for the cubic to tetragonal transformation is

$$(B-1) \quad \underline{B} = \begin{pmatrix} \eta_1 & 0 & 0 \\ 0 & \eta_2 & 0 \\ 0 & 0 & \eta_1 \end{pmatrix}$$

which is similar to Eq. 1. The statement that some vectors, $\vec{r}$, are unchanged in length when operated on by the Bain distortion is

$$(B-2) \quad |\underline{B} \vec{r}|^2 = |\vec{r}|^2.$$

Let $\vec{r}$ be a unit vector $\begin{pmatrix} \sin\phi_1 \cos\omega \\ \cos\phi_1 \\ \sin\phi_1 \sin\omega \end{pmatrix}$ expressed in cylindrical coordinates,

where ϕ_1 is the angle between $\vec{r}$ and the Y axis and ω is the angle between the projection of $\vec{r}$ on the ZX plane and the X axis. Then (B-2) becomes

$$\left| \begin{pmatrix} \eta_1 & 0 & 0 \\ 0 & \eta_2 & 0 \\ 0 & 0 & \eta_1 \end{pmatrix} \begin{pmatrix} \sin\phi_1 \cos\omega \\ \cos\phi_1 \\ \sin\phi_1 \sin\omega \end{pmatrix} \right|^2 = \left| \begin{pmatrix} \sin\phi_1 \cos\omega \\ \cos\phi_1 \\ \sin\phi_1 \sin\omega \end{pmatrix} \right|^2$$

$$\eta_1^2 \sin^2\phi_1 + \eta_2^2 \cos^2\phi_1 = \sin^2\phi_1 + \cos^2\phi_1$$

$$\sin^2\phi_1 (\eta_1^2 - 1) = \cos^2\phi_1 (1 - \eta_2^2) \quad \text{and}$$

$$(B-3) \quad \tan \phi_1 = \left(\frac{(1 - \eta_2^2)}{(\eta_1^2 - 1)} \right)^{\frac{1}{2}}$$

The angle ϕ_f between the vector after Bain distortion and the Y axis is obtained directly since the problem is really two dimensional. $\vec{r}$ can be written $\vec{r} = \sin\phi_1 \vec{i}' + \cos\phi_1 \vec{j}'$ where $\vec{i}'$ is any unit vector in the ZX plane. The final position of the vector $\vec{r}$ is

$$\begin{pmatrix} \eta_1 & 0 \\ 0 & \eta_2 \end{pmatrix} \begin{pmatrix} \sin\phi_1 \\ \cos\phi_1 \end{pmatrix} = \begin{pmatrix} \eta_1 \sin\phi_1 \\ \eta_2 \cos\phi_1 \end{pmatrix} = \begin{pmatrix} \sin\phi_f \\ \cos\phi_f \end{pmatrix}$$

since the final vector is also a unit vector, i.e., it is unchanged in length.

Thus

$$(B-4) \quad \tan \phi_f = \frac{\sin \phi_f}{\cos \phi_f} = \frac{\eta_1}{\eta_2} \tan \phi_i = \frac{\eta_1}{\eta_2} \left(\frac{(1-\eta_1^2)}{(\eta_1^2-1)} \right)^{\frac{1}{2}} .$$

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TABLE I

Classification of Solid-State Transformations^{3/}

- I. Homogeneous transformations (no new interfaces formed)
 - A. Clustering (increase in number of like atomic neighbors)
 - B. Ordering of the second kind (increase in number of unlike atomic neighbors)
 - 1. Short-range ordering
 - 2. Long-range ordering
- II. Heterogeneous transformations (accompanied by formation of new interfaces)
 - A. With attendant shape change (shear-like macroscopic displacements, surface tilts)
 - 1. Nonthermally activated growth--glissile interfaces (regular martensitic transformations)
 - 2. Thermally activated growth--nonglissile interfaces
 - a. Controlled by short-range atomic transport^{*} (some polymorphic transformations like Widmanstätten ferrite; the disordered fcc → ordered orthorhombic reaction in Au-Cu; isothermal growth in AuCd under certain conditions)
 - b. Controlled by long-range atomic transport^{2/} (bainite; probably precipitation in Cu-Be)
 - c. Controlled by relaxation processes (probably low-temperature isothermal growth in U-Cr)
 - B. Without shape change (presumably this type of growth is always isothermally activated)
 - 1. Controlled by short-range atomic transport^{*} (polymorphic transformations which are not shear-like, in contrast to IIA2a; order-disorder reactions of the first kind in contrast to IB; massive transformations as in Cu-Ga)
 - 2. Controlled by long-range transport[†] (precipitation and eutectoid decomposition)

^{*} Short-range atomic transport signifies movements by only a few jump distances; for example, across an interface or atomic interchange within an interface. Composition changes do not occur.

[†] Long-range atomic transport signifies movements of many jump distances. Composition changes do occur.

TABLE II

Comparison of Experimental and Calculated (W-L-R Theory) Crystallographic Features
of Martensitic Transformations in AuCd, InTl, and Fe--22%Ni--.8% C

System	Feature	Experimental	Theoretical	Discrepancy
Au-Cd (47.5 at. % Cd)	Interface	$\begin{pmatrix} 0.696 \\ -0.686 \\ 0.213 \end{pmatrix}_{\beta}^{(23)}$	$\begin{pmatrix} 0.6968 \\ -0.6810 \\ 0.2250 \end{pmatrix}_{\beta}^{23}$	<1.5°
	plane			
	normal			
CsCl → twinned orthorhombic		$(001)_{\beta} \parallel \text{to } (001)_{\beta}^{(28)}$	$(001)_{\beta} \quad 2 \quad 40''^{(23)}$	2.5°
			from $(001)_{\beta,1}$	
			$(010)_{\beta} \quad 2 \quad 27''$	
Orientation relationship		$[111]_{\beta} \parallel \text{to } [011]_{\beta}$	from $(010)_{\beta,2}$	0.3°
			$[111]_{\beta} \quad 18'$	
			from $[011]_{\beta,2}$	
Macroscopic shear direction		$\begin{pmatrix} 0.660 \\ 0.729 \\ 0.183 \end{pmatrix}_{\beta}^{(23)}$	$\begin{pmatrix} 0.6510 \\ 0.7322 \\ 0.2001 \end{pmatrix}_{\beta}^{(23)}$	<1.5°

TABLE II (continued)

System	Feature	Experimental	Theoretical	Discrepancy
In-Tl (18-23 at.% Tl)	Angle			
	macroscopic shear	$2.94^\circ(23)$	$3.28^\circ(23)$	0.36°
	Interface plane normal, n	$\begin{pmatrix} 0 \\ 1 \\ 1 \end{pmatrix} (38)$	$\begin{pmatrix} 0.1013 \\ 0.993 \\ 1 \end{pmatrix} (38)$	$<1^\circ$
	f.c.c. $\rightarrow$ twinned f.c.t. ($c/a > 1$)			
Fe-Ni-C (22% Ni, 0.8% C)	Interface plane normal	$\begin{pmatrix} 10 \\ 3 \\ 15 \end{pmatrix} = \begin{pmatrix} 0.5472 \\ 0.1642 \\ 0.8208 \end{pmatrix} (8)$	$\begin{pmatrix} 0.5691 \\ 0.1783 \\ 0.8027 \end{pmatrix} (22)$	$<2^\circ$
	Orientation relationship	$(111)_A \parallel (101)_M$ to within 1°	$(111)_A$ 15' from $(101)_{M_1, M_2}$	~ 0
		$[1\bar{1}0]_A$ 2 $1/2^\circ$ from $[111]_M$	$[1\bar{1}0]$ 3° from $[111]_{M_1, M_2}$	$\sim 1/2^\circ$
	Shear direction	$\begin{pmatrix} 0.7315 \\ -0.3828 \\ 0.5642 \end{pmatrix} (8)$	$\begin{pmatrix} -0.7660 \\ -0.2400 \\ 0.5964 \end{pmatrix} (22)$	$\sim 8^\circ$
	Shear angle	$10.66^\circ (8)$	10.71°	~ 0

TABLE III

Summary of Classification Scheme for Martensitic Transformation
and Martensite-like Products (after 60)

If the transformation is heterogeneous with a discontinuity in some parameter across the interface and exhibits

- (1) a shape deformation which results in surface upheavals or dihedral angle,
- (2) an irrational undistorted habit plane whose normal is characteristic of the material,
- (3) a rather precise orientation relationship between principal directions and planes in the two phases across the interface and a lattice correspondence,
- (4) a fine inhomogeneous structure such as twins, usually in the product,

and (5) all atoms move less than an interatomic distance,
then the transformation process is (at least partially) 1st order and.....orthomartensitic,
and the transformation product, as in steels, AuCd, BaTiO₃, is.....ORTHOMARTENSITE.

and (5) some atoms move more than an interatomic distance--short-range diffusion, atomic sites maintained, composition does not change,
then the transformation process is (at least partially) 1st order and.....paramartensitic,
and the transformation product, as in the ordering of AuCu II, is.....PARAMARTENSITE.

and (5) atoms of one species diffuse over large distances--long-range diffusion, composition changes,
then the transformation process is (at least partially) 1st order and.....quasimartensitic,
and the transformation product, as in the transition from β brass to α , is.....QUASIMARTENSITE.

However, if the transformation does not involve a discontinuous change in any parameter nor the formation of new interfaces between parent and product while still exhibiting features similar to some of those cited above, and, although the product may twin subsequent to the transformation to relieve stresses and may appear similar to martensite in many alloys,

then the transformation process is probably second order and is.....not martensitic,
and the transformation product, as in AuCuI, GeTe-SnTe, is.....PSUEDOMARTENSITE.

TABLE III

Summary of Classification Scheme for Martensitic Transformations
and Martensite-like Products (after)

If the transformation is heterogeneous with a discontinuity in some parameter across the interface and exhibits

(1) a shape deformation which results in surface upheavals or a dihedral angle,

(2) an irrational undistorted habit plane whose normal is characteristic of the material,

(3) a rather precise orientation relationship between principal directions and planes in the two phases across the interface and a lattice correspondence,

(4) a fine inhomogeneous structure such as twins, usually in the product,

and

(5) all atoms move less than an interatomic distance,

(5) some atoms move more than an interatomic distance--short range diffusion, atomic sites are maintained, composition does not change,

(5) atoms of one species diffuse over large distances--long range diffusion, composition changes,

then the transformation process is (at least partially) 1st Order and

ORTHOMARTENSITIC,

PARAMARTENSITIC,

QUASIMARTENSITIC,

and the transformation product is

ORTHOMARTENSITE (steels, AuCd, BaTiO₃).

PARAMARTENSITE (Ordering of AuCu II).

QUASIMARTENSITE (β brass to α).

However, if the transformation does not involve a discontinuous change in any parameter nor the formation of new interfaces between parent and product while still exhibiting features similar to some of those cited above, then although the product may twin subsequent to the transformation to relieve stresses and may appear similar to martensite in many alloys,

the transformation is 2nd Order and

the transformation product is

PSEUDOMARTENSITE

(AuCu I, GeTe-SaTe)

Table IV. Packing of various structures compared with h.c.p. - see Fig. 33

	$\theta = \angle OA, OB$	$\frac{AB}{OA}$	Efficiency of packing* in close packed plane
CsCl or b.c.c. - c	$70^\circ 32'$	1.15	0.921
Observed Orthorhombic in AuCd, - o	$66^\circ 22'$	1.09	0.945
'Theoretical' close packed orthorhombic in AuCd - o.c.p.	$61^\circ 20'$	1.02	0.985
Hexagonal close packed - h.c.p.	60°	1	1.0

*Defined here as area of ABDC of h.c.p., using $r(\text{hcp}) = \frac{r(\text{Cd}) + r(\text{Au})}{2}$,

divided by the area ABCD for each case.

FIGURE CAPTIONS

- Fig. 1 $(112)_M$ twin traces on relief surface of a pair of martensite plates formed along the surface of an austenite annealing twin in 1.35% C steel.^{83/} Oblique illumination. X250. Courtesy of J. S. Bowles.
- Fig. 2 Part of the Au-Cd phase diagram showing the two transformations in the narrow β field. The two reversible martensitic phase changes are shown in 2-b. Note that the $\sim 20\%$ change in resistivity is in opposite directions for the two transformations.^{33/}
- Fig. 3 Partially transformed AuCd specimen with single interface separating cubic (left) and orthorhombic (right) regions. The heater is at extreme left (2X).^{23/} Below is a higher magnification photomicrograph at the interface, $\sim 300X$ --the parent CsCl single crystal is on the left and the transformed twinned orthorhombic phase is on the right, as above.^{40/} Micrograph courtesy of B. S. Subramanya.
- Fig. 4 Examples of invariant plane strains. In each case, the dotted outline is deformed into the solid outline and the direction of motion, common to all points, is indicated by the arrow. The base of each figure represents the stationary invariant plane.^{14/}
- Fig. 5a Section in the X_2X_3 plane of a unit sphere and the ellipsoid into which it is transformed.^{69, ibid. in 39/}

- Fig. 5b Traces of the undistorted planes in their initial positions AB, CD, and their final positions A'B', C'D'.^{69, ibid, in 39/}
- Fig. 6a Untransformed b.c.c. structure in which a f.c.t. cell is delineated. The cubic axis system is $(\vec{i}, \vec{j}, \vec{k})$.^{23/}
- Fig. 6b Orthorhombic cell into which the face-centered tetragonal cell is transformed. Principal axes $(\vec{i}', \vec{j}', \vec{k}')$ are obtained by 45° rotation about the $\vec{k}$ axis.^{23/}
- Fig. 7 Two dimensional analogue of what the transformation looks like microscopically: a Bain distortion of the square unit cell into the rectangle and a rotation to account for the orientation relationship across the interface.
- Fig. 8 Types of deformation in martensitic transformations. (after B. A. Bilby and J. W. Christian in Ref. 39).
- Fig. 8a Original undeformed crystal block.
- Fig. 8b Lattice deformation.
- Fig. 8c Lattice invariant deformation by slip.
- Fig. 8d Lattice deformation and lattice invariant deformation combining to give zero total shape deformation.
- Fig. 8e Shape deformation caused by varying lattice deformations in different regions, lattice invariant shear is twinning in the product.
- Fig. 9 The pure distortions which (a) region 1 and (b) region 2 undergo during transformation. Unit vectors $\vec{i}, \vec{j}, \vec{k}$ are along cube edge directions; $(\vec{i}', \vec{j}', \vec{k}')$ and $(\vec{i}'', \vec{j}'', \vec{k}'')$ are along the principal axes of the pure distortions in regions 1 and 2 respectively.^{23/}

Fig. 10 Two dimensional analogue of crystallographically equivalent transformation distortions in two adjacent regions leading to a twinned product. The 'tetragonality' has been exaggerated.

Fig. 11 The equal segmented line in the parent 'austenite' ABCD...G goes into the broken line AB'CD'EF'G' during this two dimensional analogue of the transformation to a twinned product. Note that $AB' < AB$ while $B'C > BC$, but $|ABCD...G| = |AB'CD'EF'G'|$ and, therefore, this line lies in the habit plane which is, on the average, undistorted. (After 22 and 23)

Fig. 12 The two product cells which were mirror related across a $(110)_\beta$ type plane become twins when their $(111)_\beta$ planes, shaded in 9, are made to coincide by a rotation of $\sim 4.5^\circ$. (After 23 and 40)

Fig. 13 The parallel markings in this transmission electron micrograph of a martensite plate in Fe-29-29.7% Ni-0.42% C are $\{112\}_M$ transformation twins as first postulated by W-L-R many years earlier.^{22/} Courtesy of Dr. I. Tamura.

Fig. 14 Schematic showing that the same shape accommodation can be accomplished by either twinning of fraction x or slip shear by an equivalent amount of shear α . (After 69)

Fig. 15 Section through the orthorhombic region, showing the banded structure of relative amounts x of twin 2 and $(1-x)$ of twin 1. The broken line OA'B'C'D'...U'V' was the straight line OV in the original cubic crystal.^{22,23/}

Fig. 16 The shear angle α is defined in this figure. All vectors in the shear plane K_1 and the plane K_2 are unchanged in length due

to slip. All vectors in the obtuse angle between K_1 and K_2 (dotted region) are increased in length due to slip in the direction shown while all other vectors (except those in K_1 and K_2) are decreased in length.^{41,23/}

Fig. 17 Stereogram showing the undistorted K_1 , K_2 (and K'_2) planes for an arbitrary shear angle of 10° on the $(011)_A$ plane in the $[01\bar{1}]_A$ direction. X, Y, Z are the $\langle 100 \rangle_A$ and X', Y', Z' are 'martensite' plane normals and directions as indicated in Fig. 18. (After 41.)

Fig. 18 The Bain distortion takes the b.c.t. cell delineated in the f.c.c. structure in A and repeated in B into the martensite cell at C; the correspondence is clearly shown. The lattice invariant shear system is shown expressed in both austenite and martensite axis systems. (After 22,23,41)

Fig. 19 The Bain distortion transforms OV into OV' without changing its magnitude. ϕ indicates the semi-vertex angle of the cone of such unextended vectors before the Bain distortion and ϕ' the semi-vertex angle of the cone of these same vectors following the Bain distortion. All vectors in the shaded region are decreased in length by the Bain distortion while all others (except those lying on the cone OV) are increased. (After 23,40,41)

Fig. 20 Stereogram showing the two undistorted Bain cones, B_i and B_f . All vectors lying within B_i , shown shaded, are decreased in length by the Bain distortion, while all others, except those lying on the cone, are lengthened. (After 41)

- Fig. 21 Stereogram showing four unit vectors whose lengths are changed neither by slip nor Bain distortion and the regions where the vectors are changed oppositely by the two components of the total distortion. See text. (After 41)
- Fig. 22 Stereogram showing how the positions of the unit vectors $\vec{c}$, $\underline{c}$, $\underline{c}'$ depend on the amount of shear α . (After 41)
- Fig. 23 The four solution planes which are undistorted by the total transformation distortion, for each of two values of slip, α_1 and α_2 . These planes may be crystallographic variants of each other. Only the trace of the one which corresponds to a solution in the spherical triangle corresponding to experiment for the variant of shear system chosen is shown. For this shear system $(011)_A$ $[01\bar{1}]_A$ (also sketched) which corresponds to $(\bar{1}21)_M$ $[11\bar{1}]_M$ twinning--all solutions will lie in this triangle. The significance of the line connecting the solution with a $(522)_A$ type will be found in the text. (After 41)
- Fig. 24 Stereographic plot of habit planes. Grid delineates planes predicted by the theory.^{22/} Solid dots are the observed planes of Greninger and Troiano (Fe-Ni, 32.5% Ni; Ref. 8).
- Fig. 25 Electrical resistance changes during the cooling and heating of an iron-nickel and a gold-cadmium alloy, illustrating the hysteresis between the martensitic reaction on cooling and the reverse transformation on heating.^{47/}

- Fig. 26 Microstructure showing sub-bands, "diamond" figures and habit plane, in an Au Cu specimen transformed 18 hr at 400°C. Polarized light.^{55/} X150.
- Fig. 27 Transition zone between the cubic structure and the twinned tetragonal structure in a single crystal of AuCu quenched after partial transformation in a temperature gradient.^{55/} X50.
- Fig. 28 Schematic of the variation of $\underline{c}$, $\underline{a}$, $\underline{a}_0$, and $\underline{c}/\underline{a}$ for a tetragonal to cubic transformation on heating. In the transition region between the start and completion of the transformation on heating (between A_s and A_f), both phases are observed.
- Fig. 29 Stereogram comparing experimentally determined habit plane and orientation relationships and those predicted by the Lieberman-Bullough theory. The observed and calculated habit planes cannot be distinguished on a 15 cm net and the orientation relationships agree quite well,^{81/} the discrepancy between the habit plane calculated by computer and that reported is ~ 0.8 deg.^{82/}
- Fig. 30 Optical absorption coefficient as a function of temperature in KTN at $\lambda = 1985$ m μ for light polarized perpendicular to $(\vec{E} \perp \underline{c})$ and parallel to $(\vec{E} \parallel \underline{c})$ the crystal $\underline{c}$ axis.^{53/}
- Fig. 31 Stereographic projection showing that using the available lattice constants for NiMn to determine the Bain distortion, and hence the Bain cones, the trace of $(101)_c$ intersects the B_1 cone while the trace of $(112)_c$ fails to. Thus, $(111)_t$ is

a possible lattice invariant shear for an invariant habit plane solution, while $(011)_t$ is not. See text.

Fig. 32a Four unit cells of the CsCl rotated counterclockwise 45 deg. about the $\vec{i}$ axis from the orientation of Fig. 6a. The 'tetragonal' cell which 'corresponds' to the orthorhombic product cell is delineated.

Fig. 32b The product orthorhombic cell produced by the Bain distortion; half the atoms must be 'adjusted' or 'shuffled' to achieve their final positions, as indicated, since the Bain distortion only takes them to the positions marked 'X'. Recall $\underline{a} = 0.949a_0$, $\underline{b} = 1.0138(\sqrt{2}a_0)$, $\underline{c} = 1.0350(\sqrt{2}a_0)$.

Fig. 33a If the cubic structure is considered pinned at 0, then the atoms in the $(011)_c \rightarrow (001)_o$ plane will move as indicated due to the Bain distortion, with $\theta_c = 70^\circ 32' \rightarrow \theta_o = 66^\circ 22'$. However, the atoms in the plane below the one determined by the circles all shuffle to the right by $1/8 \underline{c}$ and are shown as squares. See text.

Fig. 33b The atoms in Fig. 33a have been 'expanded' as described in the text until they touch along the close packed direction OA_o . The increased packing perpendicular to the plane of the figure is a consequence of the shuffles in the plane below.

Fig. 34a Homogeneous transformation, as in single crystal to single crystal.

Fig. 34b Inhomogeneous transformation, as to a set of twin related regions. (After Ref. 23)

Figure 1

Figure 2

Figure 3

SIMPLE EXTENSION

SIMPLE SHEAR

GENERAL INVARIANT
PLANE STRAIN

Figure 4

Figure 5-a

Figure 5-b

Figure 6-a

Figure 6-b

B FOLLOWED BY Φ

Figure 7

(a)

(b)

(c)

(d)

(e)

Figure 8

Figure 9-a

Figure 9-b

Figure 10

Figure 11

Figure 12

Figure 13

Figure 14

Figure 15

Figure 16

Figure 17

B

C

Figure 18

Figure 19

Figure 20

Figure 21

Figure 22

Figure 23

Figure 24

Figure 25

Figure 26

Figure 27

Figure 28

Figure 29

Figure 30

Figure 31

Figure 32-a

Figure 32-b

Figure 33-a

Figure 33-b

Figure 34