Heats of Segregation and Segregation Profiles of BCC Metals

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Abstract

It has long been known that many multicomponent alloys exhibit surface segregation, in which the composition at or near a surface may be substantially different from that of the bulk. A number of phenomenological explanations for this tendency have been suggested, involving, among other things, differences among the components' surface energies, molar volumes, and heats of solution. In this work, we investigate via atomistic Monte Carlo computer simulation the problem of surface segregation for a variety of bcc binary metal alloys, and compute segregation profiles (that is, profiles of composition as a function of depth) in these materials. Our simulations are performed using an atomistic Monte Carlo procedure that makes use of the semi-empirical energy method of Bozzolo, Ferrante and Smith (BFS) that has been shown to provide accurate information on the bulk and surface structure of alloys. We formulate a framework for the understanding of this phenomenon that makes use of the BFS method's division of the energy into "strain" and "chemical" components, and compare this picture with available experimental results.

Introduction

The composition of metal alloy surfaces is often different from that of the bulk.

Some alloys exhibit surface segregation, where one or more species reside preferentially at or near the surface.

A detailed understanding of this behavior is necessary to correctly model such phenomena as adhesion or catalysis.

Several phenomenological approaches to the problem have been put forward, falling into two broad categories:

> Thermodynamic approaches, where the equilibrium distribution of chemical species is computed.
>
> Atomistic approaches, where the tendency of a species to segregate is determined by computation of the energies of single atoms of that species in bulk and surface environments.

We present results that combine aspects of both approaches:

Heats of segregation based on total energy calculations using the quantum-approximate BFS energy method.

Equilibrium distribution of species (i.e. segregation profiles) computed via atomistic Monte Carlo simulation.

We attempt to determine whether the heats of segregation alone are sufficient to accurately characterize the segregation behavior of binary alloys in dilute and non-dilute cases.

Segregation is usually considered to be the result of a competition between two effects:

> The effect of size mismatch among the constituent chemical species.
>
> The effect of breaking chemical bonds due to the reduced coordination at the surface.

In this work, we describe the effects of size mismatch in terms of the "strain" component of the energy, characterized by the degree of mismatch between the lattice constants of the two chemical species in a binary alloy.

We describe the effects of breaking chemical bonds in terms of the difference in "chemical" energies of bulk and surface atoms, characterized by the chemical identities of these atoms' nearest and next-nearest neighbors.

Method

The heat of segregation is defined as the difference in energies of two otherwise-identical computational cells having a single impurity atom in the bulk and in the surface layer.

Energetics are computed using the BFS quantum-approximate energy method.

The BFS method is especially suitable for analysis of this problem, since it explicitly divides the total energy into strain and chemical contributions. The strain energy is computed under the assumption that each atom's neighbors are in their actual positions, but are of the same chemical species as the atom itself. The chemical energy is computed under the assumption that the neighbor atoms maintain their actual chemical identities, but are located at crystallographic positions appropriate to a perfect crystal.

The method has been used previously to compute heats of segregation for fcc binaries that were in excellent agreement with experiment.

Dilute-limit heats of segregation

Heats of segregation of single substitutional impurities were computed for all binary combinations of Fe,Cr,V,Mo,W,Ta and Nb.

Heats were computed for the 001, 011 and 111 surfaces, with and without atomistic relaxation.

Segregation trends were characterized as follows:

E_{seg} = E(surface impurity) - E(bulk impurity), so systems with negative heats of segregation will segregate.

The segregation trend is characterized as strong or weak depending on whether the absolute value of the heat of segregation is greater than or less than 0.5 eV.

The trend is characterized as strain-dominated if $|E_{str}| > |E_{chem}|$, and chemically-dominated if $|E_{str}| < |E_{chem}|$.

Results for the 001 surface are shown in Table 1.

	Host						
Impurity	**Fe**	**Cr**	**V**	**Mo**	**W**	**Ta**	**Nb**
Fe		-0.06 Y WEAK CHEM -1.7	-0.48 Y WEAK CHEM -4.1	0.9 N STRONG CHEM -7.3	1.39 N STRONG CHEM -7.6	1.25 N STRONG CHEM -9.3	0.07 N WEAK STRAIN -9.5
Cr	-0.04 Y WEAK STRAIN 1.7		0.41 N WEAK STRAIN -2.4	0.6 N STRONG CHEM -5.7	1.45 N STRONG CHEM -5.9	1.52 N STRONG CHEM -7.7	0.63 N STRONG CHEM -7.8
V	0.01 N WEAK CHEM 4.1	-0.6 Y STRONG STRAIN 2.4		-2.26 Y STRONG CHEM -3.3	-3.36 Y STRONG CHEM -3.5	3.17 N STRONG CHEM -5.3	3.57 N STRONG CHEM -5.4
Mo	-1.94 Y STRONG STRAIN 7.3	-1.29 Y STRONG STRAIN 5.7	3.28 N STRONG CHEM 3.2		0.28 N WEAK STRAIN -0.2	1.07 N STRONG STRAIN -2	0.37 N WEAK STRAIN -2.1
W	-2.21 Y STRONG STRAIN 7.6	-2.2 Y STRONG STRAIN 5.9	4.82 N STRONG CHEM 3.5	-0.26 Y WEAK STRAIN 0.2		0.79 N STRONG STRAIN -1.8	-2.39 Y STRONG CHEM -1.9
Ta	-3 Y STRONG STRAIN 9.3	-3.02 Y STRONG STRAIN 7.7	-2.08 Y STRONG STRAIN 5.3	-1.03 Y STRONG STRAIN 2	-0.48 Y WEAK STRAIN 1.8		-0.06 Y WEAK STRAIN -0.1
Nb	-1.37 Y STRONG STRAIN 9.5	-2.34 Y STRONG STRAIN 7.8	-0.23 Y WEAK CHEM 5.4	-0.22 Y WEAK STRAIN 2.1	6.28 N STRONG CHEM 1.9	0.08 N WEAK STRAIN 0.1	

Key:
Heat of Segregation, eV
Segregation?
Strength
Strain/Chem?
Lattice Constant Mismatch, %

TABLE 1

General trends:

In the following, the size mismatch is characterized by the impurity (a_{imp}) and host (a_{host}) lattice constants.

Binaries having $a_{imp} > a_{host}$ tend to segregate, while those having $a_{imp} < a_{host}$ tend not to.

Binaries having $a_{imp} > a_{host}$ tend to be strain-driven, while those having $a_{imp} < a_{host}$ tend to be chemically-driven.

Most exceptions to the above have only a small degree of size mismatch, which tends to diminish the importance of strain effects and increase the importance of chemical effects.

Of the binaries having $a_{imp} > a_{host}$ that do not segregate, most exhibit strong chemically-driven behavior

Of the binaries having $a_{imp} < a_{host}$, the majority have chemically-dominated behavior.

While relaxation changes the values of the heats of segregation, in only three cases does it change the segregation behavior.

Conclusions:

In general, if the impurity is larger than the host, strain effects will dominate, and segregation will occur.

In general, if the impurity is smaller than the host, chemical effects will dominate, and segregation will not occur.

Segregation predictions tend to be more accurate for systems having large size mismatch.

Describing segregation behavior as the result of a competition between strain and chemical effects is a useful means of categorization.

Extension to Non-Dilute Cases

Results computed in the dilute limit may not be appropriate for non-dilute alloys:

Non-dilute alloys will have lattice constants different from those of the pure-metal hosts, as used in the dilute calculations, so the strain contribution to the heat will change with composition.

The neighbors of an "impurity" atom will not necessarily all be of the "host" species, so the chemical contribution will be composition-dependent as well.

The chemically-driven formation of large-scale structures in the bulk may add further complications.

We address the first and third of these issues in this work.

To address the strain-dependence of the heats, we have recomputed these heats in the dilute limit, but over a range of lattice constants that spans the impurity and host values, without atomistic relaxation.

This approach provides a "strain-dependent" prediction of segregation trends for non-dilute binaries which should be more accurate than predictions computed in the dilute limit.

Results:

Segregation trends (Table 2) are similar to those seen in the initial dilute calculations. If the strain-dependent results are summarized in terms of the majority segregation prediction for each system at all lattice constants, only one system, Fe(Nb), exhibits different behavior in the dilute and strain-dependent cases.

Five of the binary systems showed a "crossover" from non-segregating to segregating behavior, or vice versa. Of these, four systems showed segregation when the "impurity" species lattice constant is significantly larger than that of the alloy, but not otherwise.

General trends are consistent with earlier work:

Binaries having $a_{imp} > a_{host}$ will segregate, while those having $a_{imp} < a_{host}$ will not

Of the binaries having $a_{imp} > a_{host}$ that do not segregate, most exhibit strong chemically-driven behavior

	Host						
Impurity	Fe	Cr	V	Mo	W	Ta	Nb
Fe		YNYC	YNYC	NYNC	NYNC	NNNC	NNYS
		YNYC	YNYC	NYNC	NYNC	NNNS	NNYS
		YNYC	YNYC	NNNC	NNNC	NNNS	NNYS
		NNYS	YNYC	NNNC	NNNC	NNNS	NNYS
		NNYS	YNYC	NNNS	NNNS	NNNS	NNYS
Cr	YYNS		NNYS	NYNC	NYNC	NNNC	NNNC
	YYNS		NNYS	NYNC	NYNC	NNNC	NNNC
	YYNS		NNYS	NYNC	NNNC	NNNS	NNNS
	YYNS		NNYS	NNNC	NNNC	NNNS	NNNS
	YYNS		NNYS	NNNC	NNNC	NNNS	NNNS
V	NYNC	YYNS		YYYC	YYYC	NNNC	NNNC
	NYNC	YYNS		YYYC	YYYC	NNNC	NNNC
	NYNC	YYNS		YYYC	YYYC	NNNC	NNNC
	NYNC	YYNS		YYYC	YNYC	NNNC	NNNC
	NYNC	YYNS		YNYC	YNYC	NNNC	NNNC
Mo	YYYS	YYYS	NYNC		NNNS	NNYS	NNYS
	YYYS	YYYS	NNNC		NNNS	NNYS	NNYS
	YYYC	YNYC	NNNC		NNNS	NNYS	NNYS
	YNYC	YNYC	NNNC		NNNS	NNYS	NNYS
	NNYS	NNYS	NNNC		NNNS	NNYS	NNYS
W	YYYS	YYYS	NYNC	YYNS		NNYS	NYNC
	YYYS	YYYC	NYNC	YYNS		NNYS	NYNC
	YYYS	YYYC	NNNC	YYNS		NNYS	NYNC
	YNYC	YNYC	NNNC	YYNS		NNYS	NYNC
	YNYC	YNYC	NNNC	YYNS		NNYS	NYNC
Ta	YYNS	YYYS	YYYS	YYNS	YYNS		YYNS
	YYNS	YYYS	YYYS	YYNS	YYNS		YYNS
	YYNS	YYNS	YYYC	YYNS	YYNS		YYNS
	YYNS	YYNS	YYYC	YYNS	YYNS		YYNS
	NYNC	YYNS	YYYC	YYNS	YYNS		YYNS
Nb	YYNS	YYNS	YYYC	YYNS	NYNC	NNYS	
	YYNS	YYNS	YYYC	YYNS	NYNC	NNYS	
	NYNC	YYNS	YYYC	YYNS	NYNC	NNYS	
	NYNC	YYNS	YYYC	YYNS	NYNC	NNYS	
	NYNC	YYNC	YYYC	YYNS	NYNC	NNYS	

Key:
LC appropriate for Host/Impurity = 90/10
75/25
50/50
25/75
10/90

On each line:
Segregates? (Y/N)
Strain energy supports segregation? (Y/N)
Chem energy supports segregation? (Y/N)
Strain or chem dominance (S/C)

TABLE 2

Additional trends:

Some systems show a reversal of segregation behavior with changing lattice constant (Cr(Fe), Fe(Mo), Cr(Mo), Fe(Nb) and Cr(Nb)). For the two systems with the largest size mismatch, as the lattice constant increases toward the (larger) host value, the strain energy becomes less important and the segregation behavior is increasingly chemically-dominated.

Segregation Profiles

Segregation profiles (plots of composition versus depth) were computed via Monte Carlo computer simulation.

Monte Carlo Procedure

An initial average composition is chosen, and the chemical species distributed at random in a 5200-atom bulk computational cell. The compositions are 10/90, 25/75, 50/50, 75/25 and 90/10.

The optimum lattice constant of the cell is determined by minimizing the total energy with respect to dilation of the cell.

A surface is created at one face of the cell (001 in this case).

The chemical species are rearranged probabilistically so as to minimize the total energy using the following iterative procedure:

> A pair of atoms having different chemical species is chosen.
>
> The total energy of the two atoms and their environments (including nearest- and next-nearest-neighbors of both atoms) is computed using the BFS energy method.
>
> The chemical species of the two atoms are exchanged and the total energy recomputed.

The exchange is accepted or rejected, according to the Metropolis criterion:

If the exchange lowers the energy, it is always accepted;
If the exchange increases the energy, the exchange is accepted with probability exp($-\Delta E/kT$) where ΔE is the energy change associated with the exchange, k is the Boltzmann constant and T the absolute temperature.

Issues

If there is a significant degree of segregation, the bulk composition will differ from its initial average value.

In many cases, the average composition away from the surface after minimization is well-defined, and can be taken as the effective bulk composition.

In some cases, e.g. when compositional fluctuations are comparable in size to the computational cell, the composition away from the surface is not well-defined.

In addition to the strain/chemical competition, there may be a tendency toward bulk order that can mask the tendency toward segregation.

It is expected that the Monte Carlo simulations will be "noisier" than the simple dilute-case computations; the MC results will exhibit a degree of sensitivity to initial conditions, dependence on the particular sequence of random numbers used, etc.

Results

Segregation trends from the Monte Carlo simulations are shown in Table 3.

In most cases, the surface segregation trends from the Monte Carlo procedure agrees with those from the dilute and strain-dependent computations. Most systems show majority agreement with the strain-dependent results.

In 16 of the 42 cases there is disagreement between the MC and dilute results for at least one composition. Of these, only four systems show disagreement at a majority of compositions. Of these, the three have small size mismatches.

	Host						
Impurity	Fe	Cr	V	Mo	W	Ta	Nb
Fe		YN YN YN	YN YN YN	NN NN NY	NN NN NN	NN NN NN	NN NN NN
Cr	YN YY YY		NN NN NN	NN NN NN	NN NN NY	NN NN NN	NN NN NN
V	NN NN NY	YY YY YY		YY YN YY	YY YN YN	NN NN NN	NN NN NN
Mo	YY YY YN	YY YY YY	NN NN NN		NN NN NN	NN NN NN	NN NN NN
W	YY YY YY	YY YY YN	NN NN NY	YY YY YY		NN NN NN	YN YN YN
Ta	YY YY YY	YY YY YY	YN YY YY	YY YY YY	YY YY YY		YN YY YY
Nb	YY YY NY	YY YY YY	YY YY YY	YY YY YY	NN NN NY	NN NN NN	

Key:

Y=Segregates	First Column: Prediction from dilute heats at same lattice constant
N=Does not segregate	Second Column: Prediction from Monte Carlo simulation

Compositions:
Host/Impurity = 90/10
75/25
50/50

TABLE 3

Specifics:

Because of the large size of the computational cells, a rich set of behaviors can be observed. We consider in detail some specific binary systems of interest.

TaFe (Figs. 1-5)
The TaFe system has a large degree of size mismatch, and is strain-dominated in the Fe(Ta) case and chemically-dominated in theTa(Fe) case. This system strongly favors the formation of an ordered B_2 structure, either on the surface or in the bulk, with a surface layer of Ta. This tendency towards ordering is so strong that essentially all of the minority species appears in the B_2 region, while the rest of the cell appears as a region of majority species pure-metal.

TaNb (Figs. 6-10)
The TaNb systems has a very small degree of size mismatch. Ta segregates to the surface for all compositions. At small concentrations of Ta, the Ta segregates to the surface, but a complete layer of Ta does not form, as their is insufficient Ta in the computational cell. At intermediate concentrations, the Ta segregates to the surface, forming a layer of pure Ta. At larger concentrations of Ta, the Ta segregates to a region that includes the surface layer and several underlying layers, and Nb tends to segregate in the bulk. The Ta25Nb75 cell shows a single layer of Ta segregated to the surface, and a damped disordered modulated structure having a three-layer periodicity. A strongly-ordered B_2 structure is not observed.

NbW (Figs. 11)

The Nb75W25 system shows a region of pure Nb that includes the surface, and a region of bulk-segregated W.

VW (Figs. 12-13)

The VW system shows how competition between bulk and surface segregation can lead to varying results.

V50W50
Bulk and surface segregation of W.

V10W90
Surface segregation of V.

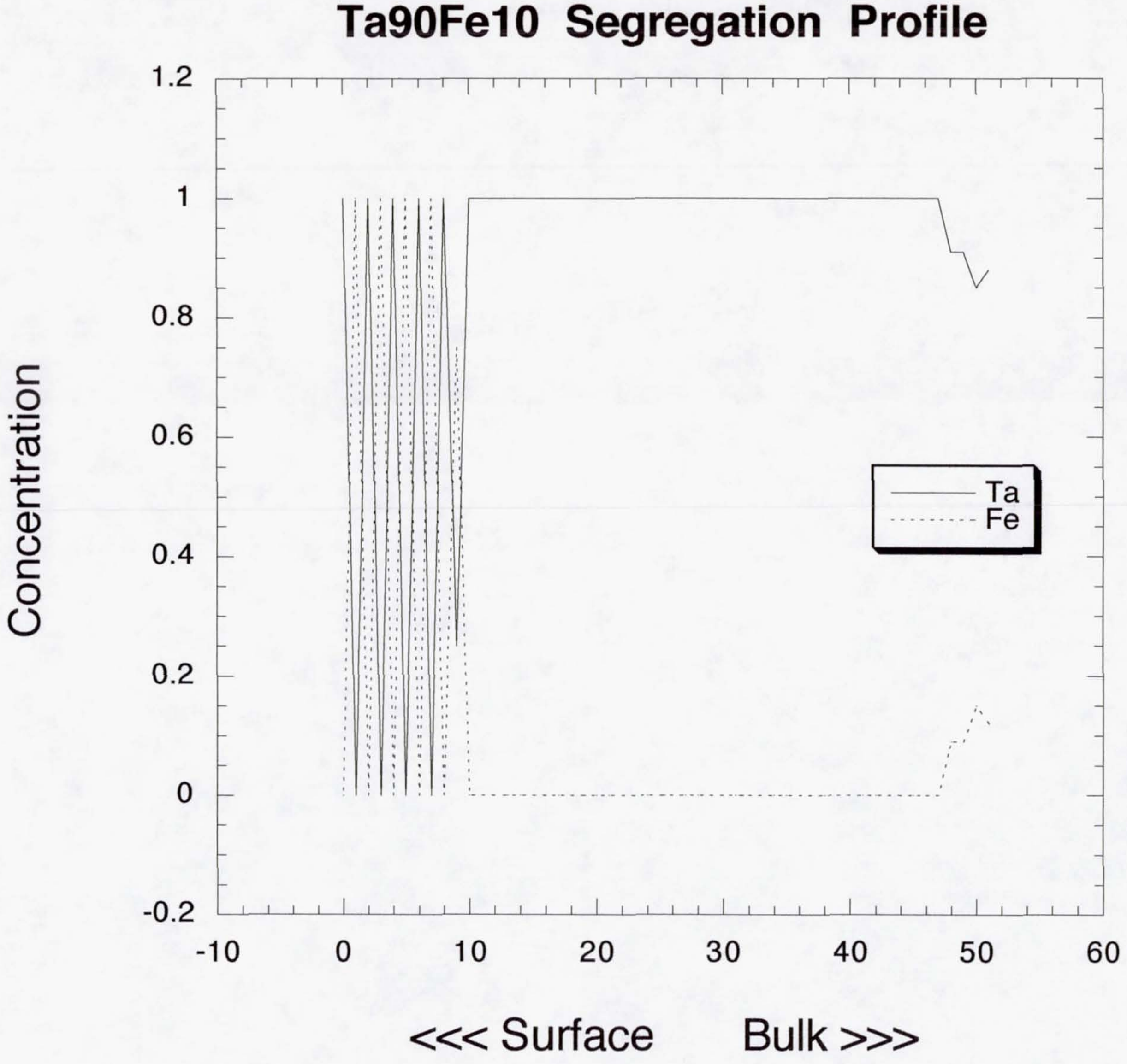

Ta90Fe10 Segregation Profile
Concentration
1.2
1
0.8
0.6
0.4
0.2
0
-0.2
-10
0
10
20
30
40
50
60
<<< Surface Bulk >>>
Ta
Fe

FIG 1

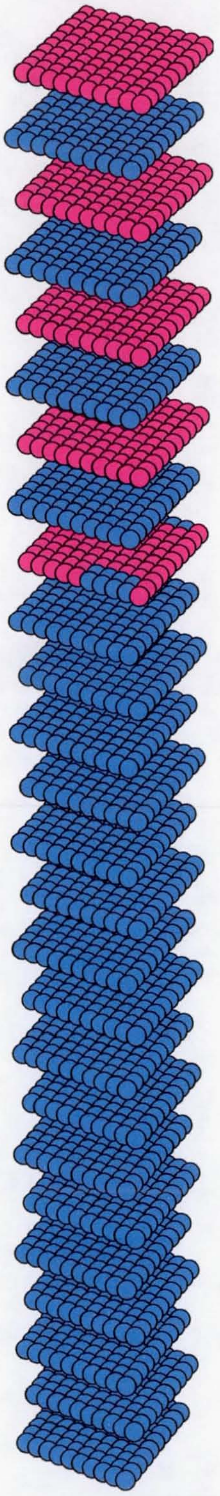
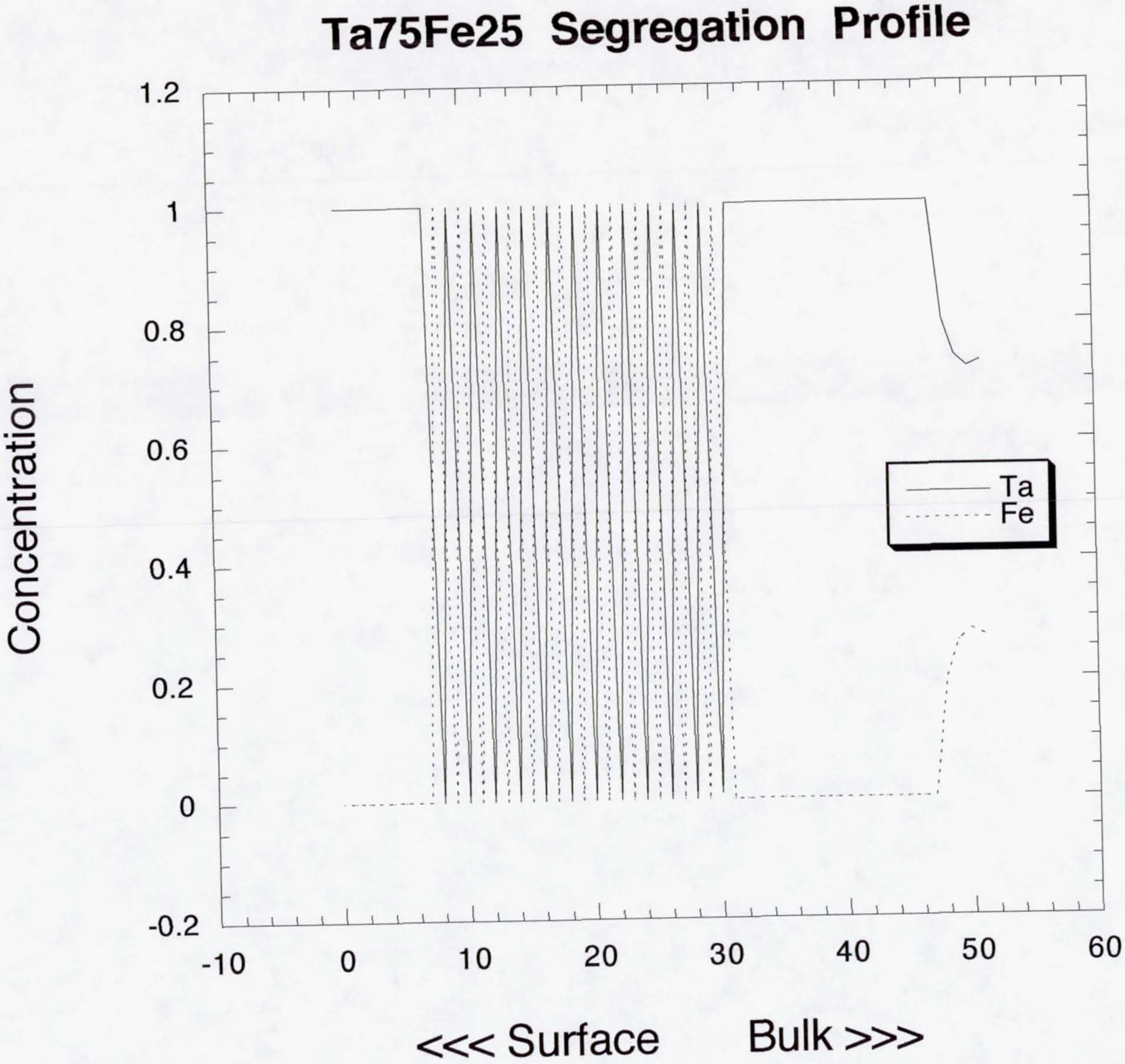


FIG 1a

Ta 10 Fe 90
Ta RED Fe BLUE



Ta75Fe25 Segregation Profile

FIG 2

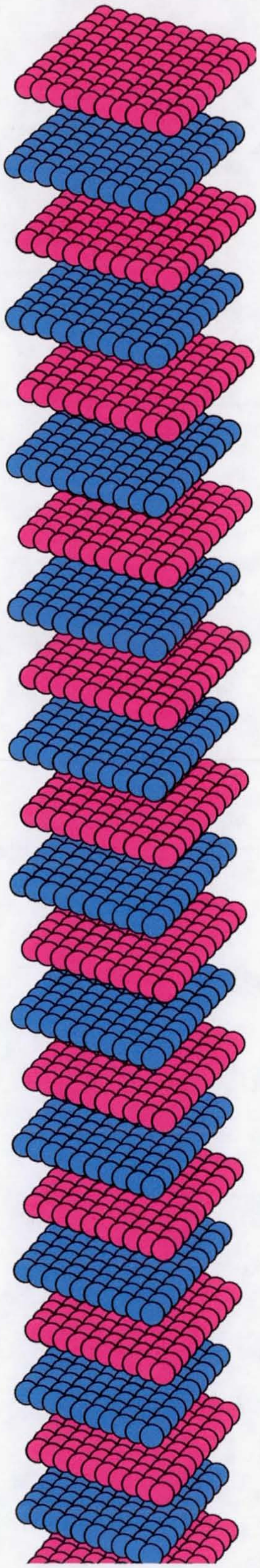


FIG 2a

Ta25 Fe75

Ta = RED
Fe = BLUE

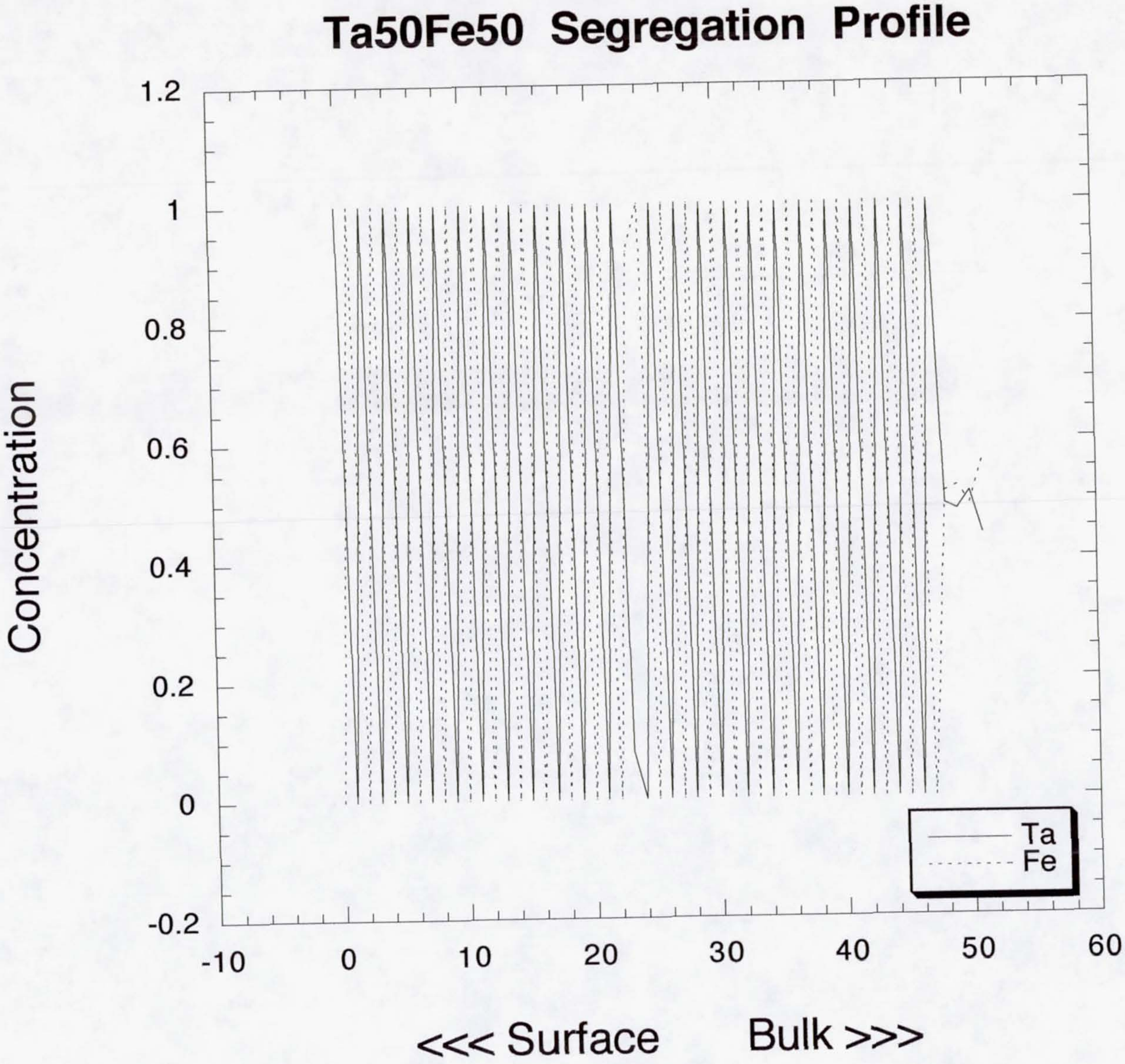

Ta50Fe50 Segregation Profile
1.2
1
0.8
0.6
0.4
0.2
0
-0.2
Concentration
-10
0
10
20
30
40
50
60
<<< Surface Bulk >>>
Ta
Fe

FIG 3

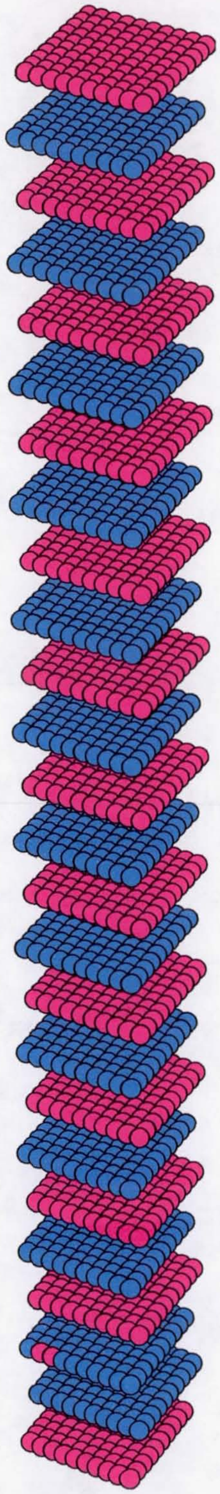


FIG 3a

Ta 50 Fe 50
Ta RED Fe BLUE

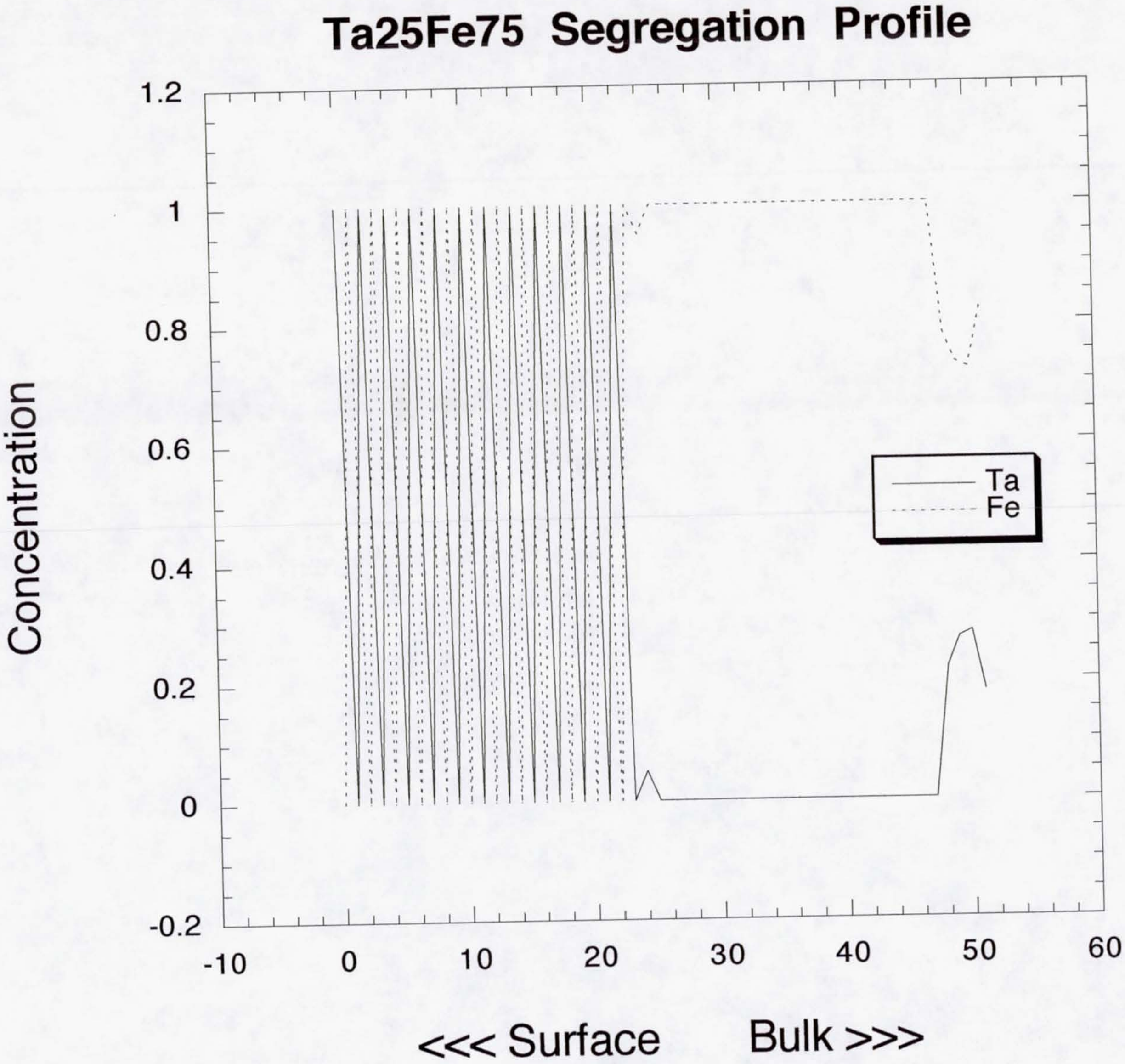

Ta25Fe75 Segregation Profile
Concentration
1.2
1
0.8
0.6
0.4
0.2
0
-0.2
-10
0
10
20
30
40
50
60
<<< Surface
Bulk >>>
Ta
Fe

FIG 4

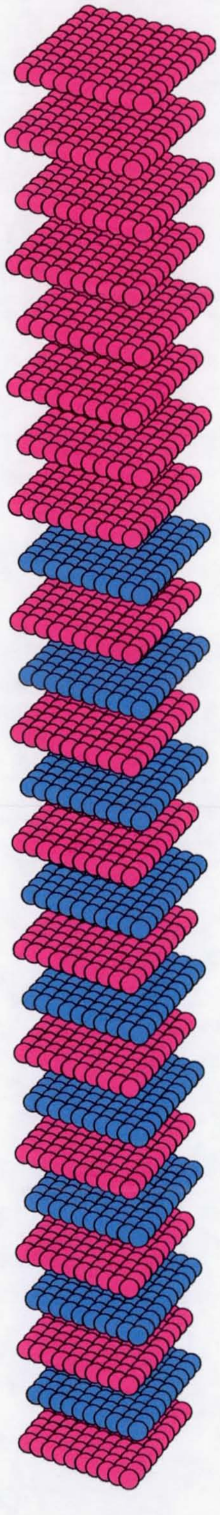


FIG 4a

Ta75 Fe25
Ta RED Fe BLUE

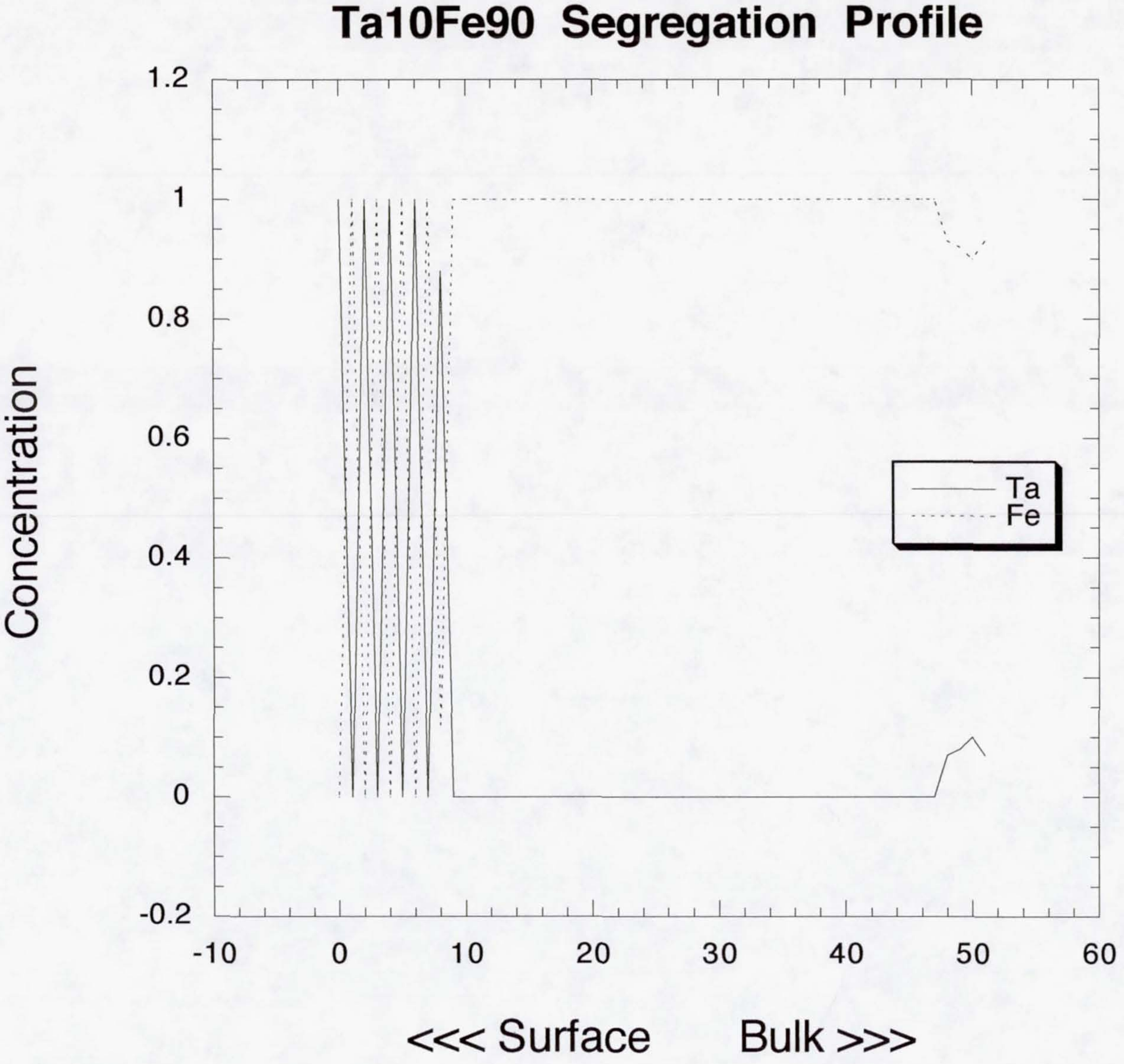

Ta10Fe90 Segregation Profile
Concentration
1.2
1
0.8
0.6
0.4
0.2
0
-0.2
-10
0
10
20
30
40
50
60
<<< Surface Bulk >>>
Ta
Fe

Fig 5

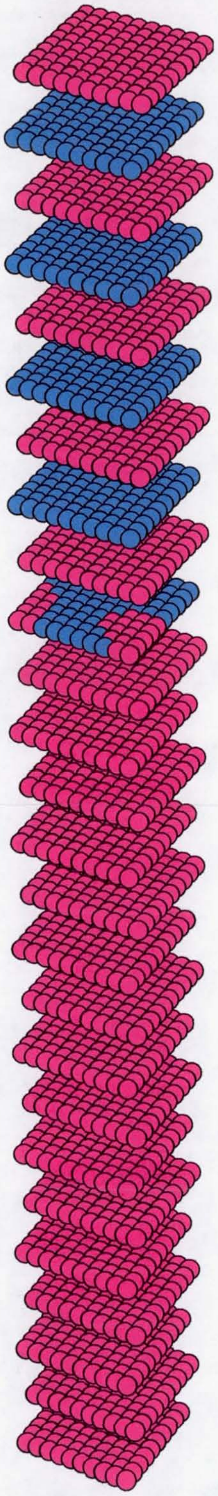


FIG 5a

Ta90 Fe10

Ta RED Fe BLUE

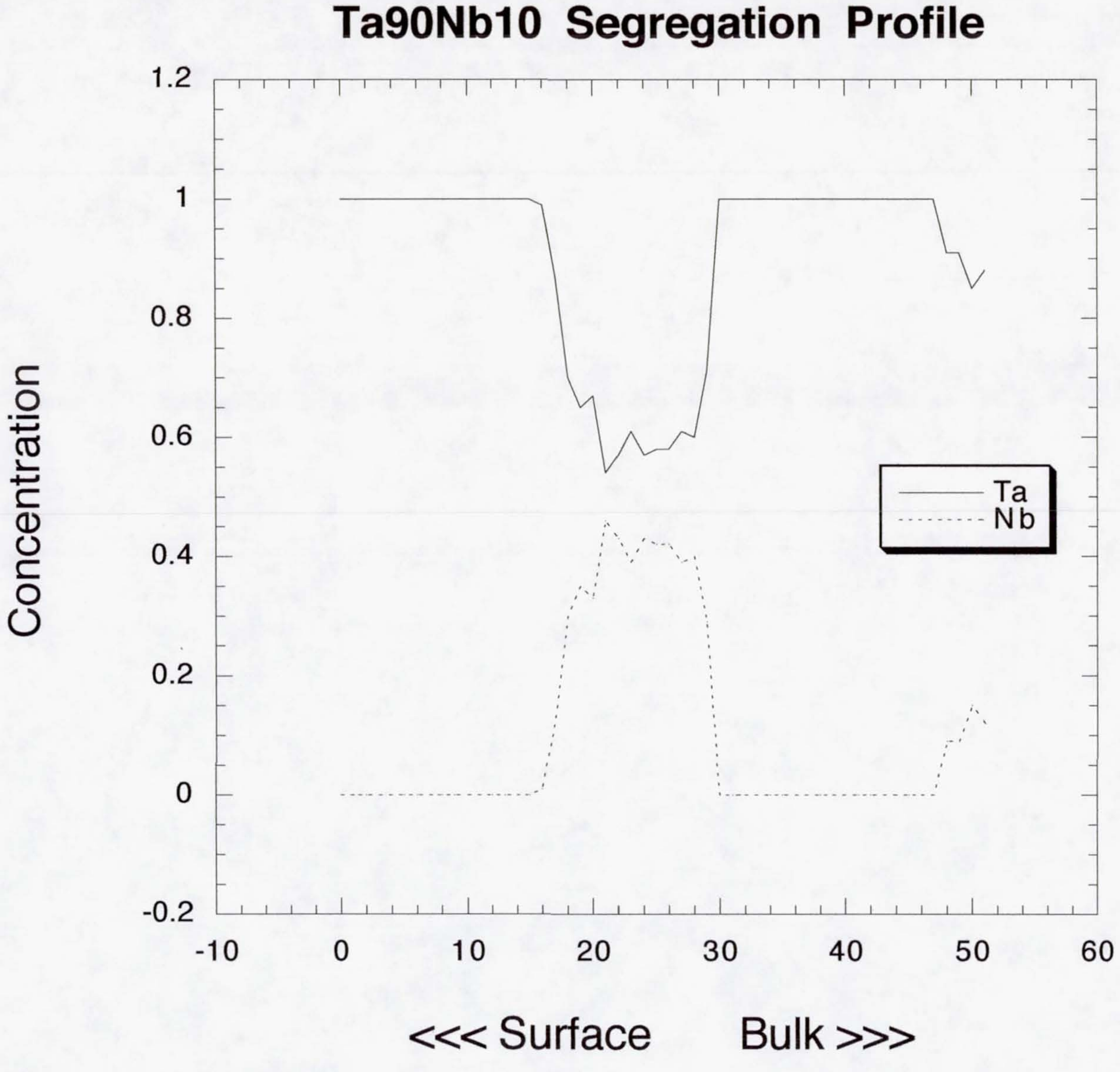

Ta90Nb10 Segregation Profile
Concentration
1.2
1
0.8
0.6
0.4
0.2
0
-0.2
-10
0
10
20
30
40
50
60
<<< Surface Bulk >>>
Ta
Nb

FIG 6

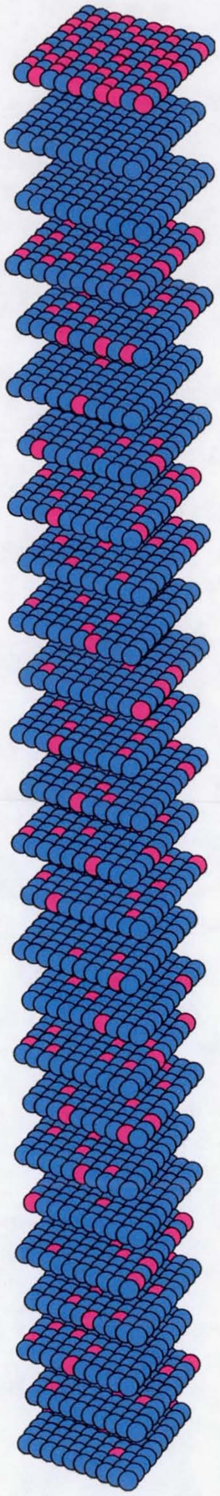


Fig 6a

Ta 10 Nb 90

Ta RED
Nb BLUE

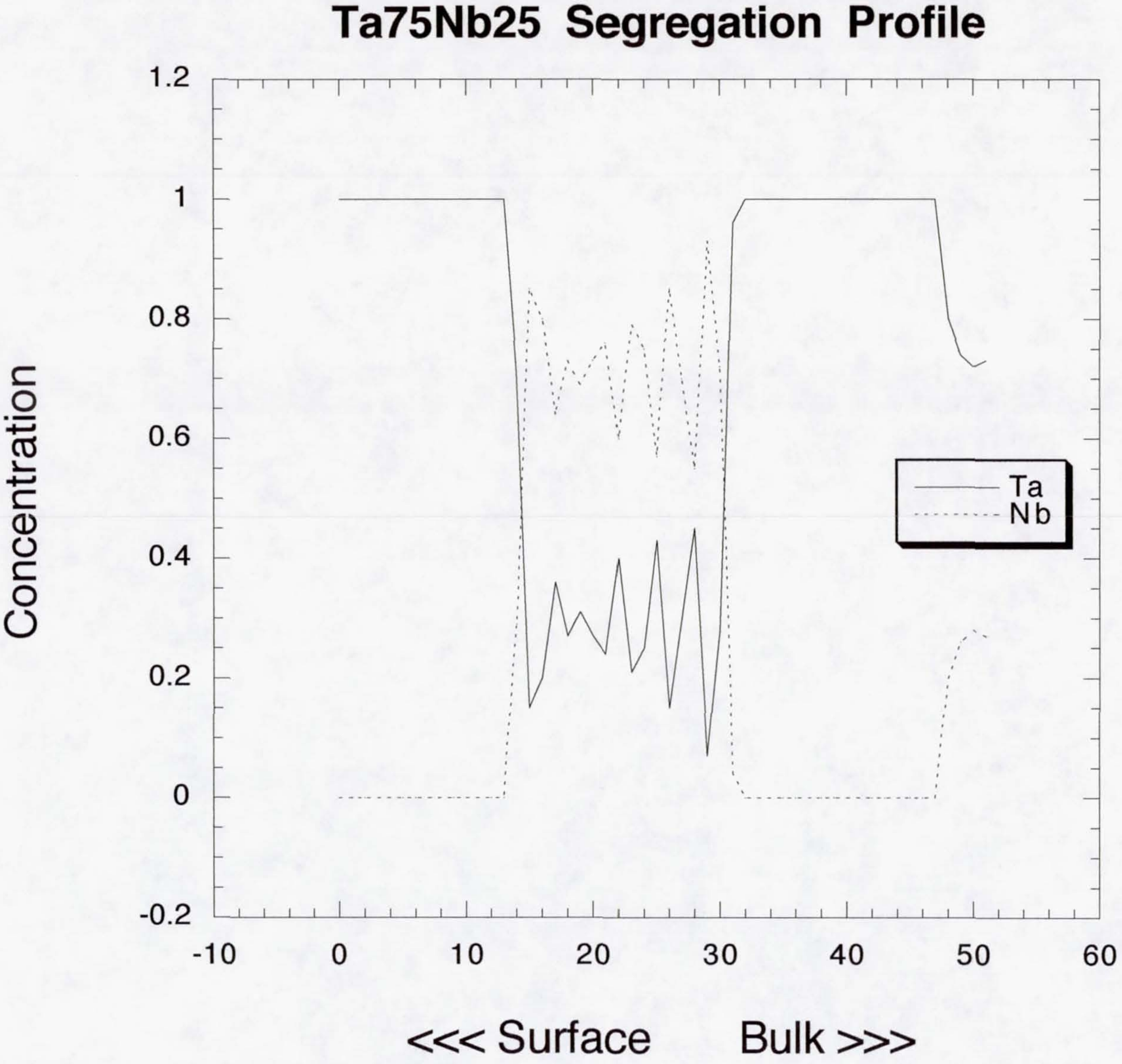

Ta75Nb25 Segregation Profile
Concentration
1.2
1
0.8
0.6
0.4
0.2
0
-0.2
-10
0
10
20
30
40
50
60
<<< Surface Bulk >>>
Ta
Nb

FIG 7

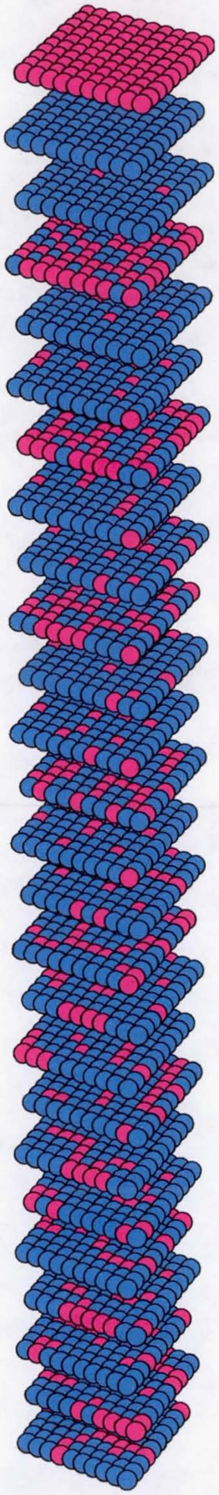


Fig 7a

Ta 25Nb75

Ta RED Nb BLUE

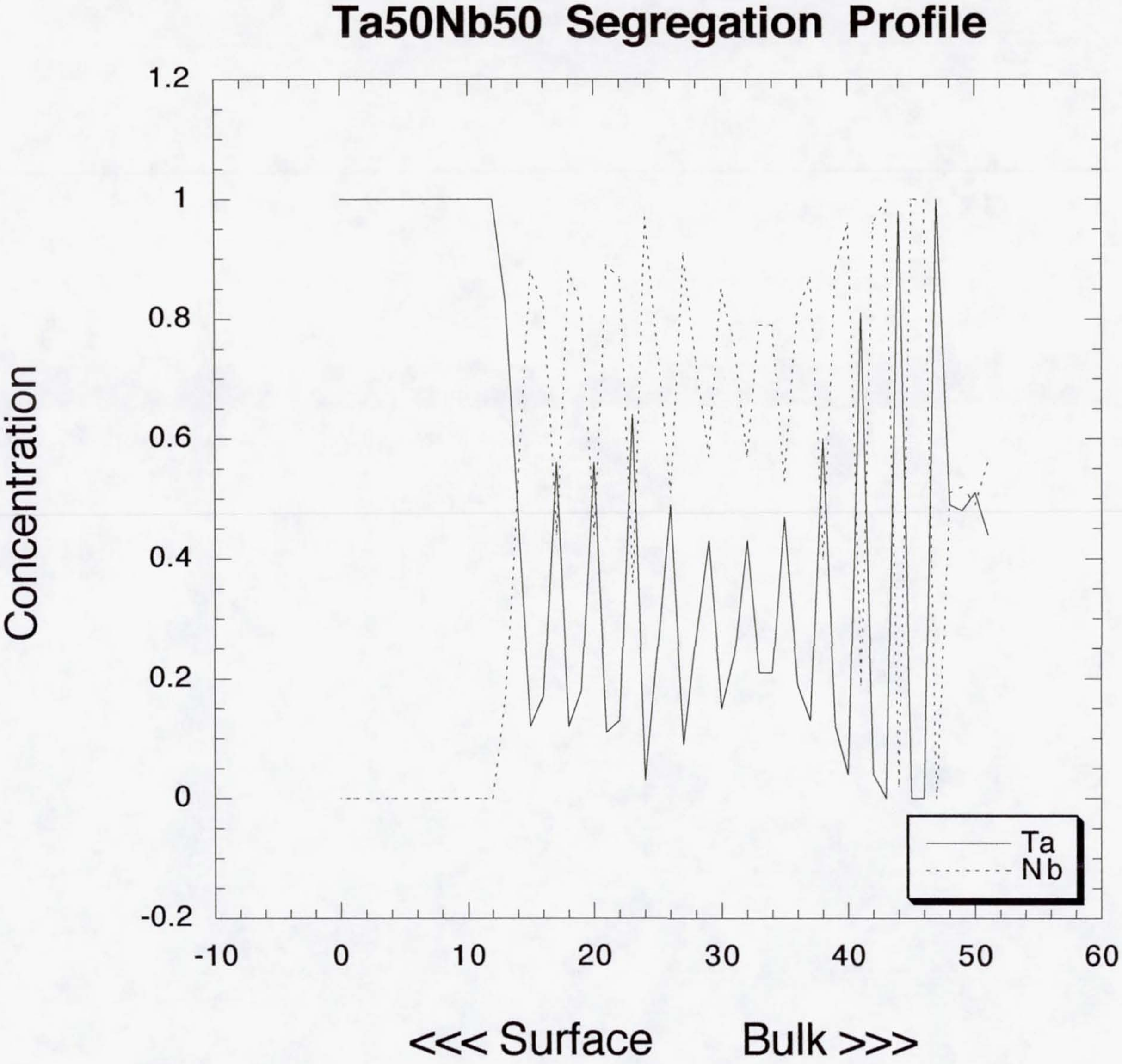

Ta50Nb50 Segregation Profile
1.2
1
0.8
0.6
0.4
0.2
0
-0.2
Concentration
-10
0
10
20
30
40
50
60
<<< Surface Bulk >>>
Ta
Nb

FIG 8

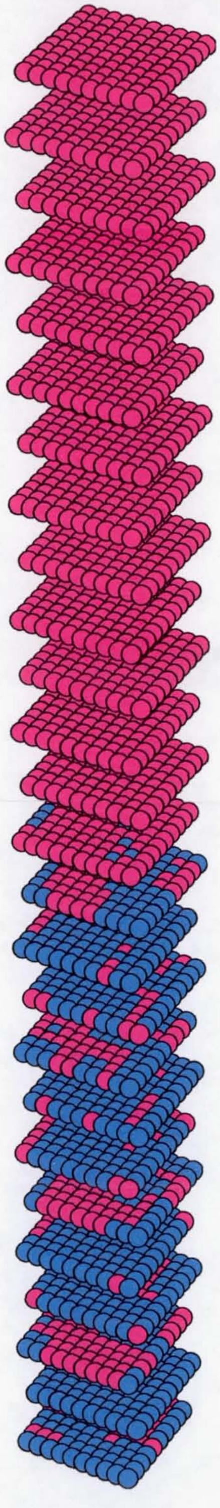


Fig 8a
Ta50Nb50
Ta RED Nb BLUE

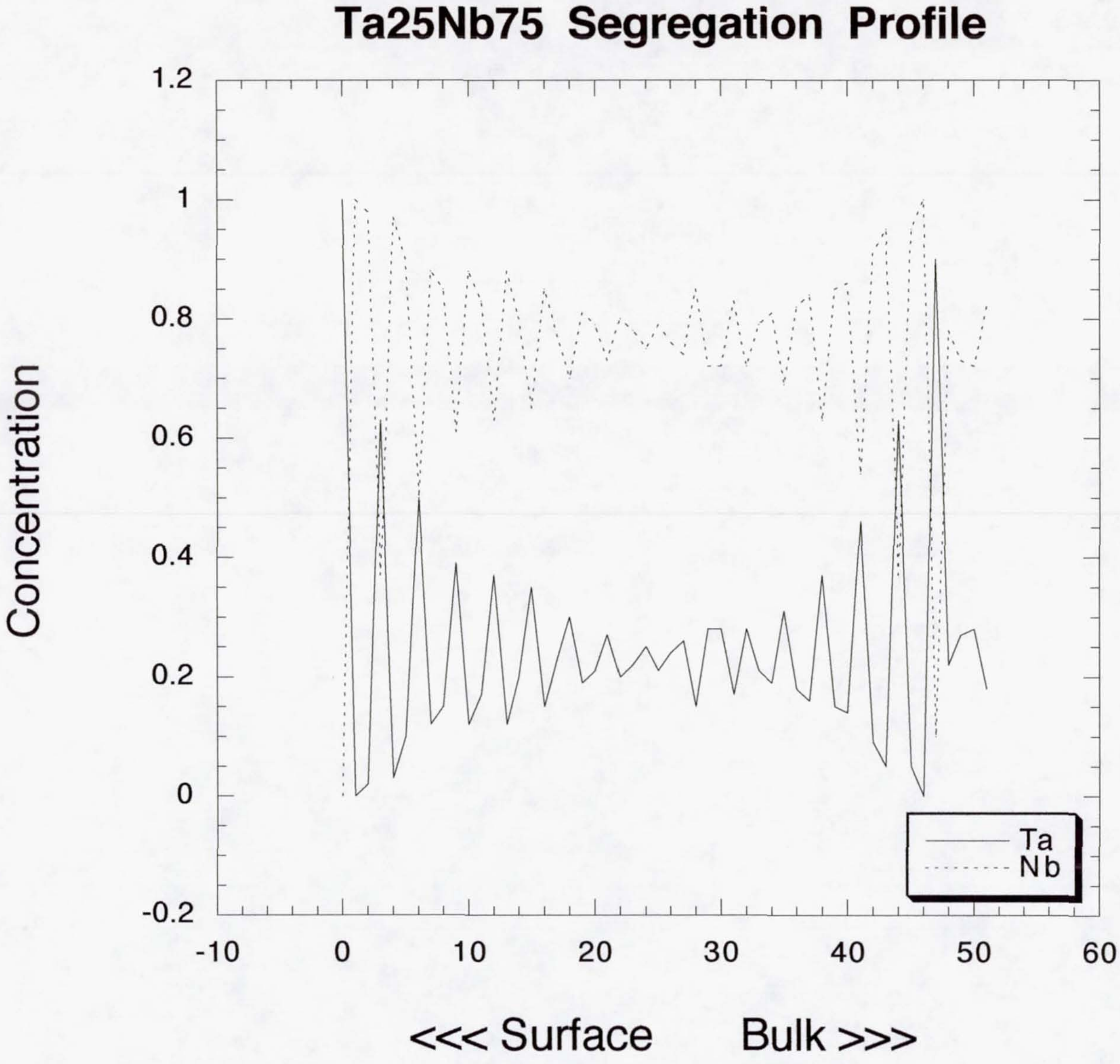

Ta25Nb75 Segregation Profile
Concentration
1.2
1
0.8
0.6
0.4
0.2
0
-0.2
-10
0
10
20
30
40
50
60
<<< Surface Bulk >>>
Ta
Nb

FIG 9

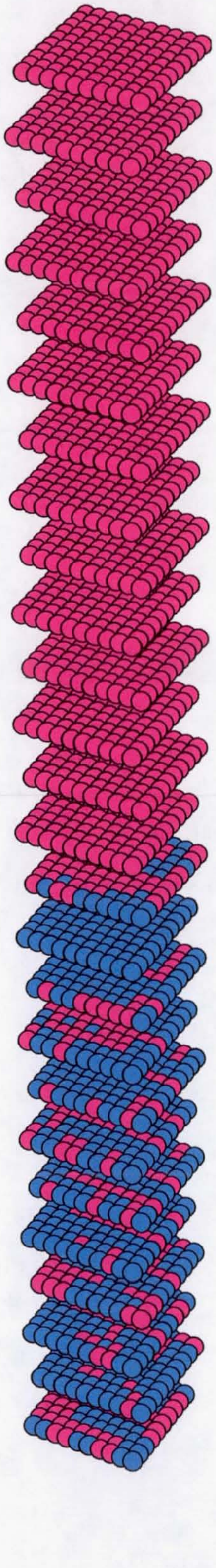


Fig 9a
Ta 75 Nb 25
Ta Red Nb Blue

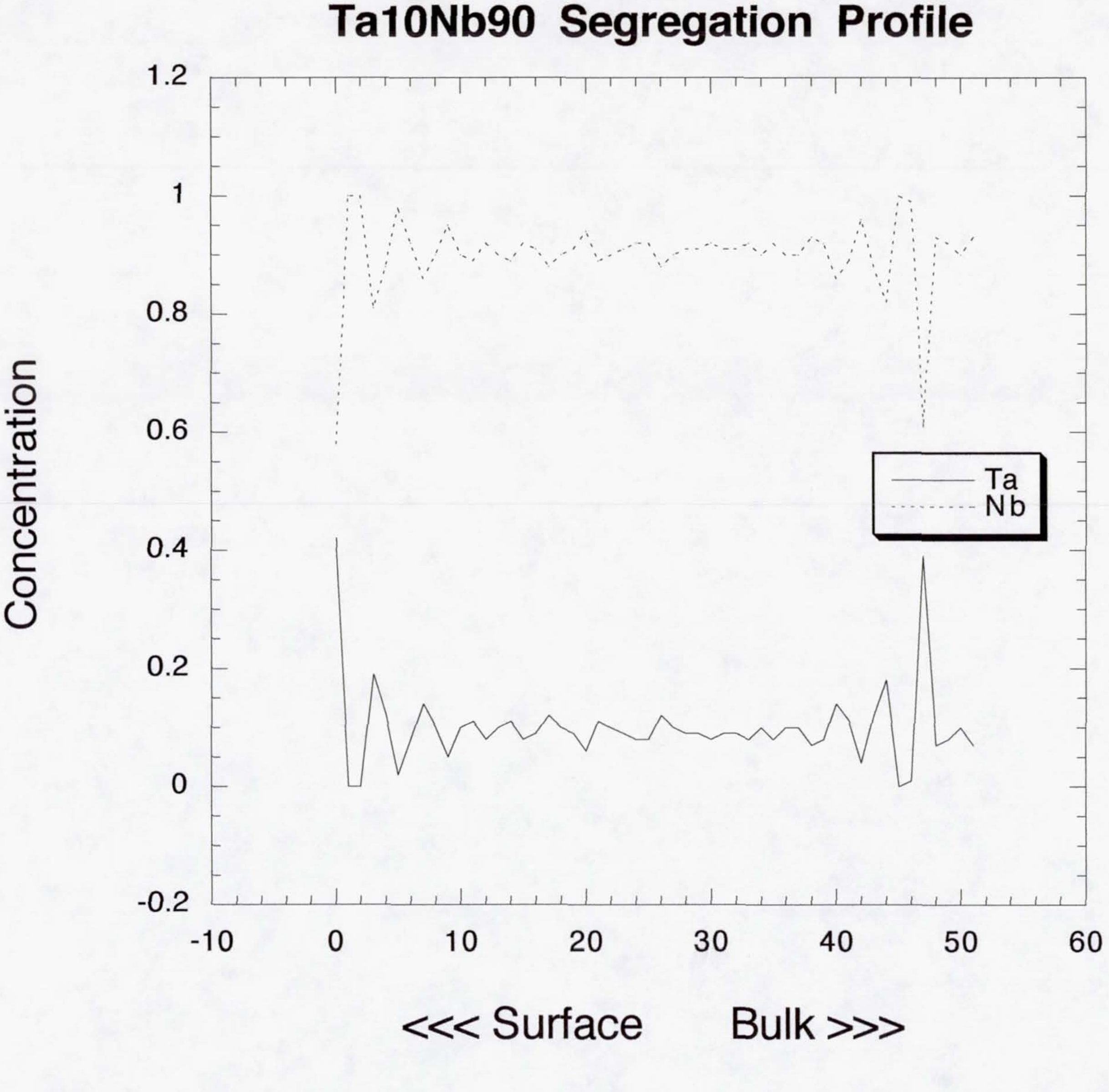

Ta10Nb90 Segregation Profile
Concentration
1.2
1
0.8
0.6
0.4
0.2
0
-0.2
-10
0
10
20
30
40
50
60
<<< Surface Bulk >>>
Ta
Nb

FIG 10

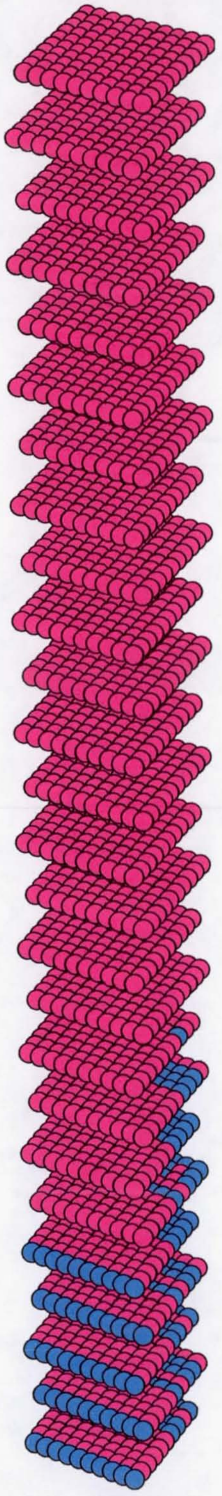


FIG 10a

Ta90Nb10

Ta RED Nb BLUE

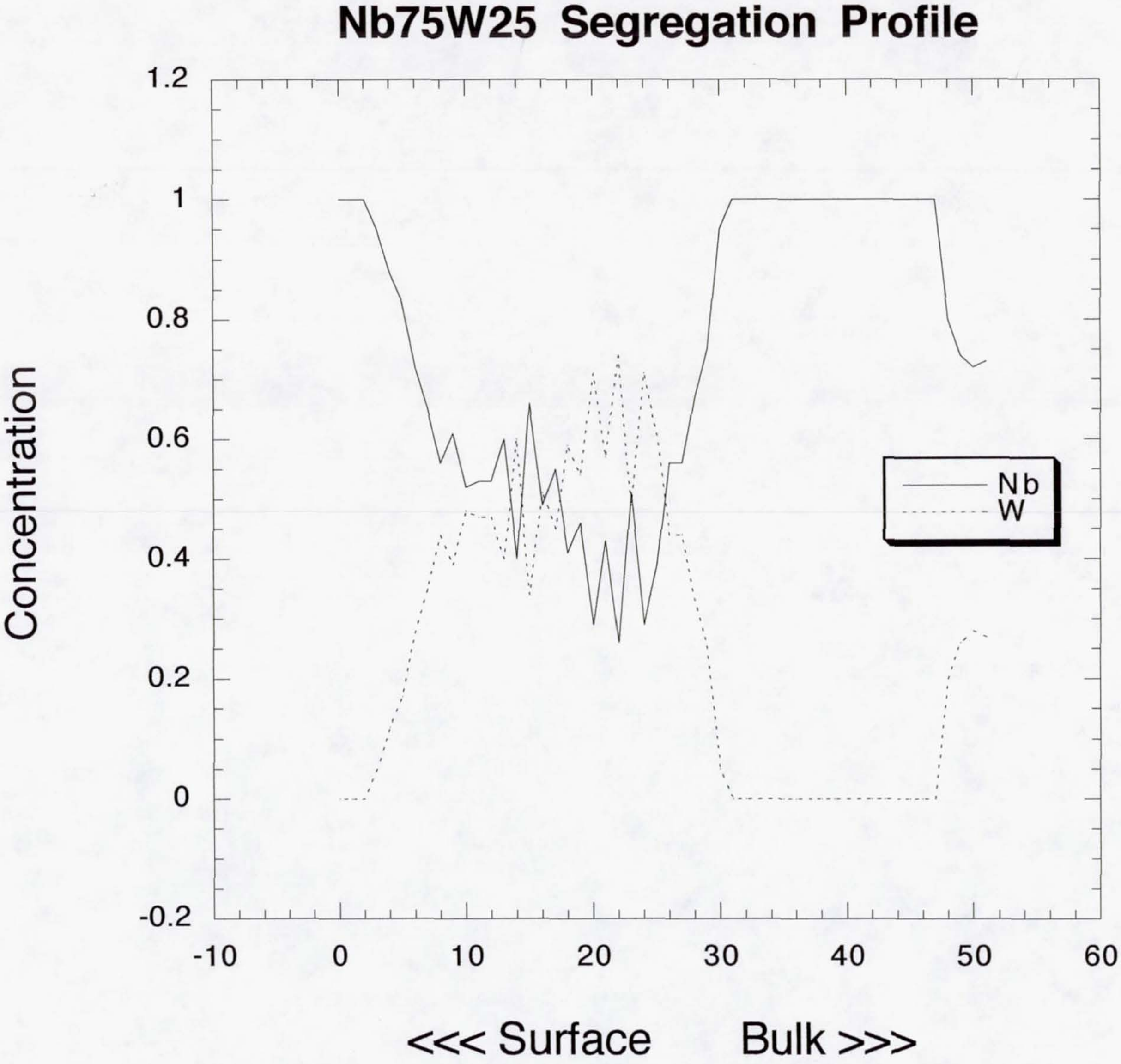

Nb75W25 Segregation Profile
Concentration
1.2
1
0.8
0.6
0.4
0.2
0
-0.2
-10
0
10
20
30
40
50
60
<<< Surface Bulk >>>
Nb
W

FIG 11

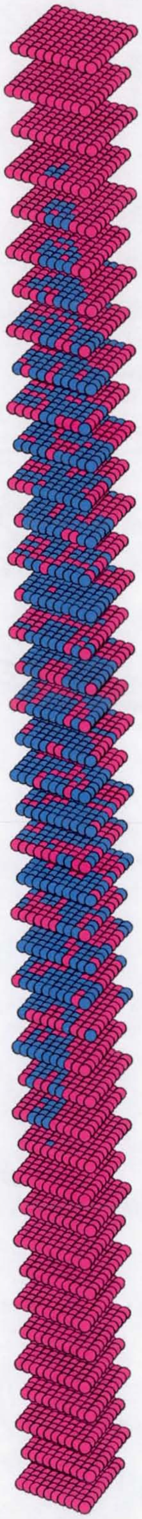


Fig 11a
Nb 75 W 25
Nb RED W BLUE

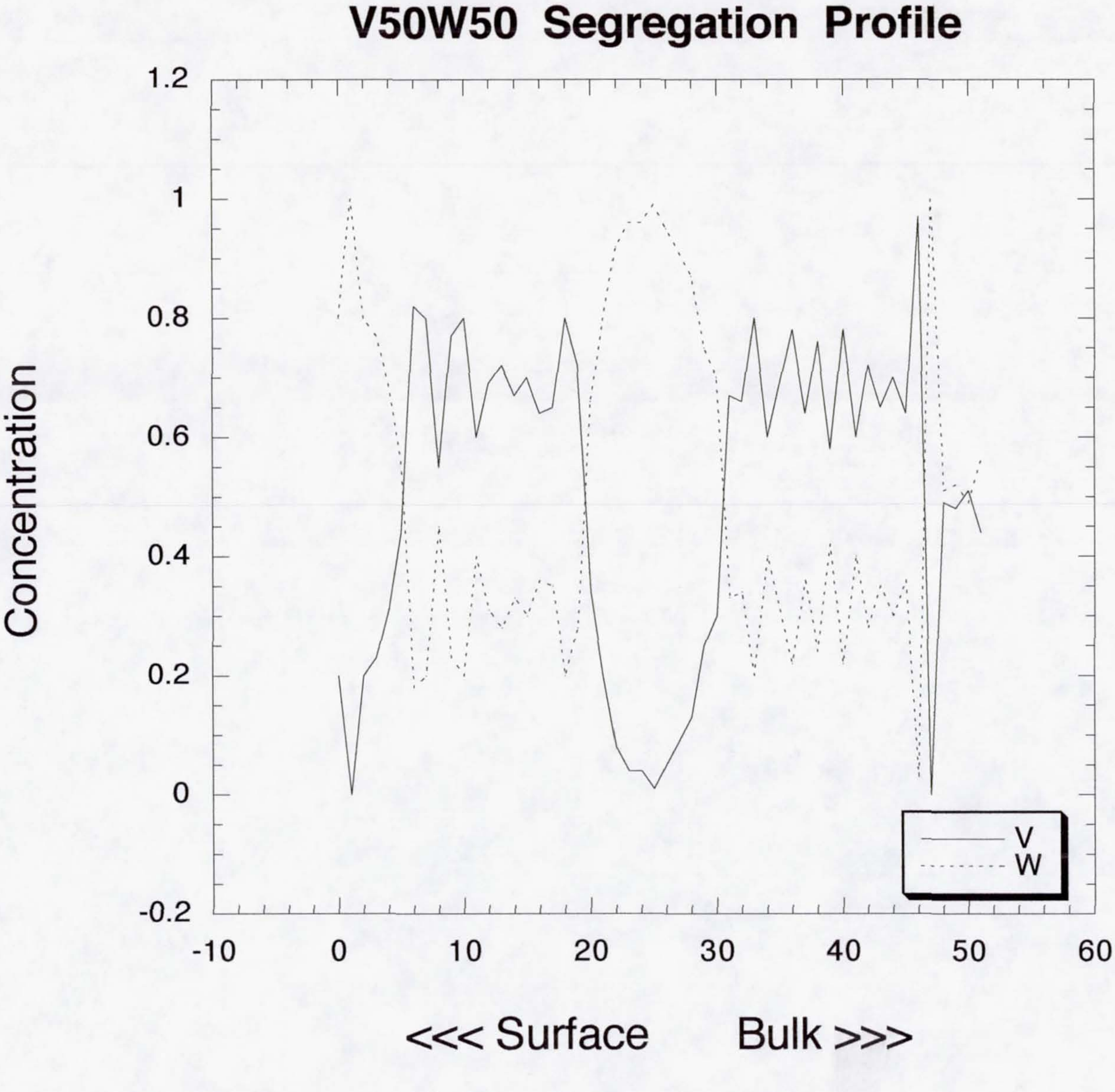

V50W50 Segregation Profile
Concentration
1.2
1
0.8
0.6
0.4
0.2
0
-0.2
-10
0
10
20
30
40
50
60
<<< Surface
Bulk >>>
V
W

FIG 12

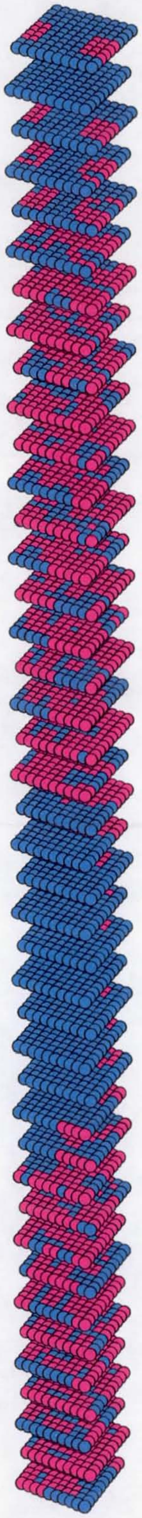


Fig 12a
V50 W50
VRED WBLUE

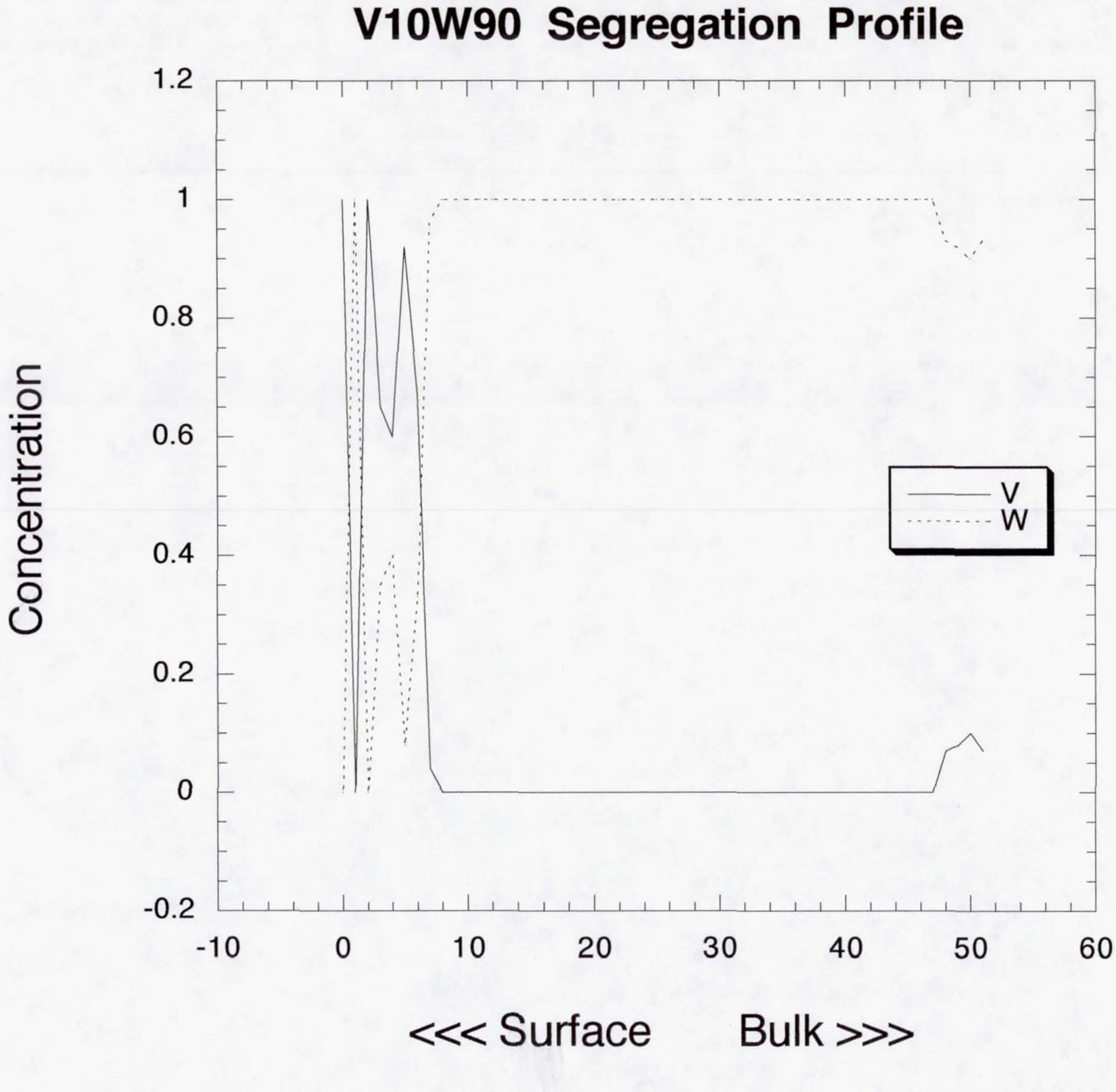

V10W90 Segregation Profile
Concentration
1.2
1
0.8
0.6
0.4
0.2
0
-0.2
-10
0
10
20
30
40
50
60
<<< Surface Bulk >>>
V
W

Fig 13

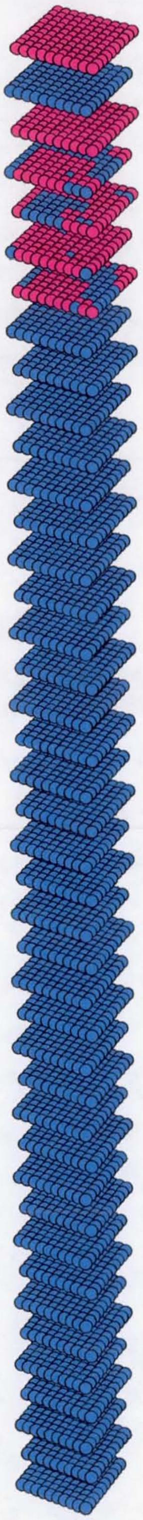


Fig 13a
V10 W90
V RED W BLUE

Conclusions

Segregation behavior from dilute heats of segregation, strain-dependent heats, and Monte Carlo simulation are in good agreement. While there is not a great deal of experimental data for the systems studied, the excellent agreement between experiment and earlier segregation predictions for fcc binaries (ref) using the BFS method suggests that this method may provide accurate results with bcc systems as well.

Somewhat surprisingly, even the heat of segregation computed in the dilute limit is a good indicator of the segregation behavior.

The good agreement between the predictions of the dilute-limit heats and the strain-dependent ones means that little additional information is gained from the strain-dependent calculations.

To obtain a level of detail comparable to that provided by the strain-dependent calculations, heats of segregation can be calculated using computational cells that have been equilibrated using the Monte Carlo scheme described above.

The MC calculations show a rich spectrum of surface and bulk behavior.