



Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

RECEIVED
LAWRENCE
BERKELEY LABORATORY

FEB 1 1982

LIBRARY AND
DOCUMENTS SECTION

Materials & Molecular Research Division

ON THE MORPHOLOGY OF GRAIN BOUNDARY SEGREGATION:
EFFECT OF GRAIN BOUNDARY STRUCTURE IN Al-Zn ALLOYS

José Mauro Briceño-Valero
(Ph.D. thesis)

November 1981

TWO-WEEK LOAN COPY

*This is a Library Circulating Copy
which may be borrowed for two weeks.
For a personal retention copy, call
Tech. Info. División, Ext. 6782*



LBL-13626
c.d

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

ON THE MORPHOLOGY OF GRAIN BOUNDARY SEGREGATION:
EFFECT OF GRAIN BOUNDARY STRUCTURE IN Al-Zn ALLOYS

José Mauro Briceño-Valero

Ph.D. Thesis

November 1981

Materials and Molecular Research Division
Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720

This work was supported by the Division of Materials Sciences,
Office of Basic Energy Sciences of the U.S. Department of Energy
under Contract No. W-7405-ENG-48.

TO:

My parents, who instilled in me the love to study.

My wife, Francelina, whose love, tenderness, encouragement, dedication and patience have been always present.

My daughter, Josmar, whose sweetness and dear companionship marked indelible prints in a transcendent part of my life.

My son, Mauro, who came at the near completion of this work, encouraging me to continue with more enthusiasm and who brought pleasant memories that last forever.

Berkeley, November 1981

CONTENTS

	page
ABSTRACT	iii
1. INTRODUCTION	1
2. THEORY	5
2.1. Grain Boundary Segregation	5
2.2. Grain Boundary Structure	9
2.2.1. Defects in Grain Boundaries	12
2.3. X-Ray Generation in the Electron Microscope	13
3. GB STRUCTURE AND SEGREGATION: BACKGROUND OF THE PROBLEM	17
4. EXPERIMENTAL PROCEDURE	20
4.1. Material Fabrication And Treatment	20
4.1.1. Bycrystal Preparation	20
4.1.2. Heat Treatment	21
4.1.3. Preparation of Specimens for the Electron Microscope	21
4.2. Microscope Preparation	22
4.2.1. Scanning Transmission Electron Microscopy	22
4.2.2. Transmission Electron Microscope	23
4.3. Making the Analysis	24
4.3.1. Choice of the Specimen	24
4.3.2. Focusing The Electron Beam	24
4.3.3. Obtaining X-Ray Signals	24
4.3.4. Foil Thickness Measurements	25

5. EXPERIMENTAL RESULTS	28
5.1. Tabulation of Boundaries Studied	28
5.2. Effect of Annealing Temperature	29
5.3. Solute Distribution along the Grain Boundary	29
5.4. Effect of Grain Boundary Structure	31
5.5. Effect of Electron Probe Size	32
6. ANALYSIS OF THE RESULTS AND DISCUSSION	33
6.1. Effect of Orientation Relationship on GB Segregation	33
6.2. Effect of Grain Boundary Structure	34
6.3. Effect of Temperature on grain Boundary Segregation	38
6.4. Comments on Technique	39
7. CONCLUSIONS	41
ACKNOWLEDGEMENTS	43
APPENDIX A: Determination of the Axis/Angle Pair of a Grain Boundary	44
APPENDIX B: Activation Energy Related to the Segregation Phenomenon	46
APPENDIX C: Error Analysis from X-Ray Data	48
REFERENCES	49
FIGURE CAPTIONS	56

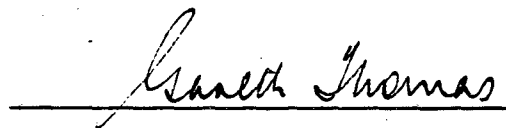
**ON THE MORPHOLOGY OF GRAIN BOUNDARY SEGREGATION:
EFFECT OF GRAIN BOUNDARY STRUCTURE IN Al-Zn ALLOYS**

José Mauro Briceño-Valero

Ph.D.

Materials Science and
Mineral Engineering Dept.

Sponsors: Universidad de Los Andes,
Mérida-Venezuela.
Division of Matls. Science,
U. S. Dept. of Energy.



Prof. Gareth Thomas
Chairman of Committee

ABSTRACT

A high spatial resolution study of the behavior of *Zn* solute in *Al* bicrystals has been conducted using x-ray energy-dispersive spectroscopy (EDS) in a TEM/STEM instrument.

The effects of relative crystal orientation were studied in order to establish the relationship between the crystallography and structure of high angle grain boundaries and grain boundary segregation phenomena. It was observed that both structure and heat treatment affect the distribution of solute at the grain boundary.

Specimens subjected to short annealing cycles were found to exhibit a periodic distribution of *Zn* along the grain boundary plane prior to the appearance of any evidence suggesting precipitation had occurred. The periodicity of the segregation event was found in several cases to agree with the expected intervals of atomic relaxations in the O-lattice. Also, the spatial distribution of certain extrinsic defects at the grain boundary was found to bear a direct relationship with higher accumulations of *Zn* solute along the boundary plane. It was found that the segregation phenomenon bears a similar relationship as the grain boundary energy to the angle of misorientation for [110] tilt boundaries.

An exponential temperature dependence of the segregation event was also observed, allowing a determination of the activation energy to be made from this relationship. Anomalous behavior at high temperatures was explained on the basis of a deviation from equilibrium coupled with the formation of impurity-vacancy pairs and higher-order complexes. The low temperature data suggests that the activation energy of grain boundary segregation is not solely due to the equivalent strain release in the classical McLean theory.

1. INTRODUCTION

Local fluctuations in solute composition at external surfaces and solid-solid interfaces (grain boundaries, stacking faults, antiphase boundaries) are generally referred as to *interfacial segregation*. This phenomenon was treated formally by J. Willard Gibbs^[1] who showed that, as a rule, solute elements which decrease the surface tension should concentrate at the surface, and those which increase the surface tension should avoid the surface. However, at least two recent developments have provided the principal impetus for renewed interest in this phenomenon. First, the capability for chemical characterization of interfaces has improved dramatically over the last decade as a result of the development of sensitive spectroscopical techniques of high resolution. Second, a growing technological need has emerged to develop improved or alternative materials after recognizing the significant influence that the chemistry of interfaces, and grain boundaries (GB) in particular, exerts upon a variety of properties, both physical and mechanical, in a wide spectrum of materials.^[2-7]

Although the segregation phenomenon has been studied mostly in connection with the effect it may have on GB cohesion in certain alloys,^[8] it is clear that a wide range of metallurgical and physical properties and processes can be affected; in some cases segregation is a governing factor, while in others it is an important contributory factor. Fig. 1 illustrates many of these material phenomena involving segregation. The phenomena comprise two broad categories: one in which some aspects of bonding or cohesion are involved and which relates to the mechanical strength of the material; the other in which the segregant species may affect some kinetic-based phenomena such as precipitation of second phase particles at the GB, surface oxidation, migration of GB's, and diffusion along GB's.^[9-15]

A distinction must be made between *equilibrium* segregation described by equilibrium thermodynamics and *non-equilibrium* segregation which is a consequence of kinetic processes, where solute interactions with point defects play an important role prior to

achieving thermal equilibrium.^[2,16,17] The segregation of solute atoms to GB's is often of the equilibrium type. This type of segregation occurs because there exist certain locations for solute atoms at GB's which are energetically more favorable than the normal sites for solute atoms in the solvent lattice.^[18] At GB's some atoms have more room around them and others have less room around them than would be provided by the undistorted lattice. Large solute atoms will tend to replace the former and small ones the latter.

Irrespective of the models which describe GB segregation on an atomic scale, it is generally agreed that the segregation is localized to within 10 nm of the boundary.^[19] Also, such segregation does not result in any detectable change in microstructure.^[20-23] Therefore a direct measurement of GB segregation tends to be difficult. However, such difficulties have been overcome in part with the advent of a range of microanalytical techniques.^[24]

The most widely used technique in the study of equilibrium segregation to GB's is Auger Electron Spectroscopy (AES). This technique, however, together with the other surface specific techniques, suffers from the disadvantage that GB microanalysis can be carried out only on a grain surface. Consequently, the specimen has to be fractured in an intergranular mode under a very high vacuum ($<10^{-6}$ Torr). Not only are such procedures both elaborate and difficult, but the spatial resolution is in the μm range and does not permit any direct correlation with detailed microstructure. Furthermore, segregation profiles up to the surface may only be obtained by sequential *ion-sputtering*. Such sputtering can introduce error due to preferential removal or redeposition of particular species.^[25,28]

Another generally useful technique for chemical analysis and simultaneous microstructural examination is electron probe microanalysis using characteristic X-ray emissions. But its spatial resolution (1000 nm in bulk specimens and 100 nm in thin foils) is inadequate when one requires the quantitative measurement of localized GB compositions, i.e., concentration gradients in the GB itself, in an attempt to localize the sites where the solute

atoms prefer to go. This type of analysis requires a high level of spatial resolution coupled with high sensitivity devices.

The introduction of the *scanning transmission electron microscope* (STEM) has eliminated the resolution problems inherent in the techniques described above. High intensity electron probes coupled with an energy dispersive spectrometer (EDS) have allowed X-ray microanalysis from areas as small as 3–20 nm in diameter on thin transmission electron microscope foils. Analysis can be carried out for elements with atomic number >11 without the need, in most cases, to correct for either absorption or fluorescence.^[29] Ultimately, the resolution of this technique depends much on the brightness of the electron source, as well as the size of the electron beam. When STEM analysis is complemented with conventional transmission electron microscopy (CTEM), weak beam (WB) imaging and convergent beam diffraction (CBD), GB segregation can be thoroughly studied.

Somewhat more sophistication can be introduced in a study of this nature by employing techniques of direct lattice resolution, electron energy loss spectroscopy or critical voltage effects. These methods are summarized by Thomas and Goringe^[30] and require substantial care in both execution and interpretation. As such they have not been generally used in studies which require larger statistical samplings. The present study seeks to classify a microstructural event on a statistical basis by employing TEM imaging and STEM microanalysis.

The objective of the present research is to understand the relationship between GB segregation and GB structure for the particular case of the *Al-Zn* system. The *Al-Zn* system was chosen here for its excellent transparency to electrons and the wide variety of thermodynamic parameters (including impurity and self-diffusivities, impurity-vacancy binding energies) previously characterized in a large number of experiments which are available in the current literature. Also the relative position of the *Zn* and *Al* peaks in the X-ray energy spectrum makes their detection straightforward. The study focusses here on the behavior of

Zn-solute atoms along the *Al*-GB's after short annealing cycles and prior to the appearance of any evidence suggesting precipitation (see phase diagram in Fig. 41). The results of these studies are interpreted in terms of current models of GB structure.

2. THEORY

2.1. Grain Boundary Segregation

The theory of solute adsorption, or segregation, to interfaces was first treated by Gibbs.^[1] In his model, he assumes the interface, in this case a grain boundary, to be represented by a second phase having only area and no thickness. The phase on either side of the interface is assumed to be of constant composition and the interface is assumed to contain all of the adsorbed solute. The model used in developing the Gibbs adsorption equation is depicted schematically in Fig. 2(a) along with a schematic depiction of true segregation and precipitation of a second phase. Using the assumptions briefly outlined above, Gibbs determined the following relationship:

$$d\gamma = -\sum \Gamma_i d\mu_i \quad (1)$$

where μ_i is the chemical potentials of the i^{th} component of a system, Γ_i is the excess of the i^{th} component at the interface in that system and γ is the surface tension of the interface. The principal difficulty encountered in using the Gibbs equation, or any other relation arrived at via classical thermodynamics, is that the equilibrium surface tension, γ , must be known as a function of bulk composition in order to determine Γ_i of the i^{th} component. This information is rarely available for metallic systems.

An alternative treatment of GB segregation has been developed by McLean,^[31] based on the original work of Gibbs,^[1] Mehl^[32] and Gorsky.^[33] McLean estimated the equilibrium concentration of solute atoms at a GB in the following manner. Assuming that there are N undistorted lattice sites with P solute atoms distributed among them, and n distorted interface sites with p solute atoms distributed among them, the free energy due to the solute atoms can be described by:

$$G = pe + PE - RT \ln W \quad (2)$$

where $RT \ln W$ is the configurational entropy caused by the solute atoms, and is expressed

as:

$$\ln W = \ln n! N! - \ln (n-p)! p! (N-P)! P!. \quad (3)$$

E is the energy of a solute atom in one of the N initially undistorted sites and e is the energy of a solute atom in one of the initially distorted sites.

By minimization of the free energy

$$\frac{p}{n-p} = \frac{P}{N-P} \exp\left(\frac{E-e}{RT}\right) \quad (4)$$

or, expressed again in a more useful form:

$$\frac{x_b}{x_{b_0} - x_b} = \frac{x_c}{1 - x_c} \exp\left(\frac{E_1}{RT}\right) \quad (5)$$

where x_b is the solute molar concentration at the grain boundary and x_{b_0} is the saturation value of x_b (which generally seems to be about one monolayer). E_1 is the free energy of adsorption at the GB. This relationship has the same behavior as that described in the Langmuir theory of gas adsorption^[34] and the Susuki^[35] theory for adsorption to stacking faults. Examples of measurements obeying this theory occur in the literature for segregation to GB's^[36] and to free surfaces.^[37]

One of the main difficulties that arises from the Mclean theory is the need to calculate the value of E_1 . McLean derived some values of E_1 using elasticity theory to calculate the release of strain energy in the matrix due to the difference in atomic volume between the solute and the solvent. Friedler^[38] made a derivation of that strain energy in a way which makes the calculations easier than the way presented by McLean. By combining both McLean and Friedler's ideas about energy of adsorption to GB's the result is:

$$\Delta H_e = -E_{el} = \frac{-24\pi KGr_0r_1(r_1-r_0)^2}{3Kr_1+4Gr_0} \quad (6)$$

where K is the solute bulk modulus, G is the solvent shear modulus, r_0 and r_1 are the

appropriate radii for solvent and solute atoms in their pure states, respectively.

The above approach for calculating E_1 is unlikely to give even an approximate estimate, unless the mismatch between the solute and the solvent atoms is very large, since it is equivalent to omitting electronic and valency effects in normal alloy formation. An alternative formulation of the Langmuir-type adsorption presented by Brunaver et.al.^[39] overcomes the above mentioned difficulty.

This new adsorption theory known better as truncated BET¹ adsorption theory served as a basis for Seah and Hondros^[37] to derive a similar relationship to that of equation 5. Thus,

$$\frac{x_b}{x_{b_0} - x_b} = \frac{x_c}{x_{c_0}} \exp(E/RT) \quad (7)$$

where E is an energy term of segregation and x_{c_0} is the solute solubility limit. The important contribution here is the introduction of the term x_{c_0} , which for slightly soluble substances is given by

$$x_{c_0} = \exp(-E_L/RT) \quad (8)$$

Now $E(=E_1 - E_L)$ is the difference between the free energy of adsorption of the first layer and the free energy of condensation of successive layers. With this new model a better appreciation can be obtained of the magnitude of E_1 and the role of x_{c_0} . In the case of dilute systems, since $E \ll E_1$ or E_L in systems of low solubility and is less than 20 KJ/mol, then

$$\left(\frac{x_b}{x_{b_0}}\right) \left(\frac{1}{x_c}\right) = \frac{C}{x_{c_0}} \quad (9)$$

where C typically has a value of 1-20. The term of the left hand side is known as GB enrichment factor B_0 . The level of complexity in the theory of GB segregation increases as more variables are taken into account. Thus the consideration of the mutual interaction of

the adsorbate with itself leads to a new expression for E_1 .^[40]

$$E_1 = E_1^0 - Z\omega \frac{x_b}{x_{b_0}} \quad (10)$$

where Z is the coordination number for the adsorbed or segregated species to the GB and ω is the interaction energy between pairs of neighbors.

So far, the above theories of GB segregation are specific to dilute systems. In the case of non-dilute systems, William and Mason^[41] derived a relation similar to equation 5 where E_1 is given by:

$$E_1 = \left(-\frac{Z_v}{Z}\right) (H_{Sub}^A - H_{Sub}^B) \quad (11)$$

where Z_v is the loss of coordination number Z at the surface and H_{Sub}^A and H_{Sub}^B are the enthalpies of sublimation of bulk A and bulk B , respectively, of a binary AB . William and Mason's theory was further developed to include the regular solution parameter Ω which describes the chemical interaction between the two constituents of the binary system, i.e.

$$2H_{Sub}^{AB} = (H_{Sub}^A + H_{Sub}^B) + Z\Omega \quad (12)$$

and

$$E_1 = \frac{(-Z_v)}{Z} (H_{Sub}^A - H_{Sub}^B) + 2\Omega_b [(Z - 2Z_v)(x_b - x_c) - Z_v(x_c - 1/2)] \quad (13)$$

A better insight into GB segregation theory can be gained by considering the two modifications to the latter model proposed by Winblatt and Ku,^[42] These investigators argued that the surface energies of the pure elements in the alloy give a better representation of the unsatisfied bonds than the $Z_v H_{Sub}/Z$ terms, and a strain energy associated with the different sizes of the solute and solvent atoms should be added to the free energy of segregation. It was expected that the strain term would be meaningful in the case of large atomic differences between the solute and solvent. This was discussed by Tsai et.al.^[43] The

¹BET stands for an abbreviation of Brunauer, Emmett and Teller.^[39]

last ideas reported here about the free energy of segregation found support and experimental evidence after a recent review study done by Seah^[43] on thirty-two published results for different systems.

Regression analysis has shown that the strain term modifies the coefficients of the terms in equation 13 to give the following relationship:

$$E_1 = -0.64(\gamma_s^A - \gamma_s^B) + 1.86\Omega + 4.64 \times 10^7 D a (\Delta a)^2 \quad \text{KJ/mol} \quad (14)$$

The last term represents the strain release term with D unity if Δa is positive, i.e. if the solute atom is larger than the solvent atom, and D zero, otherwise. The size of the solvent atom, a , and Δa are both given in nm .

2.2. Grain Boundary Structure

The structure of GB's in metallic materials has been the object of research ever since it became known that they had importance in controlling phenomena such as low and high temperature fracture, creep and corrosion. Since then, many models have been proposed to explain the relationship between GB structure and these phenomena.

The modern ideas of GB structure, unlike earlier models,^[46-52] tend to begin by considering the crystallographic relationship of the crystals delimiting the boundary and putting emphasis on the importance of periodic structure along the boundary.^[53-58] Various ways of defining this crystallography exist, but the most popular version consists of its description in terms of the so called *axis/angle pair* ($\langle h k l \rangle / \Theta$) and the boundary normal. In this description, the axis of misorientation $\langle h k l \rangle$ is a direction in the two crystals which has the same crystallographic indices and about which a rotation of Θ degrees of one crystal with respect to the other describes the relative orientation of the two crystals. (Fig. 3 and 4 give a definition of these parameters for the particular case of a symmetrical tilt boundary).

At specific values of $\langle h k l \rangle / \Theta$ certain lattice points of each crystal coincide. The space lattice made up of the coincidence sites has a periodicity of $\frac{1}{\Sigma}$. This concept of the

coincidence site lattice, CSL, (originally developed by Kronberg and Wilson,^[59] and Frank^[60] and elaborated upon by Brandon et.al.,^[54] Brandon^[61] and Ranganathan^[62]) has become very popular when studying the structure of GB's.^[55]

For the case of cubic crystal, Ranganathan^[62] has shown that a CSL can be generated if

$$\Theta = 2 \tan^{-1} \left(\frac{y}{x} \right) \sqrt{N} \quad (15)$$

where x and y are integer coordinates and N is given by

$$N = h^2 + k^2 + l^2 \quad (16)$$

The above operation leads to the definition of the generating function:

$$\Sigma = x^2 + Ny^2 \quad (17)$$

The multiplicity, Σ , is defined as the ratio of the area of the coincidence lattice cell to that of the original cell, and must have only odd values in the cubic system. Therefore, even values of Σ are divided by the correct multiple of 2 to yield an odd value.

Much work has been done on geometrical constructions of GB's following the CSL model. This has led to tables which have been published containing the axis/angle pairs for multiplicities up to $\Sigma = 19$ for cubic systems.^[63] More complete tables, with values of Σ up to 57 are reported elsewhere.^[57,64-66]

The concept of coincidence was generalized by Bollman^[55] to include not only lattice points but their interstices, as well. These new locations lie on a sub-lattice of the CSL which is called the O-Lattice. In this new lattice, each one of its points (O-lattice points) may be used as an origin for the transformation linking the two lattices; therefore the O-Lattice is considered as a lattice of origins. This model has been successfully applied in the description of the dislocation structure of certain high angle GB's by extrapolating the concept developed by Frank^[68] in the case of low angle grain boundaries. As will be described

later, a powerful application of this model occurs of the analysis of high angle grain boundary structure with further derivation of Burgers vectors for perfect grain boundary dislocations using the concept of the DSC-Lattice, i.e., a displacement of lattice-1 with respect to lattice-2 by a pattern shift which is complete, or the *Displacement Shift Complete Lattice*.

The mathematical procedure for calculating the O-Lattice first involves a point to point correlation between the two lattices comprising the boundary:

$$\bar{x}^{(1L)} = A \bar{x}^{(2L)}, \quad [A] \neq 0 \quad (18)$$

where $1L$ and $2L$ refer to lattice points in grains 1 and 2 respectively, and A refers to a homogeneous linear transformation.²

Once A is known, the whole O-Lattice is determined by the solution of

$$(I - A^{-1}) \bar{x}^{(0)} = \bar{x}^{(1)} \quad (19)$$

where $\bar{x}^{(0)}$'s are the base vectors of the O-Lattice, $\bar{x}^{(1)}$'s are the base vectors of the lattice-1 and I is the identity matrix.

As can be seen from the above definitions and formulations, the O-Lattice, unlike the CSL, defines a continuous function of the transformation, and the spacing, therefore changes continuously with crystal misorientation. This lattice permits a reasonable description of the GB structure involving dislocations, and affords a means of computing structures which might be observed particularly in the transmission electron microscope (TEM).^[63]

One more important aspect regarding the crystallography of the structure of grain boundaries is contained in the so-called DSC-Lattice. This lattice when stated for a particular GB defines all the vector displacements of lattice-1 and lattice-2 with respect to each other which are possible with the condition that the over-all pattern of atoms produced by the two interpenetrating lattices remains unchanged. One advantage of using the concepts

² A is said to be a linear transformation if: $A(\bar{x} + \bar{y}) = A(\bar{x}) + A(\bar{y})$ and $A(\alpha \bar{x}) = \alpha A(\bar{x})$, where $\bar{x}$ and $\bar{y}$ are vectors and α is a scalar.

developed from this lattice is the fact that it is possible to find the Burgers vectors of all perfect GB dislocations which may exist in the boundary. A geometrical way of finding the DSC-Lattice vectors is represented in Fig. 5. For this, it is sufficient to find a set of vectors connecting atoms of lattice-1 and atoms of lattice-2. Fig. 5 shows that for the particular case of the structure defined by the parameters $\Sigma = 5$, $\langle 001 \rangle / 36.9^\circ$, the lattice spacing of the DSC-Lattice varies reciprocally with the spacing of the CSL. Thus, as the degree of coincidence matching decreases, the CSL tends to become larger while the DSC-Lattice tends to become smaller. A general description of a graphical way of finding the DSC-Lattice is reported by Balluffi^[69] while analytical methods have been reported in the literature by Bollman^[70] and Smith and Pond.^[71]

2.2.1. Defects In Grain Boundaries

Grain boundaries may contain linear and planar defects even in equilibrium conditions. There are certain ambiguities of terminology concerning line defects in GB's which, in the literature, have been referred to as lines, steps, ledges, and dislocations.^[72-74] Throughout the context of the present work, the definitions and concepts about GB defects will be those described by Varin et.al.,^[74] and which have been summarized in Fig. 6. According to this, the first classification of GB defects is based on the character of the elastic displacement field of the defects. Thus differentiation will be made between GB steps and GB dislocations. A thorough description of GB steps has been reported elsewhere.^[73]

Depending on the origin of the defect, grain boundary dislocations (GBD) can be classified as either extrinsic GBD or intrinsic GBD. Extrinsic GB dislocations are dislocations produced by external influence (plastic deformation, quenching and so on). Intrinsic GB dislocations form part of the internal structure of the GB. This scheme is similar to that reported by Balluffi et.al.^[75] The magnitude of the Burgers vectors forms another criterion of classification of the GBD's. Thus, intrinsic GBD's with lattice Burgers vectors are known as primary dislocations, while those with Burgers vectors characteristic of the DSC-

Lattice are known as secondary dislocations. The primary dislocations are found not only in low angle GB's as was thought earlier, but their presence has been suggested to be preserved even in boundaries with misorientations higher than 15 degrees.^[76-78] The secondary dislocations exist in high angle boundaries and are thought to have Burgers vectors characteristic of the CSL which they conserve,^[55] or are supposed to accommodate slight mismatch of certain low index lattice plane across the boundary.^[54,79,80]

2.3. X-Ray Generation In The Electron Microscope

X-Ray microanalysis using modern STEM is an extremely powerful analytical tool. The ability to observe and characterize the morphology, crystallography and elemental composition at regions as small as 4 nm is a major breakthrough for material characterization. In this section, the basic theory of X-ray production and some practical aspects of the use of STEM in connection with quantitative analyses from thin foils in the electron microscope are considered.

When an electron beam strikes a solid specimen a number of interactions occur, the most important of these are illustrated in Fig. 7. Each of these events can provide information about the nature of the specimen. However, the interaction which is relevant to the subject of the present work is the generation of X-rays by high energy electrons passing through a thin specimen ($< 10\mu m$) in the electron microscope. These X-rays carry information about the atoms within the specimen in the region being irradiated, providing a means of correlating the ultrastructural information in the electron microscope image with chemical analyses of very small regions of the specimen.^[81] The emission of characteristic X-rays permits the identification and quantification of the elements present in the specimen. A suitable solid state detector collects the X-rays and the information is analyzed and displayed for its interpretation.

In order to produce an X-ray photon, the incident electron must have sufficient energy to ionize the atom concerned. This energy is called the critical excitation potential

E_c , or the absorption edge energy. [82,83]

The average number of ionizations, n , per primary beam of electrons with energy E_o ($> E_c$) incident on a specimen containing an element A is: [84,85]

$$n = \frac{NC_A\rho}{A_A} \int_{E_c}^{E_o} \frac{Q_A}{dE/dx} dE \quad (20)$$

where:

$\frac{dE}{dx}$ = mean energy change of an electron traveling a distance x

ρ = density of the material

A_A = atomic weight of A

C_A = concentration of A

Q_A = ionization cross section, i.e., the probability per unit path length that an electron with a given energy will cause ionization of a particular shell (K, L, M) in an atom A of the specimen.

Taking into consideration the fact that a fraction of the incident beam, $1-R$, is back-scattered from the target, the characteristic X-ray intensity in photons per incident electron generated in the specimen is given by:

$$I_A = \frac{const}{A_A} C_A R \omega_A a_A \int_{E_c}^{E_o} \frac{Q_A}{dE/dx} dE \quad (21)$$

where:

ω_A = fluorescent yield for element A

a_A = fraction of total K (or L) line intensity that is measured as K_α (or L_α)

R = backscatter factor

For the case of electron microscope thin films, few electrons are backscattered and the electrons lose a very small fraction of their energy in traversing the film. Therefore Q_A is

assumed constant and the trajectory of the electron in the specimen can be made equal to the thickness (t). Consequently, equation (21) becomes:

$$I_a = \frac{\text{const. } C_A \omega_A Q_A a_A t}{a_A} \quad (22)$$

The generated X-ray intensity and the X-ray intensity leaving the specimen can be considered identical if the thin film criterion is satisfied, i.e., the effects of X-ray absorption and fluorescence can be neglected if the analyzed film is sufficiently thin. This thin film criterion as detailed by Tixier and Philibert^[86] states that for each element measured in the thin foil, it must be true that:

$$\left(\frac{\mu}{\rho}\right)_{\text{spec.}}^i \csc \alpha \rho t < 0.1 \quad (23)$$

or the absorption correction is necessary. The term $\left(\frac{\mu}{\rho}\right)_{\text{spec.}}^i$ is the mass absorption coefficient for the i^{th} element in the foil, ρ is the density of the specimen, t is the thickness of the foil and α is the angle between the specimen and the detector.

Cliff and Lorimer^[87] have proposed analysis techniques in which the intensities, I_A and I_B , of two elements, A and B , in a foil are measured simultaneously. The intensity ratio, $\frac{I_A}{I_B}$, can be related directly to the mass concentration ratio $\frac{C_A}{C_B}$ by using the following expression:

$$\frac{C_A}{C_B} = \frac{A_A (Q\omega a)_B I_A}{A_B (Q\omega a)_A I_B} \quad (24-a)$$

or

$$\frac{C_A}{C_B} = K_{AB} \frac{I_A}{I_B} \quad (24-b)$$

The expression $K_{AB} = \frac{A_A (Q\omega a)_B}{A_B (Q\omega a)_A}$ depends on the operating voltage but is independent of sample thickness and composition as long as both intensities are measured simultane-

ously and the thin film criterion satisfied. This technique of measuring concentrations is known as the Cliff-Lorimer method.

Equations such as (24-b) are used together with the expression:

$$\Sigma C_i = 1 \quad (25)$$

to make quantitative analyses. C_i is the concentration of the i^{th} element in an alloy of n elements, and K_{AB} is determined in the way suggested by Cliff-Lorimer.^[87,88]

3. GB STRUCTURE AND SEGREGATION: BACKGROUND OF THE PROBLEM

Really adequate and quantitative studies of the relationship between GB structure and GB segregation have not been reported in the literature. Neither has a detailed determination of the structure of GB segregates been made. These are the goals of the present study. techniques of very high resolution.

Most of the work done in connection with the relationship between GB segregation and GB structure frequently involves determining the effect of solute atoms on GB surface tension and then employing the classical Gibbs expression given in equation 1.

Using the above concept, it has been determined that the extent of GB segregation depends on the degree of coincidence at the GB.^[89] Thus, in the case of dilute alloys of Cu in Pb, Γ is smaller for a $\langle 110 \rangle / 70.5^\circ$ tilt boundary than for a $\langle 110 \rangle / 54.8^\circ$ tilt boundary. In this example, the special boundary $\langle 110 \rangle / 70.5^\circ$ shows a smaller degree of segregation as compared to the general one $\langle 110 \rangle / 54.8^\circ$. In a similar way, it has been shown for the case of the Pb-Ag system that segregation occurs more prominently in general boundaries than in special ones such as the coherent twin $\{111\}$ ($\Sigma=3$) (see reference 90). Similar studies have shown similar results for the W-Cr system by using Field Ion Microscopy, (FIM).^[91,92]

It has also been shown that segregation can induce the formation of new GB configurations such as faceting under certain special conditions, and under other conditions it has been shown that segregation stabilizes existing boundary structures against faceting.^[93-95] Unfortunately, there exists no systematic information about the crystallographic nature of the boundaries in which enhancement or suppression of faceting has been observed.

There is also a large number of experiments which have given evidence, in an indirect way, supporting the idea that there exists a relationship between GB segregation and GB structure. These experiments have been concerned with phenomena such as grain

boundary corrosion, grain boundary diffusion and grain boundary precipitation of second phases. In the last-named case, Gronsky and Furrer^[96] have recently shown direct evidence of the effects of localized grain boundary structure on precipitation reactions by high resolution techniques of TEM and electron diffraction. In this particular example, indirect evidence of the relationship between GB structure and GB segregation can be seen. The evidence in this case suggests that dislocations present previous to the formation of precipitates served as preferential nucleation sites, and nucleation phenomena can be seen as a direct consequence of segregation.

Seah and Hondros^[34] have done extensive work to show the various degrees of segregation for different boundaries in polycrystalline specimens of Fe-Sn and Fe-Sb by using AES. A similar study has been carried out by Powell and Woodruff in Cu-Bi alloys,^[97] finding much greater apparent differences in the segregation at various boundaries. Fig. 7 and 8 show a summary of the works of Seah and Hondros, and Powell and Woodruff. Unfortunately, these data lack crystallographic information about the study of GB segregation, but show how the degree of segregation varies from boundary to boundary for the same type of material. Consequently, a systematic and unambiguous study regarding the magnitude of such effects as well as a detailed knowledge of the structure of the boundary is required.

From the theoretical point of view, there have been several attempts to study the relationship between GB segregation and GB structure. Weins and Weins^[98] and Bourquin^[99] have done the first computer calculations in an attempt to elucidate this relationship in a systematic way, taking into account the crystallographic aspects of the boundaries. Even though their results do not give a full understanding of the phenomenon, they are interesting in the sense that they indicate the existence of different behavior for the same solute atoms in different boundaries.

The work done on this particular subject had its origins in similar work done on free surfaces where the adsorption of impurities or solute atoms is known to be anisotropic. In this sense, it is expected that the amount of segregation to GB's depends on the nature and crystallography of the boundary. Even more, for GB models having periodic structures, corresponding periodicities in the distribution of segregants within the same boundary plane are expected, i.e., there should be correlation between the lateral distribution of solute atoms and the structure of the grain boundary. As was mentioned in the introduction, not many investigations of this type have been carried out, and the most recent works include those by Smith and Smith,^[100] Howell et.al.^[91] and Howell.^[92]

4. EXPERIMENTAL PROCEDURE

4.1. Material Fabrication and Treatment

4.1.1. Bicrystal Preparation

During the course of the present investigation, two types of GB's were studied; those formed during the growth of bicrystals and those analyzed from random grain boundaries in polycrystalline specimens. In both cases, the specimens were made from 99.999% purity *Al*.

A modification of the experimental setup of the Chalmers method^[101] was used to grow the aluminum bicrystals. The seeds used for the growth of bicrystals consisted of oriented pairs of single crystals. Fig. 8 shows a schematic cross section of the apparatus used for such growing. It comprises an induction furnace, a graphite mold and a glass tube. The glass tube extends through the furnace and is fixed on both ends so that it does not move when the furnace or the graphite mold is translated. The glass tube contains the graphite mold. The mold containing the seeds and the aluminum powder are placed in the furnace tube, which is evacuated and backfilled with high purity argon to a partial pressure of approximately 2×10^{-4} Torr before the furnace is turned on. The mold is then slowly heated until the upper region reaches a temperature of 730 °C as observed by a previously calibrated pyrometer.

A relative translational speed (between the furnace and the mold) of 2 cm/hr permitted a motion of the *solid-liquid* interface (seeds and molten zone) along the profile of temperature shown in Fig. 8-a to assure the growth of the bicrystal into the melt.

To determine if the growth of the bicrystal was successful with respect to orientation, the bicrystal was chemically etched in an acid mixture containing equal parts of HCL, HNO₃ and HF. The etchant exposes the {100} planes by preferential attack, so that individual grains could be seen by eye, due to their different reflectivities. The dimensions of the grown bicrystal are indicated in Fig. 8-b: 20 mils thick, 2 cm wide and 9 cm long. In the

case of wider or thicker samples, it was necessary to section them using either a diamond saw or a spark-cutter. In some cases polycrystalline specimens of *Al* were prepared from sheet material (40 mil thick) and the grains were made to grow by subsequent heat treating until grain boundaries were developed.

Three mm discs were spark-cut from the *Al* bicrystal, using care to center the grain boundary. A layer of *Zn* was then vacuum evaporated onto the *Al* discs followed by a *diffusion-annealing* process. The coated discs were encapsulated in quartz or vycor tubing and backfilled with high purity argon to a partial pressure sufficient to yield one atmosphere pressure inside the capsule at the heat treating temperature. The necessary partial pressure of Argon was determined using the ideal gas law. Residual surface films were removed after the heat treatment. Fig. 10 shows a scheme of the process followed. The specimens were examined prior to *Zn* deposition by AES in order to rule out the presence of extraneous impurities. Fig. 11 shows the results of this analysis.

4.1.2. Heat Treatment

Following encapsulation, the 3 mm discs were aged at 350 °C to ensure *Zn* saturation. The samples were then furnace cooled down to room temperature. Following this, the samples were upquenched to the desired treatment temperature. The quenching was done in iced water, breaking the capsule as soon as it entered the water. The samples were either cleaned and encapsulated again just as described above and stored at 0 °C, or they were immediately prepared as TEM foils. Specific ageing temperatures and other heat treatments are shown in Fig. 12.

4.1.3. Preparation of Specimens for The Electron Microscope

Heat treated samples were ultrasonically cleaned in acetone, methanol and distilled water. TEM specimens were then prepared by jet electropolishing in a solution of 1 part nitric acid and 3 parts methanol. The potential applied to obtain an even polishing varied from day to day and in some cases from specimen to specimen. Small deviations from the

applied potential could cause pitting or etching instead of polishing. In order to determine the origin of this sporadic behaviour it was necessary to determine the best electropolishing conditions by obtaining a current vs. potential curve such as the one shown in Fig. 12. No major difference was noticed between the polishing conditions at -25°C or -30°C . The best conditions for electropolishing^[102,103] are indicated by the plateau which developed between 15 and 30 volts at -25°C and shown in Fig. 12. These conditions were used in the preparation of the TEM foils. The polished foils were washed repeatedly in distilled water, methanol and ethanol (in that order) and finally stored in ethanol at 0°C until they were ready for examination in the microscope. This sequence of washing resulted in a minimization of contamination build-up in the microscope environment.

4.2. Microscope Preparation

4.2.1. Scanning Transmission Electron Microscope

The experimental work of the present study was mostly done in a Philips EM400 TEM/STEM equipped with a Kevex System 7000 EDS detector. A simple arrangement of this equipment is shown in Fig. 13. The microscope was operated at an accelerating potential of 100 kV. A pointed LaB_6 filament and a beam current of approximately $10\ \mu\text{amp}$ were used to guarantee high brightness and beam coherence. during X-ray microanalysis.

The sensitivity limits for STEM X-ray microanalysis, defined as either the minimum detectable mass (MDM) or the minimum mass fraction (MMF), are determined by several factors such as the X-ray count rate, the efficiency and collection geometry of the EDS detector and the excited volume of the specimen responsible for the production of X-rays. The optimization of the sensitivity has been discussed thoroughly by Joy and Maher.^[104] In order to improve MMD and MMF the electron current density (J) impinging on the sample and the counting time (τ) should be maximized and the X-ray detector configuration must also be optimized.^[105] A balance was always kept between J and τ in order to get good counting statistics and low specimen contamination rates. Typical counting times and

count rates were 200 seconds and 110 counts/sec respectively. Specimen and electronic drift were also considered when selecting the counting time. The peak/background ratio ($\frac{P}{B}$) is an important factor which has to be maximized whenever possible in order to improve MMF. As can be seen from Fig. 14 ($\frac{P}{B}$) is relatively high for the system under consideration, thus improving the MMF.

A solid state detector (SSD) such as the one shown schematically in Fig. 15-a was used to collect the X-ray signals. The detector was placed as close to the specimen as possible. The specimen was tilted 30 degrees towards the detector as is shown in Fig. 15-b. The output of the detector was used to feed a small computer which aided in the final analysis of the results.

In order to minimize spurious radiation, a low background *Be* specimen holder was used and the use of a Cu specimen retainer grid was avoided whenever possible.

As will be shown later, the STEM image was essential in the location of the regions to be microanalyzed. In order to get a STEM image, another SSD is placed between the screen and the lower lenses of the electron microscope. This detector incorporated a disc to collect the transmitted electrons when the microscope is operated in the diffraction mode. The output of this detector is connected to an electronic device capable of amplifying the signals to give a bright field image. Nominal working magnification of the STEM images was 100,000X.

4.2.2. Transmission Electron Microscopy

One of the advantages that a TEM/STEM possesses is that it can be used in both modes of operation, i.e., as a conventional transmission electron microscope and as a scanning transmission microscope. In order to do structural analysis of the specimens under consideration, it was imperative that the microscope be operated in conventional mode. In some cases it was necessary to change the specimen from a low background holder to a

double tilt holder because the relative positions of the features to be analyzed required the use of both devices. For this a JEOL 100C microscope was used.

4.3. Making The Analysis

4.3.1. Choice of the Specimen

Specimens showing even thickness were chosen for the analysis. Those foils which showed the presence of precipitation and those which had been preferentially attacked at the grain boundary during their preparation were avoided throughout the study.

4.3.2. Focusing The Electron Beam

After obtaining a reasonable TEM image of the region under study, a STEM image was obtained as described earlier. Making the proper choice of C_2 aperture and proper focusing of the C_1 lens, the electron beam was condensed to a 40 Å probe. The STEM image served as a monitor to select the position of the probe along the region of interest when microchemical analysis was performed. Chemical profiles were obtained by placing the probe at successive intervals of a few hundred angstroms.

4.3.3. Obtaining X-Ray Signals

Focusing the probe into a specific region of the specimen gives information on the chemical composition via the generation of X-rays. The generation and detection of these X-rays require some previous adjustment of the equipment as mentioned before.

The analysis was performed very carefully while striving for a dead time of less than 25%. The X-ray signal went through a multi-channel analyzer (MCA) which had been previously set to an X-ray energy range of 0-10 keV. These X-rays were displayed on a cathode ray tube as an accumulating signal during the time set for the analysis. The final spectrum is examined by identifying each peak and ascertaining its position in the energy range. A typical spectrum recorded from a plotter coupled to the CRT is shown in Fig. 16. An integration of the number of counts under each peak of interest was done by first

selecting an energy band on the MCA. Typical band widths in this work were of the order of 150 eV. The attachment of a computer to the analyzer permitted simultaneous peak integration and background subtraction. The final result was printed out on a teletype. A typical example of such an output is shown in table-1 in which the elements are listed with their respective X-ray line energies, corrected integrated peak values, count ratios with respect to the *Al* peaks, and their respective standard deviations.

The background from the obtained spectra was subtracted after some modeling was done with the computer. For this procedure, a number of background values at different positions in the spectrum at both sides of each peak of interest were sampled. After background subtraction, a set of data like the one shown in Table 2 was obtained for each position of the probe along and across the grain boundary. These data was the input for the results reported in Figs. 23, 26, 29, and 35.

4.3.4. Foil Thickness Measurements

An accurate determination of the foil thickness of the region where the microanalysis was performed was imperative. The observation of the same number of parallel Pendellösung fringes along a tilted GB with respect to the electron beam was an indication of uniform thickness;^[30] however local fluctuations in thickness could be measured using convergent beam diffraction.^[106-109] Using this technique, the thickness of the specimen was determined at different intervals along and across the boundary where the chemical analysis was done. A Joyce-Loebl MK III microdensitometer was used in the determination of the fringe spacings resulting from this technique. Fig.-18 shows a sample of such fringes at different diffraction conditions. Fig. 19 shows a plot of $(\frac{s_i}{n_i})^2$ as a function of $(\frac{1}{n_i})^2$, where s_i was the deviation from the exact Bragg reflection corresponding to each minimum in the fringes of Fig. 18 and n_i was the order of each one of those minima.

4.3.5. Grain Boundary Characterization

Following Pumphrey and Bowkett,^[64] two spot-Kikuchi diffraction patterns, SAD_{11} and SAD_{21} , one from each side of the boundary are obtained at specific orientation. The specimen is then tilted α degrees and two new diffraction patterns, SAD_{12} and SAD_{22} , are obtained from the same regions. The sense of tilting as well as the amount of tilting is recorded in order to facilitate the interpretation of the diffraction patterns. Each diffraction pattern permitted the definition of a unit vector ($\vec{t}_{ij}$) parallel to the beam direction.

A 3x3 rotation matrix, M , is obtained with the aid of Figure 20, the above defined unit vectors $\vec{t}_{ij}$, and the mathematical relationship:

$$\vec{t}_{2j} = M \vec{t}_{1j}, \quad (j=1,2,3) \quad (26)$$

Once M is known, the rotation axis is given by the expression:

$$\vec{U} = [(m_{32}-m_{23}), (m_{13}-m_{31}), (m_{21}-m_{12})] \quad (27)$$

and the angle of misorientation is obtained from the expression:

$$2 \cos \Theta + 1 = T \quad (28)$$

where T is the trace of M .

Previous to this analytical method of finding the axis/angle pair, an approximation of the same can be obtained using the graphical method of Goux[110] and which is summarized in Figure 22. The details of the analytical method are shown in appendix A for the particular case of the grain boundary with a rotation axis close to $\langle 011 \rangle$.

This method permitted the calculation of the axis of rotation with a precision of $\pm 0.1^\circ$ and the misorientation angle with a precision of $\pm 0.2^\circ$. Knowing the axis angle pair, the parameter defining the closest CSL is determined by comparison with the published tables of axis/angle pairs. Also the possible Burgers vectors of GBD's were determined using the basic concepts of the DSC-lattice.

Whenever necessary, the normal to the boundary plane is determined according to Young et.al.^[111] Tilting the specimen inside the microscope permits the formulation of a

rotation matrix for one of the crystals. With this rotation matrix and the change of projected boundary images before and after the tilt, the boundary normal is calculated with an accuracy of 2 degrees.

5. EXPERIMENTAL RESULTS

5.1. Tabulation of Boundaries Studied

Attention was given in this study to those grain boundaries which were near to a coincidence position, including a tabulation of the frequency with which they were encountered. The results are presented in Table 1, where the parameters Σ $\langle hkl \rangle$ and Θ correspond to the nearest coincidence boundary. As can be seen, most of the grain boundaries were of the type $\langle 110 \rangle$ and $\langle 100 \rangle$.

Table 1. Occurrence of Near Coincidence Boundaries in Al-Zn Alloys Studied

Multiplicity	Axis	Angle	Occurrence
Σ	$\langle hkl \rangle$	Θ (degrees)	f
17	100	62.04	5
5	100	53.13	1
7	111	38.21	2
3	111	60.00	3
9	110	38.94	2
17b	110	86.63	1
11	110	129.52	1
19	110	153.47	1
3	110	70.53	1
3	311	33.56	2
7	311	64.62	2
7	311	81.79	1
15	111	42.83	2
11	431	50.48	1
15	110	48.19	5
7	210	73.40	1
9	210	38.94	3
17	110	93.37	1
3	110	70.53	1
11	110	129.52	1

Examination of these boundaries was carried out using the TEM/STEM to monitor the distribution of solute in the vicinity of the boundary plane. A typical profile across the grain boundary is shown in Fig. 23. The extent of solute enrichment is displayed as the Zn/Al X-ray photon count rate ratio. Note that there is no difficulty detecting a marked concentration gradient which extends over approximately 50 Å on either side of the boundary, and which indicates the level of spatial resolution achieved throughout this study.

5.2. Effect of Annealing Temperature

It was observed in this analysis that for a given specimen, the amount of segregation could be directly correlated with the heat treatment the specimen had received. In particular, there was a distinct relationship between Zn concentration at the grain boundary and the equilibrium temperature used for annealing. Roughly, two regimes were indicated by the two straight lines in Fig. 24. The slopes of these lines give an indication of the magnitude of the activation energies for each regime, and their intersection yields the transition temperature between them. In one case (low temperatures) the slope was determined to be 3.2 kcal/mole, while in the other (high temperatures), a slope of 0.63 kcal/mole was determined. The intersection of the two lines occurred at $T = 560^\circ C$. These analyses were made for specimens with heat treatments as shown in Fig. 12. It was very common to observe very few boundaries with detectable levels of segregation when the specimens were quenched from temperatures relatively high for the $Al-Zn$ system, i.e., ($> 560^\circ C$). Below $560^\circ C$ the number of boundaries showing segregation increased, as did the level of segregation exhibited by each one.

5.3. Solute Distribution along the Grain Boundary

A particularly interesting aspect of this study was the observation that at very fine probe sizes, a *pattern* of solute distribution could be detected *along* the grain boundary plane. This behavior is shown in Fig. 25 displayed as plots of the (Zn/Al) count rate ratio as a function of distance along the boundary plane for boundaries of different Σ values (near-coincidence boundaries).

In general it was observed that the mean amplitude of the fluctuations decreased as the density of coincidence sites in the transition lattice increased. Note, for example, that for $\Sigma = 17$ ($\langle 110 \rangle / 38.6^\circ$) boundary shown here, the concentration profile along the boundary plane appears absolutely flat, and that fluctuations, if present, are within the statistical error. Also, note the fluctuations of up to 20% in the (Zn/Al) count rate ratio in the

boundary $\Sigma=7$ ($\langle 111 \rangle 38.21^\circ$) with a periodicity of approximately 2750 Å. Fluctuations of up to 18.8% in the (Zn/Al) count rate ratio were found in the boundary $\Sigma=7$ ($\langle 311 \rangle /64.62^\circ$). The periodicity in the solute distribution for this case was approximately 1750 Å.

Composition peaks indicating high Zn regions were detected along those boundaries where high resolution imaging failed to indicate any second phase particle. All peaks were clearly defined, with error bars as in Fig. 25 indicating the experimental uncertainties. Typically the $AL K_\alpha$ X-ray signal contained about 2500 counts when using a 230 eV energy window and 150 second minimum count time. During the present investigation, it was possible to find in certain grain boundaries a direct correspondence between the occurrence of defects along the boundary and the periodicity in the solute distribution along the same boundary. Fig. 26(a) shows a BF image of a grain boundary with dislocations spatially distributed every 3650 Å. In Fig. 26(b) a concentration profile along the same boundary is indicated, with fluctuations up to 18% and with a periodicity approximately the same as that in Fig. 26(a). Similarly, Figs. 27(a) and (b) show a BF and weak beam images respectively of a grain boundary with extrinsic dislocations in its neighborhood. The spatial distribution of these dislocations is in close accord with the periodicity of the solute distribution along the boundary plane as shown in Fig. 28.

Some boundaries, such as the one shown in Fig. 29 did not show marked periodic fluctuations in solute composition along the boundary plane. However, chemical analysis showed an abrupt change when the region marked with the arrow was reached. This corresponded to a 15% change in the (Zn/Al) count rate ratio with respect to the rest of the boundary.

Along severely distorted grain boundaries, such as the one shown in Fig. 30 there was no evidence of fluctuations along the grain boundary; at least at the level of the spatial resolution of the electron probe (40 Å).

5.4. Effect of Grain Boundary Structure

Further attempted correlations between the structural aspects of the grain boundary plane and the segregation events did yield results relating to ledge behavior as shown below. Fig. 31(a) shows a bright field image of a pure-*Al* grain boundary without any *Zn* diffused into it. After *Zn*-doping a specimen from the same bicrystal, the boundary showed a ledge structure as seen in Fig. 31(b). This boundary did not show a periodicity in solute distribution with a marked wavelength as the previous examples. However, it was noted that the regions of higher *Zn* concentration were also the regions with ledge structure. Fig. 32 is a bright field image of a rather large ledge in a low Σ boundary. The results of an EDS probe of areas 1, 2 and 3 yielded the peaks shown in Fig. 33, for a larger probe (40nm in diameter). After background stripping, the integrated peaks showed a higher *Zn* concentration on the large grain boundary step with somewhat less *Zn* in the flat, planar portions of the boundary. The lowest peak in Fig. 33 comes from the region 3 of the adjacent matrix. The overlapping *Cu* signal for the three spectra attests to the accuracy of the relative *Zn* peak heights. Using the same probe on smaller ledges was attempted but the signal-to-noise ratio fell into the uncertainty range. Table 2 shows the respective measurements after background stripping for regions 1, 2 and 3 of Fig. 32.

Table 2. Computer Analysis for the Regions 1, 2 and 3 In Fig. 32

Spectrum	Element	Region (keV)	Integral (counts)	σ_i	Count Ratio	σ_T
1	<i>Al</i>	1.12 - 1.88	2.8161E 04	0.0060	1.0000	0.0085
	<i>Cu</i>	7.78 - 8.32	1.6770E 03	0.0244	0.0771	0.0251
	<i>Zn</i>	8.44 - 8.94	2.7010E 03	0.0192	0.1242	0.0330
2	<i>Al</i>	1.12 - 1.88	2.1740E 04	0.0068	1.0000	0.0086
	<i>Cu</i>	7.78 - 8.32	1.6770E 03	0.0244	0.0771	0.0253
	<i>Zn</i>	8.44 - 8.94	2.7010E 03	0.0192	0.1242	0.0204
3	<i>Al</i>	1.12 - 1.88	2.6982E 04	0.0061	1.0000	0.0086
	<i>Cu</i>	7.78 - 8.32	1.6750E 03	0.0244	0.0621	0.0252
	<i>Zn</i>	8.44 - 8.94	3.2090E 03	0.0177	0.1189	0.0187

A summary plot of grain boundary solute enrichment as a function of misorientation angle for the particular case of boundaries with misorientation axes of the type $\langle 110 \rangle$ is presented in Fig. 35. The dashed line has been inserted in order to permit comparison between these results and the theoretical dependence of the grain boundary energy on the angle of misorientation such as indicated in Fig. 35(a).

5.5. Effect of Electron Probe Size

The detectability limits of Zn-segregation in the specimen analyzed was observed to depend upon the working microscope conditions, including in particular the size of the electron probe. For a very small probe size (40 Å), fluctuations of up to 20% in solute concentration could be detected in areas of approximately 4000 Å in diameter. The detectable degree of spatial resolution was decreased as the size of the probe was increased. Table 3 shows some of the results for this type of analysis.

Table 3. Influence of Electron Probe Size in the Spatial Resolution of the STEM

Probe Size (Å)	Lowest (Zn/Al) Count Rate Ratio	Highest (Zn/Al) Count Rate Ratio	Difference	%
40	0.481	0.575	0.094	20
100	0.497	0.578	0.081	16
200	0.542	0.580	0.038	7
400	0.565	0.590	0.025	4
1000	0.600	0.596	0.004	1

6. ANALYSIS OF THE RESULTS AND DISCUSSION

6.1. Effect of Orientation Relationship on GB Segregation

The segregation of *Zn* to *Al* grain boundaries showed a wide range of values depending on the type of boundary as well as the heat treatment of the specimen. The relative misorientation of the grains and the plane of the grain boundary were both very important in determining the extent of segregation.

The results in Figs. 25, 31-33 clearly leave no doubt about the dependence of grain boundary segregation on grain boundary structure. The micrographs of Fig. 27 and 35 demonstrate that the boundary plane runs parallel to the {200} planes of the matrix. These boundaries were the ones that showed evidence of higher solute concentration. From the structural point of view, these planes present more open volume where solute atoms can reside as compared to close packed planes such as the {111} planes. However, the {111} planes are more prone to assist the kinetics of atomic migration which explains the association of ledges in Figs. 31(b) and 32 with regions of high solute concentration.

The results depicted in Fig. 34 exhibit certain minima with misorientation near the $\Sigma=3$ and $\Sigma=11$ CSL misorientations; however, these results are difficult to rationalize completely. Note that the cusps shown with the dashed line follow a similar behavior as that of Fig. 35 where the energy of grain boundaries is plotted as a function of the misorientation angle. The exact position of these cusps is difficult to determine because of the limited data. However, the solute segregation tends to follow the energetic aspects of the grain boundaries, i.e., those boundaries away from a coincidence boundary have a tendency to give rise to more segregation than those near a coincidence position. This type of result is comparable, in part, with the results that Herbeuval et. al.^[112] on the penetration of *Zn* along the [110] tilt boundaries in aluminum as a function of the misorientation angle (see Fig. 35). The variations in the penetration of *Zn* along and across the grain boundary are intimately connected with the variations in grain boundary energy due to changes in

misorientation angle. The results of this work can be analyzed in the same way. Note that for boundaries close to the coincidence position $\Sigma=5$, $\Sigma=7$ and $\Sigma=11$ a minimum of Zn penetration has been me mecalculated,^[113] and a minimum of Zn penetration has been measure.^[112] In this study as well, a minimum in segregation has been detected. Exactly the opposite takes place for those boundaries away from an exact coincidence position and where the grain boundary energy is higher. In this case larger degree of solute concentration at the boundaries has been detected. This appears to be an obvious result, since the good atomic fit anticipated at exact coincidence does not offer much room for the solute atoms to reside. Conversely, for those boundaries away from coincidence, the presence of defects compensating the atomic misfit at the boundary makes the grain boundary an energetically attractive place for the solute atoms to reside. This analysis indicates that grain boundary energy may indeed play a role in determining the activation energy of the segregation phenomenon.

6.2. Effect Of Grain Boundary Structure

It is evident from Figs. 26-32 that extrinsic structures do influence the pattern of grain boundary segregation. The tendency for large ledges, in particular, to accumulate more solute is not surprising given the dual nature of that particular heterogeneity with respect to surface and strain energy reduction. Note that in Fig. 32, the ledge configuration lies in a plane of the type $\{200\}$ which is a plane energetically favorable for the segregation phenomenon.

The enhancement effect of ledges (see Figs. 31-32) may be explaine by a model in which strong segregation occurs to boundaries of large energy. A reduction of thos energy is therefore promoted by the segregation phenomenon to the extent that it will at least attain energy of boundaries of inherently low energy. Due to the structure itself of the boundary, this minimization or reduction of the energy occurs to a more pronounced extent in certain regions of the boundary. Consequently, there will be atomic rearrangements on a

local scale, resulting in the formation of ledges or facets. Since the reduction of the grain boundary energy is in direct relation to the amount of segregation, then those regions that lowered their energy to a larger extent would also be the regions of larger solute concentration. Consequently, this would explain the presence of larger solute aggregates at the ledge structure of Fig. 32. It is important to note that once the ledge configuration has been formed, then the solute aggregates contribute further to their energetic stabilization.

Even though the presence of extrinsic dislocations was evidently an influence on the degree of segregation, it was not possible to establish a more explicit correspondence between the nature of the dislocations and the segregation phenomenon. More experimental data about the structure of the boundary is necessary to give more precise correlation with the exact displacement fields of the defects.

Taking into consideration the small binding energy between the *Zn* atoms and the matrix,^[115] as well as the open structure in a high diffusivity path (analogous to a dislocation),^[116-120] then it is expected that accumulations of solute should be present in and at the vicinity of such defects.

It should not be overlooked that the levels of solute doping in this study were intentionally high, chiefly to avoid the limitations imposed by the experimental technique. In this way, the solute was "forced" to diffuse along the boundary. The mechanisms here started with a diffusion process and consequently, the jump frequencies of both solute and solvent atoms played an important role. Amthony^[114] has already reported that for the case of *Al-Zn* system, and at heat treatments similar to those reported here ($\frac{W_3}{W_1} < 0.26$).³ This suggests that the impurity does not strongly attract a vacancy which would cause a large decrease of W_3 . Instead, impurities experience only a small interaction with their nearest neighbors, being either a vacancy or a solvent atom. Also, this result suggests a relatively low correlation factor for diffusion in the system, as observed also in some recent

³ W_1 and W_3 stand for jump frequencies of vacancies away from and around impurity atoms respectively.

experiments.^[114] This aspect could, in principle, explain why *Zn*-enriched zones were found in the vicinity of and at extrinsic dislocations in the grain boundaries.

In cases such as that in Fig. 37 where the boundary revealed the presence of intrinsic dislocations, there was no indication of variations in solute concentration along the boundary plane. This lack of any one-to-one correspondence between the coincidence site lattice and preferential sites for segregation to occur can be attributed to the need for an even higher spatial resolution technique. The spatial resolution of the equipment here, although relatively high (40 Å), still is not enough to establish such a relationship in a direct way. Note that for $\Sigma=5$ boundaries, the spatial distribution of secondary dislocations can be as small as 50 Å, and the probe used to detect microchemical changes would not resolve such differences.^[122-125]

One of the most interesting aspects of the present study is the observed periodic nature of *Zn* segregation in *Al* bicrystals. These observations indicate the existence of a strong tendency for preferential solute clustering along the boundary plane. Unfortunately the precise identification of such sites still is not totally clear. Depending upon the degree of deviation of a boundary from its nearest exact coincidence, some agreement is found between the periodicity of solute distribution (≈ 100 nm) and the large scale relaxations in the boundaries which have slight deviations from an exact Σ boundary. It has been suggested^[69] that the relaxations which are associated with the O-points at the high angle boundaries are somewhat similar to those which occur at the low angle boundaries, but on a much coarse scale. Therefore, it is not surprising to find periodicities of the order of 100 nm in the distribution of solute atoms along the boundary plane such as indicated in Fig. 25. Furthermore, there is an indirect way of relating this type of observation with the intrinsic structure of the boundary as follows. The spacing of the intrinsic structural dislocations in grain boundaries bears an exact relationship to the magnitude of their Burgers vectors. Also there is a very large sensitivity of dislocation spacing to the angle of devia-

tion from exact coincidence; the larger the deviation, the smaller the spacing. In reference to Figs. 25(b) and 25(c), the ratio of the average wavelengths for the boundaries $\Sigma=7$ ($\langle 311 \rangle / 64.62^\circ$) and $\Sigma=7$ ($\langle 111 \rangle / 38.21^\circ$) is roughly 0.612. This number is relatively close to 0.664 which corresponds to the ratio of the estimated distances between the secondary dislocations for the same boundaries. This agreement indicates that the peaks of Figs. 25(b) and 25(c) correspond to distance equivalent to a multiple of the dislocation separation and which may be interpreted as the places where the relaxations associated with O-points occur. Nevertheless, there are difficulties in detecting these defect structures in a direct way, both due to their small strain fields and to the practical complications caused mainly by specimen contamination. These defects may act as sinks for solute atoms which may interact, as will be shown later, giving rise to the formation of even larger clusters. One mechanism by which the above described defects can become enriched in solute could be the same one already described for the case of extrinsic grain boundary dislocations.

In light of the above ideas, it is expected that all the heterogeneities at the grain boundary that have been mentioned could serve, in principle, as preferential sites for the solute atoms to reside, each site with its own characteristic interaction energy. An homologous example would be the case of the interaction of an ad-atom to a surface, where the interaction energy between the atom and the surface depends on the particular site or defect in the surface (see Fig. 38). The position of the solute atoms at the grain boundary defects can be considered as a metastable configuration. They will depend on the balance of all possible forces that an aggregate of atoms experiences; forces resulting from differences in atomic volume, forces resulting from coherency strain (strain at the boundary associated with the misfit not accommodated by misfit dislocations), different interaction forces, such as solute-dislocation interactions, dislocation-dislocation interactions, interatomic forces and so on. Thus, by direct analogy with the free surface case, each original aggregate of solute atoms at the boundary will experience a net force with two components parallel to the boundary plane but perpendicular to each other, and a third component perpendicular to

the boundary plane (see Fig. 39 for a schematic representation of these forces). The third component is responsible for the binding of the solute aggregates to the boundary, while the parallel components determine the final equilibrium position of the solute aggregates.

One cannot overlook the fact that the grain boundaries possess a periodic and "open" structure, and in many cases those structures can be seen to be or interpreted as microledges. These defects are very prone to the formation of the initial aggregates of solute atoms which subsequently interact in the manner described above.

6.3. Effect Of Temperature On Grain Boundary Segregation

One final aspect to be discussed here is the influence of temperature on the segregation phenomenon. Equilibrium solute segregation that had occurred at the solution heat treatment temperatures shown in Fig. 12 is assumed to be retained at room temperature after quenching since insufficient time would be allowed for solute atoms to go back to their original sites during their treatment. Thus, the results reported in Fig. 24 may be considered representative of each heat treatment temperature. In general these results obey equation 5 for the equilibrium segregation of solute to grain boundaries in single phase materials. Thus, higher equilibrium segregation was obtained from specimens quenched from lower temperatures and vice versa. From Fig. 24, an activation energy of 3.8 kcal/mole can be associated with the present segregation study. This seems to be valid up to a temperature close to 560 °C where a drastic change of slope is observed. This change in the slope can be due to phenomena others than segregation which occurs in that range of temperature. For example, a problem with the evaporation of Zn may be encountered. Also, a supersaturation of vacancies at high temperatures cannot be overlooked because solute-vacancy pairs and even more complex pairs may be formed, affecting the activation energy of the entire process. The value of the activation energy determined for low temperatures corresponds to the same order of magnitude as that estimated by taking into account different contributions. This is discussed further in appendix B.

Based on the classical description of equilibrium grain boundary segregation, the elastic misfit energy of the solute in the lattice is expected to decrease with increasing temperature due to a decrease in the elastic constants of equation 6. However, in making a detailed analysis of Fig. 24, one can observe that there is a general tendency for the activation energy to increase as the temperature increases when going from experimental point to experimental point. This leads to the conclusion that there are other factors, besides the elastic misfit energy, which contribute to the process of segregation. These other contributions which were detailed in the section 2.1. include the grain boundary energy and the interaction energy among the different types of constituents in the specimen, i.e., solute-solute interactions, solute-solvent interactions and solvent-solvent interactions.

Examining the boundary from a statistical thermodynamics point of view one can refer to Fig. 40, where the sketches have been labelled according to the parameters defined in section 2.1. According to this figure one can see that with the increase of temperature, certain solute atoms will be activated out of their energetically favorable sites at the grain boundary and into bulk lattice sites. The elevation of energy will not occur uniformly, however, and grain boundary sites with their energies nearest to E will be preferentially vacated. By this model the activation energy of segregation is expected to increase as the temperature increases.

6.4. Comments On Technique

The operational principle of the experimental setup appears straightforward; however, the ability to detect changes in concentrations in areas as small as $1500 \text{ \AA}$ depend in great part on the ability and skill of the operator. Problems persist from the specimen preparation up to the setting of the optimum working conditions of the microscope including specimen contamination and alignment of the microscope. The elongated error bars of Fig. 26(b) are a direct consequence of the specimen contamination in the microscope. The counting time had to be reduced in many cases in order to minimize the contamination buildup. This

resulted in a poor counting statistics as can be appreciated as one proceeds from left to right in Fig. 26(b).

The ability to obtain chemical analysis in addition to electron images and electron diffraction patterns of very small areas using a scanning transmission electron microscope was improved when the microscope was equipped with a LaB_6 filament. This suggests that using a much brighter source capable of giving higher beam currents and smaller beam diameters than the LaB_6 filament would result in great advantages for the analysis. In terms of the x-ray signal, higher spatial resolution, together with higher count rates, would increase the accuracy of the analysis. Obviously the use of a Field Emission Gun would fulfill these needs.^[121,122,125]

An accurate knowledge of the specimen thickness was critical in the present work. The results reported in Figs. 18 and 19 are a sample of the technique of determining the thickness of the specimens in the vicinity of the area where the analysis was performed. The accuracy of the thickness is observed in two ways: First, the values of thickness resulted to be within high agreement when using different reflections. Note, that the thicknesses were 1015 Å and 1023 Å for the operating reflections g_{113} and g_{200} respectively. Second, the extinction distances ξ_g as determined by the slope of the plots in Fig. 19 are in good agreement with the values tabulated in the current literature.^[122] Thus, it was determined that $\xi_{113} = 1096$ Å and $\xi_{200} = 680$ Å which are very close values to those tabulated for Al, i.e., $\xi_{113} = 1300$ Å and $\xi_{200} = 673$ Å.

Finally it should be noted that a technique of even potential resolution for local chemical analysis of the type reported here is *lattice fringe imaging*.^[126] Recent assessments^[27] have revealed the source of potential problems with this method and pointed out the need for even more extreme care than the level actually needed in this study. Nevertheless the application of lattice imaging would be extremely beneficial in the search for even higher resolution information about the atomistics of grain boundary segregation.

7. CONCLUSIONS

The need for an adequate, systematic and quantitative study of the relationship between grain boundary structure and segregation had been indicated after reviewing previous experimental and theoretical investigations in this field. Such a study was undertaken on an *Al-Zn* alloy system using a scanning transmission electron microscope to provide microstructural and microchemical analyses at relatively high spatial resolution.

The following conclusions have been drawn:

- (1) The present study allows segregation profiles down to 10 nm in extent to be measured and described to an accuracy which is limited primarily by the x-ray counting statistics and the practical consideration of orienting the boundary parallel to the incident electron beam.
- (2) A number of different observations indicate the presence of an anisotropy in the overall distribution of *Zn*-solute in the *Al* grain boundaries. This implies that the activation energy of the segregation phenomenon is not constant for a given boundary.
- (3) The presence of specific perturbations at the grain boundaries such as ledges and extrinsic dislocations are associated with higher accumulations of solute at the grain boundary as compared to the average grain boundary solute concentration.
- (4) The identification of structures on the scale of the 0-lattice as consequences of the atomic relaxations in the grain boundaries was indirectly associated with segregation behavior.
- (5) A mechanism has been suggested whereby different structural and chemical defects at the grain boundaries interact in order to produce a more stable configuration of solute atoms along the boundary plane.

- (6) The observed segregation behavior had no direct association with the CSL model through Σ values above; rather the detailed structure of the boundary was found to be the most significant influence on segregate distribution at grain boundaries.
- (7) X-ray microanalysis in the electron microscope has proven to be a powerful tool to study segregation effects in grain boundaries. This technique along with the micro-micro-diffraction technique opens the doors for new investigations in the field of grain boundary segregation, with even greater spatial resolution promised in the future.

ACKNOWLEDGEMENTS

I extend my sincere appreciation to the members of my thesis committee, Prof. Gareth Thomas, Prof. Gabor Somorjai and Dr. Ronald Gronsky, for their interest in this topic and their critical reviews of this manuscript.

I want to express my sincere deep gratitude to Dr. Ronald Gronsky for his unfailing support, encouragement and expert guidance throughout the course of this investigation.

The assistance provided by the Materials and Molecular Research Division of the Lawrence Berkeley Laboratory is gratefully acknowledged. I recognize, in particular, the help provided by Gloria Pelatowsky, Don Krieger and John Holthuis. Thanks are also extended to my colleagues in Prof. Thomas' research group for making my stay at Berkeley a pleasant one. In particular I thank R'Sue Caron, Eduardo Kamenestky and Alan Pelton for their personal and unconditional help which was extended in many ways.

I wish to thank Prof. Hans-Rudolf Wenk from the Department of Geology and Geophysics for making his department's TEM equipment available to me.

Finally, I remain forever obliged to my family for their help and encouragement. The love and tenderness of my wife Francelina, my daughter Josmar and my son Mauro throughout my staying in Berkeley will always be remembered.

I wish to acknowledge the financial support from *Universidad de Los Andes* in Mérida, Venezuela.

This work was supported by the Division of Materials Sciences, Office of Basic Energy Sciences, U. S. Dept. of Energy under contract No. W-7405-Eng-48.

APPENDIX A

Determination of the Axis/Angle Pair of a Grain Boundary

As was indicated in section 4.3.4, Figure 21 shows four diffraction patterns. These permit the definition of four beam directions as shown in Table 4-a.

Table 4-a. Beam Directions of the Diffraction Patterns in Fig. 21

Grain 1				Grain 2			
	u_1	v_1	w_1		u_2	v_2	w_2
$SAD_{11} =$	-1	1	1	$SAD_{21} =$	2	1.5	2.438
$SAD_{12} =$	0	1	1.1429	$SAD_{22} =$	0	1	1.2825

Each one of the above beam directions defines a unit vector as shown in Table 4-b.

Table 4-b. Unit Vectors along Each Beam Direction.

Grain 1				Grain 2			
	t_{11}	t_{12}	t_{13}		t_{21}	t_{22}	t_{23}
$\bar{A}_1 =$	-0.5728	-0.5728	-0.5728	$\bar{A}_2 =$	0.5727	0.4269	0.6982
$\bar{B}_1 =$	0	0.6585	0.7526	$\bar{B}_2 =$	0	0.6149	0.7886

A third unit vector can be obtained from each set above, i.e., $\bar{C} = \frac{\bar{A} \times \bar{B}}{\sin \alpha}$. Therefore:

Table 4-c. Unit Vectors Perpendicular to Each Set Defined in Table 4-b.

Grain 1				Grain 2			
	t_{11}	t_{12}	t_{13}		t_{21}	t_{22}	t_{23}
$\bar{C}_1 =$	0.0937	0.7486	-0.6556	$\bar{C}_2 =$	-0.1562	-0.7789	0.6074

Using equation 26, the matrix M is defined as:

$$M = \begin{bmatrix} -0.9978 & -0.0474 & 0.0416 \\ 0.0490 & -0.0188 & 0.9807 \\ -0.0386 & 0.9816 & 0.1890 \end{bmatrix}$$

This matrix satisfies the minimum conditions of a rotation matrix, i.e.:

- i) The sums of the squares of each row and of each column are unity.
- ii) The dot products between column vectors are zero.

The rotation axis, $\bar{U}$, can be determined from the above matrix as follows:

$$\begin{aligned}\bar{U} &= [m_{32}-m_{23}, m_{13}-m_{31}, m_{21}-m_{12}] \\ &= [0.9816-0.9807, 0.0416+0.0386, 0.0490+0.0474] \\ &= [0.0009, 0.0802, 0.0964]\end{aligned}$$

which is close to the low index direction $[011]$. The trace of the matrix is $T = -0.9965$.

This value when plugged into equation 28 gives the angle of misorientation

$$\Theta = \cos^{-1} \frac{(T-1)}{2} = 176.61^\circ.$$

The graphical method of Goux^[110] permits an easier visualization of the determination of the axis/angle pair, although it is not as accurate as the just described above. Fig. 22 shows a stereographic projection of the four beam directions $\bar{A}_1$, $\bar{A}_2$, $\bar{B}_1$, and $\bar{B}_2$. The intersection of the great circles bisecting the great circles through $\bar{A}_1$ and $\bar{A}_2$ and through $\bar{B}_1$ and $\bar{B}_2$ defines the axis direction $\bar{U}$. $\bar{A}_1'$ and $\bar{A}_2'$ represents the respective projections of $\bar{A}_1$ and $\bar{A}_2$ onto a plane perpendicular to $\bar{U}$. The angle between $\bar{A}_1'$ and $\bar{A}_2'$ represents the angle of misorientation Θ .

APPENDIX B

Activation Energy Related to the Segregation Phenomenon

The steps involved in estimating the activation energy are detailed as follows:

- (1) The elastic strain energy contribution can be estimated using equation 6. The values of the radii for solute and solvent atoms are the Seitz Radius⁴ and taken from a compilation by King.^[131] The bulk and shear moduli have been taken from a compilation by Gschneider.^[132]
- (2) The grain boundary surface energy contribution can be estimated using the first term of the right hand side of equation 13 which is equivalent to:

$$(\gamma_A - \gamma_B)\sigma - 0.174(\Delta H_{Sub}^A \frac{\sigma_B}{\sigma_A} - \Delta H_{Sub}^B)$$

where σ refers to area per atom at the GB and ΔH_{Sub} refers to sublimation energy.

- (3) The alloy interaction contribution can be estimated with the aid of the second term of equation 13, which is equivalent to:

$$\frac{-\Delta H_m}{(3X_A^b X_B^b)}$$

where ΔH_m refers to heat of mixing and whose values have been taken from the data compiled by Hultgren et.al.^[133] and X_A^b and X_B^b refers to the atomic fraction composition for elements A and B respectively in the bulk.

In using the last expression, several assumptions have been made. First, the term is compiled in the limits of infinite dilution, i.e., $X_A^b \rightarrow 0$ and high temperature, i.e., $X_A^{GB} \rightarrow 0$.

For simplicity in calculations, the number of lateral bonds (Z_l) and the number of vertical bonds (Z_v) are assumed to be equal at the grain boundary, and Z , the coordination number in fcc metal is 12.

⁴Seitz radius for an fcc metal is about 11% larger than the radius obtained from half the distance of closest approach.

Tables 5 and 6 show the values of different parameters used in the above estimations, as well as the respective contributions for the activation energy.

Table 5. Thermodynamic Data of *Zn* and *Al*.

Element	Elastic Modulus $\times 10^{-6}(\text{kg/cm}^2)$	Bulk Modulus $\times 10^{-6}(\text{kg/cm}^2)$	Shear Modulus $\times 10^{-6}(\text{kg/cm}^2)$	Poisson's Ratio	Seitz Radius $\text{\AA}$	ΔH_{Sub} (kcal/mole)	ΔH_m (kcal/mole)
<i>Al</i>	0.7240	0.7542	0.271	0.34	1.582	77.57	1.548
<i>Zn</i>	0.940	0.7460	0.379	0.29	1.538	31.55	

Table 6. Contributions to Activation Energy in the Segregation Phenomenon.

Alloy Solvent (solute)	Surface Contribution (kcal/mole)	Alloy Contribution (kcal/mole)	Strain Contribution (kcal/mole)	Activation Energy (kcal/mole)
<i>Al(Zn)</i>	7.434	2.457	0.197	10.09

APPENDIX C

Error Analysis from X-Ray Data

The arrival of X-ray quanta to a detector is random in time. Therefore, the time "t" necessary for the observation of any finite number of counts N is subject to statistical fluctuations giving rise to an error in the observed counting rate $n = \frac{N}{t}$. The type of fluctuation here obeys a Gaussian distribution.

When working with energy dispersive peaks, the standard deviation of a peak integral is taken equal to $\sqrt{N}$.^[134] Where N corresponds to the average number of counts in a time t .

Generally, the interest is not in the standard deviation in the number of counts, but rather in the standard deviation of the counting rate, i.e., $\frac{\sqrt{N}}{t}$, and the fractional standard deviation $\sigma = \frac{\sqrt{N}}{N}$, which is the one used in the present work. Most of the results are reported as ratio of measurements, in whose case the precision of the measurement is given by:

$$\sigma_{TOT} = \sqrt{\sigma_{Zn}^2 + \sigma_{Al}^2}$$

where σ_{Zn} and σ_{Al} are the fractional standard deviation from the Zn and Al peaks respectively.^[135]

One more important source of error in the present work could be the evaporation of Zn due to its volatile character. In particular, when high current densities were used in the microscope. Thus, precautions were taken to minimize this type of problem.

REFERENCES

1. J.W. Gibbs, in *The Scientific Papers of J.W. Gibbs*, vol.I, p. 219, Dover Publications, Inc., New York (1961).
2. J.H. Westbrook, *Metals Rev.*, **9**, 415 (1964).
3. J.P. Stark and H.L. Marcus, *Met. Trans.*, **8A**, 423 (1977).
4. D. Gupta, *Met. Trans.*, **8A**, 1431 (1964).
5. E.D. Hondros and M.P. Seah, *Int. Met. Rev.*, **222**, 262 (1977).
6. M.C. Inman and H.R. Tipler, *Metall. Rev.*, **8**, 105 (1963).
7. W.C. Johnson and H.B. Smarti, *Scripta Met.* **9**, 1205 (1975).
8. E.D. Hondros and D. McLean, in *Grain Boundary Structure and Properties*, G.A. Chadwick and D.A. Smith (eds.), Academic Press, New York, 1976.
9. A. Joshi and D. F. Stein, *Corrosion NACE*, **28**, 321 (1976).
10. S. P. Clough, J. K. Lee, J. R. Bradley, J. A. Carson, W. F. Lange III, K. F. Michaels, C. Seaton, H. I. Aaronson, and K. C. Russell, *Scripta Met.*, **8**, 791 (1974).
11. K. C. Russell and H. I. Aaronson, *Scripta Met.*, **463** (1976).
12. C. J. Simpson, W. C. Winegard and K. T. Aust, in *Grain Boundary Structure and Properties*, G. A. Chadwick and D. A. Smith (eds.), Academic Press, New York, 1976, p. 201.
13. H. Gleiter and B. Chalmers, in *Progress in Materials Science*, Vol. 16, J. W. Christian and T. B. Massalski (eds.), Pergamon Press, New York, 1972, p. 94.
14. R. Rosenberg and L. Berenbaum, *Appl. Phys. Letters*, **12**, 201 (1968).
15. F. M. D'Heurle and R. Rosenberg, *Phys. Thin Films*, **7**, 257 (1973).
16. K. T. Aust and J. M. Westbrook, *Lattice Defects in Quenched Metals*, Academic Press, 1965, p. 771.
17. T. R. Anthony, *Acta Met.*, **17**, 603 (1969).
18. C. L. White and W. A. Coughlan, *Met. Trans.*, **8A**, 1403 (1977).
19. P. Doig and P. E. J. Flewitt, *J. Microscopy*, **112**, 257 (1977).
20. P. W. Palmberg and T. N. Rodin, *J. Appl. Phys.*, **39**, 2425 (1968).

21. L. Smith and J. R. Low, *Metall. Trans.*, **5**, 279 (1974).
22. H. Ohtani, H. C. Feng, C. J. McMakon, Jr., and R. A. Mulford, *Metall. Trans.*, **7**, 87 (1976).
23. C. J. McMahon, Jr., E. F. Furubayashi, H. Ohtani, and H. C. Feng, *Acta Metall.*, **24**, 695 (1976).
24. P. Doig and P. E. J. Flewitt, *Phil. Mag.*, **37**, 759 (1978).
25. P. Doig and P. E. J. Flewitt, *J. Microsc.*, **110**, 107 (1977).
26. P. Doig, P. E. J. Flewitt and J. W. Edington, *Corrosion*, **33**, 217 (1977).
27. D. B. Dove, C. G. Pantano and J. B. Andrews, *J. App. Phys.*, **48**, 2776 (1977).
28. G. Carter and J. S. Collington, *Ion Bombardment of Solids*, Heinemann, London, 1968.
29. G. Cliff and G. W. Lorimer, *J. Microsc.*, **103**, 203 (1975).
30. G. Thomas and M. J. Goringe, *Transmission Electron Microscopy of Materials*, John Wiley & Sons, N. Y., 1979.
31. D. McLean, *Grain Boundaries in Metals*, Clarendon Press, Oxford, 1957.
32. R. F. Mehl, *Amer. Soc. Metals*, **29**, 752 (1941).
33. W. S. Gorsky, *Phys. Z. Sowjetunion*, **8**, 475 (1935).
34. I. Langmuir, *J. Amer. Chem. Soc.*, **40**, 1361 (1918). See also: A. W. Adamson, *Physical Chemistry of Surfaces*, John Wiley & Sons, N. Y., 1976.
35. H. Suzuki, *J. Phys. Soc. Jpn*, **17**, 322 (1962).
36. H. H. Farrel, H. S. Isaacs and M. Stragin, *Surface Sci.*, **38**, 31 (1971).
37. M. P. Seah and E. D. Hondros, *Proc. Roy. Soc. (London)*, **A335**, 191 (1973).
38. J. Friedler, *Advan. Phys.*, **3**, 446 (1954).
39. S. Brunaver, P. H. Emmett and E. Teller, *J. Amer. Chem. Soc.*, **60**, 309 (1938).
40. R. H. Fowler and E. A. Guggenheim, *Statistical Thermodynamics*, Cambridge Univ. Press, Cambridge, 1939.
41. F. L. Williams and D. Nason, *Surface Sci.*, **45**, 377 (1974).
42. P. Wynblatt and R. C. Ku, *Surface Sc.*, **65**, 511 (1977).

43. N. H. Tsai, G. M. Pound, and F. F. Abraham, *J. Catalysis*, **50**, 200 (1977).
44. M. P. Seah, *Surface Sci.*, **80**, 8 (1979).
45. P. Wynblatt and R. C. Ku, in *Interfacial Segregation*, A. S. M., Metals Park, Ohio 1962.
46. R. King and B. Chalmers, in *Progress in Metal Physics*, Butterworths Scientific Publications, London, 1949, p. 127.
47. W. Rosenshain and J. C. W. Humphrey, *J. Iron Steel Inst.*, **87**, 219 (1913).
48. S. Amelinckx and W. Dekeyser, *Sol. St. Phys.*, **8**, 325 (1959).
49. F. Hargreaves and R. T. Hills, *J. Inst. Met.*, **41**, 257 (1929).
50. N. F. Mott, *Proc. Phys. Soc.*, **60**, 391 (1948).
51. J. M. Burgers, *Proc. Phys. Soc.*, **52**, 23 (1940).
52. W. T. Read and W. Shockley, *Phys. Rev.*, **78**, 225 (1950).
53. B. Loberg and H. Norden, in *Grain Boundary Structure and Properties*, G. A. Chadwick and D. A. Smith (eds.), Academic Press, New York, 1976, p. 1.
54. D. G. Brandon, B. Ralph, S. Ranganathan and M. S. Wald, *Acta Met.*, **12**, 813 (1964).
55. W. Bollman, *Crystal Defects and Crystalline Interfaces*, Springer-Verlag, New York, 1970, p. 143.
56. H. Grimmer, *Scripta Met.*, **7**, 1295 (1973).
57. P. Chaudhari and J. W. Matthews (eds.), *Grain Boundaries and Interfaces*, North-Holland Publishing Co., Amsterdam, 1972.
58. P. H. Pumphrey in *Grain Boundary Structure and Properties*, D. Smith (ed.), Academic-Press, London, 1976, p. 139.
59. M. L. Kronberg and F. M. Wilson, *Trans. A.I.M.E.*, **85**, 26 (1964).
60. F. C. Frank, *Conference on Defects in Crystalline Solids*, The Physical Society, London, 1955, p.150.
61. D. G. Brandon, *Acta Met.*, **14**, 1479 (1966).
62. S. Ranganathan, *Acta Cryst.*, **21**, 197 (1966).
63. L. E. Murr, *Interfacial Phenomena in Metals and Alloys*, Addison-Wesley Publishing Co., Reading-Massachusetts, 1975.

64. P. H. Pumphrey, and K. M. Bowkett, *Scripta Met.*, **5**, 365 (1975).
65. H. Mykura, in *Grain Boundary Structure and Kinetics*, A. S. M., Metals Park, Ohio (1979).
66. H. Grimmer, W. Bollman and D. M. Warrington, *Acta Cryst.*, **A30**, 197 (1974).
67. G. H. Bishop and B. Chalmers, *Scripta Met.*, **2**, 133 (1968).
68. F. C. Frank, in *Carnegie Institute Technology Symposium on The Plastic Deformation of Crystalline Solids*, Office of the Naval Research, Washington D.C., 1950.
69. R. W. Balluffi, in *Interfacial Segregation*, A. S. M., Metals Park, Ohio 1977.
70. W. Bollman in *Crystal Defects and Crystalline Interfaces*, Springer-Verlag, New York, 1970, p. 206.
71. D. A. Smith and R. C. Pond, *Int. Met. Rev.*, **205**, 61 (1976).
72. R. C. Pond and D. A. Smith in *6th Eur. Conf. Elect. Mic.*, University Press, Jerusalem, Israel, 1976, p. 500.
73. J. P. Hirth and R. W. Balluffi, *Acta Met.*, **21**, 929 (1973).
74. R. A. Varin, J. A. Kozubowski and M. W. Grabski, *J. De Physique, colloque C4, Supplément au n° 10*, tome 36, C4-43 (1975).
75. R. W. Balluffi, Y. Komen, and T. Schober, *Surf. Sci.*, **68** (1972).
76. S. L. Sass, T. Y. Tan, and R. W. Balluffi, *Phil. Mag.*, **31**, 559 (1975).
77. D. Y. Guan and S. L. Sass, *Phil. Mag.*, **27**, 1211 (1973).
78. T. Y. Tan, T. Y. Tan, S. L. Sass and R. W. Balluffi, *Phil. Mag.*, **31**, 575 (1975).
79. P. H. Pumphrey, *Scripta Met.*, **6**, 107 (1972).
80. B. Ralph, W. Bollman, B. Michaut and G. Sainfort, *Phys. Stat. Sol. (a)*, **13**, 637 (1972).
81. J. A. Chandler, *X-ray Microanalysis in The Electron Microscope*, North-Holland Publishing Co., Amsterdam, 1977.
82. B. D. Cullity, *Elements of X-ray Diffraction*, Addison-Wesley Publishing Co., Menlo Park, Ca., U.S.A., 1956.
83. L. V. Azaroff, *Elements of X-ray Crystallography*, McGraw-Hill, Inc., 1968.
84. J. J. Hren, J. I. Goldstein and D. C. Joy, *Introduction to Analytical Electron*

- Microscope*, J. D. Goldstein (ed.), Plenum Publishing Co., New York, 1979.
85. R. Castaing, *Thesis, University of Paris*, ONERA Publ., sup # 55, 1951.
 86. R. Tixier and J. Philibert, in *Proc. 5th Int. Cong. on X-ray Optics and Microanalysis*, G. Mollestedt G. and K. H. Gaukler (eds.), Springer-Verlag, 1969, p. 180.
 87. G. Cliff and G. W. Lorimer, *J. Microsc.*, **103**, 203 (1975).
 88. G. Cliff and G. W. Lorimer, *Proc. 5th European Congress on Electron Microscopy*, Institute of Physics, (1972).
 98. H. Gleiter, *Acta Met.*, **18**, 117 (1970).
 90. G. F. Bolling and W. C. Winegard, *J. Inst. of Metals*, **86**, 492 (1957).
 91. P. R. Howell, D. E. Fleet, T. F. Page and B. Ralph, *Proc. 3rd International Conference On Strength of Metals and Alloys*, vol. 1, Cambridge, 1973, p. 149.
 92. P. R. Howell, D. E. Fleet, A. Hildon and B. Ralph, *J. Microsc.*, **107**, 155 (1976).
 93. G. Henry, *Rev. Met.*, **56**, 417 (1959).
 94. J. C. Rellick, C. J. McMahon, Jr., H. L. Marcus and P. W. Palmberg, *Met. Trans.*, **2**, 1492 (1972).
 95. G. H. Bishop, W. H. Hartt and G. A. Bruggeman, *Acta Met.*, **19**, 37 (1971).
 96. R. Gronsky and P. Furrer, *Met. Trans.*, **12A**, 121 (1981).
 97. B. D. Powell and D. P. Woodruff, *Phil. Mag.*, **34**, 169 (1976).
 98. M. J. Weins and J. J. Weins, *J. de Phys.*, **36**, Colloque C-4, **10**, 81 (1975).
 99. R. D. Bourquin in *Computer Simulation for Materials Applications*, R. J. Arsenault and J.R. Beeler, Jr. and J. A. Simmons (eds.), *Nucl. Met.*, **20**, Part 1, 325 (1976).
 100. D. A. Smith and G. D. W. Smith, *Proc. 3rd International Conference On Strength of Metals and Alloys*, vol. 1, Cambridge, 1973, p. 145.
 101. B. Chalmers, *Can. J. Phys.*, **31**, 132 (1953).
 102. R. D. Schoone and E. A. Fishione, *Rev. Sc. Inst.*, **57**, 1351 (1966).
 103. K. C. Thompson-Russell and J. W. Edington, *Practical Electron Microscopy in Materials Science*, vol. 5, Macmillan Press, London, 1977.

104. D. C. Joy and D. M. Maher, *SEM*, **1**, 325 (1977).
105. N. J. Zaluzec, in *Introduction to Analytical Electron Microscopy*, J. J. Hren, J. J. Goldstein and D. C. Joy (eds.), Plenum Press, New York, 1979, p. 121.
106. Bell, W. L. and G. Thomas, in *Proceedings of the 27th Conference of the Electron Microscopy Society of America*, Claitors, Baton Rouge, LA, 1969, p. 158.
107. Amelinckx, S., *Direct Observation of Dislocations*, Academic Press, N. Y., 1964, p. 158.
108. G. Thomas, *Modern Diffraction Imaging Techniques in Materials Science*, S. Amelinckx, et.al. (eds.), North Holland, Amsterdam, 1970.
109. T. Y. Tan, W. L. Bell and G. Thomas, *Phil Mag.*, **24**, 417 (1971). See also: P. M. Kelly, A. Jostons, R. G. Blake and J. G. Napier, *Phys. Stat. Sol.*, **31**, 771 (1975).
110. C. Goux, *Bull. du Cercle d'Etudes des Metaux*, **8**, 185 (1961).
111. C. T. Young, J. H. Steele, Jr. and J. L. Lytton, *Met. Trans.*, **4**, 2081 (1973).
112. I. Herbeuval, M. Biscondi and C. Goux, *Mem. Sci. Rev. Met.* **70**, 39 (1973).
113. G. Hasson, J. Y. Boos, J. Herbeuval, M. Biscondi and C. Gous, *Surface Sci.*, **31**, 115 (1972).
114. T. R. Anthony, *J. App. Phys.*, **41**, 3969 (1970).
115. N. L. Peterson and S. J. Rothman, *Phys. Rev.*, **B**, **1**, 3264 (1970).
116. B. Aufray, F. Cabane-Brouty and J. Cabane, *Acta Met.*, **27**, 1849 (1979).
117. F. Moya, G. E. Moya-Gontier and F. Cabane-Brouty, *Phys. Stat. Sol. (a)*, **2**, 101 (1970).
118. F. Moya and G. E. Moya-Gontier, *J. Phys.*, **36 C4**, 157 (1975).
119. P. Petrino, F. Moya and F. Cabane-Brouty, *J. Solid State Chem.*, **2**, 439 (1970).
120. M. E. Glicksman and R. A. Masumura, *Met. Trans.*, **8A**, 1373 (1977).
121. H. Oppalzer and U. Knauer, *SEM*, **1**, 111 (1979).
122. R. W. Carpenter and J. Bentley, *SEM*, **1**, 153 (1979).
123. P. B. Hirsch, R. B. Nicholson, A. Howie, D. W. Pashley and M. J. Whelan, *Electron Microscopy Of Thin Crystals*, Butterworths, London

(1965).

124. D. F. Kyser and R. H. Geiss, in *Eighth Int. Conf. On X-ray Optics And Microanalysis*, Boston Massachusetts, 1977.
125. J. Orloff and L. W. Swanson, *SEM*, **1**, 39 (1979).
126. R. Sinclair, R. Gronsky and G. Thomas, *Acta Met.*, **24**, 789 (1976).
128. C. L. White, *The Segregation of Impurities to Grain Boundaries with Special Reference to Sulfur Segregation in Nickel Base Alloys*, Ph.D. Dissertation, Mich. Tech. Univ., 1974.
129. R. W. Pasko, *The Effect Of Zinc On The Susceptibility Of Grain Boundaries In Al-Zn Bicrystals To Liquid Metal Embrittlement*, Master Thesis, I.I.T., Chicago, Ill., 1977.
130. N. A. Gjostein, *Acta Met.*, **11**, 957 (1963).
131. H. W. King, *J. Mater. Sci.*, **1**, 79 (1966).
132. K. A. Gschnerdner, in *Solid State Physics*, vol. **16**, F. Seitz and D. Turnbull (eds.), Academic Press, New York, 1964, p. 275.
133. R. Hultgren, P. D. Desai, D. T. Hawkins, M. Gleiser, K. K. Kelley, in *Selected Values of The Thermodynamic Properties of Binary Alloys*, A. S. M., Metals Park, Ohio, 1973.
134. L. D. Landau and E. M. Lifshitz, *Statistical Physics*, Pergamon Press, 1980.
135. Y. Beers, *Theory of error*, Addison-Wesley Publication Co., 1957.

FIGURE CAPTIONS

- Fig. 1 Outline of the materials phenomena involving segregation. (After reference 5).
- Fig. 2 Schematic diagrams of (a) The Gibbs model for adsorption to an interphase boundary. (b) True adsorption of solute to an interphase boundary. (c) Second phase at an interphase boundary. (d) True segregation to a grain boundary. (After reference 128).
- Fig. 3 Definition of a symmetrical tilt boundary in a FCC structure. Note that both grains have parallel $\langle 110 \rangle$ growth directions (GD). The tilt angle Θ is the angle between $\langle 100 \rangle$ directions which are in the plane that is perpendicular to the growth direction. (After reference 129).
- Fig. 4 Schematic representation of a bicrystal $\langle 110 \rangle$ tilt boundary. Notice the boundary plane bisects the tilt angle ($\Theta = \Theta_1 + \Theta_2$). Θ_1 and Θ_2 measure the angles between the $\langle 100 \rangle$ directions and the respective surface normals (SN_1, SN_2) to the grains 1 and 2.
- Fig. 5 DSC-Lattice, CSL and O-lattice when a simple cubic crystal 1 is rotated 36.9° around $[001]$, ($\Sigma=5$). The base vectors of the DSC lattice are shown as $\bar{b}_1$ and $\bar{b}_2$.
- Fig. 6 Outline of grain boundary defects.
- Fig. 7 The various effects of electron-specimen interaction. (After reference 81).
- Fig. 8 Histograms of segregation to grain boundaries for S and Sn in Fe At $600^\circ C$ (after reference 36), for Bi in Cu at $700^\circ C$ (after reference 96) and for P in $33Cr-0.5M$ steel at $450^\circ C$. (After reference 44).
- Fig. 9 (a) Schematic cross section of the apparatus used to grow bicrystals. (b) Schematic cross section of the bicrystal showing its dimensions.

- Fig. 10 Schematic process followed in the preparation of foils for the electron microscope.
- Fig. 11 Auger spectrum of *Al* bicrystal prior to *Zn*-deposition.
- Fig. 12 Typical heat treatments of the specimens previous to their preparation for the microscope work. These heat treatments were used to generate the experimental data in Fig. 24.
- Fig. 13 Plot of current as a function of the potential used in the selection of optimum conditions for the electropolishing process of TEM specimens.
- Fig. 14 Arrangement of the TEM and the solid state detector (SSD) for x-ray collection
- Fig. 15 Calculated Peak/Background ratio Vs. atomic number *Z* of the measured x-ray line. Various operating voltages $E_o = 25, 50, 100$ and 200 kV are considered. (After reference 105).
- Fig. 16 (a) The production of x-rays in the TEM showing the position of the solid state detector and (b) a schematic representation of a solid state detector through a thin beryllium window producing electron-hole pairs within the semiconductor crystal. The ionizations produce pulses which are amplified by a field effect transistor (FET) built into the rear of the crystal. (After reference 81).
- Fig. 17 Typical display of an energy spectrum showing the characteristic x-ray lines for the *Al-Zn* system. The *Cu* signal comes from spurious radiation of the system.
- Fig. 18 (a) Two beam: (113) convergent beam diffraction pattern (CBDP) from an *Al-Zn* foil of thickness approximately $1000 \text{ \AA}$. (b) Two beam: (200) convergent beam diffraction pattern from the same specimen as in (a).
- Fig. 19 Plots of $(\frac{S_i}{n_i})^2$ as a function of $(\frac{1}{n_i})^2$ corresponding to the CBDP in Fig. 18.
- Fig. 20 Schematic representation of the two vectors associated with each grain in a bicrystal before and after a tilting in the microscope.

Fig. 21 (a,b) Diffraction patterns, $(SAD_1)_1$ and $(SAD_2)_1$, from grains 1 and 2, respectively, of the bicrystal detailed in appendix A. (c,d) Diffraction patterns, $(SAD_1)_2$ and $(SAD_2)_2$, from the same grains after the specimen has been tilted 36° .

Fig. 22 A stereographic projection describing a Goux analysis^[110] of the diffraction patterns in Fig. 21.

Fig. 23 Typical concentration profile across a grain boundary.

Fig. 24 Plot of solute segregation as a function of annealing temperature. Two regimes are markedly differentiated with different activation energies for each regime.

Fig. 25 Plot of the Zn/Al count rate ratio as a function of the distance along the boundary plane for three bicrystals classified according to their axis angle pair:

a) $\Sigma = 17$, $\langle 100 \rangle / 61.62^\circ$

b) $\Sigma = 7$, $\langle 311 \rangle / 64.62^\circ$

c) $\Sigma = 7$, $\langle 111 \rangle / 38.21^\circ$

Fig. 26 (a) bright field image of a GB showing extrinsic dislocations with an average spatial distribution of about 2000 Å. (b) Plot of the Zn/Al count rate as a function of the distance along the GB above.

Fig. 27 Bright field (a) and weak beam (b) images of a grain boundary showing extrinsic dislocations in its neighborhood.

Fig. 28 Solute concentration profile along the GB in Fig. 27. Note the periodicity in solute distribution as compared to the dislocation separation in Fig. 27.

Fig. 29 Weak beam image of a rather irregular boundary showing the presence of secondary grain boundary dislocations. The arrow shows the only position where a marked change of solute concentration was detected as it is depicted in the attached EDX-spectrum.

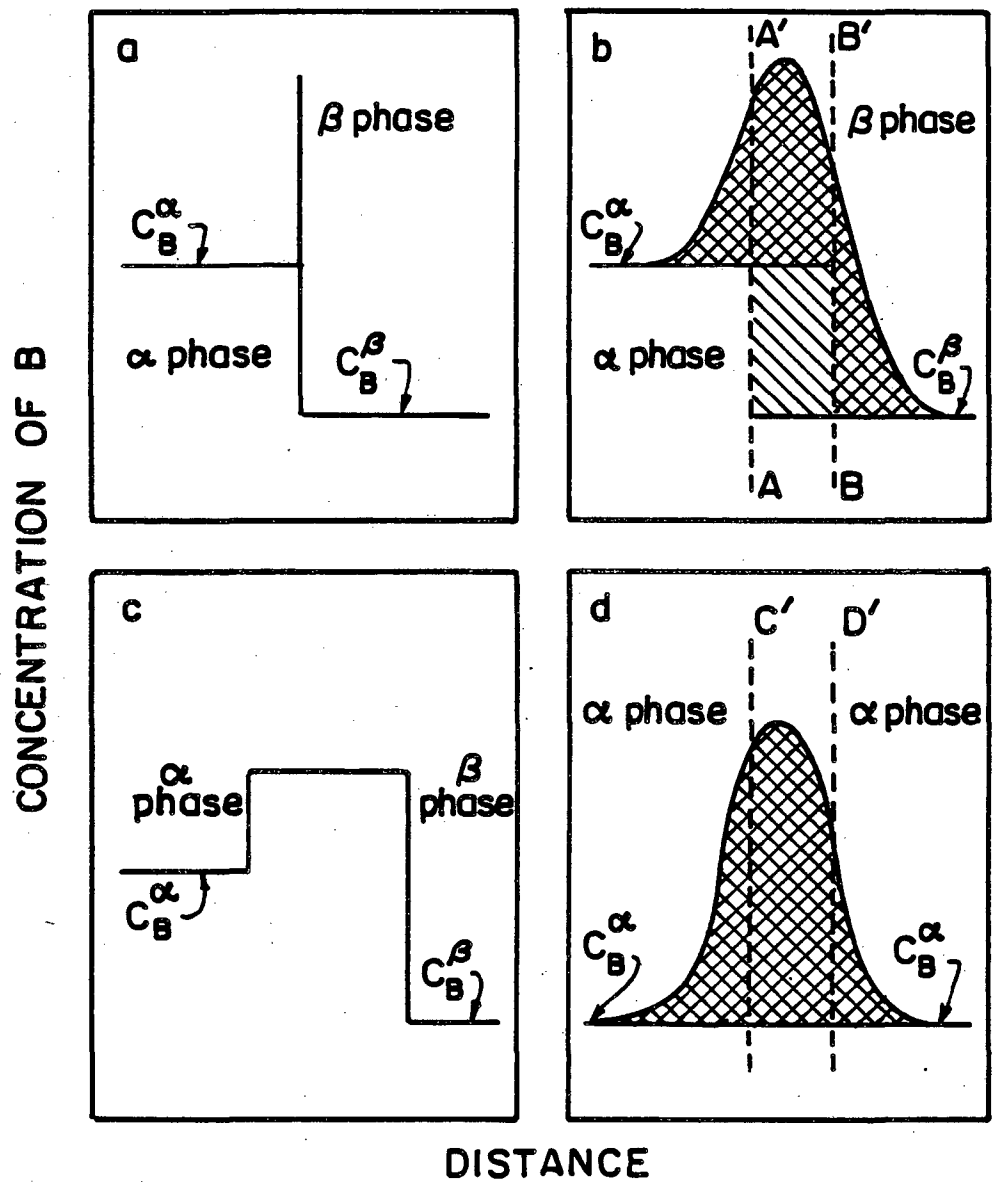
- Fig. 30 Weak beam images of distorted grain boundaries.
- Fig. 31 (a) Bright field image of an *Al* grain boundary (undoped), and (b) bright field image of an *Al* grain boundary after it has been doped with *Zn*. The small arrows show the presence of ledges attributed to the segregation phenomenon.
- Fig. 32 TEM image of a low Σ boundary showing a large central ledge structure. The numbered regions correspond to Fig. 33.
- Fig. 33 EDS output for the regions of Fig. 33. The high *Zn* signal is from the ledge region 1, the intermediate from boundary region 2 and the low from matrix region 3.
- Fig. 34 *Zn/Al* count rate ratio as a function of the misorientation angle for boundaries with misorientation axis of the type $\langle 110 \rangle$.
- Fig. 35 (a) Energy of symmetrical tilt boundaries about [011] in aluminum. (b) Penetration of Zinc parallel (solid line) and perpendicular (dashed line) in aluminum bicrystals. (After references 112 and 113).
- Fig. 36 Weak beam image of a grain boundary. The arrow shows the position where the electron probe detected a pronounced change in *Zn* concentration.
- Fig. 37 TEM image of a low Σ boundary showing the presence of closely spaced secondary dislocations.
- Fig. 38 (a) Schematic representation of the interaction of an atom with a surface (S), single ledge (L) and double ledge (D). (b) Adsorption energy diagram. (After reference 130).
- Fig. 39 Schematic representation of the resulting forces as a consequence of the different type of interactions that the microstructures and microaggregates experience along the boundary plane. Notice the space available at the maximum misfit region.

Fig. 40 A schematic diagram showing the effect of increasing temperature on the occupation of grain boundary sites by solute atoms.

Fig. 41 *Al-Zn* binary phase diagram showing limits of solid solubility at temperatures (330 °C - 600 °C) used in this study.

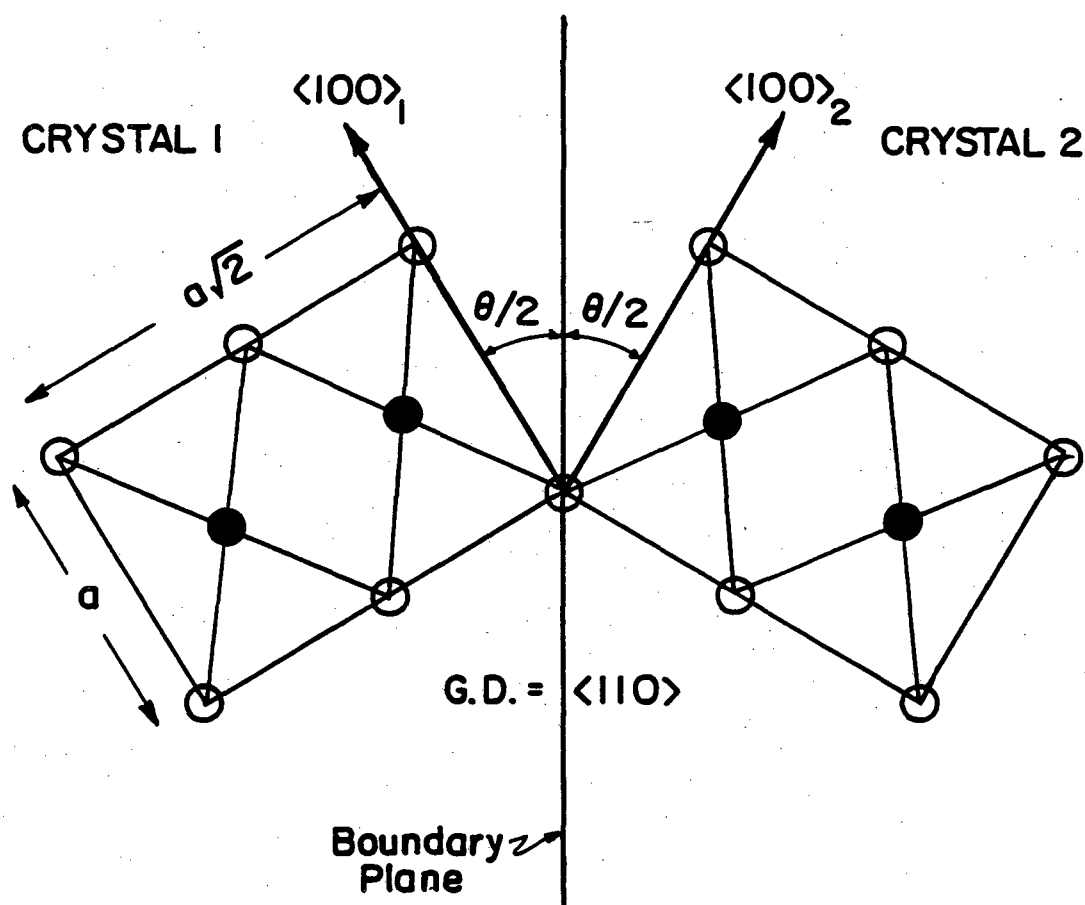
INTERFACIAL SEGREGATION	
MECHANICAL PHENOMENA	KINETIC PHENOMENA
Temper Brittleness	Controlled Precipitate Growth
	Diffusion Creep
Intergranular Fatigue Strength	Grain Boundary Diffusivity
Intergranular Stress	Intergranular Corrosion
Corrosion Cracking	Creep Cavitation
Intergranular Hydrogen Embrittlement	Stabilizing Grain Size (Sintering) or Texture
Adhesion (metal to glass, ceramics or polymers; dispersion/matrix)	Catalysis (segregate poisons and promoters)
Creep Rupture Life	Tribological Properties (surface segregation, friction, and wear)
	Surface Corrosion and Oxidation
Weld Re-Heat Cracking	Surface Hardened Layers (carburizing, boriding, nitriding)

Fig. 1



XBL 817-6175

Fig. 2



● ATOMS IN LAYER "n"

○ ATOMS IN LAYER "n + $\frac{a\sqrt{2}}{2}$ "

XBL 816-5880

Fig. 3

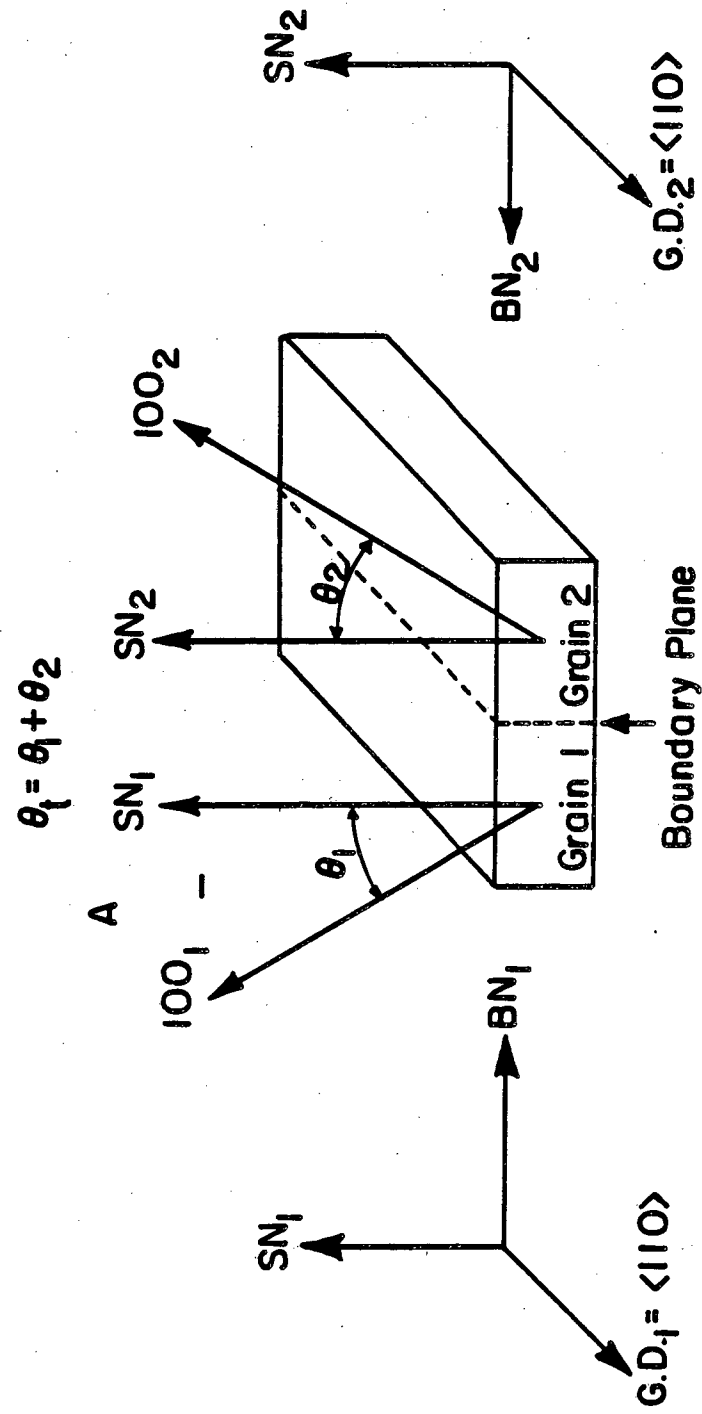
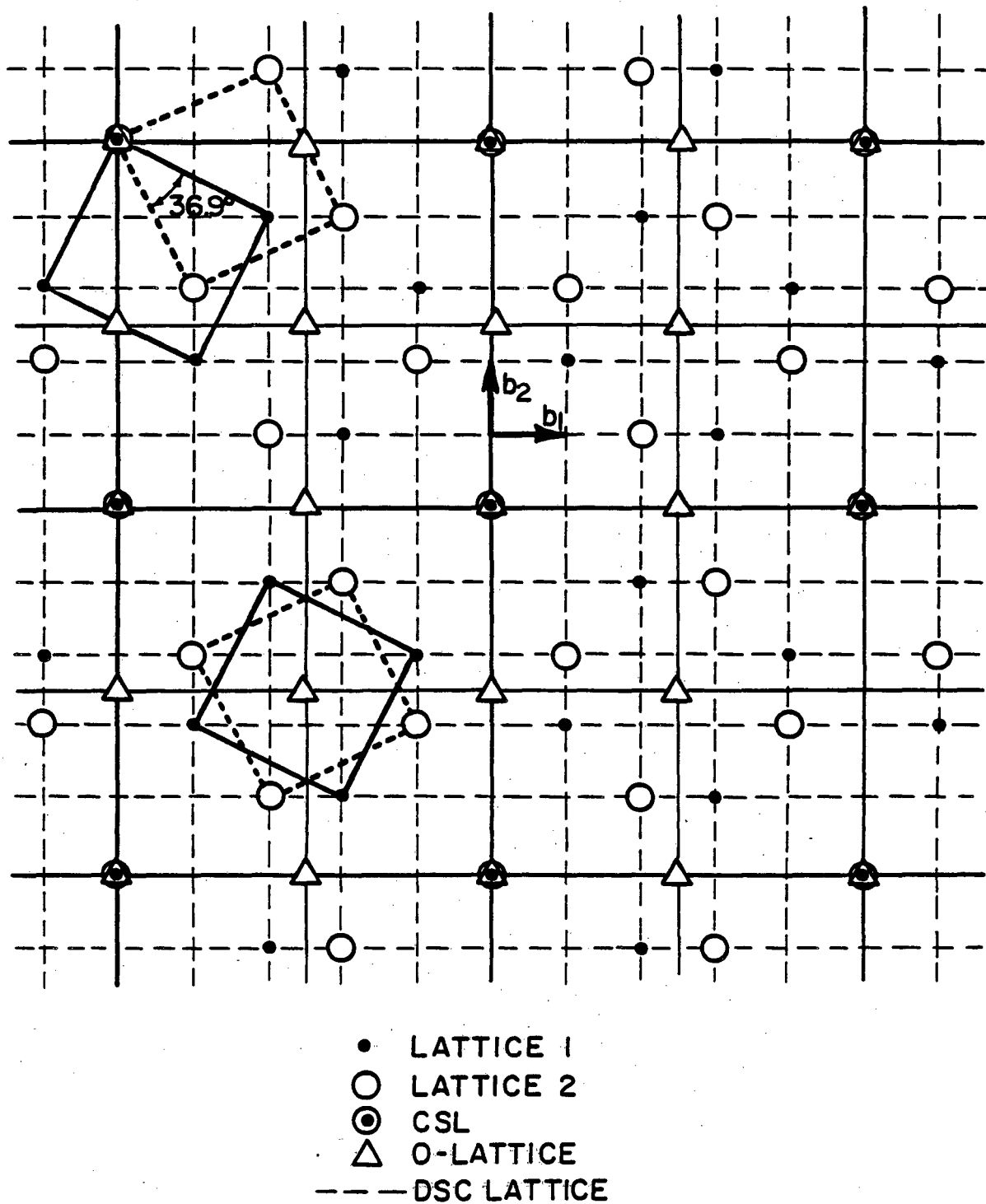


Fig. 4

XBL 816-5881

$$\Sigma = 5, \langle 001 \rangle / 36.9^\circ$$



XBL 816-5878

Fig. 5

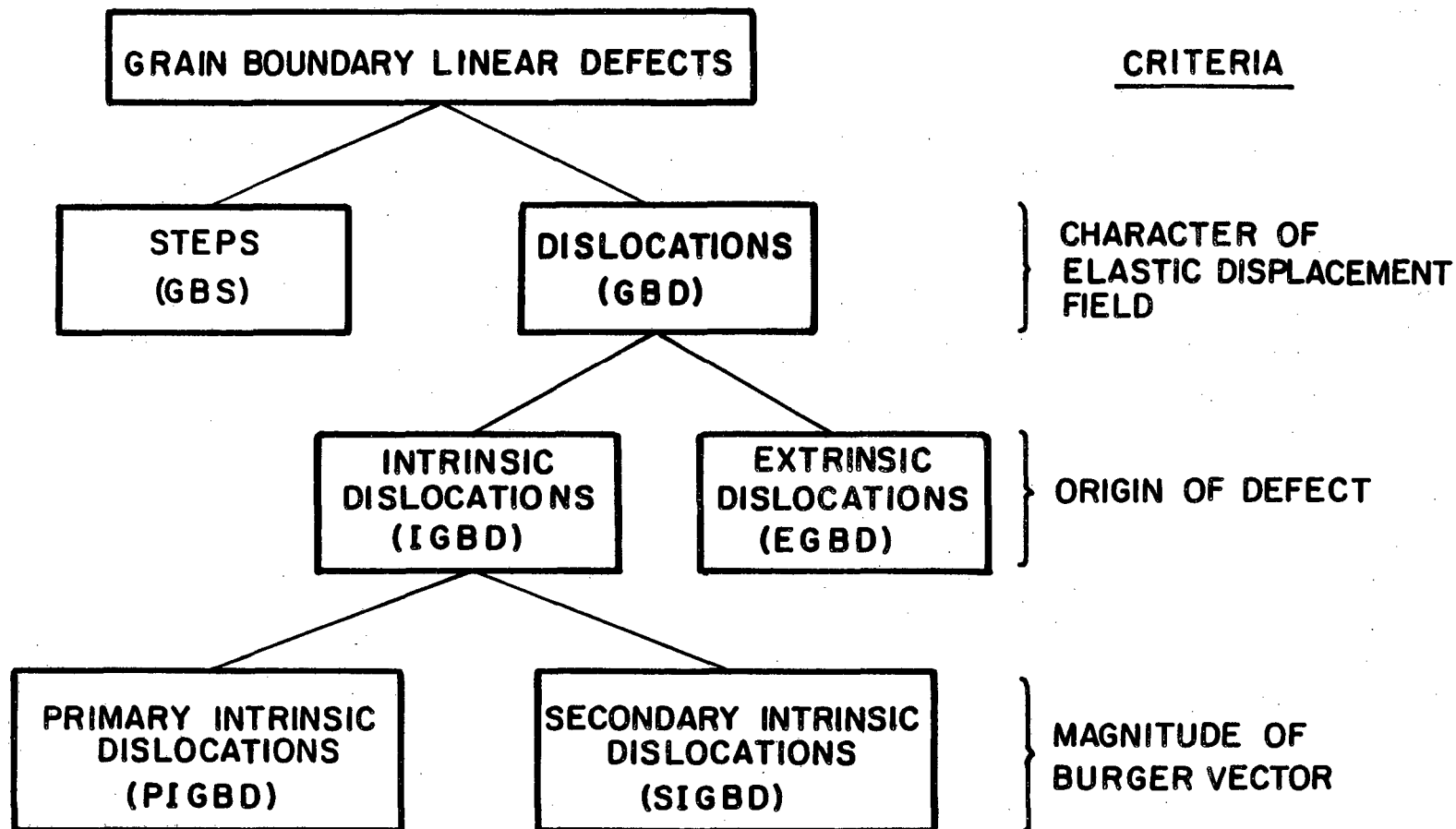
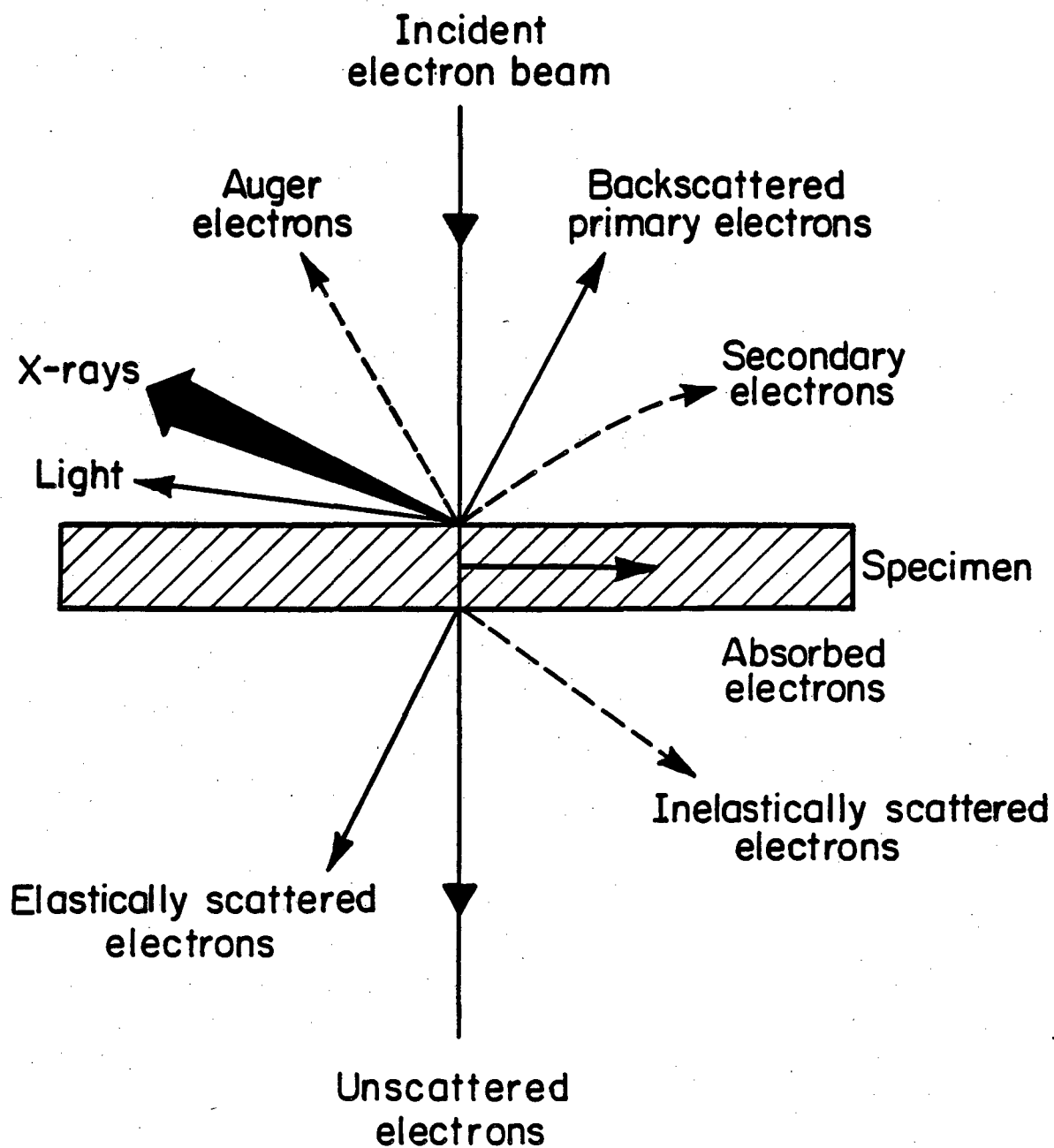


Fig. 6

XBL 816-5882



XBL 8010-6136

Fig. 7

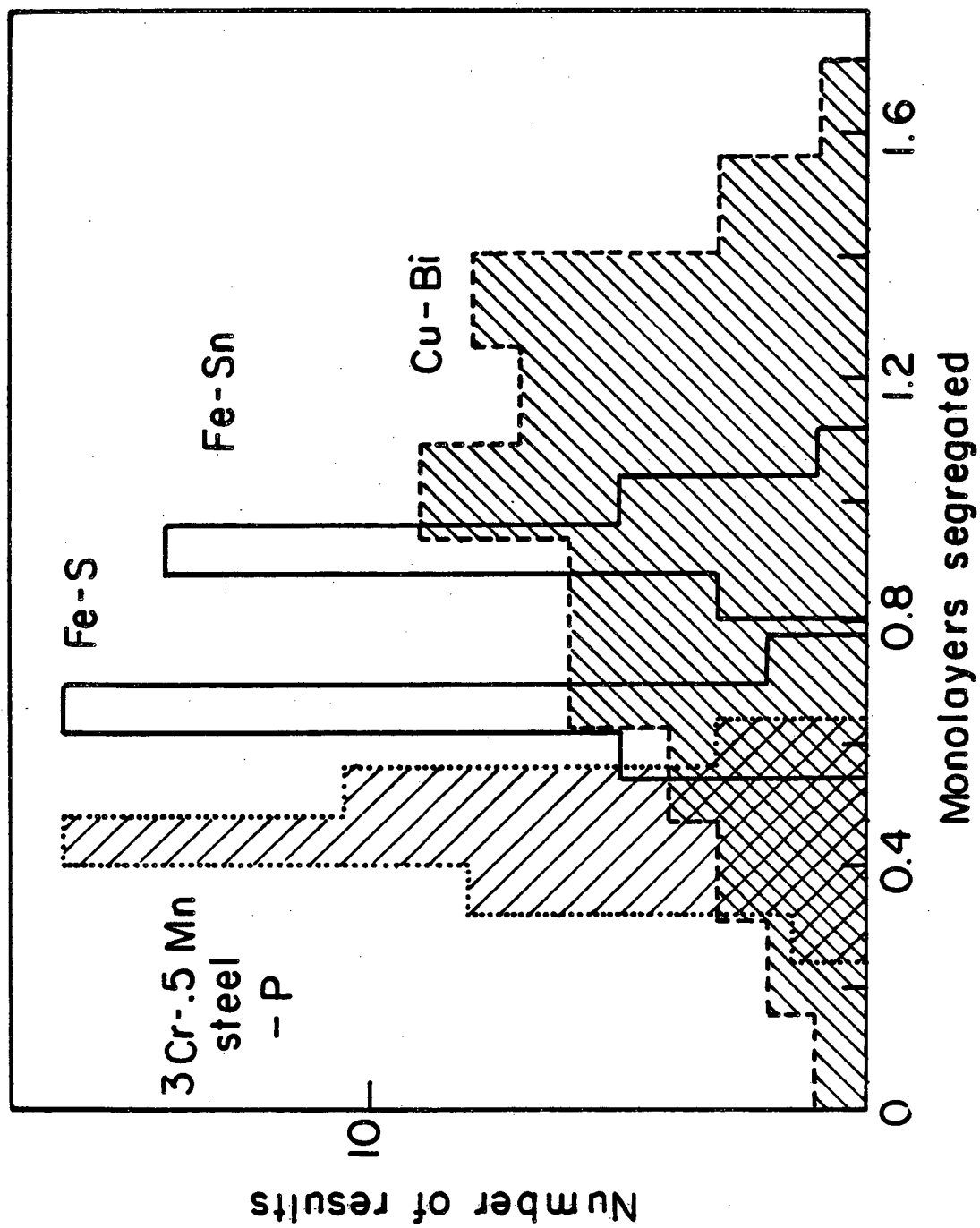


Fig. 8

XBL 819-6600

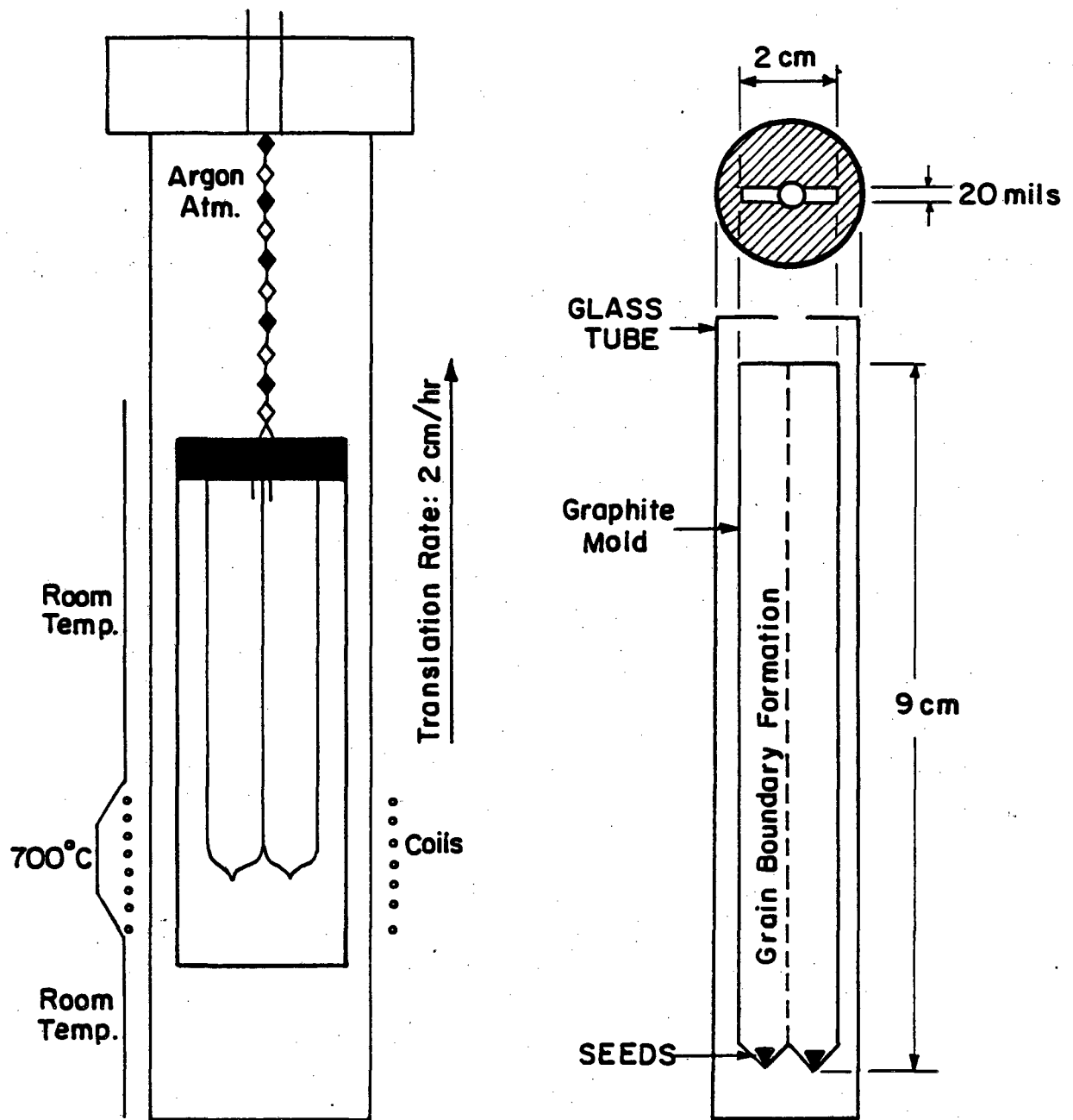
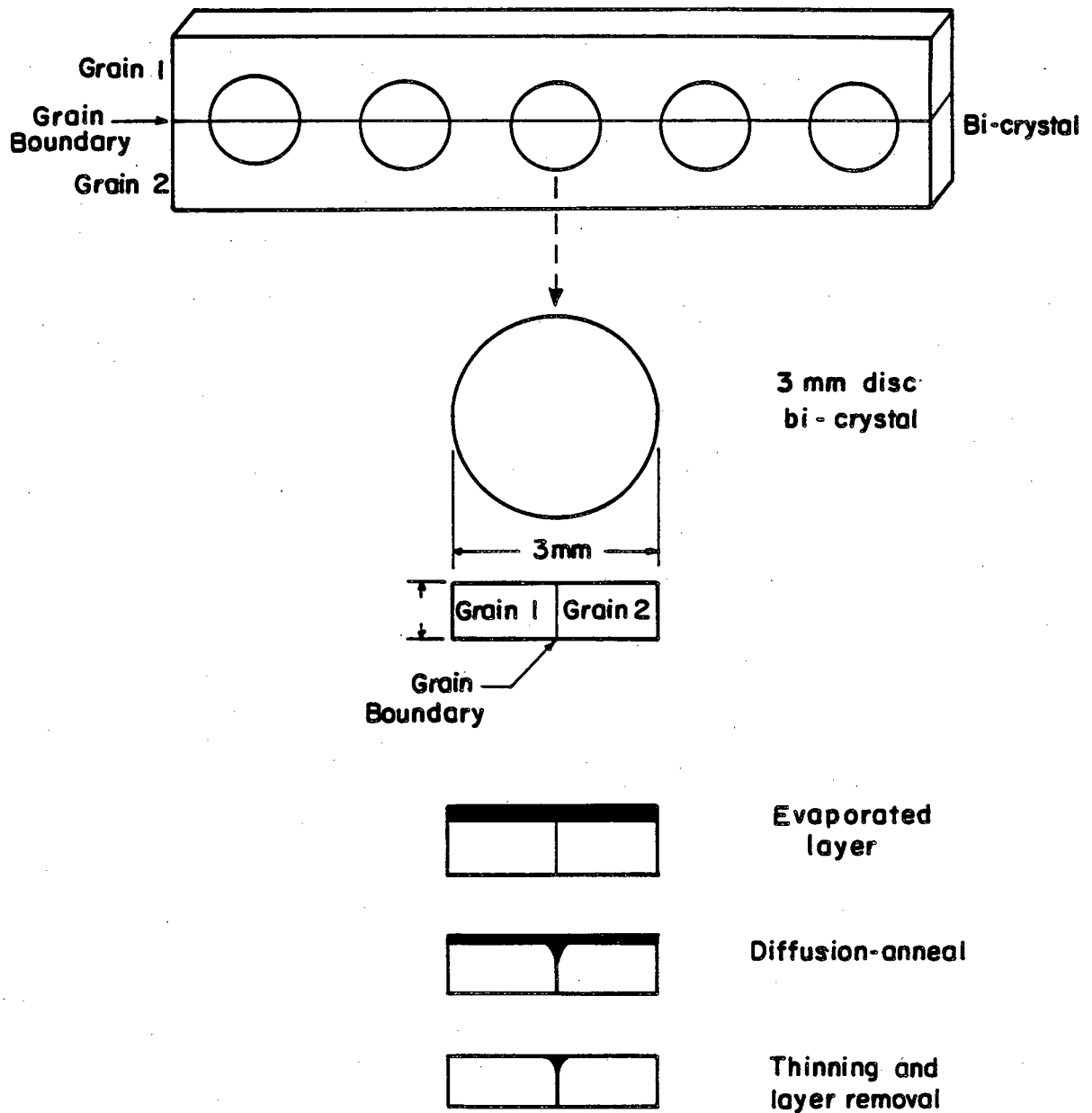


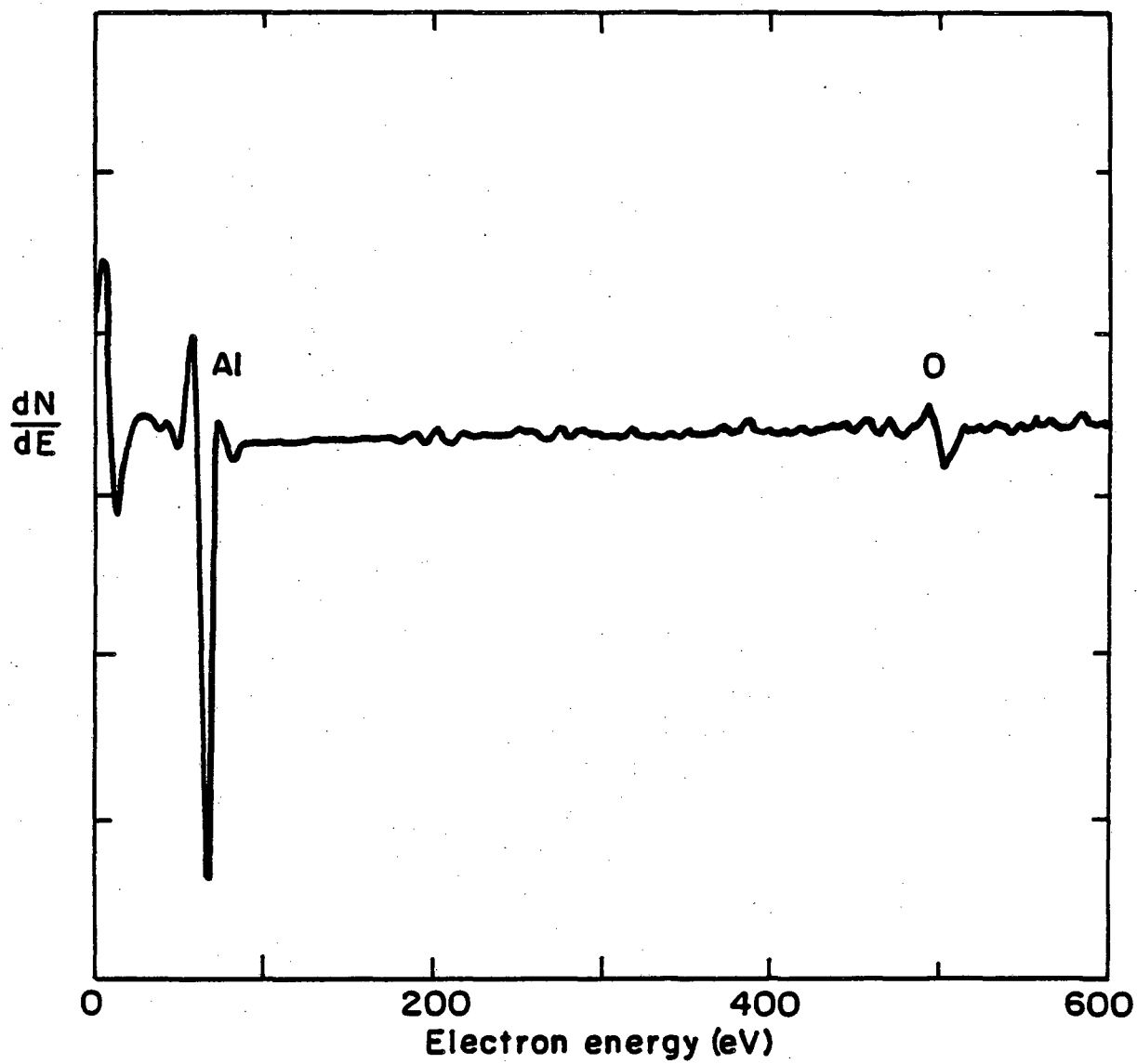
Fig. 9

XBL 802-8368A



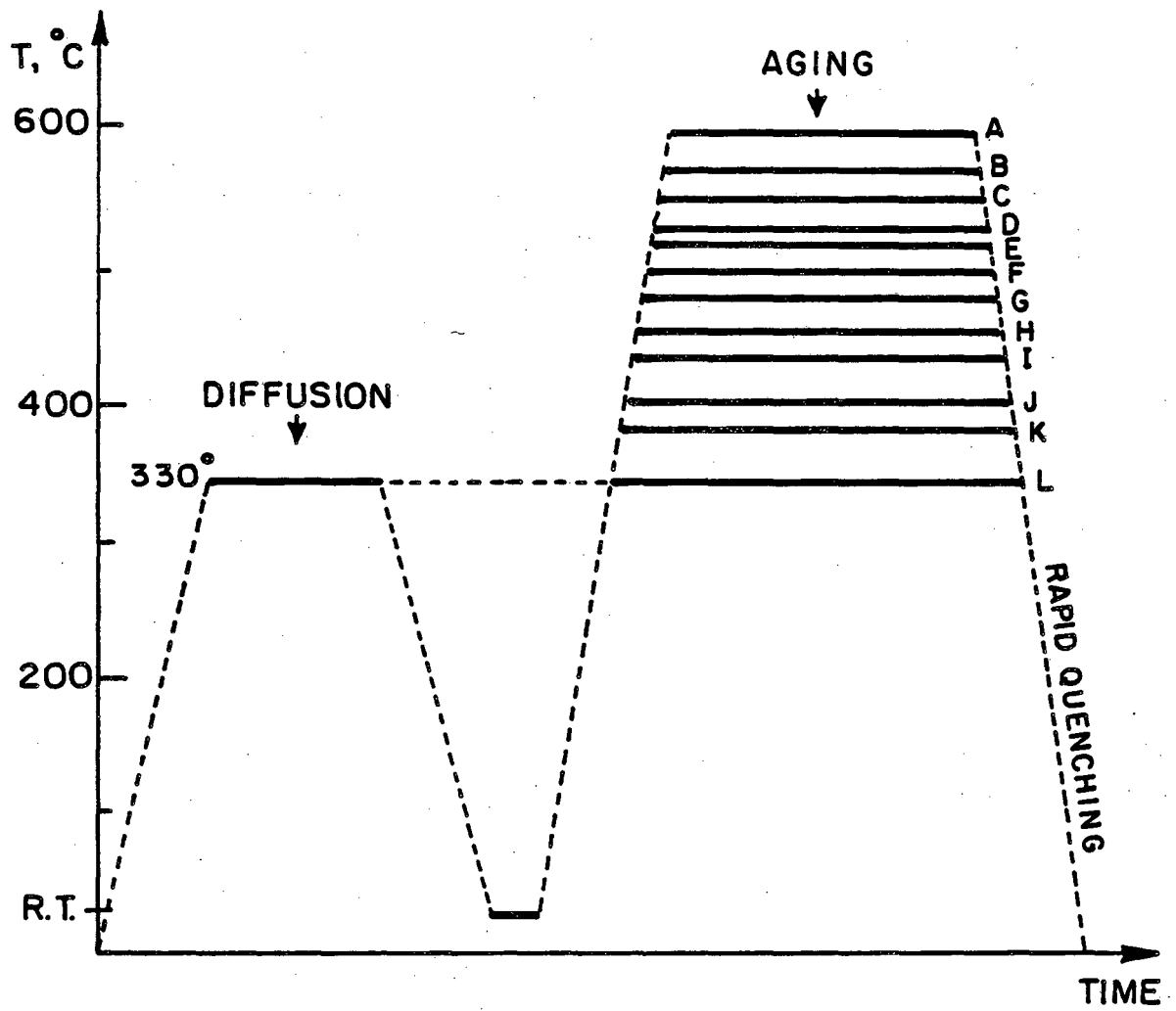
XBL819-6601

Fig. 10



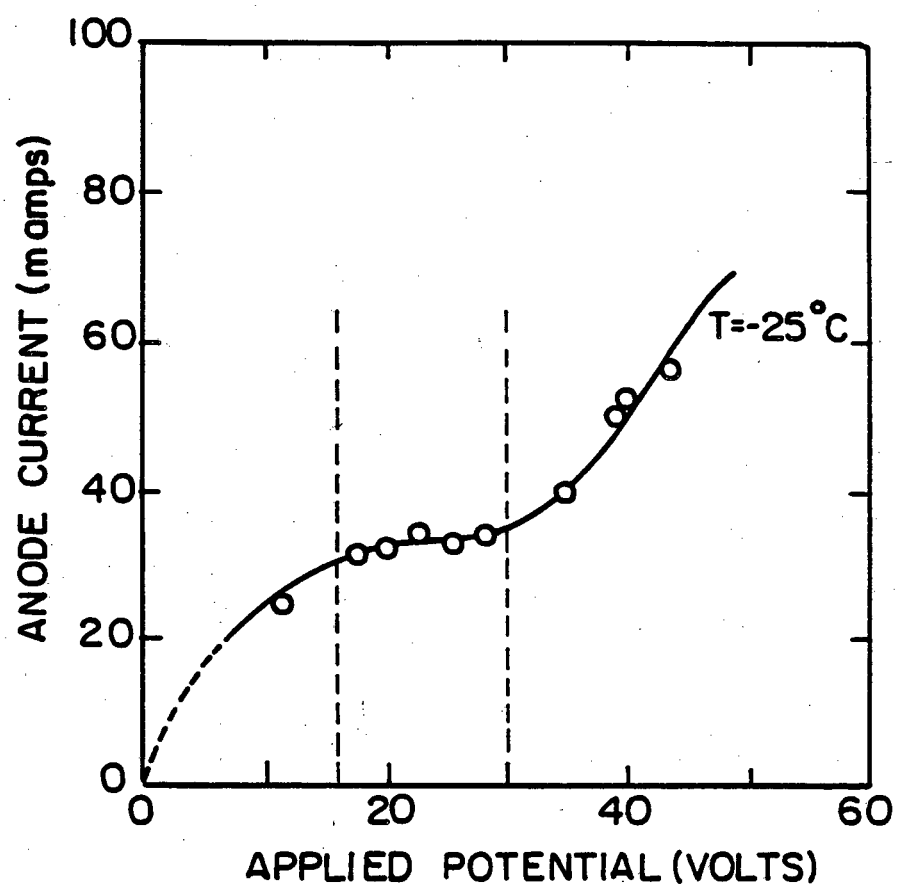
XBL819-6603

Fig. 11



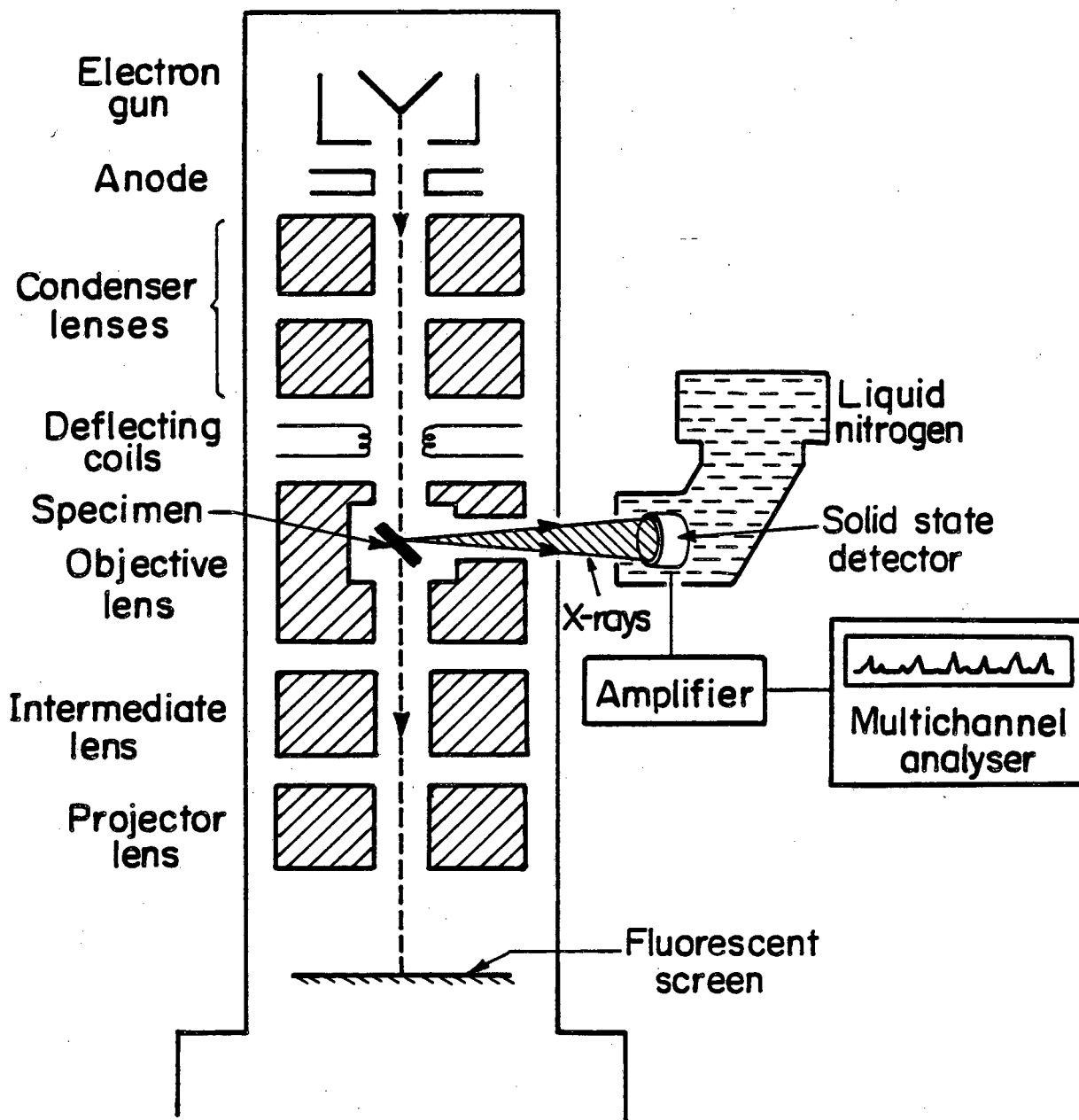
XBL8110-6804

Fig. 12



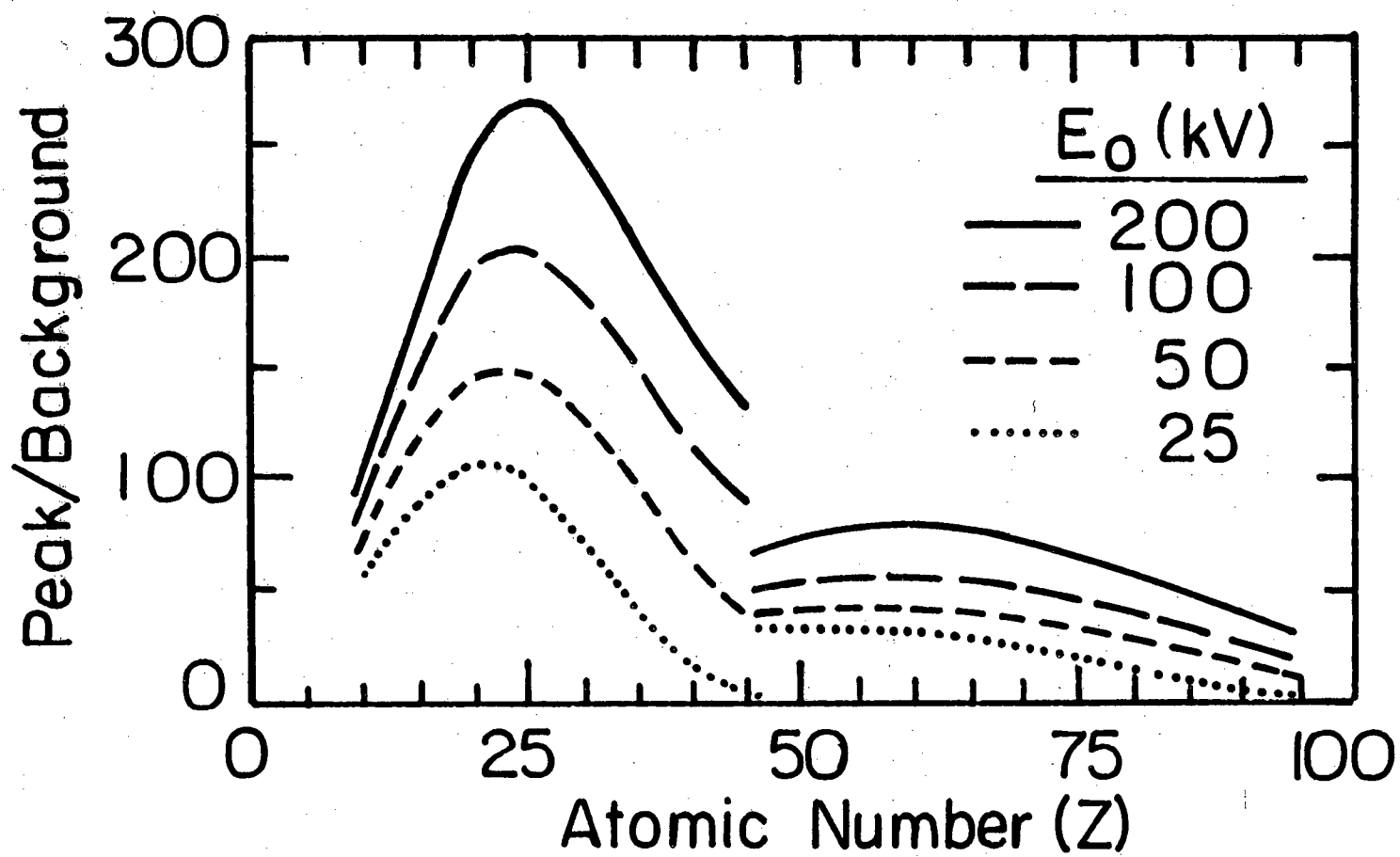
XBL 813-5436

Fig. 73



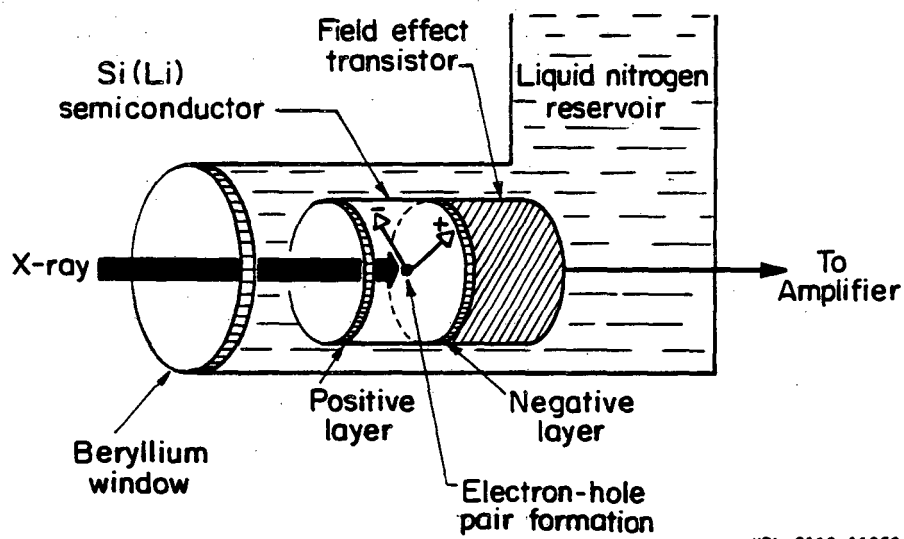
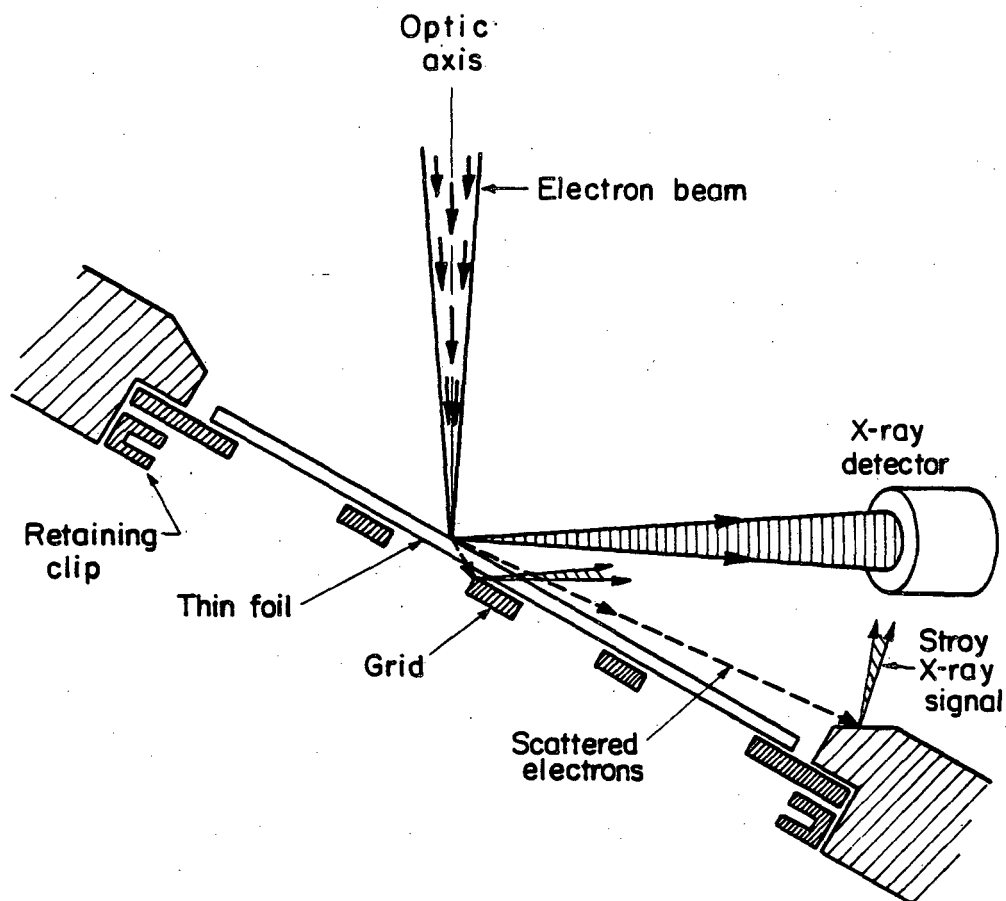
XBL 8010-6137

Fig. 14



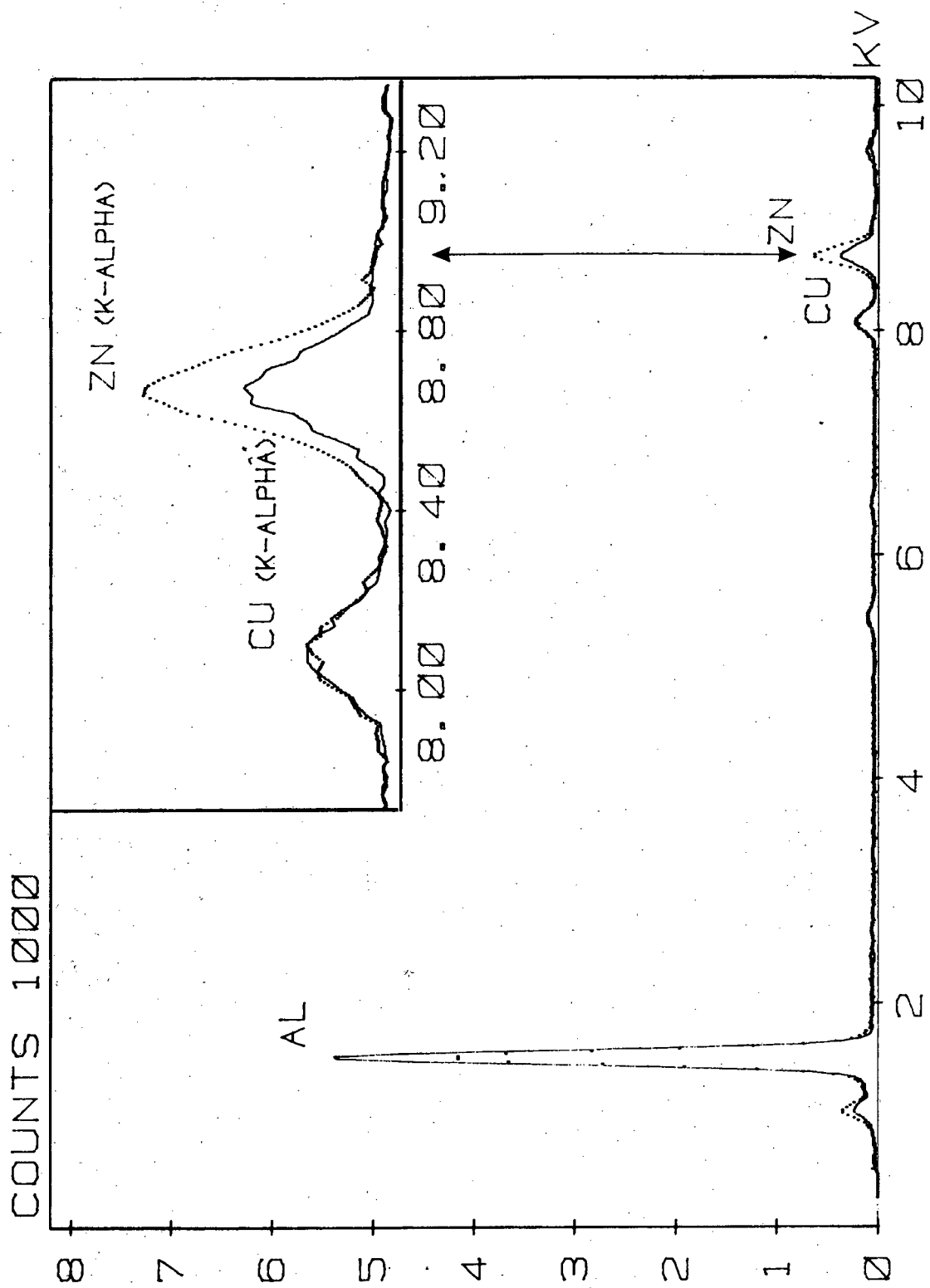
XBL 8110-11968

Fig. 15



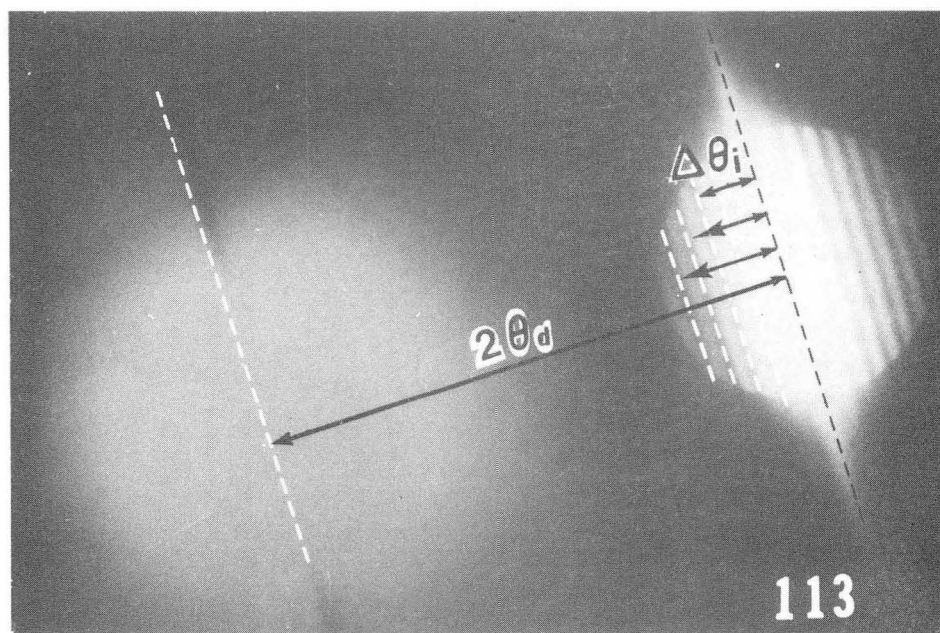
XBL 8110-11969

Fig. 16

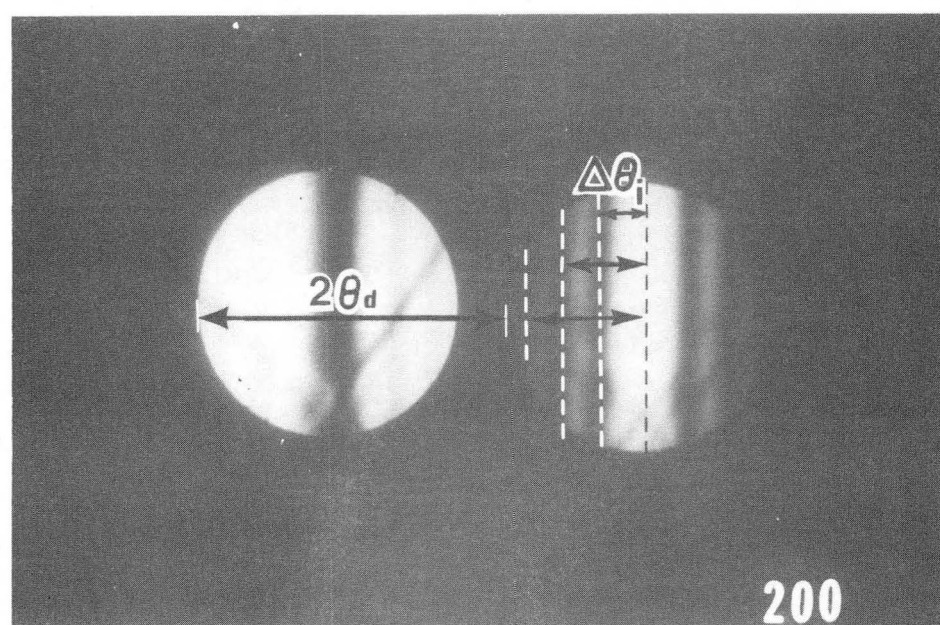


XBL 8110-11970

Fig. 17



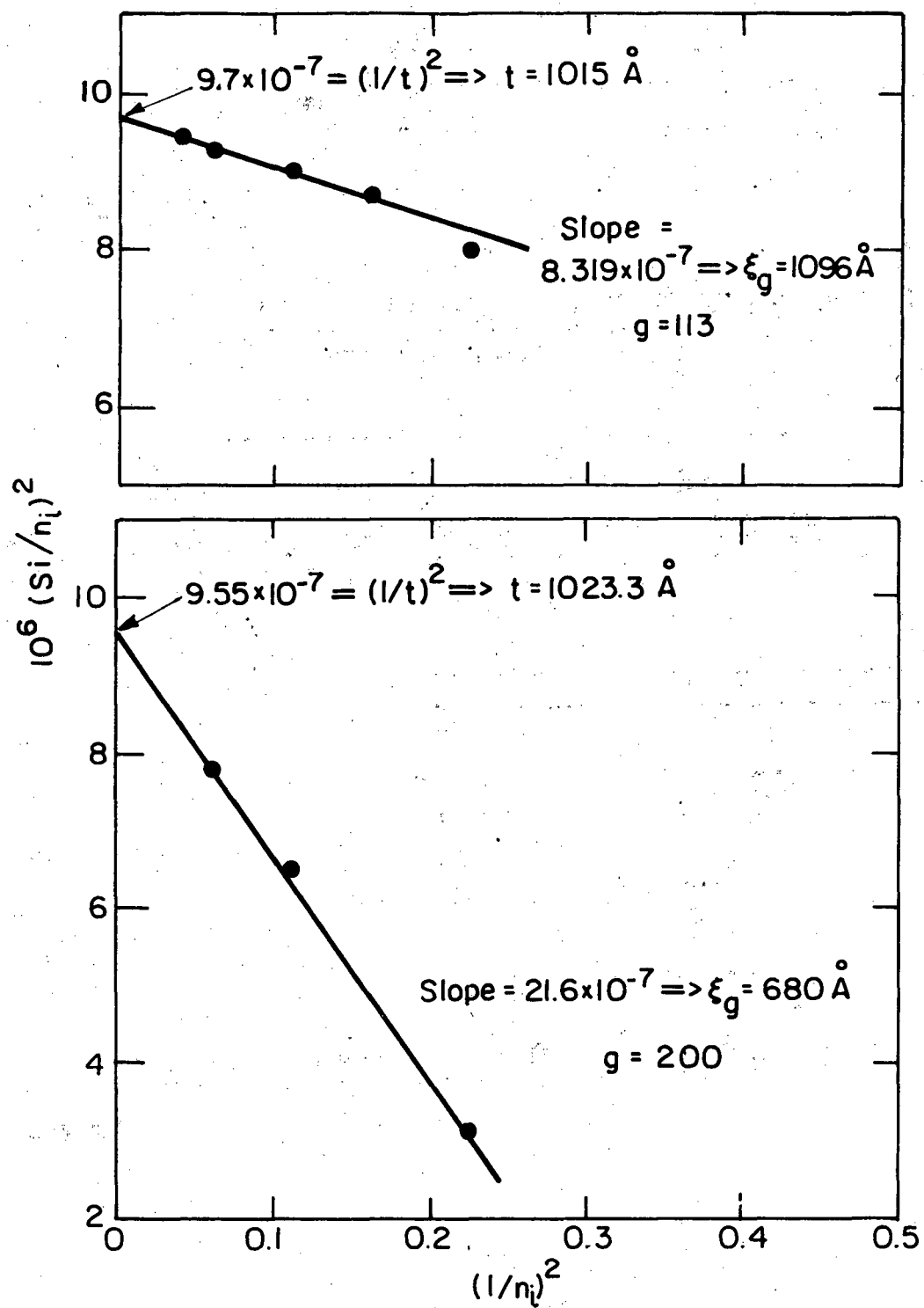
(a)



(b)

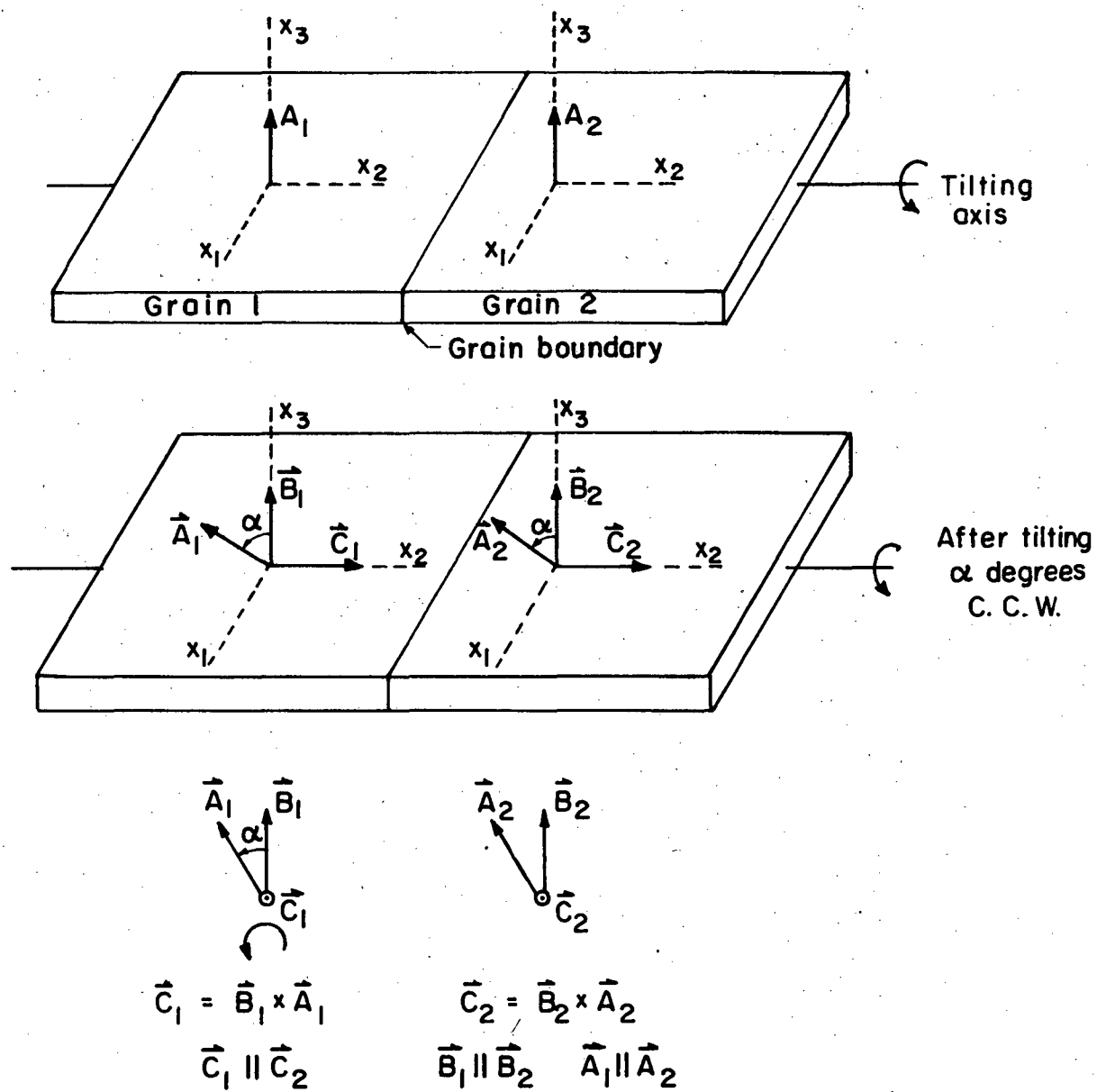
XBB 810-9967

Fig. 18



XBL8110-6732

Fig. 19



XBL 819-6602

Fig. 20

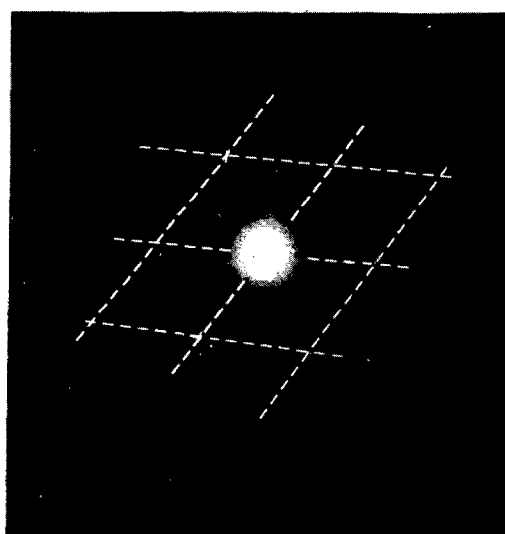
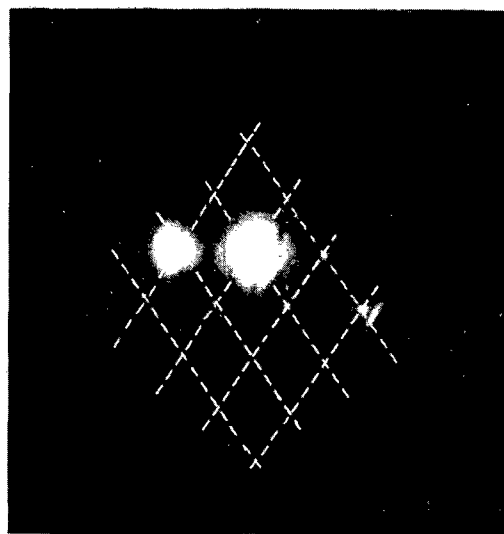
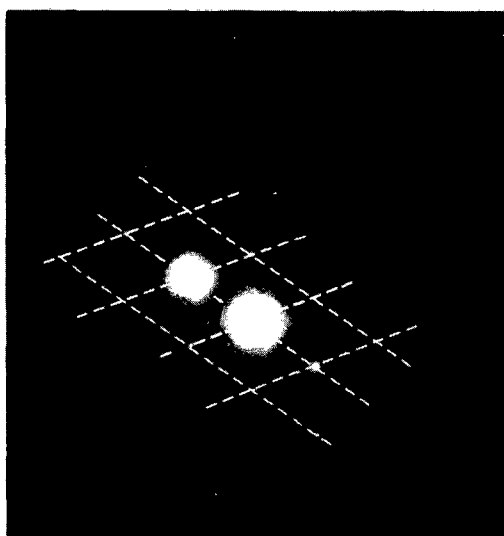
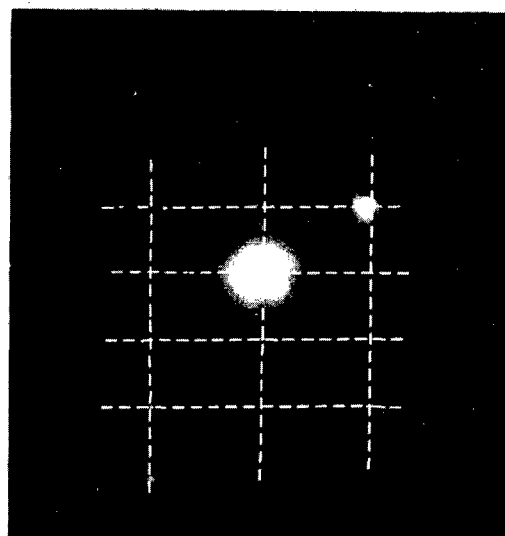
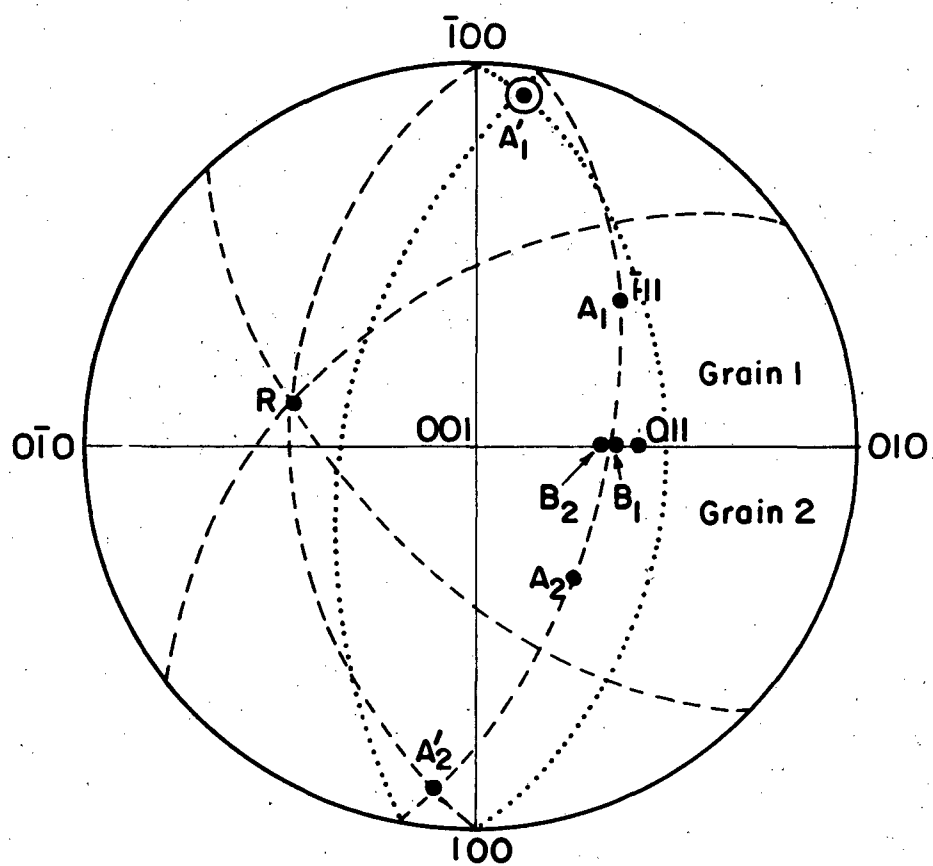
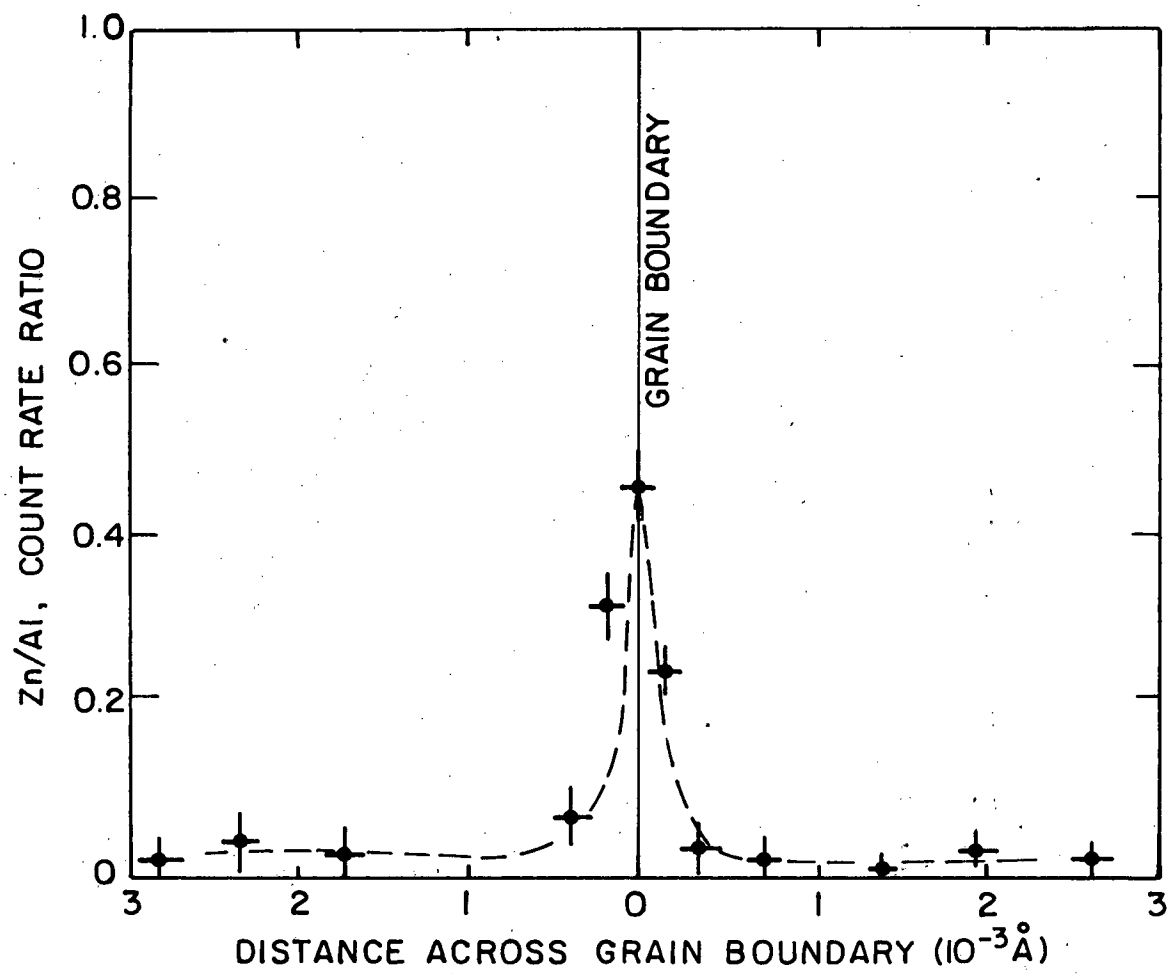
(a) $(SAD_1)_1$ (b) $(SAD_2)_1$ (c) $(SAD_1)_2$ (d) $(SAD_2)_2$ XBB 810-9972

Fig. 21



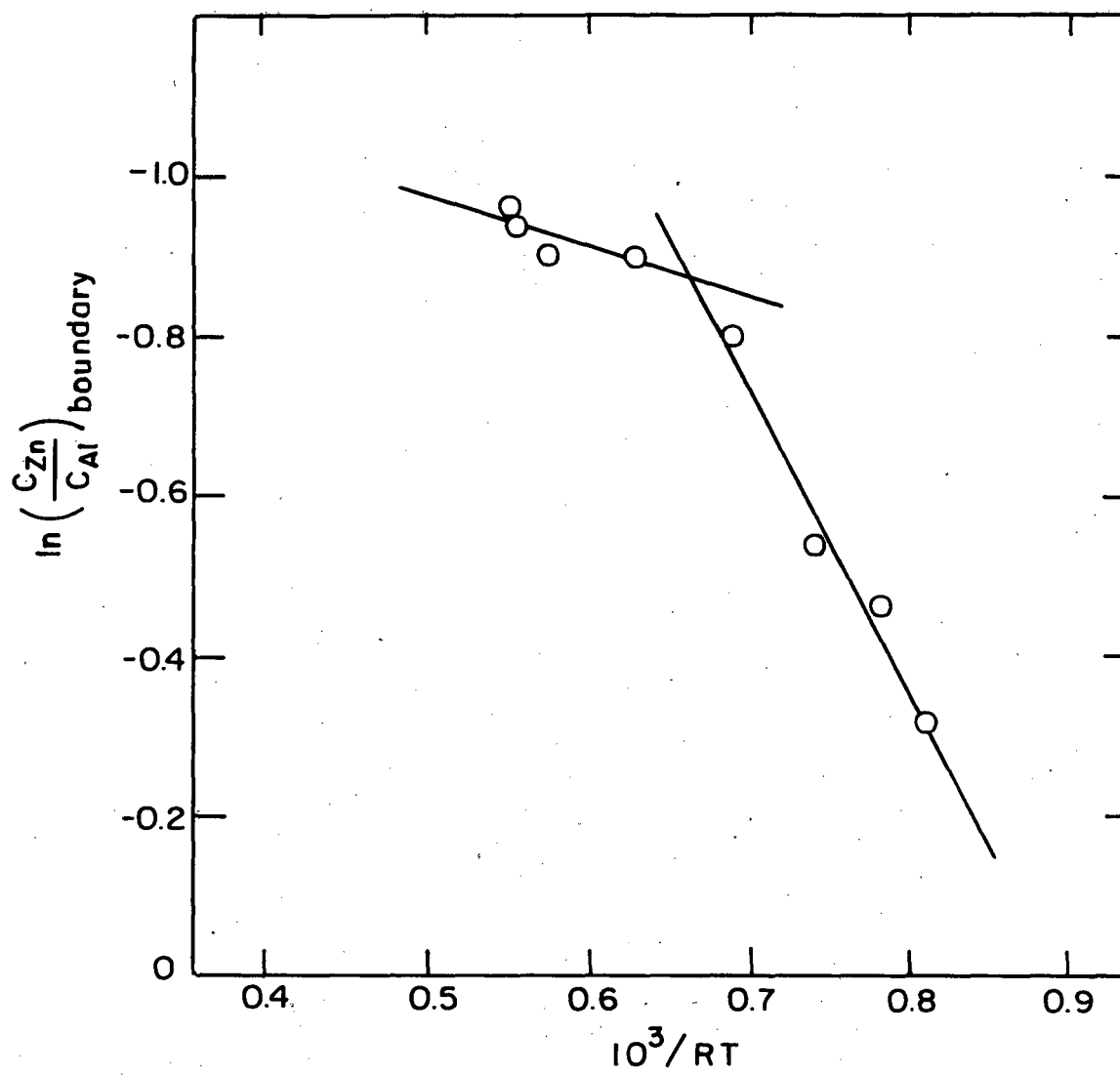
XBL 8110-6655

Fig. 22



XBL8110-6731

Fig. 23



XBL 8110-6657

Fig. 24

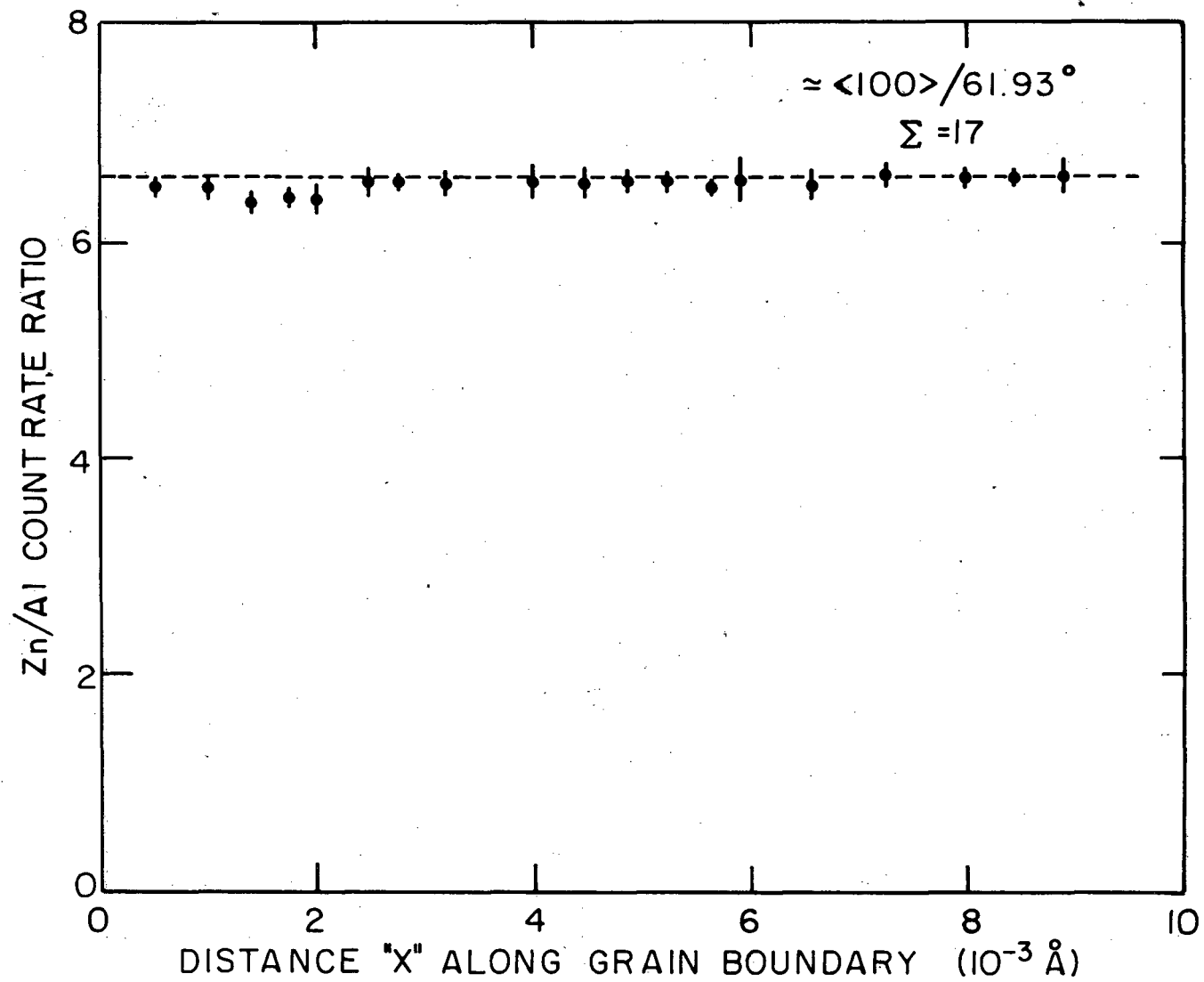


Fig. 25a

XBL 806-5283

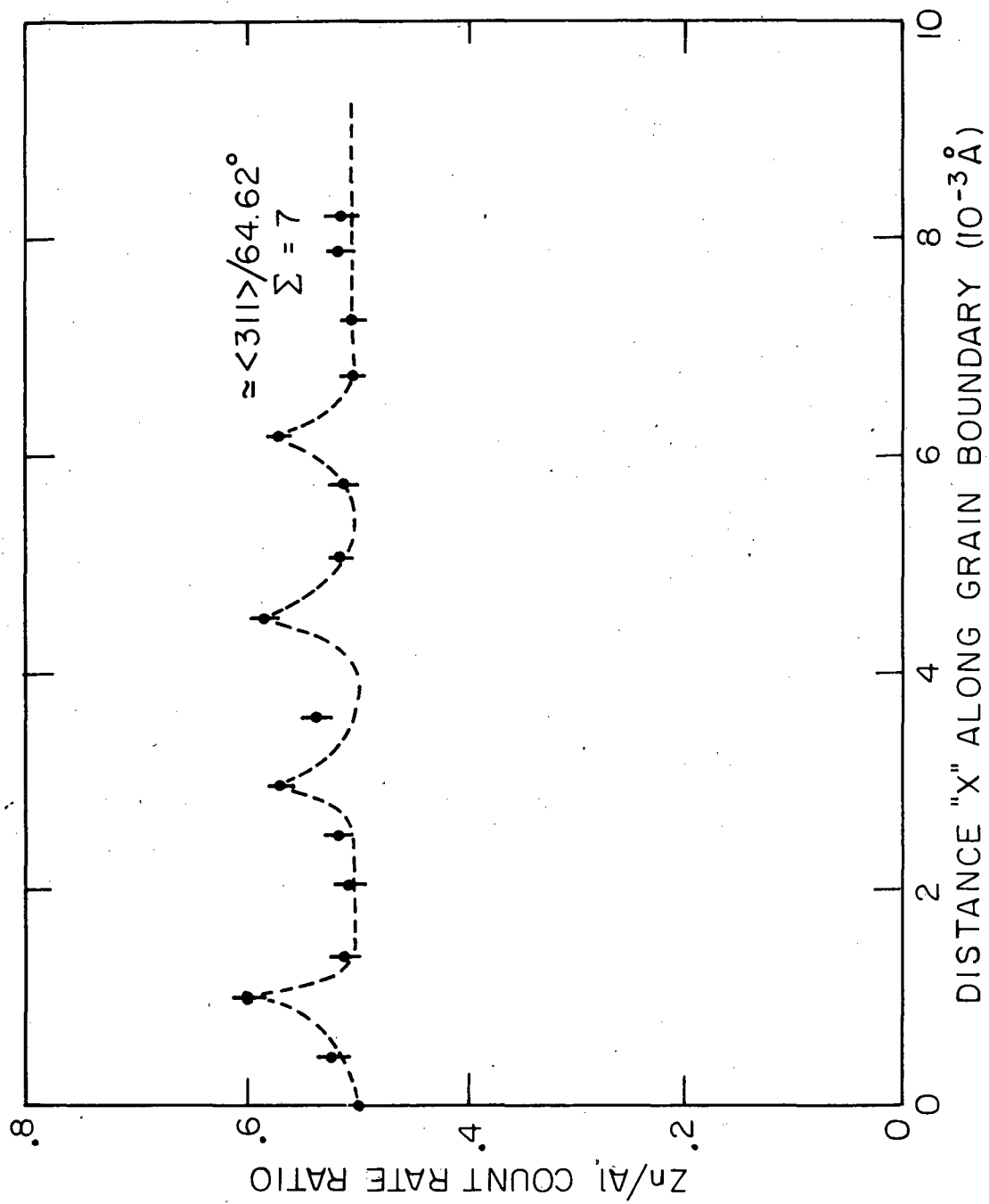
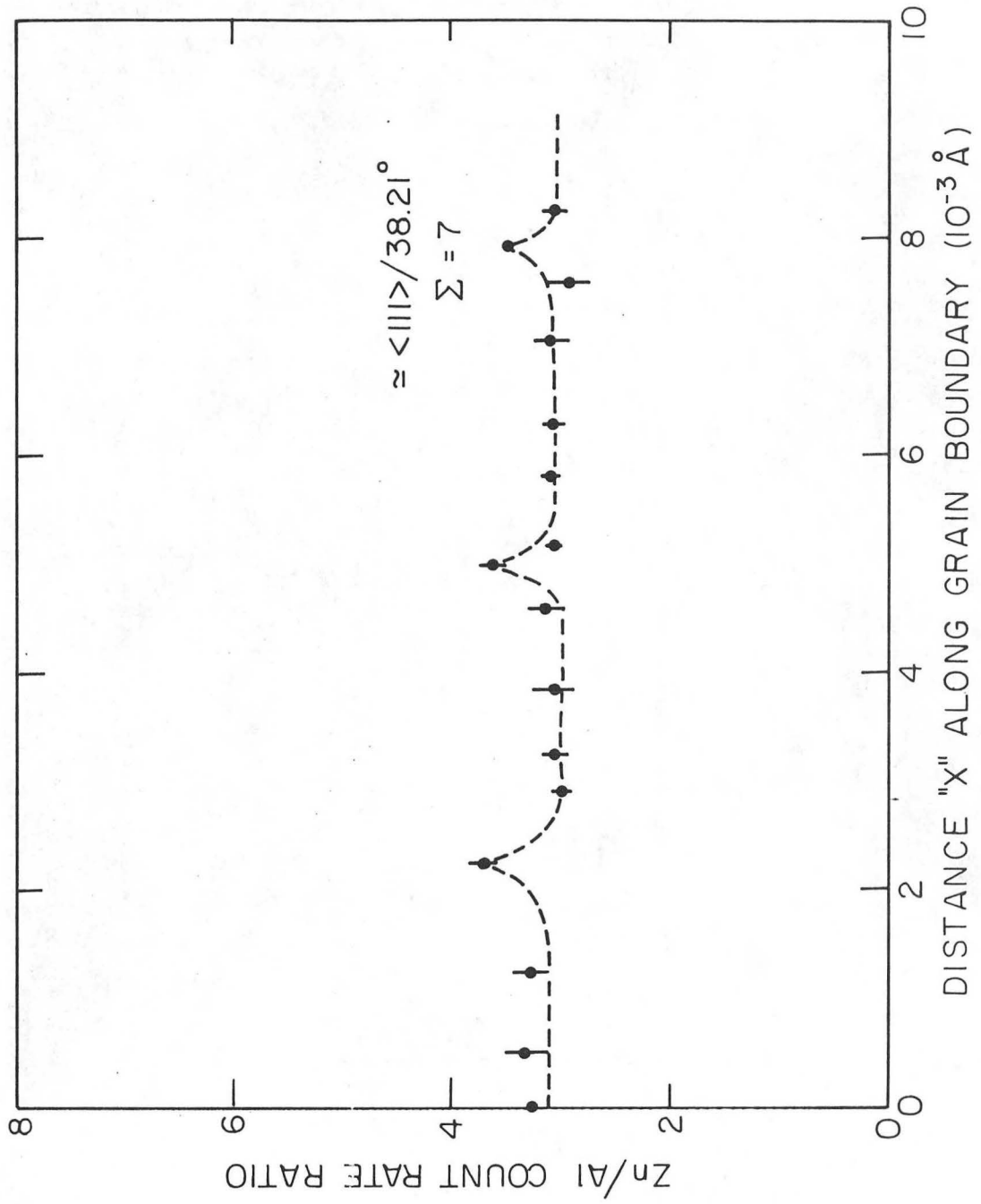


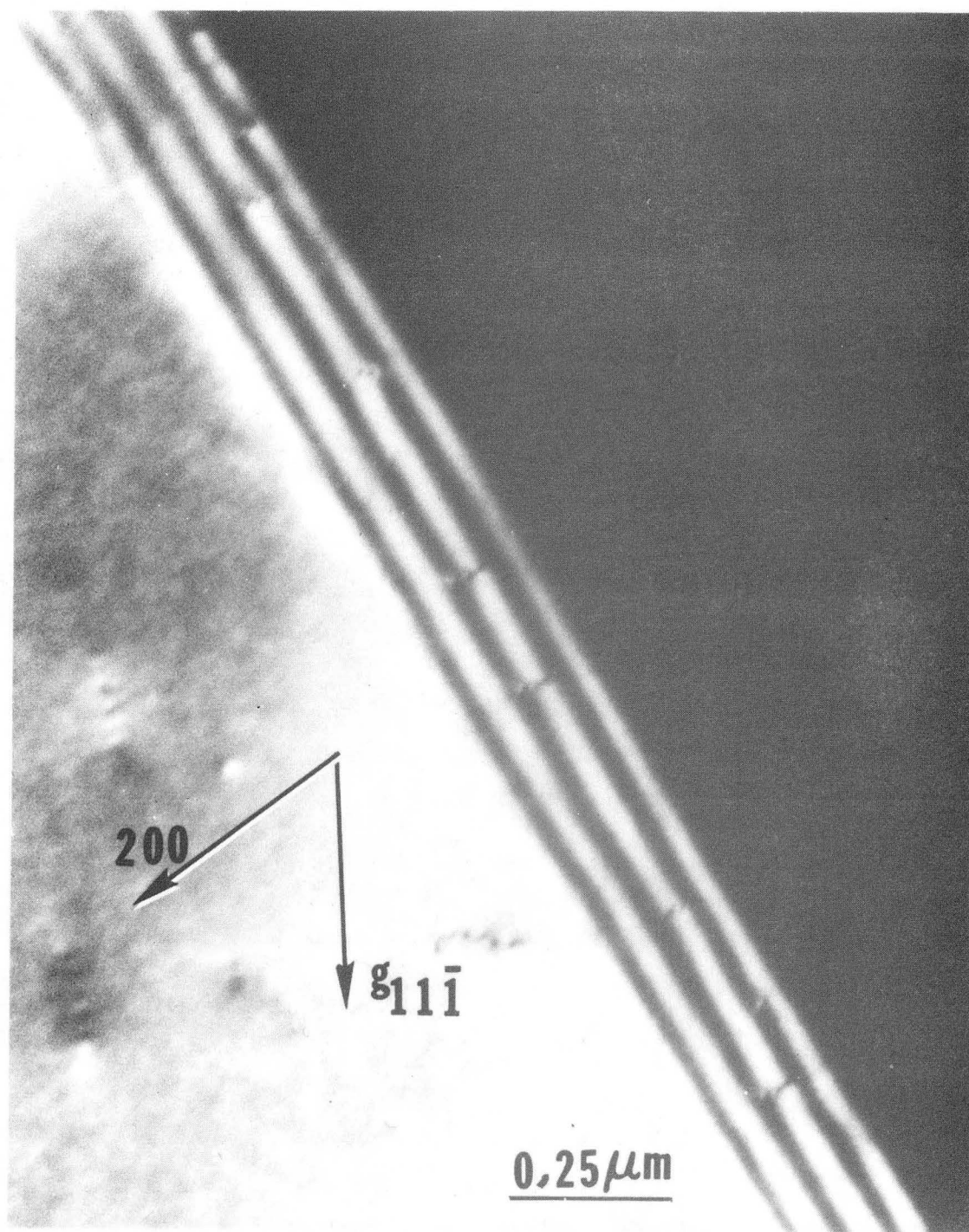
Fig. 25b

XBL 806-5282



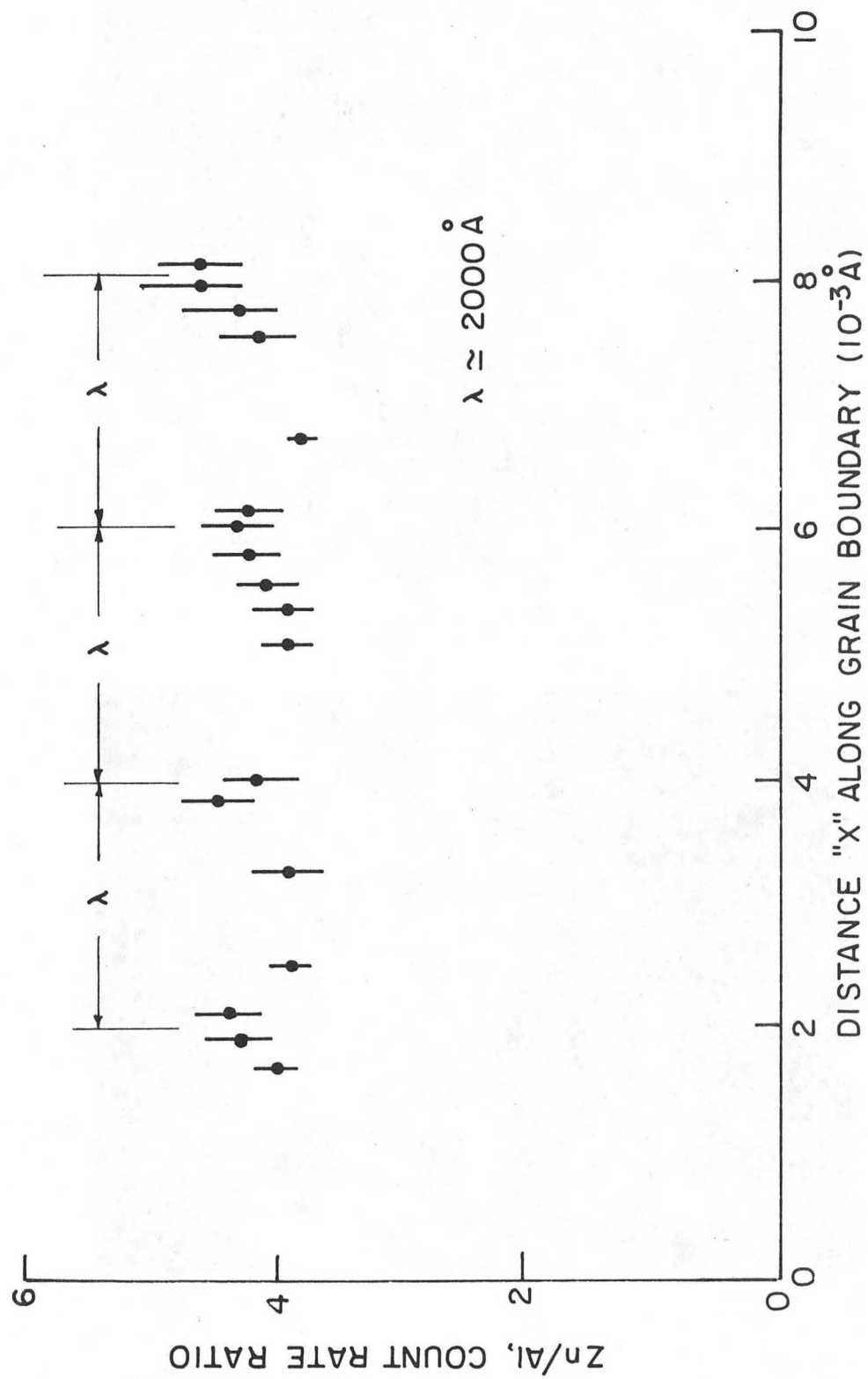
XBL 806-5284

Fig. 25c



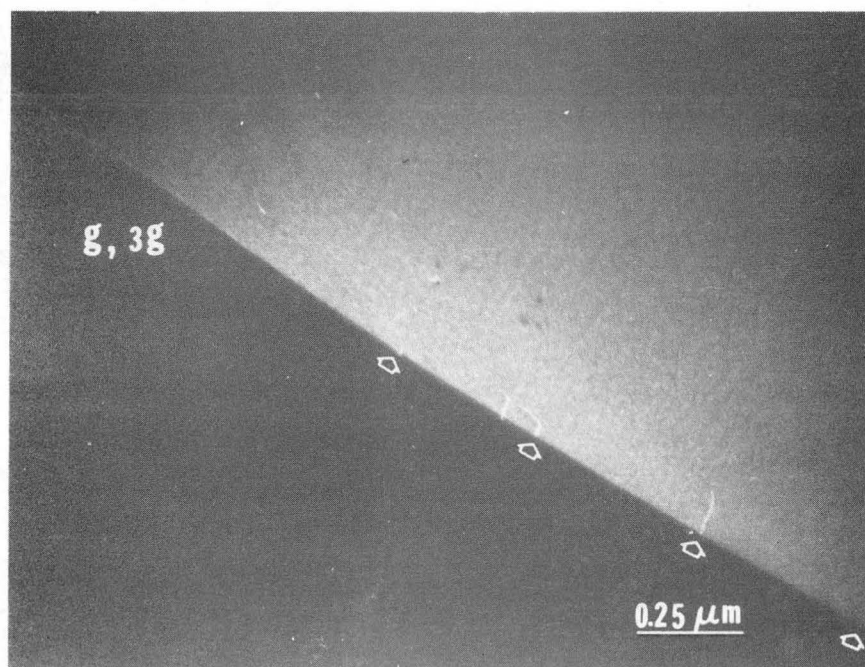
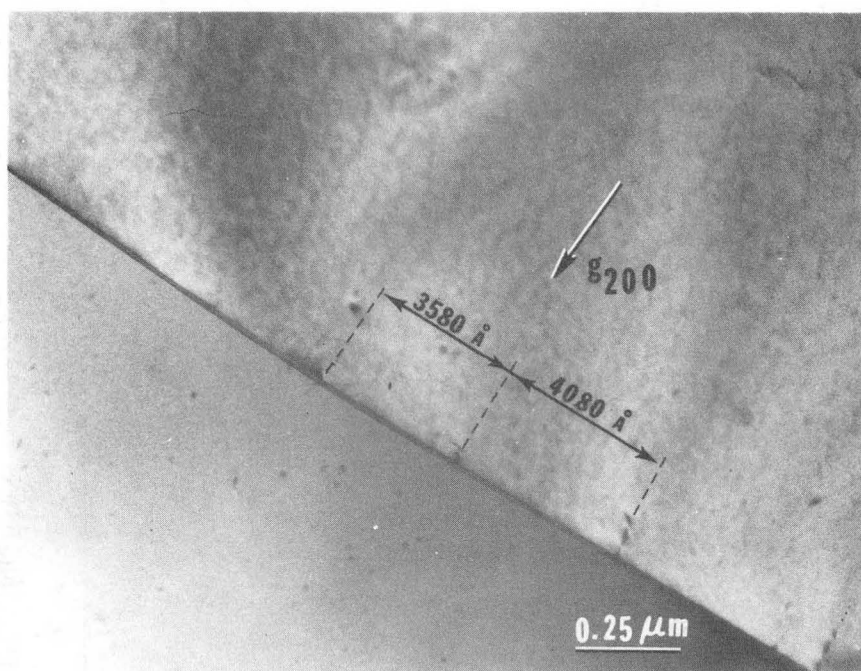
XBB 810-9963

Fig. 26a



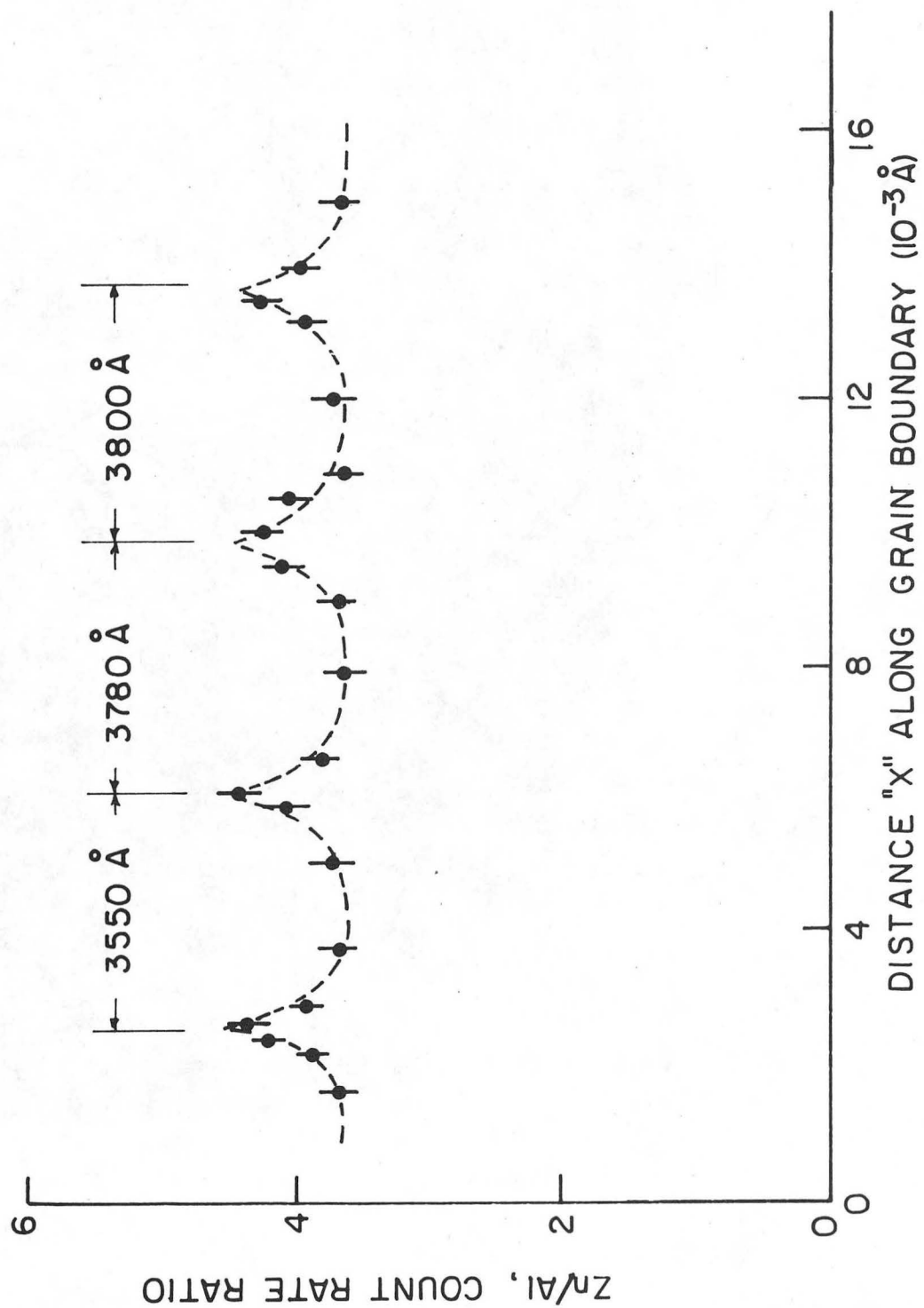
XBL 8110-6774

Fig. 26b



XBB 810-9966

Fig. 27



XBL8110-6775

Fig. 28

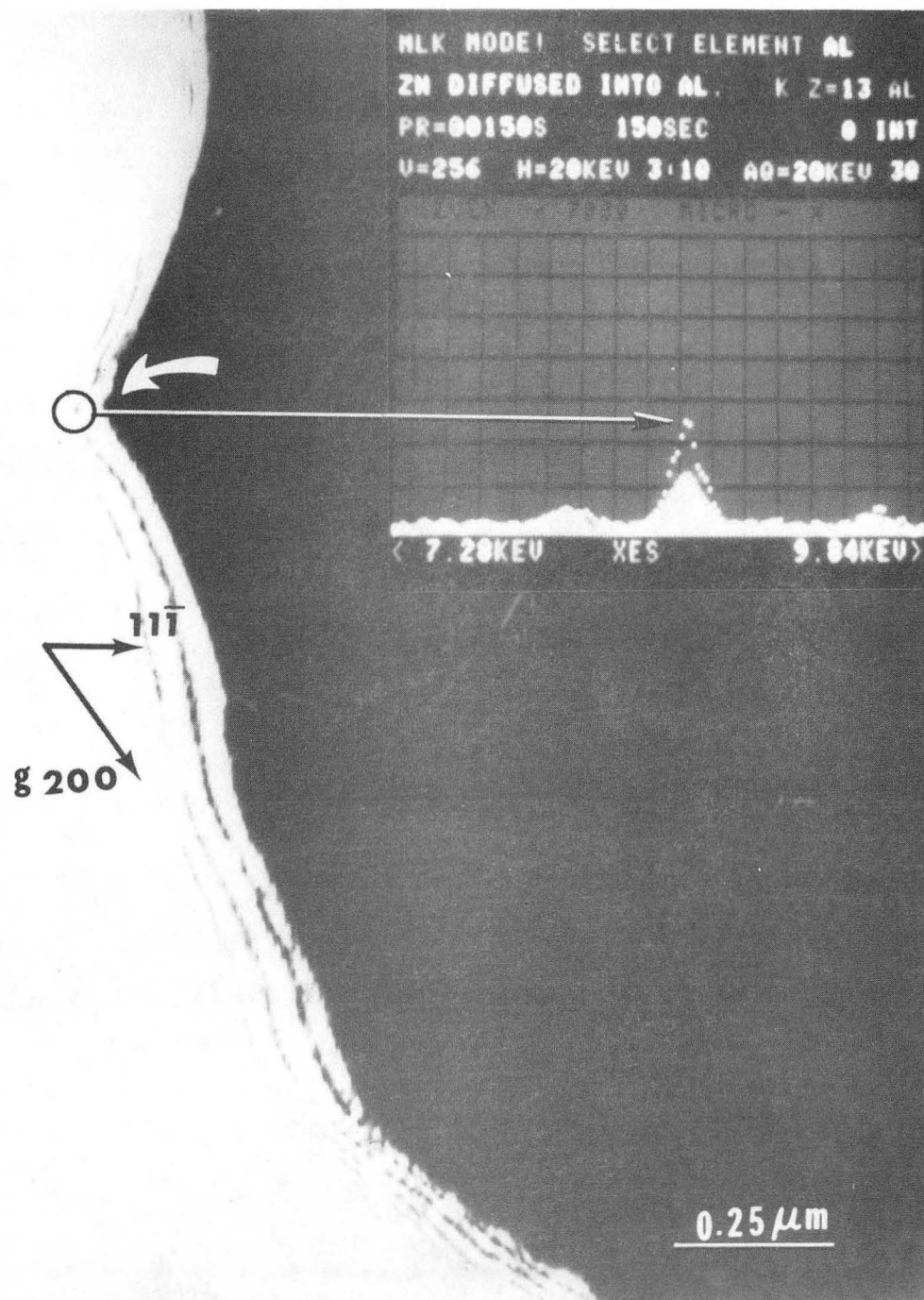


Fig. 29

XBB 810-9962

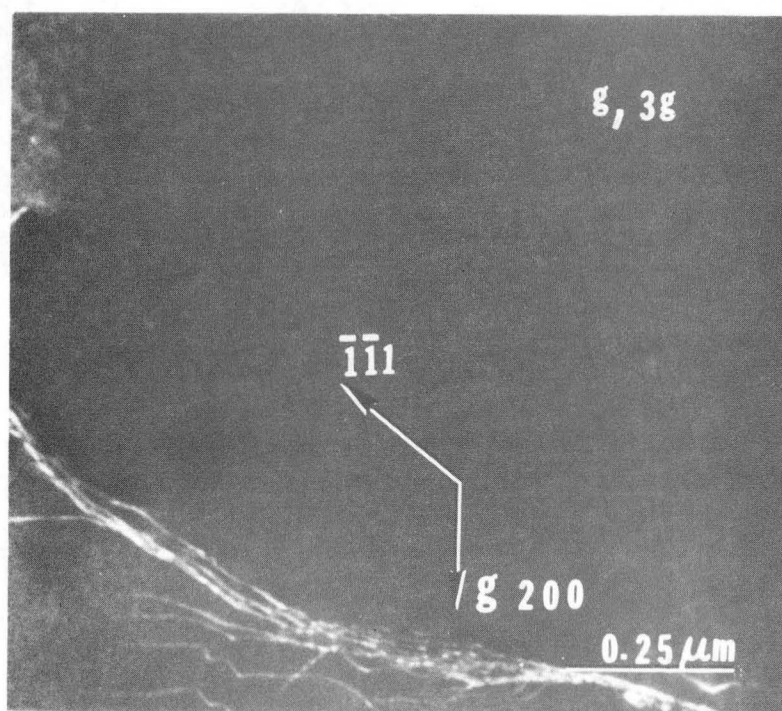
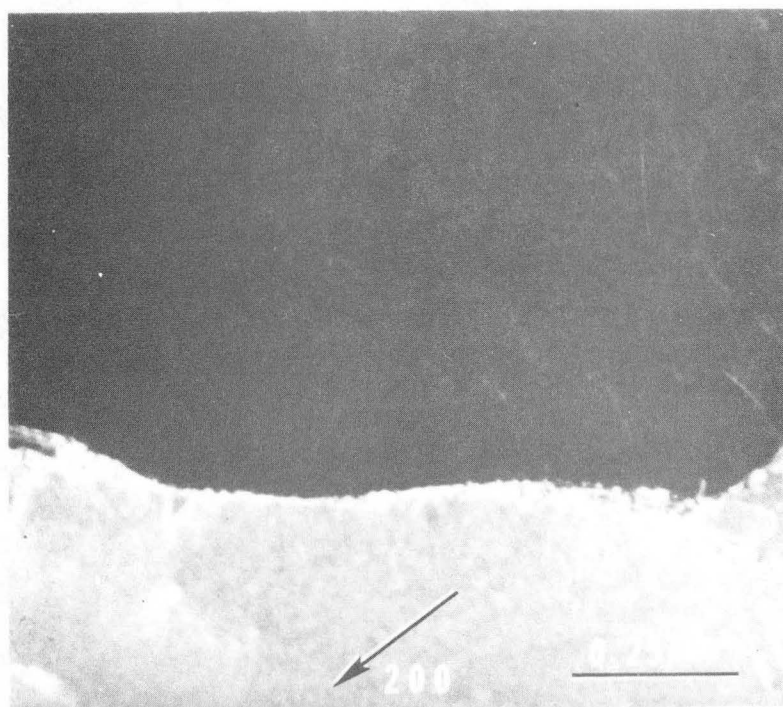
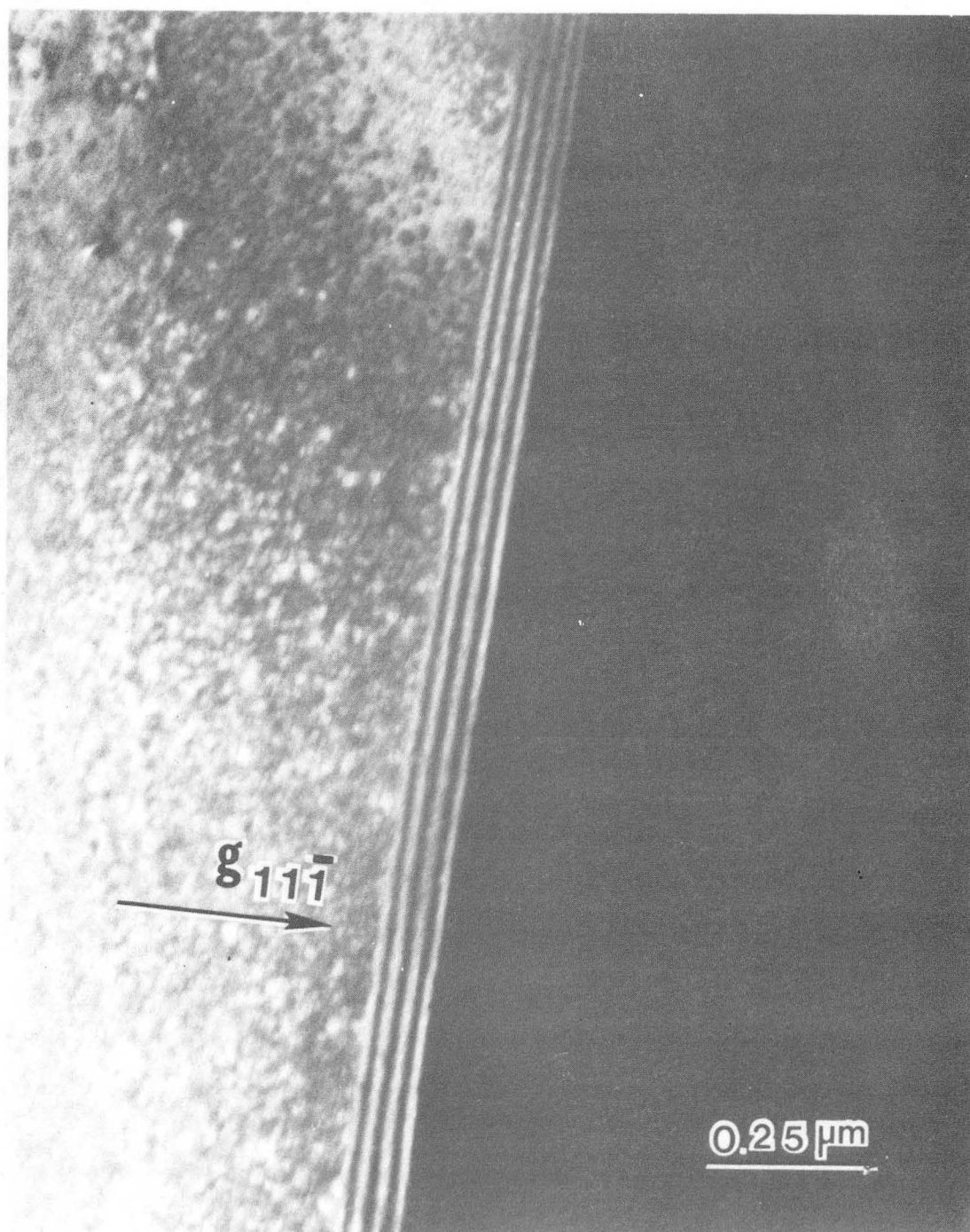


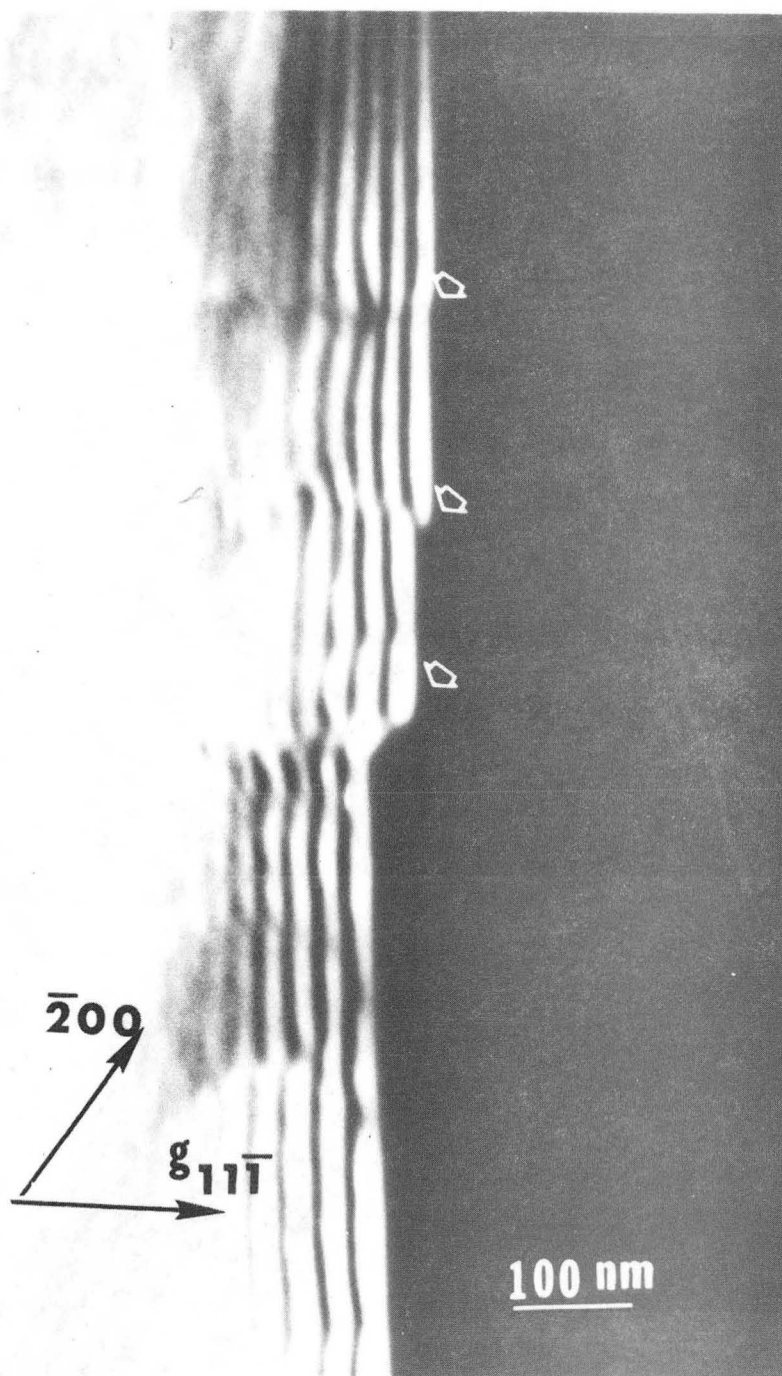
Fig. 30

XBB 810-9969



XBB 810-9964

Fig.31a



XBB 810-9965

Fig. 31b

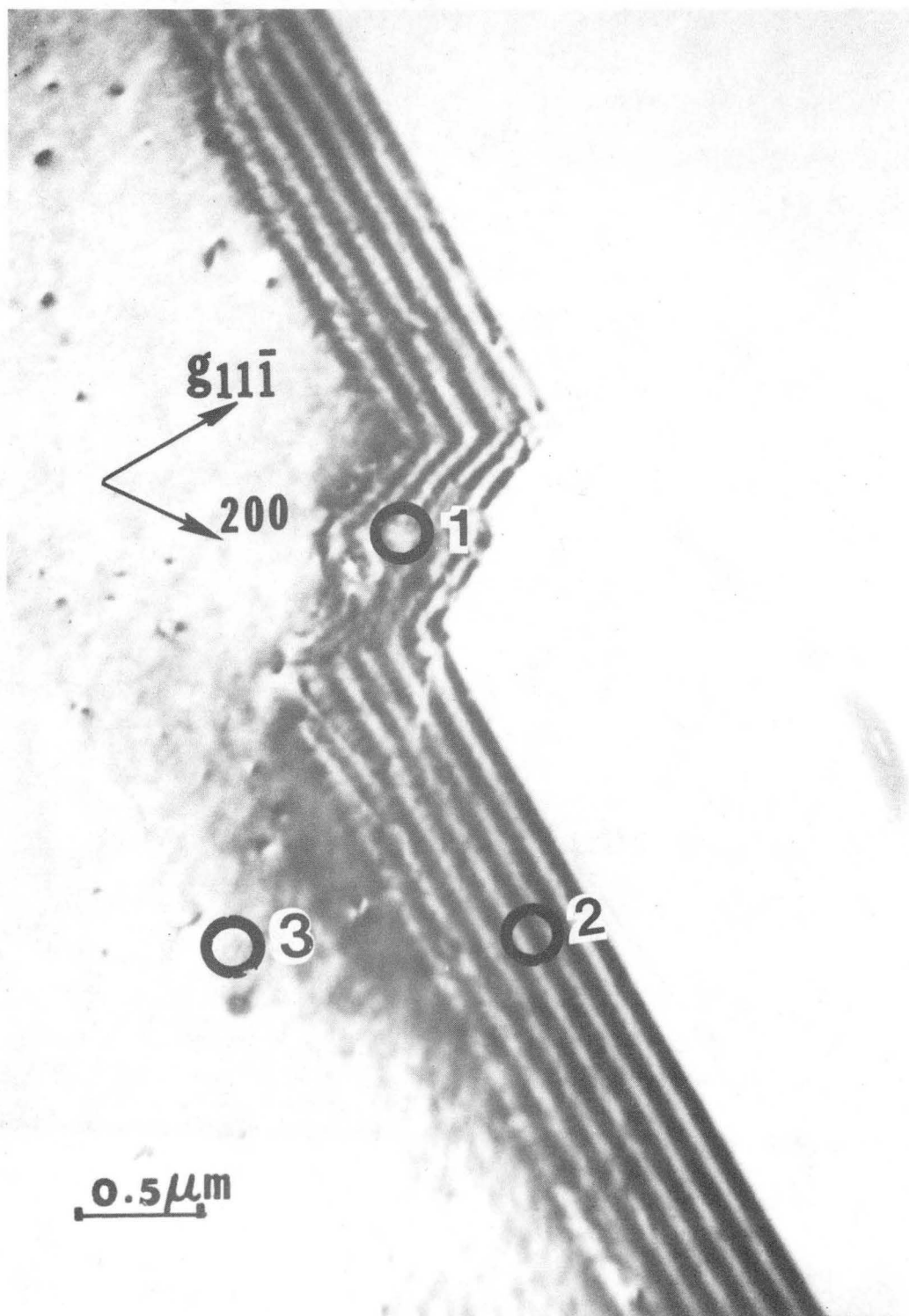


Fig. 32

XBB 810-9968

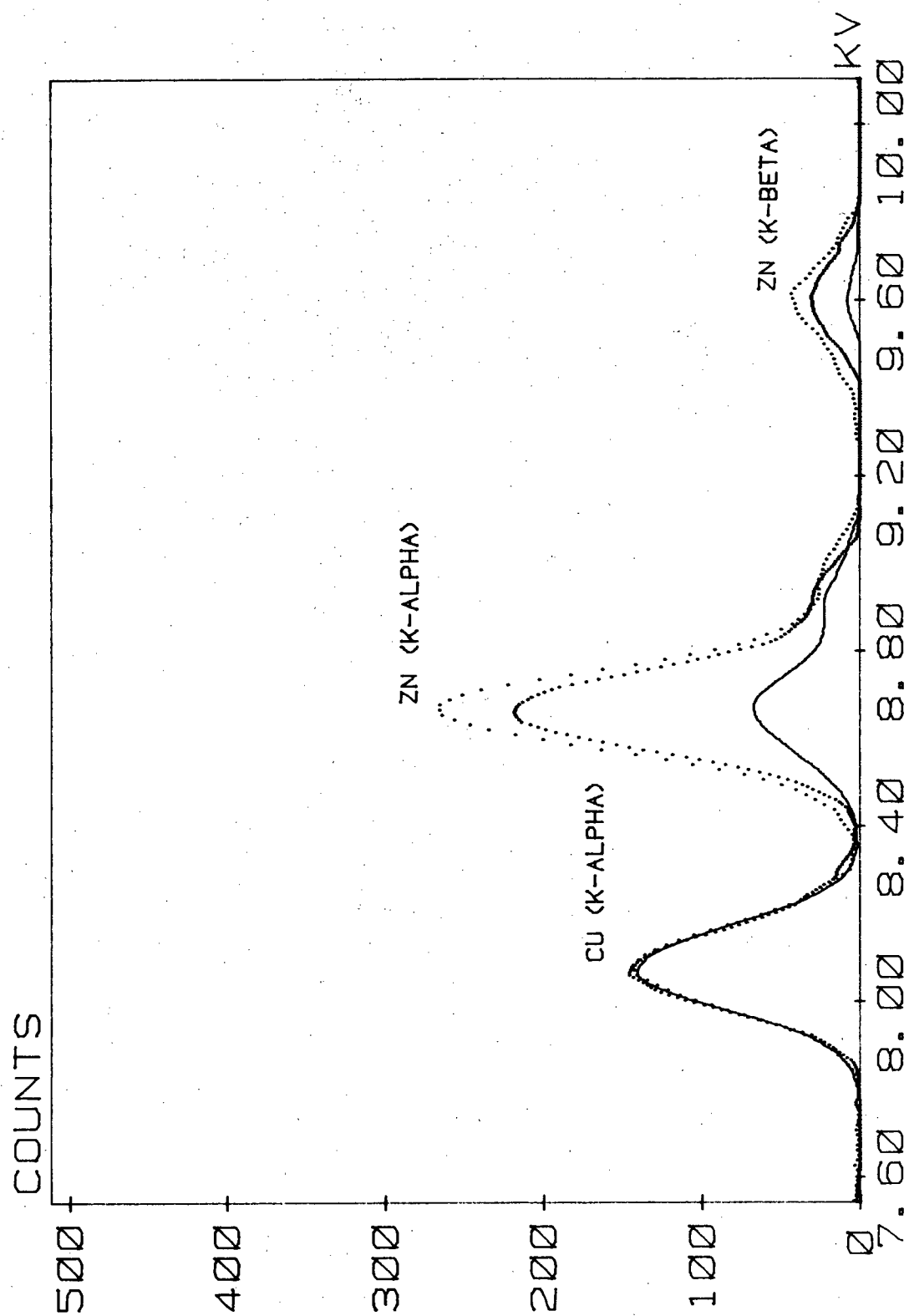
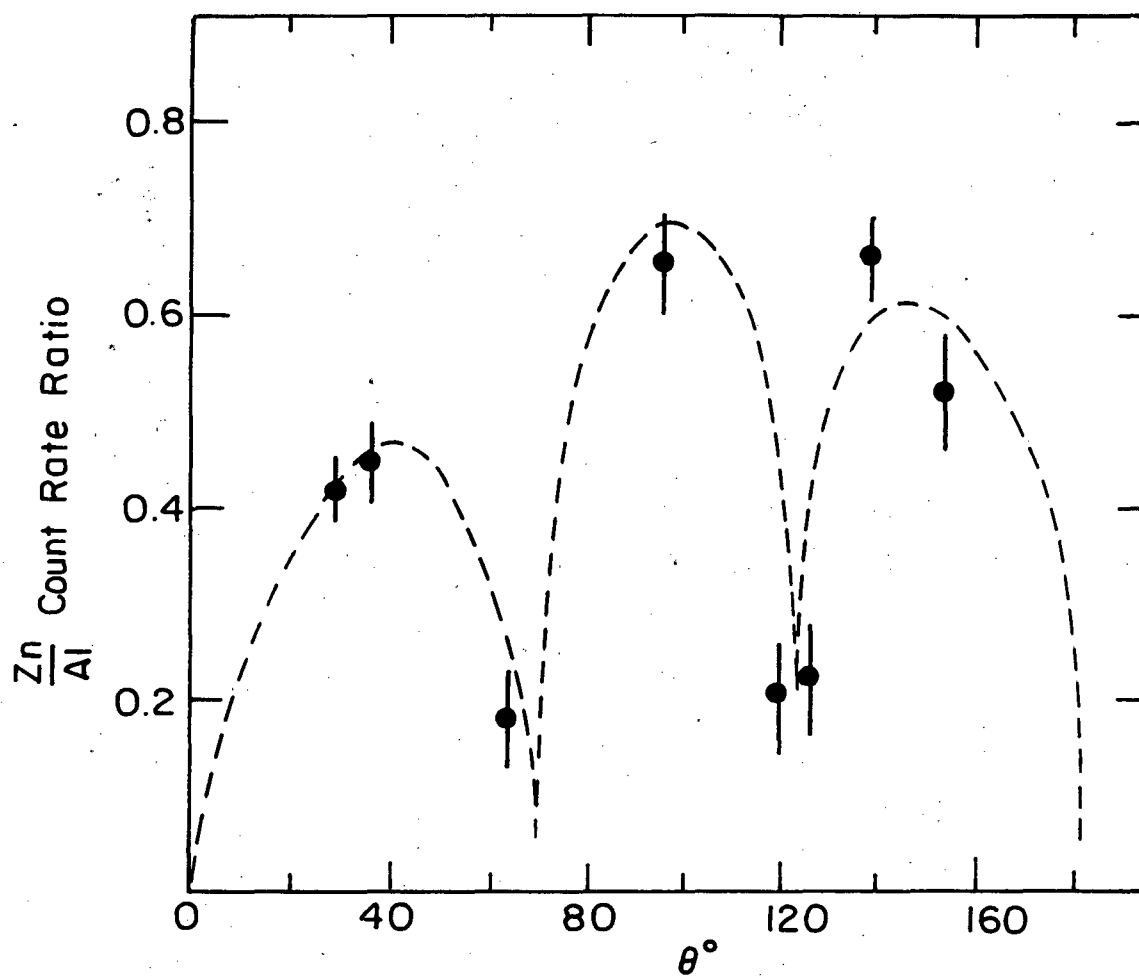


Fig. 33



XBL 8110-6656

Fig. 34.

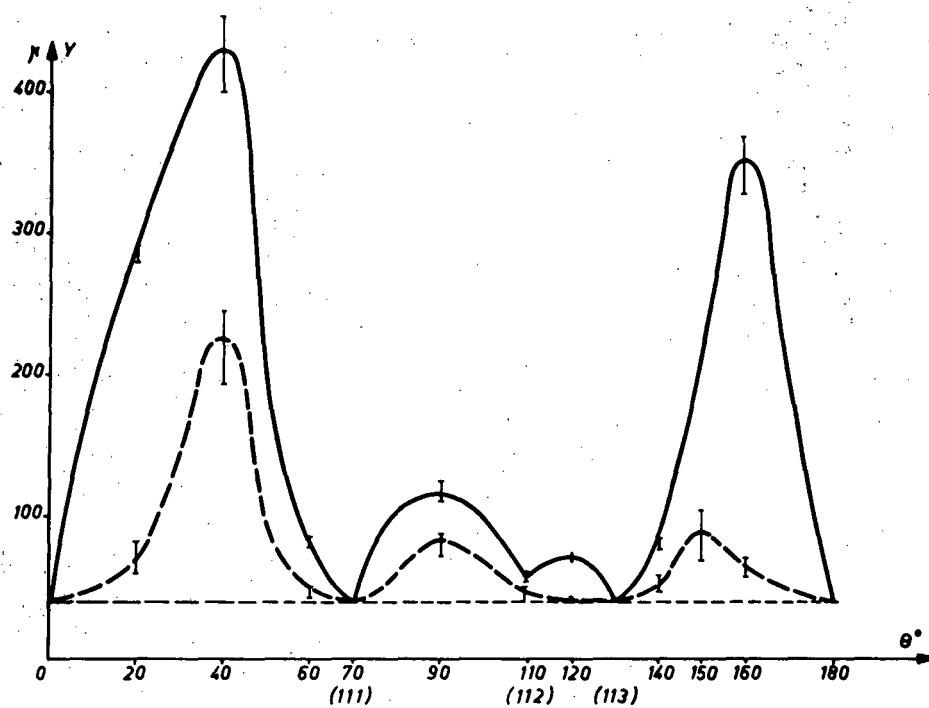
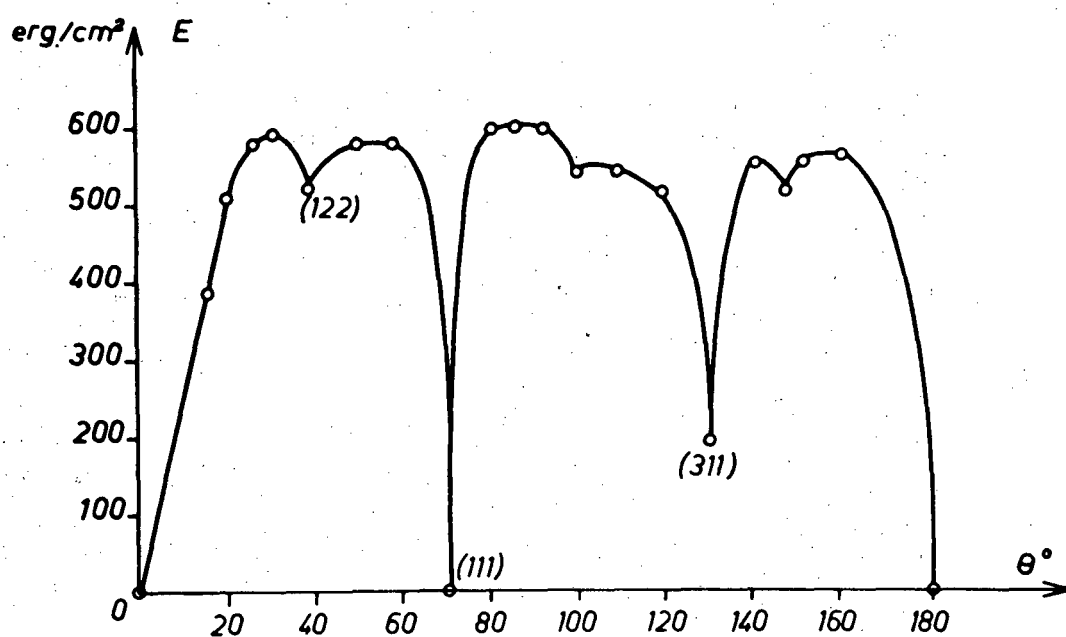


Fig. 35

XBL 776-9202A

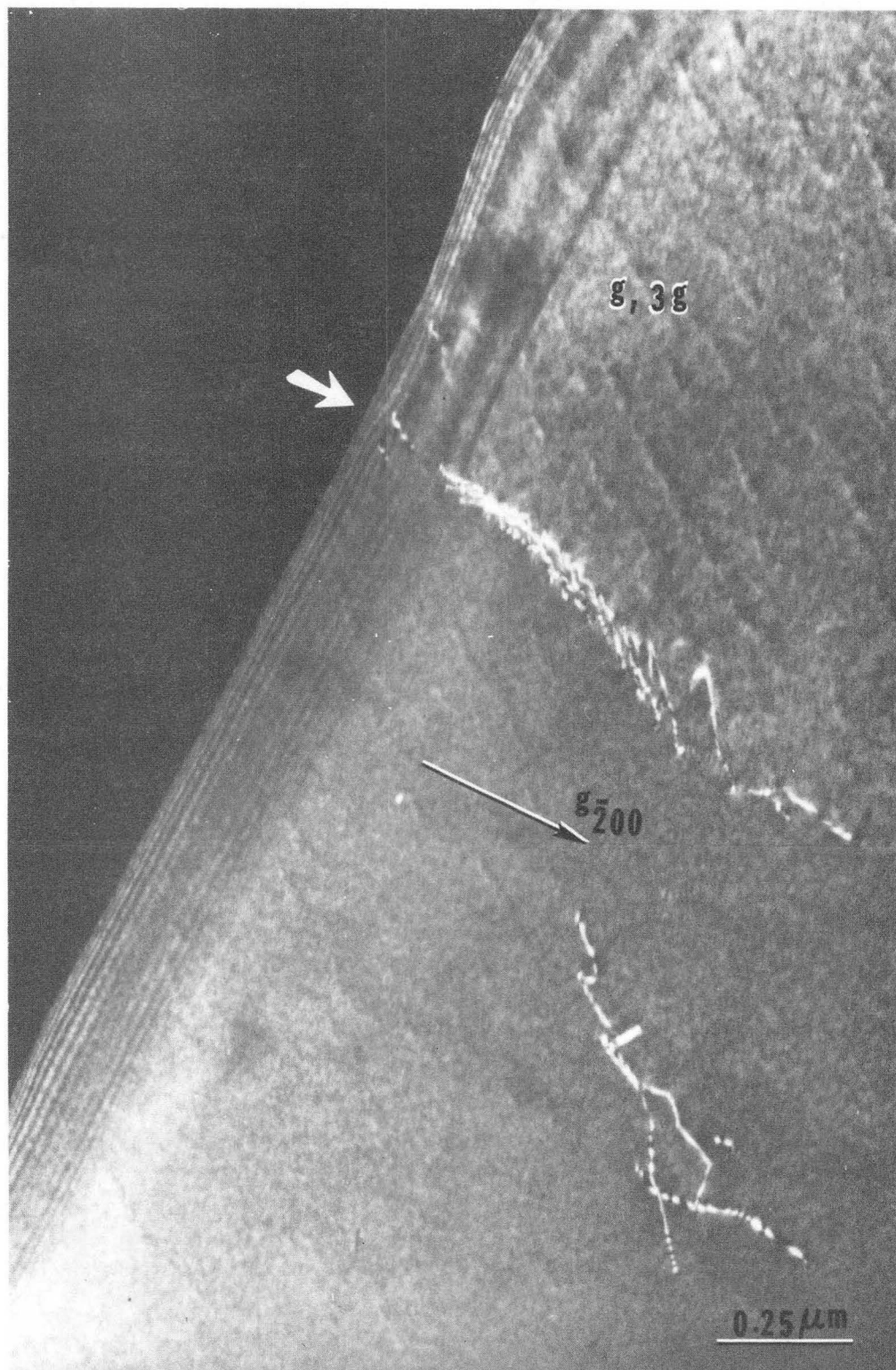


Fig. 36

XBB 810-9970

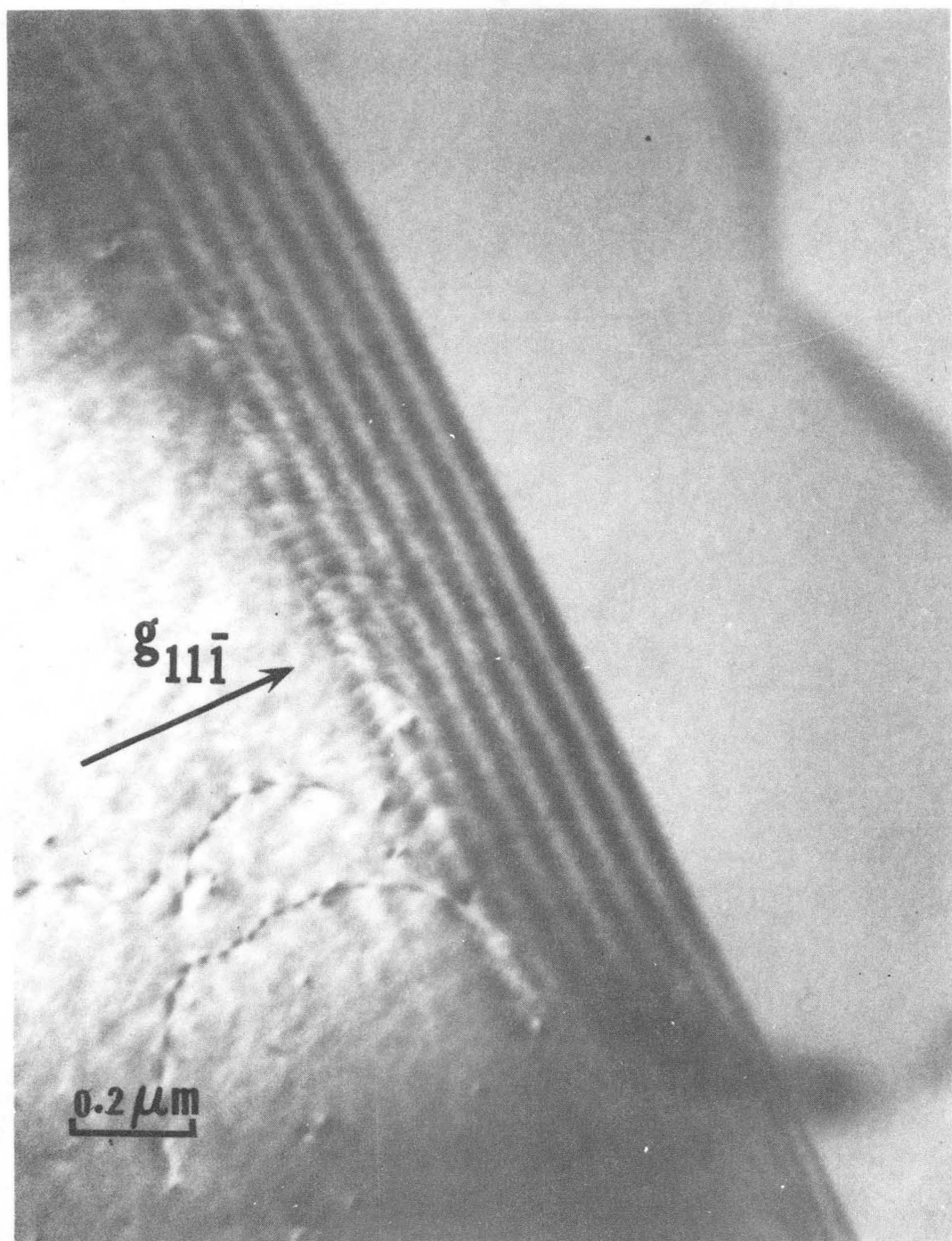
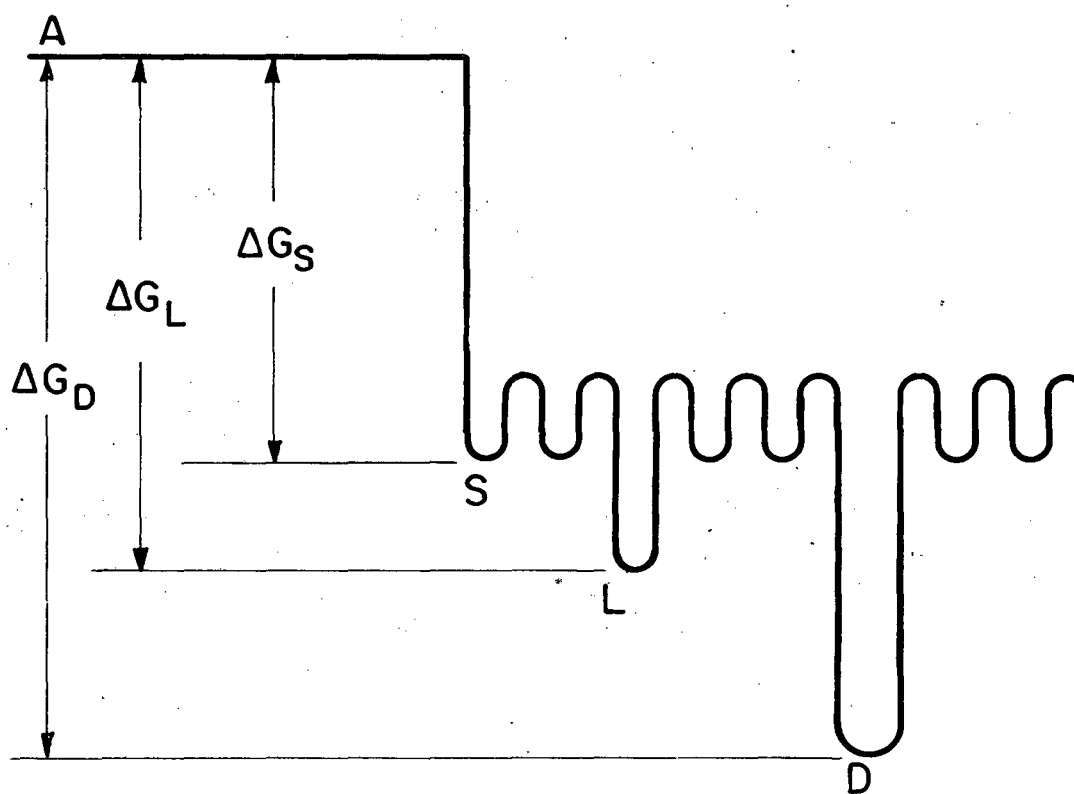
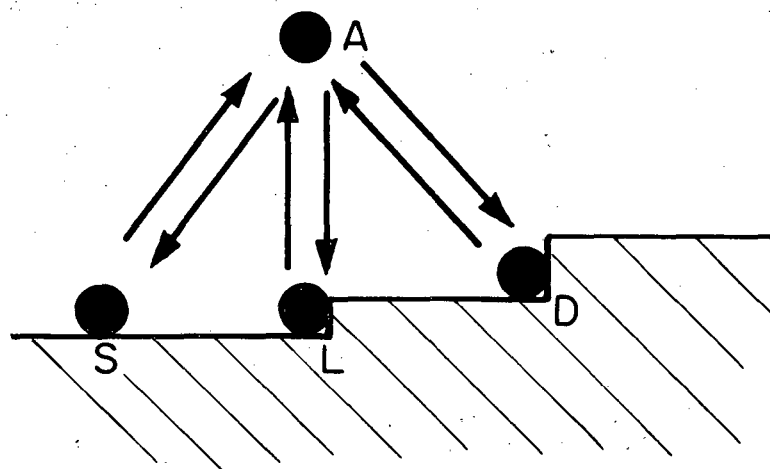


Fig. 37

XBB 810-9971



XBL 811 O-6733

Fig. 38

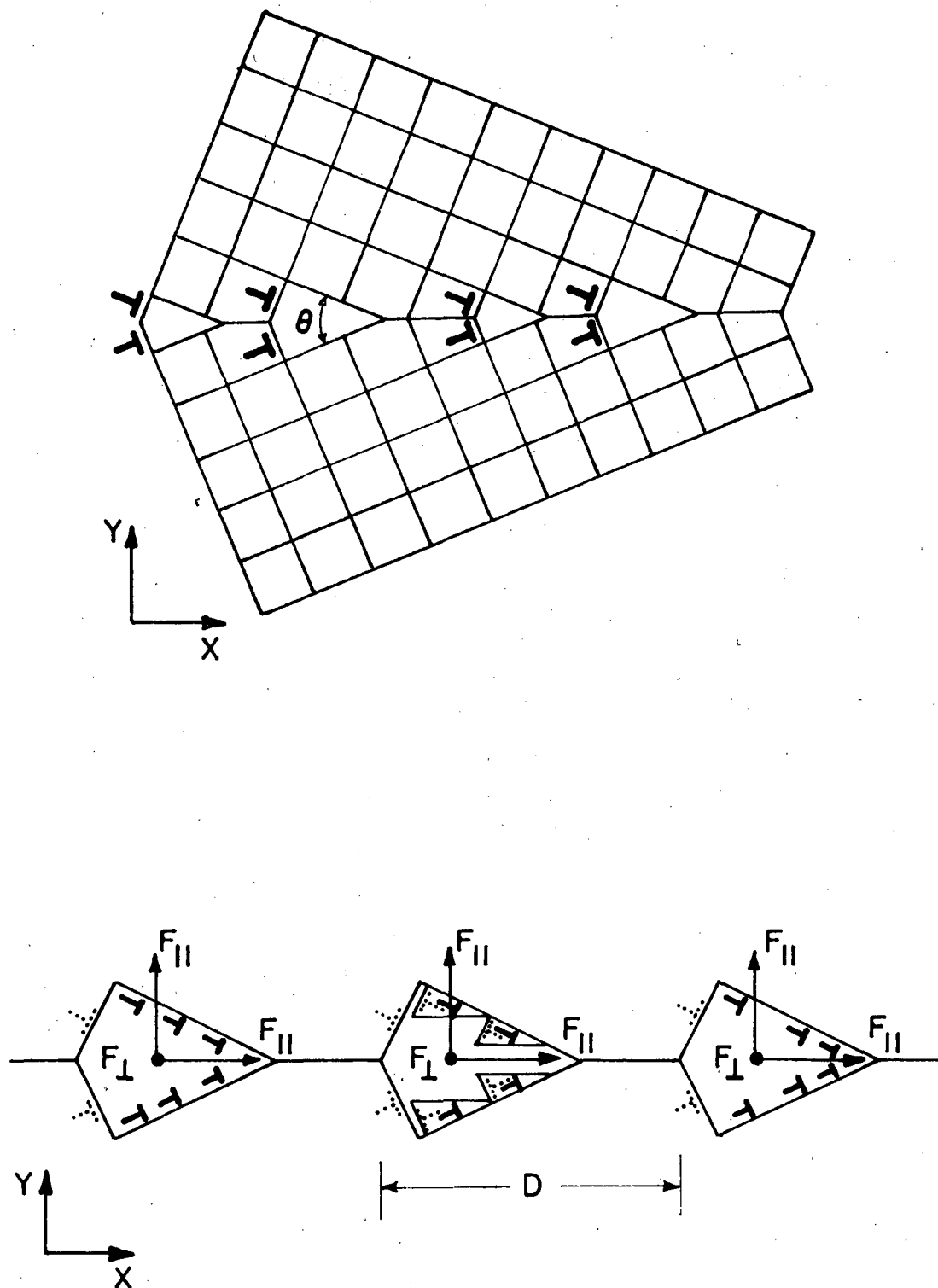
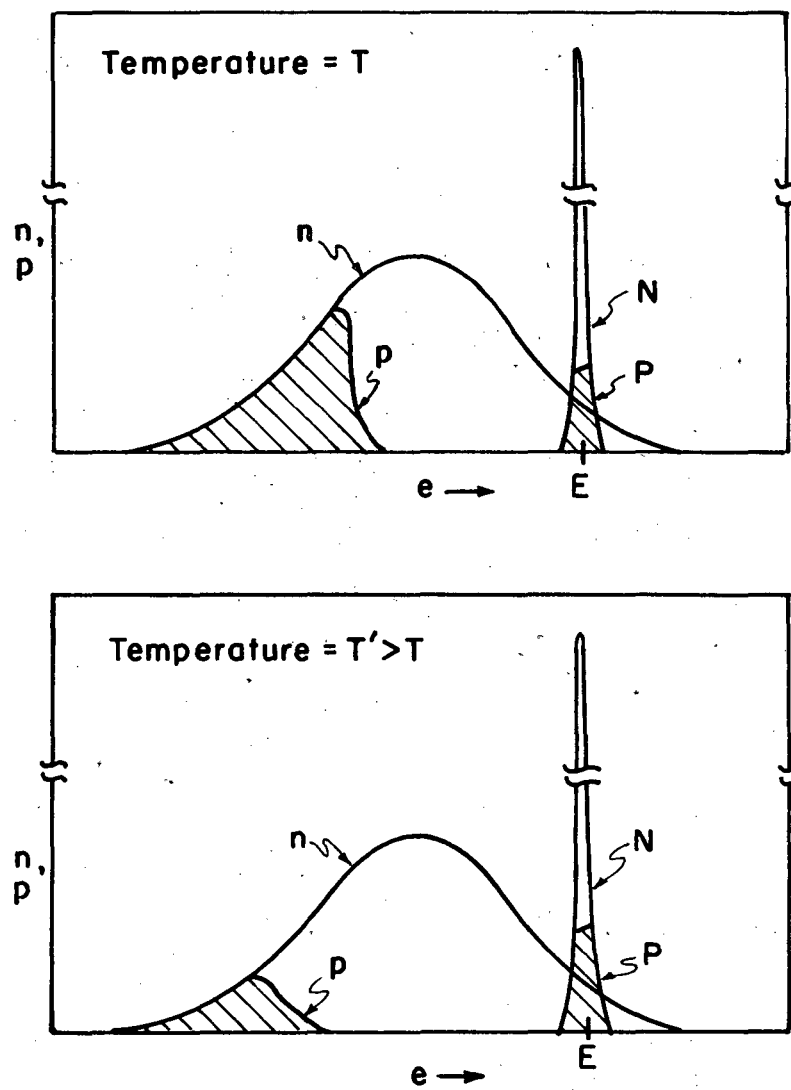


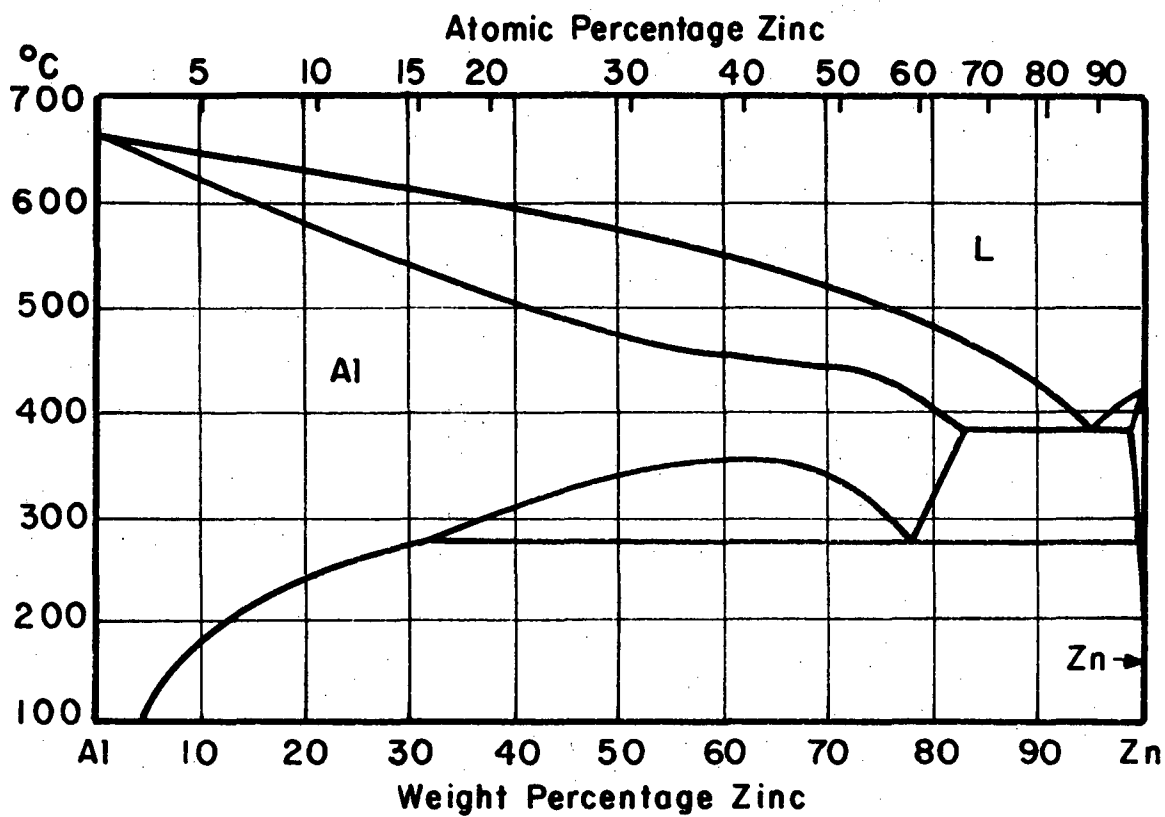
Fig. 39

XBL8110-6805



XBL 817-6176

Fig. 40



XBL 7611-7743

Fig. 41

This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Department of Energy to the exclusion of others that may be suitable.

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