Analysis of Three-dimensional Atom-probe Data by the Proximity Histogram

Olof C. Hellman,* Justin A. Vandenbroucke, Jörg Rüsing, Dieter Isheim, and David N. Seidman

Department of Materials Science and Engineering, Northwestern University, 2225 N. Campus Drive, Evanston, IL 60208-3108

Abstract: The three-dimensional (3D) atom-probe technique produces a reconstruction of the elemental chemical identities and three-dimensional positions of atoms field evaporated from a sharply pointed metal specimen, with a local radius of curvature of less than 50 nm. The number of atoms collected can be on the order of one million, representing an analysis volume of approximately $20\text{ nm} \times 20\text{ nm} \times 200\text{ nm}$ ($80,000\text{ nm}^3$). This large amount of data allows for the identification of microstructural features in a sample, such as grain or heterophase boundaries, if the feature density is large enough. Correlation of the measured atomic positions with these identified features results in an atom-by-atom description of the chemical environment of crystallographic defects. This article outlines a data compilation technique for the generation of composition profiles in the vicinity of interfaces in a geometrically independent way. This approach is applied to quantitative determination of interfacial segregation of silver at a MgO/Cu(Ag) heterophase interface.

Key words: data analysis, heterophase interface, MgO, Cu, three-dimensional atom-probe, segregation, Gibbsian interfacial excess, proxigram, ceramic/metal interfaces

INTRODUCTION

The Gibbsian interfacial excess of solute, central to the thermodynamic treatment of segregation at interfaces (Gibbs, 1948; Cahn, 1979; Sutton and Balluffi, 1995), is formulated in terms of a number of segregating atoms per unit area of interface. Experimentally, measurement of a Gibbsian excess requires a simultaneous measurement of the position of an interface and a spatially resolved measurement of local composition.

Analytical techniques such as Auger electron spectroscopy (AES), scanning transmission electron microscopy

(STEM) with electron energy loss spectroscopy (EELS), or one-dimensional atom-probe field-ion microscopy (APFIM) can be applied to the measurement of Gibbsian excesses in the case of planar, well-separated interfaces. These include grain boundaries (Krakauer and Seidman, 1993; Seidman et al., 1994; Krakauer and Seidman, 1998) and heterophase interfaces (Shashkov and Seidman, 1995, 1996; Shashkov et al., 1999). However, real interfaces often have more complex three-dimensional structures or are not well separated. Only three-dimensional (3D)-atom-probe microscopy (3DAP) is capable of both identifying the topology of interfaces and measuring the local chemical composition on a nanoscale (Letellier et al., 1994; Blavette et al., 1996; Miller et al., 1996).

3DAP (Blavette et al., 1993; Cerezo et al., 1998; Deconihout et al., 1999) is a spatially resolved field ionization/time-of-flight technique that results in a three-dimensional

Received November 15, 1999; accepted March 28, 2000.

Justin A. Vandenbroucke is now at Department of Physics, Stanford University, Stanford, CA 94305-4060.

*Corresponding author

reconstruction of approximately half of the atoms in a sample. The small radius of curvature at the end of a sharply polished sample causes a diverging electrical field, resulting in a natural magnification of ions field-evaporated from it, allowing for resolution on the atomic scale. A two-dimensional position-sensitive detector is used to identify from where on a tip's surface an ion originated. As atoms on the tip are field-evaporated, the layers beneath the surface are exposed; the sequence of field-evaporated ions is used to reconstruct the third dimension. Such a data set is visualized in Figure 1 (Rüsing et al., 2000). This image was generated using *Adam*, a custom Macintosh application developed at Northwestern University specifically to analyze data generated by a 3D atom-probe microscope (Hellman et al., submitted for publication).

GENERATION OF A PROXIMITY HISTOGRAM

The proximity histogram, or “proxigram” for short, is a profile of local atomic concentrations vs. proximity to an interface, and is the most direct way to represent experimental data for illustration of interfacial segregation. We perform three main data analysis steps to generate a proxigram: (1) a *sampling* to generate a regular grid of concentration points from the individual atomic positions; (2) an *interpolation* to identify an isoconcentration surface in the regular grid; and (3) a *correlation* of the surface to the original set of discrete three-dimensional atomic positions.

All of the data analysis described herein is performed after any data manipulation specific to the experimental setup, which may include mass windowing and time-of-flight calibration to identify elements, depth scaling, magnification calibration, and noise filtering.

Sampling

The first step in generating a proxigram is the transformation of the set of individual atomic positions and their chemical identities into a regular 3D grid of concentration values. Each point of the grid represents a local atomic fraction of each of the identified species in the analysis. We call such a grid a “concentration space.” Similar sampling techniques have been used for analysis of 3DAP data previously (Liew et al., 1999).

To generate this grid, a cubic lattice of points is defined overlaying the data set with an arbitrary grid spacing, typi-

cally 1–3 nm. Each atom in the original data set contributes to the atomic concentration calculated at the grid points close to it. The nature of the contribution is determined by a transfer function. The simplest transfer function is a square wave, where a grid point would represent the concentration calculated from the cubic volume of edge length equivalent to the grid spacing centered on a grid point, each data point contributing to a single grid point. More complex transfer functions can be constructed for the purpose of improving statistics, removing uncertainty for calculations at grid points near the edges of the data set, and preserving spatial dimensions. We commonly use a sawtooth transfer function, where each data point makes a weighted contribution to the calculation at its eight closest grid points.

The choice of a value for the grid spacing and transfer function is a tradeoff between resolution of the grid, positional error, and statistical error. For a given transfer function, larger grid spacings increase positional error and decrease statistical error. The choice of a 1.5 nm grid spacing results in approximately 200 events per grid point. This is adequate for calculating atomic fractions of majority components, but provides inadequate statistics for accurate calculations for low-concentration species; for example, for a 1 at.% component, the one sigma statistical error would be approximately 0.7 at.%.

If this composition grid is used to identify the position of interfaces, as discussed in the next section, the change in composition across the interface is usually large. This means that relatively high statistical errors can be tolerated in an interface finding algorithm, because the statistical error at one point will be small compared with the difference of the composition at an adjacent grid point on the opposite side of the interface. Defining a coarser grid would provide better statistics, but the increase in grid point spacing would result in a different source of positional error.

Interpolation

Having calculated a regular grid of concentration values, it is straightforward to generate a surface in three dimensions, which represents the surface of a concentration C_i of one of the components. The procedure is analogous to the generation in two dimensions of a contour plot from a grid of data, such as altitudes on a terrain map. This surface is referred to as an isoconcentration surface. To generate such a surface, we employ the traditional marching cubes algorithm (Lorenson and Cline, 1987). This algorithm interpo-

Figure 1. Representation of the three-dimensional reconstruction of an internally oxidized Cu(Mg, Ag) alloy by three-dimensional (3D) atom-probe microscopy; Mg (red), O (green), and Ag (blue) are represented as spheres. Cu atoms are small green dots. The cell size shown is approximately $17 \text{ nm} \times 17 \text{ nm} \times 57 \text{ nm}$.

Figure 2. Representation of the Mg 11 at.% isoconcentration surface for the sample shown in Figure 1, overlaid with the atomic positions of the Mg (red), O (green), and Ag (blue) atoms. The concentration space used was calculated with a sawtooth transfer function and a grid spacing of 1.5 nm. Atoms are drawn with a radius of 0.15 nm. The Cu atoms are not drawn for the sake of clarity.

lates linearly between adjacent grid points to identify points on an isoconcentration surface. From this set of points, a set of triangles is constructed in order to make the surface continuous. The internal representation of each triangle preserves the direction of the triangle, that is, which side of the triangle is facing toward higher composition values. This information is important in the next step of the calculation.

Isoconcentration surfaces are also useful for visualization of experimental data. We exhibit an isoconcentration surface overlaid with atomic position data in Figure 2. Generation of an isoconcentration surface from 3D atom-probe data is not uncommon. Previous work, however, has done this exclusively for data visualization. In this work, isocon-

centration surface generation is an integral part of the analysis: It is the identification of an interface for which the effect of solute segregation is measured.

The only choices of parameters at this step of the calculation are which species to analyze and at what concentration to calculate an isoconcentration surface. Ideally, the effect of changing this composition value parameter in the region of an interface with a large composition change should be small. Practically, the interface is blurred, and the exact position of the isoconcentration surface will depend on the concentration value chosen. This dependence should be weakest at the point of the steepest concentration gradient. We note that in the case of an interface of a very small precipitate, blurring of the data will not result in symmetric composition profiles of components of the precipitate and the matrix, but will produce an apparent deficit of precipitate components at the original precipitate boundary, with a corresponding increase in the matrix components. This is because the volume of layers adjacent immediately to an interface increases outside the precipitate, and the outer shell of a precipitate mixes with a larger volume of matrix. It is this same effect that is accounted for in the normalization of a proxigram, as is discussed in the next section.

The parameters that were used in generating the concentration space, i.e., the transfer function and the grid spacing can be seen in the isoconcentration surface: A grid spacing that is too large will not resolve the isoconcentration surface well. A narrow transfer function can produce poor statistics and, therefore, a rough isoconcentration surface, whereas a wide transfer function will err in its positioning. Because the isoconcentration surface is used as a reference point for the proxigram calculation, the best isoconcentration surface will have a roughness on the order of the transfer function half-width: the point at which error due to roughness is equal to error due to positioning.

Correlation

The Proximity Histogram

Having defined a surface that represents an interface in an analyzed volume of material, we proceed to correlating the initial set of atomic positions and elemental identities with that surface. We construct a one-dimensional plot of local concentration vs. proximity to that surface. We use the term proximity to include the fact that the surface has a direction, and that the proximity can have negative values. There is an intermediate step in this calculation; first, a histogram is generated of the proximity to the surface of all the atomic

positions of each identified elemental species. This histogram is then normalized by the total population in each bin of the histogram, resulting in a local composition value for each bin.

In generating a histogram, it is required to calculate the distance from each atomic position to the isoconcentration surface. As this surface is simply a set of triangles, the problem reduces to calculating the distance to every component triangle of the surface and finding the minimum value from each atomic position. This calculation can require a significant amount of CPU time; even a small precipitate might be represented by an isoconcentration surface of hundreds of triangles, and the calculation is performed at each triangle for each atomic position.

There is one subtlety in the calculation of the proximity of a point to a surface composed of a set of triangles that deserves note. It is often the case that the shortest distance to the surface is the distance to a vertex that is shared by four or more triangles. The magnitude of the proximity is equal to the distance, and the sign of the proximity is negative if the concentration gradient of the isoconcentration surface is pointing away from the atomic position. Usually, the point will be on the same side of all the triangles, and there is no ambiguity in the sign of the proximity. Recall that each triangle has a particular direction; one side faces the positive gradient of the concentration space. It is, however, possible (and for rough surfaces, increasingly likely) that some points lie on the positive side of some of the triangles, and on the negative side of the others. In this case, it must be determined on which side of the isoconcentration surface the precipitate lies. This is accomplished by calculating the distance from the point to the plane of each triangle, and using the direction of the triangle with the greatest distance thus calculated.

Normalization

The result of this calculation is a two dimensional array. One dimension represents the different species in the sample, and the second dimension represents the proximity of that array element to the surface. Each array element represents the population of a single species in a strip of volume a certain distance away from an isoconcentration surface. This representation is independent of the topological complexity of the surface; in a sample with multiple precipitates, regions in the vicinity of each separate precipitate are combined in the resulting histogram. Positive and negative proximities are defined with respect to the direc-

Figure 3. Proxigram of species in the sample with respect to the Mg 11% isoconcentration surface shown in Figure 2; the bin size is 2 nm. The calculation is made over a volume approximately 18 nm × 18 nm × 119 nm, and includes two precipitates. There are no detected atoms at a distance greater than 40 nm from the isoconcentration surface.

tion defined for the surface, which is taken to be the same sign as the concentration gradient at the surface. Normalization of the populations in each bin results in a local concentration value for each bin, and the sum of atomic concentrations in each bin is unity. A normalized proxigram is presented in Figure 3. The population of each bin of this proxigram is shown in Figure 4. The error bars in Figure 3 represent the one-sigma statistical error

$$\sigma = \sqrt{\frac{C_i (1 - C_i)}{N}}; \quad (1)$$

where C_i is the calculated atomic fraction of each species i , as shown in Figure 3, and N is the total number of atoms in each bin, shown in Figure 4. The population is the highest, and the corresponding error the smallest, in the two bins just below zero on the x-axis.

The normalization step accounts for the fact that the volume associated with each histogram bin is not constant, because a curved surface has a larger volume element of a constant thickness on its convex side. We note that this is accomplished without actually calculating the volume itself, or even calculating the area of the isoconcentration surface or its curvature. The end result of the calculation is a normalized proximity histogram, or proxigram, representing

Figure 4. Distribution of atom populations in the proxigram of Figure 3 (atoms/bin in proxigram data). Statistics are best in the region immediately outside the precipitates.

the atomic fraction of each species as a function of its proximity to an interface.

The normalization procedure also determines the upper and lower bounds of the proxigram, and the degree of statistical error at each proxigram point. At the upper and lower bounds, the population of the bins becomes zero, because of the limited spatial extent of the measured data. Close to these bounds, the population becomes very small, thus increasing the statistical error at both ends. We point out again that the x-axis (abscissa) of the proxigram is not a linear measure of distance, because the isoconcentration surface is not planar. In this sample, the upper bounds represent the interior of a precipitate, because the isoconcentration surface is wrapped around a small precipitate and the concentration gradient of the isoconcentration surface is pointing to the interior of the precipitate. The lower bounds of the proxigram represent the limits of the analyzed space far from the precipitate. At the region of the proxigram just outside a precipitate, where the statistics are best, each bin represents approximately 25,000 atoms. Even at this level, the statistical error for the low-concentration components, silver in this example, is severe; the one sigma error value for a measured concentration of 0.5% is on the order of 0.05%.

DISCUSSION

Treatment of Non-planar Interfaces

Actually, this calculation is one small step away from what is necessary for a direct comparison to a Gibbsian treatment

of interfacial segregation. That is, a calculation of the Gibbsian interfacial excess of a solute species should be performed in units of number of segregating atoms per unit interface area. If the assumption of constant atomic density is made, a simple transformation of the y-axis of the proxigram can be performed; atomic fraction can be multiplied by atoms per unit volume. As a result, the area under a proxigram plot would have units of atoms per unit area. This, however, is rigorously incorrect when compared with Gibbs' formulation.

A core assumption of the Gibbsian treatment is that the interface is planar. One of the consequences of this requirement is that the choice of the position of the interface is irrelevant for a binary system to a calculation of a Gibbsian interfacial excess, or to any true thermodynamic property of the interface. Indeed, a triumph of this treatment is that there is no need for an interface thickness to be specified; rather an interface can be assumed to be a truly two-dimensional object.

In 3D atom-probe microscopy, however, the atomic reconstruction of the sample is fine enough to identify topologically very complex interfaces, let alone non-planar interfaces. The calculation of a proxigram is done in such a way that the shape (as well as area) of the interface is irrelevant to the calculation. The effect of area, however, is embedded in the proxigram, because each bin of the proxigram represents a slice of volume at a certain distance from an isoconcentration surface, and each slice represents an effective area. Infinitesimally thin slices would represent an exact area. So, if the local atomic fraction of the proxigram is multiplied by an atomic density, the resulting number of atoms per unit area is valid for the effective area of that slice of volume. Although this effective area is not constant through the proxigram, it is independent of the choice made for the concentration parameter used to generate the isoconcentration surface.

Let us illustrate the problem by considering a spherical precipitate with a distribution of a segregant in the matrix surrounding it. The straightforward way of calculating segregation is to count the segregant atoms and divide by the area of the precipitate's surface. As in Gibbs' treatment, this method requires the identification of the position of a dividing surface. For a non-planar interface, however, the choice of the dividing surface affects the area of the interface. If a larger precipitate radius is chosen, the measured number of segregating atoms per interface area is reduced. The Gibbsian excess, however, is a true thermodynamic quantity and should not depend on such an arbitrary choice.

One approach to this problem is to link the measured quantity to the choice of the surface. The Gibbsian excess Γ would be expressed as $\Gamma[r]$, with the brackets representing the fact that the dependence of Γ on r is dependent on the arbitrary choice of the position of the interface, not on an actual change in the position of the physical interface (Fisher and Wortis, 1984). The only way to avoid this in the case of a segregation calculation is to calculate, for each atom, what the area of the surface would be if the surface were defined such that it intersected the location of that atom. The Gibbsian excess would then be the sum difference:

$$\sum_{i=1}^{N_i} (1/A_i) - C_o \sum_{j=1}^N (1/A_j). \quad (2)$$

Where the first sum is taken over all segregant atoms in the region under consideration, the second sum is taken over all atoms in that region, C_o is the bulk fraction of the segregating species, and A_i and A_j are the areas of the interface selected such that it intersects atom i or j . The first term represents the areal density of the segregating species, and the second term subtracts the areal density expected for a bulk concentration of C_o . The region considered should extend a certain distance on both sides of an interface, and should be constructed such that the area of every particle in the region is well defined. In the extreme case, an atom at the exact center of a spherical precipitate would have an effective area of zero, and the sums would not be accurate.

This is, in effect, what is done when compiling a proxigram, but without an explicit calculation of an area for each point. Instead, the effective area for a single point in the proxigram (representing a slice of volume a certain distance from the interface) is inferred from the atomic density and the count of atoms in that slice.

This count of atoms in each slice is shown in Figure 4. With the assumption of a constant atomic density, Figure 4 then also shows the trend in the effective area per point on the histogram. Figure 4 takes on its shape because of the different regimes of the intersection of the volume slices with the volume of the dataset. The highest values of proximity to the interface represent the interior of the precipitates. As proximity to the interface decreases, the effective volume of each shell increases geometrically. As the distance from the precipitate gets larger (proximity to the interface gets more negative) the slices are increasingly outside the volume of the dataset, and so their population decreases. The plateau between -35 nm and -20 nm represents the

fact that the analysis volume is very long in one direction: 12,000 atoms is approximately the population of two slices, one from each precipitate, each one 2 nm thick, which slice at right angles through the sample volume perpendicular to its long axis. The minimum value on the x-axis is at 40 nm, reflecting the fact that the particles are approximately 80 nm apart at opposite ends of the analysis volume.

Comparison to Previous Work

One study exists of a measurement of segregation in the vicinity of small precipitates (Rozdilsky et al., 1998; Rozdilsky, 1999). In this work, the authors attempt to identify segregation based on a radial distribution function of the concentration of atoms from the center of the identified precipitates. While promising, this work failed as a true measurement of compositions because of statistical noise and the fact that the precipitates were not exactly spherical. This method has not been used because of the limitation of treating only spherical precipitates and the uncertainty of arbitrarily choosing a point as the center of a precipitate.

Our method, in contrast, can treat any arbitrary interface geometry. No arbitrary choice is made for the reference point—the reference point is taken to be an isoconcentration surface calculated directly from the experimental data. In addition, because in our method the segregation at multiple precipitates is automatically combined into one diagram, statistical noise can be reduced to tolerable, though still significant, levels. Because the interface geometry is arbitrary, it plays almost no role in the generation of the proxigram data itself. Instead, microstructural features such as the density of internal interfaces or size of precipitates manifest themselves in the limits on the x-axis in the proxigram data.

The calculation of isoconcentration surfaces from a regular grid of values for visualization of data is part of standard scientific visualization packages like Research Systems' IDL (Boulder, CO). This technique has been applied to 3D atom-probe data (Isheim et al., 1999). However, the same features of commercial software packages that make it easy to perform visualization also impede the use of the isoconcentration surface data for anything other than visualization purposes.

CONCLUSIONS

When analyzing data from a 3D atom-probe for the purpose of identifying quantitative measures of segregation at interfaces, it is desirable to simplify a large set of three-

dimensional atomic positions and chemical identities into a one-dimensional set of atomic concentrations, where the parameter of interest is the proximity to an interface. This article describes how such an interface is identified, and how such data deconvolution from three dimensions to one dimension is performed, while preserving as much as possible the relevant physical properties of the data set. This new approach is applied to the problem of determining the level of interfacial segregation of silver at a MgO/Cu(Ag) heterophase interface.

ACKNOWLEDGMENTS

This research is supported by the National Science Foundation, Division of Materials Research, grant DMR-972896; Bruce MacDonald, Grant Officer. J. Vandenbroucke was supported by an NSF REU grant. D. Isheim received partial support from the Deutsche Forschungsgemeinschaft (DFG), and the Alexander von Humboldt Foundation through the Max Planck research prize of DNS. J. Rüsing was supported by the U.S. Department of Energy under grant DE-FG02-96ER45597.

REFERENCES

- Blavette D, Deconihout B, Bostel A, Sarrau JM, Bouet M, Menand A (1993) The tomographic atom probe: a quantitative three-dimensional nanoanalytical instrument on an atomic scale. *Rev Sci Instrum* 64:2911–2919
- Blavette D, Letellier L, Racine A, Hazotte A (1996) Concentration gradients near heterophase boundaries in single crystal nickel-based superalloys. *Microsc Microanal Microstruct* 7:185–193
- Cahn JW (1979) Thermodynamics of solid and fluid interfaces. In: *Interfacial Segregation*, Johnson WC, Blakely JM (eds). Materials Park, OH: ASM, pp 3–23
- Cerezo A, Godfrey TJ, Sijbrandi SJ, Smith GDW, Warren PJ (1998) Performance of an energy-compensated three-dimensional atom-probe. *Rev Sci Instrum* 69:49–58
- Deconihout B, Pareige C, Pareige P, Blavette D, Menand A (1999) Tomographic atom probe: new dimension in materials analysis. *Microsc Microanal* 5:39–47
- Fisher MPA, Wortis M (1984) Curvature corrections to the surface tension of fluid drops: Landau theory and a scaling hypothesis. *Phys Rev B* 29:6252–6260

- Gibbs JW (1948) Influence of surfaces of discontinuity upon the equilibrium of heterogeneous masses—Theory of capillarity. *The Collected Works of J. Willard Gibbs*. New Haven: Yale University Press, Vol 1, pp 219–252
- Isheim D, Hellman OC, Seidman DN, Danoix F, Blavette D (1999) Atomic scale study of second-phase formation involving large coherency strains in Fe-20 at.% Mo. *Scripta Mater* 42:645–651
- Krakauer BW, Seidman DN (1993) Absolute atomic scale measurements of the Gibbsian interfacial excess of solute at internal interfaces. *Phys Rev B* 48:6724–6727
- Krakauer BW, Seidman DN (1998) Subnanometer scale study of segregation at grain boundaries in an Fe (Si) alloy. *Acta Mater* 46:6145–6161
- Letellier L, Bostel A, Blavette D (1994) Direct observation of boron segregation at grain boundaries in astroloy by 3D atomic tomography. *Scripta Met Mater* 30:1503–1508
- Liew H, Smith GDW, Cerezo A, Larson DJ (1999) Experimental studies of the phase separation mechanism in Ti-15 at% Al. *Mat Sci Eng A* 270:9–13
- Lorensen WE, Cline HE (1987) Marching cubes: a high resolution 3D surface construction algorithm. *ACM SIGGRAPH Comput Graph* 21:163–169
- Miller MK, Cerezo A, Hetherington MG, Smith GDW (1996) Field evaporation and field desorption. *Atom Probe Field Ion Microscopy*. Oxford: Clarendon, pp 71–109
- Rozdilsky I (1999) *3-D atomic-scale characterization of growing precipitates*. DPhil Thesis, University of Oxford
- Rozdilsky I, Cerezo A, Smith GDW (1998) Atomic scale measurement of composition profiles near growing precipitates in the Cu-Co system. In: *Solidification 1998*. Marsh SP, Dantzig JA, Hofmeister W, Trivedi R, Chu MG, Lavernin EJ, Chun JH (eds). Warrendale, PA: TMS, pp 83–90
- Rüsing J, Sebastian JT, Hellman OC, Seidman DN (2000) Three-dimensional investigation of ceramic/metal heterophase interfaces by atom-probe microscopy. *Microsc Microanal* 6:445–451
- Seidman DN, Krakauer BW, Udler D (1994) Atomic scale studies of solute-atom segregation at grain boundaries: experiments and simulations. *J Phys Chem Solids* 55:1035–1057
- Shashkov DA, Seidman DN (1995) Atomic scale studies of segregation at ceramic/metal heterophase interfaces. *Phys Rev Lett* 75: 268–271
- Shashkov DA, Seidman DN (1996) Atomic scale studies of silver segregation at MgO/Cu heterophase interfaces. *Appl Surf Sci* 94/ 95:416–421
- Shashkov DA, Muller DA, Seidman DN (1999) Atomic-scale structure and chemistry of ceramic/metal interfaces—II. Solute segregation at MgO/Cu (Ag) and CdO/Ag (Au). *Acta Mater* 47: 3953–3963
- Sutton AP, Balluffi RW (1995) *Interfaces in Crystalline Solids*. New York: Oxford University Press