

Point Defects in Materials Part I: Behavior and Characteristics in Different Material Classes

David N. Seidman and Donglu Shi,
Guest Editors

Introduction

In this issue of the *MRS Bulletin* we present five papers that involve point defect phenomena in a wide variety of materials—metals, conducting ceramic oxides, semiconductors, amorphous alloys, and high T_c superconducting oxides. The unifying theme of this issue is point defects—zero-dimensional defects. Even for the high T_c oxides, where planar defects are discussed, it is the ordering of oxygen/vacancy chains that ultimately gives rise to twins in the famous $\text{YBa}_2\text{Cu}_3\text{O}_{7.8}$ (1:2:3) oxide superconductor.

Hillard Huntington, professor emeritus of physics at Rensselaer Polytechnic Institute, is an early and important pioneer in the study of point defects in metals. A theorist, he has also performed many experiments over the years; for example, he performed key early experiments on electromigration effects. Huntington's article presents a historical review of the research on vacancies and self-interstitial atoms in metals during the period that stretches from the mid-1930s to the mid-1960s. He played a crucial role in this field as a result of his seminal theoretical calculations, with Fred Seitz in 1942, on the enthalpies of formation and migration of vacancies or self-interstitial atoms in pure copper. Huntington's and Seitz's calculations indicated that diffusion occurs predomi-

nantly by a monovacancy mechanism since the enthalpy of formation of a self-interstitial atom, the [100] split form, also called the dumbbell form, is too large to be compatible with the activation enthalpy for self-diffusion in copper. It is now well established that the latter is given by the sum of the enthalpy of formation and the enthalpy of migration of a monovacancy in many face-centered-cubic (fcc), body-centered-cubic (bcc), and hexagonal-close-packed (hcp) metals.

Huntington emphasizes the importance of the now classic Kirkendall marker experiments (1947) in demonstrating that neither the direct interchange nor Zener's ring mechanism (1950) is consistent with a Kirkendall marker shift; the markers always move into the side rich in the faster diffusing element with a displacement proportional to the square root of the time. He also points out that the classic quenching and annealing experiments, pioneered by Kaufman and Koehler (1952, 1955), yield both the enthalpy of formation and the enthalpy of migration of a monovacancy, though under nonequilibrium conditions, and that the sum of these two enthalpies is equal to the activation energy for self-diffusion, as measured by the radioactive tracer technique, in pure gold.

Huntington discusses the elegant experiments pioneered by Simmons and Balluffi

(1960 to 1963) on the fcc metals aluminum, copper, gold, and silver. The Simmons-Balluffi experiment yields the fractional net change in the point defect population under thermodynamic equilibrium conditions, and simultaneously demonstrates—without any assumptions—which point defect is the dominant one. For these fcc metals, the Simmons-Balluffi experiment demonstrated conclusively that the vacancy is the dominant point defect at elevated temperatures, thus proving that vacancies mediate self-diffusion in these metals. Huntington further discusses substitutional impurity diffusion in metals, and reviews the seminal contributions of Lazurus (1954) and LeClaire (1962, 1964) to our physical understanding of this problem.

Historically, radiation damage produced by energetic particle bombardment (fast neutrons, deuterons, or 1 MeV electrons) was used to create Frenkel pairs (a vacancy plus a self-interstitial atom) in order to generate self-interstitial atoms in sufficient concentrations to study them. Electron-irradiation experiments (Meecham and Brinkman in 1954, Corbett, Smith and Walker in 1959, and Sosin and Brinkman in 1960) at 4.2 K demonstrated that the radiation damage produced at this temperature was much greater than the damage produced at room temperature, and upon subsequent annealing of a specimen irradiated at 4.2 K, the amount of recovery was extensive. A seminal model developed by Corbett, Smith and Walker (1959)—and presently called the one-interstitial model—attributes the low temperature (or Stage I) recovery behavior to the [100] split or dumbbell self-interstitial and Stage III recovery to the monovacancy in fcc metals. A great deal of research since the mid-1960s has vindicated this model in the fcc and bcc metals, as well as the hcp metals.

The equilibrium form of a self-interstitial was observed in one of the earliest applications of the molecular dynamics simulation technique. In a classic paper, Gibson, Goland, Milgram and Vineyard (1960) found that for pure copper the [001] dumbbell self-interstitial configuration is the one with the lowest energy. This result agrees with the analytical calculations of Huntington (1953), who also found the [001] dumbbell configuration to have the lowest energy and a migration enthalpy of less than 0.25 eV. In reading Huntington's historical review it is interesting to note that in the period that followed the mid-1960s, many basic and more detailed experiments were performed, but many of the seminal ideas developed before 1965 played a very important role in the fur-

ther development of studies of point defects in metals.

Arthur Nowick, the Marion Howe Professor of Metallurgy and Materials Science at Columbia University, is an expert and pioneer in the study of point defects in both metals and ceramic oxides. In a pioneering experiment, Nowick was able to deduce a limit to the enthalpy of formation of a monovacancy in a Ag-Zn alloy by studying the effect of quenched-in vacancies on the elastic aftereffect. Nowick's contribution to this issue of the *MRS Bulletin* reviews the use of electrical conductivity measurements, labeling techniques to study oxygen diffusion, and dielectric loss measurements to determine point defect mechanisms for diffusion in ceramic oxides.

Point defects in oxides behave quite differently from point defects in metals and alloys or semiconductors for several important reasons. First, oxides are highly ionic so that, in general, point defects carry an effective charge. This implies that point defect behavior is controlled by charge compensation that results in the simultaneous introduction of point defects of opposite charge to maintain the condition of charge neutrality. The point defect reactions are controlled by the law of mass action. Furthermore, the presence of oppositely charged point defects results in the formation of associated pairs or larger clusters due to Coulombic interactions. Second, the exact composition of an oxide is a sensitive function of the ambient partial pressure of oxygen. Thus the stoichiometry, and therefore the point defect concentration, can be controlled by annealing a metal oxide specimen in a specified partial pressure of oxygen at a given temperature. Third, the melting points of oxides are very high so that below approximately 1500°C the intrinsic point defect concentrations are very small. This implies that the presence of accidentally or intentionally introduced impurities strongly affects the point defect concentrations. Therefore, point defect concentrations are deliberately controlled by introducing aliovalent (heterovalent) impurities. The range of point defect concentrations in oxides that is amenable to study is from 0.01 to 1 mol%. Finally, in a binary oxide there are two different sublattices, and diffusion on each sublattice can proceed at different rates via different point defect mechanisms.

With the above general background Nowick discusses: (1) oxides of the rock-salt structure, e.g., MgO, CaO and SrO (alkaline earth oxides), and NiO, CoO, MnO and FeO (transition metal oxides); (2) oxides of the fluorite structure, e.g., CeO₂,

ThO₂ and UO₂; and (3) oxides of the perovskite structure, e.g., BaTiO₃, SrTiO₃ and KTaO₃. The most detailed discussion is reserved for oxides of the rocksalt structure. In particular, Nowick discusses MgO as a prototype metal oxide since it is the most widely studied ceramic oxide, where the intrinsic point defect is a Schottky pair (a cation vacancy plus an anion vacancy). The formation enthalpy of a Schottky pair is considerably less than that of either cation or anion Frenkel pairs.

Ulrich Gösele and Teh Tan, both professors of materials science at Duke University, have extensive experience and a great deal of expertise in the field of point defects in semiconductors. They have both made important contributions to our understanding of point defect diffusion mechanisms for self-diffusion and impurity diffusion in silicon and gallium arsenide.

Intrinsic point defects in single-crystal semiconductors have several features that distinguish them from point defects in metals or ceramic oxides. Under certain experimental conditions, however, ceramic oxides can behave as semiconductors. The distinguishing features are: (1) the point defects may be either neutral or charged; (2) the point defects may exist in significant nonequilibrium concentrations because of the low dislocation densities in single crystal semiconductors; (3) both vacancies and self-interstitials may be present simultaneously; and (4) in compound semiconductors the equilibrium point defect concentrations are a function of the vapor pressure of the more volatile component. These features play important roles in understanding diffusion mechanisms for silicon and gallium arsenide. For silicon there has been a long standing controversy concerning the relative importance of vacancies versus self-interstitial atoms, and Gösele and Tan review the status of this controversy in some detail.

The basic intrinsic point defects in silicon are vacancies and self-interstitial atoms that may occur in one or more charge states, each with its own Gibbs free energy of formation. The thermal equilibrium concentration of a charged point defect depends on the doping level, and the position of its energy level in the energy bandgap. For this reason the situation is far more complicated than for metals, where the point defects are always neutral.

In the III-V compound semiconductor gallium arsenide, the situation is even more complicated. Vacancies can form on both sublattices, and self-interstitial atoms can be created from both elements. In addition, antisite defects can form as a result of an element from one sublattice occupying the position of an element on the sec-

ond sublattice. The deep donor EL2 is an important example of an antisite defect because it causes unintentionally p-doped GaAs to become semi-insulating. Also, for GaAs the thermal equilibrium concentrations of the different vacancies and self-interstitial atoms are a function of the partial vapor pressure of As₄. This pressure dependence is both a curse and a blessing because it makes experimental point defect studies more complicated, but allows the possible point defect mechanisms to be discriminated. The latter is clearly not possible for elemental semiconductors.

Robert Averback, professor of materials science and engineering at the University of Illinois (Urbana-Champaign), has worked extensively in the fields of radiation damage, nanograined materials, and the subject of his article—diffusion in amorphous materials. He is an expert on point defect mechanisms for these phenomena. Compared to our detailed understanding of point defect mechanisms for diffusion in metals, ceramics and semiconductors, our level of understanding of precisely how diffusion occurs in amorphous materials is simply not as well developed. One reason is that the first quantitative diffusion experiment on a metallic glass was not performed until 1975. A major experimental problem is that one is restricted to performing experiments in a narrow temperature range below the so-called glass transition temperature (T_g). On the theoretical side, the absence of a three-dimensional periodic lattice makes it difficult to mathematically describe the structure of an amorphous solid or the character of defects. It is therefore difficult to formulate a description of diffusion mechanisms. Nevertheless, significant progress is being made in understanding diffusional behavior in amorphous materials.

Averback points out that there are strong similarities between diffusion in crystalline metals and in amorphous materials. He discusses the effects of atomic radius of the diffusing species, the activation enthalpies and volumes for diffusion, and radiation-enhanced diffusion, making the point that the behavior for amorphous materials is similar to that observed for crystalline materials, which suggests a direct diffusion mechanism. The two possible direct diffusion mechanisms are a vacancy diffusion mechanism and an interstitial process. Averback also points out that notable exceptions to these observations suggest a cooperative type of diffusion mechanism for the diffusion of atoms with large atomic radii, i.e., atomic motion involving excess free volume (Cohen and Turnbull, 1959). He also points out that

computer simulations of diffusion in amorphous materials have been performed employing commonly used model potentials such as Lennard-Jones type interatomic potentials for monatomic systems. Simulations using the Lennard-Jones potentials indicate that vacancies and interstitials are not stable in amorphous systems, except at very low temperatures. These simulations, however, have the major limitation that they simply may not represent real multi-component metallic glasses.

The final article is by Yimei Zhu and Masaki Suenaga (Materials Science Division, Brookhaven National Laboratory) and Johan Taftø (associate professor of physics, University of Oslo). These researchers have extensive experience and expertise in using a wide variety of electron microscope techniques to study microstructural effects. Their article discusses two-dimensional (planar) defects in high T_c cuprate superconductors, and also oxygen ordering, which is a point-defect

effect. The oxygen ordering is ultimately related to the formation of twins, so this work illustrates how point defects give rise to planar defects. The study of microstructural defects in high T_c oxide superconductors is important for understanding both phase transformations in these materials and the relationship between the critical current density and defects. Their emphasis is on defects in $YBa_2Cu_3O_{7-x}$, the so-called 1:2:3 oxide superconductor, because this oxide is studied most extensively.

The primary structural defects are twin boundaries, tweed, and oxygen/vacancy ordered planes, and they are intimately related to the phase diagram of the 1:2:3 oxide superconductor, and in particular to the oxygen content. The twin boundaries are the most commonly observed planar defect in the 1:2:3 superconductor. The twins are formed to reduce strain energy from shape and volume changes occurring during the tetragonal to orthorhombic

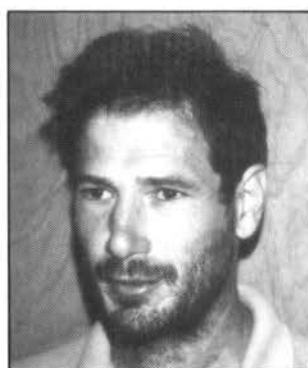
structural phase transformation. The twin boundary energy is found to be about 80 erg cm^{-2} for a pure 1:2:3 superconductor. This number is similar to the energy often found for twins in metals and alloys. The relationship of this work on planar defects to point defects comes through the role played by oxygen ordering in the basal plane containing O-Cu-O chains along the b-direction. It is this ordering that is responsible for the tetragonal to orthorhombic phase transition and therefore responsible for the formation of twins in the 1:2:3 oxide superconductor. The characteristic feature of the oxygen/vacancy ordering is that oxygen vacancies form long vacancy chains (-□-Cu-□) along the b-direction (□ represents a vacant oxygen site in the O-Cu-O chain) rather than a random distribution. The chains of -O-Cu-O- and of -□-Cu-□- order to form a superstructure. The exact period of the superstructure depends on the oxygen content. □



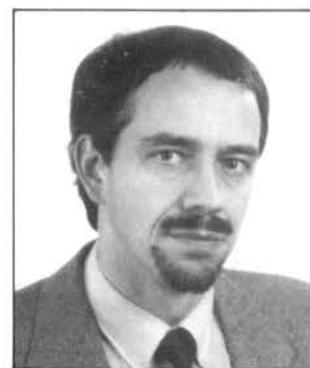
David N. Seidman



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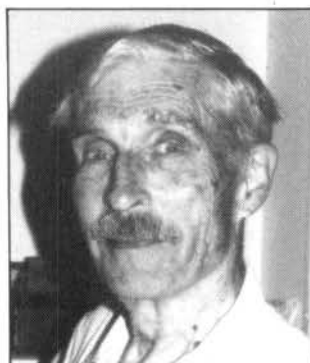


Robert S. Averback



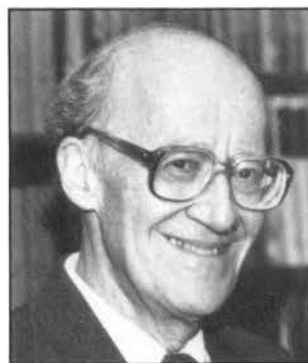
Ulrich M. Gösele

David N. Seidman, Co-Guest Editor for the November and December issues of the *MRS Bulletin*, is a professor of materials science and engineering at Northwestern University, and was a professor at Cornell University prior to 1985. Seidman's research interests have been in the areas of basic properties of point defects in quenched or irradiated materials, and displacement cascades in irradiated materials. His present research concerns phase transitions and the relationships between the structure and chemistry at internal interfaces in metal/metal, metal/metal oxide, semiconductor/



Hillard B. Huntington

semiconductor, and semiconductor/metal systems using transmission electron microscopy, atom-probe field-ion microscopy and Monte Carlo simulations.



Arthur S. Nowick

Seidman, a member of the Materials Research Society, received his PhD degree from the University of Illinois. His honors include two Guggenheim Fellowships and an

Alexander von Humboldt Senior Fellowship at the University of Göttingen.

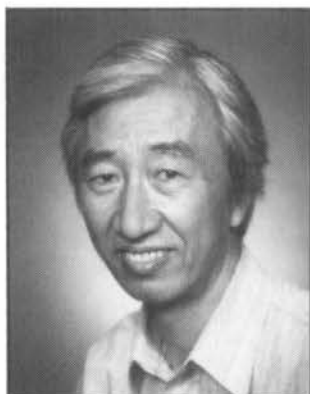
Donglu Shi, Co-Guest Editor for the November and December issues of the *MRS Bulletin*, is a research scientist at the Materials Science Division, Argonne National Laboratory. He has worked on characterizing and processing superconducting materials for the past nine years, and has concentrated on critical currents, flux pinning, vortex behavior, and microstructure analysis of conventional A-15 superconductors. Shi has also been involved in research on phase transformations, rapid solidi-

fication, crystallization, interfaces, defects analysis, alloy and ceramic processing, amorphous materials, and other aspects of the relationship between properties and structure of the metallic compounds. He holds a PhD from the University of Massachusetts and is a member of the Materials Research Society.

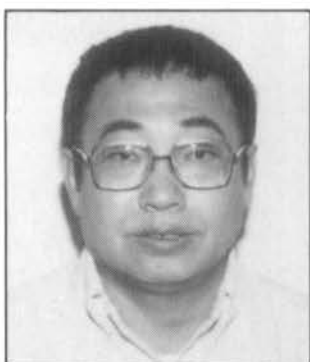
Robert S. Averback is a professor of materials science and engineering at the University of Illinois. His research interests focus on nonequilibrium processing of materials and span ion beam modification of materials, nanophase materials, and diffusion. He is a member of the Materials Research Society and the American Physical Society. Averback received his PhD in physics from Michigan State University, studying electron transport properties in metals. He has been a research associate at Cornell University and a staff physicist at Argonne National Laboratory.

Ulrich M. Gösele received his PhD from the Max-Planck-Institute for Metal Research, Stuttgart, in 1975, and afterward worked as a postdoctoral fellow or visiting scientist in industry, government, and academia in various countries, including the United States. He joined Duke University as professor of materials science in 1985. Gösele has authored or co-authored more than 100 papers on defects and diffusion in metals and semiconductors, reaction kinetics in liquids and solids, phase stability in thin films, photochemistry, semiconductor wafer bonding, and most recently, on quantum effects in porous silicon. Presently, he is on sabbatical at NTT LSI Laboratories in Atsugi, Japan.

Hillard B. Huntington is emeritus research professor at Rensselaer Polytechnic Institute, and was depart-



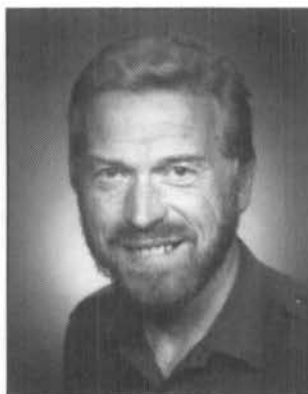
Masaki Suenaga



Teh Y. Tan

mental chairman from 1961 to 1968. His interests lie in solid state physics, and he has done work on defects, diffusion, electromigration, and surfaces, contributing nearly 100 publications to these areas. Huntington's research currently centers on computer simulation of the deterioration process through electromigration of metallic stripes as used in integrated circuitry.

Arthur S. Nowick is the Henry Marion Howe Professor of Metallurgy and Materials Science in the Henry Krumb School of Mines at Columbia University, where he has worked since 1966. His research interests are defects and mass transport, ceramic oxides, superionic conductors, and dielectric and anelastic relaxation phenomena. Nowick received his PhD in physics from Columbia University in 1950 and was head of the metallurgy



Johan Taftø



Yimei Zhu

group at IBM's T.J. Watson Research Center from 1960 to 1966. A Fellow of the American Physical Society and TMS-AIME, he has also been awarded the medal of the International Conference on Internal Friction and Ultrasonic Attenuation in Solids in 1989.

Masaki Suenaga is a senior metallurgist at Brookhaven National Laboratory. His research focuses on the relationship between microstructures, fabrication processes, and superconducting properties of high T_c superconducting oxides as well as of conventional metallic superconductors. His research has involved fabrication, characterization of electromagnetic properties and electron microscopy in microstructural studies of superconductors. Suenaga received his PhD in metallurgy from the University of California at Berkeley. He is a member of The Min-

erals, Metals, and Materials Society and the American Physical Society.

Johan Taftø, an associate professor in the Department of Physics at the University of Oslo, has been involved with transmission electron microscopy for 20 years. He is currently studying intermetallics and high T_c superconductors. He has been a research fellow at Fritz-Haber-Institute, Berlin, and at Arizona State University. From 1983 to 1986, he was at Brookhaven National Laboratory, where later he was also a visiting scientist.

Teh Y. Tan is a professor of materials science with Duke University's Department of Mechanical Engineering and Materials Science. After receiving his PhD from the University of California at Berkeley in 1971, he served as a postdoctoral fellow at Cornell University before joining IBM in 1974, and then Duke University's faculty of engineering in 1986. Tan, a co-initiator of the intrinsic gettering technology in silicon, has studied extended defects, point defects, and diffusion mechanisms in silicon as well as in gallium arsenide. He is the author or co-author of more than 100 papers.

Yimei Zhu is an associate scientist in the Materials Science Division at Brookhaven National Laboratory. His research has involved electron microscopy for studying the correlation between structures and properties in materials. His interests at Brookhaven have focused on characterization of crystal defects and interfaces in high T_c superconductors. Zhu received his PhD in materials science from Nagoya University, Japan. He is a member of the Materials Research Society and the Electron Microscopy Society of America. □