Thermodynamics of Point Defects and Their Relation with Bulk Properties

P. A. Varotsos and K. D. AlexopoulosRalph O. Simmons,

Citation: **40**, 11, 95 (1987); doi: 10.1063/1.2820277
View online: http://dx.doi.org/10.1063/1.2820277
View Table of Contents: http://physicstoday.scitation.org/toc/pto/40/11
Published by the American Institute of Physics

been the lack of a single source reference on the topic. In this, the first comprehensive book on EELS, Ray Egerton has produced a detailed description covering all aspects of theory and practice necessary to successfully implement the technique on the modern AEM.

The energy loss spectrum shows the consequences of inelastic scattering of the initially monoenergetic beam electrons. The myriad inelastic interactions can convey an extraordinary range of information about elemental composition, chemical bonding, interatomic distances, bond angles and the degree of atomic disorder. Upon first examination, it would appear that EELS offers so much more information than the x-ray signal that it would inevitably be the analytical signal of choice, but this is not the case in practice. As Egerton notes, "EELS is a fairly demanding technique, requiring for its full exploitation a knowledge of atomic and solid-state physics, electron-optics, and electronics." Egerton, who is recognized as one of the world's leading researchers in the theory and application of EELS in the electron microscope, succeeds admirably in his goal of gathering in one book a comprehensive collection of information on EELS, including detailed descriptions of instrumentation, electron optics and electron scattering theory. Such an approach is needed if EELS is to move beyond the small club of current practitioners to wider acceptance in the materials science and biological communities.

While very few members of this second tier of EELS users are ever likely to fabricate an energy-loss spectrometer from scratch, preferring rather to employ commercially available spectrometers, Egerton's detailed account of the physical basis of the design of the instrumentation will prove valuable to those who wish to know the relative strengths and weaknesses of the various types of spectrometers. With an emphasis ever on the practical, the book provides extensive details to aid the microscopist in recognizing and correcting various instrument-induced artifacts in the spectrum.

The particular strength of the book lies in its thorough and readily understandable description of electron scattering. Building upon this physical description, Egerton carefully constructs the detailed basis for quantitative analysis, including the mathematical procedures used to separate characteristic edge information from the high and rapidly varying spectral background. Appendices provide FORTRAN codes for several of the critical mathematical operations, including Fourier-log spectral deconvolution, partial cross sections based on the hydrogenic approximation for K-shell and L-shell ionization, and Kramers–Kronig transformations.

The final section of the text reviews a wide variety of practical applications, including measurement of specimen thickness, phase identification, measurement of alloy composition, detection of hydrogen and helium, EELS imaging, core-loss elemental microanalysis, measurement of radiation damage, and structural information from fine structure in the EELS spectrum.

This book will prove invaluable to a wide range of users of analytical electron microscopy, particularly in the materials science, technology and biological science communities, where EELS is usually considered an answer in search of a question. With its emphasis on practical matters in obtaining high-quality EELS spectra in the laboratory and its thorough descriptions of the underlying theory and quantitative chemical analysis, the book provides a comprehensive view of this promising technique.

DALE E. NEWBURY
National Bureau of Standards
Gaithersburg, Maryland

Thermodynamics of Point Defects and Their Relation with Bulk Properties

P. A. Varotsos and K. D. Alexopoulos
North Holland, New York, 1986. 472 pp. $115.50 hc
ISBN 0-444-86944-1

The search for correlations among physical properties of solid materials has a long tradition. Both scientists and engineers have tried various ways of summarizing existing knowledge about such properties. Sometimes the goal is to relate a variety of properties through an underlying physical model. Often the goal is to provide an empirical framework within which one can judge the justness of an existing or new measurement of a property or from which one can obtain an unknown value. Much modern technology depends on materials, increasingly used under extreme conditions, and the appearance of well-founded methods is welcome.

P. A. Varotsos and K. D. Alexopoulos detail in this book their search for a unifying framework to correlate the many measurements that have been

made of point defect properties in metals, noble gas solids and ionic crystals.

The authors devote the first third of the book to a painstaking discussion of the thermodynamics of point defects in solids. The view is refreshingly broad, looking beyond usually quoted relations, for example, to draw useful distinctions between isobaric and isochoric properties. Some care in discussion is appropriate because one must choose suitable reference states and paths. These choices are not obvious because states are sometimes arbitrarily defined and apply to a hypothetical perfect crystal. The situation is reminiscent of problems in nonlinear elasticity or in solids under finite strain, a situation that took decades to clarify. The treatment is pedagogic, with numerous interspersed sections on statistical models that help make the thermodynamic discussion concrete.

Most of the book is devoted to a comprehensive analysis of data from the literature on vacancy and Schottky defect properties, including impurity and self-diffusion. There are over 700 references. This analysis is correlated using the authors' model, which represents the defect (partial) Gibbs energy g as $cB\Omega$, where c is a proportionality constant, B the isothermal bulk modulus and Ω the mean volume per atom of the host material. The capacity of this model to correlate point defect properties with the bulk elastic properties of the respective host solid is impressive. In part this is another demonstration of the remarkable efficacy of quasiharmonic methods, which employ a succession of harmonic relations at different finite changes of volume.

A concluding chapter examines possible underlying justifications of the $cB\Omega$ model by identifying different expressions for the proportionality constant c. One looks forward to further refinements, such as a realistic incorporation of anharmonic effects, perhaps analogous to the treatment for perfect crystals in D. C. Wallace's *Thermodynamics of Crystals* (Wiley, New York, 1972). And one expects that if this approach is to be extended to nonequilibrium defects, such as dislocations, or to deformed materials, a more sophisticated use of shear elastic constants will be required. Even point defects store much of their energy in shear modes of the host material.

RALPH O. SIMMONS
University of Illinois, Urbana–Champaign