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**CALCULATED ELECTRONIC
PROPERTIES OF ORDERED
ALLOYS: A HANDBOOK**

The Elements and
Their 3d/3d and 4d/4d Alloys

V. L. Moruzzi
C. B. Sommers

World Scientific

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he numerical data of the self-consistent charge densities for the calculations presented in this handbook for both the elements and the elements within the compounds will be available via e-mail at an extra cost. Those scientists wanting to procure them for further research may do so by contacting J. B. Sommers at the following e-mail address:

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In principle a computer can only perform those operations for which it is programmed.
One day the best of the scientists programmed it to assume the role of a God.
As a consequence of which they could no longer programme the machine.
So much for principles.

cbs

To Joan

A Michelle, Rémi et Cléopâtre

PREFACE

Over the past several decades, sufficient progress has been made in the development of techniques for solving the electronic structure problem for solids to permit the accurate determination of certain ground-state properties. Energy bands, densities-of-states, equilibrium lattice constants, total energies, and bulk moduli can now be routinely calculated for a wide range of condensed systems, whether they exist in nature or not.

Most modern electronic structure calculations use the Kohn-Sham one-electron equations [1] for the ground state of electronic systems. These equations introduce the local-density approximation into the more general equations of density functional theory [2] and contain, in addition to the Coulomb potential of all charges in the system, an exchange-correlation potential which is a function of the local electron density. This function has been evaluated for a homogeneous electron gas by Hedin and Lundqvist for unpolarized electron densities, [3] and by von Barth and Hedin for polarized electron densities [4]. The calculations presented in this book are the self-consistent solutions to these one-electron equations. The evaluated total energy is the sum of the kinetic and potential energies of all electrons and nuclei in the system as a function of nuclear coordinates (which are specified by the volume or the lattice parameter for the bulk cubic systems considered here).

In 1978, Moruzzi, Janak and Williams [5] published results of a systematic study of the properties of metallic elements based on self-consistent electronic-structure calculations. This work contained the first clear recognition of the importance of total energies, and derived the properties of the metallic elements from an analysis of calculated binding (total energy versus volume) curves. The aim of this work was to provide a consistent set of calculations all based on the same set of equations and solution procedures with the atomic number, Z , as the only input parameter. The present work represents a comprehensive extension of the earlier Moruzzi-Janak-Williams work, and is similar in spirit. The basic differences are: (1) the present work uses the fast and efficient augmented-spherical-wave (ASW) method developed by Williams, Kübler and Gelatt [6] while the earlier work utilized the slower and more cumbersome Korringa-Kohn-Rostoker (KKR) method; and (2) the present work treats the elements in both bcc and fcc structures and considers ordered transition-metal alloys, while the earlier work only studied the bonding properties of each element in one of these cubic structures.

The ASW calculations employed in this study use the atomic-sphere approximation (ASA) and consider solids to consist of space-filling overlapping Wigner-Seitz spheres such that $V = (4\pi/3) \sum_{r_{ws_i}} [3]$, where V is the unit-cell volume and the sum is over all spheres in the unit cell. The sphere radii are specified by r_{ws_i} . The first operational problem in calculating the electronic structures of ordered alloys involves the detailed division of the unit cell into the individual sphere volumes. That is, the non-spherical unit cell must be partitioned and allocated to spherical constituent atoms. This is equivalent to forcing round pegs in a square hole and, of necessity, involves overlapping atomic spheres. For the bcc and fcc elements, with just one atom per unit cell the allocation is unambiguous. However, the individual volumes, V_1 and V_2 , associated with the constituent spheres in a two-constituent alloy, must be allocated in a logically consistent manner. One strategy for partitioning the unit cell for a two-constituent ordered alloy is to start with Vegard's law and the equilibrium volume, $V_0 = V_1 + V_2$, where $V_1 = (4\pi/3)r_1^3$ and $V_2 = (4\pi/3)r_2^3$, with r_1 and r_2 determined from the location of the minimum in calculated binding curves of the elemental constituents. If B_1 and B_2 are the corresponding elemental bulk moduli, the requirement that $dV_1/dV_0 = V_1 B_2 / (V_1 B_2 + V_2 B_1)$ and $dV_2/dV_0 = V_2 B_1 / (V_1 B_2 + V_2 B_1)$ insures that constituent volume changes, dV_1 and dV_2 , are proportional to the sphere volumes and inversely proportional to the bulk moduli of the constituent elements. Therefore, a change, dV_0 , (volume from Vegard's law), of the two-constituent alloy can be accomplished by volume changes which depend only upon the calculated values, V_1 , V_2 , B_1 and B_2 of the elemental constituents.

Although this is a well-defined and physically reasonable strategy, it becomes suspect for alloys made up of constituents which are not near neighbors in the periodic table and which are characterized by large differences in sphere radii and elemental bulk moduli. In this book, we eliminate the inherent uncertainties in this B/V algorithm by searching for the energy minimum in r_1 , r_2 space. That is, we systematically change r_1 and r_2 and construct the total energy surface. Analysis of the energy surface then yields the equilibrium properties of the alloy in the same way that analysis of a binding curve yields the equilibrium properties of an element. This approach assumes the existence of a minimum energy principle. Equilibrium properties obtained by the aforementioned B/V algorithm and this latter approach are almost identical for alloys consisting of near-neighbor transition-metal constituents, but show signs of progressively larger differences as $\Delta Z = Z_2 - Z_1$ increases.

Calculations using the B/V algorithm require a one-parameter survey along an axis defined by the volume-dependent ratio r_1/r_2 , while energy sur-

face calculations involve a two-parameter systematic survey of r_1 and r_2 space. Thus, the latter requires a significantly larger number of completely self-consistent calculations than the former, but yields more detailed information. In addition, we believe the B/V algorithm is only approximately valid and only for binary alloys with low values of ΔZ . The B/V algorithm and the r_1/r_2 minimization are approximations which are expected to be valid for systems with relatively small deviations from Vegard's law.

A number of different methods are available for the study of the electronic structure of solids. The different methods generally involve different degrees of accuracy and efficiency. Although it is often implied that increased efficiency can only be achieved at the expense of accuracy, the two are not necessarily mutually exclusive. The ASW method used in this work is a linear method which is simple to use and both fast and accurate. It is unencumbered by non-intuitive adjustable parameters and requires only the atomic numbers of the constituent atoms. Because of its efficiency, calculations can be readily done on very dense \mathbf{k} -space meshes, thereby minimizing the \mathbf{k} -space convergence problem which often plagues less efficient full-potential methods. In addition, the simplicity of the computer codes and the large cancellations inherent in the spherical methods employed, eliminate numerical uncertainties and noise which may occur in the more elaborate and complex numerical procedures required for full-potential methods.

The ASW method and the numerical procedures associated with the computer codes used in this study have undergone extensive evaluation and testing. The calculations are all done on uniform \mathbf{k} -space meshes containing approximately 10,000 to 15,000 \mathbf{k} -points in the full Brillouin zone. Extensive calculations on given systems using appreciably different starting potentials and calculations involving a doubling and quadrupling of the unit cell give almost identical results ($\Delta E_0 \lesssim 0.1$ mRy/atom), thereby ensuring internal consistency and a high degree of relative accuracy.

It has already been shown that the earlier Moruzzi-Janak-Williams KKR calculations [5] for nonmagnetic cubic elements yielded cohesive energies, equilibrium volumes, and bulk moduli in remarkable agreement with experiment. Our new ASW results generally agree with the earlier results. In cases where there are small differences, the new ASW calculations are usually in even better agreement with experiment. The credibility of our ordered alloy calculations is based on our success for the elements.

Although this book is primarily concerned with binary transition-metal ordered alloys, we include the results of calculations for elements constrained to metallic bcc and fcc structures. We note that, in order to be tractable, all