

INTRODUCTION

It has been suggested that analysis of wave functions will be an important aspect of the study of electronic states in the next decade. In this paper are presented results of the following calculations, which illustrate several aspects of such analysis, for crystalline solids: the cohesive energy, pressure, and enthalpy of cesium metal as a function of unit cell volume, to show computationally the isomorphic phase transition of cesium (Cs); magnetization and cohesive energy of vanadium (V) as a function of lattice parameter, to exhibit the nature of the formal transition from non-magnetic to magnetic behavior as the lattice is expanded; estimation of momentum matrix elements and interpretation of the spectral lineshapes of soft x-ray emission from the valence bands of titanium carbide (TiC) and niobium carbide (NbC). All of the energy-band calculations reported are self-consistent and are based on the $X\alpha$ exchange approximation [1], with no explicit inclusion of correlation effects.

The calculations have been done by the APW (Augmented Plane Wave) method of Slater [2], within the muffin-tin approximation [2] for the one-electron effective potential and for handling the charge density during the generation of that potential in the self-consistency iterations. (This approximation should be excellent

for fcc Cs, with its close-packed structure and metallic valence charge distribution, and adequate for bcc Cs and V, and for TiC and NbC.) Brillouin zone sampling has been done at the equivalent of 256 equally spaced points in the full zone for the fcc Bravais lattices (128 for the bcc structures); for the V calculation, additional interpolation of the bands has been performed to obtain more accurate weighting factors for the contributions of the computed $\underline{k}$ -points in the charge-density calculation [3] and to estimate electronic densities of states. A grid of the equivalent of only 32 equally-spaced points is used for states well below the valence bands when only a few percent of their charge is outside the APW spheres [4]. Wave functions and energies of true core levels are computed in atomic fashion, but in the crystal potential. The cohesive energy is calculated as the difference between the $X\alpha$ total energy per unit cell of the crystal [5] and the $X\alpha$ total energy of the isolated atom (-15,107.7719 Ry for Cs, -1885.867 Ry for the 6D multiplet of V in the $3d^4 4s^1$ configuration, and -1885.743 Ry for the 4F multiplet of the V $3d^3 4s^2$ configuration), with the same value of α used for both the crystal and the atomic calculations. (Numerical techniques used for the crystal and the atom are made as nearly identical as possible, to allow maximum cancellation of numerical errors.)

The values of α used throughout the unit cell for Cs and V and in the APW spheres for Ti and C in TiC are those for which the statistical ($X\alpha$) total energy for the isolated atom equals the expectation value of the Hartree-Fock total energy operator with