

transition could be accounted for by having the gap between the valence band and conduction band decrease with pressure, until at some critical pressure the Δ_2 tail would have a lower energy than the Γ_{15} states and the system would then be metallic. Thus, this latter model would involve only a simple band-gap closing and not any 4f delocalization.

To help furnish calculational information that possibly might distinguish between the applicability of the above two models to, in turn, each of the compounds, we have performed numerous exploratory band structure calculations for SmS, SmSe, and SmTe. The results of our calculations indicate that the model based on Figure 1(a) applies to SmS, but the model based on Figure 1(b) applies to SmSe and SmTe. In the remainder of this report, we will outline the calculations we have done, and in so doing try to convey the above indications and the limitations that exist on such indications. However, since qualitative similarities exist in our results for SmSe and SmTe, in an attempt at brevity no further mention will be made in this report concerning SmSe.

II. APPROXIMATIONS AND CALCULATIONAL DETAILS

The major approximations, which would affect any qualitative conclusions drawn from our calculations, are all involved with the procedures used in obtaining the one-electron, band-theoretic, potentials. Although the potential procedures we have adopted are somewhat standard, since they have been applied by different investigators to numerous solids with varying degrees of success, they are by no means exact. Thus, the band structures we have calculated via these potentials can honestly be considered only as first-order approximations to the actual one-particle states possessed by the respective compounds. However, it is still our feeling that such calculated band structures have at least as great, if not greater, validity than those inferred via the practice of merely postulating band structures from indirect experimental information without the use of any calculational underpinnings.

The potentials used in this investigation were obtained from a heuristic prescription^{12,13} involving free-atom charge densities. With this prescription the potential, $V(\vec{r})$, about a given lattice site is approximated by a spherically symmetric, muffin-tin, potential $V(r) = V_C(r) + V_{ex}(r)$. Both the Coulomb part, $V_C(r)$, and the exchange part, $V_{ex}(r)$, are obtained from lattice superpositions involving free-atom charge densities; thus, the resulting $V(r)$ depends directly upon the lattice parameter being used in the calculation. That is, at a given lattice site, $V_C(r)$ is the spherically averaged sum of two components. The first component is the Coulomb potential due to the free atom at the given site, while the second component is the sum of the contributions due to tails of free-atom Coulomb potentials centered on other lattice sites in the vicinity, which overlap onto the site under consideration. A Slater-type

free-electron approximation is used for the exchange part: $V_{ex}(r) = -6\alpha[3\rho(r)/8\pi]^{1/3}$. $\rho(r)$ is the spherically symmetric lattice superposition of atomic charge densities, and obtained in a manner completely analogous to that used for $V_C(r)$. The parameter α in $V_{ex}(r)$ controls the exchange contribution to the potential, with $\alpha = 1$ being full Slater exchange. In this investigation α has been varied in order to obtain calculated band gaps, at normal pressure, in agreement with experimental band gaps. Such variation of α was done in the spirit of attempting to obtain an experimentally realistic model Hamiltonian for each of the samarium compounds.

To explicitly construct the potentials for this work, free-atom Hartree-Fock wave functions tabulated by Fischer⁹ were used. Touching muffin-tin sphere radii were then determined by requiring neighboring site potentials to be equal at the point of sphere contact. The constant value of the potential between the spheres, V_0 , was equated to the potential value at sphere contact. Band structures were calculated from the resulting potentials by use of the non-relativistic form of the Korringa-Kohn-Rostoker method as formulated by Treusch and Sandrock.¹⁴ Although for fully quantitative calculations on rare-earth systems relativistic effects cannot be neglected, due to the inherently qualitative nature of this undertaking and a desire to minimize calculational details we have, at present, limited our work by omitting relativistic effects. However, the major relativistic effect expected in the calculations would be shifts in states containing large s-components, e.g., the Γ_1 's of Figure 1. But such shifts should not be large enough to qualitatively change the band structures of Figure 1, especially since the Δ_1 bands, originating at the Γ_1 's, rise and the Δ_2 bands fall as $|\vec{k}|$ increases.

III. DISCUSSION OF RESULTS

Using the procedures outlined in the preceding section, we performed a series of band structure calculations for SmTe at its normal pressure lattice parameter (cube edge = 12.46 a.u.). During this series of calculations, only the exchange multiplier, α , was varied in order to obtain a calculated band gap in agreement with the experimental absorption edge of 0.63 eV. The calculated band gaps resulting in this series of calculations were 1.59 eV for $\alpha = 1.00$, 0.89 eV for $\alpha = 0.85$, 0.28 eV for $\alpha = 0.80$, and 0.63 eV for $\alpha = 0.844$. For $\alpha = 0.844$, the resulting calculated SmTe band structure along the major symmetry directions of the Brillouin zone is displayed in Figure 2. Notice that Figure 2 verifies our previous statement that the valence band to conduction band gap is determined by the band structure for the Γ to X direction.

After the above series of calculations fixed the value of the exchange multiplier at $\alpha = 0.844$, we performed another series of band structure calculations for SmTe involving variation of the lattice parameter but using the same α value. This series used reduced values of the lattice parameter corresponding to experimentally obtainable pressures. Part of one of the band structures resulting