the calculations performed for some europium chalcogenides.[4] In an attempt to make further correlations possible, we are presently engaged in performing a systematic series of exploratory band structure calculations for most of the rare-earth monopnictides and monochalcogenides. Some qualitative features which arise in our work are illustrated in Figure 1, which contains three of our calculated band structures for nonmagnetic states of the compounds. The group theoretical notation used in Figure 1 is the standard Boukaert-Smoluchowski-Wigner notation[5]; e.g., Γ is the center of the Brillouin zone and X is the center of the square face of the surface of the zone.

Certain common features are seen to exist in the three band structures of Figure 1. First, each has the valence bands, originating at Γ_{15}, which are primarily composed of the p-states of the respective anion. Then there are the conduction bands primarily composed of the rare-earth 6s-states, originating at Γ_1, and the rare-earth 5d-states, originating at $\Gamma_{25'}$ and Γ_{12}. Of course, for a $\vec{k}$ away from Γ the corresponding energy states can reflect more hybridization. Also present in the band structures of Figure 1 are the rare-earth f-states, or "f-bands", which have little dispersion, reflecting the well established fact that the rare-earth 4f electrons are well localized. The f-states in Figure 1(c) are off the plot at lower energies. One sees a gap exists between the valence and conduction bands in Figures 1(a) and 1(b), while the valence and conduction bands overlap in Figure 1(c). It does turn out, when one investigates the band structures for other $\vec{k}$ directions, that whether the valence and conduction bands overlap is determined by whether the tail of the $\Delta_{2'}$ band has a lower energy than the Γ_{15} states. Band structures as illustrated in Figure 1 have actually been qualitatively verified by photoemission experiments reported by Eastman and Kuznietz[6]; e.g., their work shows GdS has a band structure of the type of Figure 1(b), while the band structure of EuS is of the type of Figure 1(a) except the 4f-states are slightly merged with the upper part of the valence band.

The major difficulties in performing reliable band structure calculations for the class of rare-earth compounds under discussion, as for the rare-earth metals, are connected with the f-states illustrated in Figure 1. First, it has been found[4,7,8] very difficult to energetically locate the f-states properly in the overall band structure due to their very sensitive dependence upon the exchange contribution to the one-electron, band-theoretic, potentials. Fortunately, details of the valence and conduction band structures are not so dependent upon the exchange contribution, so calculations usually have more reliability for these states. Thus it is usually necessary to perform some ad hoc adjustment in the exchange potential for the resulting calculations to properly locate the f-states if agreement with available experimental information is desired. But one must remember that it sometimes is also just as difficult to experimentally identify and locate the compound's 4f-states due to problems associated with impurities, stoichiometry, multiple

scattering, etc., so the calculational inadequacies are not unique. Whatever the experimental case, since the calculational procedures are at present not straightforward, it is necessary to caution that resulting band structures should be considered exploratory. However, at the same time, we feel that such first-attempt exploratory calculations are of value, since they do enable the interaction process between calculational and experimental results to begin, with such interaction hopefully leading to the eventual elucidation of a given compound's actual electronic band structure.

Another difficulty one might encounter with the f-states of Figure 1 is more of a conceptual character, and is concerned with the one-electron nature of the basic band-structural model. At first thought one might envision occupying the available states of, say, Figure 1(b) according to Fermi statistics. Even though this is done for the valence and conduction bands, it is not, and must not be, done for the f-states. Rather, a "correlational-configurational" argument is invoked, meaning only a given number of the f-states are filled, resulting in the expected f^n ($n \leq 14$) configuration. This should not be too surprising, since the same state of affairs, having empty states at a lower energy than filled states, occurs in Hartree-Fock calculations[9] for free rare-earth atoms. If such were not the case, self-consistent calculations would eventually produce a different energetic ordering of the one-particle states.

Turning to the three compounds which are the explicit purpose of this report, SmS, SmSe, and SmTe are all semiconductors under normal conditions, having band gaps (absorption edges) of, respectively, about 0.2 eV, 0.46 eV, and 0.63 eV.[10] Also, these three compounds do not order magnetically, presumably due to having $4f^6$ Sm-site configurations with ground-state multiplet $^7F_0$. Perhaps one of the most intriguing, and also quite recent, observations concerning the properties of these compounds is the demonstration[10] that each undergoes a pressure-induced semiconductor-to-metal transition. The pressure required for the transition increases from 6.5 kbar for SmS, to the vicinity of 40 kbar for SmSe and the vicinity of 50 kbar for SmTe. At the same time, the transition occurs discontinuously for SmS, whereas it has all appearances of taking place continuously over a broad pressure range in SmSe and SmTe.

To explain the transition in all three of the samarium compounds, Jayaraman et al.[10] postulated that each had a normal pressure band structure qualitatively like Figure 1(a). Then their explanation for the transitions was that application of pressure causes the gap between the 4f-states and the conduction band (the $\Delta_{2'}$ tail) to decrease, until at some critical pressure the conduction band merges with the 4f-states. At such merging, one 4f electron per Sm site would become delocalized,[11] and the compounds go metallic. However, without any other direct band-structural information being available, it was our feeling that one should also consider the possibility of the compounds having a normal pressure band structure qualitatively like Figure 1(b). With such a band structure, the pressure-induced

4

5