structure with the exception of Eu2S3 which does not exist (2), (6). The elements from La to Sm also form a series of compounds R_3S_4 with the same Th3P4 type cubic structure.

The R₃S4 and R₂S₃ structures are the same except R₂S₃ has 1 1/3 rare earth metal vacancies per unit cell compared to R₃S4, therefore no change in lattice parameter is found between the two types. This means there is a range of homogeniety R₂S₃ to R₃S4 with no change in diffraction pattern so that X ray diffraction analysis can not be used to differentiate between the two types of compounds. There is, however, a considerable difference in density between the two structures. This effect has been observed for the lighter rare earths from La to Sm (2). Interestingly Eu₃S4 is known but Eu₂S₃ does not exist (2). For the heavier rare earths of Gd, Tb and Dy the range of homogeniety is not observed and the R₃S4 compounds do not exist for these rare earths (2), (6).

Guittard has shown that a range of NaCl type cubic homogeniety is found in the metal rich sulfides from RS to R4S3 for the heavy lanthanides from Tb to Tm. For Lu the NaCl type homogeniety is found from LuS to Lu3S4 but does not include Lu2S3 (18). Cutler has shown that the R3S4 compounds are metallic conductors while the R2S3 compounds are semiconductors or insulators. The rare earth furnishes electrons to the conduction band when it is present at a ratio higher than is necessary to satisfy the valence

4.4

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