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# Calculated Electron Density Distributions in ScS and $Sc_3S_4$

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Previously calculated wavefunctions were used to calculate electron densities as functions of position within spheres surrounding Sc and S in scandium monosulfide and a hypothetical structure for the known scandium-deficient compound. The electron densities in the valence and conduction energy intervals are compared and interpreted in terms of the directionality of the electronic interactions in the compounds. © 1986 Academic Press, Inc.

## Introduction

Scandium monosulfide exhibits a wide range of homogeneity with in excess of 20% of the metal sites vacant on the sulfur-rich side (*1*, *2*). Until recently very little has been known about the electronic structure changes accompanying such massive metal deficiency. In a recent paper the results of self-consistent, nonrelativistic KKR calculations for ScS, with the NaCl-type structure, and $Sc_3S_4$ with a hypothetical defect structure (vacancy at the cell-center position of the NaCl-type structure) were reported (*3*). The results presented in (*3*) included electronic band structures, densities of states, and angular-resolved densities of states for the stoichiometric and hypothetical scandium-deficient compounds. The calculations have been continued, using the wavefunctions obtained in (*3*), in order to calculate distributions of electron densities in ScS and $Sc_3S_4$. It is our view that the deviations from spherical symmetry of the electron-density distributions in the intervals of energy associated with the valence and conduction electrons are indicators of the nature of directional metal–nonmetal and metal–metal interactions, respectively. The purpose here is to report the electron density distributions obtained for ScS and $Sc_3S_4$ with the view of contributing to knowledge about the nature of directional bonding interactions and their relationship to defect formation.

## Results

The densities of states (*3*) of ScS and $Sc_3S_4$ reflect the fact that the lower energy

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filled bands (between 0 and 0.36 ry, where the zero is taken to be the bottom of the lowest filled band) and the higher filled bands (0.36 ry to $E_F$) are nearly separated into a valence or $p$-band (principally, but not entirely sulfur $p$-like in character (*3*)) and a conduction or $d$-band. Accordingly, the electron densities reported here were calculated separately for states in the conduction band (0.36 ry $< E < E_F$) and in the valence band ($0 < E <$ 0.36 ry). The calculated electron densities ($\Psi\Psi^*$) were obtained as graphs on plane surfaces within the muffin–tin spheres. The planes chosen are those defined by the three points of tangency of the scandium muffin–tin sphere with the three nearest neighbor sulfur muffin–tin spheres forming an equilateral-triangular face of the coordination octahedron in stoichiometric ScS. The results are displayed as contour plots within the circles formed by the intersections of the planes with the muffin–tin spheres for Sc ("Sc circles") and for S ("S circles").

Figure 1 shows the contour plots for the valence electron density in NaCl-type ScS. The plot shows the directional nature of the interaction within the Sc sphere and the nondirectional nature of the interaction within the S sphere. The maximum electron density on the Sc sphere boundary (0.186 electrons/(a.u.)$^3$) occurs at the Sc sphere–S sphere boundaries, i.e., at the intersections of the Sc–S interatomic lines and the defined plane, and is indicative of the direct $\sigma$ bonding interaction which was shown in (*3*) to be principally a Sc $e_g$–S $p$-type interaction.

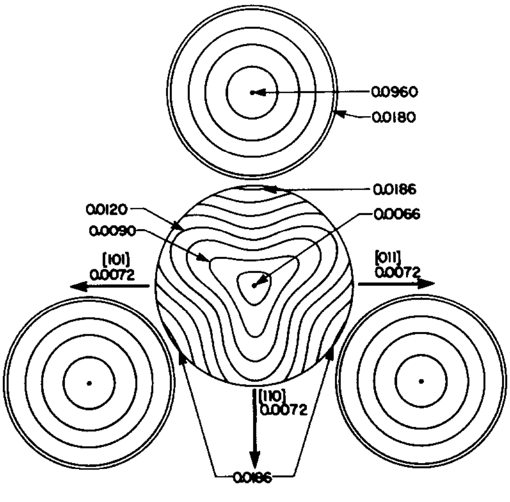

FIG. 1. Valence electron density in NaCl-type ScS ina plane perpendicular to the [111] direction. The plot plane slices the Sc muffin–tin sphere (large circle in center) and three S muffin–tin spheres (small circles).

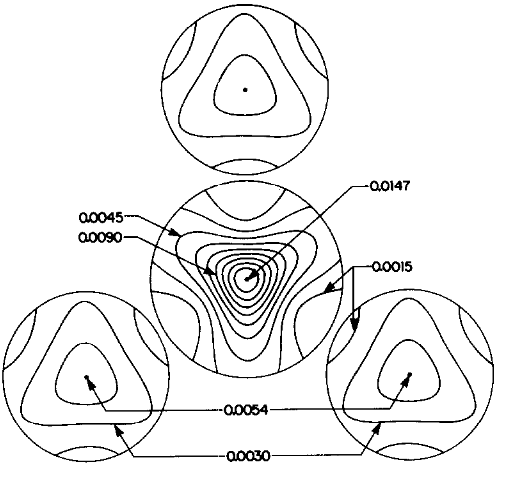

FIG. 2. Conduction electron density in NaCl-type ScS in a plane perpendicular to the [111] direction. The plot plane slices the Sc muffin–tin sphere (large circle in center) and three S muffin–tin spheres (small circles).

Figure 2 shows the contour plots for the conduction electron density in NaCl-type ScS. There are several noteworthy features of this distribution. The first is that the maximum (0.0147 electrons/(a.u.)$^3$) which occurs in the center of the Sc circle, i.e., the directions of maximum conduction electron density (principally Sc $t_{2g}$-type (*3*)) is through the centers of the triangular faces of the sulfur coordination octahedron. The second is that the electron density decreases more rapidly in the direction of the lines connecting Sc and S than in the direction of the lines connecting Sc and Sc, indicating that the conduction electron density

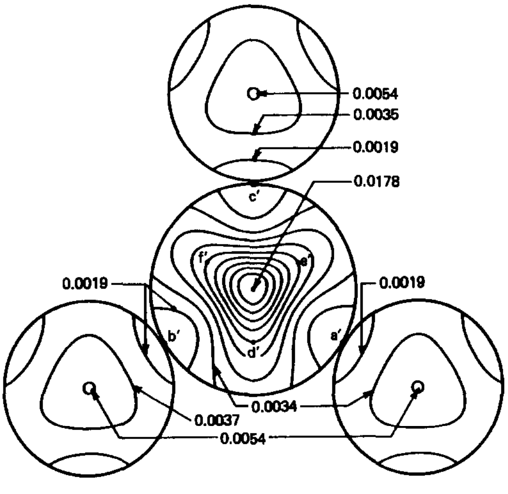

FIG. 3. Conduction electron density in NaCl-type ZrS in a plane perpendicular to the [111] direction. The points a', b', and c' denote the location at which the plot plane intersects the Zr–S bond axes. The points d', e', and f' denote the location at which the plot plane intersects the Zr–Zr bond axes.

in the Sc sphere has a shape which tends to avoid the valence electron density maximum in the Sc–S direction. Third, there is a small conduction band density in the sulfur spheres which has a maximum in the center of the sulfur circle (0.0054 electrons/(a.u.)$^3$), and which represents a small asphericity superimposed on the essentially spherical valence electron density in the sulfur sphere. Figure 3 shows a comparable electron density plot for ZrS in the NaCl-type structure obtained using the wavefunctions of Nguyen *et al.* (*4*).

Figure 4 shows the valence band electron density plots for $Sc_3S_4$. In interpreting this figure it is important to note that removal of a Sc atom from the position $\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$ of rock salt-type ScS, in order to create the model for Sc-deficient $Sc_3S_4$, creates a structure with two symmetrically inequivalent S atoms: square-planar sulfur (of which there are three per unit cell) and octahedral sulfur (of which there is one). In Fig. 4 the lower two circles are in the square-planar, i.e., 4-coordinate, sulfur atom spheres and the uppermost circle is in the sphere of an octahedral sulfur. Comparison of the electron-density distributions in this figure with those in Fig. 1 indicates a redistribution of valence electron density upon creation of a vacancy, namely an increase in the Sc–S interaction for the 4-coordinate sulfur and a decrease in the Sc–S interaction for the 6-coordinate sulfur. If the electron density at the point of contact (i.e., at the intersection of the Sc–S interatomic line with the plane of the figure) is taken as a measure of the extent of interaction, then the increase in the Sc–S bonding in the case of square-planar sulfur is the same as the decrease in the Sc–S bonding in the case of octahedral sulfur (0.0138 = 0.0186 − 0.0048 electrons/(a.u.)$^3$ in the first case and 0.0234 = 0.0186 + 0.0048 electrons/(a.u.)$^3$ in the second). Since there are six S–Sc bonds per octahedral sulfur and four per square-planar sulfur and three square-planar sulfurs per octahedral sulfur, the overall change in bond order is (taking the change per bond to be $+\Delta$ (square planar) or $-\Delta$ (octahedral)) is: $(3 \times 4 - 6)\,\Delta = 6\Delta$. The corresponding net loss of Sc–S bonds is 6. In other words,

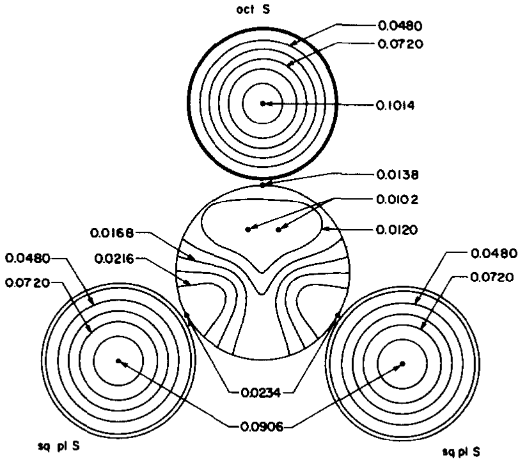

FIG. 4. Valence electron density in $Sc_3S_4$ in a plane perpendicular to the [111] direction. The plot plane slices the Sc muffin-tin sphere (large circle in center) and three S muffin-tin spheres.

there is, in response to the removal of one scandium atom and the resultant loss of six Sc–S bonds per unit cell, a net redistribution of valence electron density which increases the scandium-to-square-planar sulfur bonding interaction and decreases the scandium-to-octahedral sulfur bonding interaction. There is a net increase ($6\Delta$) in the Sc–S bonding interaction on a per bond basis which acts in the direction of compensating for the loss in bonding energy, thereby providing a stabilizing effect for the nonstoichiometry of the solid.

Figure 5 shows the conduction band electron density for $Sc_3S_4$. This figure is best understood in relationship to the proceeding discussion. For ScS it was found that the conduction band electron density distribution could be understood in terms of a valence electron–conduction electron repulsion. Furthermore, a redistribution (relative to ScS) of valence electron density which enhanced the Sc–S interaction in the case of square-planar sulfur relative to the case of octahedral sulfur was found for $Sc_3S_4$. Combining these observations and their interpretations, it would be expected that the conduction electron density in $Sc_3S_4$ would show a relative increase in repulsion by the Sc–square-planar sulfur bonding electron density in comparison with the repulsion by the Sc–octahedral sulfur bonding electron density. The observed skewing of the conduction electron density in Fig. 5 relative to Fig. 2 exhibits this increase.

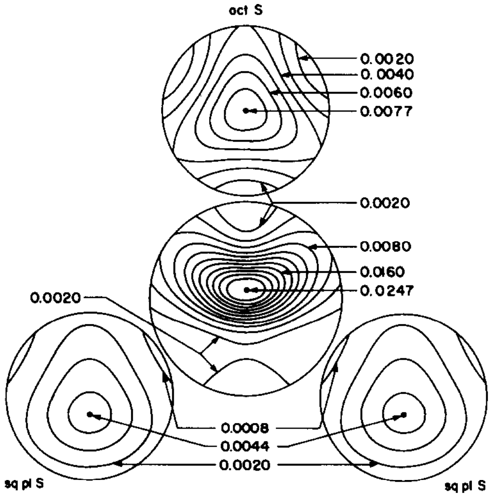

FIG. 5. Conduction electron density in $Sc_3S_4$ in a plane perpendicular to the [111] direction. The plot plane slices the Sc muffin–tin sphere (large circle in center) and three S muffin–tin spheres.

## Discussion

In view of the relatively large bond energies for binary transition-metal compounds, of which ScS is fairly typical (atomization energy = 255.7 kJ/mole (*5*)), the existence of wide ranges of homogeneity (i.e., 10–20% vacancies) requires effects which compensate for the loss of bond energy. It can be assumed with confidence, given the wealth of information pointing in this direction, that short-range ordering effects will be found to be important in massively defective solids. However, the results reported here show that even in the absence of local atomic relaxation there can be electronic rearrangement which enhances the stabilities of defective solids and contributes to the stability of grossly nonstoichiometric materials. The model discussed here, namely that covalent bonding increases in low coordinate atoms result in increased stability can be contrasted with the very elementary model that was originally proposed for $Sc_{1-x}S$, namely $Sc^{3+}_{(1+x)}S^{2-}e^{-}_{(1+3x)}$ (*6*). The calculation suggests that the supposedly free electron is not free, but is in Sc conduction band states. In other words, the charge appropriate to Sc is less than +3. Furthermore, the calculation suggests that the Sc–S interaction is more fruitfully considered to be of a covalent rather than an ionic nature. For example, the electron redistribution upon creation of the vacancy was found to be only $-0.068$ electrons within the Sc muffin–

tin sphere (33). The model suggested by the calculation, namely increasing Sc–S bond strength and decreasing number of Sc–S $\sigma$ interactions with increasing $x$, provides a mechanism for reducing the energy of creating a vacancy at a Sc position.

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