Experimental and Theoretical Studies of ScS under Pressure

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The compressibilities of ScS and a series of $Sc_{1-x}S$ metal defect structures ($x > 0$) were studied using a diamond anvil cell and synchrotron radiation at pressures up to 73 GPa. The results show that the bulk modulus increases with x, in contrast to the usual view that a less dense material is more easily compressed. The results are in qualitative agreement with existing band structure calculations designed to probe the mechanism of the ready metal atom loss from ScS at high temperatures. They are also in agreement with new calculations, both of the tight-binding and the first-principles FLAPW type. Numerically the latter show an increase in the bulk modulus of 30% between ScS and $Sc_{0.875}S$ and are in exact numerical agreement with the experimental results.

Introduction

Solid ScS is a particularly interesting material in that although compositions on both sides of the 1:1 stoichiometry are known, heating the stoichiometric or metal-poor material leads to loss of scandium. As $ScS \rightarrow Sc_{1-x}S$, the average oxidation state of Sc increases from Sc(II) toward Sc(III).[1,2] From diffraction studies, the cell side of the structure shows a small smooth decrease as vacancies are generated.[1] The driving force for metal loss in general terms can be associated with the chemists' viewpoint that Sc(III) is "more stable" than Sc(II). Certainly the dihalides of scandium are not known. (See ref 3 for a useful discussion of this topic.) A quantitative explanation of this statement is, however, not available at present.

We recently presented an electronic model,[4,5] supported by both LMTO[5] and tight-binding,[4] calculations which is able to rationalize the experimental results quantitatively. Figure 1 shows in a simple way the two parts of the electronic process. First, loss of scandium increases the average oxidation state of the remaining metal atoms. The result is that the metal levels become more strongly bound and drop to lower energy. Second, since the gap between metal 3d and sulfur 2p has now decreased, the interaction between them increases. The result is stabilization of the occupied sulfur 2p band on metal loss, the dominant effect in the overall process.

The theoretical results thus show how the defect structure is stabilized with respect to the parent. The result has other implications. Whereas the bulk modulus of a solid invariably increases with its density, the model suggests that the converse may be true for the $Sc_{1-x}S$ compounds ($x > 0$) since the Sc−S linkages are stiffer in the Sc-deficient materials. This paper addresses experimental and theoretical aspects of this problem with the aim of providing further insights into this interesting series of compounds.
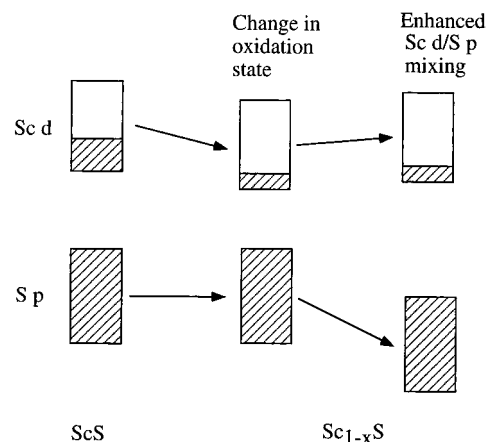

Figure 1. The two parts of the electronic process which leads to stabilization of Sc(III) and thus loss of metal from ScS.

The Structure of ScS

Different structures are found for $Sc_{1-x}S$ as a function of temperature[6] but, for small x, are all based on the rocksalt arrangement found for the ScS parent. (Sc_2S_3 has a different structure.) The high-temperature structure (>700 °C) for the $Sc_{1-x}S$ compounds ($x > 0$) is cubic with Sc vacancies arranged randomly on the metal sites ($Fm3m$). At intermediate temperatures (>300 °C) the structure ($R\bar{3}m$) contains Sc vacancies in metal sites but only in every other metal plane perpendicular to [111]. These two structures are shown in Figure 2. At temperatures lower than about 300 °C, the vacancies order within these planes in an incommensurate monoclinic structure (C2). In the intermediate defect structure all the S−Sc−S bond angle are close to 90 and 180° and the Sc−S distances very similar to (but a little smaller than) those in the ScS parent. The reorganization of the structure on metal atom loss is thus very small. All of the theoretical calculations mentioned in this paper used a large ordered cubic supercell. This is not therefore the lower symmetry (monoclinic) structure found at room temperature containing an incommensurate ordering of metal atom vacancies. However, the two are simply related.

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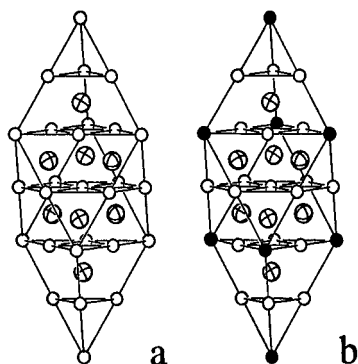
Figure 2. (a) The rocksalt structure of ScS. [111] is vertical. (b) The $R\bar{3}m$ structure of the defective material found at intermediate temperatures. The vacancies shown by solid circles appear in every other metal layer. Small circles = metal atoms; crossed circles = sulfur atoms.

Table 1. Experimentally Determined Bulk Moduli for $Sc_{1-x}S$

x in $Sc_{1-x}S$	bulk modulus (GPa)	press. deriv of bulk modulus	χ^2 of EOS fits
-0.013 ± 0.005	98 ± 12	5 ± 4	0.98
0.014 ± 0.005	108 ± 10	4 ± 1	7.47
0.108 ± 0.003	123 ± 13	3 ± 1	12.77
0.125 ± 0.006	136 ± 21	1 ± 1	2.73
0.136 ± 0.006	140 ± 21	1 ± 2	1.89
0.144 ± 0.007	140 ± 20	2 ± 3	1.06
0.162 ± 0.007	150 ± 18	-0.3 ± 1.8	11.32

Experimental Procedure

Samples of $Sc_{1-x}S$, kindly provided by Professor H. F. Franzen, were compressed at room temperature in a Mao–Bell[7] type diamond anvil cell. Type 1A diamonds with 250 μm culets were used. A gasket (of 127 μm thick Inconel) drilled with a 150 μm hole placed between the diamonds acted as the sample chamber. Samples were loaded in air with a few specks of gold for pressure measurement. No pressure medium was used. Pressure gradients were minimal, since the X-ray beam was focused to a 20 μm spot.

Energy-dispersive X-ray diffraction experiments were performed using synchrotron radiation on beam line X17C, at the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory. Each X-ray diffraction pattern was collected for 15–20 min with the detector at a 2θ angle of 12° or 15° from the incident beam. The energy (E) of each of the diffraction peaks in the spectra was estimated by fitting a Gaussian curve to the peak. The low-temperature monoclinic $C2$ structure is sufficiently close to cubic that the unit cell may be indexed using the 5–10 ScS diffraction lines observed for a $Fm3m$ lattice. The volume at each pressure was thus simply obtained. (When angular dispersion with higher resolution is used at ambient pressure in the diffraction experiment, the $C2$ structure may be identified via the splittings of some of the peaks.) Pressures were determined by using a standard equation of state for gold,[8] included as noted above with the sample. The composition of each $Sc_{1-x}S$ sample was determined using electron microprobe analysis.

Experimental Results

The $P–V$ data obtained to 30 GPa for each defect structure was fit to a third-order Birch–Murnaghan equation of state (EOS),[9] which led to an isothermal zero-pressure bulk modulus and a pressure derivative for the bulk modulus. The results are presented in Table 1 along with the χ^2 values for all the compositions. Plots of a selected set of data, those for $Sc_{1-0.014}S$, $Sc_{1-0.108}S$, and $Sc_{1-0.144}S$, are shown in Figure 3. Figure 4 shows fits to a third-order Birch–Murnaghan equation of state for these three $Sc_{1-x}S$ compositions. The unusually
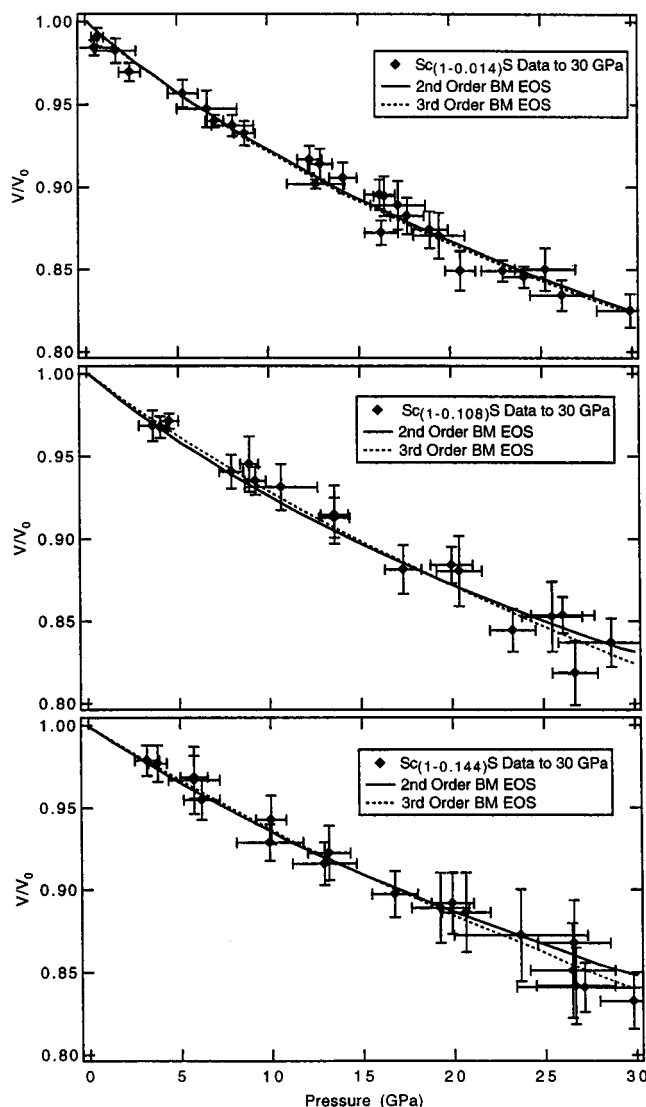
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Figure 3. Experimental pressure-volume data for three scandium sulfides, $Sc_{1-0.014}S$, $Sc_{1-0.108}S$ and $Sc_{1-0.144}S$ and second- and third-order fits to the Birch–Murnaghan (BM) equation of state (EOS).
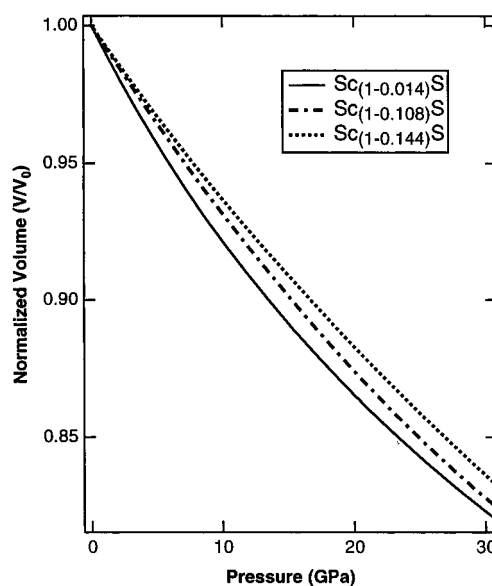

Figure 4. Third-order Birch–Murnaghan equations of state[9] for three $Sc_{1-x}S$ stoichiometries to show their different compressibilities.

low pressure derivatives of the bulk moduli of the more nonstoichiometric compositions appear not to be a statistical

artifact of the data. The negative $K_0{'}$ value obtained from the third-order equation is anomalous and possibly implies thermodynamic instability of that composition due to its high vacancy content. $P-V$ data obtained to 50 GPa require fourth-order Birch–Murnaghan equations of state to accommodate the larger compression and are consistent with those in Table 1. The most compressible composition, $Sc_{1+0.013}S$, was compressed to 73 GPa. The experiment showed that the *Fm3m* structure for that composition is stable up to that pressure. The equations of state of all seven compositions will be discussed in detail in a future publication.[10]

In Figure 4 notice the dramatic increase in bulk modulus from the $P-V$ data up to 25 GPa as metal is lost from the structure. This is quite different from the usual picture (imagine a sponge) where the structure with the largest number of defects is the most easily compressed. The behavior of the data is also different from that usually found for other metal sulfides under pressure.[11] The effect is not linearly associated with the atomic number density. The volume decreases only by about 2% over the range studied here, while the composition shows a 20% drop in sulfur content, or 10% overall.

Calculation of the Bulk Modulus

FLAPW calculations[12–14] were performed on ScS and $Sc_{0.875}S$. Both stoichiometries were calculated using $R\bar{3}m$ symmetry. The ScS cell used contained 16 atoms, and one atom was removed from the $(^1/_2, {}^1/_2, {}^1/_2)$ position to obtain Sc_7S_8. Other information regarding the calculations can be found in the appendix. The total energy was calculated for a series of cell volumes $0.91 < V/V_0 < 1.0$. V_0 is the experimentally observed volume. Calculations of the type used generally overestimate binding, and indeed values of $V/V_0 = 0.951$ and 0.947 were found for ScS and Sc_7S_8, respectively. Interpolation formulas[15] were used to obtain the calculated equilibrium volume and the second derivative of the total energy, which were then used to obtain the bulk modulus itself.

The model of Figure 1 was derived from the results[4] of both tight-binding calculations (in their extended Hückel implementation) and of first-principles LMTO[5] calculations. The movement of the scandium 3d band on loss of metal from the parent (and thus oxidation of the remaining Sc) occurs naturally in the LMTO calculations. In the tight-binding calculations, the input H_{ii} values of the metal 3d orbitals are generally assumed independent of oxidation state. Such a model showed no energetic gain for Sc atom loss. Their variation with oxidation state, however, may be mimicked by using a charge-iterated version of this method by writing $H_{ii}(q) = A + Bq + Cq^2$. Here q is the atomic charge and the parameters A, B, and C are obtained from atomic spectral data for the neutral atom and its ions. In our earlier study, use of this charge-iterated approach[4] led to the model of Figure 1. We have used these two versions of the extended Hückel ansatz to view in qualitative terms the variation in compressibility with x.

The total energy was written as $E(\text{total}) = E(\text{TB}) + \sum_{ij}(D/r_{ij}{}^n)$ where the r_{ij} are the nearest-neighbor Sc–S distances.

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Table 2. Bulk Moduli (GPa) Computed by Using Extended Hückel (EH) and FLAPW Methods Compared with Experiment

	EH			
x in $Sc_{1-x}S$	without charge iteration[b]	with charge iteration[b]	FLAPW	expt[a]
0.000	55.22 (25.10)	55.22 (25.10)	100.46	103 ± 11[c]
0.0625	52.87 (24.19)	65.81 (32.30)		
0.125	48.45 (22.04)	74.53 (38.91)	130.49	136 ± 21
0.1875	43.71 (19.70)	83.70 (46.44)		

[a] From Table 1. [b] Figures without parentheses correspond to $n = 12$; figures in parentheses, to $n = 6$. [c] By interpolation of the first two figures of Table 1.
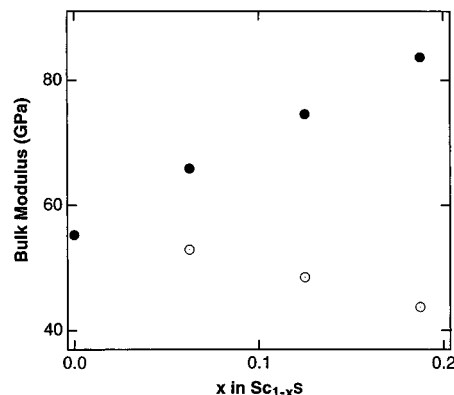

Figure 5. Bulk moduli obtained from extended Hückel calculations for $Sc_{1-x}S$ as a function of x: open circles, standard tight-binding approach using the extended Hückel implementation; closed circles, calculations with charge iteration.

D was adjusted to reproduce the equilibrium Sc–S distance and thus unit cell volume (V_{eq}) in the ScS parent.[1] Using the tight-binding parameters from ref 3, $D = 1.61 \times 10^4$ eV Å ($n = 6$) and 2.46×10^6 eV Å ($n = 12$).[6] The bulk modulus $K_0 = V_{eq}(\partial^2 E(\text{total})/\partial^2 V)_{eq}$ was evaluated for the ScS parent and for several $Sc_{1-x}S$ defect structures using both standard and charge-iterated tight-binding models. (The charge-iterated values for $Sc_{0.875}S$ are taken from ref 4.) The results are shown in Table 2. Notice that there is a decrease in the value of K_0 as x increases in the $Sc_{1-x}S$ structures using the standard approach. This is in accord with the view that the bulk modulus decreases in general as a structure becomes less dense. It is no surprise that the EH calculations, while reproducing the correct trend, quantitatively are rather poor and capture only a quarter to a half of the experimental bulk modulus. The higher values are found for the harder repulsive term ($n = 12$).

The tight-binding calculations of ref 4 only showed qualitative agreement with those of the LMTO type,[5] when the input H_{ii} values were allowed to move as a result of the change in oxidation state. The scheme of Figure 1 then results. Table 2 also shows some computations of the bulk modulus using the charge-iterated version of the model. Notice, importantly, that now the computed K_0 is larger for $Sc_{1-x}S$ ($x > 0$) than for the parent for these calculations which included charge iteration. This is a result in accord with both experiment and the FLAPW calculations reported above. Figure 5 shows the behavior of the two sets of calculations with x. Although the tight-binding calculations give (the expected) poor numerical agreement with experiment, the numerically more exact FLAPW approach gives results in excellent agreement with experiment. For ScS, the bulk moduli are 55 GPa (tight-binding; $n = 12$), 103 ± 11 GPa (experiment), and 100 GPa (FLAPW). We have noted that the computations were performed on the intermediate-temperature structure, since calculations on the incommensurate structure are not possible at present. This difference does not seem to

play a major role. The important result of course is the observed increase in bulk modulus on metal loss, a result matched by the FLAPW calculations.

The results lend general credence to the theoretical model of Figure 1. So, in this particular case, we claim that Sc(III) is stabilized by a larger covalent interaction with sulfur than Sc(II) in this particular system. It is "more stable" than Sc(II). This concept leads to a ready mechanism (in qualitative terms, at least, but confirmed[5] by good numerical calculations) for Sc loss from ScS and a larger bulk modulus for $Sc_{1-x}S$ ($x > 0$) than for the ScS parent.

As the d count increases, the importance of this effect is calculated[4,5] to rapidly decrease. It will be interesting to see if similar effects in the bulk modulus are seen experimentally in titanium and vanadium sulfides.

Appendix

The FLAPW calculations were performed with the Perdew and Wang functional.[16] The largest vector in the plane wave expansion was 10.0 au, and 15 radial functions were used inside spheres of radius 2.1 au. The potential was expanded inside the spheres using spherical harmonics with $l \leq 4$. Due to the size of the cell and the number of calculations needed to be performed, only 50/6 k points in the cell/zone were used. However, since the cell used is 8 times larger than the primitive cell and the symmetry is high, this is quite acceptable for systems of this type. The tight-binding calculations were performed using the parameters from ref 4.

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