

Defect Ordering in Early Transition-Metal Sulfides with the NaCl-Type Structure¹

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The defect rock-salt type materials $Zr_{1-x}S$, $Sc_{1-x}S$, and $Lu_{1-x}S$ have been shown to exhibit a complex variety of ordered superstructures. These superstructures are reviewed within the context of Landau's theory of symmetry and phase transitions, and it is concluded that there is a significant similarity in the transitions when they are considered from the point of view of reciprocal space.

1. Introduction

The early transition-metal sulfides with the NaCl-type structure have been found to exhibit superconductivity and nonstoichiometry, and have been shown with one exception ($Zr_{1-x}S$) to exhibit a maximum in T_c at the 1:1 composition (1). Several structural investigations over the years have shown that three of the compounds in question, $Zr_{1-x}S$, $Sc_{1-x}S$, and $Lu_{1-x}S$ exhibit long-range vacancy ordering, and that some features of the resulting ordered structures are remarkably similar. It is the purpose of this paper to call attention to and characterize these common features.

2. Vacancy Ordering

One feature common to the defect structures is that the deviations from stoichiometry arise from vacancies on the transition-metal sublattices. The vacancy concentrations in all 3 cases are observed to extend to very high values (in excess of 20%), and the defect orderings have in common, along with other features to be developed below, the fact that loss of symmetry (compared with $Fm3m$ space group symmetry of the NaCl-type substructure) results almost entirely from the distribution of vacancies on the metal sublattice with negligible distortion of the lattice as observed in diffraction experiments. The defect orderings also have in common the characteristic that they can be described in terms of population waves, which at their simplest are formed by the ordering of vacancies such that the fractional occupan-

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value of μ has no reason of symmetry to be precisely $1/6$. It is thus distinctly possible that the X-ray data have been forced into a commensurate space group symmetry framework which is slightly incorrect, the true structure being noncommensurate along the b -axis. The true symmetry would only contain a twofold in the b -direction and translational symmetry in the ac -plane and the symmetry would therefore not form a space group but instead one of the plane groups. Nevertheless, particularly if μ is very close to $1/6$, the structure obtained probably gives as accurate a picture as obtainable by X-rays since all intensities were well explained assuming $Fddd$ symmetry.

Two features of this order-disorder transition are remarkable. One is the lack of significant distortion of the cubic lattice in spite of the fact that 25% of the metal sites are unoccupied. This feature is common to Sc_{1-x}S and Zr_{1-x}S as well. The second remarkable feature is the fact that while Lu_3S_4 is an expected stoichiometry, known for the rare-earths generally (e.g., in the Th_3P_4 -type structure), it is obtained in this case in the form of a defect structure with no discernable reason for the fixed 3:4 stoichiometry.

It is interesting to note that Sc_2S_3 also crystallizes in a structure with $Fddd$ symmetry and lattice parameters 2 times ($=a$), $\sqrt{2}$ times ($=b$), and $3\sqrt{2}$ times ($=c$) the NaCl-type lattice parameter. The Sc_2S_3 structure occurs with a tripling of the periodicity perpendicular to the $(420)_{\text{cubic}}$ planes resulting from an ordered 50% occupancy of the pairs of adjacent $(420)_{\text{cubic}}$ planes interspersed by 100% occupied $(420)_{\text{cubic}}$ planes. The ordering in the half-occupied planes is such that, as in Lu_3S_4 , a sheared population wave results. The wave consists, at heights $1/4$ and $1/2$, of the sequence of populations: four (420) planes fully occupied, two (420) planes empty, four (420) planes fully occupied, two (420) planes empty . . . , and at heights $3/4$ and 0 the

same sequence occurs shifted by three interplanar spacings.

4. The Sc_{1-x}S Structure

Defect scandium monosulfide has been prepared by high-temperature vaporization of the monosulfide. The high-temperature experiments showed that $\text{Sc}_{0.80}\text{S}$ vaporizes congruently in the interval $1600 < T < 1950^\circ\text{C}$ (7). A second-order order-disorder process at ca. 700°C has been shown to yield a population wave structure ($\mathbf{k} = (\mathbf{a}^* + \mathbf{b}^* + \mathbf{c}^*)/2$) in which the vacancies are randomly distributed within the scandium containing planes perpendicular to the $[111]$ direction, and the fractional occupancies within these planes alternate along the $[111]$ direction (8, 9) resulting in the rhombohedral cell shown in Fig. 2. This process has been found to meet the Landau conditions for a second-order phase transition (see Appendix). An analysis of the order-disorder process, in comparison with other single \mathbf{k} order processes, using a point charge ionic model (8) shows that several alternate orderings would have lower Madelung energies and lower free energies, and thus that the driving force for the ordering has its origin in effects other than those associated with Madelung energies.

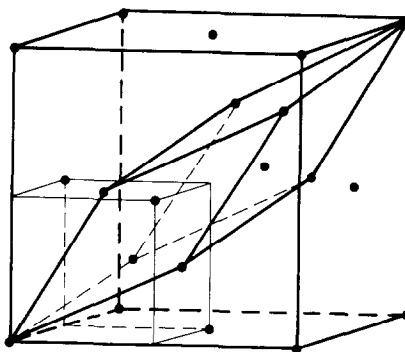


FIG. 2. Lattice of the $\mathbf{k} = (\mathbf{a}^* + \mathbf{b}^* + \mathbf{c}^*)/2$ (rhombohedral) superstructure and the cubic structure corresponding to the star of \mathbf{k} .

Electron diffraction and lattice images of Sc_{1-x}S slowly annealed to room temperature from 700°C give evidence of further ordering at temperatures in this interval (10). A variety of orderings are indicated. In one of the cases satellite diffractions in the $\langle 111 \rangle$ and $\langle 200 \rangle$ zones occur at incommensurate points nearly $1/3$ (actually 0.346) of the distance between the substructure reflections indicating the occurrence of incommensurate population waves with the average repeat distance along the waves in the directions perpendicular to the $[111]_{\text{cubic}}$ directions corresponding to 2.89 interplanar spacings along those directions (10). The diffraction patterns, and their behavior upon electron beam annealing, as discussed in Ref. (10), suggest that the principal low-temperature ordering effect is the formation of a single \mathbf{k} population wave perpendicular to the cubic body diagonal with a wavelength slightly less than 3 times the interplanar spacing and that the observed diffraction patterns exhibited threefold rotational symmetry because of diffraction maxima arising from domains corresponding to different \mathbf{k} vectors in the star of \mathbf{k} . As has been pointed out by Haas (11) a transition corresponding to an incommensurate wave vector is not subject to the fourth condition of Landau (3) and since pure, single \mathbf{k} ordering will always correspond to a single irreducible representation of the space group, the transition can be continuous provided there are no third-order invariants.

The question of third-order invariants raises an interesting point. The wave vector corresponding to an order-disorder transition in a rhombohedral lattice is equivalent by symmetry to two vectors related to it by rotation by 120° and 240° about \mathbf{c}^* . If the wave vector is perpendicular to \mathbf{c}^* the sum of these three vectors is zero, and thus the three degenerate basis functions for the translational subgroup form a product which is invariant under the translations of

the group. Since the basis functions for the order-disorder process are symmetric under the rotational symmetry operations of the point group of the wave vector, i.e., they transform as the totally symmetric small rep, it follows that there is a third-order invariant corresponding to processes with ordering perpendicular to \mathbf{c}^* . Thus if the vacancy ordering process is to occur continuously then it must correspond to a \mathbf{k} point not in the basal plane. This fact perhaps explains the observation (10) of diffuse streaking between the satellite reflections observed in the $\langle 2\bar{2}0 \rangle$ zone, i.e., there occurs a stacking disorder in the population waves along the $[111]$ direction.

Some electron diffraction patterns from some of the Sc_{1-x}S crystals exhibited diffraction maxima characteristic of doubling of lattice periodicities. Since this doubling is a prominent feature of Zr_{1-x}S the discussion of the ordered structure corresponding to the doubling is left for the next section.

5. The Zr_{1-x}S Structure

Recently X-ray analysis of Zr_{1-x}S samples annealed at $1400\text{--}1500^\circ\text{C}$ for 8–10 hr yielded the result that vacancy-ordered Zr_{1-x}S exists over a rather narrow range of homogeneity with $\text{Zr/S} = 0.775 \pm 0.010$ (12) a result which is in excellent agreement with the value 0.77 obtained previously (13). The structure has been determined by X-ray diffraction (13) and the lattice parameters of the vacancy-ordered structure ($C2/m$ symmetry) were found to be $a = 10.35 \text{ \AA}$ ($= 2 \times 5.185 \text{ \AA}$), $b = 10.31 \text{ \AA}$ ($= 2 \times 5.16 \text{ \AA}$), $c = 7.33 \text{ \AA}$ ($= \sqrt{2} \times 5.18 \text{ \AA}$), and $\beta = 135.1^\circ$ (undistorted $\beta = 135.0^\circ$). A reexamination of the data reported in Ref. (13) suggests (taking slight liberties with the occupancy data of Table I) that the sites labeled c, d, e, and f can be taken to be equally populated (within error limits), and thus the structure could be described by a: 100% occupied, b: 27% occupied, c,d,e,f: 74% oc-

TABLE I
PERCENTAGE OF OCCUPANCIES OF Zr SITES IN
 $Zr_{0.77}S$

Site (Wyckoff notation)	% Occupancy (Ref. (13))	Error
a	107	± 8
b	27	± 8
c	63	± 8
d	79	± 8
e	69	± 7
f	85	± 7

cupied. This structure is face-centered cubic with $a = 10.4 \text{ \AA}$, twice the rock-salt value. The large cubic structure arises from alternate ordering of vacancies in the metal containing planes along the body diagonals, i.e., corresponds to the vectors in the star of $\mathbf{k} = (\mathbf{a}^* + \mathbf{b}^* + \mathbf{c}^*)/2$ (see Appendix). This ordering doubles the periodicity in directions perpendicular to the [111] directions as well as along that direction. Electron diffraction patterns for $Zr_{1-x}S$ (14) show a doubling which corresponds to this structure, as well as a tripling similar to the near tripling found for $Sc_{1-x}S$. It can be concluded that the ordered structures of both $Sc_{1-x}S$ and $Zr_{1-x}S$ can be considered to have originated from essentially the same two subsequent second order processes. The first process can be labeled by the star $\mathbf{k}_1 = (\mathbf{a}^* + \mathbf{b}^* + \mathbf{c}^*)/2$ the second by the star of $\mathbf{k}_2 = (\mathbf{a}^* - \mathbf{b}^*)/3$. As shown in the Appendix the first process can either lead to a $R\bar{3}m$ cell if the ordering corresponds to one \mathbf{k} in the star of \mathbf{k} , or else in a larger cubic cell if it corresponds to a function in which all \mathbf{k} 's in the star of \mathbf{k} , are linearly combined. (In $Sc_{1-x}S$ the single- \mathbf{k} , \mathbf{k}_1 transition dominates, in $Zr_{1-x}S$ the all- \mathbf{k} transition dominates.) The subsequent \mathbf{k}_2 transition destroys the threefold symmetry in either case and allows the structure to go noncommensurate since its \mathbf{k} is not forced by reasons of symmetry to maintain a commensurate value.

Again, we should note that in "solving" the $Zr_{1-x}S$ structure the X-ray data may have been forced into a commensurate framework that was not strictly justified. Moreover we may note that a "monoclinic" departure from the large cubic cell in $Zr_{1-x}S$ could be associated with the destruction of the cubic symmetry by the non-commensurate \mathbf{k}_2 wave.

The Landau theory of symmetry and phase transitions allows second-order transitions to both the large cubic and the $R\bar{3}m$ structures from the NaCl-type (disordered, NaCl-type, $Zr_{1-x}S$ was not observed by Nguyen (12), although it seems likely that it does exist at highly temperatures and not in the quenched samples).

6. Conclusions

$Sc_{1-x}S$, $Zr_{1-x}S$, and $Lu_{1-x}S$ show some notable similarities in their defect chemistry. All occur with an excess of 20% vacancies on the metal sublattice of the NaCl-type structure. All are stable at elevated temperatures and exhibit vacancy ordering at lower temperatures. A striking feature of the three materials is that in spite of the very large concentrations of vacancies and the marked lowering of symmetry, the cubic lattices remain basically undistorted. It has, as a result, only been possible to suggest plausible structures for the vacancy-ordered solids because under this circumstance it is not possible to unambiguously differentiate diffraction effects arising from more than one domain. Nonetheless the following conclusions regarding the periodicities of the various ordered structures indicate an interesting similarity in their origins.

The low-temperature structures of the defect monosulfides mentioned above: (a) the $R\bar{3}m$ (Fig. 2a) structure that results from the $\mathbf{k} = (\mathbf{a}_c^* + \mathbf{b}_c^* + \mathbf{c}_c^*)/2$ ordering in alternate (111) planes, (b) the idealized tri-

pling of this structure that corresponds to $\mathbf{k} = (\mathbf{a}_r^* - \mathbf{b}_r^*)/3$ (equivalent to tripling along the $[420]_{\text{cubic}}$ direction), (c) the large cubic structure that results from a superposition of orderings of type a, i.e., corresponding to vectors in the star of $\mathbf{k} = (\mathbf{a}_c^* + \mathbf{b}_c^* + \mathbf{c}_c^*)/2$, (d) the incommensurate structure of Sc_{1-x}S that results from a long period mixing of b and c, and (e) the $Fddd$ structure of Lu_3S_4 and Sc_2S_3 , are closely related. The relationship between the $R\bar{3}m$ and the large cubic structures corresponding to one or more than one \mathbf{k} vector of the $(\mathbf{a}^* + \mathbf{b}^* + \mathbf{c}^*)/2$ type has been discussed.

A mixing of cases b and c results in a sextupling of the periodicity perpendicular to the $[111]_{\text{cubic}}$ direction (along the $[\bar{2}20]$ direction). Examination of an atypical $(22\bar{4})_{\text{cubic}}$ electron diffraction zone photograph from the previous study (10) shows rows of diffraction maxima midway between those arising from the NaCl substructure, as well as those at roughly 1/3 and 2/3 of the distance between the substructure rows and some weak reflections at 1/6 of the distance, providing clear evidence for this sextupling. Therefore in the case of Lu_3S_4 it is interesting to note that $2/3\mathbf{a}^* + 1/3\mathbf{b}^* + 1/2\mathbf{c}^* = (\mathbf{a}^* + \mathbf{b}^* + \mathbf{c}^*)/2 + (\mathbf{a}^* - \mathbf{b}^*)/6$ which also has a sextupling component perpendicular to a $[111]_{\text{cubic}}$ direction. It is thus apparent that the Lu_3S_4 structure is one (simultaneous) way to order vacancies corresponding to doubling along $[111]_{\text{cubic}}$ and doubling/tripling along the perpendicular to $[111]_{\text{cubic}}$, in addition to the other ways in which this can be accomplished, i.e., through two subsequent second-order transitions leading to the incommensurate structures of Sc_{1-x}S or Zr_{1-x}S .

Studies of soft-mode behavior in YS, a related NaCl-type, superconducting early transition-metal sulfide, showed a softening of the longitudinal frequencies (15) which could be correlated with population wave formation of the type described here.

Appendix

The orderings corresponding to doubling of the periodicity along the cubic body diagonals $[111]$, $[\bar{1}\bar{1}\bar{1}]$, $[\bar{1}11]$, and $[1\bar{1}\bar{1}]$ are considered. The discussion is limited to the totally symmetric small rep of the star of $\mathbf{k} = (\mathbf{a}^* + \mathbf{b}^* + \mathbf{c}^*)/2$. If the differences between the disordered electron density and that in the ordered structure are labeled ϕ_1 , ϕ_2 , ϕ_3 , and ϕ_4 , according to the diagonal along which the ordering occurs, then the most general form for the ordered electron density is

$$\rho^{\text{ordered}} = \rho^{\text{disordered}} + (\gamma_1\phi_1 + \gamma_2\phi_2 + \gamma_3\phi_3 + \gamma_4\phi_4)\eta$$

where η is a disorder parameter and the γ_i 's are normalized such that $\sum \gamma_i^2 = 1$ (3). Expansion of the Gibbs free energy yields

$$G = G^\circ + A\eta^2 + \left[C_1 \sum \gamma_i^4 + C_2 \sum_{i < j} \gamma_i^2 \gamma_j^2 + C_3 \gamma_1 \gamma_2 \gamma_3 \gamma_4 \right] \eta^4$$

where it has been recognized that $\sum \gamma_i^2 = 1$ is the only second-order invariant, there are no third-order invariants in this case, and the several fourth-order invariants are as shown. Minimization of G with respect to the γ 's yields $\gamma_1 = 1, \gamma_2 = \gamma_3 = \gamma_4 = 0$ as the stable solution if $C_1 > 0$ and $C_2 > 0$, and two solutions if $C_1 > 0$ and $C_2 > 0$, namely $\gamma_1 = \gamma_2 = \gamma_3 = \gamma_4 = 1/2$ if $C_3 < 0$ and $\gamma_1 = \gamma_2 = \gamma_3 = -\gamma_4 = 1/2$ if $C_3 > 0$. The first solution, $\rho^{\text{ordered}} = \rho^{\text{disordered}} + \eta\phi$, corresponds to the $R\bar{3}m$ ordering in Sc_{1-x}S , the second solution corresponds to a $Fm\bar{3}m$ cubic-ordered structure, with "large" cubic unit cell, and the third solution, $\rho^{\text{ordered}} = \rho^{\text{disordered}} + \eta(\phi_1 + \phi_2 + \phi_3 - \phi_4)$ corresponds to an alternative large cubic structure with $Fd\bar{3}m$ symmetry. The relationship among the cells is shown in Fig. 2.

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