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The Crystal Structure of Lu_3S_4: A New Population Wave Structure

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The monosulfide of lutetium loses lutetium preferentially upon vaporization *in vacuo* at 1750°C, and the quenched samples exhibit a new structure which is formed by an ordering of metal vacancies on the rock-salt type lattice.

Introduction

During an investigation of the high-temperature vaporization behavior of the Lu–S system (*1*) a new phase was found to occur as the result of vaporization and resultant composition change of the solid. This phase was characterized as being a line compound with composition Lu_3S_4 and an orthorhombic lattice with $a = 10.8$ Å, $b = 22.9$ Å, and $c = 7.7$ Å. A single crystal study was undertaken with the purpose of establishing the detailed structure of this solid.

Experimental

A nearly spherical crystal (diameter ~0.16 mm) was mounted on a glass fiber using Duco cement and then placed on a four-circle diffractometer. Using an automatic indexing procedure (*2*) the cell was indexed as orthorhombic, and the mm symmetry was later confirmed by oscillation pictures taken about each axis. Lattice parameters of $a = 10.747(3)$, $b = 22.813(6)$, and $c = 7.602(2)$ Å were obtained by a least-squares fit of the $\pm 2\theta(2\theta > 30°)$ measurements of twelve strong independent reflections at 27°C using graphite monochromated Mo$K\alpha$ radiation ($\lambda = 0.71002$ Å). A reevaluation of the powder diffraction patterns obtained previously produced lattice parameters in agreement with those obtained by single crystal techniques within the errors of the techniques and the variations with sample history. A total of 4251 reflections were measured in the hkl, $hk\bar{l}$, $\bar{h}k\bar{l}$, and $\bar{h}kl$ octants using an automated four-circle diffractometer (*3*). Data were collected using an ω-stepscan technique. Three reflections were remeasured every 75 reflections to monitor crystal stability. No appreciable decay was noted during the period of data collection. The extinctions hkl: $h + k \neq 2n$, $k + l \neq 2n$, $l + h \neq 2n$, and 0kl: $k + l \neq 4n$; $h0l$: $l + h \neq 4n$; $hk0$: $h + k \neq 4n$ uniquely determined the space group as *Fddd*.

The data were corrected for Lorentz and polarization effects. An absorption correction was also applied assuming a spherical crystal ($\mu = 699.3$ cm^{-1}). The data were then averaged yielding 140 observed reflections ($|F| > 3\sigma_F$).

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Results

The material LuS has been reported to crystallize in the rock-salt structure $Fm3m$ with $a = 5.323$ Å (*4*). It was noted that the data for Lu_3S_4 readily separated into two classes as a function of intensity. The strong $|F|$ data could be reindexed on a face-centered cubic lattice of dimensions $a = 5.373$ Å very similar to that of the parent LuS lattice. Thus the orthorhombic cell can be viewed as a superstructure of the cubic cell with axial relationships $a_{orth} = 2a_{cubic}$, $b_{orth} = 3\sqrt{2}a_{cubic}$, and $c_{orth} = \sqrt{2}a_{cubic}$. (It should also be noted that many samples when mounted on the diffractometer showed a diffraction pattern characteristic of a composite of orthorhombic cells disordered with respect to the cubic axes.)

Since the strong reflections in the orthorhombic cell were about an order of magnitude larger than the weak reflections, the simpler cubic cell was used as a first approximation to the structure, as follows. The strong orthorhombic reflections were averaged assuming a cubic cell and yielded 15 unique reflections. A structural model was refined using these data by full-matrix least squares (*5*) to a final $R = 0.050$ and a weighted $R = 0.059$. The weights used in the refinement were $1/\sigma_F^2$. The lutetium was placed at (0, 0, 0) with a multiplier of 0.75 and the sulfur was placed at (1/2, 0, 0) with a multiplier of 1.0. Isotropic temperature factors were varied on both atoms yielding essentially identical results: 0.78(17) for Lu and 0.77(50) for S.

This model was then refined further using the full orthorhombic data set and the assumption that the supercell is only a perturbation of the cubic cell. The lutetium atom multipliers were varied while, to reduce correlation effects, the thermal parameters were kept fixed at the values obtained from the cubic refinement. By cyclically varying three of the four lutetium multipliers at a time, convergence was found to be accelerated; only four cycles of refinement were required. The final refined lutetium multipliers and positional parameters are listed in Table I and the observed and calculated structure factors are in a table on deposit with NAPS.[1]

TABLE I

FINAL ATOMIC POSITIONAL, OCCUPATIONAL, AND THERMAL PARAMETERS[a]

	Site symmetry	Fractional occupancy	x	y	z	B
Lu1	222	0.54(2)	0.0	0.0	0.0	0.78
Lu2	222	0.84(2)	0.0	0.0	0.5	0.78
Lu3	2	0.83(2)	0.0	0.3327(1)	0.0	0.78
Lu4	2	0.75(2)	0.0	0.1661(1)	0.0	0.78
S1	2	1.0	0.25	0.0	0.0	0.77
S2	1	1.0	0.25	0.16667	0.0	0.77

[a] Estimated standard deviations are given in parentheses for the least significant figure of the parameters varied.

Discussion

The structure can be described (Fig. 1) in terms of occupation waves as follows: At a given height along a ($x = 0$, 1/4, 1/2, or 3/4), the fractional occupancies in sequential (066) planes occur periodically in the order . . . 0.54, 0.75, 0.83, 0.84, 0.83, 0.75, 0.54, ... Furthermore the occupation waves at $x = 0$ and $x = 3/4$ are in phase, as are the waves at $x = 1/4$ and $x = 1/2$; however the latter waves are exactly out of phase relative to those at $x = 0$, 3/4. Thus the structure can be described as a sheared population wave defect ordering based on the NaCl-type lattice.

[1] See NAPS document No. 03695 for 7 pages of supplementary material. Order from ASIS/NAPS c/o Microfiche Publications, P. O. Box 3513, Grand Central Station, New York, New York, 10017. Remit in advance for each NAPS Accession Number. Institutions and organizations may use purchase orders when ordering; however, there is a billing charge for this service. Make checks payable to Microfiche Publications. Photocopies are $5.00. Microfiche are $3.00. Outside of the U.S. and Canada, postage is $3.00 for a photocopy or $1.50 for a fiche.

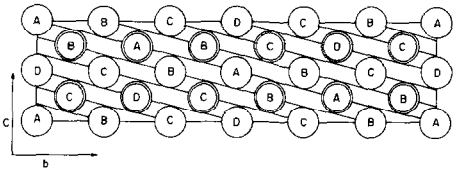

FIG. 1. Lu atom positions projected along a. Positions indicated by a single circle occur at $x = 0$ and $x = 1/2$, positions indicated by double circles occur at $x = 1/4$ and $x = 3/4$. The (066) planes are labeled by A, B, C, and D. The sites have fractional occupancies as follows. (A) 0.54 at $x = 0$, 3/4 and 0.84 at $x = 1/4$, 1/2; (B) 0.75 at $x = 0$, 3/4 and 0.83 at $x = 1/4$, 1/2; (C) 0.83 at $x = 0$, 3/4 and 0.75 at $x = 1/4$, 1/2; (D) 0.84 at $x = 0$, 3/4 and 0.54 at $x = 1/4$, 1/2.

Population waves have been previously observed in the Ti-S system by Wiegers and Jellinek (*6*). The phenomena of population wave structures are not understood from a fundamental point of view. It is not known what interactions lead to the periodicities, nor do the underlying factors yield a particular stoichiometry (S/Lu = 4/3 to a high degree of accuracy in this case) in spite of apparent disorder known. These effects provide a fruitful area for further theoretical investigation.

Acknowledgment

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