

# Synthesis, Structure, and Electrical Properties of $\text{Eu}_{0.59}\text{Nb}_5\text{Se}_8$

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Received December 14, 1987; in revised form February 22, 1988

The new compound  $\text{Eu}_{0.59}\text{Nb}_5\text{Se}_8$  has been prepared from a combination of the elemental powders at 1275 K. The material crystallizes with four formula units in space group  $C_{2h}^3-C2/m$  of the monoclinic system in a cell (at 113 K) of dimensions  $a = 17.95(2)$ ,  $b = 3.388(4)$ ,  $c = 19.30(2)$  Å,  $\beta = 107.90(2)^\circ$ . The structure has been solved and refined from single-crystal X-ray data. The asymmetric unit contains two independent Eu atoms, five independent Nb atoms, and eight independent Se atoms. Each Eu site is approximately 59% occupied; the Eu atoms are in an unusual distorted cube of Se atoms with Eu-Se interactions ranging from 3.108(6) to 3.454(6) Å. Three of the independent Nb atoms are in trigonal prisms of Se atoms with Nb-Se interactions ranging from 2.548(6) to 2.617(6) Å while the other two independent Nb atoms are in unusual distorted octahedral environments with Nb-Se interactions ranging from 2.526(9) to 2.718(7) Å. These latter two Nb atoms show short Nb-Nb interactions of about 2.95 Å. The material exhibits excellent metallic conductivity along the needle ( $b$ ) direction with  $\sigma_{298\text{ K}}$  of  $35 \times 10^3 \text{ ohm}^{-1} \text{ cm}^{-1}$  and  $\sigma_{12\text{ K}} \approx 1.4 \times 10^6 \text{ ohm}^{-1} \text{ cm}^{-1}$ . © 1988 Academic Press, Inc.

## Introduction

From an interest in ternary transition-metal/Nb-Ta/chalcogenides we have produced an assortment of new stoichiometric compounds with layer (1-6) and channel structures (2, 3, 7) as well as some new nonstoichiometric compounds with layer structures. The nonstoichiometric materials form from solid-state reactions (2, 3, 8-10) or from intercalation reactions (9). We have recently expanded exploratory studies to rare earths and have discovered the new phase  $\text{Eu}_{0.59}\text{Nb}_5\text{Se}_8$ .

Niobium selenides exhibit a wide polymorphism (11-13) and are subject to intercalation by organic (14) and inorganic materials (15-21). Although the material  $\text{Eu}_x\text{NbS}_2$  (22-24) and numerous Eu chalcogenides (25-43) have been reported, we

have found no reports of single-crystal studies within the Eu/Nb/Se system.

## Experimental

**Synthesis.** A combination of elemental powders (0.25 g), Eu (99.9%, ALFA), Nb (99.8%, AESAR), Pd (99.95%, AESAR), and Se (99.99%, ALFA), was loaded into a Ni tube under Ar. The molar ratio  $\text{Eu} : \text{Nb} : \text{Pd} : \text{Se} = 0.8 : 4 : 1 : 10$  was used in an attempt to form  $\text{Nb}_2\text{Pd}_{0.5}\text{Se}_5$  with Eu atoms occupying a rhombohedral site between the layers (3). The ends of the tube (internal diameter 4 mm, length 90 mm) were pinched off at atmospheric pressure. The tube was placed under an  $\text{N}_2$  flow and heated at 1275 K for 2 weeks. Black powder and needle-shaped crystals were produced. Analysis of four crystals (including the

crystal used for X-ray data collection) with the microprobe of an EDAX-equipped Hitachi S-570 scanning electron microscope revealed the presence of Eu, Nb, and Se but not of Pd or Ni. The lack of reliable standards prevented accurate quantitative analysis. After the final composition of  $\text{Eu}_{0.59}\text{Nb}_5\text{Se}_8$  was established from the X-ray structure determination (see below) the material (as a powder) was successfully synthesized by loading that composition into a Ta tube and proceeding as described above.

*Physical measurements.* Single crystals were mounted with Ag paint on graphite fibers. Four-probe ac conductivity measurements along the needle axis  $b$  were then carried out by methods described previously (44).

*Structure determination.* The unit-cell parameters were determined from least-squares refinement of 24 reflections in the range  $14^\circ \leq 2\theta$  ( $\text{MoK}\alpha_1$ )  $\leq 24^\circ$  that had been automatically centered on an Enraf-Nonius CAD4 X-ray diffractometer. Additional relevant crystal data are given in Table I. An examination of intensity data reveals the systematic absence  $hkl$ ,  $h + k$  odd indicative of the space groups  $C_2^3-C2$ ,  $C_3^3-Cm$ , and  $C_{2h}^3-C2/m$ . Intensity statistics led us to choose the latter group.

All calculations were performed on a Harris 1000 computer with methods and programs standard for this laboratory (45). The initial positions of the Nb and Se positions comprising the  $\text{NbSe}_2$ -type layer along  $a$  were determined by direct methods. The SHELXS-86 program (46) and a difference electron density synthesis revealed the positions of the atoms bridging the layers. As thermal motion was not large for any Nb or Se atom, we refined only the Eu atoms anisotropically. Composition of the data crystal was established through the inclusion in the final least-squares refinement on  $F_o^2$  of variable site occupancies for the two independent Eu atoms. These oc-

cupancies refined to 0.60(2) and 0.57(2), respectively, and hence to the final composition  $\text{Eu}_{0.59(2)}\text{Nb}_5\text{Se}_8$ . Scattering factors and anomalous dispersion terms were taken from the usual sources (47). A final difference electron-density map reveals no features greater than 7% the height of a Nb atom. An analysis of  $\sum w(F_o^2 - F_c^2)^2$  as a function of  $\lambda^{-1} \sin \theta$ ,  $F_o^2$ , and Miller indices revealed no unusual trends. Final positional and equivalent isotropic thermal parameters are given in Table II. Final anisotropic thermal parameters and structure amplitudes are given in Tables III and IV.<sup>1</sup>

## Results

*Description of the structure.* The structure of  $\text{Eu}_{0.59}\text{Nb}_5\text{Se}_8$  is described in terms of bond distances and angles in Table V. Figure 1 is a perspective view of the structure and provides the labeling scheme. A stereoview of the structure is provided in Fig. 2. The structure appears much like a wall of square bricks with Eu atoms as the bricks and Nb-Se chains as the mortar. Infinite  $\text{NbSe}_2$ -type chains of edge-sharing Se trigonal prisms centered by Nb atoms run parallel to  $a$ . Pairs of edge-sharing Se octahedra approximately centered by Nb atoms bridge the infinite chains. The octahedra share faces with the trigonal prisms. Chains of Eu atoms fill the resulting channels along  $b$ . The Eu atoms occupy distorted cubic sites. The coordination of atoms Nb(1), Nb(2), and Nb(3) within Se trigonal prisms is unremarkable. The Nb-Se distances range from 2.548(6) to 2.617(6) Å and the trigonal prisms are nearly regular with ap-

<sup>1</sup> Tables III and IV have been deposited with NAPS. See NAPS Document No. 04585 for 7 pages of supplementary materials from ASIS/NAPS, Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, NY 10163. Remit in advance \$4.00 for microfiche copy or for photocopy, \$7.75 for up to 20 pages plus \$.30 for each additional page. All orders must be prepaid.

TABLE I  
CRYSTAL DATA AND INTENSITY COLLECTION FOR  $\text{Eu}_{0.59}\text{Nb}_5\text{Se}_8$

Formula	$\text{Eu}_{0.59}\text{Nb}_5\text{Se}_8$
Mol. wt.	1186
Space group	$C_{2h}^2-C2/m$
$a$ (Å)	17.95(2)
$b$ (Å)	3.388(4)
$c$ (Å)	19.30(2)
$\beta$	107.90(2)°
$V$ (Å <sup>3</sup> )	1117
$Z$	4
$T$ of data coll. (K) <sup>a</sup>	113
Crystal vol. (mm <sup>3</sup> )	$2.2 \times 10^{-5}$ mm <sup>3</sup>
Crystal shape	Irregular needle $\approx 0.3 \times 0.005 \times 0.01$ mm bound by {010}, {001}, (10 $\bar{1}$ ), (40 $\bar{1}$ ), ( $\bar{4}0\bar{1}$ )
Radiation	Graphite monochromatized $\text{MoK}\alpha$ ( $\lambda(K\alpha_1) = 0.7093$ Å)
Linear abs. coeff. (cm <sup>-1</sup> )	338
Transmission factors <sup>b</sup>	0.72–0.83
Detector aperture (mm)	2 × 2
	17.3 cm from crystal
Takeoff angle (deg.)	3.0
Scan type	$\omega$
Scan speed (deg. min <sup>-1</sup> )	2° in $\omega$ /min with rescans up to 100 sec for initial $F_o^2 < 3\sigma(F_o^2)$
Scan range (deg.)	$\pm 0.8^\circ$ in $\omega$
$\lambda^{-1} \sin \theta$ , limits (Å <sup>-1</sup> )	0.049–0.618
Background counts	1/4 of scan range on each side of scan
Data collected	$+h, +k, \pm l$
$p$ factor	0.03
Number of variables	50
No. unique data including $F_o^2 < 0$	1283
No unique data with $F_o^2 > 3\sigma(F_o^2)$	501
$R(F^2)$	0.175
$R_w(F^2)$	0.207
$R$ (on $F$ for $F_o^2 > 3\sigma(F_o^2)$ )	0.088
Error in observation of unit wt. ( $e^2$ )	1.41

<sup>a</sup> The low-temperature system for the Enraf–Nonius CAD4 diffractometer is based on a design by Professor J. J. Bonnet and S. Askenazy and is commercially available from Soterem (Castanet-Tolosan, France).

<sup>b</sup> The analytical method as employed in the Northwestern Absorption program AGNOST was used for the absorption correction (57).

proximately constant Se · · · Se edges. If all Se · · · Se edges were equal the Se–Nb–Se bond angle would be 81.79° ( $\cos^{-1}(1/7)$ ) and indeed these angles range from 79.3(2) to 85.3(2)°.

However, atoms Nb(4) and Nb(5) within the bridging Se octahedra are of considerable interest. Although octahedral coordi-

nation for Nb is common in halides (48) and oxides (49, 50), only a few examples exist for octahedral Nb in chalcogenide systems. These include the high-temperature forms of NbSe<sub>2</sub> (11) and NbTe<sub>2</sub> (51) as well as materials with the Nb<sub>3</sub>FeSe<sub>10</sub> structure (52, 53) and Co<sub>2</sub>Nb<sub>4</sub>PdSe<sub>12</sub> (3). In the present instance, these octahedra are distorted,

TABLE II  
POSITIONAL PARAMETERS AND  $B_{eq}$  ( $\text{\AA}^2$ ) FOR  
 $\text{Eu}_{0.59}\text{Nb}_5\text{Se}_8$

Atom	x	y	z	$B_{eq}$ ( $\text{\AA}^2$ )
Eu(1)	0	0	$\frac{1}{2}$	2.8(4)
Eu(2)	$\frac{1}{2}$	0	0	3.5(4)
Nb(1)	0.34468(27)	0	0.24872(27)	0.11(9)
Nb(2)	0.00981(28)	0	0.25407(28)	0.08(9)
Nb(3)	0.17631(28)	$\frac{1}{2}$	0.24842(27)	0.13(9)
Nb(4)	0.24992(31)	0	0.56257(31)	0.7(1)
Nb(5)	0.29173(32)	0	0.06263(31)	0.8(1)
Se(1)	0.42877(33)	0	0.16245(33)	0.5(1)
Se(2)	0.15130(32)	0	0.34225(32)	0.2(1)
Se(3)	0.48257(32)	0	0.34471(32)	0.3(1)
Se(4)	0.08811(32)	0	0.16025(32)	0.3(1)
Se(5)	0.25577(31)	$\frac{1}{2}$	0.15693(31)	0.1(1)
Se(6)	0.31804(32)	$\frac{1}{2}$	0.33689(33)	0.4(1)
Se(7)	0.35479(36)	0	0.50030(36)	1.0(1)
Se(8)	0.14544(36)	0	0.00076(37)	1.1(1)

as can be seen from Table V. Thus the Nb–Se distances range from 2.526(9) to 2.718(7)  $\text{\AA}$ , compared with 2.57(1)  $\text{\AA}$  in high-temperature  $\text{NbSe}_2$  (11). Moreover, the Se–Nb–Se angles, which would be  $90^\circ$  in an octahedron, range from  $77.1(2)^\circ$  to  $108.8(2)^\circ$ . In addition to their rare coordination geometries, these Nb atoms are also intriguing because they interact with them-

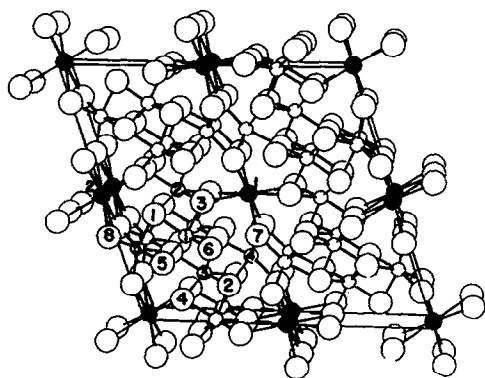


FIG. 1. A view of the structure of  $\text{Eu}_{0.59}\text{Nb}_5\text{Se}_8$  along the  $b$  axis. The small white circles are Nb atoms, the small dark circles are Eu atoms, and the large white circles are Se atoms. The numbering scheme is shown.

selves. The Nb(4)–Nb(4') distance is 2.951(10)  $\text{\AA}$  and the Nb(5)–Nb(5') distance is 2.955(10)  $\text{\AA}$ , while the Nb–Nb distance within high-temperature  $\text{NbSe}_2$  is 3.53(1)  $\text{\AA}$  (49) and within elemental Nb is 2.858  $\text{\AA}$  (54, 55). The Nb(4)–Nb(4') interaction is across the Se(7) shared octahedral face while the Nb(5)–Nb(5') interaction is across the Se(8) shared octahedral face. In essence these could be looked upon as  $\text{Nb}_2\text{Se}_9$  units. The shortest Nb–Nb distances among atoms Nb(1), Nb(2), and Nb(3), which are trigonal prismatically coordinated by Se atoms, is 3.388(4)  $\text{\AA}$ , the  $b$ -spacing.

The coordination geometry of the Eu atoms is also remarkable. Both atoms Eu(1)

TABLE V  
DISTANCES ( $\text{\AA}$ ) AND ANGLES (DEG.) IN  $\text{Eu}_{0.59}\text{Nb}_5\text{Se}_8$

Eu(1)–Se(7)	(4)	3.110(6)	Se(7)–Eu(1)–Se(7)	66.0(1)
Eu(1)–Se(3)	(4)	3.372(6)	Se(3)–Eu(1)–Se(3)	60.3(1)
Eu(2)–Se(8)	(4)	3.108(6)	Se(3)–Eu(1)–Se(7)	64.8(1)
Eu(2)–Se(4)	(4)	3.454(6)	Se(8)–Eu(2)–Se(8)	66.0(1)
Nb(1)–Se(6)	(2)	2.548(6)	Se(4)–Eu(2)–Se(4)	58.7(1)
Nb(1)–Se(1)	(2)	2.568(8)	Se(4)–Eu(2)–Se(8)	64.9(2)
Nb(1)–Se(3)	(2)	2.596(8)	Se(3)–Nb(1)–Se(6)	(2) 81.9(2)
Nb(1)–Se(5)	(2)	2.611(6)	Se(6)–Nb(1)–Se(6)	83.3(3)
Nb(2)–Se(1)	(2)	2.556(6)	Se(1)–Nb(1)–Se(5)	(2) 85.3(2)
Nb(2)–Se(2)	(2)	2.587(8)	Se(5)–Nb(1)–Se(5)	80.9(2)
Nb(2)–Se(3)	(2)	2.587(6)	Se(1)–Nb(1)–Se(3)	80.9(2)
Nb(2)–Se(4)	(2)	2.611(8)	Se(5)–Nb(1)–Se(6)	(2) 79.7(2)
Nb(3)–Se(4)	(2)	2.572(6)	Se(2)–Nb(2)–Se(3)	(2) 84.6(2)
Nb(3)–Se(5)	(2)	2.588(8)	Se(3)–Nb(2)–Se(3)	81.8(2)
Nb(3)–Se(6)	(2)	2.592(8)	Se(1)–Nb(2)–Se(4)	(2) 80.4(2)
Nb(3)–Se(2)	(2)	2.617(6)	Se(1)–Nb(2)–Se(1)	83.0(3)
Nb(4)–Se(7)	(2)	2.526(9)	Se(2)–Nb(2)–Se(4)	80.0(2)
Nb(4)–Se(7)	(2)	2.544(6)	Se(1)–Nb(2)–Se(3)	(2) 81.3(2)
Nb(4)–Se(6)	(2)	2.590(9)	Se(2)–Nb(3)–Se(6)	(2) 83.5(2)
Nb(4)–Se(2)	(2)	2.718(7)	Se(2)–Nb(3)–Se(2)	80.7(2)
Nb(5)–Se(8)	(2)	2.529(9)	Se(4)–Nb(3)–Se(5)	(2) 84.6(2)
Nb(5)–Se(8)	(2)	2.547(7)	Se(4)–Nb(3)–Se(4)	82.4(2)
Nb(5)–Se(1)	(2)	2.617(9)	Se(5)–Nb(3)–Se(6)	79.3(2)
Nb(5)–Se(5)	(2)	2.706(7)	Se(2)–Nb(3)–Se(4)	(2) 80.2(3)
Nb . . . Nb $\geq$ 2.951(10)			Se(2)–Nb(4)–Se(6)	(2) 81.6(2)
Se . . . Se $\geq$ 3.305(9)			Se(2)–Nb(4)–Se(2)	77.1(2)
			Se(7)–Nb(4)–Se(7)	83.5(2)
			Se(7)–Nb(4)–Se(7)	(2) 108.8(2)
			Se(6)–Nb(4)–Se(7)	(2) 84.7(2)
			Se(2)–Nb(4)–Se(7)	(2) 98.1(2)
			Se(2)–Nb(4)–Se(7)	(2) 84.0(2)
			Se(1)–Nb(5)–Se(5)	(2) 82.5(2)
			Se(5)–Nb(5)–Se(5)	77.5(2)
			Se(8)–Nb(5)–Se(8)	(2) 108.8(2)
			Se(8)–Nb(5)–Se(8)	83.4(3)
			Se(1)–Nb(5)–Se(8)	(2) 84.2(2)
			Se(5)–Nb(5)–Se(8)	(2) 83.7(2)
			Se(5)–Nb(5)–Se(8)	(2) 98.0(2)

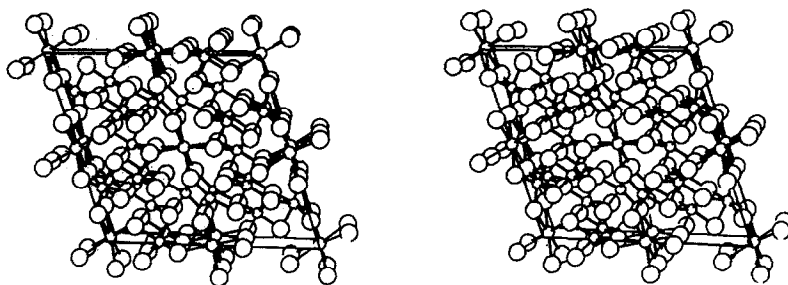


FIG. 2. A stereoview of the structure of  $\text{Eu}_{0.59}\text{Nb}_5\text{Se}_8$ . The view is the same as in Fig. 1, with the  $a$  axis going from bottom to top, the  $c$  axis from left to right, and the  $b$  axis into the paper.

and  $\text{Eu}(2)$  have four short  $\text{Eu}-\text{Se}$  and four long  $\text{Eu}-\text{Se}$  interactions (Table V) at the corners of a distorted cube. The  $\text{Se}-\text{Eu}-\text{Se}$  bond angles, which would be  $70.53^\circ$  in a perfect cube, range from  $58.7(1)^\circ$  to  $66.0(1)^\circ$ . In chalcogenide systems  $\text{Eu}$  prefers trigonal prismatic coordination, frequently capped or bicapped. The only example of  $\text{Eu}$  in a cubic environment is the bronze  $\text{EuPd}_3\text{S}_4$  (56). In the idealized composition  $\text{Eu}_{0.50}\text{Nb}_5\text{Se}_8$  there need be no short  $\text{Eu}-\text{Eu}$  interactions along  $b$  as the  $\text{Eu}-\text{Eu}$  distance could be  $2b$  ( $6.776 \text{ \AA}$ ) and the half occupancy could arise from lack of registry of  $\text{Eu}$  columns along  $b$ . Since the composition exceeds  $\text{Eu}_{0.50}\text{Nb}_5\text{Se}_8$ , some short  $\text{Eu}-\text{Eu}$  interactions are implied.

**Electrical conductivity.** As displayed in Fig. 3, the compound  $\text{Eu}_{0.59}\text{Nb}_5\text{Se}_8$  exhibits

strong metallic conductivity along  $b$ , the needle axis. Clearly not all the  $\text{Nb}$  atoms are in equivalent environments, but since there are no  $\text{Se}-\text{Se}$  bonds, the simple valence description  $\text{Eu}_{0.50}^{\text{II}}\text{Nb}_5^{\text{III}}\text{Se}_8^{-\text{II}}$  is consistent with the observed conductivity.

### Acknowledgments

This research was supported by the U.S. National Science Foundation—Solid State Chemistry—Grant DMR-83-15554. Use was made of the Scanning Electron Microscope Facility of Northwestern University's Material Research Center, supported in part under the NSF-MRL program (Grant DMR85-20280). We thank Johnson-Matthey Inc. for the loan of  $\text{Pd}$  powder. We thank Timothy Newcomb for assistance with the initial conductivity measurements down to 100 K. We are especially indebted to Eric Liimatta for extending these measurements to 12 K.

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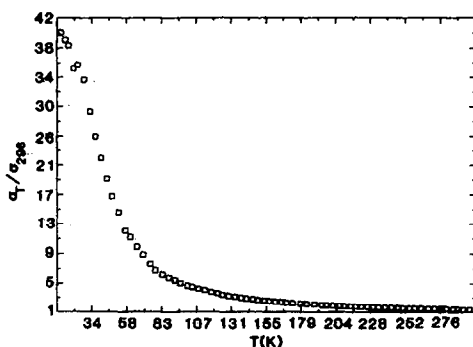


FIG. 3. Electrical conductivity along the needle ( $b$ ) direction of a crystal of  $\text{Eu}_{0.59}\text{Nb}_5\text{Se}_8$ . The value of  $\sigma_{298 \text{ K}}$  is  $35 \times 10^3 \text{ ohm}^{-1} \text{ cm}^{-1}$ .

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