Structure and electrical resistivity of CeNiSb₃

Robin T. Macaluso, a Daniel M. Wells, b Richard E. Sykora, b Thomas E. Albrecht-Schmitt, b Arthur Mar, c S. Nakatsuji, d H. Lee, d Z. Fisk, d and Julia Y. Chan a,

a Department of Chemistry, Louisiana State University, 232 Choppin Hall, Baton Rouge, LA 70803, USA
b Department of Chemistry, Auburn University, Auburn, AL 36849, USA
c Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada T6G 2G2
d National High Magnetic Field Laboratory, Florida State University, Tallahassee, FL 32306, USA

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Abstract

The ternary antimonide CeNiSb₃ has been prepared from an Sb flux or from reaction of Ce, NiSb, and Sb above 1123 K. It crystallizes in the orthorhombic space group Pbcm with Z = 12 and lattice parameters a = 12.6340(7) Å, b = 6.2037(3) Å, and c = 18.3698(9) Å at 193 K. Its structure consists of buckled square nets of Sb atoms and layers of highly distorted edge- and face-sharing NiSb₆ octahedra. Located between the \( \frac{2}{7} \) Sb and \( \frac{5}{7} \) NiSb₂ layers are the Ce atoms, in monocapped square antiprismatic coordination. There is an extensive network of Sb–Sb bonding with distances varying between 3.0 and 3.4 Å. The structure is related to that of RECrSb₃ but with a different stacking of the metal-centered octahedra. Resistivity measurements reveal a shallow minimum near 25 K that is suggestive of Kondo lattice behavior, followed by a sharp decrease below 6 K.

Keywords: Cerium; Nickel; Antimonide; Crystal structure; Resistivity

1. Introduction

Rare-earth antimonides, particularly multinary phases containing transition metals, have elicited intense interest because of their important physical properties and unusual bonding. Colossal magnetoresistance has been identified in Eu₁₄MnSb₁₁ [1,2], and relatively simple binary antimonides, such as CeSb₂ and LaSb₂, have remarkably complex and highly anisotropic magnetic and magnetoresistance properties [3]. Pronounced f–p and f–d hybridization is believed to mediate magnetic exchange mechanisms in phases such as U₃MSb₅ (M = Fe, Co, Ni, Cu, Ru, Pd, Ag, Au) [4] and CeNiSb [5]. Itinerant electron ferromagnetism has been found in LaCrSb₃ and related phases [6].

An emerging feature in the structural chemistry of antimonides is the role of Sb–Sb bonds of variable strength in the formation of diverse anionic substructures such as discrete pairs (e.g., in Yb₃In₂Sb₆) [7], one-dimensional chains and ribbons (e.g., in La₁₃Ga₈Sb₂₁ and Pr₁₂Ga₉Sb₂₃) [8,9], and most pertinent to the present work, square nets (e.g., in LaSn₀.₇Sb₂) [10]. These square nets appear frequently not only in antimonides, but also in other heavier pnictides, chalcogenides, and tetrrelides. Application of the Zintl concept and other theoretical considerations suggest that a stable electron count for such square nets is six electrons per atom [11]. However, a \( \frac{2}{7} \) Sb¹⁻ net is prone to distortion, and the resulting changes in the electronic structure affect the electrical and magnetic properties.

Herein we report the synthesis, structure, and electrical resistivity of CeNiSb₃. Its structure is related to that of REVSb₃ and RECrSb₃ [12,13] but with more varied Sb–Sb bonding interactions.

2. Experimental

2.1. Synthesis

CeNiSb₃ can be synthesized by two methods, both of which are discussed. The single crystal used for X-ray
diffraction experiments was isolated from the reaction of Ce (99.9%, Alfa-Aesar), NiSb (99.5%, Alfa-Aesar), and Sb (99.5%, Alfa-Aesar) which were loaded in a fused-silica tube in a molar ratio of 1:2:5. The tube was sealed under vacuum and heated at 1123 K for 7 days followed by annealing at 873 K for 5 days. The tube was then cooled at 0.5 K min\(^{-1}\) to room temperature. The product consisted of excess Sb, black needles of NiSb\(_2\), and black tablets of CeNiSb\(_3\). Crystals of CeNiSb\(_3\) up to 1 mm in length and uncontaminated with NiSb\(_2\) could be isolated from the reaction of Ce, NiSb, and Sb in a 1:1:2 ratio under the same heating conditions but with the cooling rate reduced to 0.25 K min\(^{-1}\).

Large, high-quality single crystals of CeNiSb\(_3\) were also synthesized by a flux growth method. Ce ingot (99.95%, Ames Laboratory), Ni (99.995%, Alfa-Aesar), and Sb (99.9999%, Alfa-Aesar) were placed in an aluminacrucibleina1:2:20 ratio. The crucible and its contents were sealed in an evacuated fused-silica tube.

A tabular crystal of CeNiSb\(_3\) with dimensions of 0.112 × 0.020 × 0.048 mm and faces indexed as \{010\}, \{010\}, and \{001\} was mounted on a glass fiber with exposures (frames). Each set had a different exposure time per frame of 30 s. A total of 1800 frames were collected with an angle of 0.048 mm and faces indexed as \{010\}, \{001\}, and \{010\}.

2.2. Single crystal X-ray diffraction

A tabular crystal of CeNiSb\(_3\) with dimensions up to 2 × 2 × 1 mm\(^3\) were mechanically separated by centrifugation. Plate-like crystals with dimensions up to 2 × 2 × 1 mm\(^3\) were collected by a combination of three sets of sealed tube equipped with a monocapillary collimator.

Data were processed with the Bruker SAINT (v. 6.02) software package using a narrow-frame integration algorithm. A face-indexed analytical absorption correction was initially applied using XPREP [14]. Individual shells of unmerged data were corrected analytically and exported in the same format. These files were subsequently treated with a semi-empirical absorption correction by SADABS [15]. The program suite SHELXTL (v. 6.12) was used for space group determination (XPREP), direct methods structure solution (XS), and least-squares refinement (XL) [14]. The final refinements included anisotropic displacement parameters for all atoms and a secondary extinction parameter. Crystallographic details are listed in Table 1. Atomic positions and displacement parameters are listed in Table 2, and interatomic distances are listed in Table 3. Further details of the crystal structure investigation may be obtained from Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (Fax: (+49)7247-808-666; e-mail: crysdata@fiz-karlsruhe.de) on quoting the depository number CSD-39122.

2.3. Electrical resistivity

The electrical resistivity of a single crystal of CeNiSb\(_3\) along the crystallographic b-axis was measured by standard four-probe ac methods between 300 and 0.6 K using a Quantum Design PPMS instrument. Measurement on another crystal of similar dimensions confirmed that the results were reproducible.

| Table 1: Crystallographic data for CeNiSb\(_3\) |
|---|
| Formula | CeNiSb\(_3\) |
| Formula mass (amu) | 564.08 |
| Space group | Pbcm (No. 57) |
| a (Å) | 12.6340(7) |
| b (Å) | 6.2037(3) |
| c (Å) | 18.3698(9) |
| V (Å\(^3\)) | 1439.78(13) |
| Z | 12 |
| T (K) | 193 |
| \(\rho_{\text{calc}}\) (g cm\(^{-3}\)) | 7.807 |
| Crystal dimensions (mm) | 0.112 × 0.048 × 0.020 |
| Radiation | Graphite monochromated MoK\(_\alpha\), \(\lambda = 0.71073\) Å |
| \(\mu\) (MoK\(_\alpha\)) (cm\(^{-1}\)) | 296.1 |
| Transmission factors | 0.0362–0.5562 |
| 2θ limits | 3.22° ≤ 2θ(MoK\(_\alpha\)) ≤ 56.54° |
| Data collected | \(-16 ≤ h ≤ 16, -8 ≤ k ≤ 8, -24 ≤ l ≤ 24\) |
| No. of data collected | 13873 |
| No. of unique data, including \(F_o^2 < 0\) | 1845 (\(R_{int} = 0.0364\)) |
| No. of unique data, with \(F_o^2 > 2\sigma(F_o^2)\) | 1730 |
| Goodness of fit | 1.11 |
| \((\Delta\rho)_{\text{max}}, (\Delta\rho)_{\text{min}}\) (e Å\(^{-3}\)) | 1.109, -1.123 |

\(a R(F) = \frac{\sum |F_o| - |F_c|/\sum |F_o|}{\sum |F_o|^2}\) 
\(b R_{int}(F_o^2) = \frac{\sum |w(F_o^2 - F_c^2)|/\sum wF_o^4}{}\) 
where \(w = \left[\frac{\sigma^2(F_o^2) + (0.0163p)^2 + 4.4358p}{\max (F_o^2, 0) + 2F_o^2}\right]^{1/2}\)
3. Results and discussion

3.1. Structure

CeNiSb$_3$ crystallizes in a new structure type. As shown in Fig. 1, the structure can be viewed as being built up by inserting Ce atoms between a layer of condensed Ni-centered octahedra, $\frac{2}{2}[\text{NiSb}_2]$, and a buckled, nearly square net, $\frac{1}{2}[\text{Sb}]$. There are also additional Sb–Sb interactions within the $\frac{2}{2}[\text{NiSb}_2]$ layer.

Each of the two crystallographically inequivalent Ce atoms is nine-coordinate and adopts a monocapped square antiprismatic geometry, in which four Sb atoms in the $\frac{2}{2}[\text{Sb}]$ net form a square base, four Sb atoms in the $\frac{2}{2}[\text{NiSb}_2]$ layer form a larger square twisted 45° relative to the first, and one Sb atom caps this larger square (Fig. 1). The Ce atoms are located above and below the $\frac{2}{2}[\text{Sb}]$ square net in a “checkerboard” pattern. The Ce1–Sb distances of 3.2225(3)–3.3112(6) Å and the Ce2–Sb distances of 3.2260(3)–3.4509(4) Å are comparable to those in CeCrSb$_3$ (3.259(1)–3.334(1) Å) where the Ce atoms have a similar coordination geometry [12].

The $\frac{2}{2}[\text{NiSb}_2]$ layer contains two kinds of Ni-centered octahedra, Ni1(Sb4)$_{2/2}$(Sb5)$_{4/4}$ and Ni2(Sb2)$_{1/2}$(Sb4)$_{1/2}$ (Sb5)$_{2/4}$(Sb6)$_{2/4}$, that share edges in the $b$-direction and both edges and faces in the $c$-direction. The Ni1–Sb distances of 2.5899(6)–2.6049(6) Å and the Ni2–Sb distances of 2.5498(7)–2.6708(7) Å are similar to the average Ni–Sb distance of 2.608 Å in NiSb (NiAs-type) where octahedrally coordinated Ni is also found [16,17].

These octahedra are highly distorted, with Sb–Ni–Sb angles as acute as 136.89(4)° and 146.72(3)° subtending trans Sb atoms about the Ni1 and Ni2 atoms, respectively. Associated with this distortion is the occurrence of a short Ni2–Ni2 distance of 2.7214(12) Å.
within a pair of face-sharing octahedra (dashed horizontal lines in Fig. 1).

The 2\textsubscript{\textit{N}}\textsubscript{1/2}Sb\textsubscript{4/C138} net is formed by four-bonded Sb1 and Sb3 atoms (Fig. 2a). Whereas the Sb atoms are spaced regularly along the b-direction (Sb1–Sb1, 3.1031(2) Å; Sb3–Sb3, 3.1035(2) Å), there are small distortions along the c-direction (Sb1–Sb3, 3.0616(3) Å; Sb1–Sb1, 3.0880(6) Å). There is a slight buckling of the 2\textsubscript{\textit{N}}\textsubscript{1/2}Sb\textsubscript{4/C138} net so that the Sb1 and Sb3 atoms are displaced above or below the mean plane by ~0.05 Å. The net is not strictly square, with Sb–Sb–Sb angles ranging from 84.95(1)° to 94.94(1)°.

Extensive Sb–Sb interactions also pervade the 2\textsubscript{\textit{N}}\textsubscript{1/2}NiSb\textsubscript{2/C138} layer, with distances ranging from 3.0395(6) to 3.4358(6) Å (Fig. 2b). This Sb substructure can be roughly described as a three-layer stacking of 4\textsuperscript{4} nets. The two peripheral nets (made up of Sb2 and Sb4 atoms) are half as dense as and rotated by 45° to the intervening net made up of Sb5 and Sb6 atoms. If an arbitrary cutoff of 3.2 Å is used, Sb2–Sb6 pairs (3.0395(6) Å) and one-dimensional bands of Sb4 and Sb5 atoms (Sb4–Sb5, 3.1568(5) Å; Sb5–Sb5, 3.1714(2) Å) become evident.

3.2. Structural relationships

In previously known Ce–Ni–Sb phases, the Ni atoms are in trigonal planar (CN3 in CeNiSb (ZrBeSi-type)), tetrahedral (CN4 in CeNiSb\textsubscript{2} (ZrCuSi\textsubscript{2}-type) and CeNi\textsubscript{2–x}Sb\textsubscript{2} (CaBe\textsubscript{2}Ge\textsubscript{2}-type)), or square pyramidal (CN5 in CeNi\textsubscript{2–x}Sb\textsubscript{2} (CaBe\textsubscript{2}Ge\textsubscript{2}-type)) coordination [18–20]. In contrast, the Ni atoms are in octahedral coordination (CN6) in CeNiSb\textsubscript{3}. The structures of CeNiSb\textsubscript{3} and CeNiSb\textsubscript{2} are related in that the layers of Ni-centered octahedra 2\textsubscript{\textit{N}}\textsubscript{1/2}NiSb\textsubscript{2/C138} in CeNiSb\textsubscript{3} are replaced by layers of Ni-centered tetrahedra 2\textsubscript{\textit{N}}\textsubscript{1/2}NiSb\textsubscript{1/C138} in CeNiSb\textsubscript{2} [19], with the 2\textsubscript{\textit{N}}\textsubscript{1/2}Sb\textsubscript{4/C138} net and the arrangement of Ce atoms remaining intact. A closer relationship is found with the ternary rare-earth antimonides REVSb\textsubscript{3} and RECrSb\textsubscript{3} (for concreteness, CeCrSb\textsubscript{3} is shown in Fig. 3a) [6,12,13]. In CeCrSb\textsubscript{3}, chains of face-sharing metal-centered octahedra extend along the c-direction; these chains are connected by edge-sharing in the b-direction to form a 2\textsubscript{\textit{N}}\textsubscript{1/2}CrSb\textsubscript{2} layer parallel to the bc-plane (Fig. 3a). In CeNiSb\textsubscript{3}, every third metal-centered octahedron in the chains extending along the c-direction is connected by edge-sharing instead of...
face-sharing (Fig. 3b). The stacking sequence of the Sb atoms along the c-direction is AB in CeCrSb₃ and ABACBC in CeNiSb₃, or in Jagodzinski notation, h and hcc, respectively. CeNiSb₃ crystallizes in the same space group (Pbcm) as CeCrSb₃, but its c parameter is tripled, reflecting the more complicated stacking sequence.

3.3. Bonding

Interpretation of the bonding in CeNiSb₃ is complicated by the possibility of mixed +3/+4 valency on the Ce atoms, by the pairing of Ni atoms across the shared face of the octahedra, and by the rich variety of Sb–Sb interactions within the Sb substructure. The similarity of Ce–Sb distances in CeNiSb₃ to those in CeCrSb₃ argues for Ce³⁺, and it is reasonable to assume that the Ce atoms participate, to a first approximation, in ionic interactions with the other atoms in the structure. The Ni²–Ni₂ distance of 2.7214(12) Å is slightly longer than the analogous distance of ~2.560 Å found in NiSb [16,17], where metal–metal bonding has long been known to be important in stabilizing its structure [21]. Magnetic measurements might also clarify the oxidation state of the Ni atoms, but the assumption of localized moments is highly suspect given the observation of itinerant electron ferromagnetism in the related series of compounds RECrSb₃ [6]. In the absence of additional experimental data, the Sb substructure can be analyzed as a starting point.

The Sb–Sb distances in CeNiSb₃ (3.0395(6)–3.4358(6) Å) are longer than the intralayer distance (2.908 Å) and comparable to the interlayer distance (3.355 Å) found in elemental Sb [22]. The four-bonded Sb atoms within the $\frac{2}{\sqrt{3}}$ [Sb] square net can be assigned oxidation numbers of −1, if the Sb–Sb interactions are considered to be one-electron bonds and two lone pairs are localized on each atom so that an octet is attained. For the Sb atoms within the $\frac{2}{\sqrt{3}}$ [NiSb₂] layer, however, the assumption of integral oxidation numbers breaks down. An elegant way, proposed by Jeitschko et al., to enumerate electrons within such complex Sb substructures is to apply a bond valence calculation to derive formal charges on these Sb atoms [23]. When bond orders are calculated from the equation $v_{ij} = \exp[(2.80/d_{ij})/0.37]$ (where $d_{ij}$ is in Å), the formal charges of the Sb atoms in CeNiSb₃ are found to be −1.2 on Sb₁, −2.5 on Sb₂, −1.1 on Sb₃, −2.6 on Sb₄, −1.4 on Sb₅, and −1.6 on Sb₆. The charges on Sb₁ and Sb₃ are consistent with those in the simple model of one-electron bonds in a $\frac{2}{\sqrt{3}}$ [Sb] square net (Fig. 2a). The one-bonded Sb₂ and Sb₄ atoms (Fig. 2b) carry the most negative charges, whereas the Sb₅ and Sb₆ atoms have intermediate charges between these extremes. If these formal charges are rounded off to the nearest half-integer and when the multiplicity of atomic sites is taken into account, the total negative charge of approximately −60 on the Sb atoms within a unit cell can be compensated by assuming +3 charges on the Ce atoms and +2 charges on the Ni atoms: (Ce³⁺)$_{12}$(Ni²⁺)$_{12}$(Sb₆₀)⁰⁺ or Ce³⁺Ni²⁺(Sb₃)$^{5−}$. It is important to appreciate that the true charges are not likely to be as extreme as implied by these formulations. The caveat about the dangers of assuming a localized electron model has already been mentioned, and significant covalent character is expected in the Ni–Sb and perhaps even the Ce–Sb bonds. It would be interesting to perform a band structure calculation to understand the bonding in more detail.
3.4. Electrical resistivity

Fig. 4 shows the temperature dependence of the electrical resistivity of a single crystal of CeNiSb$_3$ along the $b$-axis. Metallic behavior is observed with a prominent curvature in the plot, which exhibits a minimum near 25 K, followed by a steep decrease at 6 K. This behavior is typical of magnetically ordered Kondo lattices with a localized $f$ moment weakly coupled to the conduction bands. The resistivity plot bears a striking resemblance to that of CeSn$_{0.7}$Sb$_2$, a ferromagnetic layered antimonide with a similar arrangement of Ce atoms and Ce–Ce distances as in CeNiSb$_3$. It is likely that the transitions in the resistivity curve can be attributed to the Ce moments. Further experiments to measure the magnetic and transport properties would be helpful in clarifying the electronic structure of CeNiSb$_3$.

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