High-Pressure Synthesis and Properties of a Cerium Germanide $CeGe_3$ with the Cubic Cu_3Au Type Structure

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A new cerium germanide, $CeGe_3$ was prepared by the reaction of a stoichiometric mixture of $CeGe_2$ and Ge under a pressure of 5 GPa at 1600 °C. It crystallized in a cubic unit cell with $a = 4.354$ (4) Å, and was isotypic with $CeSn_3$ and $CePb_3$ having the Cu_3Au structure. It showed a Curie–Weiss paramagnetic behavior from room temperature to 20 K with a Curie constant C of 0.0495 emu mol^{-1}·K. The effective magnetic moment of 0.63 μ_B, which was much smaller than the theoretical values of 2.54 μ_B for Ce^{3+} ($4f^1$) ions, was observed. This compound showed a metallic behavior with the resistivity of 130 and 7 $\mu\Omega$·cm at room temperature and 2 K, respectively.

Among a series of the cerium intermetallic compounds, $CeSn_3$ has attracted much attention of materials scientists. It is a typical heavy fermion compound and shows many interesting physical properties including the high electronic specific heat constant, the large thermal expansion, high bulk susceptibility with a Curie–Weiss behavior, and so on.[1] These unusual properties have been extensively investigated on theoretical and experimental aspects. In the physics of this compound, the 4f electrons play the most important role.

For further investigations of the properties, it is important to study isotypic compounds like $CePb_3$ and $CeGe_3$. The latter germanide, however, has not been reported. In the present study, we have investigated the cerium–germanium binary system using high-pressure and high-temperature reactions, and found the new germanide $CeGe_3$ with the Cu_3Au type structure.

Blocks of cerium metal (Furu-uchi Chemical 99.9%) and germanium (Mitsuwa Pure Chemical 99.999%) were mixed with an atomic ratio of Ce:Ge = 1:3. The mixture was reacted in an arc furnace filled with Ar gas. The product was ground in an Ar-filled glove box, and then put into an h-BN cell (5 mm in inner diameter and 5 mm in depth). The cell was placed in a carbon tube heater, and was put in a pyrophyllite cube as pressure media ($20 \times 20 \times 20$ mm^3). A detailed cell assembly was described elsewhere.[2] The cube was pressed at a pressure of 5 GPa in a multi-anvil press and heated at 1600 °C for 30 min, followed by quenching to room temperature. After the reaction the pressure was gradually released to the ambient pressure.

X-ray powder diffraction (XRD) pattern of the product was measured with an X-ray diffractometer (Mac Science, model M18XHF) using graphite monochromated Cu Kα radiation. Magnetic susceptibility was measured from room temperature to 2 K using a SQUID magnetometer (Quantum Design MPMS-5S) under a field of 5000 Oe on a field-cooled sample. The temperature dependence of electrical resistivity was measured by four prove method (van der Pauw method). The chemical composition analysis was performed using an electron probe microanalyzer (EPMA) (JEOL, JCMA-733).

After the reaction in the arc furnace, a mixture of $CeGe_2$ with the α-$ThSi_2$ structure, and unreacted Ge was obtained. There were no additional peaks on the XRD chart of the product as shown in Figure 1a. On treating the product under a pressure of 5 GPa at 1600 °C, a new cerium germanide was obtained (in Figure 1b). The simulated XRD pattern assuming the Cu_3Au structure, which is presented in Figure 1c, was quite similar with the observed one and the new compound was identified as $CeGe_3$. It crystallized in a cubic unit cell with $a = 4.354(4)$ Å. The EPMA measurement showed that the composition of the product (b) was $CeGe_{2.99}$, in agreement with the composition of $CeGe_3$.

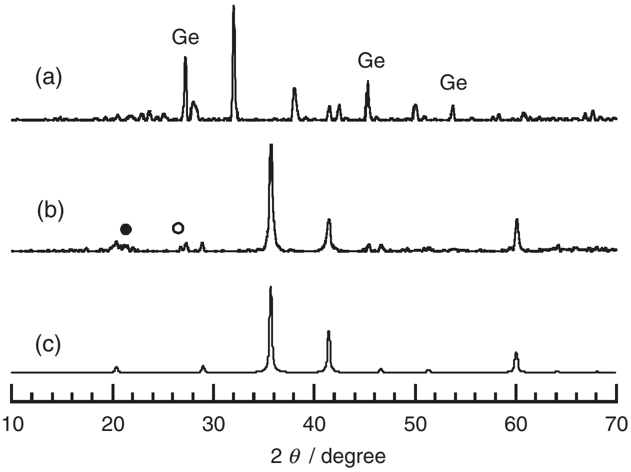

Figure 1. X-ray powder diffraction patterns of the sample (a) before and (b) after the high pressure treatment, and (c) simulated for $CeGe_3$. Peaks marked with ● and ○ are due to a glass sample folder and BN, respectively.

The structure of $CeGe_3$ is illustrated in Figure 2. The structure can be derived from the fcc structure. Putting Ge atoms on the face center positions of a cubic cell, and Ce atoms on the origin, results in this structure. The structure also can be seen as a perovskite-related structure. When the B atoms of the perovskite ABO_3 are pulled out, and Ce and Ge atoms are situated in the A and O positions, respectively, the structure of $CeGe_3$ is derived. In $CeGe_3$, each Ge atom has eight neighboring Ge, and four Ce atoms. The Ge–Ge distance is 3.077 Å. Since the covalent radius of Ge is 1.22 Å, there are only weak bondings between the neighboring Ge–Ge atoms. The Ce ions are surrounded by 12 Ge atoms with the Ce–Ge distances of 3.077 Å.

This compound is isotypic with $CeSn_3$. The Ce–Sn distance in $CeSn_3$ is 3.339 Å. Since the atomic radius of Sn is larger than that of Ge by 0.22 Å, the Ce–Ge distance is estimated to be 3.119 Å from the Ce–Sn distance. Here we used atomic radii

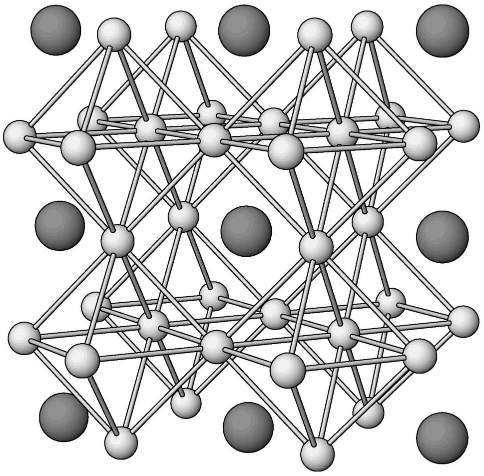

Figure 2. Schematic ball and stick illustration of the crystal structure of $CeGe_3$. Ce and Ge atoms are represented as filled large and open small balls, respectively. Neighboring Ge atoms are connected with sticks.

of Ge and Sn calculated from their allotropes with the β-Sn structure. The observed Ce–Ge distance of 3.077 Å is shorter than the estimated one. The Ce atoms are, therefore, situated in smaller spaces in $CeGe_3$ than in $CeSn_3$. This result may suggest that $CeGe_3$ contains much more tetravalent Ce ions than $CeSn_3$.

The temperature dependence of the electrical resistivity of $CeGe_3$ is shown in Figure 3. It showed a metallic property, and gradually decreased with decreasing temperature. It became constant from 20 to 2 K and the residual resistivity of $7\,\mu\Omega\cdot$cm was observed at 2 K. The resistivity of $CeSn_3$ measured on a single crystal was $30\,\mu\Omega\cdot$cm at 300 K and the residual resistivity was $10\,\mu\Omega\cdot$cm.[3] Though the resistivity of $CeGe_3$ is larger than that of $CeSn_3$ at room temperature, both compounds are metals.

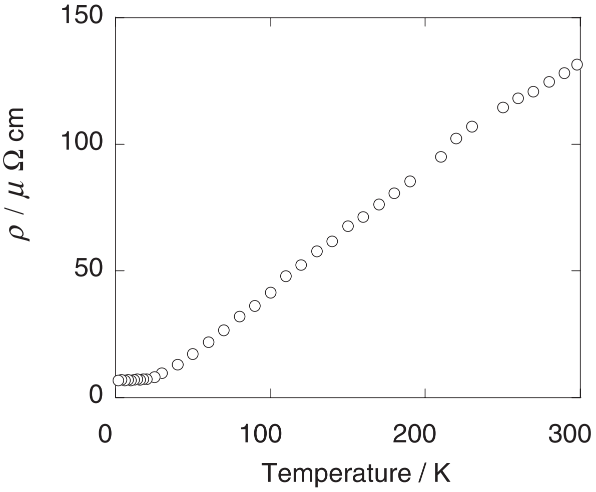

Figure 3. Temperature dependence of the resistivity of $CeGe_3$.

The magnetic susceptibility of $CeSn_3$ showed a broadened maximum at around 150 K due to the intermediate valence behavior of Ce ions.[4] No such anomaly in susceptibility was observed for $CeGe_3$. $CeGe_3$ showed Curie–Weiss behavior in the temperature region of 15 to 300 K with a Curie constant of 0.0495 emu mol$^{-1}\cdot$K. It corresponded to an effective magnetic moment of $0.63\,\mu_B$. Since the theoretical magnetic moment of Ce^{3+} ($4f^1$) ions is $2.54\,\mu_B$, about 75% of the Ce ions are in the 4+ oxidation state. $CePb_3$ also shows Curie–Weiss behavior from 200 to 600 K.[5] The magnetic moment of Ce is $2.32\,\mu_B$, close to that one expected for Ce^{3+} ions. The valence of Ce ions at room temperature increases in order of $CePb_3$, $CeSn_3$, and $CeGe_3$, respectively. $CeGe_3$ showed an antiferromagnetic transition at 12 K, though the mechanism of the transition is not clear. Further investigation should be necessary for understanding of the magnetic behavior and the valence state of Ce ions in $CeGe_3$.

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