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New intermetallic compounds found in Hf–Ni–Ge and Hf–Pt–Ge systems

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Abstract

New intermetallic compounds, $Hf_3Ni_4Ge_4$ and HfPtGe, were found and their crystallographic, electric and magnetic properties were characterized. $Hf_3Ni_4Ge_4$ has an orthorhombic structure (space group *Immm*) with lattice constants of $a=1.2873$ nm, $b=0.6484$ nm, and $c=0.3892$ nm and shows typical Curie-paramagnetic behavior between 2 K and 300 K and a metallic temperature dependence of the resistivity at temperatures between 10 and 250 K. HfPtGe has an orthorhombic structure (space group *Pnma*) with lattice constants of $a=0.6603$ nm, $b=0.3950$ nm, and $c=0.7617$ nm and shows diamagnetism and a metallic temperature dependence of the resistivity.

Keywords: Ternary hafnium compounds; Crystal structure; Magnetic properties; Electrical resistivity

1. Introduction

Since the discovery of high-T_c superconductivity many cuprate superconductors have been found. However, the use of high-T_c superconductivity has been limited to a few areas. In general, high-T_c cuprate superconductors are very brittle because they are oxides, and this is why their application has been limited. Although researchers have attempted to rectify this problem, a solution is not yet in sight. Intermetallic compound superconductors appears to have an important advantage over cuprate superconductors because their processing technology has been established. However, the superconducting transition temperature of practical intermetallic compounds still remains at low temperature below 20 K. Therefore, they must be used at temperatures below 20 K using expensive coolant and cooling systems. If a new high-T_c superconductor is discovered in an intermetallic system, superconductivity can be used more widely. From this perspective, the search for new intermetallic compounds is believed to be important. Recently, high-T_c superconductors with a superconducting transition temperature T_c as high as 23 K were discovered in Y-Ni–B–C and Y–Pd–B–C systems and their superconducting properties have been characterized [1–3]. The transition temperatures of these compounds, however, are still too low for practical use. Since there is high potential that new high-T_c superconductors can be discovered in intermetallic systems, it is still necessary to search for new superconducting compounds in them.

This study was performed based on the needs to discover new intermetallic compounds and to find new superconductors. Although new superconductors have not been found, two new intermetallic compounds $Hf_3Ni_4Ge_4$ and HfPtGe were discovered in the Hf–Ni–Ge and Hf–Pt–Ge systems. This paper presents the results of crystallographic analysis and electric and magnetic measurements performed for these compounds.

2. Experimental method

Polycrystalline specimens of $Hf_3Ni_4Ge_4$ and HfPtGe were prepared by the arc-melting and subsequent heat treatment. For $Hf_3Ni_4Ge_4$, a stoichiometric mixture of Hf (99.9%), Ni (99.9%) and Ge (99.999%) was melted in an arc-furnace in a zirconium gettered argon atmosphere. The mixture was further sealed in a quartz ampoule with argon gas (194 Torr) after being evacuated to 5×10^{-5} Torr. The mixture was heated to 900°C in a quartz ampoule using an electric furnace. An inner argon gas pressure of 760 Torr is established at 900°C. After the temperature was maintained at 900°C for three days, the ampoule was quenched into

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water. HfPtGe, on the other hand, was prepared by arc-melting a stoichiometric mixture of Hf (99.9%), Pt (99.999%) and Ge (99.999%) and subsequent heat treatment of the mixture. The heat treatment was performed by the same procedure as that used for $Hf_3Ni_4Ge_4$.

The chemical composition of the compounds was determined by electron-probe micro-analysis (EPMA) using wave-length dispersive spectrometers. Crystallographic analysis was performed by X-ray powder diffraction using CuKα radiation, and the diffraction data were refined by the Rietveld method. The electrical resistivity was measured by a conventional DC four-probe method at temperatures from 10 K to 300 K. Electrical leads were made by spark-bonding gold-wires (50 μm) onto a polished surface of the specimen. Magnetic measurements were performed by a superconducting quantum interference device (SQUID) magnetometer at temperatures between 2 and 300 K in an applied magnetic field up to 10 kOe.

3. Results and discussion

3.1. $Hf_3Ni_4Ge_4$

A single phase specimen was obtained when an as-cast specimen, which was prepared by arc-melting raw materials that had a stoichiometric composition, was annealed at 900°C for 3 days. The results of X-ray powder diffraction and subsequent refinement of the diffraction data are shown in Fig. 1. The diffraction data can be explained by assuming an orthorhombic structure of a space group of *Immm* and lattice constants of $a=1.2873$ nm, $b=0.6484$ nm, and $c=0.3892$ nm. The crystallographic parameters are listed in Table 1 and the possible crystal structure of $Hf_3Ni_4Ge_4$ is shown in Fig. 2. This structure is analogous to that of $Hf_3Cu_4Si_4$ [4].

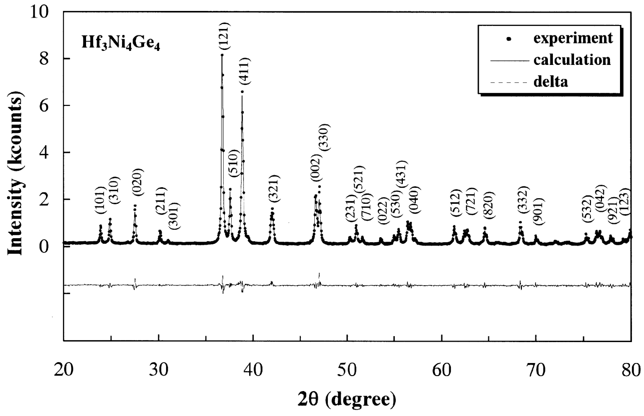

Fig. 1. The results of X-ray powder diffraction and refinement of the diffraction data for $Hf_3Ni_4Ge_4$.

Table 1
Crystal structure parameters of $Hf_3Ni_4Ge_4$

Space group:	*Immm*, orthorhombic				
Lattice parameters:	$a=1.2873$ nm, $b=0.6484$ nm, $c=0.3892$ nm				
Structure type:	$Hf_3Cu_4Si_4$				
Density:	10.845 g cm^{-3}				
Atomic parameters:	Atom	Site	*x*	*y*	*z*
	Hf 1	2*d*	0.5	0	0.5
	Hf 2	4*e*	0.1276	0	0
	Ni	8*n*	0.3239	0.2013	0
	Ge 1	4*f*	0.2149	0.5	0
	Ge 2	4*h*	0	0.1963	0.5

In Fig. 3 the temperature dependence of molar magnetic susceptibility which was measured in a magnetic field of 10 kOe is shown. The susceptibility $\chi_{obs}(T)$ shows paramagnetic behavior at temperatures between 2 K and 350 K and decreases as the temperature increases. The $\chi_{obs}(T)$ can be fitted by the equation $\chi_{obs}(T)=\chi_0+C_{mol}/(T-\theta)$, where the second term indicates the Curie-Weiss law and χ_0, θ and C_{mol} are, respectively, the temperature independent susceptibility, the paramagnetic Curie temperature, and the Curie constant. $\chi_0=1.23\times10^{-4}$ emu mol^{-1} was obtained by the fitting. When χ_0 is subtracted from $\chi_{obs}(T)$, the residual susceptibility $\chi_{obs}(T)-\chi_0$ shows typical paramagnetic behavior. The reciprocal of $\chi_{obs}(T)-\chi_0$ is also shown in Fig. 3. The reciprocal susceptibility appears to have a linear temperature dependence and the data can be fitted by the reciprocal of the Curie-Weiss law which is given by $1/\chi_{mol}=(T-\theta)/C_{mol}$. $\theta=0.29$ K and $C_{mol}=3.38\times10^{-3}$ emu mol^{-1} were obtained by the fitting. Since the paramagnetic Curie θ is very close to zero, $Hf_3Ni_4Ge_4$ is thought to be a paramagnet. The effective magnetic moment $P_{eff}=0.165$ μ_B/formula-unit was deduced from the Curie constant C_{mol}. Since there are four nickel atoms in the formula of $Hf_3Ni_4Ge_4$, magnetic moment of 0.041 μ_B is assigned to one nickel atom. Therefore, a magnetic moment of 0.041 μ_B localizes at the Ni sites and the paramagnetism originates from the localized Ni moments. The value 0.041 μ_B is considerably small in comparison with the value $0.6\mu_B$ of fcc Ni. Presumably, the unoccupied 3d band of Ni is partially filled by electrons that were introduced by hybridization between Ni and Ge electron orbitals and the Ni moment is suppressed almost in $Hf_3Ni_4Ge_4$. The reason why χ_0 has a considerably large value is unclear at present.

In Fig. 4 the temperature dependence of the electrical resistivity of $Hf_3Ni_4Ge_4$ is shown. The resistivity increases as the temperature increases. At high temperatures, however, the behavior of $\rho(T)$ differs from that of conventional metals; and the slope $d\rho/dT$ decreases as the temperature increases. This behavior cannot be explained by the Bloch-Grüneisen formula. Since Ni has a negligibly small moment, the magnetic contribution to $\rho(T)$ must be very small. Therefore, $\rho(T)$ of $Hf_3Ni_4Ge_4$ could be explained by taking account of impurity- and phonon-scattering of conduction electrons. Wiesmann et al. and Ramakrishnan et al. used a parallel resistor model to explain the transport

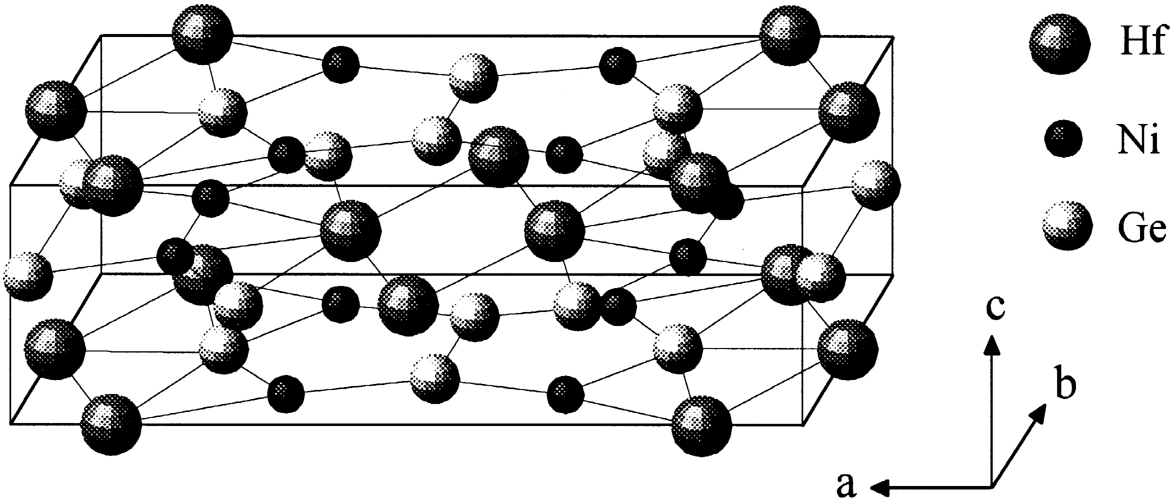

Fig. 2. Possible crystal structure of $Hf_3Ni_4Ge_4$.

properties of silicides and germanides [5,6]. According to the model $\rho(T)$ is represented by the expression

$$\frac{1}{\rho(T)}=\frac{1}{\rho_{rp}(T)}+\frac{1}{\rho_{max}}, \tag{1}$$

where $\rho_{rp}(T)$ is the sum of the residual resistivity ρ_0 and phonon-assisted resistivity $\rho_{ph}(T)$ and ρ_{max} is the saturation resistivity which is independent of temperature. The parallel resistor model was applied to explain $\rho(T)$ of $Hf_3Ni_4Ge_4$. Although the Grüneisen-like formula has been used for the phonon-assisted resistivity $\rho_{ph}(T)$, in this study a simple formula which was derived by the Bose-Einstein statistics was used for $\rho_{rp}(T)$. If it is assumed that the phonon-assisted resistivity is caused by thermal phonons with a flat energy distribution from E_1 to E_2, $\rho_{ph}(T)$ is given by

$$\rho_{ph}(T)=\alpha[(E_1-E_2)/k_B + T\ln\{(e^{E_2/k_BT}-1)/(e^{E_1/k_BT}-1)\}], \tag{2}$$

where α and k_B are the fitting coefficient and Boltzmann's constant. The result of the fitting is shown by the solid line in Fig. 4 and the parameters ρ_0, α, E_1, E_2, and ρ_{max} obtained by the fitting are, respectively, 1.63×10^{-5} Ωcm, 1.28×10^{-5}, 11.1 meV, 11.8 meV and 4.31×10^{-4} Ωcm. Since the difference between E_1 and E_2 is very small, the thermal phonon which contributes to $\rho_{ph}(T)$ appears to have an energy of about 11 meV.

3.2. HfPtGe

In Fig. 5 the results of X-ray powder diffraction for an as-cast specimen of HfPtGe and subsequent refinement of

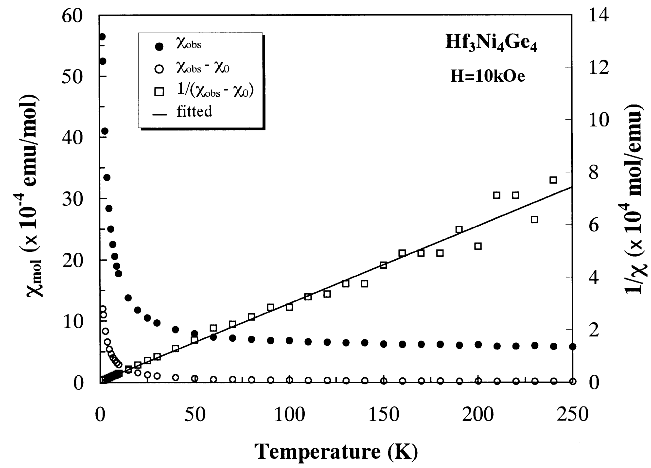

Fig. 3. Temperature dependence of the molar magnetic susceptibility and the reciprocal magnetic susceptibility as measured for $Hf_3Ni_4Ge_4$ at 10 kOe. The solid line shows the result of calculation by means of the Curie-Weiss law.

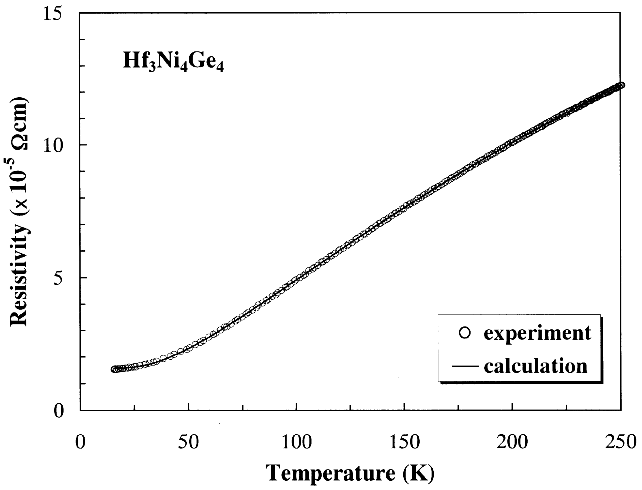

Fig. 4. Temperature dependence of the electrical resistivity as measured for $Hf_3Ni_4Ge_4$. The solid line shows the results of the least mean squares fitting by means of parallel resistor model.

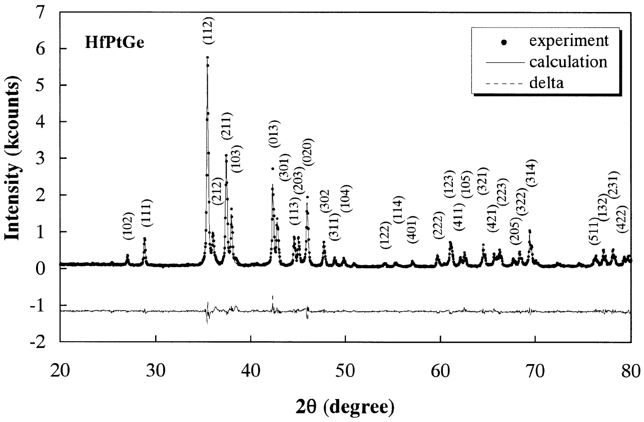

Fig. 5. The results of X-ray powder diffraction and refinement of the diffraction data for an as-melt specimen of HfPtGe.

the diffraction data are shown. Unlike $Hf_3Ni_4Ge_4$, a single phase specimen was obtained by melting a stoichiometric mixture of Hf, Pt, and Ge without any heat treatment. The diffraction data can be fitted by assuming an orthorhombic structure of space group of *Pnma* and lattice constants of $a=0.6603$ nm, $b=0.3950$ nm and $c=0.7617$ nm. This structure is very similar to that of the silicide Co_2Si [7]. The crystal structure parameters are listed in Table 2 and the possible crystal structure of HfPtGe is shown in Fig. 6.

In Fig. 7 the temperature dependence of magnetic susceptibility χ_{mol}, which was measured at a magnetic field of 10 kOe, is shown. The susceptibility shows diamagnetic behavior and appears to be almost constant at temperatures between 10 K and 350 K. In Fig. 8 the field dependence of the magnetization measured at 5 K is shown. The magnetization shows an almost linear field dependence with a negative slope. This clearly indicates the diamagnetism of HfPtGe. In general, the magnetic susceptibility of metals is given by $\chi=\chi_{\mathrm{Pauli}}+\chi_{\mathrm{core}}+\chi_{\mathrm{vV}}+\chi_{\mathrm{Landau}}$, where χ_{Pauli}, χ_{core}, χ_{vV} and χ_{Landau} are, respectively, Pauli-, core-, van Vleck- and Landau-susceptibility. Among these, the diamagnetic susceptibility is caused by χ_{core} and χ_{Landau}. Since χ_{core} and χ_{Landau} are, respectively, independent and dependent of temperature, the diamagnetic susceptibility of HfPtGe appears to come from χ_{core}: However, details about the diamagnetism of HfPtGe are as yet unclear. More data are necessary for a further understanding of the magnetism of HfPtGe.

Table 2
Crystal structure parameters of HfPtGe

Space group:	*Pnma*, orthorhombic				
Lattice parameters:	$a=0.6603$ nm, $b=0.3950$ nm, $c=0.7617$ nm				
Structure type:	Co_2Si				
Density:	14.917 g cm^{-3}				
Atomic parameters:	Atom	Site	*x*	*y*	*z*
	Hf	4*c*	0.0299	1/4	0.1863
	Pt	4*c*	0.1425	1/4	0.5617
	Ge	4*c*	0.7506	1/4	0.6215

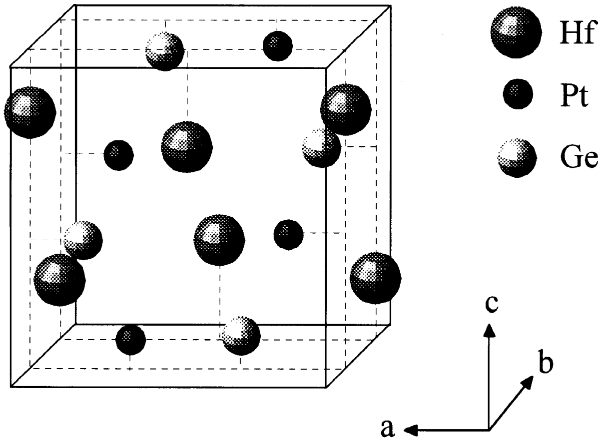

Fig. 6. Possible crystal structure of HfPtGe.

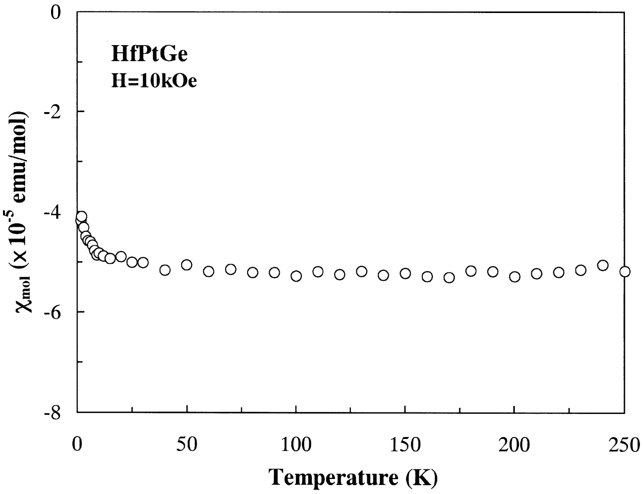

Fig. 7. Temperature dependence of the molar magnetic susceptibility as measured for HfPtGe at 10 kOe.

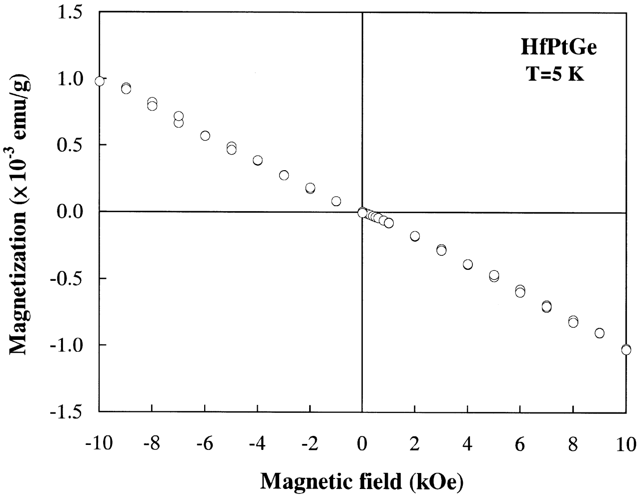

Fig. 8. The field dependence of the magnetization as measured for HfPtGe at 5 K.

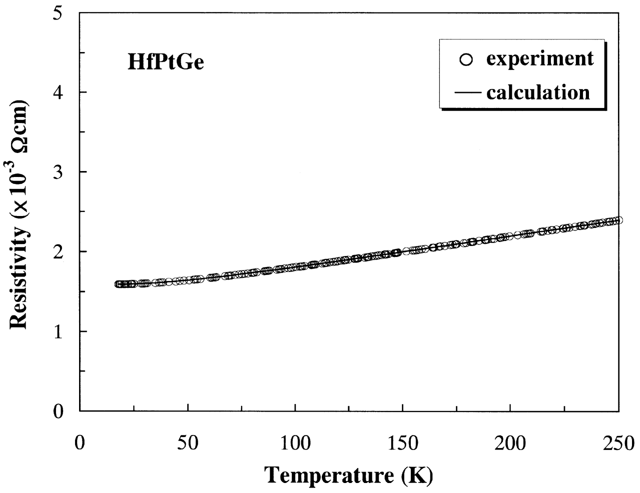

Fig. 9. Temperature dependence of the electrical resistivity as measured for HfPtGe. The solid line shows the result of the least mean squares fitting by means of parallel resistor model.

In Fig. 9 the temperature dependence of the electrical resistivity of HfPtGe is shown. Although the resistivity shows metallic behavior, the temperature dependence is much smaller than that of $Hf_3Ni_4Ge_4$. Moreover, a considerably large residual resistivity was observed at low temperature. This suggests that the purity of the specimen is still low. $\rho(T)$ can be explained by the parallel resistor model that was used for $\rho(T)$ of $Hf_3Ni_4Ge_4$. The experimental results could be fitted when $\rho_0 = 1.59 \times 10^{-3}$ Ωcm, $\alpha = 4.41 \times 10^{-5}$, $E_1 = 9.49$ meV, $E_2 = 10.4$ meV and $\rho_{\max} = 7.66$ Ωcm were used, and the result of fitting is shown by the solid line in Fig. 9. The value of E_1 is very close to that of E_2: Therefore, thermal phonons with an excitation energy of about 10meV are thought to have contributed to $\rho_{ph}(T)$.

4. Conclusion

New intermetallic compounds were found in the Hf–Ni–Ge and Hf–Pt–Ge systems and their crystallographic, electric and magnetic properties were characterized. One of the compounds has the chemical formula $Hf_3Ni_4Ge_4$ and has an orthorhombic structure (space group *Immm*) with lattice constants of $a = 1.2873$ nm, $b = 0.6484$ nm and $c = 0.3892$ nm. The resistivity of $Hf_3Ni_4Ge_4$ shows metallic behavior at temperatures between 10 and 250 K and the magnetic susceptibility shows typical Curie-paramagnetic behavior between 2 K and 300 K. The other compound, HfPtGe, has an orthorhombic structure (space group *Pnma*) with lattice constants of $a = 0.6603$ nm, $b = 0.3950$ nm and $c = 0.7617$ nm and shows diamagnetic behavior and a metallic temperature dependence of the resistivity.

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