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Structure, Stoichiometry, and Properties of the Chimney-Ladder Phases Ru_2Ge_{3+x} ($0 < x < 1$)

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The preparation and physical characterization of non-stoichiometric Ru_2Ge_{3+x} ($0 \leq x \leq 1$) are reported for the first time. The defect $TiSi_2$-type chimney-ladder structure is maintained for the full stoichiometry range. The resistivity of Ru_2Ge_{3+x} increases systematically with x from 300 mΩ cm, $x = 0$–3 Ω cm, $x = 1$ at 300 K. The temperature dependence is consistent with a variable range-hopping mechanism for $x \geq 0.6$. The Seebeck coefficients of samples do not evolve simply with x. A low thermal conductivity ($\kappa_{300\,K} = 0.03$ W/K cm) suggests that Ru_2Ge_3 has some of the properties of a phonon-glass–electron-crystal. The low value of the thermoelectric figure of merit $ZT = 3.2 \times 10^{-3}$ ($T = 300$ K) calculated for Ru_2Ge_3 is due primarily to a low conductivity. © 2002 Elsevier Science (USA)

Key Words: **Ru_2Ge_3; electronic properties; incommensurate structure.**

INTRODUCTION

The search for new thermoelectrics is dominated by the need to minimize the thermal conductivity of materials while maximizing their electronic conductivity. The traditional strategy to optimize these conflicting parameters involves selecting semiconducting compounds containing heavy elements and then reducing their thermal conductivity by introducing crystallographic disorder. Recent investigations, however, have utilized the concept of the phonon-glass–electron-crystal (PGEC) proposed by Slack (1) as being optimal for good thermoelectric properties. The PGEC concept describes a material which has an open semiconducting or semimetallic framework (electron-crystal) containing loosely bound guest atoms (phonon–glass). These guest atoms rattle within the framework producing low–frequency anharmonic modes, which strongly scatter the heat–carrying acoustic modes of the material, thus reducing the thermal conductivity to glass–like values without serious detriment to the electronic conductivity. A similar kind of dampening of the heat–carrying phonon modes may also be possible for structures displaying incommensurate lattices.

The two-component nature of the Nowotny chimney-ladder structure suggests that it may have some of the desirable characteristics of a PGEC material. The Nowotny chimney-ladder compounds, $TX_{2-\delta}$, sometimes found for transition metal silicides and germanides, have crystal structures based on $TiSi_2$ (2). This structure consists of a rigid T sublattice (the chimneys) formed by hexagonal close-packed layers of metals stacked in a four-layer repeat. The X atoms, the "ladders", are located within this framework, as shown in Fig. 1. As the T:X ratio is reduced (i.e., as δ is increased) the T lattice remains virtually unchanged. The X lattice, however, becomes extended due to its reduced density. The periodicities of the two sublattices are in general not equal, and are incommensurate with respect to each other. Commensurate structures are observed in the special cases where δ is a rational fraction, as shown in Fig. 1 (2–6).

The Ru_2X_3 ($X = $ Si, Ge, Sn) binary compounds all exhibit Nowotny chimney-ladder structures, and are reported to be semiconducting for $X = $ Si and Ge (7). In addition, electronic band structure calculations performed for Ru_2Ge_3 indicate that the electronic states near the Fermi energy have dominant contributions from the Ru d-orbitals (8, 9). This suggests that the picture of the interconnected Ru lattice as an electron-crystal containing within it a Ge phonon-glass may be applicable, and that these may be good thermoelectric materials.

The Ru_2X_3 ($X = $ Si, Ge, Sn) binary compounds all exhibit diffusionless phase transitions at elevated temperatures. In the specific case of Ru_2Ge_3, this involves a transformation from a high-temperature tetragonal structure (space group P-4c2) to a low-temperature orthorhombic structure (space group $Pbcn$) associated with the displacement of the group

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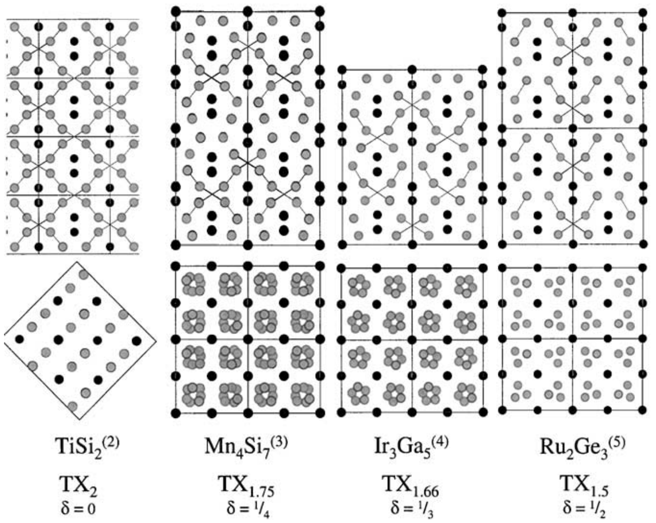

FIG. 1. The evolution of the idealized crystal structures of Nowotny chimney-ladder phases $TX_{2-\delta}$. The quasi-static T lattice is marked with dark atoms and the expansion of the stoichiometrically variable X lattice is indicated by the light atoms. The bonds marked between light atoms are meant only as a guide to the eye.

IV atoms within the static Ru lattice ($T_{\text{trans}} \approx 500°\text{C}$) (10). The transformation is reversible and occurs over a relatively wide temperature range. There are only limited data available on the electronic properties of the ruthenium-based chimney-ladder phases, suggesting that a thorough examination with an emphasis on possible thermoelectric properties is of interest.

EXPERIMENTAL

Chimney-ladder structures have been observed over a large stoichiometric range, (Fig. 1). Ru_2Ge_3, however, has not previously been reported to have a significant stoichiometric variation. This prompted us to investigate the range of Ru:Ge stoichiometry over which this structure type is stable in the Ru–Ge system. To this end, samples of stoichiometry Ru_2Ge_{3+x} ($x = 0$, 0.2, 0.4, 0.6, 0.8, 1) were prepared, and their physical properties measured. All samples were prepared by arc melting the elements three times under an Ar atmosphere. The melted buttons were then individually wrapped in Ta foil, sealed in evacuated quartz ampoules and annealed for 7 days at 950°C. The ampoules were then quenched to room temperature in water. Samples were weighed prior to and after annealing to confirm that no material was lost during sample preparation (maximum observed mass loss: 0.3%). The phase purity and structural evolution of the annealed samples were assessed by X-ray powder diffraction (Rigaku miniflex, Cu$K\alpha$ radiation). The annealed buttons were cut into bars (approximate dimensions: $1 \times 1 \times 4\,\text{mm}^3$) which were employed in resistivity and Seebeck coefficient measurements. Resistivity measurements were performed using a standard four-point AC method utilizing a Quantum Design PPMS instrument. The Seebeck coefficients of samples were measured using commercially available apparatus (MMR Technologies). Field-cooled magnetic susceptibility measurements were performed on powder samples in an applied field of 10 000 Oe using a Quantum Design PPMS magnetometer. The thermal conductivity of samples was measured by the longitudinal steady-state method.

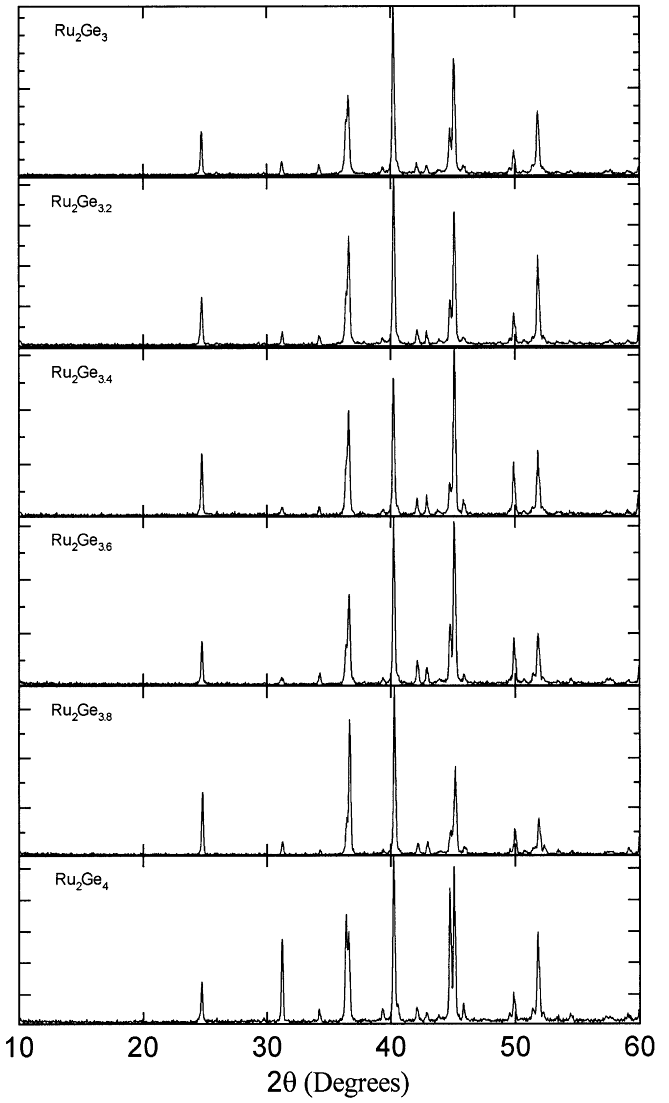

FIG. 2. The X-ray powder diffraction data showing the structural evolution of Ru_2Ge_{3+x} with x. All patterns can be indexed using the high-temperature orthorhombic unit cell proposed for Ru_2Ge_3.

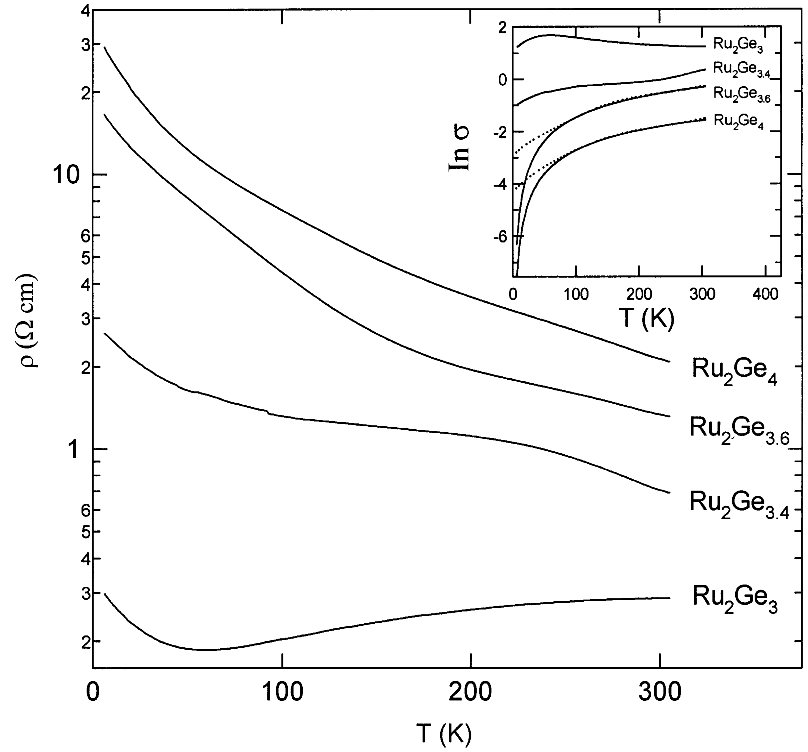

FIG. 3. Resistivity data for selected Ru_2Ge_{3+x} samples showing the evolution from a low-temperature dependence at $x = 0$ to a strong temperature dependence at $x = 1$. The inset plots $\ln\sigma$ against temperature. The fits for the $x = 0.6$ and 1 data correspond to a $T^{1/4}$ dependence, characteristic of three-dimensional variable range hopping.

RESULTS

The evolution of the X-ray powder diffraction pattern of Ru_2Ge_{3+x} with x is shown in Fig. 2. It can be seen that all the Ru:Ge ratios prepared react to form single phase samples which can be readily indexed using the orthorhombic unit cell reported for $Ru_2Ge_{3.0}$ (space group *Pnca*, $a = 5.718$ Å, $b = 11.436$ Å, $c = 9.240$ Å (5)). This is contrary to reports that Ru_2Ge_3 adopts a non-centrosymmetric tetragonal structure at high temperatures ($T > 550$°C (10)) and suggests that excess Ge stabilizes the lower symmetry structure.

There is no evidence, in the diffraction data, of a structural transition or any significant expansion of the lattice parameters with increasing x (Δvolume$<0.2\%$). This indicates that the additional Ge is inserted into the incompletely filled channels formed by the Ru sublattice with almost no change in the size of the Ru sublattice. Close examination of the powder diffraction data do not reveal any supercell reflections or unindexed peaks associated with the evolution of the Ge sub-lattice crystallographic repeat, relative to the quasi-static Ru lattice. The lack of such reflections suggests that the Ge sublattice displays a significant level of disorder, a situation common in materials which have been rapidly quenched from high temperatures. Samples which were slow cooled, rather than rapidly quenched, displayed elemental germanium in their diffraction patterns (the amount observed increasing with x). This indicates that phase separation occurs at some temperature below 975°C, presumably to form stoichiometric $Ru_2Ge_{3.0}$ and elemental Ge.

A detailed structural analysis of the prepared material is beyond the scope of the present study. However, the observations are sufficient to conclude that Ru_2Ge_3 tolerates gross non-stoichiometry, an observation not previously reported. All compositions in the range Ru_2Ge_{3+x}, $0 < x < 1$, when annealed at 975°C and quenched to avoid low-temperature phase separation, crystallize in a continuous set of structures which are related by the incommensurate filling of the almost invariant Ru sublattice with Ge, in a manner akin to the scheme shown in Fig. 1.

Figure 3 shows the evolution of the temperature-dependent electrical resistivity of Ru_2Ge_{3+x} with increasing x. The resistivity of all samples is relatively high, and increases with Ge content ($\rho_{300\,\mathrm{K}} \sim 300\,\mathrm{m\Omega\,cm}$ at $x = 0$, and $\rho_{300\,\mathrm{K}} \sim 3\,\mathrm{m\Omega\,cm}$ at $x = 1$). The weak temperature dependence of the resistivity of all samples, but especially $Ru_2Ge_{3.0}$, is unusual and more typical of materials several orders of magnitude less resistive. This is confirmed by the

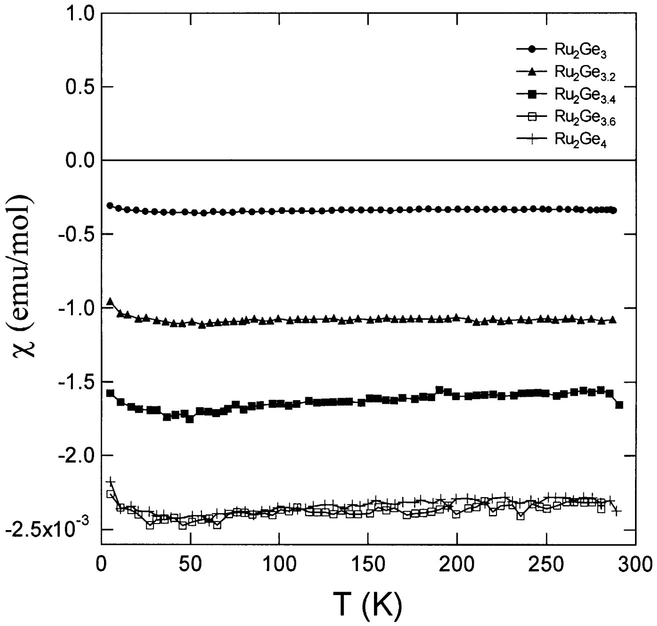

FIG. 4. Field-cooled magnetic susceptibility data for Ru_2Ge_{3+x} measured in a DC field of 10 000 Oe. All samples display a strong, temperature-independent diamagnetic susceptibility typical of low-carrier concentration, low-mobility semiconductors.

observation that plots of $\ln \sigma$ vs. $1/T$ contain no linear regions for any of the measured compositions, demonstrating that activated behavior is not followed in the temperature range studied. The inset to Fig. 3 shows that a $\ln \sigma$ vs $T^{-1/4}$ dependence is observed for high Ge contents at high temperatures. This behavior is indicative of three-dimensional variable range hopping, as often observed in disordered materials.

The magnetic susceptibility data (Fig. 4) show that all the Ru_2Ge_{3+x} samples have a surprisingly strong, temperature-independent diamagnetic susceptibility ($\chi < 0$). There is no evidence of a local Ru moment in any of the compositions measured. This is in agreement with measurements by Susz *et al.* (7) performed on Ru_2Ge_3 samples. In contrast to these previous measurements, however, our samples do not exhibit a low-temperature paramagnetic tail indicating a higher sample purity. The magnetic susceptibility of semiconductors is usually evaluated as the combination of two major contributions: the core or lattice contribution, χ_{core} and the carrier contribution. The carrier contribution consists of a paramagnetic part, χ_{Pauli} and a diamagnetic contribution due to the orbital electronic motion induced by the applied magnetic field, χ_{Landau}, typically $\chi_{\mathrm{Landau}} = -\frac{1}{3}\chi_{\mathrm{Pauli}}$. The core contribution is too small to account for the observed diamagnetism in the Ru_2Ge_{3+x} samples ($\chi_{\mathrm{core}} \sim 1 \times 10^{-4}\,\mathrm{emu\,mol^{-1}}$) indicating that $\chi_{\mathrm{Landau}} > \chi_{\mathrm{Pauli}}$. This situation is possible if the effective mass of carriers is low or if they have a very low carrier mobility (11). Hall-effect measurements suggest that Ru_2Ge_3 does indeed have a low carrier mobility (12) providing some explanation for the surprisingly large diamagnetic susceptibility observed. The data in Fig. 4 show that the susceptibility of Ru_2Ge_{3+x} becomes systematically more diamagnetic with increasing x. This suggests that there is a reduction in the mean-carrier mobility with increasing x.

Figure 5 shows the temperature dependence of the Seebeck coefficient of Ru_2Ge_{3+x} and its evolution with x. The Seebeck coefficients of all samples increase smoothly and continuously with temperature in the range measured (200–500 K). The inset to Fig. 5 shows the variation of the Seebeck coefficient, measured at 300 K, with sample composition. The value of $S_{300\,\mathrm{K}}$ initially decreases with increasing x, passing through a minimum at intermediate values, before rising sharply at large values of x to regain its initial value of around 325 μV/K at Ru_2Ge_4. This behavior is contrary to the standard model for small band-gap semiconductors, in which the Seebeck coefficient varies simply as the reciprocal of the carrier concentration. The observed behavior is more typical of a series of materials in which both holes and electrons carry current, with the relative ratio of carriers changing as a function of composition.

Figure 6 shows the thermal conductivity of Ru_2Ge_3 as a function of temperature. The overall temperature dependence is typical of well-ordered crystalline materials. The room-temperature thermal conductivity ($\kappa_{300\,\mathrm{K}} = 0.03\,\mathrm{W/K\,cm}$), however, is comparable to that observed for heavy metal intermetallics (e.g., HoPdSb (13)). Such a low thermal conductivity in a material with no "heavy" elements gives some credence to the suggestion that Ru_2Ge_3 has some of the features of a phonon-glass–electron-crystal.

Combining the measured resistivity and Seebeck coefficients of Ru_2Ge_3 and Ru_2Ge_4 to gain the thermoelectric power factor, at 300 K, values of: $S^2/\rho = 3.2 \times 10^{-7}$ and $3.5 \times 10^{-8}\,\mathrm{W/K^2\,cm}$ are obtained, respectively. When combined with the reported low thermal conductivity at 300 K, a thermoelectric figure merit $ZT = 3.2 \times 10^{-3}$ at 300 K is obtained for Ru_2Ge_3.

DISCUSSION

The electronic and magnetic behavior of the Ru_2Ge_{3+x} system is unusual. A plausible explanation for the observed behavior describes the Ru_2Ge_{3+x} system as a series of semiconductors with a large number of states in the band gap. At high temperatures, thermally excited carriers dominate the electronic conduction. Ru_2Ge_3 displays the Arrhenius behavior expected for such a system, as measured by Susz *et al.* (7). Below 400 K, the resistivity of Ru_2Ge_3 has a weak positive temperature dependence

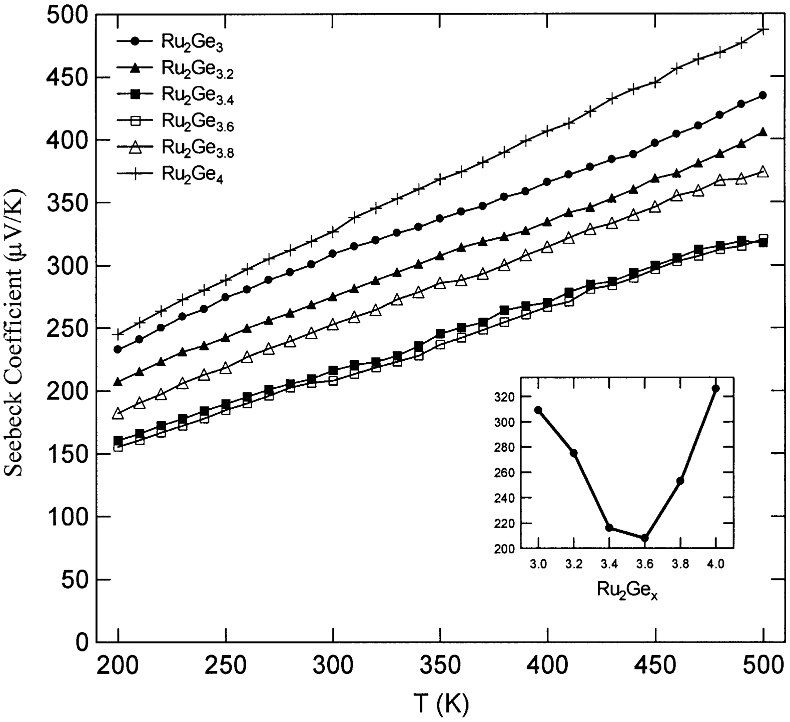

FIG. 5. Seebeck coefficient data for Ru_2Ge_{3+x} measured on heating from 200 to 500 K. The inset shows the compositional dependence of the Seebeck coefficient at 300 K.

(ρ increases with temperature). This demonstrates that the temperature dependence is no longer dominated by the change in the number of thermally excited carriers that is observed in the high-temperature intrinsic regime. This weak temperature dependence can be explained by the presence of an extrinsically populated impurity band in the band gap. Such an impurity band would have carrier concentration with a weak temperature dependence by virtue of its extrinsically populated nature and would also have relatively few carriers leading to the relatively high observed resistivity. The diamagnetic susceptibility of Ru_2Ge_3 and reported Hall-effect measurements (12) indicate that the charge carriers have a relatively low mobility.

The addition of Ge leads to a change in the electronic conduction behavior from the weak temperature dependence observed for Ru_2Ge_3 at low temperatures to the variable range hopping observed for Ru_2Ge_4. This clearly shows that there is a large reduction in the mean carrier mobility with increasing x. This is further evidenced by the accompanying increase in the diamagnetic susceptibility of Ru_2Ge_{3+x} with x. The variation in the Seebeck coefficient of Ru_2Ge_{3+x} with composition is also consistent with such a change in carrier type. At low and high values of x, one type of carrier dominates. At intermediate values of x, both carriers types (those due to the impurity states and the intrinsic carriers) are present and in combination this leads to the observed reduction in the Seebeck coefficient at these compositions. The origin of the impurity bands may lie in the disordered or incommensurate nature of the Ge sublattice.

CONCLUSION

We have shown that materials in the composition range Ru_2Ge_{3+x} $(0<x<1)$ form a continuous structural series in which a nearly invariant Ru framework is filled with an almost crystallographically independent Ge sublattice. A composite structure is formed in which the two sublattices are, in general, incommensurate with respect to each other. The addition of Ge leads to a reduction in the carrier mobility, evidenced by an increase in the resistivity and diamagnetic susceptibility of samples. The temperature dependence of the resistivity for values of $x>0.6$ is consistent with a variable range-hopping conduction mechanism. The Seebeck coefficients of these materials do not vary in the expected simple manner, instead they suggest a change in carrier type with increasing x. When the Seebeck data are combined with resistivity, the data yield power factors too small to be thermoelectrically useful. This study of the electronic properties of the Ru–Ge Nowotny chimney-ladder phases shows that in spite of a promising combination of structural (potential PGEC material) and electronic (small band-gap semiconductor)

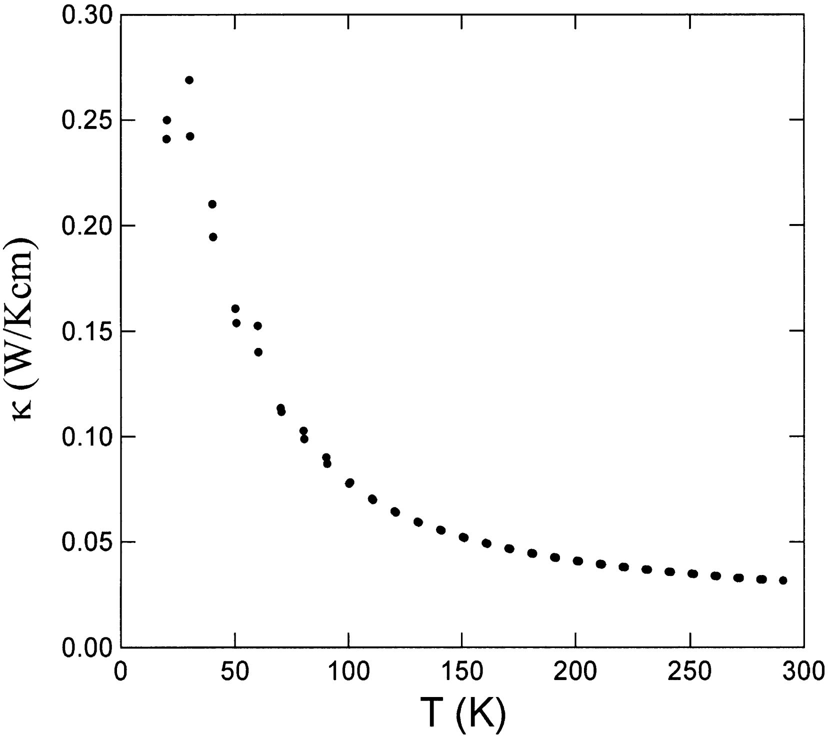

FIG. 6. Thermal conductivity of Ru_2Ge_3 plotted against temperature.

properties, these materials in their current state are not good thermoelectrics. However, doping experiments designed to increase conductivity through ruthenium-site substitution with 3*d* transition elements are currently in progress and will be reported later.

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