PHYSICAL REVIEW B VOLUME 58, NUMBER 7 15 AUGUST 1998-I

Unusual transport and large diamagnetism in the intermetallic semiconductor $RuAl_2$

D. Mandrus, V. Keppens, and B. C. Sales
Solid State Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6056

J. L. Sarrao*
National High Magnetic Field Laboratory, Tallahassee, Florida 32306-4005

(Received 10 June 1997; revised manuscript received 20 April 1998)

We report measurements of the resistivity, thermopower, thermal conductivity, Hall coefficient, and magnetic susceptibility of $RuAl_2$ over a wide temperature range. Room-temperature sound velocity measurements are also reported. We find that at low temperature $RuAl_2$ behaves as a low carrier-density semimetal. As the temperature is raised, excitations across a 0.6-eV pseudogap dominate the transport, and $RuAl_2$ behaves effectively as a semiconductor. The diamagnetic susceptibility of $RuAl_2$ is anomalously large, and has an unusual temperature dependence that can be attributed to a Pauli term that reflects underlying structure in the density of states. We also suggest that the large diamagnetic response is a universal feature of hybridization gap semiconductors. The potential of $RuAl_2$ for thermoelectric applications is evaluated. We find that even if the lattice component of the thermal conductivity could be reduced to its minimum value, the electrical properties of $RuAl_2$ are not good enough to make it an attractive thermoelectic material.

[S0163-1829(98)09031-6]

INTRODUCTION

Unconventional semiconductors such as FeSi,[1,2] $Ce_3Bi_4Pt_3$,[3] and $LaFe_3CoSb_{12}$ (Refs. 4 and 5) have attracted attention recently both because of their unusual transport and thermodynamic properties and their potential for thermoelectric applications. Theoretically, too, many of these materials have attracted attention, both as hybridization gap semiconductors[6,7] and as Kondo insulators.[8] Gap formation in these materials is thought to arise from the hybridization of a narrow band of f or d electrons with a broad sp band. This hybridization gives the valence and conduction bands a strong f or d character, and leads to sharp structures in the density of states close to the band edges. As pointed out by Mahan and Sofo,[9] narrow peaks in the density of states a few k_BT from the Fermi energy can be beneficial for thermoelectric performance.

$RuAl_2$ crystallizes in the orthorhombic $TiSi_2$ structure (space group $Fddd$, 24 atoms per unit cell). This structure is built from layers in which each Ru atom is surrounded by a hexagon of Al atoms. There are four layers per unit cell, and the layers are arranged such that the Ru atoms are never nearest neighbors (see Fig. 1). The $TiSi_2$ structure is the building block of a large series of defect-$TiSi_2$ structures adopted by materials known as Nowotny chimney-ladder compounds.[10] The general formula for these compounds is T_nB_{2n-m} (T is transition metal; $B = $ Al, Ga, Si, Ge, or Sn; n, m are integers). It was pointed out by Jeitschko[11] that chimney-ladder compounds with 14 valence electrons per T atom were semiconducting, and he proposed a rigid-band model in which electrons are transferred from the B atom to the T atom, filling all of the d levels and half of the sp levels. Recent electronic structure calculations,[12,13] however, have clearly shown that gap formation in $RuAl_2$ results from the hybridization of Ru d with Al sp states, with little static charge transfer. Given that all known chimney-ladder compounds with 14 valence electrons per T atom are semiconductors, it is likely that the electronic structure and transport properties of these compounds are quite similar; however, the increasing complexity of the unit cell means that the lattice dynamics of these compounds may be profoundly different, especially since it has been argued that in materials with a large number of atoms per unit cell the concept of a phonon loses its validity.[14]

EXPERIMENTAL DETAILS

The $RuAl_2$ sample used in these experiments was prepared as follows. Ru (99.99%, Johnson Matthey, Puratronic) and Al (99.9999%) were arc melted together under an Ar atmosphere. The sample was flipped and remelted several times. Due to the volatility of the Al at high temperature, we

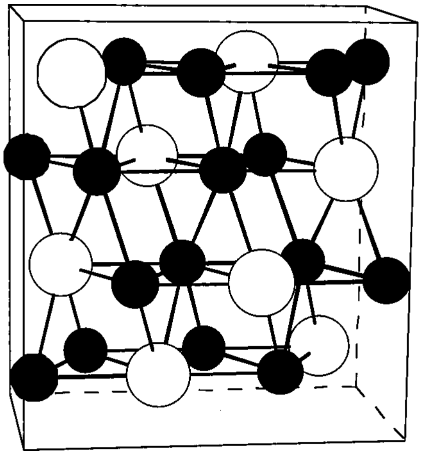

FIG. 1. Diagram of the $RuAl_2$ structure. This orthorhombic structure is built up from layers of Ru atoms (empty spheres) surrounded by hexagons of Al atoms (filled spheres). There are four layers per unit cell.

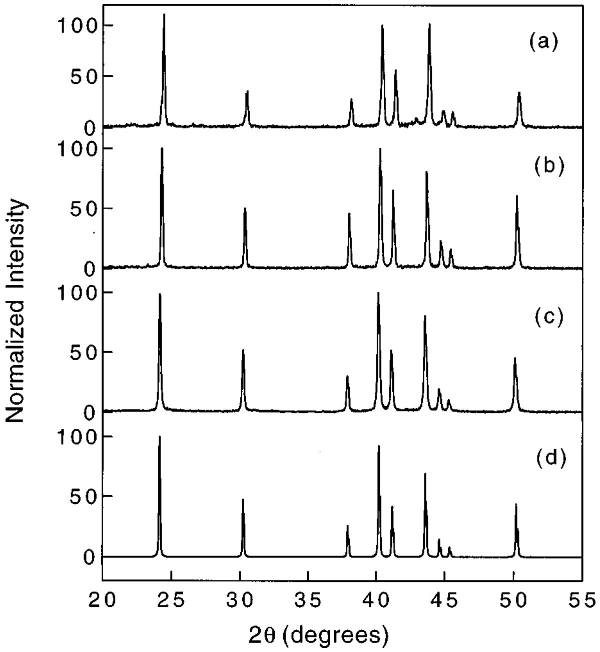

FIG. 2. X-ray powder diffraction pattern of $RuAl_2$. These patterns were obtained (a) after arc melting, (b) after annealing one day at 750 °C and one day at 950 °C, and (c) after hot pressing. Pattern (d) is a calculated pattern.

started with 3% excess Al. After arc melting, if we assumed all the weight loss was attributable to the Al, the sample was then stoichiometric. The sample was then ground thoroughly in a ball mill, pressed into a pellet, and annealed one day at 750 °C and one day at 950 °C. The sample was then reground in a ball mill and hot-pressed for 1/2 h at 1150 °C and 315 kg/cm^2. The resulting sample was single phase according to its powder diffraction pattern (see Fig. 2), and was 92% of its x-ray density. The intensities of a powder diffraction pattern obtained on a bar cut from the pellet agreed well with the calculated pattern, thereby indicating that the sample had no appreciable texture.

Resistivity, Seebeck, and thermal conductivity measurements were performed on a sample with dimensions $12\times6\times3$ mm^3. Measurements from 10 to 300 K were performed in a closed-cycle refrigerator. A 50-Ω RuO_2 chip resistor was attached to one end of the sample using a thermally conductive but electrically insulating epoxy; this served as a heater for the Seebeck and thermal conductivity measurements. Conventional linear dc methods were employed throughout. The Seebeck coefficient was obtained against copper, and the data were not corrected for the small ($\sim$1 μV/K) absolute thermopower of Cu. A NIST stainless-steel standard was used to verify the accuracy of the thermal conductivity measurements; agreement to better than 5% was obtained. Because the thermal conductivity of $RuAl_2$ is rather high, the data were not corrected for radiation losses.

Hall measurements were performed from 5 to 325 K and in magnetic fields from 10 to 70 kOe. Two longitudinal current leads and two transverse voltage leads were attached to the sample using Epo-Tek H20E silver epoxy and 25 μm-diameter Pt wire. At each temperature, the sample was rotated 180° and the current reversed in order to eliminate misalignment and thermal voltages, respectively. The Hall coefficient was found to be independent of magnetic field between 5 and 325 K, and from 10 to 70 kOe.

Magnetic susceptibility measurements were performed below room temperature using a quantum design superconducting quantum interference device (SQUID) magnetometer. Above room temperature a homemade Faraday system was employed, using Lewis coils and a furnace supplied by George Associates. A NIST MnF_2 standard was used to calibrate the Faraday magnetometer. An applied field of 1 kOe was used for the low-temperature measurements, and 7 kOe for the high-temperature measurements.

The room-temperature elastic constants of polycrystalline $RuAl_2$ were obtained dynamically using resonant ultrasound spectroscopy.[15] In this method the free-body resonances of a small ($3\times2.5\times2$ mm^3) rectangular parallelepiped are measured very precisely using tiny $LiNbO_3$ transducers and a sensitive heterodyne receiver. Once the resonances are known, the elastic constants are determined using nonlinear optimization as described in Ref. 15. Although an orthorhombic crystal has nine elastic constants, a polycrystal without texture has just two: a shear modulus (c_{44}) governing transverse waves, and a compressional modulus (c_{11}) governing longitudinal waves. Since a good description of the elastic response of the $RuAl_2$ specimen was obtained using two elastic constants, this is a further indication that the sample had little or no texture.

RESULTS AND DISCUSSION

The magnetic susceptibility of $RuAl_2$ from 2 to 900 K is plotted in Fig. 3. Although the observed diamagnetism is typical of semiconductors, both the magnitude and temperature dependence of the susceptibility are very unusual. In a conventional semiconductor, the total susceptibility can be understood as the sum of a diamagnetic ''core'' or ''lattice'' susceptibility χ_A, and a conduction electron susceptibility χ_C. The lattice susceptibility is expected to be essentially independent of temperature. The conduction electron susceptibility χ_C can itself be broken down into a paramagnetic Pauli term χ_P, and a diamagnetic Landau term χ_L. Typically, $-\chi_L=1/3\chi_P$, but if the effective mass of the carriers is very small the magnitude of χ_L can exceed that of χ_P.[16]

In $RuAl_2$ the hybridized *d*-like bands are expected to give rise to carriers with fairly large effective masses. As discussed below, Hall effect measurements are consistent with this expectation. It is therefore unlikely that Landau diamagnetism is playing an important role in $RuAl_2$. What is more plausible is that the temperature dependence of the susceptibility is due to a Pauli term that reflects structure in the density of states near the chemical potential. According to band-structure calculations,[13] $RuAl_2$ is not a true semiconductor but rather a low carrier density semimetal; small pockets of light holes and heavier electrons exist near the Fermi energy. The calculations predict that although there is a marked depression in the density of states around the Fermi energy, the density of states at E_F is nonzero. The semiconducting gap, therefore, is not a true gap but a pseudogap. As the temperature is raised, the chemical potential should move toward the center of the pseudogap, and the Pauli contribution should decrease. The observed behavior is consistent with this picture.

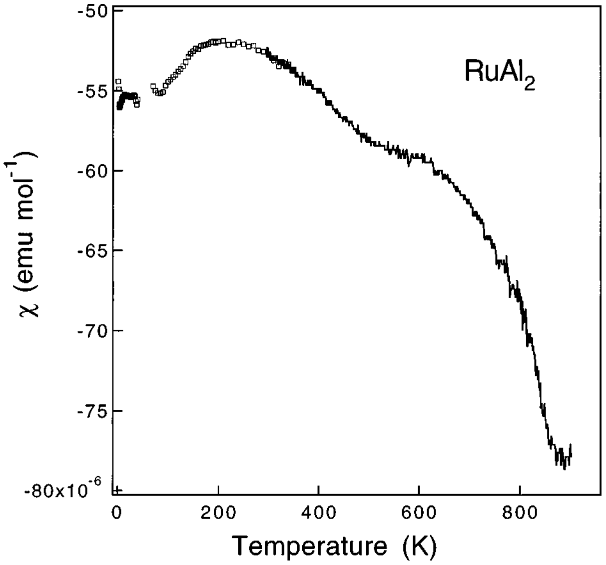

FIG. 3. Magnetic susceptibility of RuAl$_2$. The open squares represent data obtained using a commercial SQUID magnetometer. The solid line represents data obtained using a homemade Faraday magnetometer. Some data near 50 K were excised because the O_2 ordering peak (from a small amount of O_2 in the sample chamber) was still visible after the background was subtracted.

The magnitude of the susceptibility is also noteworthy, in that at high temperatures it approaches $-27\ \mathrm{cm}^3$/mol atom. Since Al typically has a very small ''core'' diamagnetism, we might consider associating all of the diamagnetic response to the Ru atom. In that case we have $\chi \cong -80\ \mathrm{cm}^3$/mol Ru. This magnitude is larger than any of the ionic diamagnetic susceptibilities reported in Ref. 17. Interestingly, anomalously large diamagnetic susceptibilities have also been observed in other transition-metal intermetallic semiconductors such as CrSi$_2$,[18] CoSb$_3$,[19] and Ru$_2X_3$ (X $=$Si, Ge, or Sn).[20] It appears that enhanced diamagnetism may be a signature of a hybridization gap material, although we are unaware of any theory that purports to explain this phenomenon.

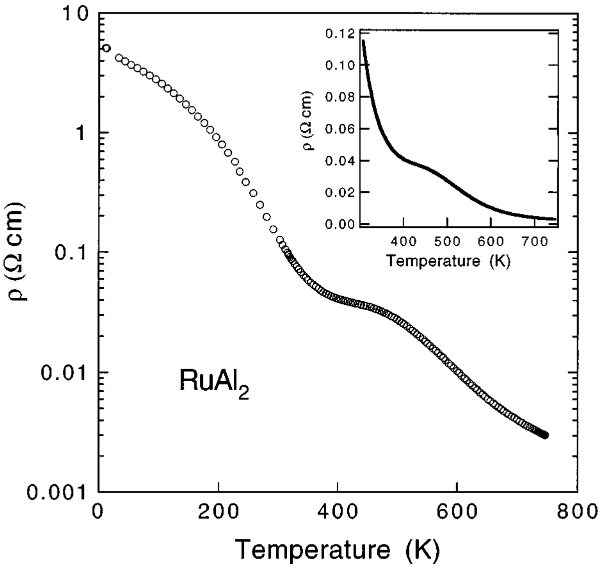

FIG. 4. Resistivity of RuAl$_2$. The inset is the high-temperature portion of the data plotted on a linear scale.

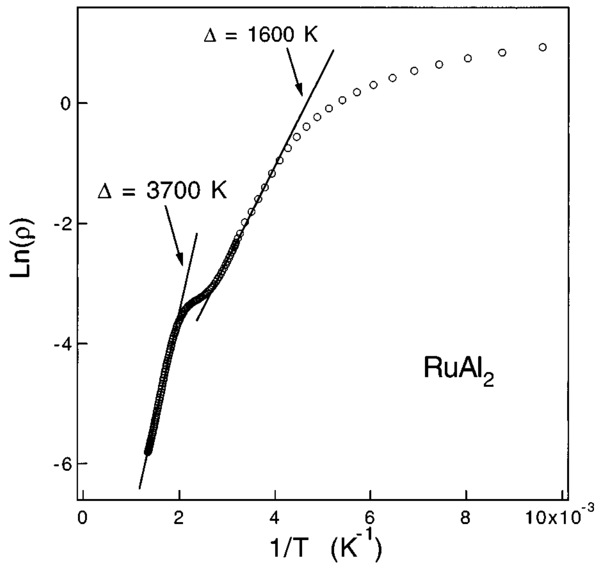

FIG. 5. Natural logarithm of the resistivity of RuAl$_2$ vs inverse temperature. Above 500 K, the data are well described by an Arrhenius law $\rho(T)=\rho_0\exp(\Delta/T)$ with $\Delta=3700$ K. This behavior is consistent with excitations across a 0.62 eV pseudogap. From 250 to 450 K another energy scale is apparent with an activation energy of 1600 K. Below 250 K the resistivity peels off in a manner typical of extrinsic conduction mechanisms.

The resistivity of RuAl$_2$ from 10 to 750 K is plotted in Figs. 4 and 5. The resistivity is clearly semiconducting, and changes by more than three orders of magnitude between 10 and 750 K. Above 500 K the resistivity obeys an Arrhenius law $\rho(T)=\rho_0 e^{\Delta/T}$ with $\Delta=3700\ \mathrm{K}\cong 0.31$ eV. This yields a value of $2\Delta=0.62$ eV for the pseudogap, which is in reasonable accord with the value of $\approx$0.05 Ry ($=$0.68 eV) expected from band-structure calculations.[12,13] Between 300 and 500 K the resistivity has an unusual shape. As Volkov and Poon point out,[21] this shape is insensitive to sample quality, and so is most likely not of extrinsic origin but rather represents behavior intrinsic to RuAl$_2$. In an effort to parametrize this

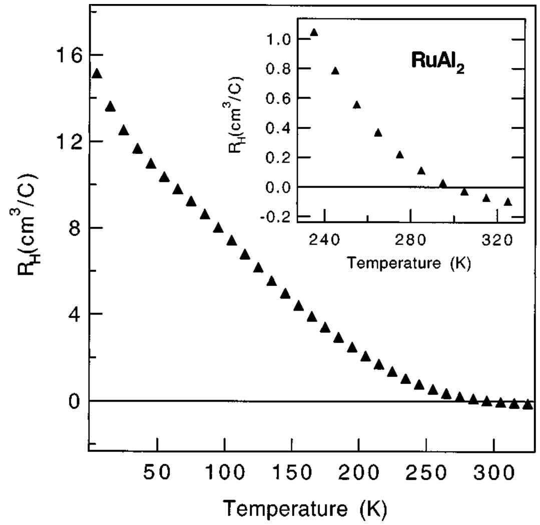

FIG. 6. Hall coefficient of RuAl$_2$ obtained in a field of 30 kOe. The inset shows the high-temperature portion of the data on an expanded scale.

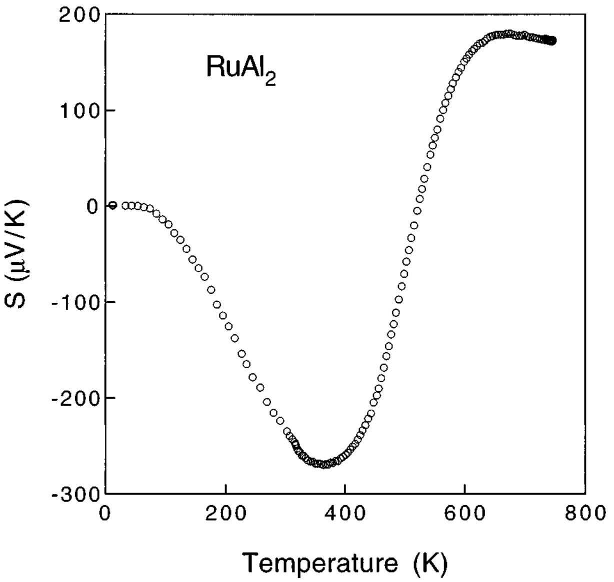

FIG. 7. Seebeck coefficient of RuAl$_2$. The rapid change from a large negative to a large positive thermopower is quite unusual.

behavior, we find (Fig. 5) that the resistivity in the range 25–450 K is characterized by an activation energy of $\Delta = 1600\ \mathrm{K} \cong 0.13\ \mathrm{eV}$. It is likely that this activation energy is related to structure in the density of states within the pseudogap.

The Hall coefficient (R_H) of RuAl$_2$ from 5 to 325 K is plotted in Fig. 6. R_H displays a moderately strong temperature dependence and changes sign near room temperature. Such behavior is indicative of competition between at least one electron and one hole band. As mentioned previously, the Hall coefficient is independent of field from 10 to 70 kOe in the temperature range studied. This field independence suggests that the charge carriers traverse only a small fraction of a cyclotron orbit before they are scattered, and thus always remain in the weak-field limit ($\omega_c \tau \ll 1$). This is expected if the states near the Fermi energy have significant *d* character, leading to high effective masses and correspondingly low mobilities.

The Seebeck coefficient of RuAl$_2$ from 10 to 750 K is plotted in Fig. 7. The most remarkable feature in the data is the rapid change from a large negative to a large positive thermopower. Given that the low-temperature Hall coefficient is *positive*, it is clear that both electrons and holes are contributing to the conduction. This observation is consistent with band-structure calculations, which predict that RuAl$_2$ is a semimetal with a light hole pocket and heavier electron pockets.[13] As the temperature is raised the transport in RuAl$_2$ is increasingly governed by excitations across the 0.6 eV pseudogap, and in this (effectively semiconducting) high-temperature regime the holes are now heavier and dominate the thermopower. RuAl$_2$, therefore, behaves as a low-carrier

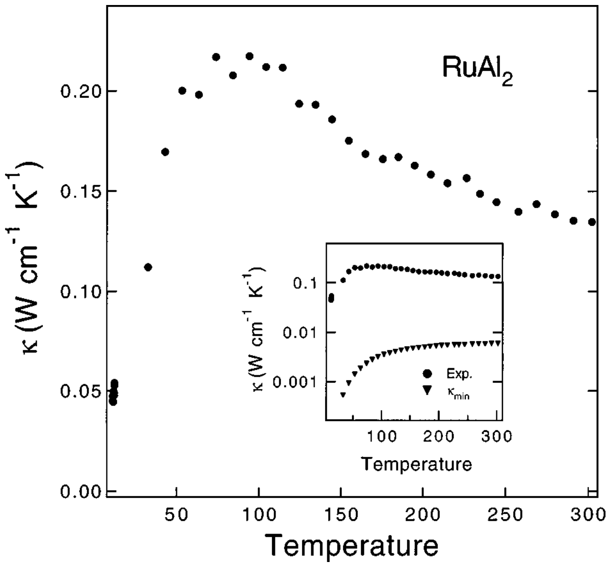

FIG. 8. Thermal conductivity of RuAl$_2$. The inset shows, on a logarithmic scale, the measured thermal conductivity and the minimum thermal conductivity calculated according to the prescription in Ref. 21.

TABLE I. Theoretical and experimental densities, elastic moduli, bulk modulus, longitudinal and transverse sound velocities, and Debye temperature obtained on RuAl$_2$ at room temperature using resonant ultrasound spectroscopy.

	RuAl$_2$
ρ_{theor} (g/cm^3)	6.247
ρ_{expt} (g/cm^3)	5.765
c_{11} (10^{11} N/m^2)	2.60
c_{44} (10^{11} N/m^2)	0.92
B (10^{11} N/m^2)	1.37
v_l (m/s)	6720
v_t (m/s)	3990
θ_D (K)	535

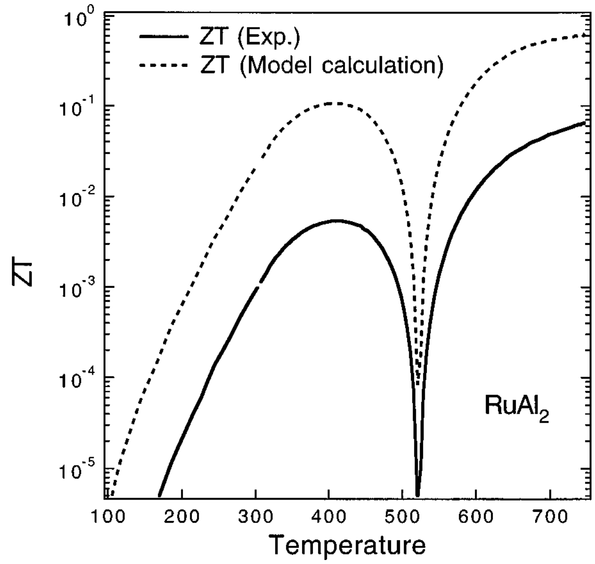

FIG. 9. The thermoelectric figure of merit ZT vs temperature for RuAl$_2$. Solid line: ZT vs temperature obtained using measured values of the thermal conductivity below 300 K. Above 300 K a conventional $1/T$ behavior was assumed for the thermal conductivity. Dashed line: ZT vs temperature calculated using κ_{min} for the lattice component of the thermal conductivity and the measured thermopower and resistivity. The Wiedemann-Franz law was used to estimate the electronic contribution to the thermal conductivity.

density semimetal at low temperatures and as an intrinsic semiconductor at high temperatures.

The thermal conductivity of $RuAl_2$ is plotted in Fig. 8. Also plotted in Fig. 8 is a model calculation of the minimum (lattice) thermal conductivity following the prescription of Cahill, Watson, and Pohl.[22] In this model, heat is transported as a random walk of thermal energy between neighboring atoms vibrating with random phases. The inputs to the calculation are simply the longitudinal and transverse sound velocities (Table I) and the number density of atoms. The minimum thermal conductivity represents a lower limit to the achievable thermal conductivity of a given material. In the context of thermoelectric materials, the minimum thermal conductivity represents a ''best of all possible worlds'' value for the lattice thermal conductivity and is useful for estimating the maximum value of the thermoelectric figure of merit $ZT=S^2T\rho^{-1}\kappa^{-1}$ that can be hoped for in a given material. A plot of ZT vs temperature for $RuAl_2$ appears in Fig. 9. Also plotted in Fig. 9 is the value of ZT vs temperature obtained using κ_{min} for the lattice component of thermal conductivity (the electronic component of the thermal conductivity was estimated using the Wiedemann-Franz law). It is apparent that, despite the large thermopower and reasonably high electrical conductivity of $RuAl_2$, the thermal conductivity is much too high for $RuAl_2$ to be considered as a promising thermoelectric material. Moreover, as Fig. 9 illustrates, even if the lattice component of the thermal conductivity could be successfully reduced to κ_{min}, the electrical properties of $RuAl_2$ are simply not good enough to make it an attractive thermoelectric material.

Finally, to the extent that other chimney-ladder materials have similar electronic properties to $RuAl_2$, the present results indicate that this class of intermetallic compounds is probably not a fruitful place to search for new thermoelectric materials.

ACKNOWLEDGMENTS

We thank the late Bryan R. Coles for stimulating our interest in $RuAl_2$. Oak Ridge National Laboratory is managed by the Lockheed Martin Energy Research Corporation for the U.S. Department of Energy under Contract No. DE-AC05-96OR22464. The National High Magnetic Field Laboratory is supported by the NSF and the State of Florida through Grant No. DMR-9016241.

---

*Permanent address: Materials Science and Technology Division, MST-10, Los Alamos National Laboratory, Los Alamos, NM 87545.

[1] D. Mandrus, J. L. Sarrao, A. Migliori, J. D. Thompson, and Z. Fisk, Phys. Rev. B **51**, 4763 (1995), and references therein.

[2] B. C. Sales, E. C. Jones, B. C. Chakoumakos, J. A. Fernandez-Baca, H. E. Harmon, and J. W. Sharp, Phys. Rev. B **50**, 8207 (1994).

[3] Z. Fisk, P. C. Canfield, J. D. Thompson, and M. F. Hundley, J. Alloys Compd. **181**, 369 (1993).

[4] B. C. Sales, D. Mandrus, and R. K. Williams, Science **272**, 1325 (1996).

[5] D. Mandrus, B. C. Sales, V. Keppens, B. C. Chakoumakos, P. Dai, L. A. Boatner, R. K. Williams, T. W. Darling, A. Migliori, M. B. Maple, D. A. Gajewski, and E. J. Freeman, in *Thermoelectric Materials—New Directions and Approaches*, edited by T. M. Tritt, G. Mahan, H. B. Lyon, and M. G. Kanatzidis, MRS Symposia Proceedings No. 478 (Materials Research Society, Pittsburgh, PA, 1997), pp. 199–209.

[6] M. A. Continentino, G. M. Japiassu, and A. Troper, J. Appl. Phys. **79**, 6345 (1996).

[7] S. Ögüt and K. M. Rabe, Phys. Rev. B **54**, R8297 (1996).

[8] For a review see G. Aeppli and Z. Fisk, Comments Condens. Matter Phys. **16**, 155 (1992).

[9] G. D. Mahan and J. O. Sofo, Proc. Natl. Acad. Sci. USA **93**, 7436 (1996).

[10] H. Nowotny, in *The Chemistry of Extended Defects in Non-Metallic Solids*, edited by L. R. Eyring and M. O'Keefe (North-Holland, Amsterdam, 1970), p. 223.

[11] W. Jeitschko, Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem. **B33**, 2347 (1977).

[12] D. Nguyen Manh, G. Trambly de Laissardiere, J. P. Julien, D. Mayou, and F. Cyrot-Lackmann, Solid State Commun. **82**, 329 (1992).

[13] S. E. Burkov and S. N. Rashkeev, Solid State Commun. **92**, 525 (1994).

[14] P. B. Allen, X. Du, L. Mihaly, and L. Forro, Phys. Rev. B **49**, 9073 (1994).

[15] A. Migliori, J. L. Sarrao, W. M. Visscher, T. M. Bell, M. Lei, Z. Fisk, and R. G. Leisure, Physica B **183**, 1 (1993).

[16] See N. W. Ashcroft and N. D. Mermin, *Solid State Physics* (Saunders, Philadelphia, 1976), pp. 664–666 for a concise discussion.

[17] *Diamagnetic Susceptibility*, edited by R. R. Gupta, K.-H. Hellwege, and A. M. Hellwege, Landolt-Börnstein, New Series, Group II, Vol. 16 (Springer-Verlag, Berlin, 1986).

[18] D. Shinoda and S. Asanabe, J. Phys. Soc. Jpn. **21**, 555 (1966).

[19] D. Mandrus, A. Migliori, T. W. Darling, M. F. Hundley, E. J. Peterson, and J. D. Thompson, Phys. Rev. B **52**, 4926 (1995).

[20] C. P. Susz, J. Muller, K. Yvon, and E. Parthé, J. Less-Common Met. **71**, 1 (1980).

[21] P. Volkov and S. J. Poon, Europhys. Lett. **28**, 271 (1994).

[22] D. G. Cahill, S. K. Watson, and R. O. Pohl, Phys. Rev. B **46**, 6131 (1992).