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Low-temperature heat-capacity study of superconducting ternary silicides and germanides with the $Sc_5Co_4Si_{10}$-type structure

L. S. Hausermann-Berg and R. N. Shelton
Ames Laboratory and Department of Physics, Iowa State University, Ames, Iowa 50011

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The results of low-temperature specific-heat experiments on eleven superconducting compounds belonging to the ternary system $R_5T_4X_{10}$ (R=Sc, Y, and Lu; T=Co, Rh, Ir, and Os; X=Si and Ge) are presented. Analysis of the data yields relatively high Debye temperatures for the silicides (300–600 K), as well as large values for $\Delta C/\gamma T_c$ (2.8–4.9) and the electron-phonon interaction λ (0.60–0.75) for the high-T_c compounds $Sc_5Rh_4Si_{10}$, $Sc_5Ir_4Si_{10}$, and $Y_5Os_4Ge_{10}$, indicating that these are strong-coupled superconductors. The analysis also indicates that a large contribution of the anharmonic term to the total specific heat in the normal state is present in the low-T_c compounds. It is apparent that the phonon spectra of these $Sc_5Co_4Si_{10}$-type materials are quite complex.

INTRODUCTION

Until recently, the interest in ternary superconductors has focused on the chevrel phases and rhodium borides. However, the discovery of the coexistence of superconductivity and a regular sublattice of magnetic rare-earth atoms has prompted the search for more ternary systems with this property. Eleven new superconducting structure types were reported in 1980 alone.[1–10] In two separate silicide phases, $Lu_2Fe_3Si_5$ and $Sc_5Co_4Si_{10}$, superconductivity still exists ($T_c = 4.7$ K or greater) in the presence of a significant amount of a magnetic $3d$ transition metal; 30% in the former and 21% in the latter. However, neither the Fe nor Co atom was reported to exhibit a magnetic moment in these compounds.[11,12]

As mentioned, the $R_5T_4X_{10}$ series,[5,6] first reported in 1980, is one successful example of the search for additional ternary superconductors. This new class of superconducting and magnetic compounds is constituted as follows: R = rare earth, including Sc and Y, T = Co, Rh, Ir, or Os, and X = Si or Ge. The system crystallizes in the $Sc_5Co_4Si_{10}$-type structure which is primitive tetragonal, space group $P4/mbm$, and has 38 atoms per unit cell. The projection of the $Sc_5Co_4Si_{10}$ structure along the c axis yields Co and Si atoms in planar nets of pentagons and hexagons stacked parallel to the basal plane and connected along the c axis via Co-Si-Co zigzag chains. The pentagon-hexagon layers are separated by layers of Sc.[6] One interesting feature of this structure is the absence of transition-metal–transition-metal bonds. This is quite different from what is found in the Mo chalcogenides[13] and the rhodium borides,[14] both well studied ternary systems, in which the transition metals form clusters. In this paper, we present the low-temperature heat-capacity data for the 11 superconducting compounds in this system as part of a systematic study of ternary rare-earth transition-metal silicides and germanides.

EXPERIMENTAL DETAILS

All samples were prepared by arc melting stoichiometric amounts of the elements in a Zr-gettered high-purity argon atmosphere. After melting, the samples were sealed in quartz ampoules under 150 Torr of argon and subjected to a heat treatment of 18 days at 1050 °C followed by a water quench to room temperature.

X-ray powder diffraction work was carried out on a Rigaku diffractometer and lattice parameters were determined by the method of least-squares using 20–24 reflections including an internal silicon standard ($a = 5.430\,83$ Å). These are in good agreement with those reported by Braun *et al.*[12] and Venturini *et al.*[15] The ambient-pressure superconducting transition temperatures (T_c) of the samples were determined from low-frequency ac-susceptibility measurements. Low-temperature heat-capacity measurements were carried out at temperatures ranging from 0.5 to 30 K in a heat-pulse type semiadiabatic calorimeter. Two features of the colorimeter were a ^{3}He pot-bellows together with a mechanical heat switch serving to cool the samples without exchange gas, and a continuously operating ^{4}He cold plate. Details of the low-temperature heat-capacity measurement technique may be found in Ref. 16.

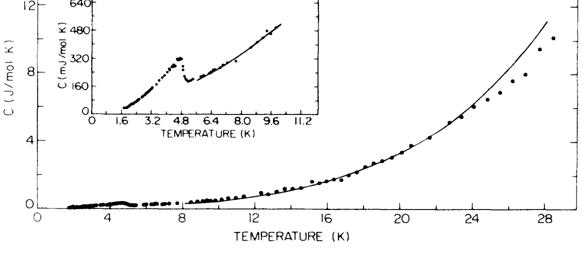

FIG. 1. Specific heat vs temperature for $Sc_5Co_4Si_{10}$ with an inset focusing on the specific-heat jump at T_c. The solid line represents the best fit to the data.

TABLE I. Superconducting and normal-state properties of the $R_5T_4X_{10}$ compounds.

Compound	T_c (K)	ΔC (mJ/mol K)	γ_n (mJ/mol K^2)	β_n (mJ/mol K^4)	α_n (mJ/mol K^6)	$\Delta C/\gamma_n T_c$	$N^*(0)$ (states/atom eV spin)	Θ_D	λ
$Sc_5Co_4Si_{10}$	4.89	160	30.9	0.182	4.14×10^{-4}	1.08	0.35	584	0.47
$Sc_5Rh_4Si_{10}$	8.43	400	17.1	0.412	5.17×10^{-4}	2.82	0.19	448	0.60
$Sc_5Ir_4Si_{10}$	8.57	250	9.93	0.571	6.67×10^{-4}	2.96	0.11	402	0.62
$Y_5Ri_4Si_{10}$	2.29	55	21.8	0.687	6.92×10^{-4}	1.10	0.24	377	0.45
$Lu_5Rh_4Si_{10}$	3.45	112	16.7	1.41	1.46×10^{-4}	1.95	0.19	297	0.52
$Lu_5Ir_4Si_{10}$	3.77	124	23.4	0.752	2.20×10^{-3}	1.41	0.26	366	0.50
$Y_5Rh_4Ge_{10}$	1.25	34	19.2	1.06	2.44×10^{-3}	1.42	0.21	326	0.41
$Y_5Ir_4Ge_{10}$	2.75	85	17.6	1.34	2.03×10^{-3}	1.76	0.20	302	0.49
$Y_5Os_4Ge_{10}$	9.10	570	13.2	1.78	3.37×10^{-4}	4.74	0.15	275	0.74
$Lu_5Rh_4Ge_{10}$	2.74	104	24.6	2.06	2.94×10^{-3}	1.54	0.26	262	0.51
$Lu_5Ir_4Ge_{10}$	2.54	77	20.0	2.30	2.62×10^{-3}	1.52	0.22	252	0.50

RESULTS

The heat-capacity data for the superconducting compounds belonging to the ternary system $R_5T_4X_{10}$ are presented in Figs. 1–11. For each of the 11 samples studied there is one graph of C versus T over the entire temperature range investigated with an inset of C versus T focusing on the specific heat jump at the transition temperature. We will first discuss the low-temperature heat-capacity results for the samples individually and then point out any systematic trends discovered.

For each compound, the total heat capacity, after correcting for the addenda, was expressed as

$$C = C_e + C_l \ , \tag{1}$$

where C_e is the usual electronic contribution and C_l is the lattice contribution. The heat capacity data from above T_c to 26 K were then fitted to an equation of the form

$$C_n = \gamma_n T + \beta_n T^3 + \alpha_n T^5 \ , \tag{2}$$

where γ_n is the electronic specific heat coefficient in the normal state, β_n is the lattice specific heat coefficient in the normal state, and α_n is a term to account for the anharmonicity of the lattice. Using these coefficients, we calculated $N^*(0)$, the enhanced density of electronic states per spin at the Fermi level,

$$N^*(0) = \frac{3\gamma_n}{2\pi^2 N r k_B^2} \tag{3}$$

as well as the Debye temperature ($T < \Theta_D/10$),

$$\Theta_D^3 = \frac{12\pi^4 N r k_B}{5\beta_n} \tag{4}$$

for each compound. In the above equations, N is Avogadro's number, r is the number of atoms per formula unit, and k_B is Boltzmann's constant. For most of the data sets, the root-mean-square deviation of the fit was about 2%. Exceptions to this were $Sc_5Rh_4Si_{10}$, $Sc_5Ir_4Si_{10}$, and $Y_5Os_4Ge_{10}$ where the rms deviation was between 4% and 5%. This increased difficulty in fitting the data for these three high T_c samples is considered in the discussion section below. In order to calculate λ, the electron-phonon coupling constant for each sample, McMillan's formula with $\mu^* = 0.1$ (μ^* is the Coulomb coupling constant) was used:

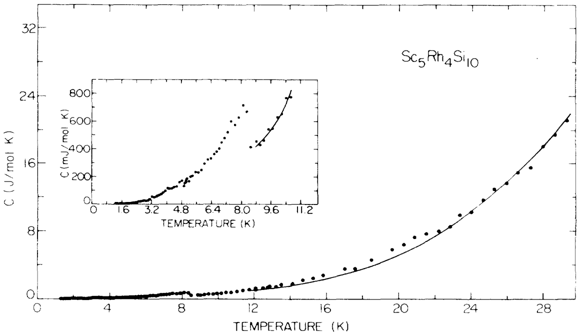

FIG. 2. Specific heat vs temperature for $Sc_5Rh_4Si_{10}$ with an inset focusing on the specific heat jump at T_c. The solid line represents the best fit to the data.

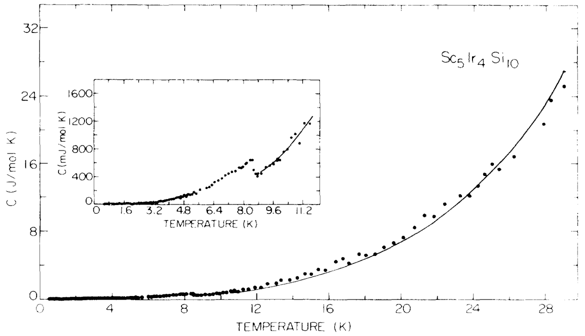

FIG. 3. Specific heat vs temperature for $Sc_5Ir_4Si_{10}$ with an inset focusing on the specific heat jump at T_c. The solid line represents the best fit to the data.

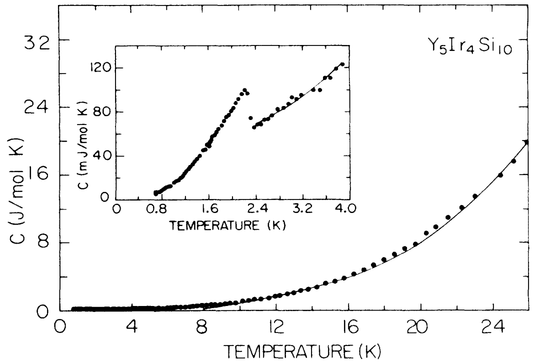

FIG. 4. Specific heat vs temperature for $Y_5Ir_4Si_{10}$ with an inset focusing on the specific heat jump at T_c. The solid line represents the best fit to the data.

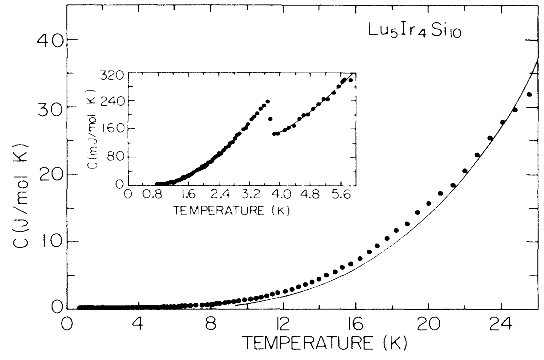

FIG. 6. Specific heat vs temperature for $Lu_5Ir_4Si_{10}$ with an inset focusing on the specific heat jump at T_c. The solid line represents the best fit to the data.

$$\lambda=\frac{1.04+\mu^*\ln(\Theta_D/1.45T_c)}{(1-0.62\mu^*)\ln(\Theta_D/1.45T_c)-1.04}\ . \tag{5}$$

Quantitative data for all samples are presented in Table I.

The low-temperature heat-capacity data for $Sc_5Co_4Si_{10}$ are presented in Fig. 1. The inset of the C-versus-T graph indicates that the calorimetric T_c is 4.89 K, whereas the heat, capacity jump ΔC is 163 mJ/mol K. Analysis of the data yields a value of $\Delta C/\gamma_n T_c = 1.08$, somewhat reduced from the Bardeen-Cooper-Schreiffer (BCS) value of 1.43, as well as a very high Debye temperature, $\Theta_D = 584$ K. The value of λ indicates the sample is an intermediate-coupled superconductor. The low-temperature heat-capacity data for $Sc_5Rh_4Si_{10}$ are presented in Fig. 2. The values of $T_c = 8.43$ K and $\Delta C = 404$ mJ/mol K are evident from the graph. As for $Sc_5Co_4Si_{10}$, the value of the Debye temperature for this sample, $\Theta_D = 448$ K, is large compared to most ternary superconducting compounds. We note the value of $\Delta C/\gamma_n T_c = 2.82$ is much larger than the BCS value. This result, combined with the value of $\lambda = 0.60$, indicates that $Sc_5Rh_4Si_{10}$ is a strong-coupled superconductor. The low-temperature heat-capacity data for $Sc_5Ir_4Si_{10}$ are presented in Fig. 3. The graph yields values of $T_c = 8.57$ K and $\Delta C = 252$ mJ/mol K. The value of the Debye temperature, $\Theta_D = 402$ K, though not as large as the previous two samples is still high. However, the data for $Sc_5Ir_4Si_{10}$ yield even higher values for $\Delta C/\gamma_n T_c = 2.96$ and $\lambda = 0.62$ than for $Sc_5Rh_4Si_{10}$. Again, one may draw the same conclusion: $Sc_5Ir_4Si_{10}$ is a strong-coupled superconductor. The low-temperature heat-capacity data for $Y_5Ir_4Si_{10}$ are presented in Fig. 4. From the graph one notices $T_c = 2.29$ K and $\Delta C = 55$ mJ/mol K. The ratio $\Delta C/\gamma_n T_c = 1.05$ for this compound is less than the BCS value. The Debye temperature is close to that of $Sc_5Ir_4Si_{10}$, having a value of 377 K. The low-temperature heat-capacity data for $Lu_5Rh_4Si_{10}$ are presented in Fig. 5. We obtain values of $T_c = 3.45$ K and $\Delta C = 112$ mJ/mol K. The ratio $\Delta C/\gamma_n T_c = 1.95$ is larger than the BCS value. Fitting the heat capacity data above T_c yields a relatively large value for $\beta_n = 1.41$ mJ/mol K^4 and a Debye temperature of 297 K. The low-temperature heat

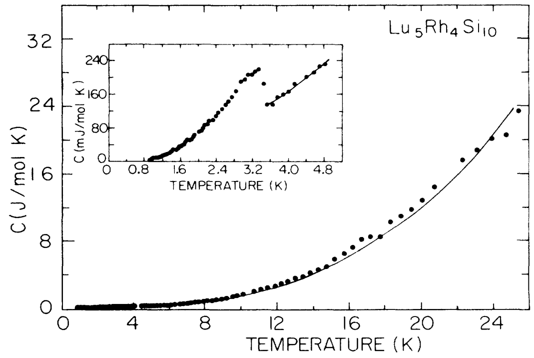

FIG. 5. Specific heat vs temperature for $Lu_5Rh_4Si_{10}$ with an inset focusing on the specific heat jump at T_c. The solid line represents the best fit to the data.

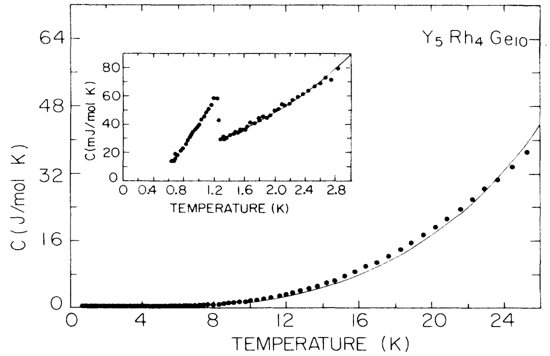

FIG. 7. Specific heat vs temperature for $Y_5Rh_4Ge_{10}$ with an inset focusing on the specific heat jump at T_c. The solid line represents the best fit to the data.

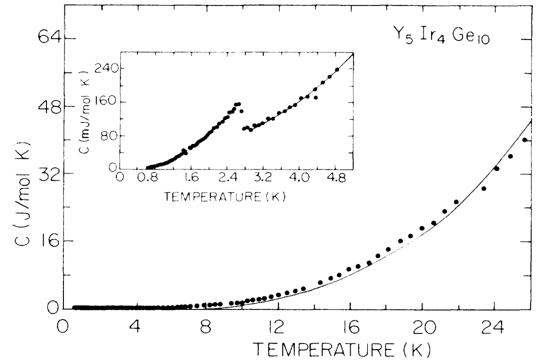

FIG. 8. Specific heat vs temperature for $Y_5Ir_4Ge_{10}$ with an inset focusing on the specific heat jump at T_c. The solid line represents the best fit to the data.

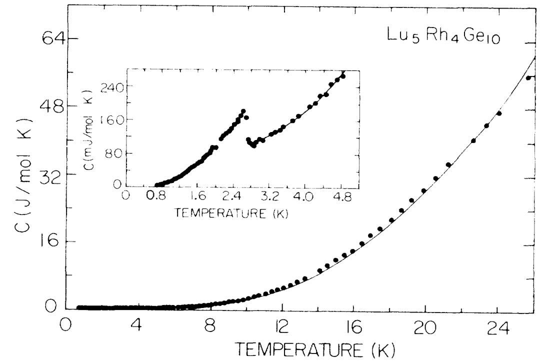

FIG. 10. Specific heat vs temperature for $Lu_5Rh_4Ge_{10}$ with an inset focusing on the specific heat jump at T_c. The solid line represents the best fit to the data.

capacity data for $Lu_5Ir_4Si_{10}$ are presented in Fig. 6. The values of $T_c = 3.77$ K and $\Delta C = 124$ mJ/mol K are evident from the graph. Compared to the BCS value of 1.43, the value of $\Delta C/\gamma_n T_c = 1.41$ for this compound is quite close. A value of $\Theta_D = 366$ K is obtained from the fit of the normal-state data.

Turning to the isostructural, germanium-based compounds, we present the low-temperature heat-capacity data for $Y_5Rh_4Ge_{10}$ in Fig. 7. This figure indicates that $T_c = 1.25$ K and $\Delta C = 34$ mJ/mol K. The calorimetric transition temperature for this compound is quite sharp being about 0.05 K wide. The Debye temperature for this material has a value of 326 K. The low-temperature heat-capacity data for $Y_5Ir_4Ge_{10}$ are presented in Fig. 8. From the graph one obtains $T_c = 2.75$ K and $\Delta C = 85$ mJ/mol K. From a fit of the normal state data, one gets $\Theta_D = 302$ K. The low-temperature heat-capacity data for $Y_5Os_4Ge_{10}$ are presented in Fig. 9. One obtains values of $T_c = 9.10$ K and $\Delta C = 570$ mJ/mol K from the graph. Utilizing the parameters from the fit yielded values of 4.74 for $\Delta C/\gamma_n T_c$, exceptionally large compared to the BCS value of 1.43, and 0.74 for λ. Note also the relatively small values for $\gamma_n = 13.2$. mJ/mol K^2 and $\Theta_D = 275$ K. The same conclusion may be drawn as for $Sc_5Rh_4Si_{10}$ and $Sc_5Ir_4Si_{10}$: $Y_5Os_4Ge_{10}$ is a strong-coupled superconductor. One also notes the existence of a second superconducting phase in this sample, having a $T_c = 1.47$ K. The presence of a heat-capacity jump at this temperature confirms the bulk nature of the superconductivity of this unknown phase. The phase is yet to be determined. The low-temperature heat-capacity data for $Lu_5Rh_4Ge_{10}$ are presented in Fig. 10. A $T_c = 2.74$ K and $\Delta C = 104$ mJ/mol K, are evident from the figure. Fitting the heat capacity data above T_c yields a large value of $\beta_n = 2.06$ mJ/mol K^4 and hence, a relatively small value of $\Theta_D = 262$ K. The low-temperature heat-capacity for $Lu_5Ir_4Ge_{10}$ are presented in Fig. 11. It is evident from the graph that $T_c = 2.54$ K and $\Delta C = 77$ mJ/mol K. This sample has the highest value of $\beta_n = 2.30$ mJ/mol K^4 and hence, the lowest value of $\Theta_D = 252$ K.

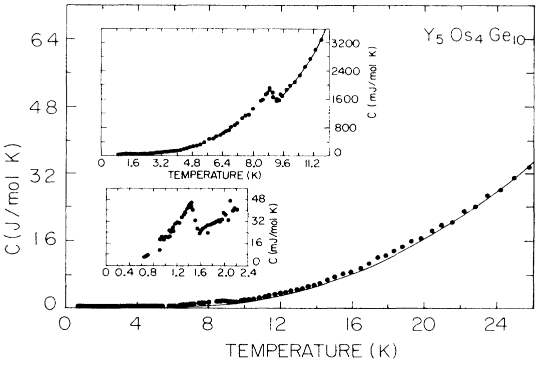

FIG. 9. Specific heat vs temperature for $Y_5Os_4Ge_{10}$ with an inset focusing on the specific heat jump at T_c. The solid line represents the best fit to the data.

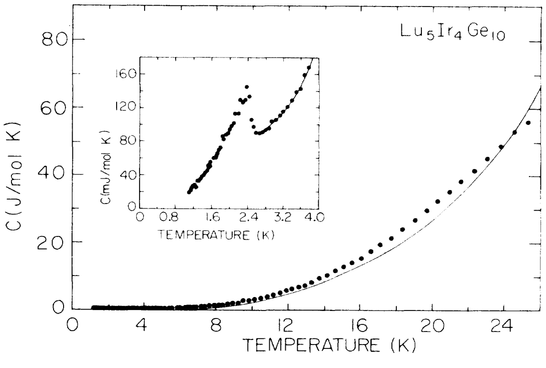

FIG. 11. Specific heat vs temperature for $Lu_5Ir_4Ge_{10}$ with an inset focusing on the specific heat jump at T_c. The solid line represents the best fit to the data.

DISCUSSION

Having presented the low-temperature heat-capacity data of the superconducting compounds in the $R_5T_4X_{10}$ series, we now concentrate on systematic trends observed in these data, referring to Table I for quantitative comparisons. As mentioned previously, the fits of the normal state data to the modified Debye model [Eq. (2)] were poorer for the three highest T_c materials; namely, $Sc_5Rh_4Si_{10}$, $Sc_5Ir_4Si_{10}$, and $Y_5Os_4Ge_{10}$. One consideration is that the high T_c's of these compounds might render the extrapolation of this fit below T_c less reliable and thus introduce greater uncertainty in the fit parameters. Quenching the T_c's by the application of a magnetic field would be useful in understanding the normal state behavior of these compounds. We believe that a more probable reason for the difficulty in fitting the heat capacity data of these three samples is that the phonon spectrum of these structurally complex compounds is too complicated to be adequately described by the Debye model which utilizes just one characteristic temperature. This problem has already been noted in other ternary compounds as well as the high-T_c A-15 materials.[17–20] The high T_c materials investigated thus far seem to have an excess of phonon modes at the low frequencies.

Another systematic result of the analysis that distinguishes the three highest T_c compounds is the extraordinarily large enhancement of $\Delta C/\gamma_n T_c$ from the BCS value of 1.43. The values of the electron-phonon interaction parameter λ are also distinctly larger for these three materials, with $\lambda \geq 0.60$. Although the other eight compounds have respectable λ values (0.41 to 0.52) indicative of intermediate-coupled superconductors, there is a clear distinction between this group of eight compounds and the three highest T_c samples. The presence of the strong electron-phonon interaction in these and high T_c A-15's is one additional reason for the systematic deviations of the normal state lattice contribution from the Debye model. In that case, the BCS theory, which assumes weak coupling between the electrons and phonons, is no longer strictly valid in its application to the materials. A more complete treatment of this interaction, already handled by many scientists, is then necessary to afford a better description of the various superconducting and normal state behaviors exhibited by these strong-coupled superconductors.

The Debye temperatures of the silicides in this system are generally much higher than what is found in other ternary superconducting systems. This is most likely attributable to the fact that Si has a Debye temperature of 630 K and is a major constituent in these materials forming important interatomic bonds (Ge has a $\Theta_D = 370$ K). The Debye temperatures cover a wide range for these eleven isostructural superconductors, varying by more than a factor of 2 from 584 K for $Sc_5Co_4Si_{10}$ to 252 K for $Lu_5Ir_4Ge_{10}$. This variation is not surprising since the molecular weight of these compounds also varies greatly. In fact, the Debye temperature scales reasonably well as the reciprocal of the square root of the molecular weight as one expects.

Lastly, we note that the contribution to the normal state heat capacity by the anharmonic term (α_n) is significant; the data could not be fit when this term was omitted. This is another indication of a complicated phonon structure in this class of compounds. Deviation from a T^3 law in the phonon contribution to the heat capacity has been reported for other ternary superconductors.[21,22] This effect may be a rather general consequence of the complex phonon density of states which may be expected from the involved crystal structure of these materials.

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