# Low Temperature Specific Heat of The Ternary Superconductor $LuRuB_2$

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The detailed specific heat C vs. temperature $T$ for $LuRuB_2$ will be shown in this report. The superconducting and normal state properties were obtained from the calculation of a, $\beta, \gamma$ parameters. High Debye temperature (487 K), electron phonon coupling constant $\lambda=0.59$ and the moderate density of states (0.24 states/eV-atom-spin direction) are the characteristics of this superconducting compound $LuRuB_2$. Modified Debye model can be used to describe this compound entirely.

## I. INTRODUCTION

FOR $(Lu_{1-x}Er_x)RuB_2$, their reentrant phenomenon induced by the onset of magnetic order as displayed in a concentration region $0.35 \leq x \leq 0.50$ provides a good chance for studying the coexistence problem" '. Some ferromagnetic-like order has been suggested by the resistivity measurements at low temperature for reentrant samples under various megnetic fields. The evidence of reentrant phenomenon is clear in either ac magnetic susceptibility measurements or upper critical field determination. If one neglects the second set of magnetic transitions, the low temperature phase diagram for the $(Lu_{1-x}Er_x)RuB_2$ system exhibits the normal state, reentrant superconductivity behavior analogous to the other reentrant systems.

Low temperature and high temperature resistivity data showed no $T^2$ or $T^5$ dependence, which would correspond to electron-electron or s-s intraband scattering. The evidnece we find in the normal state resistivity for strong electron-phonon coupling, which is also observed in A-15 compounds, could have important implications for understanding the high $T_c$ of orthorhombic $LuRuB_2$[1].

From the measurement of low temperature heat capacity, we can characterize the superconducting and normal state properties of sample. Parameters such as the energy gap $\Delta$ may be derived from the superconducting state properties while the detailed electronic and phonon spectrum may be inferred from the normal state. The importance for such measurement is obvious for the advanced understanding on $LuRuB_2$ sample.

## II. SAMPLE PREPARATION AND EXPERIMENTAL METHOD

The sample used in the low temperature heat capacity measurement is about 4 g bulk sample. The correct amount of boron was arc-melted into the ruthenium ingot first, then followed by arc-melting appropriate pure Lu element. The final product was melt several times in order to improve the homogeneity. Finally the sample was sealed in a Ta tube with an argon atmosphere, which is then in quartz tube, and annealed 2 days at 1250°C, 3 weeks at 1000°C. At last, a fast quench in water is necessary.

(1) H. E. Horng, the previous paper "The reentrant properties and upper critical field $H_{c2}$ in the orthorhombic pseudoternary system $(Lu_{1-x}Er_x)RuB_2$", 1984.

A standard isolated heat-pulse type, $He^3$, semi-adiabatic low temperature calorimeter with a mechanical heat switch was used in the measurements of low temperature heat capacity at zero field. The heat capacity data were taken between 0.6K and 26K for a four-gram superconducting ingot of $LuRuB_2$. Temperature was monitored with calibrated Ge thermometers while a heat pulse *was* applied by passing current through high resistance 0.001' diameter Pt-W wire heater wound on the gold plated copper sample holder.

## III. LOW TEMPERATURE SPECIFIC HEAT RESULTS

The detailed heat capacity C vs. temperature $T$ of $LuRuB_2$ between 0.6K and 26K *is* shown in Fig. I. Heat capacity data were taken with increasing temperature in this temperature range. The four-gram sample used for this purpose has a normal to superconducting transition temperature at 8.9K which is lower than the $T_c=9.9K$[1] obtained for a small sample in $\chi_{ac}$ data performed on the same sample. Shown in the inset of Fig. 1 is a detailed plot of $C/T$ *vs.* $T^2$ from 0.6K to 26K. A marked departure from simple Debye type behavior about $T_c$ is apparent by inspecting this inset.

Since $LuRuB_2$ cannot be characterized by a Debye type specific heat of the form $C=\gamma T+\beta T^3$ for the temperature above $T_c$, an additional term $\alpha T^5$ will be added to the normal state heat capacity; therefore, the expression becomes $C=\gamma T+\beta T^3+\alpha T^5$. In this modified Debye model, the $\gamma T$ term is the electron contribution to the heat capacity while $\beta T^3$ is the lattice contribution to the heat capacity and the $\alpha T^5$ term accounts for anharmonicity in the lattice. Then, the plotting $(C-S)/T^3$ *vs.* $T^2$ above $T_c$ yields a linear function with $y$ intercept $(2/3)\beta$ and slope $(4/5)\alpha$. Shown in Fig. 2 is the least-squares fit of the data points to a function $(C-S)/T^3=(2/3)\beta+(4/5)\alpha T^2$. It gives the values of $\beta=6.75\times10^{-2}$ mJ/mole-K$^4$ and $\alpha=1.77\times10^{-4}$ mJ/mole-K$^6$. Using the obtained $\alpha$ and $\beta$ value, the normal state heat capacity fitted by the function $C=\gamma T+\beta T^3+\alpha T^5$ is shown

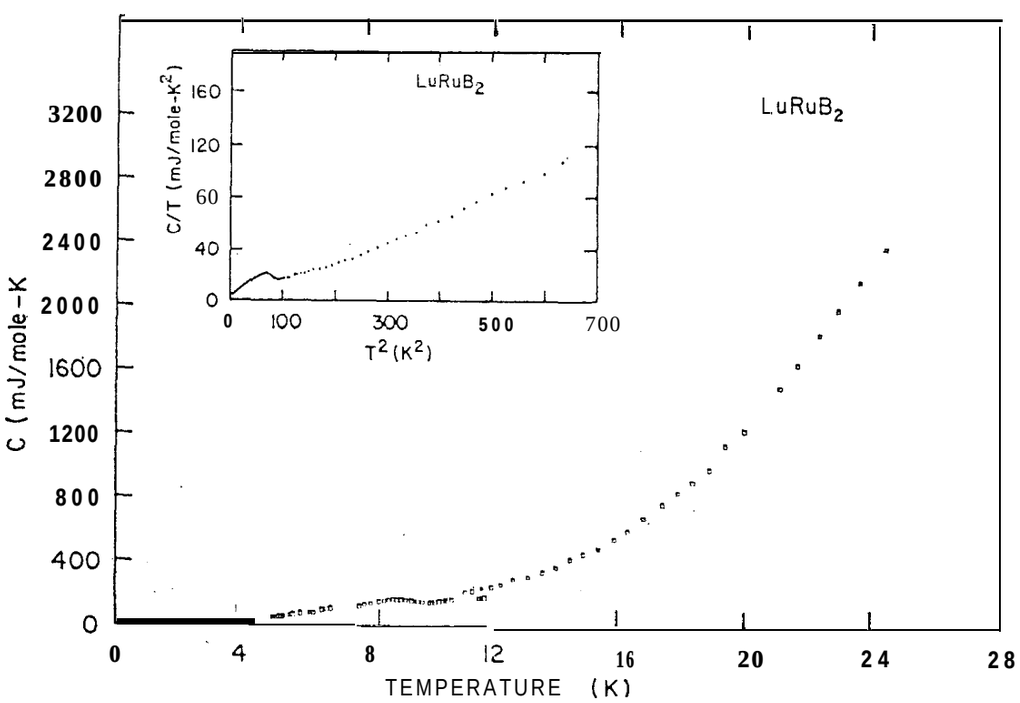


Fig. 1. Specific heat C vs. temperature $T$ for $LuRuB_2$. The inset shows $C/T$ *vs.* $T^2$ in the same temperature range.

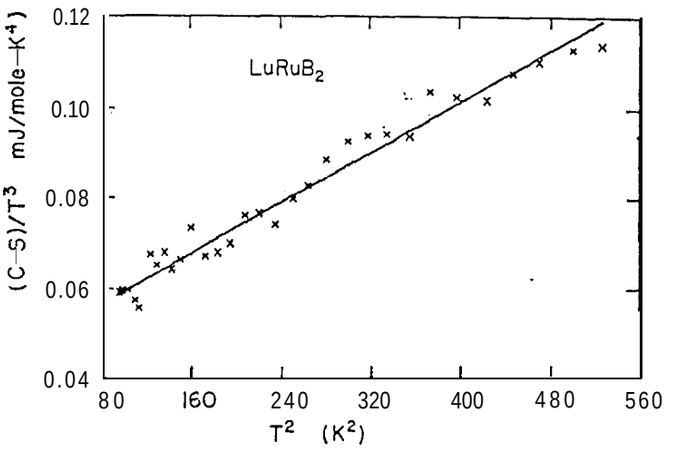


Fig. 2. A plot of $(C\text{-}S)/T^3$ vs. $T^2$ for $LuRuB_2$. The (x) are the data points while the solid line is the least square fit to the function $(C\text{-}S)/T^3 = 2/3\ \beta + 4/5\ \alpha T^2$.

in Fig. 3 with the fitting coefficient $\gamma = 7.05$ mJ/mole-K$^2$. The calculated curve fits excellently to the data points in the temperature range $T_c$ to 23K with a standard deviation of less than 2%.

In order to calculate the enhanced density of state at Fermi energy $N^*(E_F)$, a conveniennt formula is expressed by[2]

$$N^*(E_F) = 0.212\gamma/N \qquad (1)$$

where the units of $N^*(E_F)$ are states/eV-atom-spin direction, the units of $\gamma$ are mJ/mole-K$^2$ and

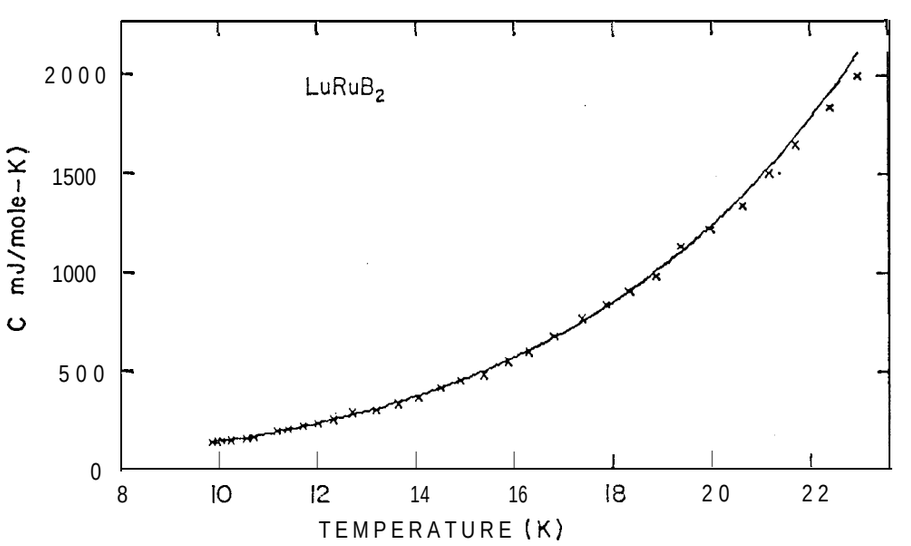


Fig. 3. The normal state heat capacity C of the sample $LuRuB_2$ as a function of temperature between the temperature above $T_c$ to 23K with the fitting equation $C = \gamma T + \beta T^3 + \alpha T^5$ (fixed constants $\beta = 6.75 \times 10^{-2}$ mJ/mole-K$^4$ and $\alpha = 1.77 \times 10^{-4}$ mJ/mole-K$^6$). The solid line represents the fit to tho data.

(2) L. D. Woolf, Ph.D. thesis, University of California, San Diego, 1980.

N is the number of atoms per formula unit. If the units of $\beta$ are mJ/mole-K$^4$, then the Debye temperature $\theta_D$ in Kelvin may be calculated from the lattice contribution to C derived from Debye model :

$$C_e = 9N_A k_B \left(\frac{T}{\theta_D}\right)^3 \int_0^{\theta_D/T} \frac{x^4 e^x}{(e^x-1)^2}\, dx$$

with $N_A$ being Avogadro's number. At temperature $T \leq D/50$, $C_e$ becomes

$$C_e = 234 N_A k_B \left(\frac{T}{\theta_D}\right)^3 = \beta T^3$$

If one compares both sides of this equation, it yields a convenient relation between $\theta_D$ and $\beta$:

$$\theta_D = (1.946 \times 10^6 N/\beta)^{1/3} \qquad (2)$$

Thus, $N^*(E_F) = 0.37$ states/eV-atom-spin direction and $\theta_D = 487$K are found by using Eqs. (1) and (2). If one defined AC as the jump between the extrapolations of heat capacity in both normal and superconducting states at $T_c$, the ratio $\Delta C/\gamma T_c = 1.09$ is the experimental result, which is smaller than the predicted BCS value[3] of 1.43.

The strength of electron-phonon interaction $\lambda$ for $LuRuB_2$ may be derived theoretically by using McMillan's equation[4]

$$T_c = \frac{\theta_D}{1.45} \exp\left[-\frac{1.04(1+\lambda)}{\lambda - \mu^*(1+0.62)}\right] \qquad (3)$$

where $\mu^*$ is the Coulomb pseudopotential and taken to be 0.1, then $\lambda$ is calculated to be 0.59. Finally, the bare density of state $N_b(E_F)$ is given by

$$N^*(E_F) = N_b(E_F)(1+\lambda) \qquad (4)$$

with $N^*(E_F) = 0.37$ states/eV-atom-spin direction obtained from Eq. (1). A value of $N_b(E_F) = 0.24$ states/eV-atom-spin direction is calculated for $LuRuB_2$. Comparing this value to 0.35 states/eV-atom-spin direction for $LuRh_4B_4$ ($T_c = 11.5$K) and $YRh_4B_4$ ($T_c = 10.8$K)[5,6], one notes that $N_b(E_F)$ for $LuRuB_2$ is smaller than that of these superconducting borides. Meanwhile, using the $N_b(E_F)$ value along with $N_b(E_F)J^2 = 2.876 \times 10^{-4}$ eV-atom-states/spin direction in Ref. 1, the estimated strength of pair breaking interaction $J$ is obtained as $3.5 \times 10^{-2}$ eV-atom, which is larger than the value $2.2 \times 10^{-2}$ eV-atom for $(Lu_{1-x}Ho_x)Rh_4B_4$[7] system.

The energy gap at $T=0$, A(O), can be deduced from the superconducting state heat capacity data $C_s$ in the temperature range below $T_c$. Assume that $C_{es}$ is the electronic and $C_{ls}$ the lattice contribution to the specific heat in the superconducting state. Then, $C_{es}$ is obtained from $C_{es} = C_s - C_{ls}$. In the modified Debye model described previously, the lattice part of heat capacity $C_{ls}$ is in the form $C_{ls} = \beta T^3 + \alpha T^5$ while the electronic part near the superconducting transition can be expressed as

$$C_{es} = A_1 \exp\left[-\frac{\Delta(0)}{k_B T}\right] \qquad (5)$$

where $k_B$ is Boltzmann constant. A least square fit of $C_{es}$ vs. temperature $T$ is shown in Fig. 4. The fitting parameters are $A_1 = 592$ mJ/mole-K and $\Delta(0)/k_B = 13.4$K in the temperature range $4.5\text{K} \leq T \leq 7.9\text{K}$. The linear tendency of $C_{es}$ plotted in log-scale vs. $1/T$ is shown in the inset of Fig. 4 and confirms the exponential relation of $C_{es}$. Thus, the energy gap A(0) is found to be $1.16 \sim 10^{-3}$ eV and therefore yields the quantity $2\Delta(0)k_B T_c = 3.02$ which is smaller than the BCS prediction of 3.52. Table 3 provides a convenient summary these heat capacity data and analysis.

(3) J. Bardeen, L. N. Cooper and J. R. Schrieffer, Phys. (Rev. 108, 1175 (1957).
(4) W. L. McMillan, Phys. Rev. 167, 331 (1968).
(5) T. Jarlborg, A. J. Freeman and T. J. Watson-Yang, Phys. Rev. Lett. **39**, 1032 (1977).
(6) A. J. Freeman and T. Jarlborg, J. Appl. Phys. **50**, 1876 (1979).
(7) M. B. Maple, H. C. Hamaker, D. C. Johnston, H. B. Mackay and L. D. Woolf, J. Less Common Metals 62, 251 (1978).

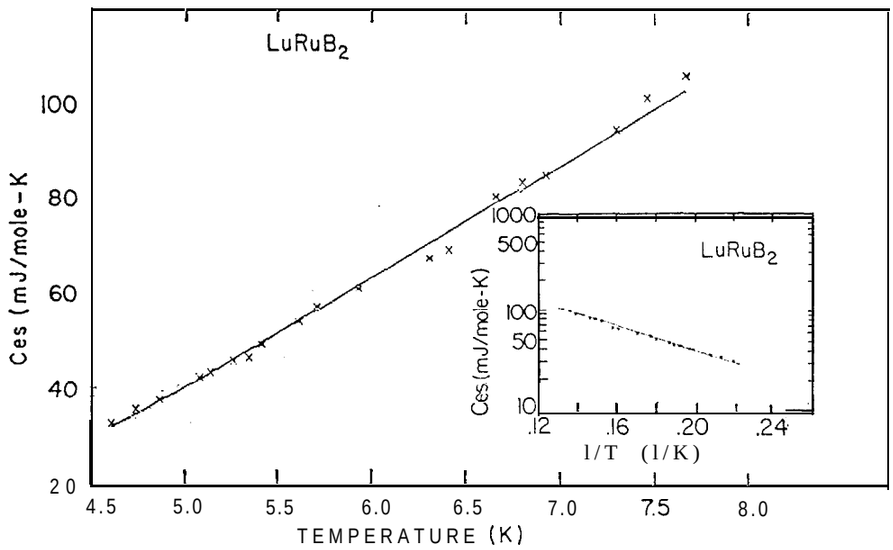


Fig. 4. Electronic contribution to the superconducting state heat capacity $C_{es}$ vs. temperature $T$ for ***Lu Ru*** $B_2$. The solid line is a least square fitof the data for 4.5 K$<T<$7.9 K with the functon $C_{es}=A_1\exp(-A_2/T)$. Shown in the inset is the plotted of C,, on a log scale vs. $1/T$ in which a straight solid line was drawn through the data points.

Extrapolation of the curve fitted to the normal state data, $C=\gamma T+\beta T^3+\alpha T^5$, to $T=0$ allows calculation of the total entropy from $T=0$K to $T=10$K by counting the area under the curve in ***C/T vs. T*** diagram. This value is in good agreement with the experimentally determined entropy and provides an independent check on our fitting procedure.

## IV. DISCUSSION AND CONCLUSION

We obtain different values of $\gamma$ and $N(E_F)$ from the analysis of heat capacity data and critical field measurements (see Table 1). This 20% discrepancy can be attributed to the uncertainty

***Table 1.*** Superconducting and normal state properties of ***Lu Ru*** $B_2$

| Parameter | Units | Heat capacity data | BCS prediction | Critical field results |
|---|---|---|---|---|
| $T_c$ | K | 8.9 | | |
| $\Delta C$ | mJ/mole-K | 68 | | |
| $\gamma$ | mJ/mole-K$^2$ | 7.05 | | 8.67 |
| $\beta$ | mJ/mole-K$^4$ | $6.75\times10^{-2}$ | | |
| $\alpha$ | mJ/mole-K$^6$ | $1.77\times10^{-4}$ | | |
| $\theta_D$ | K | 487 | | |
| $N^*(E_F)$ | states/eV-atom-spin direction | 0.37 | | 0.46 |
| $\lambda$ | | 0.59 | | |
| $N_b(E_F)$ | states/eV-atom-spin direction | 0.24 | | |
| $\Delta C/\gamma T_c$ | | 1.09 | 1.43 | |
| $2\Delta(0)/k_B T_c$ | | 3.02 | 3.53 | |
| $J$ | eV-atom | 3.5x10-2 | | |

in measuring the room temperature resistivity which is an important quantity in determining $\rho_{res}$. Therefore, the values of $\gamma$ and $N(E_F)$ obtained via low temperature heat capacity measurements should be considered more accurate.

An anharmonic term was added to the normal state specific heat data when a modified Debye model was applied. This term is important for fitting due to the curvature in the $C/T$ *vs.* $T^2$ graph in the inset of Fig. 1. The moderate density of states (0.24 states/eV-atom-spin direction obtained from heat capacity data), high Debye temperature (487K) and electron phonon coupling constant $\lambda=0.59$ are the characteristics of the superconducting compound $LuRuB_2$. The critical field measurements" ' show the linearly decreasing tendency of $N^*(E_F)$ as $Er^{3+}$ concentration increases for the the superconducting materials. This decrease in $N^*(E_F)$ is related to the linear decrease in the superconducting transition temperature. Fewer conduction electrons at the Fermi surface lead to a lower temperature for the formation of Cooper pairs. From results of resistivity, upper critical field and heat capacity measurements plus the theoretical intepretation, we suggested that $LuRuB_2$ may be described as a BCS superconductor.

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