PHYSICAL REVIEW B VOLUME 6, NUMBER 9 1 NOVEMBER 1972

Low-Temperature Heat Capacity of $LaRu_2$, $CeRu_2$, and $CeRu_{2-x}Pt_x$

R. R. Joseph,* K. A. Gschneidner, Jr., and D. C. Koskimaki
Ames Laboratory-U. S. Atomic Energy Commission and Department of Metallurgy,
Iowa State University, Ames, Iowa 50010

(Received 6 March 1972)

The heat capacity of two samples of $CeRu_2$ and one sample each of $CeRu_{1.9}Pt_{0.1}$, $CeRu_{1.8}Pt_{0.2}$, and $LaRu_2$ were measured from 1.3 to 9 °K (to 20 °K for $LaRu_2$). All samples are superconducting, have high γ values (10–14 mJ/g atom °K^2) and moderately low Debye temperatures (144–158 °K). None of these materials behaves as a BCS-type superconductor. All of these materials exhibit a departure from the normal T^3 behavior at a temperature $\frac{1}{3}$ to $\frac{1}{2}$ of that which might be expected from the Debye theory. The departure is unusual in that the Debye temperature increases with increasing temperature, while other Laves-phase compounds that we have recently examined show the opposite and more normal(?) behavior. These different behaviors are explained on the basis of the structural nature of the Laves phase.

INTRODUCTION

Cerium metal is known to exist in several allotropic forms and electronic configurations. Until recently, it has proven difficult to isolate any one form at low temperatures to study its electronic character. For this reason we decided to examine some of the cerium compounds as a means of isolating a particular electronic structure of cerium at low temperature. In particular, we have examined the *C*15-type Laves phases AB_2 in which the cerium atom is the *A* atom. It has been observed that the cubic Laves phase $CeRu_2$ becomes superconducting at 4.9 °K.[1] Because a large localized magnetic moment prohibits superconductivity, the electrons in $CeRu_2$ must have little or no localized $4f$ character. Therefore, in this compound cerium must be approximately tetravalent. Also, a plot of the lattice parameters of the compounds RRu_2 (where R stands for a rare-earth element) versus atomic number shows an anomaly for the cerium compound in that its lattice parameter is 1.6% smaller than that expected from the lattice parameters of the other trivalent lanthanides.[2] If the entire change in lattice parameter was due to a shrinkage of the cerium atom this would correspond to a volume change of 14.4%, which compares with a 17% change observed for pure cerium when it transforms from γ to α. In contrast to $CeRu_2$, the lattice parameter of the cubic Laves phase $CePt_2$ shows no deviation when compared to that of the other lanthanide RPt_2 compounds, thereby indicating that cerium is trivalent in this compound. This has been confirmed by magnetic susceptibility measurements.[3–6]

At the time this study was begun $CeRu_2$ was the only known cerium Laves-phase superconductor. For this reason we decided to examine $CeRu_2$ as the material in which cerium had no localized $4f$ electrons. $CePt_2$ was examined because platinum is about the same size as ruthenium, and the cerium in the $CePt_2$ compound has one localized $4f$ electron. Furthermore, it was hoped that the pseudobinary alloys $CeRu_{2-x}Pt_x$ could be formed to study how the properties change as the valence of cerium changes.

EXPERIMENTAL

Sample Preparation

The highest-purity component metals available at the time the study was started were used to prepare these compounds. The La and Ce were prepared at the Ames Laboratory, Iowa State University, and the Ru and Pt were purchased from commercial sources. Chemical analyses of the components used in this study are given in Table I.

A review of the literature on these compounds revealed that the Ce-Ru phase diagram had been investigated[7] and that $CeRu_2$ formed peritectically from ruthenium and liquid alloy between 1539[8] and 1570 °C.[7] Nothing is known about the melting behavior of the other compounds.

A metallographic examination of an ingot of stoichiometric $CeRu_2$ prepared by arc melting revealed three phases and evidence of peritectic rimming. An attempt was made to remove the nonequilibrium microstructure by annealing the ingot at temperatures just below the eutectic temperature 645 °C. An arc-melted sample, heat treated 84 h at 625 °C, showed no change in the amounts of the phases present, suggesting that at 625 °C diffusion rates are too low for any homogenization to take place in a reasonable amount of time. At higher homogenization temperatures the low-melting liquid would wet the tantalum crucibles making removal of the brittle Laves phase in the form of a single solid sample suitable for calorimetry measurements impossible.

TABLE I. Analysis of component materials (impurity levels are given in ppm by weight) [· · · : none found; <: less than; T: trace; FT: faint trace; VFT: very faint trace; (X): interference].

	La	Ce	Ru	Pt
H	2	2	1	21
N	350	33	4	145
O	395	665	15	103
Mg		<55	FT	VFT
Al			VFT	VFT
Si	<15	<30	VFT	FT
Ca	<15	<90	FT	VFT
Cr		<80	FT	VFT
Fe	105	<20	FT	· · ·
Ni	<10		· · ·	VFT
Cu		<20	FT	VFT
Zr		<200		
Ru				T(X)
Rh				T
Pd				FT
Ag				VFT
La		<200		
Ce	<300			
Pr	<600	<200		
Nd	<200	<200		
Ta	660	<500		

An alloy was prepared which had a cerium concentration greater than 35-at.% Ce to avoid the peritectic reaction and leave elemental ruthenium present in the arc-melted button. The problem was to eliminate the cerium-rich eutectic which was intermixed with the Laves phase. Leaching a powdered sample with nitric acid was found to work, but the process was messy and the resulting samples were not suited for calorimetry. Another solution was arc-zone melting.[9] In this technique a sample is placed in a trough of a water-cooled copper hearth and a molten zone is established at one end of the bar. As the hearth is moved under the arc the molten zone will move along the bar. The material freezing out of this molten zone as it moves is the desired $CeRu_2$ and is found at one end of the bar and the eutectic at the other end. The hearth was moved at a velocity of 6.4 mm/h (0.25 in./h) for preparing $CeRu_2$ I. In practice, conditions could not be found in which the phase separation is complete, probably because it is difficult to get the molten zone to extend to the bottom of the bar.

Because subsequent heat-capacity measurements revealed the existence of a second phase which has a large heat capacity, another $CeRu_2$ sample was prepared. This sample, $CeRu_2$ II, was prepared by arc melting stoichiometric amounts of cerium and ruthenium and then annealing it on a water-cooled silver hearth at 1300 ± 50 °C. The inductively heated sample was annealed for 24 h, after which the power was reduced slowly so the sample cooled at a rate of 20 to 30 °C/min down to 800 °C. The power was then shut off and the material cooled to room temperature in about 5 min.

Microscopic examination revealed a small amount of eutectic in the grain boundaries of both $CeRu_2$ samples, and a point-count analysis of the samples showed 3% Ce-rich eutectic in $CeRu_2$ I and 1% in $CeRu_2$ II. From the phase diagram it is estimated that $CeRu_2$ I contains (1.3 ± 0.1)% γ-Ce-Ru solid solution and $CeRu_2$ II (0.43 ± 0.03)% γ-Ce-Ru solid solution. Both samples were chemically analyzed. The metallic impurity concentrations were essentially the same and about what one would expect for levels found in the starting materials (Table I). The nonmetallic concentrations were 406 and 142 ppm (by weight) oxygen, 6 and 1 ppm hydrogen, and 33 and 30 ppm nitrogen for $CeRu_2$ I and $CeRu_2$ II, respectively. Thus, in all respects the $CeRu_2$ II sample was the purer.

The $CeRu_{2-x}Pt_x$ samples were prepared in the same manner as CeRu II, except the annealing times were 30 h for $CeRu_{1.9}Pt_{0.1}$ and 47 h for $CeRu_{1.8}Pt_{0.2}$. Metallographic analysis revealed that there was a small amount of eutectic present in both samples. The two components of the eutectic are the Laves-phase compound and cerium solid solution.

It was observed that a 35-at.% lanthanum arc-melted $LaRu_2$ sample consisted of three phases, not two phases as the off-stoichiometric $CeRu_2$ I sample, and thus, the arc-zone method would not be expected to succeed. An arc-melted sample of the $LaRu_2$ stoichiometry was put into a tantalum crucible which was welded closed under a helium atmosphere, and then homogenized at 1200 ± 50 °C for 16.5 h after which the power was turned off allowing the sample to cool to room temperature in about 30 min. There was no sign of attack of the tantalum crucible, and the alloy was 99.5% single phase but with many voids present. The 0.5% of second phase present was thought to be ruthenium.

The lattice parameters of the $CeRu_{2-x}Pt_x$ alloys were investigated to determine if a continuous series of solid solutions exist in the pseudobinary system. Figure 1 shows the result of this investigation. In addition to the change in the lattice parameter as the concentration is varied, extra lines begin appearing in the x-ray patterns as one moves away from the end components, indicating the existence of a new phase in the $CeRu_{2-x}Pt_x$ system. A sample of the composition CeRuPt was prepared by melting appropriate amounts of $CePt_2$ and $CeRu_2$ in an arc melter and then annealing at 1375 °C for 213 h. An electron microprobe examination of the sample revealed that the two phases present had the approximate compositions CePt and Ru. An x-ray analysis showed that most of the lines could be accounted for by CePt (*B*33, *Tl*I type)[10] and Ru, confirming the microprobe analysis.

The solid solubility limit of Pt in $CeRu_2$ is about 20 mol% at 1000 °C, but there is little solubility of Ru in $CePt_2$ even near the melting point (see Fig. 1). Recent work by Wilhelm and Hillenbrand[11] indicates that the solubility of Pt in $CeRu_2$ can be extended up to about 30 mol% (i.e., $CeRu_{1.4}Pt_{0.6}$) by quenching into ice water small samples which were annealed at 1380 °C.

The lattice parameters of the samples used in the calorimetry experiments are

$LaRu_2$:	$a = 7.7187 \pm 0.0002$ Å,
$CeRu_2$ I:	$a = 7.5386 \pm 0.0004$ Å,
$CeRu_2$ II:	$a = 7.5379 \pm 0.0003$ Å,
$CeRu_{1.9}Pt_{0.1}$:	$a = 7.5461 \pm 0.0002$ Å,
$CeRu_{1.8}Pt_{0.2}$:	$a = 7.5539 \pm 0.0004$ Å.

It is noted that the samples used for the calorimetry measurements are not the same as those used to establish the results shown in Fig. 1. The lattice parameters for the various samples of the same composition, however, agree well with one another within experimental error.

Heat-Capacity Measurements

Heat-capacity measurements[12] were made in an adiabatic heat-pulse type of calorimeter, which was designed to fit between the pole pieces of a 9-kOe magnet. A mechanical heat switch was used to isolate the sample from the helium bath. The temperature was measured with a Honeywell type-II germanium-resistance thermometer (GRT). The GRT was calibrated in the range 1.4–4.2 °K against the vapor pressure of He^4 and in the range 4.2–22 °K against a second GRT which had been calibrated by gas-bulb thermometry.[13] The heat capacity of the addenda was determined in separate runs and subtracted from total heat capacity to give the heat capacity of the sample.

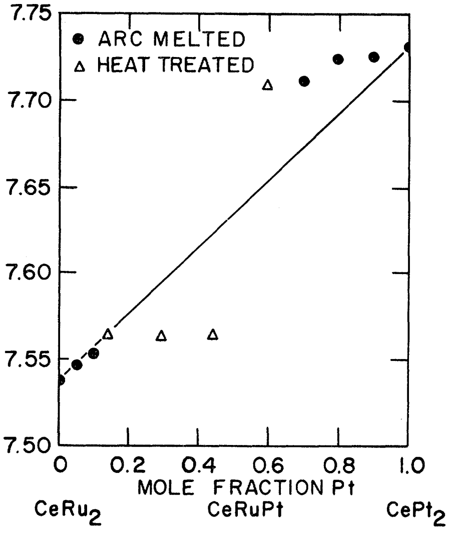

FIG. 1. Lattice parameters of some $CeRu_{2-x}Pt_x$ alloys. The solid line connecting the end members ($CePt_2$ and $CeRu_2$) is the Vegard's law line. The lattice parameters were obtained from arc-melted (●) and heat-treated (△) samples. The heat-treated samples were initially examined after arc melting, but the poor x-ray patterns did not allow us to obtain precise lattice constants. Good x-ray patterns were obtained by annealing the samples at 1000 °C for 48 to 300 h followed by quenching.

The operation of the calorimeter and the validity of the thermometry was checked by measuring the heat capacity of a 1.1-mole Calorimetry Conference Copper Standard[14] sample from 1.4 to 8 °K. All but two of the points fall within 2% of the standard reference equation[14] with no systematic deviations. Furthermore, our results also agree quite well with critically evaluated low-temperature heat-capacity data for copper.[15] Thus, our results for copper give additional confidence to the two thermometer calibrations.

Measurements of heat capacity in a magnetic field were made by using an electromagnet with 10-cm-diam pole tips and a 5-cm pole gap. It was found that the change of resistance of the GRT above 4.2 °K was negligible (< 0.5%) in fields of 9 kOe. Below 4.2 °K the change in resistance varied from 1.3% at 3.3 °K to 2.3% at 1.6 °K. The change in resistance of the GRT as a function of field was fit to an equation and incorporated into the computer program to correct for the effect of field.

All heat-capacity data in zero field were taken in at least two separate runs with the sample warmed to room temperature between runs. No systematic deviation of the heat capacity from one run to the next was found. Since the heater current and Δt are known to 0.1% or better, it is felt that most of the errors associated with the heat-capacity measurements are random in nature and associated with determing ΔT by extrapolation to the center of the heat pulse. The scatter in the data varied from 5% for the addenda to 2% for the copper standard. The heat capacity of the addenda ranged from 20% to 30% of the total heat capacity of the Laves phases investigated in this study. Systematic errors may exist from the thermometry, but their magnitudes are difficult to estimate.

RESULTS

$CeRu_2$

The heat capacity of a 14.9-g sample of $CeRu_2$ I was measured from 1.4 to 8.3 °K (see Fig. 2).[16] The superconducting transition temperature T_s was found to be 5.9 °K. The heat capacity above T_s yielded $\gamma = 23.3 \pm 0.6$ mJ/g atom °K^2 and $\Theta = 171$

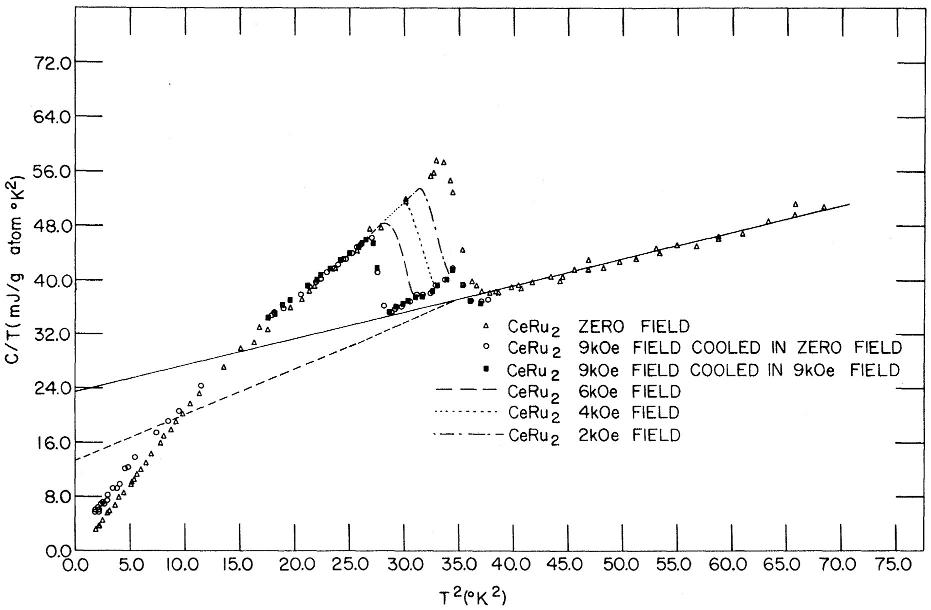

FIG. 2. Heat capacity of $CeRu_2$ I. The solid line is the normal-state behavior based on the extrapolation of the high-temperature data points. The dashed line is the normal-state behavior required for $S_n = S_s$ at T_s, where S is the entropy.

± 2 °K. Measurement of the heat capacity in fields of 2, 4, 6, and 9 kOe revealed a bump in the C/T-vs-T^2 plot at approximately 6 °K. This bump is believed due to the β-Ce (dhcp) second phase which was observed metallographically as the γ-Ce phase at room temperature, but upon cooling transforms to β-Ce.[2] β-Ce is known to order antiferromagnetically at 12.8 °K.[17] but T_N is probably lower since Ru is soluble in Ce.[7] Because of the large heat-capacity contribution due to the β-Ce impurity, a second $CeRu_2$ sample was prepared to see if a purer specimen could be obtained.

The heat capacity of a 18.9-g sample of $CeRu_2$ II was measured over the temperature range 1.4 to 9 °K (see Fig. 3).[16] The T_s of this sample was 6.18 °K. Transition temperature of 4.9 to 6.2 °K have been reported previously for this compound.[1,11,18,19] We believe the differences in transition temperature are due to the varying amounts of Ce-rich solid solution which is present as a second (impurity) phase and lowers T_s by the proximity effect. Our evidence for this is based on the following facts. The early determinations of T_s were made on arc-melted samples[1,18] which were not examined metallographically. However, our study has indicated that samples prepared by arc melting may have as much as 10% of the Ce-rich solid solution present. Furthermore, a transition temperature of 5.9 °K was found for $CeRu_2$I, which contained 1.3% β-Ce solid solution, but $CeRu_2$II, which had 0.4% β-Ce second phase, had a transition temperature that was 0.3 K higher.

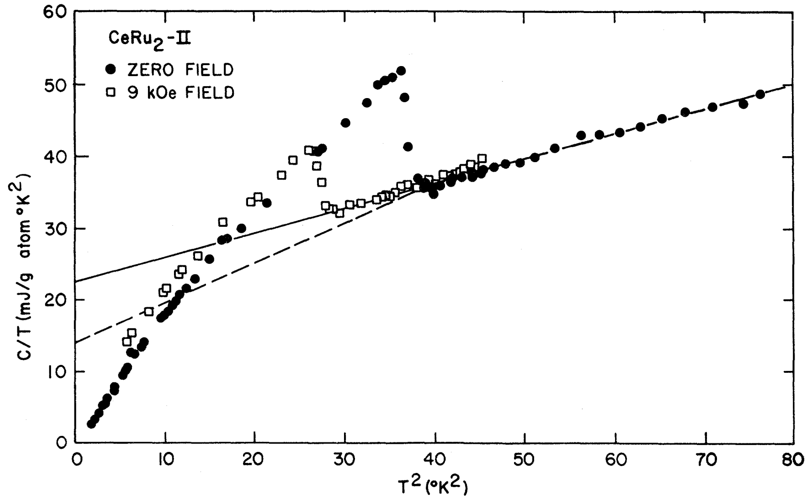

FIG. 3. Heat capacity of $CeRu_2$ II. The solid line is the normal-state behavior based on the extrapolation of the high-temperature data points. The dashed line is the normal-state behavior required for $S_n = S_s$ at T_s, where S is the entropy.

ond phase, had a transition temperature that was 0.3 K higher.

Examination of the heat capacities of $CeRu_2$ I (Fig. 2) and $CeRu_2$ II (Fig. 3) at 9 kOe shows that the entropy of the β-Ce bump in $CeRu_2$ II is about three times less than that seen in the lower-purity sample, $CeRu_2$ I. The relative amount of entropy associated with the bump for the two samples is consistent with the metallographic data. A least-squares fit of the heat-capacity data above 6 °K gives $\gamma = 22.6 \pm 0.5$ mJ/g atom °K^2 and $\Theta = 179 \pm 1$ °K for $CeRu_2$ II (Fig. 3).

Recently, Cooper *et al.*[20] reported preliminary results of their heat-capacity measurements on $CeRu_2$. They find $\gamma = 30 \pm 5$ mJ/g atom °K^2 and $\Theta = 202 \pm 10$ °K. Both of these values are significantly higher (33 and 13%, respectively) than our values for $CeRu_2$ II. Peter *et al.*[21] and Junod[22] have also recently measured the heat capacity of $CeRu_2$, and their γ and Θ values are 20 mJ/g atom °K^2 and 180 °K, respectively. These values are in good agreement with our results for $CeRu_2$ II. A comparative analysis of the three sets of heat-capacity measurements shows that (i) our $CeRu_2$ II sample has the highest T_s and smallest ΔT_s (width of the superconducting transition temperature); (ii) the sample of Peter *et al.*[21] and Junod[22] has intermediate T_s and ΔT_s values; and (iii) the sample of Cooper *et al.*[20] has the lowest T_s and largest ΔT_s (nearly three times our ΔT_s value). These data suggest that our $CeRu_2$ II sample is the purest sample measured to date. It is also noted that the sample of Peter *et al.* and Junod contained about 2% γ-Ce-Ru solid solution.[22]

Further analysis of our $CeRu_2$ data showed that the entropy of the superconducting state S_s at the transition temperature is smaller than that of the normal state S_n by 26% (44 mJ/g atom °K) for $CeRu_2$ I and 27% (45 mJ/g atom °K) for $CeRu_2$ II. This difference is clearly unacceptable. But, if normal-state behavior follows the $C = \gamma T + \beta T^3$ behavior, then the difference can be reconciled if the γ and Θ values are significantly lower than that obtained from the high-temperature data (> 6 °K). Examination of the C/T-vs-T^2 plots for the $CeRu_{2-x}Pt_x$ alloys (Figs. 4 and 5) shows a change in slope around 6 °K. The plots show that two straight lines can be drawn through the points, and the resultant γ and Θ values are smaller for the heat-capacity data points below 6 °K than the γ and Θ values obtained from the heat-capacity data points above 6 °K. The behavior of the $CeRu_{2-x}Pt_x$ alloys reinforces our conviction that the approach used to equate the two entropies is the correct one.

By assuming that the normal-state heat capacity can be expressed as $C/T = \gamma + \beta T^2$, then the heat capacity of the normal state at T_s is $C/T_s = \gamma + \beta T_s^2$. The entropy at T_s is

$$S_n = S_s = \int_0^{T_0} (C/T)dT = \gamma T_s + \tfrac{1}{3}\beta T_s^3.$$

By solving the last two equations simultaneously, the following γ and Θ values are obtained:

$CeRu_2$ I: $\gamma = 13.3 \pm 1.3$ mJ/g atom °K^2,
$\Theta = 144 \pm 2.4$ °K;
$CeRu_2$ II: $\gamma = 13.6 \pm 1.1$ mJ/g atom °K^2,
$\Theta = 147 \pm 2.6$ °K.

The γ and Θ values which give S_n values within ± 5 mJ/g atom °K of S_s are considered to be acceptable solutions for $S_n = S_s$ at T_s. This criterion was used to estimate the above error limits for γ and Θ.

Junod[22] also found $S_n \neq S_s$ for his $CeRu_2$ sample. A behavior similar to that found for $CeRu_2$ has been observed by Vieland and Wicklund[23] for the heat capacity of Nb_3Sn.

$CeRu_{2-x}Pt_x$ Alloys

The heat-capacity data of the pseudobinary alloy $CeRu_{1.9}Pt_{0.1}$ are shown in Fig. 4.[16] The superconducting transition temperature is 4.08 °K. A least-squares fit of the data between 4 and 6 °K gives $\gamma = 10.3 \pm 0.2$ mJ/g atom °K^2 and $\Theta = 143.5 \pm 0.5$ °K.

The heat-capacity data[16] (Fig. 5) of $CeRu_{1.8}Pt_{0.2}$ were too sparse in the vicinity of the superconducting transition to define the transformation temperature. The transition temperature was found to be 3.40 ± 0.04 °K by measuring the magnetic susceptibility versus temperature. As seen in Fig. 5, this transition temperature is consistent with the heat-capacity data. A least-squares fit of the data between 3.4 and 5.4 °K gives $\gamma = 11.1 \pm 0.2$ mJ/g atom °K^2 and $\Theta = 144.5 \pm 0.5$ °K.

The bump found in Figs. 4 and 5 at $T^2 = 37$ °K^2 is thought to be due to the excess cerium solid solution (containing ruthenium and platinum) which probably orders antiferromagnetically, just as the two $CeRu_2$ samples discussed previously. However, for the $CeRu_{2-x}Pt_x$ alloys the bumps are visible in zero field since the superconducting transition has been lowered by the platinum additions.

For both of these alloys S_n is slightly greater than S_s at T_s (~ 6%), but the absolute difference is less than 5 mJ/g atom °K for both alloys. It is thought that this difference in entropies lies within the experimental error and thus no adjustment was made in the γ and Θ values given above.

$LaRu_2$

The heat capacity of $LaRu_2$ (Fig. 6)[16] was measured in an attempt to understand the effect of the extra valence electron in $CeRu_2$. These data show a well-behaved heat-capacity curve with the transition temperature between the normal and super-

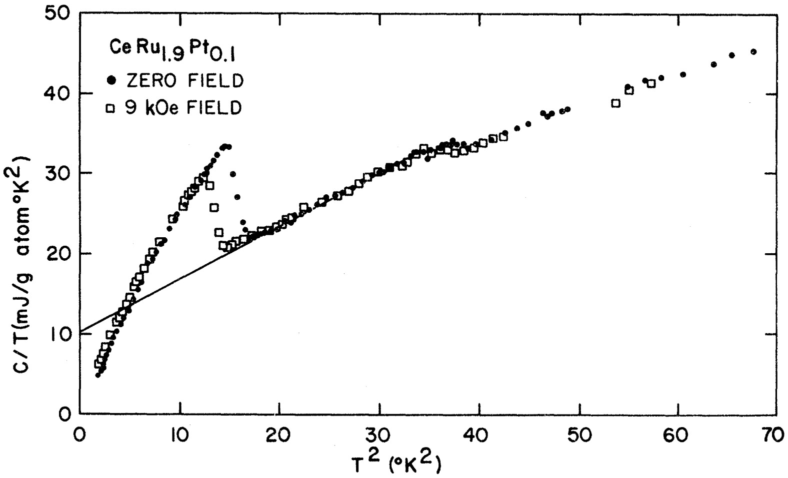

FIG. 4. Heat capacity of $CeRu_{1.9}Pt_{0.1}$.

conducting states occurring at 3.08 °K. The constants determined from the data between 3 and 6 °K were $\gamma = 13.85 \pm 0.09$ mJ/g atom °K and $\Theta = 158.4 \pm 0.3$ °K.

The heat capacity was redetermined in order to confirm the drop off of the C/T values from the linear line established between 3 and 6 °K (Fig. 6). Although the data shown in Fig. 6 cover the range 1.2–7.7 °K, the C/T values up to 20 °K lie on a smooth curve which continues to depart from the linear line. The later data are thought to be more reliable (± 1% compared to ± 2%) because of improvements in the calorimeter. The largest deviation between the two sets of runs occurs in the 6–7 °K region. The earlier data points fall within ± 1% of the smooth curve drawn through the later data points, except between 6 and 7 °K where the spread is ± 2%.

The entropy difference between the normal and superconducting states at the superconducting-transition temperature for $LaRu_2$ is 5% (3mJ/g atom °K) and thus, S_s and S_n are considered to be equal within experimental error.

DISCUSSION

The experimental results for these Laves-phase compounds are summarized in Table II. The data have been arranged as a function of increasing electron concentration, assuming La contributes three electrons, Ce contributes four, Ru contributes eight, and Pt contributes ten. It is seen that γ and Θ decrease initially with increasing electron concentration and that T_s has a maximum at an electron concentration of 6.67 (i.e., $CeRu_2$). These data also suggest that just beyond $CeRu_2$ (on an electron-concentration scale) the density of states (γ) falls as the electron concentration is increased by a few hundredths per atom.

The decrease in the density of states for electron concentrations greater than 6.67 is consistent

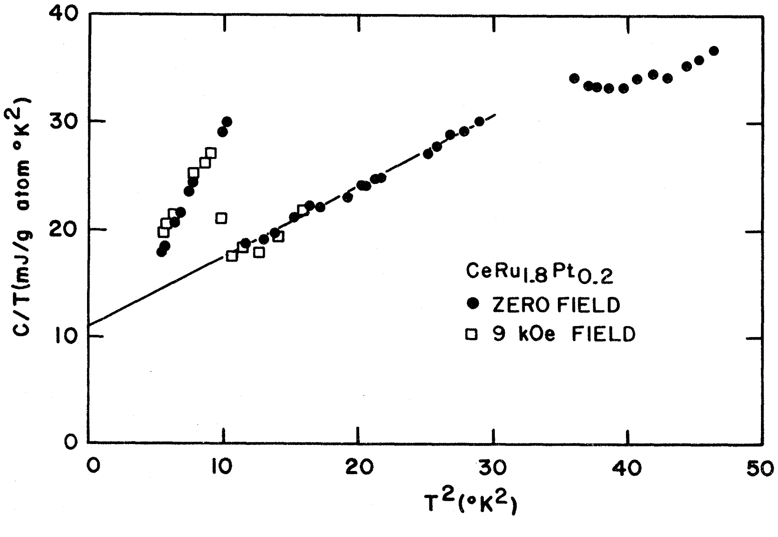

FIG. 5. Heat capacity of $CeRu_{1.8}Ru_{0.2}$.

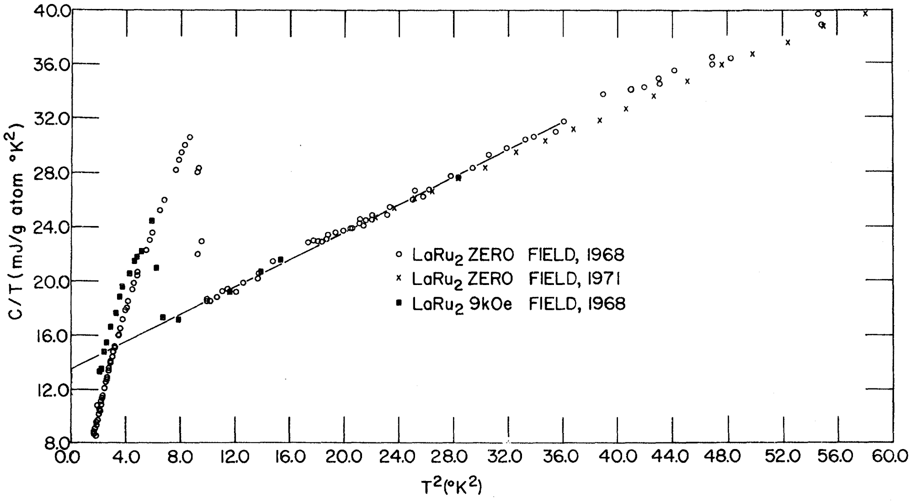

FIG. 6. Heat capacity of $LaRu_2$.

with the decrease in the superconducting transition temperature and the termination of the solid-solution region, $CeRu_2$-$CeRu_{2-x}Pt_x$. The former will be discussed later. The termination of Laves-phase solid-solution regions, according to Klee and Witte,[24] is due to a drop in the density of states as the solid-solution region approaches its equilibrium-solubility limit. Their model is an extension of Jones's theory originally proposed for the termination of Cu solid solutions.[25]

Debye Temperature

The variation in the Debye temperatures (Table II) is reasonable, especially for the $CeRu_{2-x}Pt_x$ compounds. From elementary theory as a first approximation the Debye temperature for these closely similar materials should vary inversely to the square root of the mass of the atoms per formula unit M. This is most readily seen by comparing the product $\Theta M^{1/2}$ (see Table II). For the three $CeRu_{2-x}Pt_x$ compounds the deviation from the mean is 1.1%. The $\Theta M^{1/2}$ value for $LaRu_2$ is about 7% smaller than the values for the $CeRu_{2-x}Pt_x$ compounds. It is difficult to say whether or not this difference is significant.

The change in slope in the C/T-vs-T^2 plots for these Laves phases and also the direction of the change is interesting. For these compounds, the Debye temperature as determined from heat-capacity data above 6 °K for the $CeRu_{2-x}Pt_x$ compounds increased by 10% and for $LaRu_2$ by 20% from the Debye temperatures deduced from the lower temperature data (see Fig. 7). In contrast to this behavior, Hungsberg and Gschneidner[26] noted that Debye temperatures for the RAl_2 Laves phases (R = Y, La, and Lu) decrease with increasing temperature above ~6.5 °K (see Fig. 7). The same also occurs for $LaPt_2$ above ~3.5 °K.[6] In an attempt to understand this behavior the heat capacity was fitted to a power series $C = AT + BT^3 + DT^5$. As one might expect for those Laves phases for which Θ decreases with increasing temperature (Fig. 7), the sign of the D coefficient is positive, and for those for which Θ increases, the sign is negative. We believe that A, B, and D are only fit parameters and have no physical significance. Our reasons for this are the following: (i) Although good fits are obtained for the Laves phases which have positive D values, the fits are poor for the three compounds which have negative D values and the power series chosen to fit the data is unsatisfactory. (ii) For $LaAl_2$ and YAl_2 the Debye temperatures have been calculated from the single-crystal elastic constants measured at 4.2 °K.[27] A comparison shows that the Θ values obtained from the C/T vs T^2 plot are smaller than the elastic Θ by 6.1% and 2.5%, respectively, but the above three-parameter equation yields Θ values which are larger than the elastic Θ by 11.5 and 7.2%, respectively, depending upon the temperature range over which the data are fitted. One can get

TABLE II. Summary of the heat-capacity results and some derived quantities.

Compound	Electron conc.	T_s (°K)	γ $\left(\frac{\text{mJ}}{\text{g atom °K}^2}\right)$	Θ (°K)
$LaRu_2$	6.33	3.08	13.85	158.4
$CeRu_2$-II	6.67	6.18	13.6	147
$CeRu_{1.9}Pt_{0.1}$	6.73	4.08	10.3	143.5
$CeRu_{1.8}Pt_{0.2}$	6.80	3.40	11.1	144.5

Compound	$\Theta M^{1/2}$	$\frac{\Delta C}{\gamma T_s}$	H_0 (Oe)	T_s at 9 kOe (°K)	Entropy under bump (mJ/g atom °K)
$LaRu_2$	2920	1.07	617	2.49	...
$CeRu_2$-II	2720	1.33	1420	5.20	10
$CeRu_{1.9}Pt_{0.1}$	2690	1.39	832	3.64	20
$CeRu_{1.8}Pt_{0.2}$	2750	1.22	669	3.14	10

the elastic Θ to agree with the heat capacity Θ by merely choosing the particular temperature range over which the three-parameter equation gives the right answer—but this is unethical and unscientific. A calculated phonon spectrum for the hexagonal MgZn_2 Laves phase[28] suggested that there may be low-lying optical branches. Therefore, we attempted to explain the temperature variation of Θ by adding an Einstein-type term to the Debye term. This was not successful since such a term can only account for a decrease in the Debye temperature.

The variation of the Debye temperature with increasing temperature can be correlated to the radius ratio and Debye temperatures of the component atoms in their pure states by the use of a simple hard-sphere model. The Laves phases AB_2 can be considered to be constructed of a close-packing arrangement of hard spheres of two different size atoms, which have radius ratio r_A/r_B near 1.2.[29-31] When the radius ratio is ideal ($r_A/r_B = 1.225$) there are both A-A and B-B contacts; when it is larger there are only A-A contacts, and when it is less there are only B-B contacts. There are never any A-B contacts, regardless of radius ratio value; and the Laves phases can be considered to consist of two semi-independent lattices, one being composed of only A atoms and the other of only B atoms. Although the materials studied in this investigation are cubic, the unit cell of the cubic Laves phase is large and contains 24 atoms. Because of the complexity of the cubic Laves phase no experimental or theoretical phonon frequency spectrum is available and thus we are unable to discuss the temperature dependence of the Debye temperature in terms of a phonon spectrum.

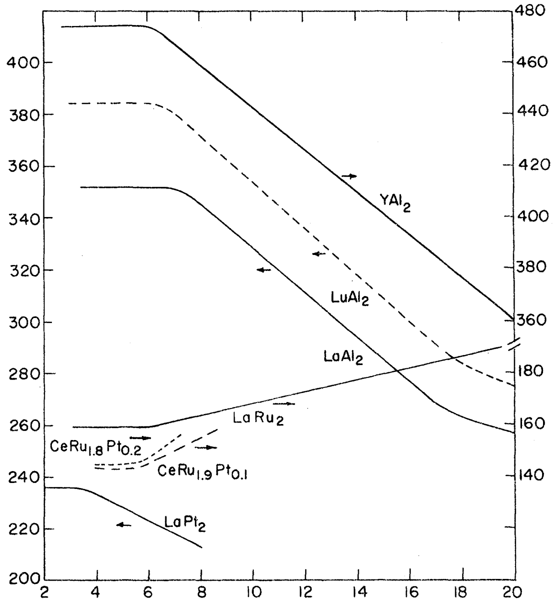

FIG. 7. Debye temperature for several Laves-phase compounds as a function of temperature. The Debye temperature was calculated from the measured heat capacity after subtracting the electronic contribution (γT). At the lowest temperature shown in the figure the uncertainty in Θ assuming a 1% error in the heat capacity is ±17 °K for YAl_2, ±9 °K for LaAl_2, ±7 °K for LuAl_2, ±3 °K for LaPt_2, and ±1 °K for the $R\text{Ru}_{2-x}\text{Pt}_x$ compounds. At 7 °K the estimated uncertainty in Θ is ±5 °K for YAl_2, ±3 °K for LaAl_2 and LuAl_2, and <1 °K for LaPt_2 and the $R\text{Ru}_{2-x}\text{Pt}_x$ compounds. At 20 °K the uncertainty in Θ is about 1 °K for all three $R\text{Al}_2$ Laves phases, and 0.7 °K for LaRu_2.

The vibrational frequency of an atom in a linear chain is proportional to $(c_i/M_i)^{1/2}$, where c_i is the force constant of the ith atom and M_i is its mass. From the structural nature of the Laves phase it is expected that $c_A \neq c_B$. Since c_i cannot be determined uniquely for these compounds, we have assumed that the $(c_i/M_i)^{1/2}$ is proportional to Θ_i, where Θ_i is the Debye temperature of either pure A or pure B, and the vibrational characteristics of the ith atom are given by Θ_i. At temperatures near 0 °K, the dominant contribution to the lattice dynamics are expected to be due to the kind of atoms which are in contact with one another (e.g., A-A). As the temperature is raised, higher vibrational modes are excited and contribute to the heat capacity. Some of these higher modes arise from the other kind of atom (B) which is not in contact with other B atoms at 0 °K. As the temperature is increased the B atom contribution to the total lattice dynamics of the crystal would increase. Thus, at 0 °K the Θ of the Laves phase would be approximately Θ_A and at higher temperatures it would change in the direction toward Θ_B. If $\Theta_A > \Theta_B$, then at higher temperatures the C/T-vs-T^2 plot would rise above the straight line established at low temperatures. In the case where there are B-B contacts at 0 °K and $\Theta_B > \Theta_A$, the same behavior would be expected. This is the situation for the $R\text{Al}_2$ and LaPt_2 phases, (Fig. 7), which exhibit B-B contacts at 0 °K[26,32] with Θ_R (268, 142, and 210 °K, respectively, for R = Y, La, and Lu) $< \Theta_{\text{Al}}$ (423 °K) and Θ_{La} (142 °K) $< \Theta_{\text{Pt}}$(234 °K).

Conversely, in the case where there are A-A contacts at 0 °K and $\Theta_B > \Theta_A$, the Θ of the Laves phase at 0 °K would expected to be $\simeq \Theta_A$, but the C/T values on a C/T-vs-T^2 plot would fall below the straight line established at low temperatures. This is the situation for LaRu_2 and the $\text{CeRu}_{2-x}\text{Pt}_x$ phases (Figs. 4–7) which exhibit A-A contacts at 0 °K[32] with Θ_{Ru} (600 °K) $> \Theta_{\text{La}}$(142 °K) and $\Theta_{\text{Ru,Pt}}$ (600 °K, 234 °K) $> \Theta_{\text{Ce}}$(~ 140 °K). In the case where there are B-B contacts at 0 °K and $\Theta_A > \Theta_B$ the same behavior would be expected.

Qualitatively, the heat-capacity behavior of these Laves phases has been explained by an oversimplified model. *But its greatest utility is that it can be used to predict the Debye temperature at 0 °K and its temperature dependence from a knowledge of the Laves-phase lattice parameter(s) (to calculate the radius of A*[32]*) and the radius of pure metal B, which together give the radius ratio required to apply this model.*

Superconductivity

Wilhelm and Hillenbrand[11] have made a study of the variation of T_s with Pt concentration for the CeRu$_{2-x}$Pt$_x$ alloys. Our results are in reasonable agreement with their data: A $T_s = 4.08$ °K for our CeRu$_{1.9}$Pt$_{0.1}$ compares to 3.9 °K and a $T_s = 3.40$ for our CeRu$_{1.8}$Pt$_{0.2}$ compares to 3.3 °K. These differences could easily be due to slight errors in the Pt concentration and/or internal stresses and/or sample inhomogeneities in the two sets of alloys. Furthermore, our results confirm the shape of the T_s-vs-composition curve reported by these authors.[11]

The superconducting transition temperature for these Laves-phase compounds has been calculated by using the BCS equation[33]

$$T_s = (1.14\hbar\omega/k)e^{-1/N(0)V^*} ,$$

where $\hbar\omega/k$ is the Debye temperature, $N(0)$ is the density of states at the Fermi surface and is calculated from γ, and V^* is the net electron-interaction energy and is assumed to be the same for all of the RRu$_{2-x}$Pt$_x$ Laves phases. A value of $0.105 \pm .009$ for V^* was calculated for CeRu$_2$ II by substituting T_s in the above equation. It can be shown that T_s, according to the above equation, has a weak dependence on Θ but is quite sensitive to the exponential term. The calculated T_s values for the other compounds (observed values given in parentheses) using the above equation are 2.1 ± 1.0 °K (4.08) for CeRu$_{1.9}$Pt$_{0.1}$, 2.9 ± 1.1 °K (3.40) for CeRu$_{1.8}$Pt$_{0.2}$, and 7.0 ± 2.0 °K (3.08) for LaRu$_2$. The error limits are obtained by taking into account the error limits associated with the γ values for the four compounds. The agreement between the calculated and observed superconducting transition temperatures can be considered to be only fair. Furthermore, the calculated values suggest a minimum in or a flattening out (considering the error limits) of the T_s-vs-composition curve, neither of which is observed. The (dT_s/dc) value derived from the calculated T_s is much smaller than that observed.

The BCS theory states[33] that the ratio $\Delta C/\gamma T_s$ should be equal to 1.52, where ΔC is the jump in the heat capacity at the superconducting transition temperature. It is not unusual to see deviations from this value, but they are usually in the direction of higher ratios. As can be seen in Table II, the ratio is smaller than predicted by theory for all four compounds, and this is what has been observed for rare-earth compounds which have been measured to data.[26,34]

The temperature dependence of the electronic contribution to the heat capacity of the superconducting phase was examined. The electronic contribution was determined by subtracting the lattice contribution as calculated from a T^3 dependence, from the total heat capacity. The data given in Fig. 8 show that the heat capacity of the electrons have a temperature dependence that is considerably different than that predicted by the BCS theory.

The above analyses indicate that LaRu$_2$ and CeRu$_{2-x}$Pt$_x$ do not behave as BCS-type superconductors. This may be due to a complex Fermi surface,[34] or to overlapping conduction bands,[35] or to a combination of both. Either or both of these conditions could exist in the RRu$_{2-x}$Pt$_x$ Laves-phases materials, but in the absence of theoretical calculations and/or experimental Fermi-surface measurements, it is not possible to know if this

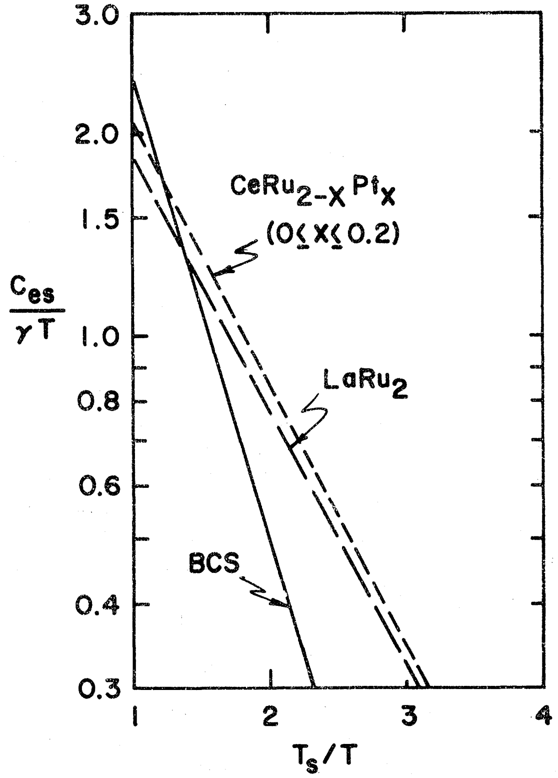

FIG. 8. Electronic heat capacity as a function of the reduced temperature for LaRu$_2$ and CeRu$_{2-x}$Pt$_x$. The curve labeled BCS is the theoretical temperature dependence expected for a material behaving as a BCS superconductor.

is the explanation for the observed departure from BCS behavior.

The thermodynamic critical field at $T = 0$ °K, H_0, was calculated by using Rutgers's formula[36]

$$\Delta C = \frac{VT_s}{4\pi}\left(\frac{dH_c}{dT}\right)^2_{T=T_s} ,$$

and assuming that temperature of the critical field H_c obeys the standard form found experimentally for most superconductors,[36]

$$H_c = H_0[1 - (T/T_s)^2] ,$$

where V is the atomic volume (cm^3/g atom). All of the other terms have been defined previously. The calculated H_0 values are listed in Table II. Comparing these values with the observed field dependence for these compounds (see Figs. 2–6), indicates that $LaRu_2$ and $CeRu_{2-x}Pt_x$ are type-II superconductors with H_{c2} greater than 9 kOe.

It is of interest to calculate the field required to quench superconductivity at 0 °K, but a recent study of the variation of T_s of $CeRu_2$ as a function of field by Hillenbrand *et al.*[37] shows that H_{c2} has an unusual S-shaped temperature dependence from ~ 1 to 6.2 °K (T_s at $H = 0$). Their data show that $H_{c2}(0)$ is of the order of 80 kOe. Comparing the lowering of T_s by a field of 9 kOe (see Table II), it is found that our $CeRu_2$ II exhibits a significantly larger decrease in temperature (0.98 °K/9 kOe) than their sample (0.7 °K/9 kOe), which is essentially the same as observed for our CeRu I sample (0.72 °K/9 kOe). Since the superconducting transition temperature of the sample of Hillenbrand *et al.* sample is the same as that of our $CeRu_2$ II alloy, the difference in temperature dependence of H_{c2} is not due to excess Ce impurities (the likely reason for the differences between our two samples). The most reasonable explanation for the difference in the temperature dependence of H_{c2} is the difference in the metallurgical microstructure of our $CeRu_2$ II and their $CeRu_2$ sample. The description of the heat treatment of their samples (annealing at 1380 °C and quenching) suggests that their sample is more highly strained than our $CeRu_2$ II sample, which was slow-cooled from the annealing temperature (1300 °C) to 800 °C before rapidly cooling it to room temperature.

β-Ce Solid-Solution Impurity

As noted earlier, metallographic examination revealed the presence of a cerium-rich eutectic composed of the $CeRu_{2-x}Pt_x$ Laves phase and a Ce solid-solution phase, which probably contained dissolved Ru and perhaps Pt. The bump in the heat capacity curves at ~ 6 °K is believed to be due to the Ce solid-solution phase which orders magnetically at ~ 6 °K. The entropy associated with the bump is listed in Table II (the value for $CeRu_2$-I is 30 mJ/g atom °K).

One would expect the entropy[17] associated with the ordering to be

$$S = R\ln 2 = 5760 \text{ mJ/g atom Ce °K}$$

because the crystal field splits the $J = \frac{5}{2}$ multiplet into three doublets in a hexagonal field or a doublet (ground state) and a quartet (excited state) in a cubic field. The entropy under the bump indicates 0.52 at.% excess Ce is present in $CeRu_2$ I, 0.17 at% in $CeRu_2$ II and $CeRu_{1.8}Pt_{0.2}$, and 0.34 at.% in $CeRu_{1.9}Pt_{0.1}$. These values are four times lower than the Ce concentrations estimated from metallographic data. There are several explanations rationalizing this difference. One reason is that the metallographic data is based on several observations of the surface of the samples and thus is not necessarily representative of the bulk of the specimen. The heat capacity, however, is a bulk measurement and thus should be more representative of the whole specimen, provided all of the Ce present orders. In pure Ce and many Ce-rich alloys (up to ~ 5 at.% solute), only part of the Ce (the dhcp phase) orders magnetically, while the remainder (the α-fcc phase) does not. Whether the dissolved Ru prevents the formation of the fcc α-Ce phase is not known. We consider these two methods of estimating the amount of second phase Ce as giving us the upper and lower limits of the amount of impurity phase present in our samples.

One might wonder whether the excess Ce phase could account for some of the unusual behavior noted above. We do not think so, primarily because it is difficult to see how such a small amount of second phase could have such large anomalies (the two different slopes in the C/T-vs-T^2 curves and departures from BCS theory). Furthermore, the anomalies appear to be independent of the amount of impurities present. Another reason is that similar anomalies were found in $LaRu_2$ and Nb_3Sn, and there are no magnetic impurities present in these materials. In conclusion, we note it is regrettable that we were unable to prepare samples which were free from second-phase material, but we believe that the data and results presented herein are reliable and accurate within the limits stated.

ACKNOWLEDGMENTS

The authors wish to thank their co-workers, O. D. McMasters, J. E. Ostenson, Nancy Kippenhan, and F. A. Schmidt, for their assistance in some aspects of this investigation; F. H. Spedding and his group for furnishing the rare-earth metals; D. K. Finnemore, C. A. Swenson, and J. F. Smith for their helpful discussions; and the Ames Laboratory Spectrochemical and Analytical Chemistry Groups for analyzing the samples.

Acknowledgement is also due to D. W. Osborn and H. E. Flotow, Argonne National Laboratory, for furnishing the Calorimetry Conference Copper Standard; to J. R. Cooper, Institute di Fisica, Universita di Genova and to Dr. A. Junod, Département de Physique de la Matière Condensée, Université de Geneve for sending us more detailed information on their heat-capacity results for $CeRu_2$; and to R. J. Schiltz, Jr., Iowa State University, Ames, Iowa, for furnishing us with his results of the elastic constant measurements on the RAl_2 phases before publication.

---

*Present address: Components Division, IBM, Hopewell Junction, N. Y. 12533.

[1] B. T. Matthias, H. Suhl, and E. Corenzwit, Phys. Rev. Letters 1, 92 (1958).

[2] K. A. Gschneidner, Jr., *Rare Earth Alloys* (Van Nostrand, Princeton, N. J., 1961).

[3] G. L. Olcese, Boll. Sci. Fac. Chim. Ind. Bologna 24, 165 (1966) [U. S. AEC Report No. IS-Trans-70, (National Technical Information Service, Springfield, Va. 1967)].

[4] R. Vijayaraghavan, V. U. S. Rao, S. K. Malik, and V. Marathe, J. Appl. Phys. 39, 1086 (1968); and R. Vijayaraghavan, S. K. Malik, and V. U. S. Rao, Phys. Letters 20, 106 (1968).

[5] H. J. van Daal and K. H. J. Buschow, Phys. Status Solidi 3 (a), 853 (1970).

[6] R. R. Joseph, K. A. Gschneidner, Jr., and R. E. Hungsberg, Phys. Rev. B 5, 1878 (1972).

[7] W. Obrowski, Z. Metallk. 53, 736 (1962).

[8] R. D. Reiswig and K. A. Gschneidner, Jr., J. Less-Common Metals 5, 432 (1962).

[9] O. N. Carlson, F. A. Schmidt, and W. M. Paulson, Trans. Am. Soc. Metals 57, 356 (1964).

[10] A. E. Dwight, R. A. Conner, Jr., and J. W. Downey Acta Cryst. 18, 835 (1965).

[11] M. Wilhelm and B. Hillenbrand, Z. Naturforsch. 26a, 141 (1971).

[12] More details are available in the Ph. D. thesis of R. R. Joseph (Iowa State University, Ames, Iowa, 1968) (unpublished); or in *The Low Temperature Specific Heat of Some Cerium and Lanthanum Laves Phase Compounds*, US AEC Report No: IS-T-229 (National Technical Information Service, Springfield, Va., 1968).

[13] D. K. Finnemore, D. L. Johnson, J. E. Ostenson, F. H. Spedding, and B. J. Beaudry, Phys. Rev. 137, 550 (1965).

[14] D. W. Osbourne, H. E. Flotow, and F. Schreiner, Rev. Sci. Instr. 38, 159 (1967).

[15] G. T. Furukawa, W. G. Saba, and M. L. Reilly, *Critical Analysis of the Heat Capacity Data of the Literature and Evaluation of Thermodynamic Properties of Copper, Silver, and Gold from* 0 *to* 300 °K, Natl. Bur. Std. Ref. Data Series-Natl. Bur. Std. 18, (U. S. GPO, Washington, D. C., 1968).

[16] The experimental heat capacity versus temperature data may be obtained by ordering NAPS Document No. 01868 from ASIS National Auxiliary Publications Service c/o CCM Information Corp., 909 Third Avenue, New York, N. Y. 10022; remitting $2.00 for microfiche or $5.00 for photocopies; or from K. A. Gschneidner, Jr., Ames Laboratory, Iowa State University, Ames Iowa 50010 (free).

[17] N. T. Panousis and K. A. Gschneidner, Jr., Phys. Rev. B 5, 4767 (1972).

[18] T. E. Smith and I. R. Harris, J. Phys. Chem. Solids 28, 1846 (1967).

[19] M. Wilhelm and B. J. Hillenbrand, J. Phys. Chem. Solids 31, 559 (1970).

[20] J. R. Cooper, C. Rizzuto, and G. Olcese, in *Conference Digest No. 3, Rare Earths and Actinides, Durham*, 1971 (The Institute of Physics, London, 1971), pp. 183–185. The experimental heat capacity data points were not published in the paper but were kindly furnished by Dr. J. R. Cooper.

[21] M. Peter, P. Donzé, O. Fischer, A. Junod, J. Ortelli, A. Treyvaud, E. Walker, M. Wilhelm, and B. Hillenbrand, Helv. Phys. Acta 44, 345 (1971).

[22] A. Junod (private communication).

[23] L. J. Vieland and A. W. Wicklund, Phys. Rev. 166, 424 (1968).

[24] H. Klee and H. Witte, Z. Physik. Chem (Leipzig) 202, 352 (1954).

[25] H. Jones, Proc. Phys. Soc. (London) 49, 250 (1937).

[26] R. E. Hungsberg and K. A. Gschneidner, Jr., J. Phys. Chem. Solids, 33, 401 (1972).

[27] R. J. Schiltz, Jr. (private communication).

[28] H. Eschrig, P. Urwank, and H. Wonn, Phys. Status Solidi 49, 807 (1972).

[29] R. L. Berry and G. V. Raynor, Acta Cryst. 6, 178 (1953).

[30] W. Hume-Rothery, R. E. Smallman, and C. W. Haworth, *The Structure of Metals and Alloys* (Institute of Metals, London, 1969).

[31] G. E. R. Schulze, Z. Krist. 111, 249 (1959).

[32] R. R. Joseph and K. A. Gschneidner, Jr., Scripta Met. 2, 631 (1968).

[33] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. 108, 1175 (1957).

[34] T. Satoh and T. Ohtsuka, Phys. Letters 20, 565 (1966).

[35] I-Ming Tang, Phys. Letters 35A, 39 (1971).

[36] D. Schoenberg, *Superconductivity* (Cambridge U. P. Cambridge, England, 1965).

[37] B. Hillenbrand, K. Schuster, and M. Wilhelm, Phys. Letters 36A, 383 (1971).