

Low-temperature specific heat of two platinum-based ternary alloy systems

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The specific heat C_p of pure platinum and of the ternary alloys Pt₉₀Ir₅Au₅, Pt₈₀Ir₁₀Au₁₀, Pt₈₆Rh₉Au₅, and Pt₇₄Rh₁₇Au₉ was measured between 0.5 and 30 K. C_p is analyzed primarily in terms of lattice and electronic contributions, and the latter is discussed in terms of several models of metallic alloying. A constant contribution to C_p was apparent in all of the alloys at the lowest temperatures.

I. INTRODUCTION

We have measured the specific heat, C_p , of two platinum-based disordered alloy systems having nominal concentrations Pt₉₀Ir₅Au₅, Pt₈₀Ir₁₀Au₁₀, Pt₈₆Rh₉Au₅, and Pt₇₄Rh₁₇Au₉, over the temperature range 0.5 to 30 K. Pure platinum was also measured to serve as a calorimetric reference. The alloy series was chosen specifically to examine the effects of alloying on the electronic specific heat for compositions at, or close to, pseudo-platinum, i.e. with equal additions of elements electronically adjacent to platinum, in contrast to the more usual binary-alloy studies.

Recent photoemission experiments¹⁻⁴ have demonstrated that the band structure of alloy systems does not in general behave according to any simple model. However, simple models do appear to provide an adequate description for some binary-alloy systems and for those specific systems the models have value, and one can consider their extension to ternary or more complex alloys. We have applied three models to the alloys we have measured: the rigid-band approximation, an empirical model proposed by Miedema,⁵ and a calculation suggested by Guthrie.⁶ We find that although the rigid-band approximation provides an adequate description of binary alloys of some of our constituents it cannot be extended to their ternaries. Miedema's model does not provide an accurate description at present, but there is good agreement with the calculations of Guthrie when applied to the Pt-Ir-Au series. Changes in the electron-phonon enhancement factor $(1 + \lambda)$ in an alloy system may be responsible for changes in γ which are comparable to or larger than changes due to purely electronic effects on the density of states $N(E_F)$. Our studies of $\Theta_D(T)$ over the temperature range of our measurements indicate that $\Theta_D(T)$ of most alloys is very similar to $\Theta_D(T)$ of pure platinum. Consequently, changes in $(1 + \lambda)$

are expected to be small, minimizing the effect of the electron-phonon enhancement on changes in γ .

The Pt-Ir-Au and Pt-Rh-Au ternary systems are particularly suited to testing recent energy-band calculations of disordered alloy systems, such as those of Stocks^{7,8} because they provide data complementary to those obtained previously in the Pt-Ir and Pt-Au binary systems,⁹ the Pd-Rh and Pd-Ag binary systems,¹⁰ and an associated ternary system Pd-Rh-Au.¹¹ In addition, our Pt-Rh-Au alloys provide a useful link between ternary series involving $5d$ and $4d$ constituents.

II. EXPERIMENTAL TECHNIQUES

The measurements were made in a pumped ³He calorimetry system using a standard heat-pulse technique. Between 200 and 300 measurements of the specific heat were made for each sample in the temperature range from 0.5 to 30 °K. Both ³He vapor pressure (0.4–2 °K) and a four lead germanium standard resistor¹² (1.5–30 °K) were employed to calibrate a two lead germanium resistive thermometer in an ac bridge circuit. The ³He vapor pressure was accurately determined by use of a capacitance manometer, and care was taken to provide a substantial overlap between the vapor pressure and standard resistor calibration regions. The agreement was good in the overlap region. We have since cross-calibrated the ³He vapor pressure capacitance manometer with a four lead germanium standard resistor¹³ calibrated from 0.3 °K. Details of the systems and methods involved are available elsewhere.^{14,15} The excellent agreement of our pure platinum results with previously published values provides a useful check of our technique.

All the samples measured were prepared by Materials Research Corporation. The constituent elements were all Marz grade (99.998% pure).

TABLE I. List of compositions and contaminants of the samples studied.

Nominal concentration	Atomic percentages				Contaminants ^c (ppm)	
	Pt	Ir	Rh	Au	Fe	Ni
Pure Pt ^a	99.998 ^a	5 ^a	<1 ^a
Pt ₉₀ Ir ₅ Au ₅ ^b	89.14	5.45	...	5.40 ^b	<20	<200
Pt ₈₀ Ir ₁₀ Au ₁₀ ^a	80.04	10.08	...	9.88 ^a	260	<200
Pt ₈₀ Ir ₁₀ Au ₁₀ ^b	80.10	9.52	...	10.38 ^b		
Pt ₈₆ Rh ₉ Au ₅ ^a	86.28	...	9.00	4.72 ^a	130	<200
Pt ₇₄ Rh ₁₇ Au ₉ ^a	73.88	...	16.87	9.25 ^a	180	<200

^a Concentrations provided by manufacturer.

^b Concentrations obtained using Physics Dept., University of Delaware/Bartol Research Foundation proton microprobe facility (see Ref. 16).

^c Except in the case of pure Pt all contaminant concentrations provided by Schwartzkopf Microanalytical Laboratory, Woodside, N.Y.

Each sample was approximately 50 g, and consequently the contribution of the addenda to the total heat capacity was always less than 10% and usually much smaller. The composition of each sample is listed in Table I. The nominal figures are the results of the manufacturer's analysis, conducted before the samples were prepared. As a check, the samples were reanalyzed by two independent techniques. A standard chemical analysis was attempted but difficult to execute because of the chemical properties of the elements involved. To avoid these complications, a proton microprobe analysis was completed using the University of Delaware/Bartol Research Foundation facility based on a 2.5-MeV Van de Graaff accelerator.¹⁶ The results of this analysis agree within experimental error with the concentrations cited by the manufacturer. The iron and nickel concentrations of the alloys quoted by the manufacturer are comparable to those of the pure platinum sample. Results of the chemical analysis, however, indicate significantly higher concentrations of iron, and we are currently attempting to verify this analysis using the proton microprobe.

III. RESULTS

Below about 8 K the specific heat for our alloys was analyzed according to the equation

$$C_P = \gamma T + \beta(0)T^3 + C_{ex}, \quad (1)$$

where

$$\gamma = \frac{2}{3}\pi^2 k^2 N(E_F), \quad (2)$$

$N(E_F)$ being the density of electronic states at the Fermi level. From β the low-temperature limiting value of Θ_D can be obtained from

$$\beta(T) = 12\pi^4 R / 5\Theta_D^3(T) \quad (3)$$

when $T \rightarrow 0$. The third term in Eq. (1) C_{ex} represents the remaining specific heat when the two contributions mentioned above are removed. It is apparent only at the lowest temperatures, and was found to be almost constant throughout our temperature range. Similar contributions have been observed in other alloy systems and are generally attributed to the formation of magnetic clusters, either spontaneously or due to impurities.¹⁷

Above about 10 K [i.e., $\Theta_D(0)/25$] Eq. (1) no longer provided an adequate description of C_P . The variations could be encompassed by determining an effective Debye temperature $\Theta_D(T)$ obtained from $\beta(T)$ according to Eq. (3) after subtracting the small electronic and C_{ex} contributions from C_P . Comparison of the resulting temperature dependence of $\Theta_D(T)$ for the pure platinum and the alloys gives an indication of possible

TABLE II. Summary of the specific-heat results when analyzed according to the equation $C = \gamma T + \beta T^3 + C_{ex}$.

	γ (mJ/mole °K ²)	$\Theta_D(0)$ (°K)	C_{ex} (mJ/mole °K)
Pure Pt	6.50 ± 0.024	239.7 ± 1.1	-0.02 ± 0.020
Pt ₉₀ Ir ₅ Au ₅	5.59 ± 0.022	232.8 ± 0.20	0.64 ± 0.027
Pt ₈₀ Ir ₁₀ Au ₁₀	4.77 ± 0.015	237.0 ± 0.16	0.65 ± 0.018
Pt ₈₅ Rh ₉ Au ₅	5.91 ± 0.021	236.7 ± 0.22	1.64 ± 0.022
Pt ₇₄ Rh ₁₇ Au ₉	6.21 ± 0.025	248.5 ± 0.48	2.08 ± 0.036

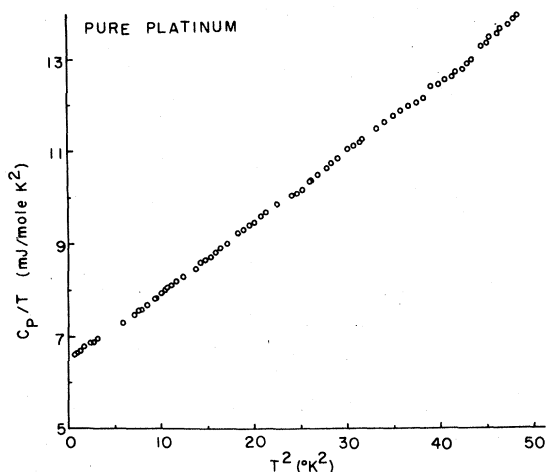
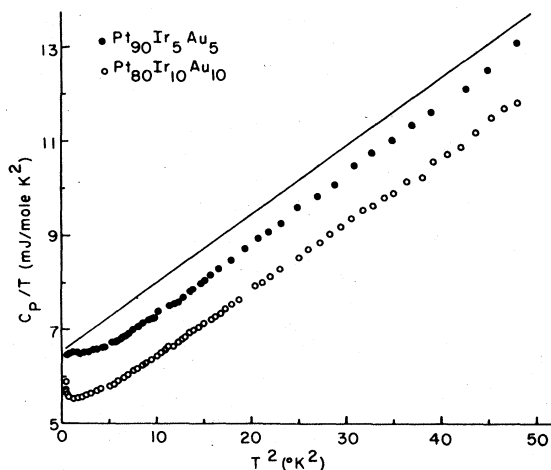


FIG. 1. Specific heat of pure platinum.

FIG. 2. Specific heat of $\text{Pt}_{90}\text{Ir}_5\text{Au}_5$, $\text{Pt}_{80}\text{Ir}_{10}\text{Au}_{10}$, and smoothed pure Pt (solid line).

changes in phonon behavior arising from alloying.

Fitting to Eq. (1) was carried out by multiple regression analysis over successive temperature regions since C_{ex} is best determined at the lowest temperatures where it is a major contribution, while γ and $\beta(0)$ are best determined between 2 and about 8 K. We caution that data above 2.5 K can be interpreted without the third term of Eq. (1) since the standard plots of C_p/T vs T^2 (see below, Figs. 1–3) do not show the clear upturn characteristic of the C_{ex} contribution until below 1.5 K. Values of γ and $\beta(0)$ obtained from such a two-term analysis will be in error, consistently overestimating γ . This suggests that much alloy data of the past, limited to a lowest temperature of 1.5–2 K, may be providing misleading values of γ , and should be redetermined down to at least 0.5 K. In a few cases, notably Pt-Ir and Pt-Au binary alloys, the contribution of C_{ex} has been carefully recognized.⁹

For comparative purposes we present all of our data at low temperatures in the form of C_p/T vs T^2 plots, while for $T \gtrsim 10$ K we plot

$\Theta_D(T)$ vs T , γ , and C_{ex} being considered constant. The numerical values of γ , $\beta(0)$, and C_{ex} are summarized in Table II and discussed in detail in the sections below.

A. Platinum

The results for the pure platinum sample are shown in Fig. 1, where it is seen that our data are in excellent agreement with Eq. (1), with $C_{\text{ex}} = 0$. Resulting γ , $\Theta_D(0)$, and C_{ex} values obtained from the least-square fit are listed in Table II. The value of C_{ex} obtained from the computer fit show that contributions other than phonon and electronic are negligible.

In Table III we list several recent measurements of γ and $\Theta_D(0)$ for pure platinum as well as our own results. The agreement of our results with the published values is excellent.^{18,19} Figure 4(a) is a plot of $\Theta_D(T)$ as a function of temperature together with a solid line representing the smoothed values of Shoemake and Rayne.²⁰ Again, the agreement is good over the same temperature range.

TABLE III. Comparison of the specific-heat results of pure platinum.

Reference	Purity (at.% Pt)	γ (mJ/mole $^{\circ}\text{K}^2$)	$\Theta_D(0)$ ($^{\circ}\text{K}$)
Shoemake and Rayne (Ref. 20)	99.999	6.56 ± 0.03	234.4 ± 2.5
Sacchi <i>et al.</i> (Ref. 18)	99.999	6.60 ± 0.01	240.0 ± 5.0
Martin (Ref. 19)	99.999	6.49 ± 0.008	238.7 ± 0.7
This work	99.998	6.50 ± 0.02	239.7 ± 1.1

B. Pt-Ir-Au alloys

The low-temperature results for the $\text{Pt}_{90}\text{Ir}_5\text{Au}_5$ and the $\text{Pt}_{80}\text{Ir}_{10}\text{Au}_{10}$ samples are shown in Fig. 2 and tabulated in Table II. Clearly, γ is strongly affected by the alloying process. While the value for the $\text{Pt}_{90}\text{Ir}_5\text{Au}_5$ sample is depressed below the Pt value to 5.59 mJ/mole K, γ for the $\text{Pt}_{80}\text{Ir}_{10}\text{Au}_{10}$ sample has been depressed to 4.77 mJ/mole K or approximately twice the change ($\Delta\gamma$) seen in $\text{Pt}_{90}\text{Ir}_5\text{Au}_5$. The fact that $\Theta_D(0)$ changes very little would suggest that the lattice properties of the samples have not been significantly altered by the alloying process. Figure 4(b) displays $\Theta_D(T)$ as a function of temperature for each of the alloys, as well as a dashed line representing the smoothed data for our pure platinum sample. Comparison shows that $\Theta_D(T)$ is also relatively unaffected by alloying over the temperature range of our measurements.

C. Pt-Rh-Au alloys

Figure 3 shows the low-temperature results for $\text{Pt}_{86}\text{Rh}_9\text{Au}_5$ and $\text{Pt}_{74}\text{Rh}_{17}\text{Au}_9$ with the numerical values in Table II. The γ value for $\text{Pt}_{86}\text{Rh}_9\text{Au}_5$ is depressed below the Pt value to 5.91 mJ/mole K² while in contrast to the results for the Ir-based series above, the value of γ for $\text{Pt}_{74}\text{Rh}_{17}\text{Au}_9$ is depressed only slightly below that of Pt to 6.21 mJ/mole K².

The value of $\Theta_D(0)$ for $\text{Pt}_{86}\text{Rh}_9\text{Au}_5$ is very close to that of pure Pt, as is the general trend of $\Theta_D(T)$ vs T [Fig. 4(c)]. However, for $\text{Pt}_{74}\text{Rh}_{17}\text{Au}_9$, $\Theta_D(0)$ shows a marked shift from the values of Pt and the other alloys, and $\Theta_D(T)$ as a function of

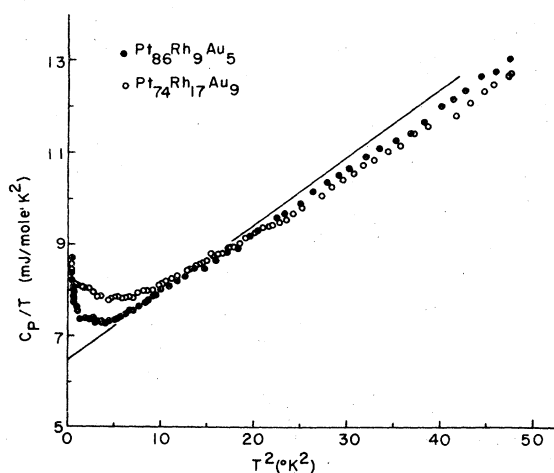


FIG. 3. Specific heat of $\text{Pt}_{86}\text{Rh}_9\text{Au}_5$, $\text{Pt}_{74}\text{Rh}_{17}\text{Au}_9$, and smoothed pure Pt (solid line).

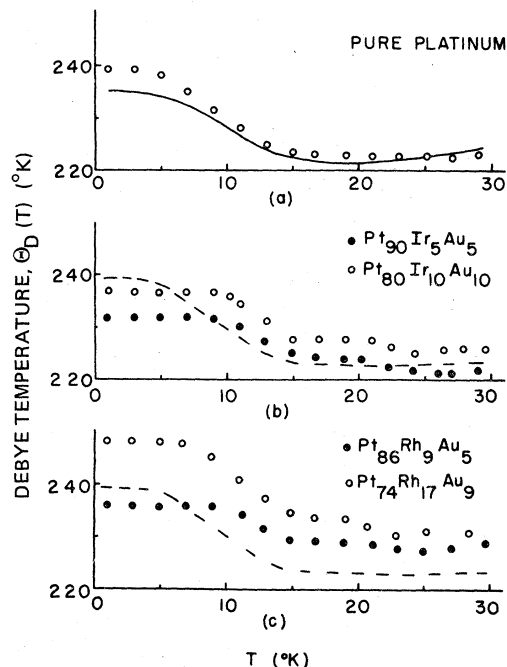


FIG. 4. Debye temperature for (a) pure Pt (this work) and smoothed Pt data of Shoemaker and Rayne (Ref. 20) (solid line); (b) $\text{Pt}_{90}\text{Ir}_5\text{Au}_5$, $\text{Pt}_{80}\text{Ir}_{10}\text{Au}_{10}$, and smoothed pure Pt data of this work (dashed line); (c) $\text{Pt}_{86}\text{Rh}_9\text{Au}_5$, $\text{Pt}_{74}\text{Rh}_{17}\text{Au}_9$, and smoothed pure Pt data of this work (dashed line).

temperature reflects that shift throughout the temperature range, while retaining the general shape of the other curves. This trend in Θ_D is consistent with the increasing amount of the lighter Rh atoms in the lattice, and suggests also that we are exceeding the region of dilute alloy behavior.

IV. DISCUSSION

The purpose of the series of measurements reported here was to initiate a study of the dependence of the electronic specific heat of ternary alloys which are isoelectronic with elements as a test of theoretical models and empirical calculations of alloying behavior. Although the isoelectronic condition was met quite accurately for our Pt-Ir-Au series, the Pt-Rh-Au series was not as well balanced, making interpretation of the results more difficult. Recent advances in photoemission spectroscopy have provided, in some ways, more complete information on the density of electronic states of elements and alloys than can be provided by measurement of C_P , but the latter does provide a direct quantitative measurement of the electronic density of states at the

Fermi level $N(E_F)$ for comparison with theoretical calculations.

In general only binary alloy systems and pure elements have been compared with recent theoretical determinations of band structure and density of states, with almost no attempts to apply models to ternary alloy systems. This is in part because few ternary alloy systems have been studied experimentally, and also because of the relative difficulty of extending all but the simplest theoretical models to such multicomponent systems. Consequently we are only able, at this point, to compare our result to three relatively simple model calculations. Although recent photoemission experiments clearly show that the detailed electronic density of states function of an alloy cannot, in general, be predicted by a simple model, there are clear instances where the simple models do adequately describe the behavior of $N(E_F)$ over limited concentration regions.

In addition, the interaction between electrons and phonons in a lattice may result in an enhancement in γ . The low-temperature electronic specific heat is proportional to the thermal effective mass of the electron, m^* :

$$m^* = m_b(1 + \lambda),$$

where m_b is the band mass and $1 + \lambda$ is the electron-phonon enhancement factor. It is possible that changes in γ for a particular alloy system may be partially caused by changes in λ , the electron-phonon enhancement parameter.

There are several methods presently employed to extract information concerning the electron-phonon enhancement of γ . One of these techniques is to measure the specific heat at high temperatures,²¹ where the electron-phonon interaction parameter is negligible and the band-structure value of γ can be determined. Comparing this quantity with the low-temperature experimental value of γ , it is possible to calculate λ . Another method, based on high-temperature electrical resistivity measurements, is described by Grimvall²² and has been used to obtain values of λ for transition-metal elements as well as noble metals and their alloys.

Each of our ternary alloy systems is unique and has not been subject to experiments of the type mentioned above. Consequently, data concerning λ , or more importantly, $d\lambda/dc$, the rate of change of λ with solution concentration, are not presently available. The fact that $\Theta_D(T)$ of most of the alloys is very similar to $\Theta_D(T)$ of pure platinum in the temperature range of this work (see Fig. 4) suggests that changes in the phonon spectrum arising from alloying are small. The electron

density-of-states calculations that follow are based on the assumption that $d\lambda/dc$ is negligible, and consequently, the results of these calculations must be regarded with caution until further study of these and related ternary alloy systems establishes the role of electron-phonon enhancement.

We discuss the results of the two alloy systems separately.

A. Pt-Ir-Au

The rigid-band approximation (RBA) was used for many years as the principal theoretical construct for discussing the behavior of $N(E_F)$ for binary alloys, and for a few ternary systems. The RBA suggests that the electron-to-atom ratio \mathfrak{z} is the most important determinant of $N(E_F)$, and assumes that the band shape of dilute alloys will retain the form of the band shape of the host metal. Thus, as alloying occurs, \mathfrak{z} changes and traces out the band shape. For some alloy systems (e.g., Cu-Ni),²³ this has been shown to be an inaccurate picture, but nevertheless the behavior of other alloy systems (e.g.,²⁴ Al-Zn and¹⁸ Pt-V) can still be well described in RBA terms.

A sensitive test of the applicability of the RBA then is to create an alloy isoelectronic with a particular element. Provided that this is a dilute alloy and the phonon spectrum is not changed enough to affect electron-phonon contributions, the value of γ for such an alloy should agree with the dominant element. Our results for the alloys in the sequence Pt-Ir-Au, which is isoelectronic with Pt, show instead a sharp decrease in γ with alloying, ruling out the RBA in this instance. Previous measurements of the corresponding binary-alloy series show that Pt-Au dilute alloys do seem to obey the RBA, although Pt-Ir alloys do not.^{9,18}

An alternative to the RBA was proposed by Miedema.⁵ In this calculation, the individuality of the density-of-states function of each element is preserved. The γ value of the alloy consists of a weighted sum of adjusted γ values of the constituent elements. The key parameters in determining the weighting factors are concentration, difference in electronegativity, and the quantity $d\gamma/dZ$ evaluated at the Z value of interest. The predicted value of γ for the binary alloy consisting of elements having atomic numbers Z_1 and Z_2 is given by

$$\gamma_{\text{alloy}} = c_1\gamma_1(Z_1) + c_2\gamma_2(Z_2), \quad (4)$$

where

$$\gamma_1(Z_1) = \gamma(Z_1) + (d\gamma/dZ)_{Z_1}\Delta Z_1 \quad (5)$$

TABLE IV. Comparison of experiment γ to a γ value determined by applying Guthrie's calculation to the Pt-Ir-Au and Pd-Rh-Ag ternary-alloy series.

Sample	Experimental	Guthrie's calculated
Pt ₉₀ Ir ₅ Au ₅ ^a	5.59 ± 0.022	5.72
Pt ₈₀ Ir ₁₀ Au ₁₀ ^a	4.77 ± 0.015	4.75
Pd _{90.7} Rh _{3.8} Ag _{5.5} ^b	8.97 ± 0.42	8.70
Pd _{82.4} Rh _{8.1} Ag _{9.5} ^b	8.02 ± 0.20	7.80

^aThis work.

^bGilchrist (Ref. 11).

and $\gamma_2(Z_2)$ has identical form. The second term in $\gamma_1(Z_1)$ is the correction term where ΔZ is linearly dependent upon the difference in electronegativity between constituent elements. Using his own values of electronegativity,²⁵ Miedema's calculations have accurately predicted the behavior of many binary-alloy systems.

Applications to our ternary-alloy system was simplified by the nature of our constituent elements. According to Miedema, Pt and Ir have the same electronegativity and the Rh value is very close. Also, $d\gamma/dZ$ for the Au contribution will be quite small. In every case, the correction term will be zero or very nearly zero. Consequently we do not find agreement between predictions based on the model and the results for γ . This suggests the Miedema model is not applicable to this series or, possibly, that modifications of the electronegativity scale are required for more accurate calculations.

Finally, we compared our γ values for the Pt-Ir-Au alloys with an empirical calculation of the type performed by Guthrie⁶ on his Cu_{1-2x}Zn_xNi_x pseudometal series. Using values of $d\gamma/dc$ determined from the appropriate binary series, the γ values of the alloy is calculated as follows:

$$\gamma_{\text{alloy}} = \gamma_{\text{Pt}} + c_{\text{Au}}(d\gamma/dc)_{\text{Pt-Au}} + c_{\text{Ir}}(d\gamma/dc)_{\text{Pt-Ir}}. \quad (6)$$

Utilizing the Pt-Ir and Pt-Au binary series data of Dixon *et al.*⁹ to determine $d\gamma/dc$ for each series, we have found excellent agreement between calculated and experimental values of γ as can be seen in Table IV.

A possible explanation for the success of this calculation may be obtained from the Pt-Ir and the Pt-Au binary-alloy series data of Dixon *et al.*⁹ As noted by Sacli *et al.*,¹⁸ Pt-Au appears to obey a rigid-band approximation but Pt-Ir does not. Using a rigid-band approach, the addition of Au to Pt would result in a change given by $c_{\text{Au}}(d\gamma/dc)_{\text{Pt-Au}}$, where $d\gamma/dc$ is obtained from the

γ versus concentration curve of Dixon's Pt-Au data. The corresponding value of the Pt-Au combination would be given by the first two terms in Eq. (6). This is reasonable since the band shape is assumed to be unchanged and the addition of the gold conduction electrons will shift the Fermi level and change γ . The third term in Eq. (6) has the double effect of changing the band shape and of shifting the band on the energy axis. The Fermi level shifts, resulting in γ values that agree reasonably with experimental data. It is of interest to note that when Guthrie's calculation is applied to the near pseudometals of Gilchrist's¹¹ Pt_{1-x-y}Rh_xAg_y series the agreement is also reasonable (see Table IV).

B. Pt-Rh-Au

The Pt-Rh-Au alloys do not behave in accordance with any of the simple electronic models. Although the Pt-Rh-Au alloys are not isoelectronic, the surprisingly high value of γ for the Pt₇₄Rh₁₇Au₉ alloy indicates that the RBA is inapplicable. Calculations based on Miedema's model also failed to agree with our results. Application of Guthrie's calculation to this series is not possible at this time. The experimental value of $(d\gamma/dc)_{\text{Pt-Rh}}$ is unavailable because the Pt-Rh binary-alloy series has escaped investigation.

Figure 4(c) is a plot of the $\Theta_D(T)$ functions of the Pt-Rh-Au alloys as compared to $\Theta_D(T)$ for pure Pt. Although $\Theta_D(T)$ of Pt₈₆Rh₉Au₅ is very similar to that of pure Pt, the $\Theta_D(T)$ function of Pt₇₄Rh₁₇Au₉ changes significantly from $\Theta_D(T)$ of pure Pt over the entire temperature range of these measurements, and may be a result of the relatively high concentration of Rh atoms. The significant departure of $\Theta_D(T)$ of this alloy from $\Theta_D(T)$ of pure Pt raises the question of differences in the electron-phonon enhancement. It is possible that the unexpectedly high value of γ for Pt₇₄Rh₁₇Au₉ is a result of an increased electron-phonon enhancement and is not due solely to changes in its electron density-of-states function.

C. Excess specific heat C_{ex}

As shown by the data in Figs. (2) and (3) and by the analysis in Table II, all of our alloys showed an additional excess specific heat C_{ex} at low temperatures, although in most cases this was only apparent because we obtained data below 1.5 K. In the pure platinum, the computer analysis showed $C_{\text{ex}} = 0$ within experimental scatter. In

Pt₈₀Ir₁₀Au₁₀ and Pt₉₀Rh₅Au₅, C_{ex} was analyzed as temperature independent within experimental error giving the listed values in Table II. In the other two alloys C_{ex} could be described by a constant only within $\pm 5\%$ at the lowest temperature which is outside our accepted experimental error of $\pm 2\%$, but no other simple functional form provided a better fit.

Such contributions to C_P have been seen in other noble-metal alloys⁹ and may arise from magnetic impurities. Although our alloys as supplied were stated to have iron concentrations less than 10 ppm based on composition of constituents, subsequent chemical analysis showed an order of magnitude higher figures as in Table I. We plan to confirm these figures by proton microprobe analysis.

Analyzing C_{ex} as due to magnetic clusters according to the model of Hahn and Wohlfarth,¹⁷ which at temperatures in our region would give a constant contribution to C_P , we find that for the Pt-Ir-Au alloys the cluster concentration would be 150 ppm and proportionally higher for the alloys with Rh. These concentrations are comparable to the iron impurity concentrations listed in Table I.

Measurements to lower temperatures on alloys of lower and better known impurity concentrations would be needed to clarify the source of C_{ex} .

V. SUMMARY AND CONCLUSIONS

We have determined the specific heat of two series of ternary alloys based on Pt, of which one, Pt-Ir-Au, was always isoelectronic with Pt, while the other, Pt-Rh-Au, was nearly so. We find that for the Pt-Ir-Au sequence the behavior of the electronic contribution coefficient γ can be described by an empirical calculation due to Guthrie⁶ which is seen to combine the rigid-band behavior of the Pt-Au binary-alloy series with the non-RBA behavior of the Pt-Ir binaries. Our results for the Pt-Rh-Au series cannot be described by existing simple models. Although changes in the electron-phonon enhancement factor may be partially responsible for changes in γ of the alloys, the close similarity of $\Theta_D(T)$ of most alloys to $\Theta_D(T)$ of pure Pt suggests that the effect is small. A complete explanation of our results must clearly await further development of theoretical models of alloying, and their extension to ternary-alloy systems. Further specific-heat studies of ternary alloys isoelectronic with specific elements are planned.

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