Phonon and electron components of the thermal conductivity of tantalum at intermediate temperatures

R. K. Williams, R. S. Graves, T. L. Hebble, D. L. McElroy, and J. P. Moore
Metals and Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830
(Received 25 January 1982)

Thermal conductivity, electrical resistivity, and absolute Seebeck-coefficient values for Ta and four Ta-base alloys are reported. The data, which cover the temperature range 80—400 K, were analyzed to identify the phonon and electron contributions to the thermal conductivity of Ta. Reflecting the strong electron-phonon interaction, the phonon thermal conductivity is rather small and equal to about $\frac{2}{3}$ of the prediction of a theoretical formula. At the highest temperatures investigated, the electronic thermal conductivity and electrical resistivity are consistent with the Sommerfeld-Lorenz number. The electrical resistivity and Seebeck-coefficient results can be satisfactorily fitted to standard theoretical formulas, and these results indicate that deviations from Matthiessen's rule are small and positive.

I. INTRODUCTION

This study is a part of a systematic experimental investigation of the phonon λ_p and electronic λ_e thermal conductivity components of the bcc transition elements at intermediate[1] and high[2] temperatures. The experimental λ_p values are currently of interest to theorists because they give a relatively unambiguous and sensitive[3] measure of the electron-phonon interaction. First-principles calculations of this interaction are now possible for some cases[4] and the connection with superconductivity is well established. In some alloys, λ_p can make a significant contribution to the total thermal conductivity λ,[5] which leads to interest in the experimental λ_p values from a more practical viewpoint.

The high-temperature thermal conductivities of the transition elements are largely electronic in origin, and several experimental studies have shown[6] that λ_e is frequently larger than that predicted by the experimental electrical resistivity ρ and the Sommerfeld-Lorenz number L_0. Subtraction of λ_p from λ to obtain λ_e helps to reduce the difficulty, but several cases of significant positive deviations from the Sommerfeld prediction remain.[6,7] Detailed applications of the Mott-Fermi smearing model have met with some success[6] but do not appear to be applicable to Nb.[4] However, in this case L_0 seems to be consistent with the data.[2] An experimental investigation of the validity of the Sommerfeld law for Ta forms the second goal of this study.

The apparatus and experimental techniques have been described elsewhere[1,8] and the remaining sections of this paper contain sample characterization data, the experimental results, and a comparison of the results with available theory. Most of this discussion is centered around the magnitude and temperature dependence of λ_p at intermediate (80—300 K) temperatures.

II. SAMPLE CHARACTERISTICS

Two Ta and four Ta alloy specimens were studied and their characteristics are summarized in Table I. One of the Ta specimens and the two ternary alloy samples were electron-beam melted at our laboratory. The Ta sample was then swaged into rod form, machined, cleaned, and annealed. This sample was also used for high-temperature (2600-K) ρ measurements before the low-temperature data were taken. These ρ measurements were conducted in an ultrahigh-vacuum furnace and this heat treatment appeared to lower the room temperature ρ by about 1%. The two ternary alloy specimens were machined from electron-beam melted ingots and annealed in another ultrahigh-vacuum furnace. The ρ of these two specimens was also measured at three positions along the length and the results showed ρ inhomo-

 ©1982 The American Physical Society

TABLE I. Sample characteristics.

	Electron-beam melted Ta	Zone-refined Ta	Ta−6 wt.% W	Ta−12 wt.% W	Ta−2.5 wt.% Hf−2.5 wt.% W	Ta−5 wt.% Hf−5 wt.% W
Specimen dimensions (length)× (diameter) (mm)	76×3.8	76×9.1	76×6.3	76×6.3	76×6.2	76×6.4
Residual resistivity (10^{-8} Ω m)	0.077	0.0534	2.72	5.53	3.30	5.67
T_c (K)			a	a	4.17	3.57
Density (10^3 kg/m^3)		16.64	16.76	16.88	16.66	16.69
Lattice parameter (nm)		0.3302	0.3295	0.3286	0.3293	0.3295
Diamond pyramid hardness (0.5-kg load)	86		143	255	220	230
wt.% W	0.03	0.0002[b]	5.8	12	2.3	4.5
Hf	ND	ND	ND	0.02	2.5	5.1
ppm C	31	10	29	29	44	32
O	27	3	41	44	40	21
H	4	<1	2	<1	1	<1
N	3	<3	5	14	9	2
Cr	100	0.3	10	7	1	3
Cu	0.05	0.6	0.05	0.2	<0.5	<0.4
Fe	3	0.5	2	1	5	10
Mo	2	0.15	2	300	200	5
Nb	1000	2.0	1000		5000	<250
Re	<0.2		<0.2	0.5		
V	1	0.2	0.3	1		
Zr	20	<0.1	1	30	200	100
Annealing conditions (h, K)	24, 2573	4, 2473 + 96, 2273	1, 2073	1, 2073	4, 2273	4, 2273

[a]Literature values were used in making calculations (Ref. 10).
[b]Vendor's analysis of lot 96916.

geneities of 0.55% and 0.04% for the nominally 2.5:2.5 and 5:5 Hf-W specimens. The two Ta-W samples, which were of unknown origin, were also annealed in an ultrahigh-vacuum furnace. The zone-refined Ta specimen, which had a resistivity ratio of about 250, was purchased from Materials Research Corp., Orangeburg, N. Y. and was supplied as a cold worked rod. The sample was machined from this rod, cleaned, and annealed in ultrahigh vacuum as shown in Table I. The data for this specimen are somewhat more accurate than values for the electron-beam melted (EBM) sample because the diameter was about 2.4 times larger than the EBM sample. Samples from all the alloy specimens were examined metallographically and by x-ray diffraction. This showed that the test samples were large grain size, bcc solid solutions. One somewhat surprising observation was that the lattice parameters a_0 of the two ternary alloys are smaller than that of pure Ta, while data on binary alloys[9,10] would suggest larger a_0 values for the isoelectronic ternary alloys.

III. EXPERIMENTAL RESULTS

Smoothed values for the λ and ρ of the six samples are shown in Table II. The procedure used for smoothing the data has been described[1] and the two sets of experimental λ data for Ta are shown in Fig. 1 to illustrate the excellent precision and the small differences between two sets of results for samples of about equal purity. The thermopower values, which were measured with a Pt (Ref. 11) standard, are shown in Fig. 2. All values are based on the International Practical Temperature Scale (IPTS) 1968. The experimental uncertainties in λ and ρ probably fall somewhere between the two sets of estimates[1,8] which have been presented for an apparatus of this type. The maximum determinate uncertainties calculated in these two cases were $0.5-1.8\,\%$ for λ and $0.3-0.7\,\%$ for ρ. The smoothed values contain extra digits to eliminate the effects of rounding errors. The λ values for the two ternary alloys were also confirmed by 300–360 K measurements with a comparative heat-flow apparatus. These checks were as good ($1-2\,\%$) as our previous comparisons.[12]

At 100 K the λ values for Ta are in good (1.8%) agreement with the Thermophysical Properties Research Center (TPRC, Ref. 13) recommendations and about 5% higher than the results of a recent Russian[14] study. At 100 K the ideal resistivity values for Ta are about 0.6% higher than those of White and Woods,[15] and the difference decreases at higher temperatures. The 300-K ρ values for the two Ta-W alloys are $12-14\,\%$ lower than those of Thomas,[16] and the cause of this difference is unknown. In making theoretical calculations, a single set of transport property data for Ta was required. This set was obtained by assigning an arbitrary 3:1 weighting factor favoring the data on the zone-refined sample. This bias was based on better purity, smaller geometrical uncertainties and a more extensive set of data, especially at the lowest temperatures.

IV. DISCUSSION

The transport property data obtained in this study yield values of the phonon thermal conductivity λ_p of Ta; deriving λ_p and comparing it with theoretical estimates is the principal topic of this paper. The electronic thermal conductivity is also of interest; and, in addition, the composition and temperature variations of the electrical resistivity and Seebeck coefficients yield information which can be used in interpreting the behavior of the two derived λ components. This is especially true in the case of the two isoelectronic Ta-Hf-W alloys because our literature survey indicates that these alloys have not been studied before.

A. Thermopower

The absolute Seebeck coefficients S of Ta and all four alloys are relatively small and the results are shown in Fig. 2. In this temperature range, the absolute thermopowers of all four alloys are somewhat greater than that of Ta and isoelectronic alloying produces smaller S increments. The curves diverge at higher temperatures and this behavior is not predicted by the dilute-solution model which Fulkerson *et al.*[17] used to treat data for iron samples of differing purity. Application of the Nordheim-Gorter rule[18] to the two groups of S data for Ta-W and Ta-W-Hf alloys predicts S values for pure Ta which generally fall within about 0.2 μV/K of the experimental values. The good general description of S given by the Nordheim-Gorter equation seems to be another case in which the equation applies although the alloys do not obey Matthiessen's rule and the Wiedemann-Franz law is not valid.[18]

B. Electrical resistivity

The temperature and composition variations of the ρ of Ta and the four alloys yield some infor-

TABLE II. Smoothed thermal conductivity and electrical resistivity values λ (W/mK) and ρ (10^{-8} Ω m). These values contain extra digits to prevent rounding error effects and the small fluctuations in the values for the λ of the electron-beam melted Ta sample are not real.

Temperature	Electron-beam melted Ta		Zone refined Ta		Ta−6 wt.% W		Ta−12 wt.% W		Ta−2.5 wt.% Hf−2.5 wt.% W		Ta−5 wt.% Hf−5 wt.% W	
(K)	λ	ρ	λ	ρ	λ	ρ	λ	ρ	λ	ρ	λ	ρ
80	59.66	2.563	59.38	2.566	34.75	5.464	25.93	8.043	31.65	6.090	23.68	8.668
100	58.24	3.634	58.18	3.628	37.31	6.503	28.64	9.036	34.21	7.174	26.36	9.772
120	57.93	4.676	57.97	4.672	39.39	7.503	31.12	10.001	36.47	8.226	28.67	10.831
140	57.98	5.698	58.06	5.689	41.23	8.480	33.31	10.936	38.41	9.239	30.68	11.858
160	57.95	6.701	58.12	6.690	42.86	9.445	35.30	11.843	40.00	10.231	32.44	12.856
180	57.87	7.688	58.12	7.669	44.17	10.355	37.00	12.723	41.31	11.206	33.97	13.823
200	57.78	8.664	58.08	8.634	45.29	11.243	38.49	13.584	42.42	12.162	35.30	14.778
220	57.72	9.629	58.00	9.589	46.20	12.151	39.81	14.430	43.38	13.100	36.47	15.712
240	57.69	10.584	57.88	10.536	46.96	13.052	40.94	15.267	44.23	14.023	37.52	16.631
260	57.68	11.528	57.79	11.479	47.66	13.946	41.94	16.095	44.98	14.944	38.49	17.538
280	57.71	12.458	57.73	12.415	48.28	14.830	42.91	16.916	45.64	15.860	39.40	18.436
300	57.77	13.381	57.71	13.348	48.83	15.706	43.81	17.727	46.21	16.770	40.21	19.325
320	57.85	14.323	57.71	14.283	49.34	16.473	44.69	18.530	46.70	17.671	40.95	20.209
340	57.92	15.248	57.68	15.210	49.77	17.431	45.45	19.342	47.15	18.567	41.63	21.085
360	57.96	16.164	57.63	16.128	50.09	18.280	46.10	20.154	47.56	19.459	42.26	21.953
380	57.96	17.072	57.56	17.035	50.34	19.127	46.63	20.962	47.96	20.343	42.83	22.816
400	57.94	17.973	57.48	17.929	50.48	19.967	47.03	21.760	48.40	21.207	43.27	23.680

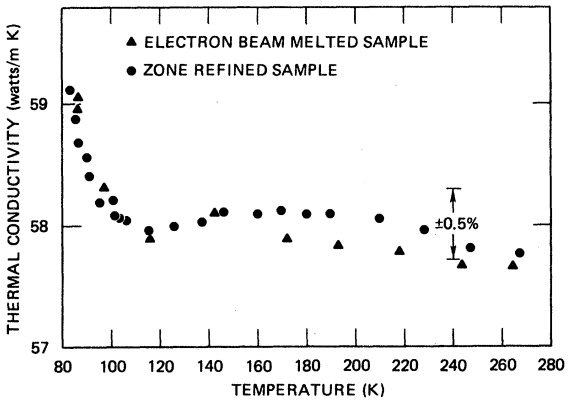

FIG. 1. Experimental thermal conductivity values for two Ta samples.

mation which is useful in analyzing the thermal conductivity results. If it is assumed that the effects of W and Hf are additive, the residual resistivity data (Table I) can be used to evaluate the impurity resistivities of W and Hf in Ta. The ρ increment for Hf is about 1.6 times larger than the impurity resistivity for W, which may be due to a lattice strain effect. Neither impurity resistivity is unusually large.[19]

The temperature variation of the ρ of pure Ta has been discussed by several authors.[15,20,21] Our data on Ta can be described to within $\pm 0.04\%$ by

$$\rho-\rho_0=\rho_{\mathrm{BG}}-\alpha T^2 . \tag{1a}$$

In this equation ρ_0 is the residual resistivity, ρ_{BG} is the Bloch-Grüneisen formula for the electron-phonon resistivity and includes the assumption that the Debye temperature Θ_R is a constant. The last term accounts for the combined effects of thermal expansion[22] and negative deviations from linearity (DFL). The mechanism repsonsible for the negative DFL in Nb has been the subject of a recent debate,[23,24] and the theoretical calculations of Pinski *et al.*[4] indicate that the *s-d* model does not apply to Nb.

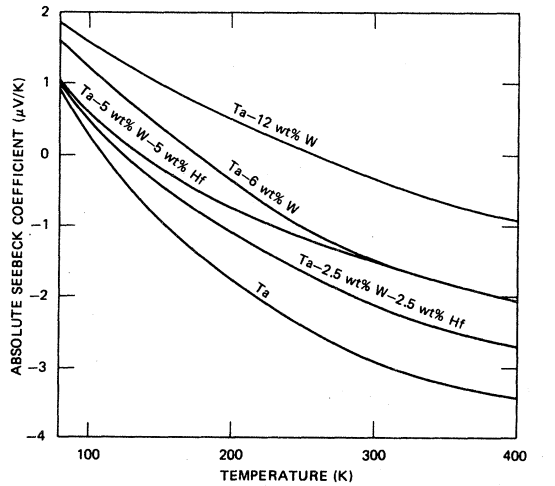

FIG. 2. Smoothed absolute Seebeck-coefficient values for Ta and four Ta-base alloys.

If the impurity term is assumed to be an adjustable constant, Eq. (1a) also gives a good description of the data for the four alloys:

$$\rho-A=\rho_{\mathrm{BG}}-\alpha T^2 . \tag{1b}$$

Presumably this additional parameter is required to account for deviations from Matthiessen's rule. The parameters derived from the data are summarized in Table III. For the alloys, the temperature-independent impurity terms are about 5–10% greater than the measured residual resistivity values, and this sign and magnitude is typical of observations of deviations from Matthiessen's rule.[25] The Debye temperature derived for Ta is about 0.93 of the value obtained from intermediate-temperature specific-heat data, 235 K,[26] and also smaller than an earlier value[27] obtained from resistivity data. However, our Θ_R value is in good agreement with the results of Semler and Riehl,[20] 217.5 K.

Inclusion of additional higher-temperature[28] data increases Θ_R(Ta) by only a few degrees and α then tends to approach the values derived for the four alloys. These data do not define α very well, since it only contributes a few percent at 400 K. For the Ta-W alloys, other results[16,29] indicate that α should gradually decrease with increasing W content, but the α values shown in Table III do not have this variation. The αT^2 contribution to the electrical (and presumably thermal) resistivities is very small, in the range 80–200 K, where accurate λ_p values can be derived from the data.

The linear resistivity coefficients R/Θ_R (Ref. 19) indicate a gradual decrease with W content and a smaller increase relative to Ta for the two isoelectronic alloys. The dependence on W content is similar to the observations on Nb-Mo alloys[2] and indicates a gradual decrease in the intrinsic strength of the electron-phonon scattering. The factors responsible for this variation have been discussed by Butler[30] and the variation of the electron-phonon mass enhancement factor Λ derived from ρ is similar to that predicted by McMillan's formula.[31] Isoelectronic alloying does not seem to disturb the electron-phonon scattering

TABLE III. Parameters derived by fitting experimental electrical resistivity values (Table II) to Eq. (1a). Temperature range 80—400 K.

Material	Average percent deviation of calculated values	ρ_0 (Table I) (10^{-8} Ω m)	A Eq. (1a) (10^{-8} Ω m)	α (10^{-14} Ω m/K^2)	$\frac{R^a}{\Theta_R}$ (10^{-8} Ω m/K)	Θ_R (K)	Θ_D[b] (K)
Ta	0.04	0.0534	0.0534	1.72	0.04618	218	235
Ta—6wt.% W	0.08	2.72	2.83	5.00	0.04544	192	240
Ta—12 wt.% W	0.11	5.53	5.79	5.30	0.04268	219	245
Ta—2.5 wt.% W—2.5 wt.% Hf	0.05	3.30	3.49	5.21	0.04708	208	229
Ta—5 wt.% W—5 wt.% Hf	0.08	5.67	6.15	7.74	0.04765	218	224

[a]Blatt's notation (Ref. 19).
[b]The methods used to obtain these Debye temperature estimates from the available literature are discussed in the text.

as much, and this is important because this is an assumption about the intrinsic electronic thermal resistance W_{ei}, which is used in deriving λ_p values.

Table III also shows a comparison of Debye temperatures Θ_R derived from the ρ fits with Θ_D values inferred from the literature. The Θ_R values do not form a completely consistent pattern (note the low value for Ta—6 wt.% W) and the literature values are also somewhat uncertain because inelastic neutron scattering measurements are not available. Specific-heat data[9] indicate that W additions increase Θ_D of Ta, but these values are not appropriate for intermediate temperatures because the real phonon spectrum can only be described by the Debye model if Θ_D is allowed a considerable temperature variation.[26] The temperature variations found for Ta (Ref. 26) and W (Ref. 32) were interpolated to derive the intermediate-temperature Θ_D values (Table III) for Ta-W alloys from the low-temperature specific-heat values. These Θ_D values increase with W content. The Θ_D values for the two isoelectronic alloys were obtained by assuming that the composition dependence is similar to that of isoelectronic Nb-Mo-Zr alloys[33] and the temperature dependence is equal to that of Ta. These Θ_D values decrease as the solute content increases, and, for both binary and isoelectronic alloys, the Θ_R values do not show consistent trends with composition.

Overall, the differences in intermediate temperature Θ_R and Θ_D values average about 25 K and the Θ_R values are always smaller than Θ_D. These differences are large enough to preclude the use of composition-dependent Θ_D values in the analysis of the derived λ_p values.

C. Phonon thermal conductivity

As a first step in identifying the phonon conductivity of Ta, four λ_p estimates were calculated at each temperature using the equations described by Williams and Fulkerson.[34] The principal assumptions are that the ideal electronic thermal resistance W_{ei} and λ_p are not altered by alloying and the Sommerfeld-Lorenz number L_0 applies to the total electrical resistivity contribution from impurity scattering. One set of λ_e and λ_p values can then be calculated from the λ and ρ data on Ta and each of the alloys. The relatively concentrated alloys used in this study were required because the intrinsic scattering is strong in Ta, and the experimental identification of the phonon conductivity becomes less uncertain as the relative strength of

the impurity scattering increases. The use of concentrated alloys must, however, put a considerable strain on the assumptions that the phonon conductivity and intrinsic electronic thermal resistivity of Ta are unchanged in the alloys. It therefore would not be surprising if the λ_p values calculated from these equations[34] showed a systematic composition dependence similar to that observed for bcc Fe solutions.[1]

The four λ_p curves are presented in Fig. 3, with the results plotted as λ_p^{-1} to show that they do not extrapolate to zero thermal resistance at absolute zero. This large positive intercept ($\sim$0.2 mK/W) gives a rough measure of the strength of the electron-phonon scattering. These calculations indicate that the phonon conductivity accounts for about 7% of the total conductivity of Ta at 100 K, and experimental indentification of this component is thus a stringent test of the accuracy of the experimental data.

All four sets of calculations are reasonably consistent up to about 200 K and the difficulties at higher temperature presumably arise because the thermal conductivities of the alloys tend to approach that of Ta at higher temperatures. At 300 K the λ of Ta–6 wt. % W (Table II) is only 17% less than that of Ta. In the 80–200 K range, the four calculated λ_p values are within $\pm$11% of the average λ_p, and it should be noted that this average λ_p is considerably lower than the value derived by Butler and Williams.[35] This earlier estimate was based on an extrapolation of calculated values for two Ta-W alloys at 80 K.

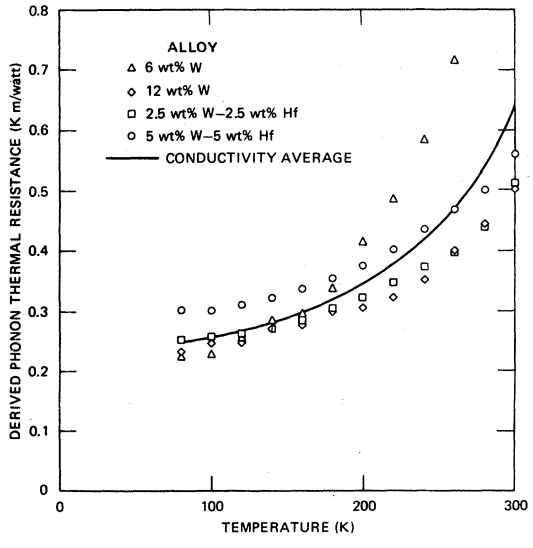

FIG. 3. Phonon thermal resistance (λ_p^{-1}) estimates for Ta obtained by using the equations presented in Ref. 34.

Near 100 K, where the λ_p results are least subject to experimental uncertainties, the four sets of calculations show a consistent pattern; with lower lattice resistance λ_p^{-1} values calculated from the data on the alloys with lower solute contents. This is reminiscent of the behavior noted for bcc Fe (Ref. 1) and Nb (Ref. 36) alloys. If these trends were real, they would also indicate that at lower temperatures λ_p of Ta is at least 20% larger than the average value shown in Fig. 3.

The significance of these compositional trends was investigated by two methods. A calculation of the maximum determinate error[8] based on optimistic estimates of the λ ($\pm$0.5%) and ρ ($\pm$0.2%) experimental uncertainties yields maximum λ_p uncertainties of about $\pm$40% at 100 K. This is not too surprising because λ_p is small relative to λ, and, since the calculated uncertainty is about 4 times larger than the maximum compositional variation, this result indicates that the concentration variations are not significant. However, since the method does not allow for possible cancellation of errors, and the two λ determinations for Ta differ by less than 0.5%, a statistical method for estimating the errors was also used. This analysis was based on the two equations[34] used to calculate the λ_p values shown in Fig. 3. Independence of random variables was assumed and subjective estimates of the variances of the experimentally determined quantities were made by examining the data scatter. The variance var$[L(T)]$ of the electronic Lorenz function $L(T)$ was obtained from the Taylor's series expansion of $L(T)$. var$[L(T)]$ was then used with the equation for the thermal conductivity of the element[34] to estimate the variance of λ_p. Estimates of standard deviations for λ_p and 95% confidence limits about the mean of λ_p show that, for a given temperature, the large variation masks any real differences which may exist among the alloy means. Nevertheless, more complicated λ_p calculations were performed, principally to determine the sensitivity of the λ_p results to some of the basic assumptions.

The phonon conductivity calculation can be improved by generalizing the original equations[34] to account for changes in the intrinsic electronic thermal resistance and alloy phonon conductivities caused by the presence of W and Hf in the lattice.

The thermal conductivity of Ta, λ_1 is taken to be the sum of two contributions, $\lambda_e^{(1)}$ and $\lambda_p^{(1)}$:

$$\lambda_1=\lambda_e^{(1)}+\lambda_p^{(1)}=\left[\frac{\rho_0}{L_0T}+W_{ei}^{(1)}\right]^{-1}+\lambda_p^{(1)}$$
$$=\left[\frac{\rho_0}{L_0T}+\frac{\rho_1-\rho_0}{LT}\right]^{-1}+\lambda_p^{(1)}\,. \quad (2)$$

This is the equation used to relate λ_1 and the ρ of Ta, ρ_1, in the original calculation.[34] If both W_{ei} and λ_p are altered by alloying, the thermal conductivity of the alloy would be given by

$$\lambda_2=\lambda_e^{(2)}+\lambda_p^{(2)}=\left[\frac{\rho_I}{L_0T}+W_{ei}^{(2)}\right]^{-1}+\lambda_p^{(2)}\,. \quad (3)$$

In this equation, ρ_I is the total impurity contribution to the ρ of the alloy ρ_2 and this quantity was originally taken to be $\rho_2-(\rho_1-\rho_0)$. However, the analysis of the alloy ρ data (Table III) showed significant shifts in the intrinsic scattering component. This component is given by Eq. (1b) and by defining

$$f\equiv\frac{\rho_2-A}{\rho_1-\rho_0}\simeq\frac{\rho_{\rm BG}-\alpha T^2}{\rho_1-\rho_0}\,, \quad (4)$$

$$\rho_I=\rho_2-f(\rho_1-\rho_0)=A\,. \quad (5)$$

An analogous modification of $W_{ei}^{(2)}$ is required, and assuming that the intrinsic Lorenz function L is unchanged,

$$W_{ei}^{(2)}=\frac{f(\rho_1-\rho_0)}{LT}\,. \quad (6)$$

Defining the ratio of the two phonon conductivities as a temperature-dependent parameter β and substituting Eqs. (5) and (6) into (3) yields

$$\lambda_2=\left[\frac{[\rho_2-f(\rho_1-\rho_0)]}{L_0T}+\frac{f(\rho_1-\rho_0)}{LT}\right]^{-1}+\beta\lambda_p^{(1)}\,. \quad (3')$$

Then if β and f are known, Eqs. (2) and (3′) can be solved for L and $\lambda_p^{(1)}$ in terms of λ_1, λ_2, ρ_1, ρ_2, and T. Note that both β and f are ratios, which is a relatively undemanding method for introducing the corrections.

Values for f appropriate for each alloy and T were calculated from Eq. (4), the experimental ρ data (Table II), and the A values shown in Table III. At higher temperatures these values approach the (R/Θ_R) ratios which are also related to the respective Λ values.

Estimates of β, the phonon conductivity ratio, were obtained from an approximate theoretical calculation. Ratios for each alloy and temperature were calculated from the approximate equation[1]:

$$\beta=\frac{W_{ep}(\text{alloy})+W_p}{W_{ep}(\text{Ta})+W_{pp}(\text{Ta})}\,, \quad (7)$$

where the phonon-phonon resistance for Ta, W_{pp}(Ta), was calculated from the modified[37,38] Leibfried-Schlömann equation. W_p was calculated from Abeles's formula[39] for the high-temperature thermal resistance of an insulating solid solution. The temperature-dependent electron-phonon scattering resistance W_{ep}(Ta) values were obtained by using Butler's formula[35] for the T dependence and by deriving W_{ep}(Ta) from the lower-temperature (80–120 K) estimates shown in Fig. 3 by making a small ($\sim$10%) correction for phonon-phonon scattering. Analogous alloy W_{ep} values then were obtained from the superconducting transition temperatures,[10] McMillan's formula,[31] and electronic specific-heat values. This calculation suggests that W_{ep} for all the alloys is smaller than the value for Ta, but the difference is more pronounced in the binary Ta-W alloys.

Abeles's formula[39] for W_p requires a value for the N to U process relaxation time ratio, and this parameter was taken to be $\frac{9}{5}$ for all calculations. The atomic volumes of Ta and W were obtained from their lattice parameters and the value for bcc Hf was estimated from the lattice parameter of a Ta–30 wt.% Hf alloy.[9] These size values are critical because the point defect scattering is controlled by the lattice strain term. It should also be noted that the cancellation[40] of strain and mass difference terms is not important in this case because the mass difference part is always small. The proportionality factor used to evaluate the strain contribution (Ref. 40) was obtained by comparing Abeles's formula with λ data on electrically insulating solid solutions.[41]

These estimates of β range from 1.07 (Ta–12 wt.% W at 80 K) to 0.75 (Ta–5 wt.% Hf–5 wt.% W at 280 K). The β values also suggest that linear extrapolation of λ_p^{-1} from Fig. 3 against solute concentration will probably yield low λ_p estimates for pure Ta. This is particularly true for the binary alloys because the model suggests λ_p passes through a minimum in our composition range.

The results of the modified λ_p calculation are shown in Fig. 4, which also includes the average curve from Fig. 3 for comparison. The new calculation does not reduce the scatter of the four curves and produces only small changes at lower

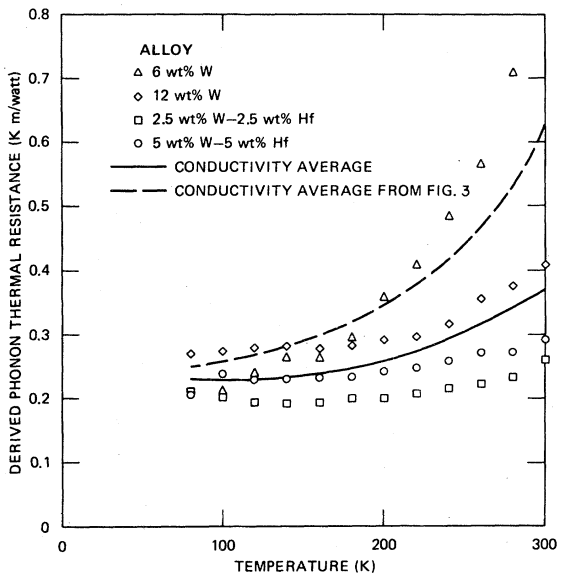

FIG. 4. Phonon thermal resistance (λ_p^{-1}) estimates for Ta obtained from Eqs. (2) and (3').

temperatures. The major effect is at higher temperatures, where the corrections lower λ_p^{-1}, reducing the temperature coefficient toward the value (1.9×10^{-4} mK/W) predicted by theory.[37] In our opinion the average curve shown in Fig. 4 is the best currently available determination of the phonon conductivity of Ta. The uncertainty of these results is smallest at the lowest temperatures, as shown by insensitivity to the choice of β and f.

Between 80 and 200 K, these λ_p^{-1}(Ta) values can be described by

$$\lambda_p^{-1}(\mathrm{Ta}) = W_{pp} + W_{ep} = 5.7\times10^{-4}T + \frac{0.14}{2}\left[\frac{223}{T}\right]^2 \Big/ J_3\left[\frac{223}{T}\right]\left[\frac{\mathrm{K\,m}}{\mathrm{W}}\right]. \quad (8)$$

Theoretical estimates[35,37] of these two resistance terms are both smaller: the calculated phonon-phonon scattering is 33% of the value shown above the electron-phonon term is 60%. Inspection of Figs. 3 and 4 shows that W_{pp} is not well defined by the experimental results and the theory[38] also frequently underestimates this contribution. The W_{ep} disagreement is more serious because this relatively large resistance is better defined and the theory[35] tends to overestimate this term. The W_{ep} found from these intermediate-temperature results is also over four times greater than the results obtained[42] from low-temperature experiments.

D. Electronic Lorenz function

The experimental Lorenz function of Ta is shown in Fig. 5. This curve was obtained by making the phonon conductivity correction with Eq. (8) and including the small impurity scattering (ρ_0/L_0T) correction to derive the intrinsic electronic thermal resistance of Ta. The experimental values for Cu fall below this curve by about 10% and two theoretical curves are also included for comparison. The Wilson theory[43] was normalized at T/Θ of 0.5 and falls about 2.5% below the experimental curve at T/Θ of 1.4.

Niobium is a very similar element and a detailed and successful treatment of its electronic transport properties has recently appeared.[4] A comparison to these results was made by assuming that they also apply to Ta if an adjustment is made for the differences in phonon properties. This was done by assuming that $\Theta(\mathrm{Ta})/\Theta(\mathrm{Nb})\approx235/280$. The comparison is very encouraging ($\sim2\%$) at lower temperatures and the difference increases to about 3% at Θ. This divergence at higher temperatures suggests that the phonon-phonon scattering term in Eq. (8) may be too strong, and using the theoretical value,[37] 1.9×10^{-4} K m/W, for W_{pp}(Ta) in Eq. (8) brings the experimental L values at higher temperatures into uniformly good agreement with the Pinski *et al.*[4] calculation.

This suggests an alternate method for calculating the λ_p of Ta. Assuming that the Pinski *et al.*[4] L

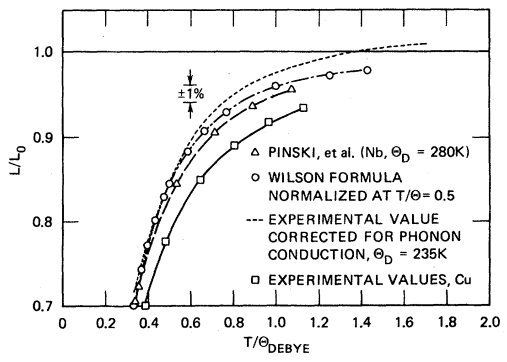

FIG. 5. Experimental and theoretical temperature variations of the electronic Lorenz function of Ta. An experimental curve for Cu is included for comparison.

calculations apply exactly defines the electronic thermal conductivity versus temperature and λ_p can then be obtained from the measured λ values by subtraction. The results of this calculation can be described by

$$\lambda_p^{-1}(\mathrm{Ta}) = 0.027T + \frac{0.13}{2}\left[\frac{223}{T}\right]^2 \Big/ J_3\left[\frac{223}{T}\right]\left[\frac{\mathrm{K\,m}}{\mathrm{W}}\right]. \quad (9)$$

Comparison to Eq. (8) shows that the principal change is in the phonon-phonon term and the electron-phonon resistance decreases only 7% and remains considerably larger than the theoretical value.

We note in passing that the electronic Lorenz function of Ta is essentially equal to the Sommerfeld value at the highest temperatures investigated. The fact that there is no evidence of deviations from the theoretical value is similar to the observations for Nb, and, in that case, the data extend to 1300 K.

ACKNOWLEDGMENTS

D. W. Yarbrough wrote the computer program used to treat the resistivity data, F. J. Weaver obtained some of the experimental data, and O. B. Cavin supplied lattice parameter results. The manuscript was prepared by S. J. Phillips. Research was sponsored by the Division of Materials Sciences, U. S. Department of Energy, under Contract No. W7405-ENG-26 with the Union Carbide Corporation.

[1]R. K. Williams, D. W. Yarbrough, J. W. Masey, T. K. Holder, and R. S. Graves, J. Appl. Phys. 52, 5167 (1981).
[2]J. P. Moore, R. S. Graves, and R. K. Williams, High Temp. High Pressures 12, 579 (1980).
[3]W. H. Butler, ORNL, private communication, 1980.
[4]F. J. Pinski, P. B. Allen, and W. H. Butler, Phys. Rev. B 23, 5080 (1981).
[5]R. K. Williams, R. S. Graves, F. J. Weaver, and D. L. McElroy, *Proceedings of the Seventeenth International Conference on Thermal Conductivity, Gaithersburg, Maryland, 1981* (Plenum, New York, in press).
[6]M. J. Laubitz and T. Matsumura, Can. J. Phys. 50, 196 (1972).
[7]J. P. Moore, R. K. Williams, and R. S. Graves, J. Appl. Phys. 48, 610 (1977).
[8]J. P. Moore, D. L. McElroy, and R. S. Graves, Can. J. Phys. 45, 3849 (1967). Also see J. P. Moore, R. K. Williams, and R. S. Graves, Rev. Sci. Instrum. 45, 87 (1974).
[9]E. Bucher, F. Heiniger, and J. Muller, *Proceedings of the 9th International Conference on Low Temperature Physics* (Plenum, New York, 1965), Part B, p. 1059.
[10]W. DeSorbo, Phys. Rev. 130, 2177 (1963).
[11]J. P. Moore and R. S. Graves, J. Appl. Phys. 44, 1174 (1972).
[12]R. K. Williams, R. S. Graves, and J. P. Moore, ORNL Report No. 5313 (unpublished).
[13]C. Y. Ho, R. W. Powell, and P. E. Liley, J. Phys. Chem. Ref. Data 3, Suppl. 1, 631 (1974).
[14]A. M. Ermolaev, G. M. Zlobintsev, A. V. Krasnokutskii, B. A. Merisov, and V. I. Khotkevich, Fiz. Nizk. Temp. 1, 1071 (1975) [Sov. J. Low Temp. Phys. 1, 516 (1975)].
[15]G. K. White and S. B. Woods, Philos. Trans. R. Soc. (London) Ser. A 251, 273 (1959).
[16]L. Thomas, Z. Metallkd. 59, 127 (1968).
[17]W. Fulkerson, J. P. Moore, and D. L. McElroy, J. Appl. Phys. 37, 2639 (1966).
[18]F. J. Blatt, P. J. Schroeder, C. L. Foiles, and D. Greig, *Thermoelectric Power of Metals* (Plenum, New York, 1976), p. 38.
[19]F. J. Blatt, *Physics of Electronic Conduction in Solids* (McGraw-Hill, New York, 1968), p. 189.
[20]T. T. Semler and J. P. Riehl, NASA Report No. TMX2320 (unpublished).
[21]V. Ye. Startsev, V. I. Cherepanov, R. Sh. Nasyrov, and N. V. Volkenshteyn, Phys. Met. Metallogr. (USSR) (English Trans.) 44, 194 (1977).
[22]N. F. Mott and H. Jones, *The Theory of the Properties of Metals and Alloys* (Dover, New York, 1958), p. 268.
[23]P. B. Allen, Phys. Rev. Lett. 37, 1638 (1976).
[24]M. J. Laubitz, C. R. Leavens, and Roger Taylor, Phys. Rev. Lett. 39, 225 (1977).
[25]J. Bass, in *Advances in Physics* edited by N. F. Mott (Taylor and Francis, London, 1972), Vol XXI, p. 431.
[26]V. K. Clusius and C. G. Losa, Z. Naturforsch. Teil A 10, 939 (1955).
[27]W. Meissner and B. Voight, Ann. Phys. (Leipzig) 7, 893 (1930).
[28]R. E. Taylor and R. A. Finch, J. Less Common Metals 6, 283 (1964).
[29]R. K. Williams, J. Appl. Phys. 47, 574 (1975).
[30]W. H. Butler, Phys. Rev. B 15, 5267 (1977).
[31]W. L. McMillan, Phys. Rev. 167, 331 (1968).
[32]S. H. Chen and B. N. Brockhouse, Solid State Commun. 2, 73 (1964).
[33]M. Ishikawa and R. L. Cappelletti, J. Low Temp. Phys. 20, 407 (1975).
[34]R. K. Williams and W. Fulkerson, *Thermal Conduc-*

tivity, Proceedings of the 8th Conference, edited by C. Y. Ho and R. E. Taylor (Plenum, New York, 1969), p. 389.
[35]W. H. Butler and R. K. Williams, Phys. Rev. B 18, 6483 (1978).
[36]J. P. Moore, R. K. Williams, R. S. Graves, F. J. Weaver, F. J. Pinski, and W. H. Butler, ORNL Report No. 5672, (unpublished), p. 143.
[37]C. L. Julian, Phys. Rev. 137, A128 (1965).
[38]M. Roufosse and P. G. Klemens, Phys. Rev. B 7, 5379 (1973).
[39]B. Abeles, Phys. Rev. 131, 1906 (1963).
[40]J. A. Krumhansl and J. A. D. Matthew, Phys. Rev. 140, A1812 (1965).
[41]D. W. Yarbrough and R. K. Williams, ORNL Report No. 5434 (unpublished).
[42]J. B. Sousa, J. Phys. C 2, 629 (1969).
[43]A. H. Wilson, Proc. Cambridge Philos. Soc. 33, 371 (1937).