

involved. It seems likely that many of the Auger processes involve valence-band electrons. If this is the case then this region should be investigated more fully for chemical effects due to chemisorption as the density of states for these electrons are most apt to be affected by chemical change.

V. SUMMARY

The Auger transitions in the intermediate-energy range for most of the transition metals in periods 4-6 have been investigated. On the basis of these results,

assignments of the transitions have been made. In all cases it appears as though electrons in only the outermost shells and subshells participate in these transitions, even though incident beam energies are many times the binding energies for more tightly bound electrons. In order to calculate the Auger electron energies, it is necessary to use a correction to take account of the fact that the Auger electrons are being ejected from ionized atoms. Good agreement was obtained when using the energy levels from the next higher element for the binding energy of the ejected electron.

Rigid-Band Behavior in the Specific Heats of PbTl and PbBi Alloys: Electron-Phonon Enhancement Effects*†

LAVERN C. CLUNE‡ AND BEN A. GREEN, JR.§

Department of Physics and Condensed State Center, Case Western Reserve University, Cleveland, Ohio 44106

(Received 7 April 1969)

The normal-state specific heats of pure lead and four dilute PbTl and PbBi alloys have been measured in the temperature range 1.0-2.3 K. The fractional rate of change of the electronic specific-heat coefficient γ with respect to the number of conduction electrons per atom was found to be 0.25 ± 0.06 for PbTl alloys and 0.51 ± 0.04 for PbBi alloys. When changes in the electron-phonon enhancement factor as determined from tunneling measurements are included, good agreement is found between the measured changes in γ and those expected from the rigid-band model. Semiquantitative calculations indicate that changes in the electron-phonon enhancement factor may also account for the apparent discrepancy between previous experimental results and the rigid-band model in noble-metal alloys. The Debye temperature was found to decrease for both lead alloy series.

INTRODUCTION

THE electronic specific heats of simple alloys of the noble metals have puzzled investigators ever since it became known that the Fermi surface of copper makes contact with the first Brillouin-zone boundary. For Rayne¹ had found that addition of Zn to Cu increases the coefficient of the linear term in the specific heat, which is proportional to the density of electron states at the Fermi energy, and it was thought that adding Zn should merely increase the Fermi energy without seriously distorting the shape of surfaces of constant energy. Most calculations of the band structure of Cu, however, agree that the density of states should

decrease with energy for energies beyond that at which said contact occurs.^{2,3}

Examples of this phenomenon have since multiplied to include several alloy systems based upon each of the noble metals⁴⁻¹³ in an attempt to explore the effects of solute valence, size, and mass on the rate of increase of γ with concentration. Size of the solute atom appears to have little to do with the rate of increase, while both valence and mass are significant variables. (Although atomic mass and size are strongly correlated, giving rise to ambiguity of interpretation, the comparison of

² J. M. Ziman, *Advan. Phys.* **10**, 1 (1961).

³ J. S. Faulkner, H. L. Davis, and H. W. Joy, *Phys. Rev.* **161**, 656 (1967).

⁴ B. A. Green Jr. and H. V. Culbert, *Phys. Rev.* **137**, A1168 (1965).

⁵ H. Montgomery, G. P. Pells, and E. M. Wray, *Proc. Roy. Soc. (London)* **A301**, 261 (1967).

⁶ L. C. Clune and B. A. Green, Jr., *Ref. 1*.

⁷ B. A. Green, Jr., *Phys. Rev.* **144**, 528 (1966).

⁸ T. A. Will and B. A. Green, Jr., *Phys. Rev.* **150**, 519 (1966).

⁹ L. J. Badar and B. A. Green, Jr., *Bull. Am. Phys. Soc.* **12**, 20 (1967).

¹⁰ B. A. Green, Jr., and H. M. Wu (to be published).

¹¹ B. A. Green, Jr., and A. A. Valladares, *Phys. Rev.* **142**, 374 (1966).

¹² H. J. Blythe, T. M. Holden, M. Dixon, and F. E. Hoare, *Phil. Mag.* **11**, 235 (1965).

¹³ D. A. Dicke and B. A. Green, Jr., *Phys. Rev.* **153**, 800 (1967).

* Manuscript preparation supported by National Science Foundation Departmental Science Development Grant No. GU 2603 to Ohio University.

† Part of a thesis by L. C. C. submitted to Case Western Reserve University in partial fulfillment of the requirements for the Ph.D. degree.

‡ National Defense Education Act Fellow during part of this research. Present address: Ohio University, Athens, Ohio 45701.

§ Present address: Massachusetts Institute of Technology, Cambridge, Mass. 02139.

¹ J. A. Rayne, *Phys. Rev.* **108**, 22 (1957). These results were probably slightly in error because of paramagnetic impurities but the increase (although smaller) was confirmed by B. W. Veal and J. A. Rayne [*ibid.* **130**, 7156 (1963)] and by L. C. Clune and B. A. Green, Jr. [*ibid.* **144**, 525 (1966)].

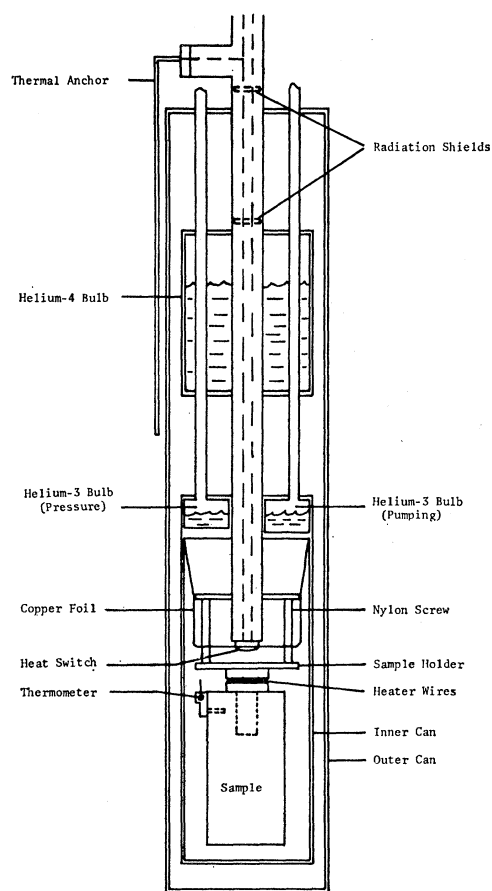


FIG. 1. Calorimeter.

CuAl and CuBe show that mass effects dominate.¹⁰) The mass of the solute can affect the density of states of electrons through the electron-phonon interaction responsible for superconductivity. To explain the experiments in this way would require that the factor by which the density of states is enhanced be itself sensitive to alloying in a regular way.

The present paper concerns results of electronic specific-heat measurements on dilute Pb alloys in the normal state. Pb as a base for alloys in these studies offers the following advantages: (i) The addition of, say, Bi (valence 5) to Pb (valence 4) causes less fractional increase in average valence per atom added than occurs when Zn (valence 2) or any other polyvalent solute is added to Cu (valence 1). (ii) The ionic core of a Pb atom occupies a smaller fraction of the atomic volume than does Cu or any noble metal. (iii) The electron-phonon enhancement factor λ for Pb and its superconducting alloys is susceptible of independent measurement through electron tunneling experiments. The results reported below show a strong rise in γ with electron concentration for PbTl and PbBi alloys. This is shown to be in quantitative agreement with the rigid band model when the measured changes in λ are in-

cluded. Semiquantitative calculations are presented which indicate that changes in λ also make a significant contribution to the increase in γ for the noble-metal alloys.

EXPERIMENTAL DETAILS

The specific-heat measurements were made in a He³ calorimeter very similar to a He⁴ calorimeter used by Green and Culbert^{4,14} for similar measurements on noble metal alloys. The present calorimeter is narrow enough to fit inside the 2-in. bore of a superconducting solenoid (which is operated at 10 kG for normal-state measurements) and, of course, provision has been made to use He³ as a refrigerant and for temperature measurement.

The calorimeter is shown in Fig. 1. The outer can isolates the inner can from the surrounding He⁴ bath at 4.2 K. The sample is screwed to a sample holder which is rigidly supported by three No. 4 nylon screws, only two of which are shown. A 0.1-W Allen-Bradley carbon resistor, nominally 10 Ω , is moulded into a cylindrical cavity in a brass holder with a rubber adhesive (Silastic RTV 732) and the holder is attached to the sample by a No. 4 brass screw. Two manganin heater wires, 0.001 in. in diam, are wrapped around the sample holder and are held in place with wax; we call them the "differential" heater (2000 Ω) and the "main" heater (600 Ω).

Two He³ bulbs are located at the top of the inner can: one (labeled "Pumping") is connected to a special oil-sealed Welch mechanical pump (1402 KBG) by which a temperature of less than 0.3 K can be obtained; the other (labeled "Pressure") is connected to a Texas Instrument Precision Pressure Gauge (Model 142A) for temperature measurement.

A mechanical heat switch is provided to make contact between the sample and the He³ bulbs. When tension in a central control rod is released by a control outside the cryostat, a spring forces an indium-coated copper plug into contact with the sample holder. This plug connects to the wall of the He³ bulbs through two copper foils $\frac{1}{4}$ in. wide by $\frac{1}{64}$ in. thick.

A 50-cc He⁴ bulb (located just above the He³ bulbs) is pumped to 1.3 K to condense the He³ and to minimize the heat leak into the He³ bulbs. A needle valve

TABLE I. Values of γ and A for pure Cu. Results are listed in chronological order.

Authors	Field (kG)	γ (mJ/mole K ²)	A (mJ/mole K ⁴)
Osborne <i>et al.</i> ^a	0	0.695	0.0475
Current work	0	0.698 \pm 0.001	0.0471 \pm 0.0002
Current work	10	0.701 \pm 0.001	0.0467 \pm 0.0003
Current work	0	0.696 \pm 0.002	0.0468 \pm 0.0004

^a Reference 15.

¹⁴ H. V. Culbert, Ph.D. thesis, Western Reserve University, 1964 (unpublished).

TABLE II. Values of γ , A , B , and θ_D for pure Pb as determined by different authors and methods.

Author	Method	γ (mJ/mole K ²)	A (mJ/mole K ⁴)	B (mJ/mole K ⁶)	θ_D (K)
This work	Calorimetric	3.04±0.02	1.65±0.02	0.018±0.002	105.7±0.4
van der Hoven and Keesom ^a	Calorimetric	3.00±0.04	1.66±0.04	0.016±0.008	105.4±0.8
Decker <i>et al.</i> ^b	Magnetic	3.06±0.04			
Waldorf and Alers ^c	Velocity of sound				105.3

^a Reference 21.^b Reference 22.^c Reference 23.

allows easy filling of the He⁴ bulb from the surrounding 4.2 K bath.

A thermal anchor and two radiation shields reduce the heat leak into the helium bulbs and the sample. This heat leak is further minimized by right-angle bends in all vacuum lines except the central line (whose radiation traps are indicated) leading into the outer can. The 50-cc He⁴ pumping bulb lasts at least 10 h at 1.3 K; the 5-cc He³ pumping bulb, approximately 6 h at 0.3 K.

The specific heat is measured by the technique previously used in this laboratory: One measures the time the sample requires to warm through a 5% temperature interval centered at the nominal temperature of measurement \bar{T} . The heat leak from the sample is first balanced out with the main heater to achieve a steady temperature \bar{T} . Then the sample is briefly cooled below the starting temperature by the heat switch. The differential heater is then switched on. An electric clock is automatically gated on and off as the temperature of the sample traverses the measurement interval. This process can easily be repeated until the standard error of the mean heating time is less than 0.1%. The heat capacity of the addenda (sample holder, etc.) is determined by a separate run.

The carbon resistance thermometer was calibrated immediately after each specific-heat run against the vapor pressure of He³ (T_{62} scale). The temperature is allowed to drift upward at the rate of less than 2×10^{-5} K/sec by turning off the pump attached to the He³ pumping bulb and controlling the temperature of the large He⁴ bulb to be just above that of the He³ bulb. Estimates of the time constants involved show that the calibration process is subject to less than 10^{-4} K error from temperature drift.

The carbon resistance thermometer was stable within 1 mdeg between consecutive measurements at the same field. Thus, if a satisfactory calibration was not obtained following a particular measurement, the average of preceding and following calibrations in that magnetic field was used.

The measurements of a particular sample in the normal and superconducting states were, in general, made on separate days. The superconducting magnet was removed during the superconducting run and the sample was allowed to warm to room temperature between runs. Thus there is no possibility that flux remained trapped in the specimens.

It is estimated that the systematic errors introduced by the unusual measurement and calibration techniques are less than 0.1% and that the total systematic error is less than 0.5%. A further check was made by measuring the specific heat of pure Cu in 0- and 10-kG fields at the beginning of the series of runs on PbTl and PbBi and in zero field near the end. The results were fitted to the expression $C = \gamma T + AT^3$, where C is the specific heat and T is the temperature. The values of the coefficients γ and A are compared to the value given in the reference equation by Osborne, Flotow, and Schreiner in Table I.¹⁵ There is reasonable agreement between the various coefficients, and it is therefore assumed that any systematic errors were small and did not change significantly during the course of this work.

SAMPLES

Samples, approximately 1 mole in size, were prepared from 99.9999% pure Pb, Tl, and Bi, obtained from Cominco American Inc. Appropriate amounts of starting materials for each sample were sealed in fused quartz tubes. They were heated approximately 100 K above their liquidus point in an electric furnace and mixed several times by removing the tubes containing the molten alloys from the furnace and shaking vigorously. The samples were quenched in cold water from just above the liquidus point. The samples were drilled and tapped as required for attachment in the calorimeter, etched to remove any impurities left by the tool bits, sealed under vacuum in vycor tubes, and annealed at approximately 235 K for periods of time varying from two days to two weeks.

It has been shown that concentrations of Mn,¹⁶ Fe,¹⁷ Co,¹⁸ and Ni¹⁹ of a few ppm can have large effects on the low-temperature specific heats. The present samples were analyzed by an independent laboratory²⁰ and concentrations of these paramagnetic impurities were found to be less than 1 ppm in all samples. It is

¹⁵ D. W. Osborne, H. E. Flotow, and F. Schreiner, *Rev. Sci. Instr.* **38**, 159 (1967).

¹⁶ J. E. Zimmerman and F. E. Hoare, *J. Phys. Chem. Solids* **17**, 52 (1960).

¹⁷ G. L. Guthrie, S. A. Friedberg, and J. E. Goldman, *Phys. Rev.* **113**, 45 (1959).

¹⁸ L. T. Crane and J. E. Zimmerman, *Phys. Rev.* **123**, 113 (1961).

¹⁹ J. R. Frank, F. D. Manchester, and D. L. Martin, *Proc. Roy. Soc. (London)* **A263**, 494 (1964).

²⁰ Done by National Spectrographic Laboratories, Inc., Cleveland, Ohio.

TABLE III. Values of γ , A , B , and θ_D for PbTl and PbBi alloys in the normal state as determined by fitting the specific heat to the expression $C = \gamma T + AT^3 + BT^5$ and where $A = (12R\pi^4/5)(1/\theta_D)^3$.

All	Solute concentration (at. %)	Z	γ (mJ/mole K ²)	A (mJ/mole K ⁴)	B (mJ/mole K ⁶)	θ_D (K)
Pb	0.0	4.0	3.045	1.637	0.019	105.9
Pb ^a	0.0	4.0	3.026	1.653	0.017	105.5
PbTl	4.6	3.954	2.975	1.729	0.017	104.0
PbTl	4.6	3.954	3.019	1.707	0.022	104.4
PbTl	9.8	3.902	2.962	1.798	0.025	102.6
PbBi	4.6	4.046	3.117	1.713	0.019	104.3
PbBi	8.9	4.089	3.169	1.818	0.014	102.2
	Mean standard deviation		0.007	0.005	0.001	0.1

^a Same sample remeasured.

therefore assumed that such impurities introduced no significant error in the present specific-heat results.

RESULTS

The results were fitted by the method of least squares to the expression

$$C = \gamma T + AT^3 + BT^5,$$

where C is the specific heat. The term γT is interpreted as the electronic specific heat. The coefficient A is related to the Debye temperature at 0 K, θ_D , by the expression $A = (12\pi^4 R/5)(1/\theta_D)^3$. Random error limits were assigned to γ , A , B , and θ_D on the basis of scatter of the measured points from the above expression for C .

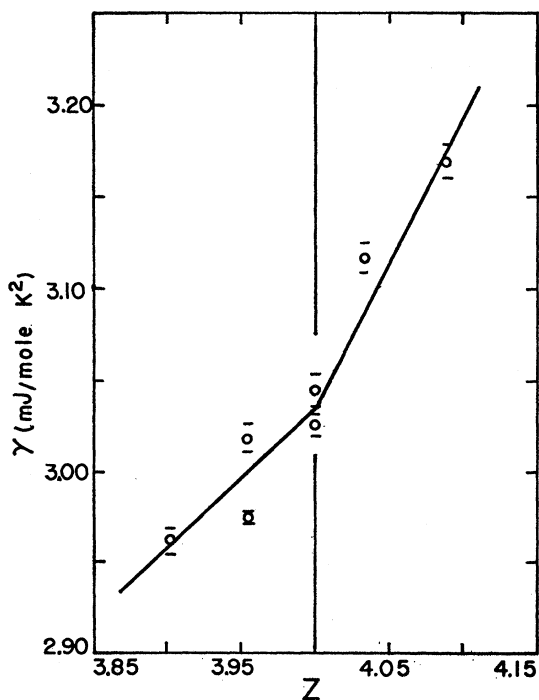


FIG. 2. γ versus electron per atom ratio Z for PbTl and PbBi alloys.

The average values of γ , A , B , and θ_D determined from two measurements of pure Pb made during the present research are compared to the recently published values of van der Hoven and Keesom²¹ in Table II. Also given are the values of γ as obtained from critical magnetic-field measurements by Decker, Mapother, and Shaw²² and the value of θ_D obtained from velocity of sound measurements by Waldorf and Alers.²³ The absolute error limits for the present results are estimated from the consistency of results between the two Pb runs and the previously mentioned results for pure Cu. The random errors for a given measurement are actually much smaller than this. The agreement between the various values is considered quite satisfactory.

The values of γ , A , B , and θ_D for the alloys as well as the results for the two measurements of pure Pb are given in Table III. The quantity Z is the average number of valence electrons per atom defined on the basis of Tl, Pb, and Bi having 3, 4, and 5 valence electrons, respectively. Graphs of γ , θ_D , and B are shown in Figs. 2 and 3.

Figure 2 indicates that γ is an increasing function of Z . Least-square fits of the results for each alloy series to straight lines forced to pass through the average value of γ for pure Pb give the results

$$\gamma = 3.035 + (0.77 \pm 0.21)(Z - 4)$$

for the PbTl alloys and

$$\gamma = 3.035 + (1.56 \pm 0.11)(Z - 4)$$

for the PbBi alloys in units of mJ/mole K². These lines are indicated in Fig. 2 and the values of $d(\ln\gamma)/dZ$ calculated from these lines are given in Table IV. The scatter in the data is sufficient that a single straight line through both alloys series would also adequately represent the results. The scatter of the points from the lines (or line) per degree of freedom is only slightly reduced when the two lines are used. However, the

²¹ B. J. C. van der Hoven, Jr., and P. H. Keesom, Phys. Rev. **137**, A103 (1965).

²² D. L. Decker, D. E. Mapother, and R. W. Shaw, Phys. Rev. **112**, 1888 (1958).

²³ D. L. Waldorf and G. A. Alers, J. Appl. Phys. **33**, 3266 (1962).

cusps in the Debye temperatures reported below suggests that it is unnatural to expect the properties of PbTl and PbBi alloys to vary linearly through pure Pb.

There have been some recent estimates of γ for PbTl alloys from magnetization data, but the large hysteresis in the magnetization curves for these alloys make such estimations uncertain. Bon Mardion, Goodman, and LaCaze²⁴ find that γ remains essentially constant for small concentrations of thallium. Because of the limitations of their approximations this seems to be in reasonable agreement with the present results. Sekula and Kernohan²⁵ find a large initial increase in γ which probably results from their determination of the thermodynamic critical fields based on the integral of the magnetization curve corresponding to increasing field (which has the largest magnetization at a given field).

The graph of θ_D versus Z in Fig. 3 shows a definite cusp at pure Pb. The straight lines correspond to the best estimate of a straight-line fit to each alloy series. The values of $d(\ln\theta_D)/dZ$ calculated from these lines are 0.29 and -0.34 for PbTl and PbBi alloys, respectively. The results for the PbTl alloys are in reasonable agreement with the values of θ_D as calculated from elastic moduli by Alers and Karbon²⁶ and Shepard and Smith.^{27,28}

The coefficient B is seen to decrease slowly with Z with a straight line giving a reasonable fit of the data.

DISCUSSION

Comparison to Rigid-Band Model

The observed change in the electronic specific-heat coefficient is opposite to that expected from the slope of the band-structure density of states curve of pure Pb and the rigid-band model. The band-structure density of states, $N(E)$, was calculated recently by Anderson and Gold,²⁹ who found that near the Fermi energy the density of states is a smoothly decreasing function of energy:

$$\frac{d \ln N(E_F)}{dZ} = -0.24,$$

evaluated at E_F for pure lead. If changes in the enhancement factors are neglected, this should equal the fractional rate of change of γ with Z . The measured values of $d(\ln\gamma)/dZ$, however, are positive and equal to 0.51 and 0.38 for PbBi and PbTl alloys, respectively. This is

²⁴ G. Bon Mardion, B. B. Goodman, and A. LaCaze, *J. Phys. Chem. Solids* **26**, 1143 (1965).

²⁵ S. T. Sekula and R. H. Kernohan, *J. Phys. Chem. Solids* **27**, 1863 (1966).

²⁶ G. A. Alers and J. A. Karbon, *J. Appl. Phys.* **37**, 4252 (1966).

²⁷ M. L. Shepard and J. F. Smith, *Acta Met.* **15**, 357 (1967).

²⁸ T. Claeson and G. Grimvall, *J. Phys. Chem. Solids* **29**, 387 (1968).

²⁹ J. R. Anderson and A. V. Gold, *Phys. Rev.* **139**, A1454 (1963).

TABLE IV. Comparison of values of $d(\ln\gamma)/dZ$ "measured" from specific heats to the values "calculated" from the rigid-band model and determinations of the electron-phonon enhancement factor $(1+\lambda)$ by electron tunneling.

	$\frac{d \ln(1+\lambda)}{dZ}$	$\frac{d[\ln N(E_F)]}{dZ}$	$\frac{d(\ln\gamma)}{dZ}$	
			Calculated	Measured
PbTl	0.44 ± 0.05	-0.24 ± 0.03	0.20 ± 0.06	0.25 ± 0.06
PbBi	0.86 ± 0.05	-0.24 ± 0.03	0.62 ± 0.06	0.51 ± 0.04

the same phenomenon found in noble-metal alloys discussed earlier.

However, the electron-phonon enhancement factor for the density of states of Pb at E_F is known to be large. When enhancement factors are included the expression for γ can be written in the form

$$\gamma = \frac{1}{3} \pi^2 k_B^2 (1 + \lambda + \lambda_1) N(E_F),$$

where λ and λ_1 represent the enhancements due to the electron-phonon and electron-electron interactions, respectively. The electron-phonon factor determined from the tunneling measurements of Jackson, Wu, and Adler³⁰ is $\lambda = 1.51$ so that $1 + \lambda = 2.51$. Anderson and Gold find that λ is 2.23 times that expected from $N(E_F)$. Thus the enhancement due to electron-electron interactions is verified to be small and will be neglected.

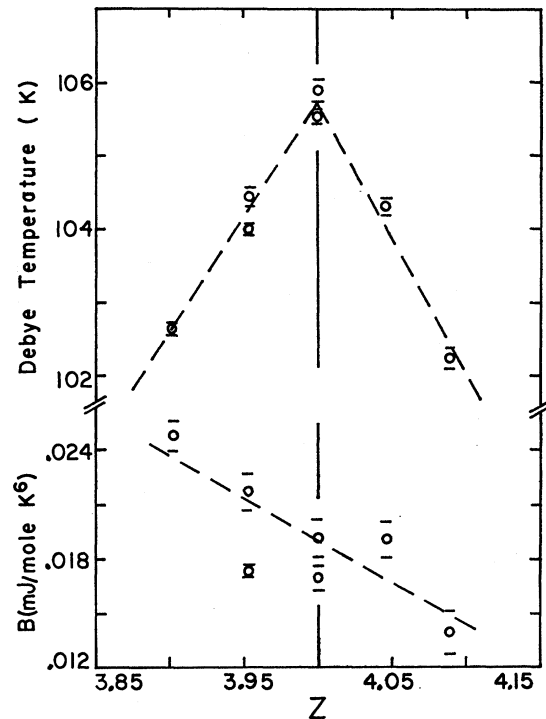


FIG. 3. θ_D and B (the coefficient of the T^5 term) versus electron per atom ratio Z for PbTl and PbBi alloys.

³⁰ J. E. Jackson, T. M. Wu, and J. G. Adler (to be published).

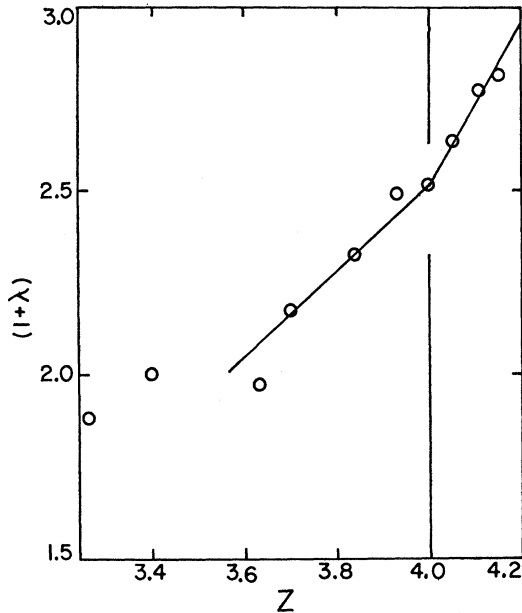


FIG. 4. Electron-phonon enhancement factor $(1+\lambda)$ versus electron per atom ratio Z for PbTl and PbBi alloys.

The electron-phonon enhancement factors in PbTl and PbBi alloys have been measured by Will, Wu, and Adler,^{31,32} whose results are shown in Fig. 4. The straight lines are forced to pass through the value 2.51 for pure Pb. Of the PbTl alloys only those with Z equal to or greater than 3.7 were used for the fit, since nonlinear behavior of λ is expected for alloys with lower Z due to nonlinear changes in $N(E_F)$ as will be discussed later.

The fractional rate of change of γ may now be calculated from the expression

$$\frac{d \ln \gamma}{dZ} = \frac{d \ln(1+\lambda)}{dZ} + \frac{d \ln N(E_F)}{dZ}. \quad (1)$$

The results for these alloys are summarized in Table IV. The values of $d \ln(1+\lambda)/dZ$ are calculated from the straight lines in Fig. 4. The calculated values of $d(\ln \gamma)/dZ$ are just the sum of the previous two columns as required by the previous equation. Measured values are from the specific heat measurements. The agreement between the calculated and measured values is very reasonable.

Thus, the rigid-band model satisfactorily accounts for the changes in γ for dilute PbTl and PbBi alloys after changes in the electron-phonon enhancement factor are allowed for. Further support is given to the rigid-band model in the PbTl alloys by the apparent minimum and then rise of $(1+\lambda)$ at a Z of approximately 3.6 in the data of Will, Wu, and Adler shown in Fig. 4. There is a sharp peak in the density of states

curve of Anderson and Gold at an energy of approximately 0.64 Ry. On the rigid-band model this point corresponds to the Fermi energy for an alloy with Z of 3.57. Thus, the minimum in $(1+\lambda)$ can be associated with the peak in the density-of-states curve. A reason for this inversion will be presented later; but the fact that the structure in the pure-metal density-of-states curve can predict irregularities in the alloy results at the appropriate concentration is itself a strong argument in favor of the rigid-band model for lead alloys.

As an attempt to explain the initial decrease in γ for AgAu, Haga³³ proposed γ is of the form

$$\gamma = \frac{1}{3} \pi^2 k_B^2 (1+\lambda G) N(E_F),$$

where G has been introduced to include the effects of scattering, and the electron-electron interaction has again been ignored. He argues that G is one for pure metals but that it decreases rapidly with scattering in alloys. The present results are inconsistent with this hypothesis.

Jones^{34,35} and Brailsford³⁶ have indicated that electron scattering can also have an effect on the change in the unenhanced density of states $N(E_F)$ upon alloying. Brailsford has rigorously analyzed the effect of "scattering" in terms of the shift in energy of each level due to introduction of the solute. The effect on the density of states is the rigid-band contribution plus a term, whose sign depends upon details of the system, proportional to the energy derivative of the level shift. In the analysis of our results we obtain good agreement by including only the dependence of the electron-phonon enhancement factor and $N(E_F)$ upon Z . Small discrepancies remain, however, which may arise from scattering effects.

Relevance to Noble-Metal Alloys

Since the noble metals are not superconducting, there is no possibility of getting the same direct measurement of their electron-phonon enhancement factors we have just appealed to for lead. Thus if we wish to explain the change of γ with alloying for noble metals by this mechanism we must appeal to theory. In this section we apply the results of one calculation to the case of lead to verify that it leads to the correct order of magnitude of enhancement factor and the proper sensitivity to alloying factors. Then these results are applied to noble metals.

Second-order perturbation theory³⁷ leads to the following expression for λ :

$$\lambda = \sum_{\nu} \sum_{\mathbf{g}} \int \frac{d^3 k'}{(2\pi)^3} |M_{\mathbf{k}\mathbf{k}'}|^2 \left(\frac{2}{\omega_{\mathbf{q}\nu}} \right) \left(- \frac{\partial f(E_{\mathbf{k}'})}{\partial E} \right),$$

³³ E. Haga, Proc. Phys. Soc. (London) **91**, 169 (1967).

³⁴ H. Jones, Phys. Rev. **134**, A958 (1964).

³⁵ H. Jones, Proc. Roy. Soc. (London) **285**, 461 (1964).

³⁶ A. D. Brailsford, Proc. Roy. Soc. (London) **292**, 433 (1966).

³⁷ S. Nakajima and M. Watabe, Progr. Theoret. Phys. (Kyoto) **29**, 341 (1963).

³¹ T. A. Will, T. M. Wu, and J. G. Adler (to be published).

³² T. A. Will, Ph.D. thesis, Case Western Reserve University, 1968 (unpublished).

where k is fixed on and k' runs over the Fermi surface, $\omega_{\mathbf{q}\nu}$ is the frequency of phonon of wave vector \mathbf{q} and polarization ν , \mathbf{g} is the reciprocal-lattice vector, $|M_{\mathbf{k}\mathbf{k}'}|$ is the matrix element for scattering of an electron from state \mathbf{k} to state \mathbf{k}' by the electron-phonon interaction, f is the Fermi distribution function, and $\hbar=1$. The general form of $|M_{\mathbf{k}\mathbf{k}'}|$ is given by³⁸

$$|M_{\mathbf{k}\mathbf{k}'}|^2 = |\alpha_{\mathbf{q}\nu}|^2 |\mathbf{K} \cdot \hat{\epsilon}_{\mathbf{q}}|^2 |U(K)|^2,$$

where $\mathbf{K}=\mathbf{k}-\mathbf{k}'$ is the scattering vector; $\alpha_{\mathbf{q}\nu}$ is the amplitude of phonon of wave vector \mathbf{q} and polarization ν , $\hat{\epsilon}_{\mathbf{q}}$ is the polarization vector of the mode of wave number \mathbf{q} ; and $U(K)$ is the Fourier transform of the electron-ion interaction potential. In the limit as $T \rightarrow 0$, $\alpha_{\mathbf{q}\nu}$ is simply given by

$$\alpha_{\mathbf{q}\nu} = (2Mn\omega_{\mathbf{q}\nu})^{-1/2},$$

where M is the mass of an ion and n is the number density of ions. For atoms having small ionic cores, $U(K)$ can be approximated³⁹ by

$$U(K) = \frac{-4\pi Ze^2 n / K^2 + n\beta}{\epsilon(K)},$$

where $-e$ is the electronic charge of an electron, Ze is ionic charge, β represents the effects of core potentials, $\epsilon(K)$ is the Hartree dielectric function, and n is the number density of ions. Let us use the Thomas-Fermi model for $\epsilon(K)$:

$$\epsilon(K) = 1 + (k_s/K)^2,$$

where k_s is the inverse screening length:

$$k_s^2 = 4\pi e^2 N(E_F) / V,$$

and V is the molar volume. Then $U(K)$ can be rewritten as

$$U(K) = \frac{-VZn/N(E_F) + n\beta(K/k_s)^2}{1 + (K/k_s)^2}.$$

Approximate values of β ³⁹ indicate that only for $K \cong 2k_s$ does the term $-\beta(K/k_s)^2$ approximately equal the term $VZ/N(E_F)$ and at this point the denominator is increased by a factor of 3 or 4 from its value at $K=0$. Since λ is an integral over all K and since values of β are only approximate, the core potential term will be ignored.

With these approximations λ can be rewritten in the form

$$\lambda = \frac{Z^2 n V^2}{8\pi^2 M N^2(E_F)} \sum_{\nu} \sum_{\mathbf{g}} \int d^3 k' \left(\frac{1}{1 + (K/k_s)^2} \right)^2 \times \left(\frac{\mathbf{K} \cdot \hat{\epsilon}_{\mathbf{q}}}{\omega_{\mathbf{q}\nu}} \right)^2 \left(-\frac{\partial f(E_{k'})}{\partial E} \right),$$

³⁸ L. J. Sham and J. M. Siman, *Solid State Phys.* **15**, 221 (1963).

³⁹ W. A. Harrison, *Pseudopotentials in the Theory of Metals* (W. A. Benjamin, Inc., New York, 1966).

or simply

$$\lambda = [Z^2 n V^2 / 8\pi^2 M N^2(E_F)] \Sigma. \quad (2)$$

This expression for λ has the correct dependence on Z and $N(E)$ to account for increases of γ with Z for both the Pb alloys and the noble-metal alloys, if the changes in Σ are assumed to be small. For both alloy series $N(E)$ is a decreasing function of Z . The average ionic charge Z is just Z . So both of the factors Z^2 and $1/N^2(E_F)$ will produce an increase in λ with increasing Z .

Furthermore, the expression predicts a stronger effect in noble metals than in Pb. The fractional rate of change of Z^2 with Z will be larger for dilute Cu alloys (with $Z=1$) than for dilute Pb alloys (with $Z=4$). This is essential if the electron-phonon enhancement is going to account for the difference between γ and the presumed band-structure density of states in noble-metal alloys. It is $d \ln(1+\lambda)/dZ$ which accounts for the difference between $d(\ln\gamma)/dZ$ and $d \ln N(E_F)/dZ$ and this is related to $d(\ln\lambda)/dZ$ by the relation

$$\frac{d \ln(1+\lambda)}{dZ} = \frac{\lambda}{1+\lambda} \frac{d(\ln\lambda)}{dZ}, \quad (3)$$

where λ is the enhancement for the pure metal and is assumed to be small for the noble metals, certainly much less than 1.5.

Finally, Eq. (2) predicts that $1+\lambda$ will be inversely proportional to $N^2(E_F)$ and therefore tends to explain the inversion observed in λ for PbTl alloys remarked upon above.

If we assume that the fractional rate of change of Σ with Z is small we may pursue this discussion to a quantitative conclusion. From Eq. (2), we have

$$\frac{d(\ln\lambda)}{dZ} = 2 \frac{d(\ln Z)}{dZ} + \frac{d(\ln n)}{dZ} + 2 \frac{d(\ln V)}{dZ} - \frac{d(\ln M)}{dZ} - 2 \frac{d \ln N(E_F)}{dZ}. \quad (4)$$

If we choose, however, to improve on this approximation by including the effects of changes in $\omega_{\mathbf{q}\nu}$ through the Debye model

$$\omega_{\mathbf{q}\nu} = qs = q\theta_D / (6\pi^2 n)^{1/3},$$

where s is the sound velocity; the expression (2) for λ can be rewritten as

$$\lambda = \frac{Z^2 V^2 n (6\pi^2 n)^{2/3}}{8\pi^2 M N^2(E_F) \theta_D^2} \Sigma', \quad (5)$$

where the changes of Σ' with alloying are now assumed

TABLE V. Comparison of measured values of $d \ln(1+\lambda)/dZ$ to the values calculated using the approximations discussed in the text.

Alloy	$d \ln(1+\lambda)/dZ$		Measured
	Eq. (7)	Eq. (8)	
PbTl	0.61	0.24	0.44
PbBi	0.62	1.00	0.86

to be negligible, and we find

$$\frac{d(\ln\lambda)}{dZ} = 2 \frac{d(\ln Z)}{dZ} + \frac{5}{3} \frac{d(\ln n)}{dZ} + 2 \frac{d(\ln V)}{dZ} - \frac{d(\ln M)}{dZ} - 2 \frac{d[\ln N(E_F)]}{dZ} - 2 \frac{d(\ln \theta_D)}{dZ}. \quad (6)$$

We use the average values in the alloys to rewrite each of these Eqs. (4) and (6). Equation (4) becomes

$$\frac{d(\ln\lambda)}{dZ} = \frac{2}{(Z)} + \frac{d(\ln V)}{dZ} - \frac{1}{Z'} \left(\frac{\Delta M}{M} \right) - 2 \frac{d[\ln N(E_F)]}{dZ}, \quad (7)$$

and Eq. (6) becomes

$$\frac{d(\ln\lambda)}{dZ} = \frac{2}{(Z)} + \frac{1}{3} \frac{d(\ln V)}{dZ} - \frac{1}{Z'} \left(\frac{\Delta M}{M} \right) - 2 \frac{d[\ln N(E_F)]}{dZ} - 2 \frac{d(\ln \theta_D)}{dZ}, \quad (8)$$

where ΔM and Z' are the difference in mass and valence, respectively, of the solute and solvent atoms. Each of these expressions were used to compare the calculations with experimental data below.

The calculations of $d[\ln(1+\lambda)]/dZ$ for PbTl and PbBi alloys are summarized in Table V. The volume changes with Z were obtained from the lattice spacings of these alloys as given by Pearson.⁴⁰ The values of the other variables are taken from the normal-state specific-heat data, the band-structure density of states of Anderson and Gold, and the known atomic masses of the elements. The experimental value $\lambda=1.51$ for pure Pb was used. The measured values are from the tunneling measurements of Will, Wu, and Adler previously quoted and repeated here for ease of comparison.

The agreement between the results is reasonable considering the crudeness of the approximations. Under Eq. (7), which neglects any change in the phonon spectrum, the calculated values of $d \ln(1+\lambda)/dZ$ for the two alloy systems are approximately equal, lying between the measured values. Use of Eq. (8), in which the Debye model is used to allow for changes in the

phonon spectrum in alloying, increases the calculated value for PbBi, alloys above that for PbTl alloys, as is found experimentally.

In the above calculation, we use Eq. (7) or (8) to find $d(\ln\lambda)/dZ$ and convert the result to $d[\ln(1+\lambda)]/dZ$ by multiplying by $\lambda/(1+\lambda)$, which is evaluated from tunneling measurements on Pb. When we come to apply this procedure to noble metals, there is no problem in evaluating $d \ln\lambda/dZ$, but there is no independent measure of λ to use to complete the calculation. Equations (1) and (3) can be combined and solved for $\lambda/(1+\lambda)$ in the form

$$\frac{\lambda}{1+\lambda} = \left(\frac{d(\ln\gamma)}{dZ} - \frac{d \ln N(E_F)}{dZ} \right) / \frac{d(\ln\lambda)}{dZ}.$$

We shall therefore evaluate the denominator from Eq. (7) or (8), the first term in the numerator from specific-heat measurements, and the second term from band-structure calculations. The result then should be (i) independent of solute for any given solvent and (ii) of the right magnitude of λ to explain the value of γ for the pure solute.

The results are given in Table VI. The calculations were made using values of $d(\ln\gamma)/dZ$ and $d(\ln\theta_D)/dZ$ taken from the specific-heat measurement and of $d(\ln V)/dZ$ as obtained from Pearson.⁴⁰ The value of $d[\ln N(E_F)]/dZ$ was assumed to be the same for all noble-metal alloys and to have a value of 0.33 as determined from the recent calculation of $N(E)$ for copper by Faulkner *et al.*³ The values of $(1+\lambda)$ for each noble metal and even between the different noble metals seem reasonably consistent considering the crudeness of the approximations.

For elements alloyed with solutes having approximately equal or heavier masses (CuZn, AgCd, and AgSn) the value of $\lambda/(1+\lambda)$ is approximately 0.2, corresponding to the value of $\lambda=0.25$. Thus, if changes in the electron-phonon enhancement factor as evaluated here are to account for the observed increases in γ upon alloying, the enhancement factor in the pure noble metals must be approximately 0.25.

Only for Cu have there been extensive comparisons between the band structure and measured values of γ . Calculations by Segall⁴¹ using the Korringa-Kohn-Rostoker (KKR) method indicates that both γ and the cyclotron period (which is assumed to be affected the same as γ by the electron-electron and electron-phonon interactions⁴² are enhanced by about 18%. Zornberg and Mueller⁴³ found an enhancement of 25% for the neck and belly cyclotron periods. The most recent calculations by Faulkner, Davis, and Joy,³ again using the KKR method, indicates a maximum enhancement of about 10%.

⁴¹ B. Segall, Phys. Rev. **125**, 109 (1962).

⁴² N. W. Ashcroft and J. W. Wilkins, Phys. Letters **14**, 285 (1965).

⁴³ E. I. Zornberg and F. M. Mueller, Phys. Rev. **151**, 557 (1966).

⁴⁰ W. B. Pearson, *Handbook of Lattice Spacings and Structures of Metals and Alloys* (Pergamon Press, Inc., New York, 1958).

The above are estimates of the total enhancements and include both electron-electron and electron-phonon enhancements. The estimate of λ from such comparisons is further obscured since the total enhancement is actually a sum of $\lambda + \lambda_1$. From the above it would seem reasonable to assume that this sum $\lambda + \lambda_1$ was approximately 0.10–0.15. Estimates of λ_1 are extremely difficult to make; it is not even certain that λ_1 is positive, although it is generally assumed to be small.^{42,44} Perhaps the discrepancy between the measured values⁷ for lead of $1 + \lambda = 2.51$ obtained from tunneling and the calculated enhancement of 2.23 should be interpreted to indicate that λ_1 is negative and has a value of -0.28 . The closest theoretical value to this is the value of approximately $\lambda_1 = -0.05$ by Watabe⁴⁴ for essentially all metals (or perhaps slightly more negative with a slight correction he discusses to give agreement with the measured enhancement of Pauli paramagnetism). Thus, the value of $\lambda = 0.25$ required to account for the differences between measured and expected changes in γ for noble-metal alloys is not unreasonable.

The above considerations, crude as they may be, nevertheless make it plausible that at least part of the initial increase in the electronic specific-heat coefficients when noble metals are alloyed with polyvalent non-transition metals can be attributed to an increase in the electron-phonon enhancement factor.

If the electron-phonon interaction is a rapidly increasing function of Z in noble-metal alloys one might expect to find a superconducting transition in these alloys. The noble metals have been found to remain normal down to temperatures of 0.05, 0.35, and 0.006 K for Cu, Ag, and Au, respectively.⁴⁵ The only reported check for superconductivity in the fcc noble-metal alloys has been on a 92 Ag+8 Sn alloy which remained normal down to 1.2 K.⁴⁵ A further search would be interesting.

SUMMARY

Specific-heat measurements on dilute PbTl and PbBi alloys in the normal state indicate that the electronic

⁴⁴ M. Watabe, Progr. Theoret. Phys. (Kyoto) **29**, 519 (1963).

⁴⁵ B. W. Roberts, Progr. Cryogenics **4**, 1959 (1964).

TABLE VI. Calculated values of $d(\ln\lambda)/dZ$ and the corresponding values of $\lambda/(1+\lambda)$ required to account for the measured changes in γ for noble alloys.

Alloy	$\frac{d(\ln\gamma)}{dZ}$	$\frac{d(\ln\lambda)}{dZ}$		$\frac{\lambda}{1+\lambda}$	
		Eq. (7)	Eq. (8)	Eq. (7)	Eq. (8)
CuBe	0.6 ^a	3.24	3.13	0.29	0.30
CuAl	0.4 ^a	3.05	2.84	0.24	0.26
CuZn	0.33 ^b	2.82	3.15	0.23	0.21
CuSn	0.24 ^c	2.65	3.54	0.22	0.16
AgAl	0.4 ^d	2.99	...	0.24	...
AgZn	0.65 ^e	2.92	3.01	0.34	0.33
AgCd	0.26 ^f	2.79	2.96	0.21	0.20
AgSn	0.22 ^g	2.74	2.95	0.20	0.19
AuSn	0.82 ^h	2.88	3.42	0.40	0.34

^a See Ref. 10.

^b See Ref. 3.

^c See Ref. 6.

^d See Ref. 9.

^e See Ref. 7.

^f See Ref. 5.

^g See Ref. 4.

^h See Ref. 8.

specific-heat coefficient is an increasing function of Z , with the rate of increase being greater for PbBi alloys than for PbTl alloys. The differences between these results and those expected from a rigid-band model using the calculated density of states for pure Pb are accounted for quantitatively by the experimentally observed rate of change in the electron-phonon enhancement factor λ . These results indicate that the rigid-band model is valid in PbTl and PbBi alloys.

By making several simplifying approximations, the changes in λ for the Pb alloys were calculated and found to be in reasonable agreement with the measured values. These same approximations applied to noble-metal alloys indicate that at least part of the discrepancy between the rigid-band model and the measured changes in γ for these alloys can also be attributed to the changes in λ .

ACKNOWLEDGMENTS

The authors are grateful to Dr. T. A. Will for indicating the availability of the electron-phonon enhancement factor from tunneling measurements, and to Dr. T. A. Will, Dr. T. M. Wu, and Dr. J. G. Adler for providing these data in advance of publication.