resonant oscillations in cadmium in a longitudinal field, which they ascribe to orbits which have a net velocity in the direction of the field, and which are sufficiently convoluted to allow a resonant absorption when the displacement during one period is a multiple of the acoustic wavelength. Such orbits can arise from pieces of Fermi surface having the form of a distorted cone, and the period of the resonant oscillations allows the determination of the rate of change of Fermi surface area with wave vector in the field direction, for those orbits which are responsible for the resonance.

The attenuation of longitudinal waves in lead appears to approach a constant value at high magnetic fields. This is in accord with the theory since there are no open orbits present when the magnetic field is along the axes of the specimens used in these experiments.[19] The attenuation of transverse waves in tin is decreasing with field at the highest fields in all the specimens measured, but it is not clear whether it is tending towards a finite or zero limiting value. According to Alekseevskii, Gaĭdukov, Lifshits, and Peschanskii[20] open orbits exist when the field is in the [100], [110], and [101] directions, but not in the [001] direction. It may be significant that the attenuation at high fields has fallen to a considerably lower value in the crystal with no open orbits than in the others. Experiments in higher fields and further consideration of the theory are required for a complete understanding of the limiting behavior of ultrasonic attenuation in high longitudinal magnetic fields.

ACKNOWLEDGMENTS

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Valuable discussions with Professor R. H. Good, Jr., and Professor J. M. Keller are also gratefully acknowledged.

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Specific Heats of Zirconium Alloys at Low Temperatures

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The specific heats of dilute alloys of silver, cadmium, indium, tin, and antimony in hexagonal zirconium have been measured from 1.2 to 4.5°K. For each alloy the specific heat obeys the relation $c=\gamma T+\beta T^3$ within the experimental error. All of these solutes increase γ linearly with concentration and $d\gamma/dx$ is linearly related to the chemical valence of the solute. The increase in γ in the tin-zirconium alloys shows that all electrons outside closed shells cannot be treated as equivalent in the rigid band model of alloying. All of these solutes increase the density of states of zirconium, providing evidence for a zone overlap in the zirconium d band and for a small number of electrons in a new band. All of the solutes increase the lattice specific heat and the Debye temperature is a linear function of solute concentration for each of these alloy systems. $d\theta/dx$ is not simply related to the solute valence but shows a close correlation with the magnitude of the rate of change of the distance between atoms at (0,0,0) and ($\frac{1}{3},\frac{2}{3},\frac{1}{2}$) of the hexagonal cell. Additions of tin to zirconium do not change the average interaction potential of the BCS theory appreciably.

I. INTRODUCTION

The electronic specific heat provides one of the best methods for experimentally determining the changes in the density of electronic states which take place during alloying and, thus, indirectly the band structure of the solvent metal.[1–3] Although the original conception of the rigid band model[4] of alloying did not allow for the screening by the conduction electrons of the additional charge of the solute ions, Friedel[5] has shown that this model does correctly predict the affect of alloying on the density of states using the Thomas-Fermi approximation and assuming that exchange and correlation effects do not change during alloying. For alloys of metals containing closed d shells, the rigid band model describes the situation fairly well. Rayne[6] has shown that for germanium and zinc in

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[1] N. F. Mott and H. Jones, *The Theory and Properties of Metals and Alloys* (Clarendon Press, Oxford, 1936), p. 179.

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copper the density of states is proportional to the electron concentration providing suitable corrections are made for the change in volume during alloying. Further support is found in the dependence of the elastic constants[7] and, hence, the Debye temperature[6] on the electron concentration. The rate of increase of the density of states with increasing electron concentrations is much greater than expected for parabolic valence bands and the rapid increase in the density of states is attributed to the distortion of the Fermi surface due to approaching contact with the {111} faces of the Brillouin zone. The electronic specific heat of dilute alloys of bismuth and indium in tin also are in agreement with the rigid band model.[8] The Debye temperatures are not simply related to the electron concentration as in the copper alloys but are related to the change in the magnitude of the electron concentration. When both the solvent and solute are transition metals with unfilled d bands, the rigid band model is applicable in many cases. Thus, the density of states and the Debye temperatures of body-centered titanium-vanadium[9] and titanium-molybdenum[10] alloys are functions of the electron concentration if the valences of titanium, vanadium, and molybdenum are taken as 4, 5, and 6, respectively.

If the solvent is a transition metal with partially filled d bands and the solute contains filled d shells, the situation is more complicated. Investigations of electronic and lattice specific heats of zirconium-alloys with silver, cadmium, indium, tin, and antimony were undertaken in order to compare the alloying behavior of an early transition metal, zirconium, with the alloying behavior of the noble metals copper, silver, and gold. An understanding of these alloys is important because this is one of the principle methods of interpolating experimentally between the properties of the pure elements. The strong cohesion, high-field superconductivity, good neutron properties and rapidly changing properties with electron/atom ratio in this part of the periodic table makes these results of particular interest. In Secs. II and III, the preparation of the alloys and experimental techniques are described. In Sec. IV, the experimental results for both the electronic and vibrational specific heats are presented and in Sec. V the electronic specific heat is discussed in terms of a modified rigid band model. In Sec. VI the effect of alloying on the vibrational specific heat is shown to correlate with the change in distance between the atoms whose coordinates are (0,0,0) and $(\frac{1}{3},\frac{2}{3},\frac{1}{2})$. The BCS (Ref. 11) interaction potential V is shown to be unchanged by the addition of tin to zirconium in Sec. VII.

Table I. Impurities in arc-melted zirconium.[a]

Impurity	Amount (ppm)
Hafnium	~130
Silicon	14
Iron	55
Copper	14
Tungsten	8
Hydrogen	11
Nitrogen	<5
Oxygen	70
Carbon	30

[a] Zirconium 99.95%. Vickers hardness 68.

II. ALLOY SPECIMENS

Alloys of the systems Zr-Ag, Zr-In, Zr-Sn, and Zr-Sb approximately one mole in size were prepared by arc melting iodide-zirconium and 99.99% pure solute on a water-cooled copper hearth in an argon atmosphere. Uniform solute concentration was attained by repeated melting on opposite sides of the ingot, shearing the ingot to small pieces, and remelting. Each ingot was cut up at least twice and remelted a minimum of 12 times. The more dilute alloys were annealed at 1100°C for at least five days to remove minor concentration gradients, annealed in the α solid solution range for a minimum of 25 days, and then quenched in water to retain the α solid-solution structure. Because of the limited solubility of these elements in hexagonal zirconium the more concentrated alloys were annealed in the β solid-solution region for periods between 10 days at 1100°C and 1 day at 1200°C and then quenched in water. This heat treatment yields a strained hexagonal structure, denoted α', similar to the equilibrium α structure with the solute atoms as randomly distributed as possible. The zirconium-cadmium alloys could not be prepared by arc melting because of the high vapor pressure of cadmium but were made by diffusing controlled amounts of cadmium into zirconium at 1000 to 1100°C. Diffusion times of 20 to 30 days were found to yield a substantially uniform cadmium concentration in 1.6-mm-thick zirconium disks. The alloys were then annealed in the α solid solution region and quenched to room temperature. All annealing treatments were carried out in evacuated or argon-filled quartz capsules using procedures which introduced a minimum of impurities into the alloys. In order to establish the impurity content of the alloys, a pure zirconium sample was subjected to the same melting and annealing treatments as the alloys and then analyzed for minor constituents. The analytical results are listed in Table I and indicate that hafnium is the major impurity and that the total impurity content is not greater than 500 ppm. The metallic elements were assayed by neutron activation analyses, the gases by vacuum fusion, and carbon by the

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combustion method. The composition of each alloy was determined by chemical analysis.[12] Analytical samples were taken from three different locations on most of the specimens, the variation in the analytical values indicating a maximum solute inhomogeneity of ±0.2 at.%.

III. EXPERIMENTAL PROCEDURE

The specific heat of each alloy sample was measured at about 30 points between 1.2 and 4.5°K in an adiabatic calorimeter. Errors in the specific heat due to adsorbed helium gas on the samples were eliminated by using a mechanical heat switch to cool the specimen to the working temperature. Errors due to thermal coupling between the bath and the sample and due to the curvature of the specific heat in a heating interval were small so that the controlling source of error, approximately ±0.2%, was caused by the uncertainty in the measurement of the temperature rise of the sample during the heating period. The calorimeter and the experimental procedures have been described in detail in another report.[13] After subtracting the heat capacity of the heater and thermometer which were determined in a separate experiment, the data were fitted to the equation

$$c=\gamma T+\beta(T/\theta_D)^3 \qquad (1)$$

by the method of least squares to obtain the coefficient of the electronic term γ, and the Debye temperature θ_D, for each alloy.

TABLE II. Coefficient of the electronic specific heat and Debye temperatures of zirconium alloys.

Alloy	Structure	γ (mJ/mole deg^2)	θ_D (°K)
Zr	α	2.808±0.024	291.2±1.3
Zr-0.38% Ag	α	2.825±0.019	294.7±1.7
		2.813±0.016	294.3±1.4
		2.821±0.010	292.7±0.9
Zr-0.54% Ag	α	2.763±0.017	290.0±1.5
Zr-0.86% Ag	α	2.771±0.014	292.5±1.2
		2.805±0.012	290.4±1.1
Zr-1.87% Ag	α'	2.849±0.012	288.9±1.0
Zr-3.65% Ag	α'	2.891±0.015	282.3±1.1
Zr-5.66% Ag	α'	2.864±0.019	276.0±1.3
Zr-1.44% Cd	α	2.804±0.023	284.1±1.7
		2.767±0.025	290.3±2.4
		2.834±0.024	287.0±2.0
Zr-5.37% Cd	α	2.959±0.035	280.2±2.9
		3.023±0.019	283.0±1.2
Zr-8.15% Cd	α	3.208±0.020	278.4±1.4
Zr-1.79% In	α	2.858±0.012	289.3±1.1
Zr-3.65% In	α	2.956±0.015	287.7±1.5
Zr-5.33% In	α	3.090±0.015	286.8±1.5
Zr-8.19% In	α	3.243±0.014	284.5±1.1
	α'	3.223±0.024	284.1±2.2
Zr-9.40% In	α'	3.271±0.015	283.4±1.4
Zr-11.26% In	α'	3.319±0.017	282.6±1.6
Zr-1.60% Sn	α	2.952±0.019	290.6±1.9
Zr-3.09% Sn	α	3.043±0.015	287.5±1.3
Zr-4.58% Sn	α	3.152±0.015	282.6±1.4
Zr-6.11% Sn	α'	3.242±0.023	278.2±1.9
Zr-7.60% Sn	α'	3.329±0.018	277.5±1.5
Zr-9.06% Sn	α'	3.376±0.035	275.3±2.7
Zr-0.69% Sb	α	2.873±0.013	292.1±1.2
Zr-1.23% Sb	α'	2.919±0.014	287.1±1.2
Zr-1.85% Sb	α'	3.005±0.031	282.8±2.5

IV. EXPERIMENTAL RESULTS

Except for the two higher composition zirconium-tin alloys which undergo a superconducting transition at approximately 1.25°K, the specific heats were found to obey Eq. (1) from 1.2 to 4.5°K within the experimental error. A typical set of data is shown in Fig. 1 plotted as c/T versus T^2 to show the linear relation, and as $\Delta c/c$ versus T, where $\Delta c=c-\gamma T-\beta T^3$, to display the scatter more clearly. The random nature of the scatter shows clearly that below 4.5°K the Debye approximation is adequate for the lattice specific heats of these alloys and that the measurements would have to be extended to higher temperatures to establish the presence of T^5 or higher terms. No evidence was found for electronic terms nonlinear in temperature. The results of the least-square fit of the data to Eq. (1), the confidence limits at the 99% confidence level, and the metallurgical structure of each alloy are listed by alloy composition in Table II. The γ values and Debye temperatures were found to be linearly related to the solute concentration for each of the alloy systems as shown in Fig. 2 for the zirconium-indium alloys where the filled symbols denote the α' alloys. That the additional strains introduced in the α' alloys do not significantly affect either γ or the Debye temperature is shown by the measurements on the 8% indium alloy after both α and α' heat treatments and by the fact that the γ's and Debye temperatures of the higher composition α' indium and the tin alloys fall on the curves established by the α alloys. For this reason, the results of the specific heat measurements of the α' alloys of each alloy series were considered to be equal in weight to those of the α alloys in establishing the effect of the solutes on the specific heat of zirconium. The results for the other alloying systems were similar

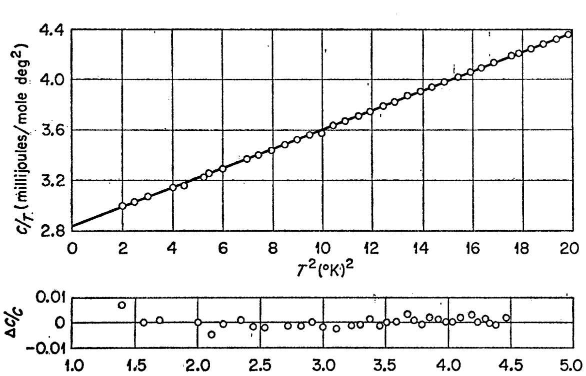

FIG. 1. The specific heat of zirconium-0.86% silver.

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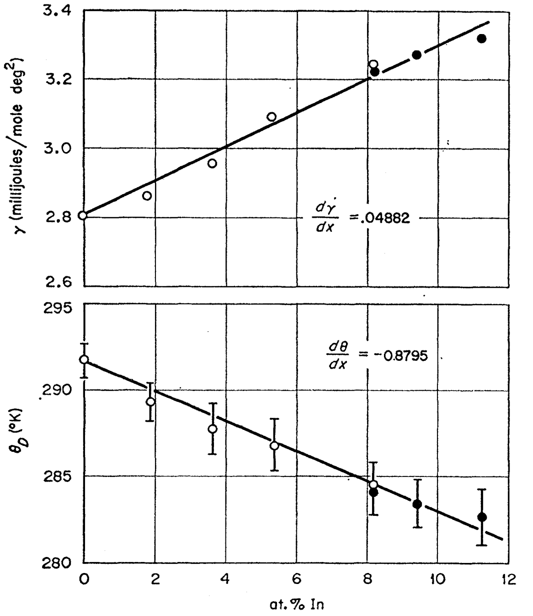

FIG. 2. The electronic specific heats and Debye temperatures for zirconium-indium alloys.

to those for Zr-In with only changes in the slopes of the curves. These effects are shown together in Fig. 3 where the data have been omitted for clarity in drawing and the numerical values of the slopes of the curves are tabulated in Table III.

V. THE ELECTRONIC SPECIFIC HEAT

In order to discuss the increases in γ which occur during alloying it is necessary to consider the relationship between γ and $N(E)$ and the changes in $N(E)$ with alloying. Although in the one-electron approximation,[1–3] $\gamma=\frac{2}{3}k^2N(E)$, several authors[14–16] have recently shown that when interactions between electrons are considered this relationship is not valid and that the effect of the exchange and correlation energies is to modify the density of states at the Fermi surface and, thus, the specific heat from the one-electron values. Using the collective description of electrons of Bohm and Pines,[17] Nozières and Pines[18] show that the correlation energy may be found for the electronic densities which occur in metals by an interpolation between the exact results for high densities of Gell-Mann and Brueckner[19] and the low-density calculation of Wigner.[20] That this correction can be appreciable even for the alkali metals has been shown by Fletcher and Larson.[21] The effect of including the electron interactions to the second order in H_{Sr}, the Hamiltonian of a screened electron-electron interaction, is to increase the electronic specific heat by 20–70%. Luttinger[15] has treated the interactions in a different fashion using perturbation theory and draws somewhat different conclusions. The result of the electron-electron interactions in this case is that even at the absolute zero of temperature some of the states having momenta less than the Fermi momenta are only partially occupied, and the electrons which would be in these states in the single-particle approximation are now in states above the Fermi surface. The picture of the Fermi surface as being a discontinuity in the density of states is still valid although the magnitude of the discontinuity is reduced. The electronic specific heat of interacting fermions in a periodic potential field has a similar form to the noninteracting case except that the original unperturbed single particle energies are replaced by the interacting particle energies. The specific heat is still a linear function of temperature and a measure of the dis-

TABLE III. Rate of change of the electronic coefficient and Debye temperature of zirconium upon alloying.

Alloy system	$d\gamma/dx$ (mJ/mole deg² at.%)	$d\theta_D/dx$ (°K/at.%)
Zr-Ag	0.01303	−2.492
Zr-Cd	0.03778	−1.766
Zr-In	0.04882	−0.8795
Zr-Sn	0.06811	−1.881
Zr-Sb	0.1016	−4.037

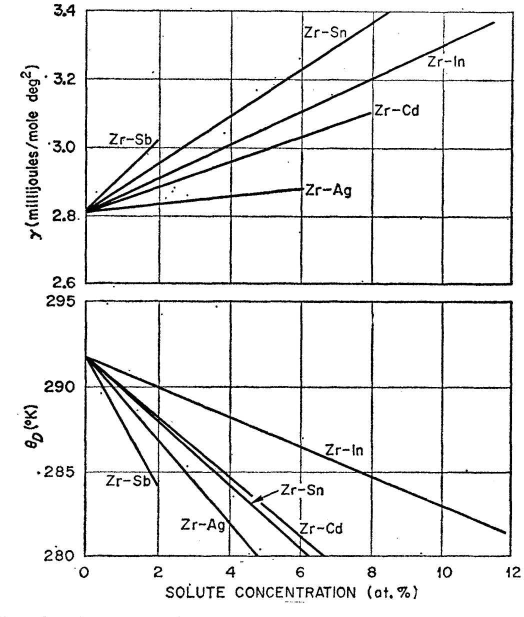

FIG. 3. The electronic specific heats and Debye temperatures for zirconium-B-subgroup alloys.

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continuity in occupied states at the Fermi surface. In addition to these interactions, Jones[22] has proposed that an increased linear term of the specific heat occurs when the Fermi surface lies close to but not touching the zone boundaries. This term arises from an electron-lattice interaction and the change of the Fermi surface with temperature. These electron-electron and electron-phonon interactions appear to be important in determining the density of states in zirconium as Altmann[23] has recently calculated the band structure using a cellular method and found the one-electron density of states to be 12% smaller than the experimental value. This difference is assumed to be due to the interaction energies and suggests that the interaction effects are fairly small in zirconium.

To simplify the discussion of the changes in γ with alloying, we shall assume that the interaction effects are independent of the solute additions and that the density of states is not appreciably affected by the small changes in volume which occur in these systems or by the changes in axial ratio which occur during alloying. In the usual treatment of alloying, the rigid band model[4] is assumed to relate the changes in the filling of the energy bands to the electron to atom ratio. Although this model does not take into account the screening of the perturbing potential of the solute atom by the conduction electrons, Friedel[5] has shown that it may be used in studying the density of states at the Fermi surface or other properties which depend on the displacement of the Fermi surface relative to the bottom of the band. The screening effect leaves the shape of the band unchanged and causes the band as a whole to shift along the energy scale.

The band structure of zirconium is assumed to be similar to that of other transition metals and consists of a narrow d band with a high density of states overlapped by a broad s band as shown schematically in Fig. 4. The general shape is similar to those computed by LCAO methods for titanium,[24] copper,[25] tungsten,[26] and with the cellular calculation for zirconium by Altmann and Bradley.[23] The minimum in the curve arises from the splitting of the d band due to the symmetry of the crystal potential and the symmetry of the d atomic orbitals.

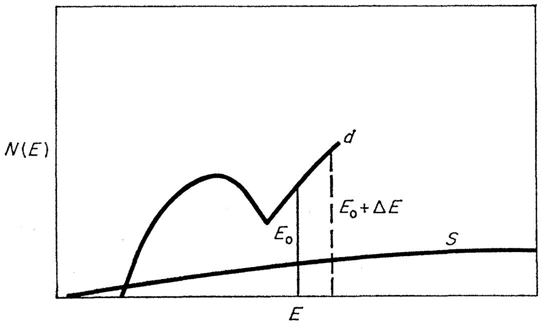

FIG. 4. Schematic band structure of zirconium.

Tin, like zirconium, has four electrons outside of closed shells so that the substitution of a tin atom for a zirconium atom in an alloy would leave the electron concentration and, hence, the Fermi level and density of states, unchanged if all of the electrons are assumed to be equivalent in the rigid band model. This is contrary to the experimental results, tin being one of the most effective alloying elements in changing the electronic specific heat; thus, all of the electrons must not be equivalent or the conduction band of the alloy must be changed by these solutes. Either of these ideas can be incorporated into the rigid band model and lead to expressions for the density of states as a function of solute concentration and valence which agree with the experimental results. We shall consider first the case where the wave functions of the solute valence electrons do not combine with the wave functions of the electrons in the zirconium d band and, secondly, the case where the bottom of the s and d bands are shifted with respect to each other during alloying.

We shall assume that the zirconium d electrons are tightly bound and do not penetrate into the atomic polyhedra of the solute atom, that the s and d bands do not change in energy during alloying, and that the two bands may be treated independently. The conduction band of the alloy then consists of the zirconium s band combining with the s and p bands of the solute. If the alloying process is considered in steps, the substitution of a solute atom for a zirconium atom results in the removal of d states as well as d electrons from the d band, leaving the band unchanged except that it extends over one less atom; a change in the s band resulting from the change in the electron concentration; finally, spilling of the electrons from the s band to the d band to equalize the Fermi surface in the two bands. The change in the Fermi energy then can be shown to be for small x

$$\Delta E=\frac{n-n_s}{N(E_0)}x, \tag{2}$$

where n and n_s are the solute valence and the number of electrons in the zirconium s bands, respectively, x is the solute concentration, and $N(E_0)$ is the density of states in the pure metal. The d electrons influence the change in the Fermi surface and any properties which depend explicitly on the Fermi surface only through the density of d states at the Fermi surface. The change in the density of states and hence the change in γ is

$$\frac{d\gamma}{dx}\sim\frac{dN(E_0)}{dx}=\frac{1}{N(E_0)}\frac{\partial N(E_0)}{\partial E}(n-n_s)-N_d(E_0). \tag{3}$$

The change in the electronic specific heat then is a linear function of the solute valence and of the solute

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concentration. As shown in Fig. 5, this linear relation between $d\gamma/dx$ and the solute valence is obeyed for the solutes silver, cadmium, indium, tin, and antimony in zirconium. All of these solutes increase the density of states at the Fermi surface with the highest valent solute giving the largest value of $d\gamma/dx$.

Although neither the number of s nor d electrons can be determined uniquely in this way, the slope of the density of states versus energy curve can be evaluated from the slope of this curve. The value computed in this manner is very high, and assuming this slope is constant, the portion of the d band past the minimum must contain approximately one-half electron/atom. For $n=n_s$, $d\gamma/dx$ must equal the negative of the d contribution to γ for pure zirconium. As shown in the figure, this does not occur for any positive value of the number of s electrons, since γ is 2.8 for zirconium and the s contribution is assumed to be relatively small. Thus, although this alloying model agrees with the experimentally observed dependence of the electronic specific heat on the solute concentration and solute valence, it leads to a physically unacceptable value for the number of electrons in the s band of zirconium.

Another way the rigid band model may be improved is to allow the individual bands to shift with respect to each other. Such band shifts can occur as a result of the strong perturbations which occur in the zirconium d band upon alloying with solute atoms with completely filled d shells or as a result of dimensional changes in the Brillouin zone as the hexagonal lattice relaxes to new axial ratios during alloying. Assuming that the bands do not change in shape but that they may shift with respect to each other and that the shift in the relative positions is proportional to the solute concentration, then

$$\frac{d\gamma}{dx}\sim\frac{dN(E_0)}{dx}=\frac{1}{N(E_0)}\frac{\partial N(E_0)}{\partial E}(n-n_0)+\frac{A}{N(E_0)}\left[N_d(E_0)\frac{\partial N_s}{\partial E}-N_s(E_0)\frac{\partial N_d}{\partial E}\right], \quad (4)$$

where A is the constant relating the relative shift of the bands to the solute concentration. In this case n_0 is the total number of electrons in zirconium. The electronic coefficient of the specific heat is linearly dependent on both the solute concentration and valence as in the other model and the slope of the $d\gamma/dx$ versus solute valence curve is again proportional to the derivative of the density of states with respect to the energy. The value of $dN(E)/dx$, when $n=n_0$, however, is now a more complicated function of the densities of states and their derivatives for the two bands. No internal inconsistencies now exist since the sign of the constant term and thus the direction of the relative movement of the s and d bands, are determined from the experimental data. Using similar arguments as before about the relative position of the s and d bands in pure zirconium, we again have a rapidly rising density of states with additions of the five solutes. The relative shift in energy of the bottom of the two bands turns out to be approximately 1 eV for a 10% solute concentration.

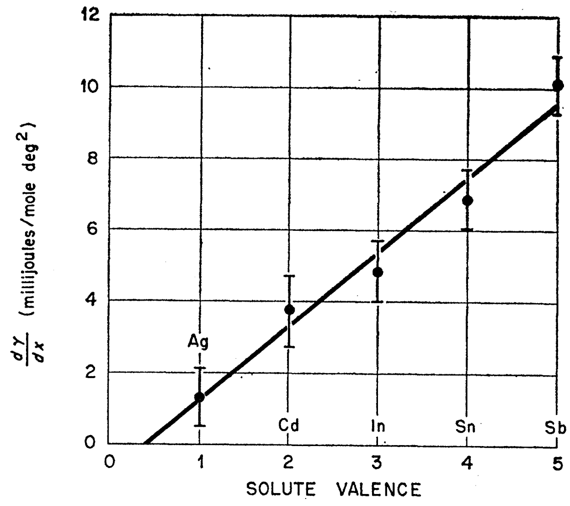

FIG. 5. The effect of silver, cadmium, indium, tin, and antimony on the electronic specific heat of zirconium.

Equation (3) represents the case where no band shifts occur and Eq. (4) represents the case where a fairly large band shift occurs proportional to the solute concentration without assuming solute holes in the $4d$ band of zirconium. The intermediate situation is also possible where another term is added to Eq. (3) which corresponds to the final term of Eq. (4). The band shift constant A in this case would be considerably smaller than that required to fit the data where Eq. (4) pertains. In this intermediate case, the argument is made that the unusually large increase in resistivity of alloys of B-subgroup solutes in zirconium[27] is due to the solute holes in the $4d$ band and that these holes perturb the d-wave functions strongly with an upward shift in their energies. Thus, the alloying of a transition metal with a B-subgroup metal will have such shifts, while alloying two transition metals with each other would not, and a simple rigid band model might be more appropriate in the latter case. This interpretation assumes that the volume and axial ratio changes that take place during alloying have a small effect on the band structure. The x-ray emission spectra of zirconium are in agreement with these models. The L spectra measurements[28] indicate a narrow d band and the M spectra[29] implies that some of the $4d$ electrons are in a hybridized band with P symmetry. The magnetic field dependence of the Hall coefficient and the magnetoresistance of zirconium as

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[27] J. O. Betterton, Jr., and D. S. Easton, in *Proceedings of the Seventh International Conference on Low-Temperature Physics*, edited by G. M. Graham and A. C. Hollis Hallet (University of Toronto Press, Toronto, 1961), p. 270.

[28] C. H. Shaw and E. L. Jossem, Final Report RF Project 471 (1959), Ohio State University Research Foundation (unpublished).

[29] J. E. Holliday, Bull. Am. Phys. Soc. **7**, 416 (1962).

measured by Berlincourt[30] also indicate an overlapped band structure. A simple two-band structure, however, is not adequate to explain the experimental results for these transport properties and the anisotropy of the Fermi surface should be evaluated in further experimental and theoretical study of the band shifts.

VI. THE DEBYE TEMPERATURES

The lattice specific heat is increased by each of these solutes as indicated by the decreased Debye temperatures shown in Figs. 3. As might be expected, the solute and solvent atoms do not act as independent oscillators in these alloys and the lattice specific heats do not obey the Kopp-Neumann[31] rule at low temperatures. At these temperatures only the long-wavelength phonons are thermally excited so that the lattice specific heat and, hence, the Debye temperature is determined by elastic waves whose wavelength is several atomic distances. The alloy then can be considered to approximate a solid whose vibrational spectra is similar to that of pure zirconium. The changes in the Debye temperature upon alloying arise from changes in the elastic constants and the average atomic mass. Figure 6 shows that the rate of change of the Debye temperature with concentration is not simply related to the solute valence so that factors other than the electronic energy as reflected by the density of states are important in determining the elastic constants.

If we consider the interatomic forces to be central forces, then, as a first approximation the Debye temperature is proportional to the square root of an average interatomic force constant divided by an average atomic mass. The Debye temperature then can be written as

$$\theta \sim (F/M)^{1/2}, \tag{5}$$

and if the average force constant is assumed to be a function of the solute concentration x, then

$$\frac{d\theta}{dx}=\frac{\theta_0}{2}\left[\frac{1}{F}\frac{dF}{dx}-\frac{M_s-91.22}{91.22}\right], \tag{6}$$

where M_s is the atomic weight of the solute.

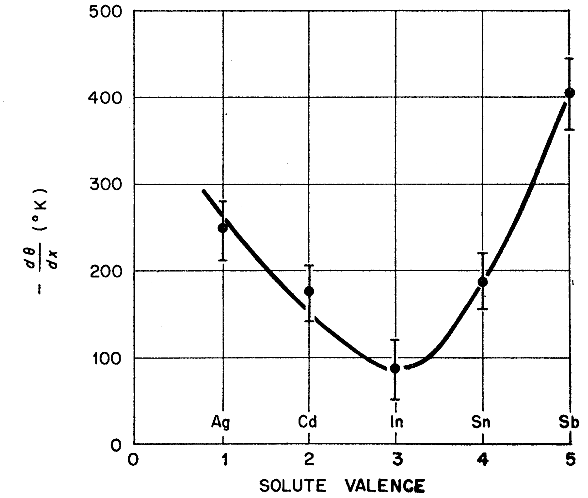

FIG. 6. The effect of silver, cadmium, indium, tin, and antimony on the Debye temperature of zirconium.

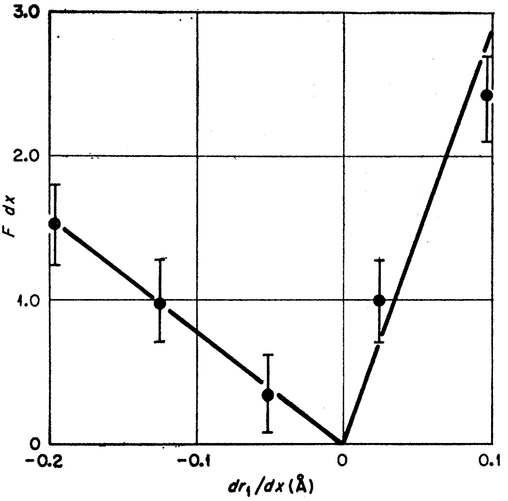

FIG. 7. The rate of change of the average interatomic force constants of zirconium alloys.

Intuitively, the force constants are expected to be dependent upon the lattice distortion which occurs during alloying, and it is of interest to compare the force constants obtained from the Debye temperatures with interatomic spacings for these alloys. Betterton and Easton[32] have found that the axial ratios for these alloy systems are dependent upon solute valence and concentration, while the a parameter is a function of the solute concentration only. Thus, the distance between the atoms at 000 and 100 is a function of the alloy concentration only while the distance r_1 between the atoms at 000 and $\frac{1}{3}, \frac{2}{3}, \frac{1}{2}$ is a function of solute valence as well as the solute concentration. The apparent correlation between the rate of change of the Debye temperature and the absolute value of the rate of change of the interatomic spacing with solute concentration as shown in Fig. 7 suggests that the mechanism which is responsible for the changes in the interatomic spacing also changes the interatomic force constants. The asymmetry of the curve shows then that increasing the distance between atoms reduces the average force constant more than decreasing the distance. In terms of the force constant model, the correlation between the r_1 distances and the force constants would suggest that any deviation of r_1 from the value it has in α-Zr results in large second deri-

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[30] T. G. Berlincourt, Phys. Rev. **114**, 669 (1959).

[31] F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), p. 38.

[32] J. O. Betterton, Jr., and D. S. Easton, J. Metals **13**, 86 (1961).

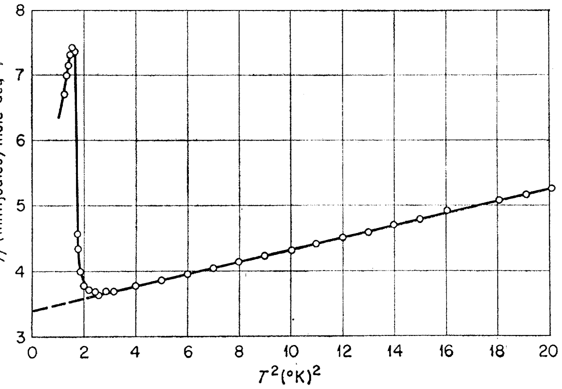

FIG. 8. The specific heat of zirconium-9.06 at.% tin.

vatives of the electronic energy density with respect to thermal motion of the atoms.

VII. SUPERCONDUCTING TRANSITIONS OF Zr-Sn ALLOYS

Pines[33] has suggested that the mean interaction parameter V, in the BCS[11] relation

$$kT_c = 1.4\langle\hbar\omega\rangle_{\text{av}} \exp(-1/NV), \tag{7}$$

should be relatively constant for the transition metals. This has been shown to be true experimentally for U-Mo,[34] U-Nb,[34] and Ti-Mo [10] alloys where both the solute and solvent are transition metals with unfilled d shells. The interaction parameter can be computed for the zirconium-tin alloys using Eq. (7) and assuming that $\langle\hbar\omega\rangle_{\text{av}} = \frac{3}{4}\theta_D$. The results shown in Table IV indicate that the interaction parameter of zirconium is not appreciably changed by additions of tin, so that V does not change appreciably over this range of alloy compositions although γ does change by approximately 25%. The discontinuity in the specific heat at the transition temperature is not spread out in these alloys indicating good alloy homogeneity and relative freedom from strains as shown in Fig. 8.

TABLE IV. Superconducting transition temperatures and the BCS-interaction potential for zirconium-tin alloys.

Alloy	T_c (°K)	θ_D (°K)	γ (mJ/mole deg²)	(N_0V/γ) (mole deg²/mJ)
α-Zr	0.55	291.7	2.807	58.3
Zr-7.6% Sn	~1.14	277.5	3.329	~56.3
Zr-9.1% Sn	1.29	275.3	3.375	56.9

VIII. CONCLUSIONS

The electronic specific heat of hexagonal zirconium is increased by the alloying elements silver, cadmium, indium, tin, and antimony. The coefficient of the electronic specific heat is proportional to the solute concentration for each alloy system and the rate of increase is proportional to the usual chemical valence of the solute. The present experiments show that a modified rigid band model is applicable for alloys of silver, cadmium, indium, tin, and antimony in hexagonal zirconium. It is necessary to assume, however, that the electrons in the conduction band are not all equivalent, those filling the band identified with the atomic s levels forming the conduction band of the alloy. The wave functions of the electrons in the band associated with the atomic d states of the solvent are considered not to penetrate into the solute cells and to form a separate band with electron density holes near the solute atoms. This follows for solute ions of the above type with $4d^{10}$ configurations in their outer shells, since only states other than $4d$ states can be orthogonal to electrons of the ion near such solute nuclei. On the other hand, if the $4d$ wave functions do penetrate the solute cells the d band, as a whole, is shifted in energy by the perturbing potential of the solute atoms. The results indicate that all of these solutes increase the density of states of zirconium, and that in terms of a two-band model of alloying, a zone overlap possibly has occurred in the zirconium d band, and that the number of electrons in the new band is small. All of these solutes also increase the lattice specific heat, as shown by a decrease in the Debye temperature. Although the Debye temperature is a linear function of the solute concentration for each of the alloy systems, it is not simply related to the solute valence.

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[33] D. Pines, Phys. Rev. **109**, 208 (1958).

[34] B. L. Goodman, J. Hillairet, J. J. Veyssié, and L. Weil, in *Proceedings of the Seventh International Conference on Low-Temperature Physics*, edited by G. M. Graham and A. C. Hollis Hallet (University of Toronto Press, Toronto, 1961), p. 350.