

Low-Temperature Specific Heats of Zr-Ti, Zr-Hf, and Zr-Sc Alloys*

J. O. BETTERTON, JR., AND J. O. SCARBROUGH

Metals and Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830

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The specific heats of hexagonal Zr-Ti, Zr-Hf, and Zr-Sc alloys were measured at 1.1 to 4.2°K. Maxima in both the electronic specific-heat coefficient γ and the superconducting transition temperature T_c were observed at 60 at.% Ti in the Zr-Ti system. No superconductivity was found in the Zr-Sc system, although γ rose to high values for pure scandium, and a minimum in γ occurred near 10 at.% Sc. In the Zr-Hf system γ was nearly linear between pure element values. The Debye temperatures Θ_D , after correction for atomic mass and volume, deviate negatively near 60 at.% Ti in Ti-Zr, positively near hafnium in Zr-Hf, and in an S-type manner in Zr-Sc. The effects of scandium in depressing γ in the zirconium-rich region are in qualitative agreement with dependence on electron/atom ratio indicated by earlier *B*-subgroup solute effects in zirconium-rich alloys. The γ for Zr-Sc alloys, after a correction for phonon enhancement and with the assumption of a rigid band in the alloys, correlates fairly well with the electronic density of states for pure zirconium, calculated by Loucks. The rigid-band approximation, on the other hand, cannot explain the maxima in γ and T_c in Zr-Ti alloys, which involve no change of electron/atom ratio. Rather the maximum may arise from differences in the relative energies of the third and fourth bands in titanium and zirconium, with a crossing of these bands in the alloys. The γ and T_c are related to both the density of states and the electron-electron interactions, and although a clear separation of the two factors is not possible, a reasonable interpretation can be made, assuming that the electron-phonon interaction is nearly constant.

INTRODUCTION

THE effects of transition elements as alloying elements in zirconium were investigated because an earlier study¹ with *B*-subgroup solutes showed that zirconium acted as if it were zero valent in these alloys, and the electronic specific-heat coefficient γ increased linearly in proportion to the numbers of *s*, *p* electrons added by the solutes. It was expected that the transition element solutes with incomplete *d* shells would have a different alloying behavior from the *B*-subgroup elements, where the *d* shells are complete. The addition of elements Ti and Hf was intended to show the effect of large changes in atomic mass and of atomic potential by alloying along the group IV A column of the Periodic Table without changes in the electron to atom ratio e/a . The Zr-Ti alloys were of particular interest because a maximum in the superconductivity transition temperature T_c at 50 at.% Ti had been reported by Hulm and Blaugher.²

The addition of scandium to zirconium illustrated the alloying of zirconium with a lower valent solute, from group III A and up diagonally in the Periodic Table. Zirconium-scandium alloys were important because only the Zr-Sc system permitted continuous hexagonal solid solutions in zirconium with a lower e/a , and because superconductivity had not been found near scandium in spite of the large γ of this element.

Effects of the electron-phonon reactions, such as are implied by the existence of superconductivity in these metals, have been discussed by Clogston,³⁻⁵ Krebs,⁶

TABLE I. Impurities (ppm) in metals used to make the alloys. All analyses are in weight ppm. Italicized values are more accurate ones, obtained by neutron activation, except for the very low levels in Zr a, which are from mass spectrometry. Carbon analyses are by the combustion method; oxygen and nitrogen, by vacuum fusion. Other nonitalicized values are from optical spectroscopy. Elements analyzing less than 10 ppm were deleted except those indicated above. Vickers Diamond Pyramid Hardness is with 10-kg load. Electrical resistivities were measured at 4.2°K.

Sample	Analysis
Ti ^b	C190, <i>Fe200</i> , Hf300, <i>Mn2.4</i> , O100, <i>Zr400</i> , hardness 63, resistivity 0.78 $\mu\Omega$ cm
Ti ^c	Al150, Cr250, Cu20, Fe150, Hf80, Mg25, Mn200, Mo10, N20, Ni25, O150, Pb35, hardness 72, resistivity 2.16 $\mu\Omega$ cm.
Zr ^a	C80, Cr7, <i>Fe70</i> , <i>Hf570</i> , <i>Mo25</i> , <i>Ni14</i> , O10, <i>Si15</i> , hardness 75, resistivity 0.53 $\mu\Omega$ cm
Zr ^d	C15, <i>Cr3</i> , <i>Fe45</i> , <i>Hf100</i> , <i>Mn0.1</i> , O20, hardness 63, resistivity 0.20 $\mu\Omega$ cm
Zr ^e	C < 5, <i>Cr0.01-0.20</i> , <i>Fe0.04-2.0</i> , <i>Hf45</i> , <i>Mn0.02</i> , O4-10, hardness 45, resistivity 0.07 $\mu\Omega$ cm
Hf ^f	C130, <i>Ca10</i> , Cr6, <i>Fe200</i> , <i>Mo43</i> , <i>Ni7</i> , O18, <i>Si65</i> , <i>Zr500</i> , hardness 135, resistivity 1.7 $\mu\Omega$ cm
Hf ^g	Al30, Cr6, Fe230, N50, Ni50, O50-500, Si20, Zr28000, hardness 147, resistivity 2.9 $\mu\Omega$ cm
Hf ^h	Al10, Fe10, Si20, Zr46000, hardness 170, resistivity 2.66 $\mu\Omega$ cm
Sc ⁱ	Al < 30, Cu30, <i>Fe118</i> , H30, Ni15, O450, rare earths < 100, hardness 55, resistivity 2.97 $\mu\Omega$ cm

^a Westinghouse Atomic Power Division, lot 1684 iodide zirconium.

^b New Jersey Zinc Company, lot IT 160 iodide titanium.

^c New Jersey Zinc Company, lot IT 424 iodide titanium.

^d Westinghouse Atomic Power Division, lot 1436 iodide zirconium.

^e ORNL zone refined zirconium.

^f ORNL-Battelle Memorial Institute, lot 8496 iodide hafnium.

^g Westinghouse Atomic Power Division, R 189 A iodide hafnium.

^h Westinghouse Atomic Power Division, R 838 iodide hafnium.

ⁱ Johnson, Matthey, and Son, Ltd., vacuum distilled scandium after Li reduction of fluoride.

Garland,⁷ and Bucher.⁸⁻¹⁰ In our earlier study¹ we

⁷ J. W. Garland, Jr., Phys. Rev. Letters **11**, 111 (1963); **11**, 114 (1963).

⁸ E. Bucher, F. Heiniger, and J. Muller, Physik Kondensierten Materie **2**, 210 (1964).

⁹ E. Bucher, F. Heiniger, J. Muller, and J. L. Olsen, in *Proceedings of the Ninth International Conference on Low-Temperature Physics at Columbus, Ohio*, edited by J. G. Daunt, D. O. Edwards, F. J. Milford, and M. Yaqub (Plenum Press, Inc., New York, 1965), pp. 616 and 1059.

¹⁰ E. Bucher, J. Muller, J. L. Olsen, and C. Palmy, Phys. Letters **15**, 303 (1965).

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¹ G. D. Kneip, Jr., J. O. Betterton, Jr., and J. O. Scarbrough, Phys. Rev. **131**, 2425 (1963).

² J. K. Hulm and R. D. Blaugher, Phys. Rev. **123**, 1569 (1961).

³ A. M. Clogston and V. Jaccarino, Phys. Rev. **121**, 1357 (1961).

⁴ A. M. Clogston, V. Jaccarino, and Y. Yafet, Phys. Rev. **134**, A650 (1964).

⁵ A. M. Clogston, Phys. Rev. **136**, A8 (1964).

⁶ K. Krebs, Phys. Letters **6**, 31 (1963).

TABLE II. Materials and heat treatments used in preparation of the alloys.

Alloy	Pure materials				High-temperature anneal	Low-temperature anneal	Cooling method ^a	Structure	Vickers hardness 10-kg load	
	Type	Ti	Zr	Hf						Sc
Ti, 9.6±0.8 at.% Zr	2	c	e	1300°C, 8 h	750°C, 10 days	w	α	142
Ti, 30.6±0.5 at.% Zr	2	c	e	1300°C, 12 h	620°C, 12 days	w	α	234
Ti, 30.6±0.5 at.% Zr	2	c	e		725°C, 12 days	w	α'	273
Ti, 39.5±0.08 at.% Zr	1	d	f	1200°C, 3 h	520°C, 35 days	a	α'	254
Ti, 39.5±0.08 at.% Zr	1	d	f	1200°C, 3 h		r	α'	259
Ti, 49.4±0.5 at.% Zr	1	d	f	1200°C, 1 day	520°C, 16 days	a	α	251
Ti, 49.4±0.5 at.% Zr	1	d	f	1200°C, 1 day		w	α'	260
Ti, 50.2±0.3 at.% Zr	2	c	e	1300°C, 8 h	500°C, 70 days	a	α	244
Ti, 59.5±0.09 at.% Zr	1	d	f	1300°C, 3 h; 520°C, 35 days		a	α	232
Ti, 59.5±0.09 at.% Zr	1	d	f	1300°C, 3 h		r	α'	249
Ti, 69.1±0.8 at.% Zr	2	c	e	1300°C, 8 h	500°C, 35 days	a	α	194
Ti, 89.6±0.1 at.% Zr	2	c	e	1300°C, 8 h	700°C, 25 days	a	α	100
Hf	1	h	...	1000°C, 3 days		a	α	151
Hf, 6.5±0.2 at.% Zr	2	...	e	i	...	1200°C, 8 h		r	α	148
Hf, 8.5±1.4 at.% Zr ^b	3	j	...	1200°C, 8 h		r	α	128
Hf, 27.8±0.7 at.% Zr	2	...	e	i	...	1200°C, 8 h		r	α	146
Hf, 48.0±0.4 at.% Zr	2	...	e	i	...	1000°C, 9 days		a	α	142
Hf, 69.5 at.% Zr	2	...	e	i	...	1200°C, 8 h; 900°C, 12 days		a	α	102
Hf, 90.5 at.% Zr	2	...	e	i	...	1200°C, 8 h; 850°C, 10 days		a	α	96
Sc	2	k	950°C, ¼ h		r	α	36-73
Sc, 11 ±1 at.% Zr	2	...	f	...	k	1000°C, 3 days		a	α	43-90
Sc, 28.2±0.2 at.% Zr	2	...	f	...	k	950°C, 5 days		a	α	79
Sc, 48.7±1.2 at.% Zr	2	...	f	...	k	900°C, 3 days		a	α	116
Sc, 69.1±0.2 at.% Zr	1	...	g	...	k	950°C, 1 day		r	α	109
Sc, 79.8±0.2 at.% Zr	2	...	f	...	k	1000°C, 3 days		a	α	91
Sc, 82.1±3 at.% Zr	1	...	g	...	k	950°C, 3 days		r	α	107
Sc, 88.6±0.8 at.% Zr	2	...	f	...	k	950°C, 6 h		r	α+α'	96

^a Cooling methods were w: quenched in ice and water; r: radiation cooling in vacuum; and a: rapidly cooled in argon inside silica capsule under ice and water.

^b Crystal bar, not arc cast.

^c New Jersey Zinc Company, lot IT160 iodide titanium.

^d New Jersey Zinc Company, lot IT424 iodide titanium.

^e Westinghouse Atomic Power Division, lot 1684 iodide zirconium.

^f Westinghouse Atomic Power Division, lot 1436 iodide zirconium.

^g ORNL zone refined zirconium.

^h ORNL-Battelle Memorial Institute, lot 8496 iodide hafnium.

ⁱ Westinghouse Atomic Power Division, R189A iodide hafnium.

^j Westinghouse Atomic Power Division, R838 iodide hafnium.

^k Johnson, Matthey, and Son, Ltd., vacuum distilled scandium after Li reduction of fluoride.

assumed that electron-electron effects were independent of alloying but in view of the later work above, the γ of the Zr-Ti, Zr-Hf, and Zr-Sc alloys may depend upon changes in electron-electron interactions as well as upon band structure and alloying effects. Although the main object of this paper is to present experimental specific heats on the alloys, some preliminary discussion will be given of two extreme cases—first, γ and T_c change because of changes in the density of states, and secondly, all the major changes reflect changes in the electron-phonon interaction.

Since the start of this research,¹¹ other work on the low-temperature specific heats and superconductivity of Zr-Ti and Zr-Sc have been published. Hake and Cape¹² and Bucher, Heiniger, Muheim, and Muller^{13,14}

have also shown that the maximum¹⁵ in T_c at Ti, 50 at.% Zr is associated with a similar maximum in γ . Hake and Cape showed that small amounts of manganese impurity depress T_c in Ti, 50 at.% Zr, and Bucher and his co-workers noted effects of both quenching stresses and impurities upon T_c in the same alloys. Jensen and Maita¹⁶ have recently determined the low-temperature specific heats and T_c of Zr-Sc alloys, and showed a sharp drop in T_c with dilute scandium additions to zirconium. They attributed this effect to an abrupt increase in the effective Coulomb interaction, as one decreased the number of d electrons.

The present work will present the low-temperature specific heats of Zr-Ti and Zr-Sc in greater detail and

¹¹ J. O. Betterton and J. O. Scarbrough, *J. Metals* **15**, 686 (1963).

¹² R. R. Hake and J. A. Cape, *Phys. Rev.* **135**, A1151 (1964); also *Bull. Am. Phys. Soc.* **8**, 419 (1963).

¹³ E. Bucher, F. Heiniger, J. Muheim, and J. Muller, *Rev. Mod. Phys.* **36**, 146 (1964).

¹⁴ E. Bucher, F. Heiniger, and J. Muller, in *Proceedings of the*

Ninth International Conference on Low-Temperature Physics at Columbus, Ohio, edited by J. G. Daunt, D. O. Edwards, F. J. Milford, and M. Yagub (Plenum Press, Inc., New York, 1965), p. 482.

¹⁵ The alloys are identified by solute component, followed by atomic percentage of zirconium.

¹⁶ M. A. Jensen and J. P. Maita, *Phys. Rev.* **149**, 409 (1966).

TABLE III. Analysis of minor impurities in Zr-Ti and Zr-Sc alloys in parts per million by weight.

Element	Ti, 50% Zr Type 1	Ti, 50% Zr Type 2	Sc, 70% Zr Type 2	Sc, 28% Zr Type 2
Copper ^a	7	10	10	20
Hydrogen ^b	7	3	8	21
Hafnium ^a	81	282	79	45
Iron ^a	47	78	72	97
Manganese ^a	67	6.3	0.1	0.4
Nickel ^a	14	21	9	...
Nitrogen ^b	<5	7	7	11
Oxygen ^b	100	150	130	360
Silicon ^a	8	26	3	...
Tungsten ^a	1.8	10	19	12

^a Neutron activation.
^b Vacuum fusion.

accuracy, and with samples of higher purity. New results will be presented for Zr-Hf, and more accurate coefficients γ and Θ_D will be given for pure scandium.

EXPERIMENTAL METHODS

The alloys were prepared from pure metals by multiple casting on a copper hearth in a pure argon atmosphere. The impurity content of the pure metals are given in Table I. Two impurity sensitive properties, Vickers Hardness and low-temperature resistivity, are indicated with each pure metal in the same table.

The identification letters with the pure metals in Table I correspond to sources of the metals and to their employment in the alloys, as described in Table II.

TABLE IV. Coefficient of the electronic specific heat, Debye temperature, and superconducting transition temperatures.

Alloy	Type	Structure	γ mJ mole ⁻¹ deg ⁻²	Θ_D (°K)	T_c (°K)	$S-J$ (eV)
Ti, 9.62 at.% Zr	2	α	3.648±0.012	396.4± 3.8	<1.12	...
Ti, 30.6 at.% Zr	2	α	4.144±0.018	347.3± 3.1	1.15±0.02	0.199
Ti, 30.6 at.% Zr	2	α'	4.159±0.027	342.2± 4.3	1.22±0.1	0.201
Ti, 39.5 at.% Zr	1	α	4.231±0.018	330.8± 2.5	1.15±0.1	0.197
Ti, 39.5 at.% Zr	1	α'	4.243±0.008	320.9± 1.0	1.15±0.1	0.197
Ti, 49.4 at.% Zr	1	α	4.190±0.025	324.4± 3.7	1.08±0.15	0.197
Ti, 49.4 at.% Zr	1	α'	4.222±0.011	314.1± 1.4	1.22±0.05	0.201
Ti, 50.2 at.% Zr	2	α	4.124±0.036	318.1± 4.6	1.30±0.02	0.208
Ti, 50.2 at.% Zr	2	α	4.117±0.018	317.6± 2.1	1.30±0.02	0.208
Ti, 59.5 at.% Zr	1	α	3.955±0.035	305.3± 3.5	1.08±0.1	0.211
Ti, 59.5 at.% Zr	1	α'	4.013±0.026	307.5± 2.8	1.11±0.1	0.209
Ti, 69.1 at.% Zr	2	α	3.666±0.029	299.1± 2.7	1.03±0.15	0.227
Ti, 89.6 at.% Zr	2	α	3.097±0.019	301.2± 1.9	<1.27	...
Hf ^a	1	α	2.146±0.022	252.2± 1.0	<1.62	...
Hf, 6.5 at.% Zr	2	α	2.224±0.027	251.0± 1.2	<1.36	...
Hf, 8.5 at.% Zr	3	α	2.300±0.018	257.5± 0.9	<1.64	...
Hf, 27.8 at.% Zr	2	α	2.367±0.025	256.8± 1.3	<1.41	...
Hf, 48.0 at.% Zr	2	α	2.546±0.022	264.6± 1.3	<1.25	...
Hf, 48.0 at.% Zr	2	α	2.545±0.016	263.9± 0.9	<1.31	...
Hf, 69.5 at.% Zr	2	α	2.636±0.021	271.8± 1.3	<1.31	...
Hf, 90.5 at.% Zr	2	α	2.757±0.009	287.2± 0.7	<1.43	...
Sc	2	α	10.717±0.033	425.6±13.7	<1.14	...
Sc, 11 at.% Zr	2	α	9.317±0.025	360.0± 4.2	<1.19	...
Sc, 28 at.% Zr	2	α	6.899±0.040	356.5±10.2	<1.20	...
Sc, 49 at.% Zr	2	α	4.870±0.031	344.1± 5.6	<1.28	...
Sc, 69 at.% Zr	1	α	3.025±0.014	333.4± 2.3	<1.30	...
Sc, 80 at.% Zr	2	α	2.651±0.016	333.1± 2.4	<1.16	...
Sc, 82 at.% Zr	1	α	2.607±0.019	329.7± 3.4	<1.32	...
Sc, 89 at.% Zr	2	α	2.512±0.016	310.6± 1.8	<1.15	...

^a Hafnium values, plotted in Fig. 4, were the average of the above experiment, and two earlier measurements (see Ref. 16) which gave γ 2.157 mJ mole⁻¹ deg⁻² and Θ_D 252.0°K, respectively. Earlier measurements (see Ref. 16) for titanium and zirconium were as follows: γ 3.3485 and 2.807 mJ mole⁻¹ deg⁻² and Θ_D 428.5 and 291.7°K, respectively.

TABLE V. Impurity effects in 50% Ti, 50 at.% Zr.

Material	Electrical resistivity at 4.2°K, $\mu\Omega$ cm	Superconducting transition temperature °K	Electronic specific-heat coefficients mJ mole ⁻¹ deg ⁻²	$S-J$ interaction eV atom
Alloy type 1	42.7	1.08	4.19	0.197
Alloy type 2	44.1	1.30	4.12	0.208
Alloy Hake and Cape ^a	51	1.60	4.21	0.214

^a R. R. Hake and J. A. Cape, Phys. Rev. **135**, A1151 (1964); Bull. Am. Phys. Soc. **8**, 419 (1963).

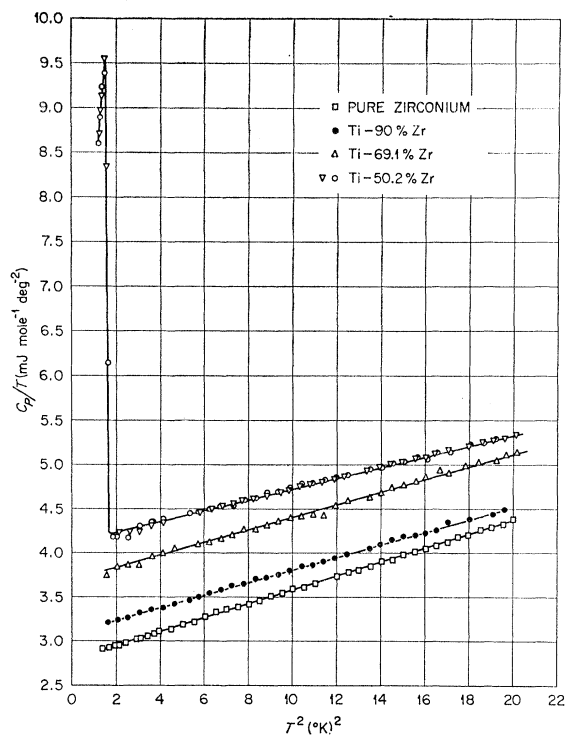


FIG. 1. The specific heats of Zr-Ti alloys.

Most heat treatments were carried out in silica capsules, baked out under vacuum at the annealing temperature, and then sealed off with an atmosphere of pure argon. Silica reaction was suppressed by foils of zirconium and molybdenum. Some anneals were done with specimens suspended in a vacuum with tungsten wire followed by a radiation cooling, as indicated by the letter r in Table II. Other details in the preparation of the specimens were similar to those in the earlier report.¹⁷

The phase diagrams of Zr-Ti, Zr-Hf,¹⁸ and Zr-Sc¹⁹ show continuous body-centered cubic solid solution at higher temperatures and continuous close-packed hexagonal solid solutions at lower temperatures. In the Zr-Ti system, specimens were homogenized a few hours in the cubic region and then reannealed for 10-70 days at a lower temperature in the hexagonal region (α specimens). The values of T_c in the present Zr-Ti alloys were lower than had been reported by Hulm and Blaugher² and for this reason some effects of transformation strains and of minor impurities in these alloys were studied. To investigate the effect of strains, several Zr-Ti specimens were annealed in the cubic β region and were then rapidly cooled in water, and

several alloys were annealed in the cubic region and were cooled by radiation cooling in vacuum. Both treatments result in a strained, hexagonal structure α' , similar to the equilibrium α phase, through diffusionless transformation in cooling. To investigate the effects of minor impurities, a second set of alloys was made from different lots of zirconium and titanium. In the Zr-Sc and Zr-Hf systems, the cubic region of the phase diagram occurs at quite high temperatures. In order to avoid risks of contamination at high temperatures, the Zr-Sc and some Zr-Hf alloys were given only a single anneal in the hexagonal region.

Minor impurities were analyzed in four typical alloys and the results are shown in Table III. As can be seen in the table, the sum of major components is of the order 99.95%. The composition of the major components of the Zr-Ti, Zr-Hf, and Zr-Sc alloys was determined by chemical analysis²⁰ of samples taken at the top, center, and bottom of the ingot. The analyzed composition and their inhomogeneity ranges are given for each alloy in Table II.

The low-temperature specific heats were measured using the same technique as that described in an earlier report.¹⁷ An adiabatic calorimeter, with a mechanical heat switch to avoid helium exchange gas errors, was employed over the temperature range 1.1 to 4.5°K. Addendum heat capacity was evaluated in a separate experiment, and a graphite resistance thermometer was calibrated against the vapor pressure of liquid helium (T_{88} scale) after each cooling to low temperatures.

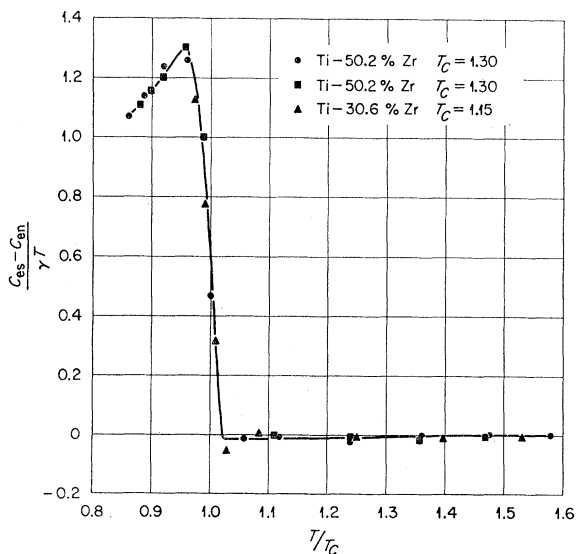


FIG. 2. Superconducting transition of Zr-Ti alloys in α -annealed condition.

¹⁷ G. D. Kneip, Jr., J. O. Betterton, Jr., and J. O. Scarbrough, *Phys. Rev.* **130**, 1687 (1963).

¹⁸ Rodney P. Elliott, *Constitution of Binary Alloys, First Supplement* (McGraw-Hill Book Co., Inc., New York, 1965).

¹⁹ B. J. Beaudry and A. H. Daane, *Trans. AIME* **227**, 865 (1963).

²⁰ Zirconium titanium and zirconium scandium were chemically analyzed by Johnson, Matthey, and Company, Ltd. The analyses of Zr-Hf alloys were averages of results from x-ray spectroscopy and neutron activation at Oak Ridge National Laboratory and at Johnson, Matthey, and Co., Ltd.

EXPERIMENTAL RESULTS

The specific heats of these alloys in the temperature range 1.1–4.5°K were typical of nonmagnetic normal state metals with the form $C = \gamma T + \beta(T/\Theta_D)^3$, where $\beta = (12/5)\pi^4 N_A k = 1.94373 \times 10^6$ mJ/mole deg and $\gamma = \frac{2}{3}\pi^2 k^2 N(E_f)$ mJ/mole $^{-1}$ deg $^{-2} = 4.7128 N(E_f)$ atom $^{-1}$ eV $^{-1}$. A deviation from this form of the specific heats was observed at lower temperatures when superconductivity occurred. Typical specific-heat data are shown in Fig. 1 for pure zirconium and three Zr-Ti alloys. After removal of points affected by the superconducting transition, the electronic specific-heat coefficient γ and the Debye temperature Θ_D were evaluated by least squares and are given in Table IV with 99% confidence limits.

Superconducting transition temperatures were observed above 1.1°K for the Zr-Ti alloys between 30–70 at.% Zr. The transitions are illustrated for the α alloys in Fig. 2 and for the α' alloys in Fig. 3. The physical defects of the α' alloys increased the width of the transition relative to that observed in the equilibrium α alloys. Because of the temperature limitations in the calorimeter some of the specific-heat curves did not extend through the transformation, and these temperatures were estimated approximately by selecting temperatures T_c so that the T/T_c curves had approximately the same shape as a T/T_c curve which had been measured earlier for another α' sample in the Zr-Sn system. This is illustrated in Fig. 3. The transition

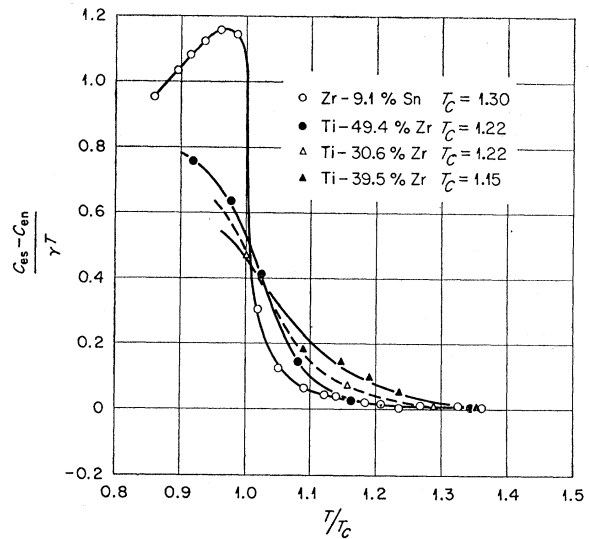


FIG. 3. Superconducting transition of some α' zirconium alloys.

temperatures with estimated uncertainties are given in Table IV.

In Fig. 4, γ , Θ_D , and T_c of the Zr-Ti and Zr-Hf alloys are plotted as a function of alloy composition. In the lower plot, the dashed line represents the superconducting transition temperatures determined by Hulm and Blaugher.² T_c from the present work are

FIG. 4. Variation of γ , θ_D , and T_c for Zr-Hf and Zr-Ti alloys. Present data are indicated by symbols \circ , Δ , \square ; open symbols— α -annealed, closed symbols— α' -quenched, triangles—alloys of purity type 1, circles—alloys of purity type 2, and squares—alloys of purity type 3. The symbol \pm indicates not superconducting down to this temperature. Measurements by Hulm and Blaugher (see Ref. 2) are indicated by symbols ∇ for T_c and \perp for not superconducting down to this temperature.

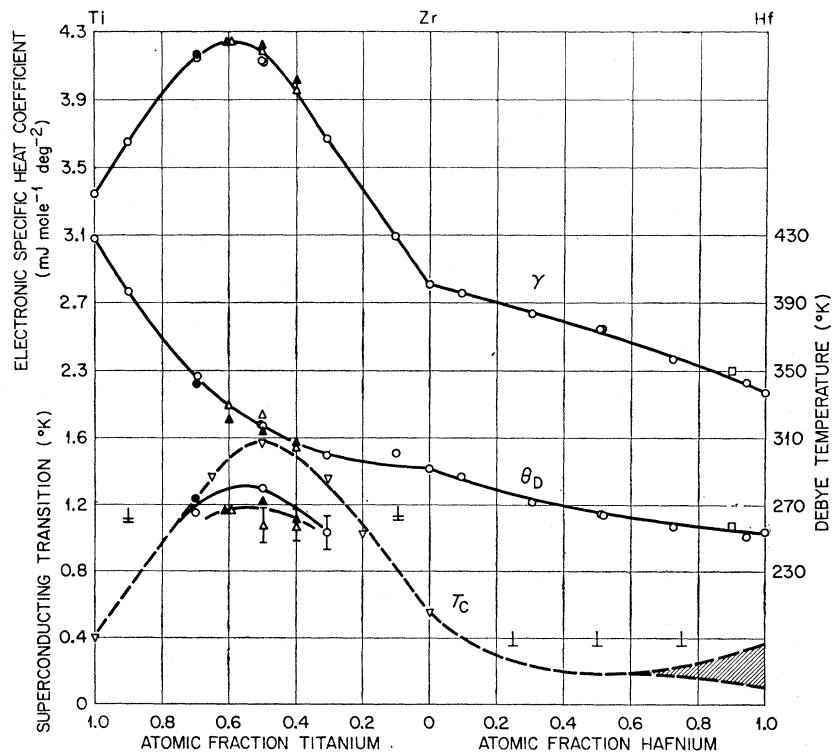


TABLE VI. Comparison of the low-temperature specific-heat coefficients of scandium with literature values.

Reference	γ mJ/mole deg ²	Θ_D °K
a	11.3 ±0.1	470 ±80
b	10.8 ±0.5	470 ±80
c	10.9 ±0.1	344 ±25
Present results	10.717±0.033	425.6±13.7

^a H. Montgomery and G. P. Pells, Proc. Phys. Soc. (London) **78**, 622 (1961).

^b H. Montgomery, private communication cited by K. A. Gschneider, Jr., in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1964), Vol. 16, p. 351.

^c P. Lynam, R. G. Scurlock, and E. M. Wray, *Proceedings of the Ninth International Conference on Low-Temperature Physics* (Plenum Press, Inc. New York, 1965), p. 905.

shown by the solid curves between 0.70 and 0.30 atomic mole fraction titanium. Superconducting transition temperatures are about 0.3°K lower than the results of Hulm and Blaughner for pure alloys of type II, and about 0.4°K lower for still purer alloys of type I. The transition temperatures are slightly higher in the α' samples with transition defects than in the equilibrium α samples. Larger effects were observed in Ti, 30.6% Zr and Ti, 49.4% Zr alloys which were water quenched through the transformation than in Ti, 39.5% Zr and Ti, 59.5% Zr alloys which were cooled through the transformation by radiation.

As shown by the upper curve in Fig. 4, γ has a pronounced maximum at 60 at.% Ti, correlating with the maximum in transition temperature. The values of γ reported by Hake and Cape¹² and Bucher¹³ for Ti-Zr alloys agree within 4% with this curve. In the Zr-Hf system, γ is nearly linear with composition, in contrast to the Zr-Ti case, but in agreement with the usual absence of any large changes in properties, alloying along a column in the Periodic Table. The Debye temperatures are shown by the middle curve, decreasing from titanium to zirconium, and from zirconium to hafnium.

Measurements of electrical resistivities provide support for correctness of the lower values of the superconducting transition temperature in Zr-Ti. Residual electrical resistivities at 4.2°K are compared in Table V for a type-1 alloy, a type-2 alloy, and the alloy studied by Hake and Cape, and show that resistivities are increasing in the same order as the transition temperatures. Hake and Cape¹² showed that an addition of manganese decreased T_c of Ti, 50% Zr rapidly (2°K/at.%) in the same manner as manganese decreases T_c in pure Ti (15°K/at.%).²¹ Even with effects of this size, our manganese impurity levels (Table III) are too small to account for an error of more than 0.1°K. We believe that significant other impurities and transformation strains have the opposite effect on T_c , and account for the abnormally high values in the earlier work.

²¹ R. F. Falge, Jr., Phys. Rev. Letters **11**, 248 (1963).

The γ and Θ_D of Zr-Sc alloys are listed in Table IV. In the continuous hexagonal solid solution of the Zr-Sc system, γ first decreases with scandium additions to zirconium to minimum at 10% Sc and then rises nearly linearly to a value for scandium which is 3.8 times the value for pure zirconium. In spite of this increase, no superconductivity was observed for the alloys tested to 1.15°K. Our results are in agreement with the work of Jensen and Maita¹⁶ who show rapid depression of the superconductivity transition temperature by addition of scandium to zirconium and essentially the same variation of electronic specific heat and Debye temperatures. Further note that in zirconium-rich Zr-Sc alloys the decrease in γ and the increase in Θ_D with scandium, which reduces the electron concentration, is opposite in sense to the changes in these same properties with electron concentration additions by the B-subgroup solutes in zirconium alloys.¹

The present values for γ and Θ_D of pure scandium are compared to other values which have been reported for this metal in Table VI. The new results are intermediate to previous work in Θ_D and slightly lower in γ . Lynam, Scurlock, and Wray²² have found a T^{-2} -type specific-heat component in the temperature range 0.3–3°K but were unable to determine whether it was due to a nuclear hyperfine interaction or incipient superconductivity or long-range magnetic ordering of gadolinium impurities. The purity of the present scandium sample, given in Table I, is greater than that of the earlier specimen. Down to 1.14°K, the lowest temperature investigated, we were unable to see any sign of a T^{-2} -type component in the specific heat.

ELECTRONIC SPECIFIC HEAT AND SUPER-CONDUCTIVITY TRANSITION TEMPERATURES

Clogston^{4,5} has discussed the paramagnetic spin susceptibility and the electronic specific-heat coefficients of transition metal superconductors at low temperatures in terms of the effective screened Coulomb interaction²³ J and the electron-phonon interaction S . The density of states of the interacting electron gas, $N_p(E_f)$, is given in terms of the noninteracting density of states, $N_0(E_f)$, by the following expression: $N_p(E_f) = N_0(E_f) \times [1 - N_0(E_f)S]^{-1}$. The S and J also appear in the Bardeen-Cooper-Schrieffer formula for the superconducting transition temperature,²⁴ with substitution of $0.88k\Theta_D$ for the average phonon energy:

$$T_c = \Theta_D \exp\{-1/N_p(E_f)(S - J)\}.$$

²² P. Lynam, R. G. Scurlock, and E. M. Wray, *Proceedings of the Ninth International Conference on Low-Temperature Physics* (Plenum Press, Inc., New York, 1965), p. 905.

²³ A repulsive exchange interaction for superconductivity, in addition to the screened Coulomb interaction, has been suggested by N. F. Berk and J. R. Schrieffer, Phys. Rev. Letters **17**, 433 (1966). Thus J , in their view, would be the sum of a screened Coulomb and a repulsive exchange interaction.

²⁴ J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1186 (1957).

The Sommerfeld formula $C_{e1} = \frac{2}{3}\pi^2 k^2 N_0(E_f) T = \gamma_0 T$, relating the electronic specific heat C_{e1} linearly with temperature and $N_0(E_f)$, is not valid in the presence of interactions, but Krebs⁶ has already obtained a rather similar correction of the electron-phonon interaction for the linear term in the low-temperature expansion of the specific heats. Krebs analyzed vanadium specific heats using a known lattice specific heat from neutron data and by means of a theory by Buckingham and Schafroth²⁵ for an electron gas, with electron-phonon interaction, but which is otherwise free. He obtained an enhanced linear term and a term proportional to the cube of the temperature also proportional to the electron-phonon interaction, and this latter term results in a correction to the effective Debye temperature.

Since Ti, Zr, and Hf are superconductors, $S-J$ and S for these metals are positive numbers of such size that these corrections should be appreciable. Bucher, Muller, Olsen, and Palmy¹⁰ measured the isotope effect in zirconium and found negligible mass dependence, i.e., $T_c \sim M^{-1/2}(1-\xi)$, with $\xi = 1 \pm 0.05$. By means of the formula $N_p(E_f)S = (1 + \sqrt{\xi}) / \ln(1.14\Theta_D/T_c)$ due to Garland⁷ and experimental values of γ and Θ_D , they obtained values for zirconium as follows: $N_p(E_f) = 0.60$ eV⁻¹ atom⁻¹, $J = 0.25$ eV atom, $S = 0.52$ eV atom, and $S - J = 0.27$ eV atom. According to Clogston's formula, the interacting density of states should be 31% greater than the noninteracting density of states.

The γ coefficient should also be enhanced by 31%, and a lower apparent Debye temperature would be observed, due to the addition of Krebs's electronic cubic term to the lattice specific heat. However, in Ti, Zr, and Hf the value of Θ_D obtained from elastic constants by Fisher and Renken²⁶ agreed excellently with the Θ_D from specific heats, and thus the T^3 term in the electronic specific heat was not indicated. Recently Keesom and Radebaugh²⁷ showed that in vanadium there is a significant discrepancy between Θ_D from elastic constants and from specific heats, which, however, is smaller than the correction estimated by Krebs for vanadium. This inconsistency with respect to the T^3 term could arise for errors in the Debye model, in relating elastic constants to specific heats, or it could arise from too literal use of the formulas from the isotope effect in superconductivity, or from inconsistencies in the theories of Krebs and Clogston. This is an open question that cannot be resolved without additional work, and casts some doubt on parts of the discussion below.

Nevertheless, the electronic specific heat of Zr-Ti, Zr-Hg, and Zr-Sc alloys and the superconducting transition temperature of Zr-Ti alloys will be discussed

²⁵ M. J. Buckingham and M. R. Schafroth, Proc. Phys. Soc. (London) **67**, 828 (1954).

²⁶ E. S. Fisher and C. J. Renken, Phys. Rev. **135**, A482 (1964).

²⁷ P. H. Keesom and Ray Radebaugh, Phys. Rev. Letters **13**, 685 (1964); Phys. Rev. **149**, 209 (1966).

TABLE VII. Values of S and J or $N_0(E_f)$ and J for extreme cases.

Alloy	$S - J^a$ eV atom	First case $N_0(E_f)$ constant		Second case S constant	
		S eV atom	J eV atom	$N_0(E_f)$ eV ⁻¹ atom ⁻¹	J eV atom
Ti	0.20	0.79	0.58	0.52	0.32
Ti, 31 at.% Zr	0.20	1.06	0.86	0.60	0.32
Ti, 39 at.% Zr	0.20	1.08	0.88	0.61	0.32
Ti, 49 at.% Zr	0.20	1.07	0.87	0.61	0.32
Ti, 60 at.% Zr	0.21	1.00	0.79	0.58	0.31
Ti, 69 at.% Zr	0.23	0.91	0.68	0.55	0.29
Zr	0.26	0.52	0.26	0.46	0.26
Sc, 99 at.% Zr	0.24	0.50	0.26	0.45	0.28
Sc, 95 at.% Zr	0.23	0.31	0.08	0.42	0.29
Sc, 89 at.% Zr	<0.20	0.32	>0.12	0.42	>0.32
Sc, 80 at.% Zr	<0.17	0.42	>0.24	0.44	>0.34
Sc, 69 at.% Zr	<0.17	0.64	>0.46	0.48	>0.35
Sc, 49 at.% Zr	<0.10	1.23	>1.1	0.67	>0.42
Sc, 28 at.% Zr	<0.07	1.51	>1.4	0.83	>0.45
Sc, 11 at.% Zr	<0.05	1.69	>1.6	0.97	>0.47
Sc	<0.05	1.75	>1.7	1.04	>0.47
Hf, 70 at.% Zr	<0.27	0.41	>0.14	0.43	>0.25
Hf, 48 at.% Zr	<0.28	0.34	>0.06	0.42	>0.24
Hf, 28 at.% Zr	<0.30	0.20	>-0.10	0.40	>0.22
Hf, 9 at.% Zr	<0.31	0.14	>-0.17	0.39	>0.21
Hf	0.28	0.01	-0.28	0.37	0.25

^a The value of $S - J$ are derived from γ , Θ_D , and T_c given in Table IV, except as follows. The transition temperatures Zr, 0.49°; Ti, 0.42°; Hf, 0.09°; and Sc, <0.032°K are from Bucher *et al.* (see Ref. 10), Flage⁸ (see Ref. 21), and Jensen and Maita (see Ref. 16). Interpolated transition temperatures, or upper limits, for Zr-Sc and Zr-Hf alloys are from Jensen and Maita (see Ref. 16) and Hulm and Blaughner (see Ref. 2). γ , Θ_D , and T_c for Sc, 95% Zr is taken from Jensen and Maita (see Ref. 16), while T_c for Sc 99% Zr is taken from Jensen and Maita with γ and Θ_D interpolated from present results.

as dependent upon $N_0(E_f)$, S , and J as in the formulas, and we will consider two extreme cases. In the first case, assume that $N_0(E_f)$ remains constant in the alloys, and assign the changes in γ to variations in the electron-phonon interaction S . For the second case assume that S is constant in the alloys so that variations in γ would be attributed to changes in $N_0(E_f)$. Since zirconium is involved in all of the alloys, either the $N_0(E_f)$ value or the S value of pure zirconium was taken as the arbitrary constant in these respective cases. The Clogston formula was then used in the first case to evaluate values of S from experimental values of γ . The same formula was used in the second case to evaluate values of $N_0(E_f)$ from γ . The Bardeen, Cooper, and Schriffer formula allows the interaction $S - J$ to be evaluated from experimental values of γ , Θ_D , and T_c . In the first case, combining S from γ with $S - J$ gives values of J , and in the second case, S has been assumed so that $S - J$ gives J . The results for both cases are tabulated in Table VII for the Zr-Ti, Zr-Sc, and Zr-Hf alloys. Our specific-heat measurements did not extend below 1.15°K, and the upper limits for T_c , as determined by Jensen and Maita¹⁶ for Zr-Sc alloys and by Hulm and Blaughner² for Zr-Hf alloys were used in preparing Table VII.

The values of $S - J$ for the alloys are plotted in

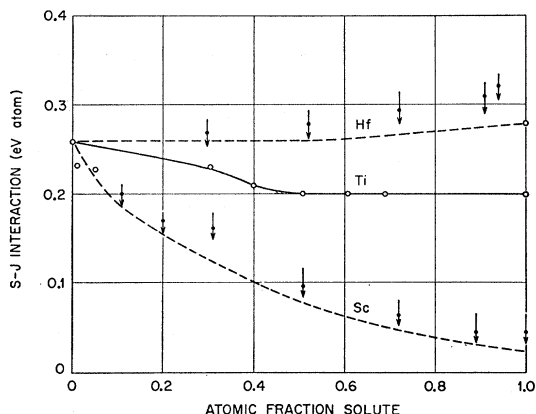


FIG. 5. Effect of alloy composition on the interaction $S-J$ in Zr-Ti, Zr-Hf, and Zr-Sc alloys. The symbols \downarrow represent upper limits for the interaction assuming superconductivity would be observed in these alloys at some temperature below that tested.

Fig. 5 against atomic fraction solute. Unfortunately, only the upper limit of the interaction $S-J$ is available for most of the Zr-Hf and Zr-Sc alloys. We can see, nevertheless, that $S-J$ does not change greatly in the Zr-Ti and Zr-Hf alloys, but rapidly decreases with the addition of scandium to zirconium.

The values of S and J for the two extreme cases are plotted in Fig. 6. The first case, where $N_0(E_f)$ remains

unchanged, shows that large variations of both S and J are required in order to account for the observed γ and T_c . Further because $S-J$ is smaller and more slowly varying, the curves for S and J are nearly parallel, which seems to be an unreasonable result. At pure hafnium and in hafnium-rich Hf-Zr alloys, the effective screened Coulomb interaction has become negative, or attractive in the present sense, and the electron-phonon interaction has nearly vanished. In pure scandium both the S and J values are unreasonably large. Finally a comparison of the $S-J$ curve of Zr-Ti alloys in Fig. 5 to the γ curve for the same alloys in Fig. 4 shows that $S-J$ remains unchanged in the composition range from pure titanium to 50 at.% Zr, while the γ curve rises to a maximum at 40 at.% Zr. Thus the first case does not seem to be physically realistic and any hope that phonon enhancement would provide a convincing interpretation of the γ and T_c maxima in the Zr-Ti alloys is not evident.

The second extreme case with S constant during alloying is illustrated by the dashed curves on Fig. 6. This case results in smaller and more reasonable variations in J . It follows Jensen and Maita,¹⁶ who earlier assumed the constancy of the electron-phonon interaction for a range of transition metals and alloys in their interpretation of T_c , Θ_D , and γ in the Zr-Sc system. Jensen and Maita related the drop in T_c , as scandium

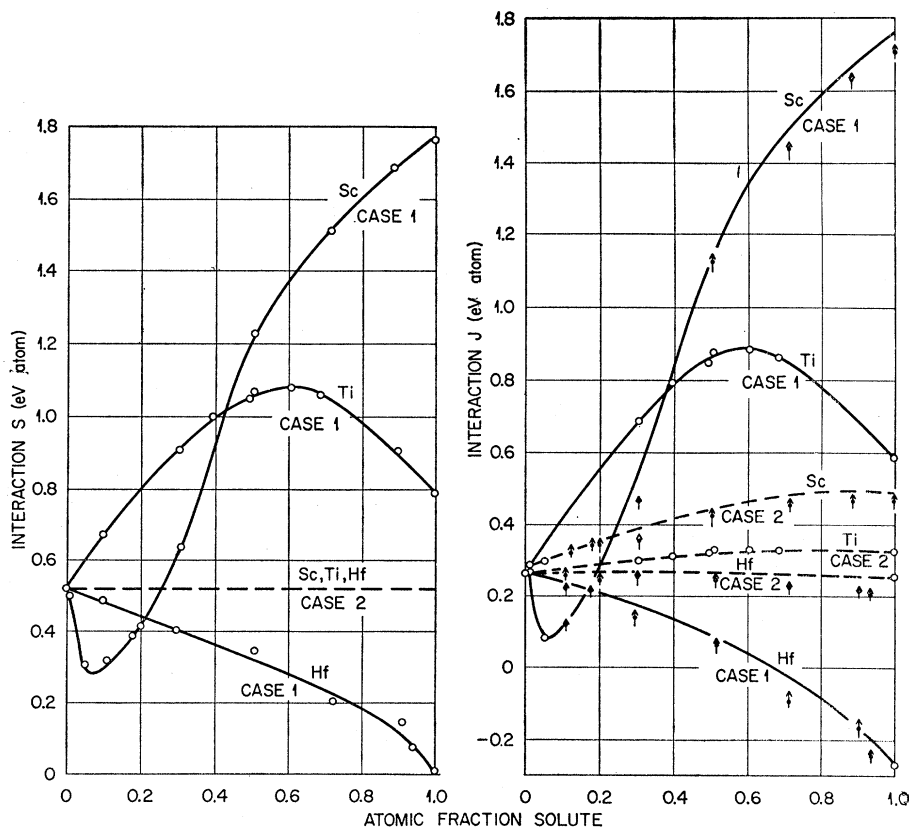


FIG. 6. S and J variations with composition in Zr-Ti, Zr-Hf, and Zr-Sc alloys. The solid curves represent the extreme case where $N_0(E_f)$ is assumed constant, and phonon enhancement is responsible for the variations in γ . The dotted curves represent the extreme case where S is constant and the electronic structure is responsible for variations in γ .

is added to zirconium, to a rapid rise in the Coulomb and other repulsive interactions. Another result for the second case in Fig. 6 is that the values of J in Zr-Ti and Zr-Hf alloys decrease in agreement with the trend for lower J in transition metals of the lower rows of the Periodic Table, noted earlier by Bucher *et al.*⁹

With this assumption that S is constant, the decline in γ from pure scandium to a minimum near pure zirconium can be understood in terms of gradual filling of the partially occupied bands of hexagonal scandium to a near filling of the four lower bands at zirconium. This behavior is illustrated by Fig. 7 where $N_0(E_f)$ values, obtained from γ and $S=0.52$ eV atom, are plotted against energy content using the rigid-band approximation.

T. L. Loucks²⁸ has calculated the density of states of zirconium by the augmented plane-wave method. His results are shown on Fig. 7 by the dashed curve. They correlate fairly well with the experimental curve, corrected for phonon enhancement in the above manner. The difference in Fermi energy corresponding to three electrons/atom and four electrons/atom according to Loucks agrees within 5% with Fermi energy difference between scandium and zirconium according to the alloys. Loucks²⁸ has pointed out that all the density of states curves calculated by the augmented plane-wave method for hexagonal transition metals have been

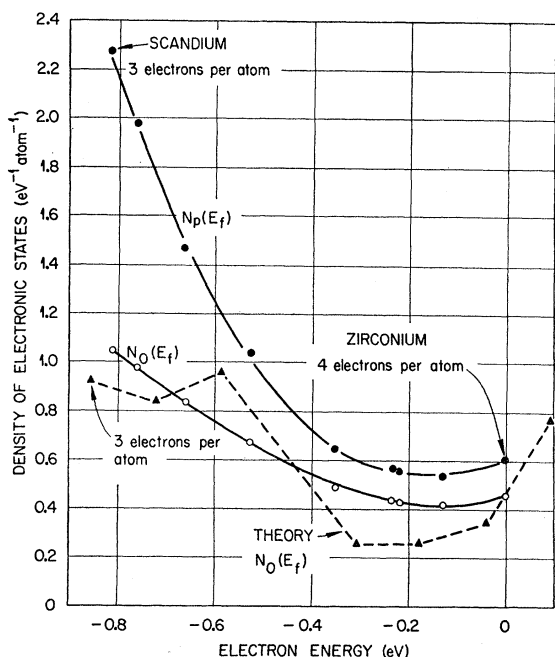


FIG. 7. Density of electronic states between scandium and zirconium for the extreme case of constant S at 0.52 eV atom, and with the rigid-band approximation. Upper curve $N_p(E_f)$ shows experimental values with phonon enhancement and the lower solid curve $N_0(E_f)$ shows the density of states after correction of this effect. The lower dashed curve represents density of states calculated theoretically by T. L. Loucks.

²⁸ T. L. Loucks, Phys. Rev. (to be published).

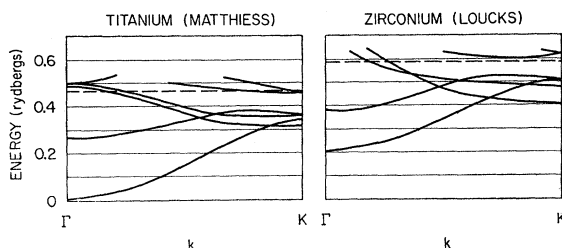


FIG. 8. Band structure in ΓK direction of hexagonal titanium and zirconium.

quite similar at a given number of electrons/atoms, so that in this case dissimilar band structures in the pure elements does not complicate alloying. The agreement has some imperfections since the experimental curve does not show as deep a minimum as the theory, and the hump in $N_0(E_f)$ at 0.6 eV below the Fermi surface of zirconium does not exist in the alloy data.

In contrast to the above, the γ maximum in the Zr-Ti alloys cannot be explained in terms of a rigid-band assumption, since no change occurs in the electron/atom ratio. However, for the second case where no change in the phonon enhancement of γ occurs, a different interpretation with a maximum in $N_0(E_f)$ is required. The difference in potential for zirconium and titanium reverses the relative energy of the third and fourth bands near point Γ in K space, so that at an intermediate composition a peaking of $N_0(E_f)$ might occur through crossing of these bands. The band structures for titanium and zirconium in the ΓK direction, $\langle 2\bar{1}\bar{1}0 \rangle$, as calculated by Mattheiss²⁹ and Loucks,²⁸ are illustrated in Fig. 8 in order to show reversed order of the energies of the third and fourth bands near the point Γ .

Based on the above, our choice between these extreme cases would favor the second one with $N_0(E_f)$ and J as the more important variables in determining γ and T_c of these alloys. However, more precise interpretations of γ and T_c must await development of a more satisfactory understanding of alloying. In the above discussion we have neglected the effects of moderate differences in atomic size and of the changes of the hexagonal axial ratio. The atomic size factors³⁰ for Zr-Ti, Zr-Hf, and Zr-Sc are 0.91, 0.98, and 1.03, respectively, while the measurements^{19,31,32} of the axial ratio show that the deviation from zirconium is at most 1% in these alloys.

The study of the transformation stresses and the impurities in Zr-Ti alloys showed that these factors change T_c mainly through their effects on J rather than through changes in γ , S , and Θ_D . This may be seen in Table V and in Fig. 4 where changes in transition temperature are proportionately much larger than changes in γ and Θ_D for different purity levels. The BCS formula

²⁹ L. F. Mattheiss, Phys. Rev. **133**, A1399 (1964).

³⁰ Ratio of atomic radius of solute to that of zirconium.

³¹ R. B. Russell, J. Appl. Phys. **24**, 232 (1953).

³² P. Duwez, J. Inst. Metals **80**, 525 (1952).

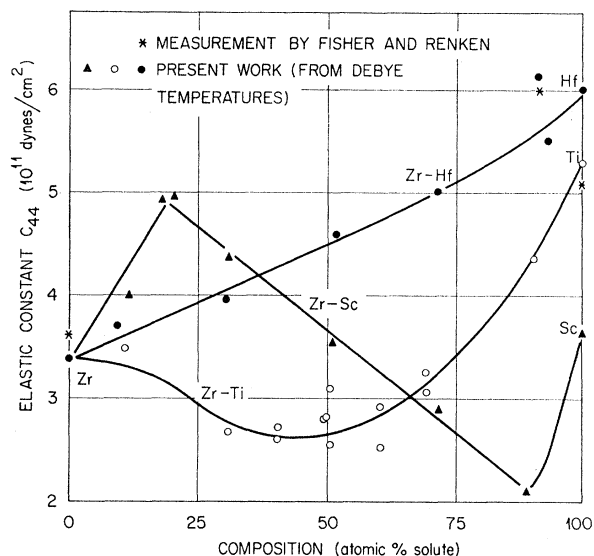


FIG. 9. Variation of C_{44} in Zr-Hf, Zr-Ti, and Zr-Sc alloys.

then relates T_e largely to $S-J$. However, the main dependence is upon J because, assuming Clogston's formula, a change in S should change γ , except for certain unlikely compensating changes in $N_0(E_F)$ and S .

DEBYE TEMPERATURES

Debye temperatures, as measured by low-temperature specific heats, are based on long-wavelength elastic waves in a crystal acting as a continuum. With long wavelengths we can assume that the mass parameter entering into the Debye temperature should be the average atomic mass of the alloy. Since transverse elastic waves have lower frequencies than longitudinal waves, the Debye temperatures are largely dependent upon shear constants. Leigh³³ has pointed out that small pieces of Fermi surface from electron or hole bands may contribute to the shear constants and hence one might expect that the Debye temperatures would be altered with changes in the electronic structure during alloying.

Wolcott³⁴ has given the following formula for the Debye temperature of a crystal with hexagonal symmetry:

$$\Theta_D = 23.105 M^{-1/2} \Omega^{1/6} C_{44}^{1/2} \{g(C_{ij}/C_{44})\}^{1/3},$$

where M is the atomic mass (g), Ω is the atomic volume (cm^3), C_{ij} are elastic constants (dynes/cm^2), and g is a numerically evaluated integral, which depends upon ratios of elastic constants.

In Zr-Ti, Zr-Sc, and Zr-Hf alloys, the main part of the variation in the Debye temperature corresponds to changes in M and Ω , and with correction for these variations, an approximate elastic constant C_{44} can be derived from the specific-heat data. Values were cal-

culated with Wolcott's formula and by linear interpolation of $C_{ij} \neq C_{44}$ between Zr, Ti, Hf, and in the case of Zr-Sc alloys, by assuming $C_{ij} \neq C_{44}$ to have the same values as in pure zirconium. The resulting C_{44} for the alloys are shown in Fig. 9. Single-crystal elastic constants are not known for scandium but measurements of Young's and shear moduli on polycrystalline scandium³⁵ at 300°K show values which are 14-18% lower than these properties for polycrystalline zirconium. The present values of C_{44} for pure scandium and pure zirconium at 4°K are nearly equal, as shown in Fig. 9, whereas from the room-temperature polycrystalline properties one would infer that C_{44} should be lower for scandium than for zirconium. Hence errors may be present in the C_{44} of Zr-Sc alloys of about this magnitude.

The measurements of C_{44} by Fisher and Renken²⁶ for Ti, Zr, and Zr, 92% Hf are indicated on Fig. 9 by asterisks. The curves for Zr-Ti and Zr-Hf agree well with these points, as would be expected from the close agreement of Debye temperatures from specific heats and elastic properties²⁶ and the method of calculating these curves.

In the Zr-Hf alloys C_{44} increases nearly linearly from zirconium to hafnium. With completion of the 4f shell in hafnium, increased nuclear charge is not completely screened so that outer electrons are more strongly attracted to these hafnium atoms, and elastic constants increase. In Zr-Ti a negative deviation from linearity occurs, which may indicate negative contributions to C_{44} from a redistribution of electrons and holes, as occurs in Leigh's theory for aluminum. In Zr-Sc, C_{44} had an S shape again suggestive of an influence on C_{44} of changes in the electronic structure. The negative contributions to C_{44} from electrons outside the hexagonal faces of the Brillouin zone in aluminum were proportional to the density of states in Leigh's theory, and similar considerations may account for the trend for C_{44} to be inverse to the density of states in Zr-Hf, Zr-Ti, and in Zr-Sc alloys over most of the composition range.

SUMMARY

Measurements have been made of the coefficient of the electronic specific heat γ and the Debye temperature Θ_D in Zr-Sc, Zr-Ti, and Zr-Hf alloys, and of the superconducting transition temperature T_e in Zr-Ti alloys in the composition range 30-70% Zr. The coefficient γ depends upon the band structure of the alloys and upon enhancement by electron-phonon interaction S , as suggested by Clogston. We have discussed the alloys for two extreme cases: (1) S does not change and the variations in γ arise entirely from changes in the band structure, and (2) the band-structure effects are absent and changes in γ arise entirely from changes in S .

³³ R. S. Leigh, *Phil. Mag.* **42**, Ser. 7, 139 (1951).

³⁴ N. M. Wolcott, *J. Chem. Phys.* **31**, 536 (1959).

³⁵ H. L. Brown, P. E. Armstrong, and C. P. Kempter, *J. Less-Common Metals* **11**, 135 (1966).

Although specific-heat data alone do not provide sufficient information to definitely separate the effects, the simpler and more reasonable interpretation is with S nearly constant. This interpretation is consistent with the zirconium band structure calculated by Loucks,²⁸ with nearly constant values of $S-J$ observed from pure titanium to Ti, 50% Zr while γ and T_c increased significantly, with the assumptions of Jensen and Maita¹⁶ that decreases of T_c in Zr-Sc alloys are due to rising J rather than decreasing S , and with the probable dependence of T_c in Ti, 50% Zr upon J during changes with impurities and physical defects.

On the other hand, the moderately good correlation of the theory of Loucks with γ of the Zr-Sc alloys, which one obtains by assuming a rigid-band model as

well as near constancy of S , seems to be accidental since the rigid-band approximation cannot explain the maximum in the γ of the Ti-Zr alloys. Additional assumptions and the variety of models which are needed to explain the data show the inadequacy of our present understanding of alloys. The study of Θ_D shows this property to be mainly dependent upon atomic mass and volume, and after correction for these variables, the corrected values show appreciable alloying effects, which related to the effect of the electronic structure on the shear constants.

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Random Impurity Problem*

P. S. PERSHAN† AND W. B. LACINA

Division of Engineering and Applied Physics, Harvard University, Cambridge, Massachusetts

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The problem of determining the vibrational properties of a random distribution of defects in an otherwise perfect lattice has most conveniently been treated by Green's-function techniques. The quantities of physical interest, such as the phonon density of states and the infrared or Raman spectra, are obtained from an average Green's function which has previously been obtained by means of a diagrammatic technique due to Langer. The purpose of this paper is to show that the average Green's function, or alternatively the "proper self-energy," for the random impurity problem can be obtained by a differential method which is conceptually much simpler than the diagrammatic technique. For a number of specific examples, the results previously obtained are rederived. With the differential method the relation between the single-defect problem and the random crystal problem becomes very clear, even for crystal systems with many phonon branches or for defects in the force constants as well as in the mass. The particular significance of this is that it provides an immediate qualitative explanation for the diverse experimental results on mixed crystals. The method is also amenable to numerical calculations and can be used to obtain quantitative results.

I. INTRODUCTION

A GREAT number of workers have studied the vibrational properties of impure lattices. Ample review articles exist for both the case of a single isolated impurity and a random distribution of a finite concentration of impurities.¹⁻⁴ Except for some very recent work by Taylor,⁵ the basic theoretical method has been an iterative technique in which one sums an infinite series of Feynman-type diagrams. This procedure, first

carried out by Langer⁶ for a simple mass defect on a one-dimensional lattice, is complex, and for many experimentalists not familiar with diagram techniques it represents a formidable obstacle to the understanding of disordered crystals. Furthermore, although the iterative procedure can readily be applied to the simple mass-defect problem, it becomes exceedingly complex when one attempts treatment of a random crystal containing many phonon branches and for which the defect is of a tensor nature. For example, a defect which, in addition to having a different mass, induces changes in the force constants between nearby atoms would be of a "tensor nature."

A general feature of this approach is that the infinite series of diagrams cannot be summed exactly for even the simplest of problems. The best efforts to date have only been able to obtain low-concentration approximations and although these have very definite short-

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† Alfred P. Sloan Foundation Fellow.

¹ Yu A. Izyumov, *Advan. Phys.* **14**, 569 (1965).

² A. A. Maradudin, *Rept. Progr. Phys.* **28**, 331 (1965).

³ A. A. Maradudin, *Solid State Phys.* **18**, 273 (1966).

⁴ R. J. Elliott, in *Phonons in Perfect Lattices and in Lattices with Point Imperfections*, edited by R. W. H. Stevenson (Plenum Press, Inc., New York, 1966).

⁵ D. W. Taylor, *Phys. Rev.* **156**, 1017 (1967).

⁶ J. S. Langer, *J. Math. Phys.* **2**, 584 (1961).