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Low-Temperature Specific Heat of Body-Centered Cubic Ti-V Alloys

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The electronic specific heat coefficient, γ, of V and of bcc Ti-V alloys was measured. A maximum of γ occurs at approximately 60 at.% V. The electronic specific heat coefficients were found to correlate quite well with the superconductive transition temperatures according to the Bardeen-Cooper-Schrieffer theory, with an interaction coefficient V independent of composition. From the exponential dependence of the electronic specific heat in the superconductive state on the reciprocal temperature, an energy gap of 0.0014 to 0.0025 ev was calculated, depending on the composition.

INTRODUCTION

In a previous paper,[1] it was predicted that a peak in the electronic specific heat coefficient is attained for bcc solid-solution alloys between Ti and V. Hulm and Blaugher[2] recently published data for the superconductive transition temperature of bcc Ti-V alloys. They compared these with transition temperatures calculated from electronic specific heat values on the basis of the BCS theory of superconductivity.[3] The accuracy of the electronic specific heat values for four Ti-V alloy compositions listed in their Table III, and attributed to reference 1, were questioned by these authors, since the agreement between their measured and calculated transition temperatures was poor. Actually no data were available for the alloy compositions listed, and the calculations of Hulm and Blaugher were presumably based on the rough predictions shown by dashed line in Fig. 13 of reference 1. The present work was undertaken to determine experimentally the electronic specific heat of bcc Ti-V alloys, and to use it for comparison in the light of the BCS theory with the corresponding transition temperatures.

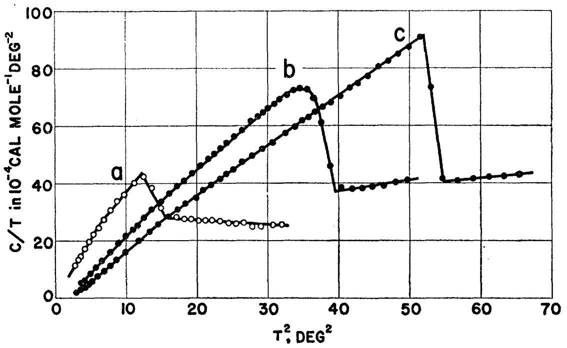

FIG. 1. C/T vs T^2 for $Ti_{0.8}V_{0.2}$ (a), $Ti_{0.7}V_{0.3}$ (b), and $Ti_{0.5}V_{0.5}$ (c).

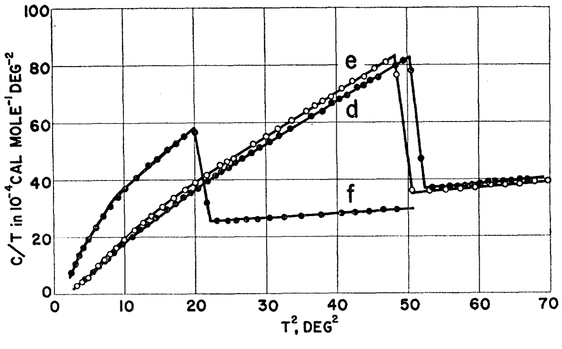

FIG. 2. C/T vs T^2 for $Ti_{0.25}V_{0.75}$ (d), $Ti_{0.15}V_{0.85}$ (e), and V (f).

EXPERIMENTAL PROCEDURES

Five Ti-V alloy specimens were prepared. Two buttons of each alloy were made by melting 99.8% pure vanadium and iodide titanium in an arc furnace with a water-cooled copper crucible under argon atmosphere. All specimens were annealed in vacuum for 3 days at 1200°C, then oil quenched without breaking the vacuum. The total weight of the two buttons of each specimen was about 1 mole. Metallographic examination showed that these alloys consisted of a single phase at room temperature, i.e., the bcc β phase, stable at the annealing temperature, was retained on quenching. However, the possibility of partial transformation to the ω phase on cooling could not be excluded in the case of the 20% and 30% V alloys. The experimental procedure used in measuring the specific heat was described in previous publications.[1,4] In the present work, the "1958 He temperature scale"[5] was used for the calibration of the carbon resistance ther-

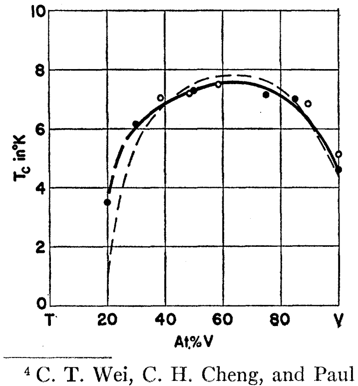

FIG. 3. Superconductive transition temperature T_c vs composition for Ti-V alloys. Empty circles: Data from reference 2; solid circles: Present work. Dashed line calculated from BCS theory, using $V=0.1288$ ev atom.

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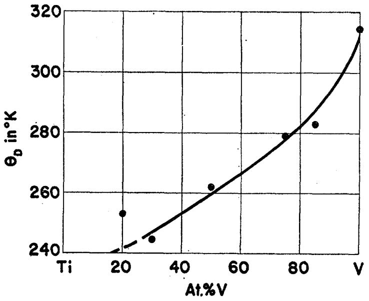

FIG. 4. Debye temperature θ_D vs composition for Ti-V alloys.

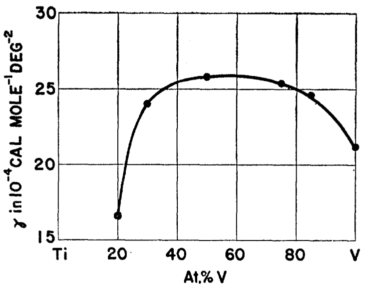

FIG. 5. Electronic specific heat coefficient vs composition for Ti-V alloys.

mometer. The thermometer calibration was extrapolated according to the relation[6] $[(\log R)/T]^{\frac{1}{2}} = A + B \log R$ for temperatures above 4.2°K, where no calibration was made.

RESULTS

The C/T vs T^2 data are shown in Figs. 1 and 2. The T_c for each alloy is taken as the midpoint of the usually narrow transition range. The wide transition temperature range for $\mathrm{Ti}_{0.8}\mathrm{V}_{0.2}$ is presumably due to partial transformation of the β phase, in spite of the homogeneity apparent in the microstructure.

The θ_D value can be calculated from the slope of the straight line portion of each C/T vs T^2 curve, corresponding to the normal state. The variation of T_c and θ_D with the composition is shown in Figs. 3 and 4. The T_c values, measured by Hulm and Blaugher[2] by a magnetic method, are also given in Fig. 3 for comparison. The agreement with the T_c values obtained in the present work is very good. The γ values can be obtained by calculation from the entropy in the superconducting state and from T_c, both of which were obtained from the measured data. The calculation makes use of the fact that at T_c the difference in entropy between the normal and superconductive states is zero. The lattice specific heat is assumed to be the same in the normal and the superconductive states. The γ values, calculated in this manner, were found to agree well with the intercept at $T=0$ of the extrapolated straight line (normal state) portion of the C/T vs T^2 curves. The variation of γ with composition is shown in Fig. 5.

The electronic specific heat coefficient for vanadium, obtained in the present work, is in good agreement with the value previously reported[7] for V metal of comparable purity, namely 21.1×10^{-4} cal mole^{-1} deg^{-2}. The only γ value for a Ti-V alloy previously published was approximately 22×10^{-4} cal mole^{-1} deg^{-2} for $\mathrm{Ti}_{0.5}\mathrm{V}_{0.5}$.[1] A new specimen of the same composition was measured in the present investigation, and the γ value was found to be 25.8×10^{-4} cal mole^{-1} deg^{-2}. It is probably significant that in the earlier investigation the specimens were annealed in a He+8% H_2 gas mixture and that the H_2 content of the $\mathrm{Ti}_{0.5}\mathrm{V}_{0.5}$ specimen was particularly high, namely 0.1% by weight,[1] while the present specimens were annealed in vacuum. Apparently, in this alloy, H_2 in solution has a rather important effect on the electronic specific heat coefficient, as well as on the superconductive transition temperature.

DISCUSSION

As shown in Figs. 3 and 5, up to about 40 at.% Ti the addition of Ti to V increases both T_c and γ. At still higher Ti contents both T_c and γ decrease. The parallelism between T_c and γ is in agreement with Daunt's rule[8] and with qualitative expectations based on the BCS theory. With the present experimental data, it is also possible to make a quantitative comparison with the BCS theory. The latter requires

$$kT_c = 1.14\langle\hbar\omega\rangle_{\mathrm{av}} e^{-1/N(0)V}. \tag{1}$$

Here $\langle\hbar\omega\rangle_{\mathrm{av}}$ is the mean energy of phonons, and V is the interaction parameter for superconductivity. By substituting $(3/4)k\theta_D$ for $\langle\hbar\omega\rangle_{\mathrm{av}}$, as suggested by Goodman *et al.*,[9] we have

$$T_c/\theta_D = 0.855 e^{-1/N(0)V}. \tag{2}$$

Using $\gamma = (2/3)\pi^2 k^2 N(0)$, the values of V were calculated and they are listed in Table I. These values are

TABLE I. Results of low-temperature specific heat measurements for Ti-V alloys.

Alloy	γ (10^{-4} cal mole^{-1} deg^{-2})	θ_D (°K)	V (ev atom)	T_c (°K) meas.	T_c (°K) calc.	a	b	E_G (ev)
$\mathrm{Ti}_{0.8}\mathrm{V}_{0.2}$	16.5	...	...	3.5	1.08	...	...	...
$\mathrm{Ti}_{0.7}\mathrm{V}_{0.3}$	24.0	244	0.1304	6.14	5.46	9.27	1.60	0.0021
$\mathrm{Ti}_{0.5}\mathrm{V}_{0.5}$	25.8	262	0.1275	7.30	7.56	10.3	1.65	0.0025
$\mathrm{Ti}_{0.25}\mathrm{V}_{0.75}$	25.4	279	0.1265	7.16	7.63	8.01	1.48	0.0022
$\mathrm{Ti}_{0.15}\mathrm{V}_{0.85}$	24.6	283	0.1294	7.02	6.92	10.2	1.56	0.0023
V	21.2	315	0.1304	4.59	4.36	8.85	1.45	0.0014

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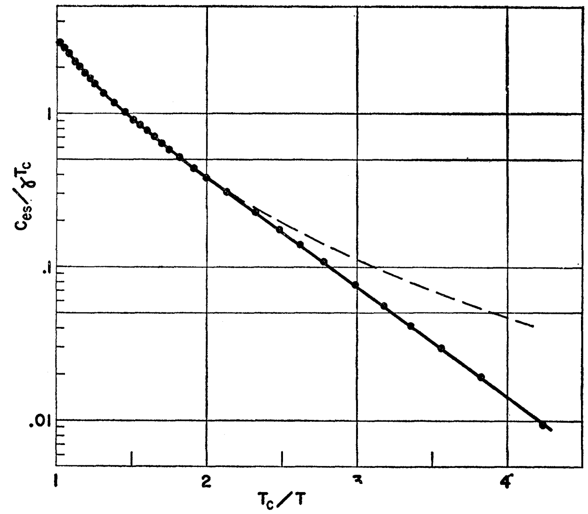

FIG. 6. $C_{es}/\gamma T_c$ on logarithmic scale vs T_c/T for $Ti_{0.5}V_{0.5}$ alloy. Dashed curve represents T^3 law.

constant within ±2%, as was also found in the case of U-Mo alloys by Goodman *et al.*[9] This result can be expressed graphically by plotting T_c, calculated from the average value of V, as a function of composition. It shows reasonably good agreement with the experimental values of T_c, Fig. 3. The discrepancy found by Hulm and Blaugher,[2] between the T_c values from magnetic measurements and from the BCS theory, was most likely due to the incorrect γ and θ_D vs composition values used by them. Lacking measured θ_D values for Ti-V alloys, Hulm and Blaugher used values for the bcc alloys obtained by linear interpolation between the measured values of 430°K for hcp α-Ti [10] and 338°K for bcc V.[11] The present data, Table I, indicate that such an interpolation leads to gross errors. The value of θ_D, as obtained by low-temperature specific heat measurements, actually decreases with increasing Ti content in the bcc alloys, Fig. 4, rather than increasing, as would follow from the interpolation.

The BCS theory requires exponential temperature dependence of the specific heat for a superconductor.[3] Such an exponential relationship has been experimentally found in the case of V and Nb by Corak *et al.*[12] according to the expression

$$C_{es}/\gamma T_c = a e^{-bT_c/T}. \qquad (3)$$

The present data are in good agreement with this expression, up to a temperature of $T_c/2$. The corresponding values of the empirical constants a and b are listed in Table I for each Ti-V alloy. At temperatures above $T_c/2$, however, the data fit much better the T^3 law of Gorter and Casimir.[13]

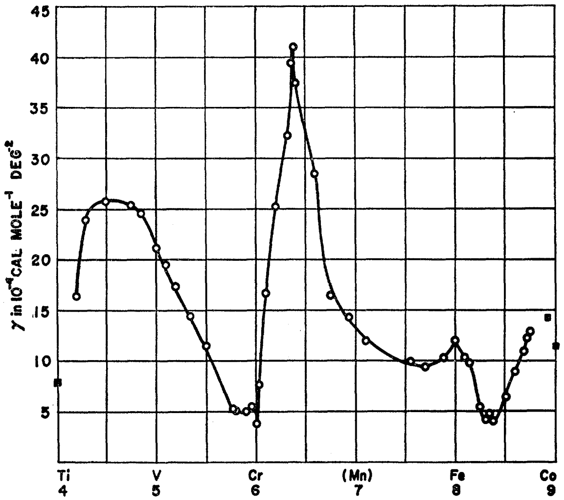

FIG. 7. Electronic specific heat coefficient of bcc alloys of first long period transition elements,[1] incorporating the present data for the Ti-V system, and new data for $V_{0.9}Cr_{0.1}$, $V_{0.8}Cr_{0.2}$, and $V_{0.65}Cr_{0.35}$, using vacuum-annealed specimens. Points marked by filled squares represent data for close-packed structures.

Figure 6 gives $C_{es}/\gamma T_c$ on a logarithmic scale vs T_c/T for the $Ti_{0.5}V_{0.5}$ alloy, as obtained from the measured data. The corresponding curves for all the other alloys are also very similar. The value of the energy gap, E_G, corresponding to the BCS theory, can be calculated[14] from the data for $T<T_c/2$. These values range from 0.0014 to 0.0025 ev (Table I), for the alloys studied.

Hake recently published[15] low-temperature specific heat measurements for four Ti-Mo alloys, which show that the γ values drop rapidly with increasing Ti-content near the Ti-rich end of the bcc solid-solution field. These results are very consistent with those given in Fig. 5 for Ti-V alloys. Electronic specific heat data are not yet available for bcc alloys of other second or third long-period transition elements. However, superconductive transition temperatures were recently measured by Hulm and Blaugher,[2] for several of these binary alloy systems. They found maxima in the T_c vs composition curves for all systems homologous with Ti-V which they studied, namely Ti-Nb, Zr-Nb, Hf-Nb, and Hf-Ta. In view of the close correlation between T_c and γ predicted by the BCS theory of superconductivity and experimentally confirmed by Goodman *et al.*[9] for U-Mo alloys and by the present work for Ti-V alloys, such a correlation may be expected to hold for these other alloy systems as well. Accordingly, it is very probable that the electronic specific heat coefficient (and the density of states at the Fermi surface) have corresponding maxima, in all these cases, near the average electron concentration of 4.6. Similarly, the maxima in T_c found by Hulm and Blaugher[2] in the Mo-Re and W-Re

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systems, and by Compton *et al.*[16] in the Mo-Tc system, correspond to the maximum of γ for Cr-Fe alloys at an electron concentration of about 6.4,[1] Fig. 7. It is, therefore, very likely that γ also has a maximum in the Mo-Re, W-Re, and Mo-Tc systems at approximately the same electron concentration. The data, now available, strongly suggest that the general features of the shape of the *d* band, including the separation into subbands, as established by low-temperature specific-heat measurements for the bcc alloys of the first long period,[1] Fig. 7, are reproduced also in the second and third long periods.

ACKNOWLEDGMENTS

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Multiphonon Processes Occurring in First-Order Perturbation Theory*

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An estimate of the effect of the multiphonon processes in first-order perturbation theory on the electrical conductivity in metals is made, according to a simplified model of the electron-phonon interaction, and a correspondingly simple model of the electron wave functions (plane waves). A method for taking Umklapp processes into account is worked in detail and the calculation is set up in the framework of the variational principle. A sample computation of the effect of double-phonon processes on the conductivity of the alkali metals is performed using a nonisotropic phonon spectrum, the result being a decrease by less than four percent (1% being more characteristic for the lighter elements). The method is not restricted to long-wave phonons, but does not include the effects of higher-order perturbation theory or of interference terms, which may be considerable.

I. INTRODUCTION

In studying electron transport phenomena, we are concerned with the interactions of a two-component system—the electrons and the phonons. The scattering of electrons by the phonon field gives rise, for example, to electrical resistance. Such a scattering is ordinarily described in terms of the creation and annihilation of single phonons and expressions for electron-phonon collision probabilities are obtained with the aid of first-order, time-dependent perturbation theory. Multiphonon processes, in which two or more phonons are created or annihilated while the electron changes its state, are also possible. We may analyze the types of possible transitions in the following way. It is well known that the electron-lattice perturbation energy may be expanded as an infinite series in the displacements of the atoms. Application of first-order perturbation theory to a given term in the expansion leads to one certain type of process (for example single-phonon processes from the first term, double-phonon processes from the second and so on) in which the electron changes its state, in each case, by a single transition without recourse to any intermediate states. On the other hand, treatment of even the first term of the perturbation energy expansion in conjunction with perturbation theory of higher order than first leads to double-phonon processes with one intermediate state, triple-phonon processes with two intermediate states, and other similar processes all involving intermediate states which are transitory in nature. The other terms of the perturbation potential lead to additional, more complicated, higher-order effects. Now a consideration of multiphonon processes involving intermediate states presents formidable mathematical difficulties, but those not involving such states may be treated in a systematic manner which is also mathematically tractable if the electronic states are characterized by plane waves. The purpose of this paper is to investigate the latter type of process. In the plane wave approximation the matrix element of the electron-lattice interaction may be separated into two factors. The first is a matrix element of a single ionic potential shielded in some fashion by the conduction electrons, and the second is a matrix element involving the annihilation and creation operators characteristic of multiphonon processes. Such a separation is carried out in Sec. II and explicit expressions are derived for the single-, and double-phonon transition probabilities. Evaluation of the electronic portion of the matrix element is described in Sec. III on the basis of a Fermi-Thomas statistical model.

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