Specific heat of bcc $Mo_{1-x}Tc_x$

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The low-temperature specific heats of four compositions of bcc $Mo_{1-x}Tc_x$ ($x=0.25$, 0.45, 0.50, and 0.54) have been measured. Results indicate that the large normalized energy gaps $2\Delta/kT_c$ found previously in both bcc and $A-15$ $Mo_{0.4}Tc_{0.6}$ exist also at other compositions in the bcc phase away from the bcc phase boundary at $x=0.6$. A possible cause of this strong-coupling behavior is the presence of a very sharp d-band for $0.5 \leq x \leq 0.6$ as revealed by the linear term in the specific heat for the three Tc-rich samples reported here and the previous data for bcc $Mo_{0.4}Tc_{0.6}$. The method for extracting $2\Delta/kT_c$ values from specific-heat data is discussed, along with possible uncertainties of this method.

I. INTRODUCTION

The discovery[1] of extreme strong coupling ($2\Delta/kT_c > 6.0$) in both bcc and $A-15$ $Mo_{0.4}Tc_{0.6}$ makes the Mo-Tc system of special interest for further study. Recently, we reported[2] specific-heat measurements on hcp $Mo_{0.2}Tc_{0.8}$, which has the highest T_c ($T_c=13.7$) found in the Mo-Tc system. The low normalized energy gap $2\Delta/kT_c$ found for $Mo_{0.2}Tc_{0.8}$ ($2\Delta/kT_c=3.6$) prompted the present specific-heat study of the bcc solid solution $Mo_{1-x}Tc_x$ system to see if the strong coupling found in $Mo_{0.4}Tc_{0.6}$ is unique to this composition. In addition to furthering understanding of the unique strong coupling in $Mo_{0.4}Tc_{0.6}$, this study will be an important aid in the preparation of sputtered films for tunneling studies by showing the range of compositions in which films can be prepared and still be of interest.

II. EXPERIMENTAL

A. Sample preparation

Small beads of molybdenum and technetium metal were prepared by arc melting small pressed pellets of the high-purity (99.9+%) metal powders. The compositions $Mo_{0.75}Tc_{0.25}$ and $Mo_{0.46}Tc_{0.54}$ were then prepared by arc melting weighed amounts of the metal beads in a zirconium-gettered argon atmosphere. Two other compositions were prepared from the $Mo_{0.46}Tc_{0.54}$ sample by adding successive amounts of Mo to first make $Mo_{0.50}Tc_{0.50}$ and then $Mo_{0.55}Tc_{0.45}$. Each composition was fully characterized by specific-heat and x-ray diffraction (see Table I) measurements. In earlier studies,[3,4] lattice parameters for various compositions of the bcc phase of Mo-Tc were reported. A plot of these data, Fig. 1, yields a straight line showing that the bcc ($A-2$) type solid solution obeys Vegard's Law. The following linear equation relating composition to lattice parameter was calculated by the method of least squares:

$$x = 3962.5 - 1259.2a_o \ ,$$

where x is the atomic percent technetium and a_o is the lattice parameter of the bcc phase in Å. Nominal compositions agreed within 0.5% with the composition calculated from the lattice parameter.

B. Calorimetry

The apparatus used for the specific-heat measurements is a low addenda, small sample calorimeter described fully in the literature.[1,5] The $Mo_{0.75}Tc_{0.25}$ sample weighed 73.20 mg. The weights of the $Mo_{0.46}Tc_{0.54}$, $Mo_{0.50}Tc_{0.50}$, and $Mo_{0.55}Tc_{0.45}$ were 99.00,

TABLE I. Lattice parameters for bcc $Mo_{1-x}Tc_x$.

Compound	a_0 (Å)
Mo	3.1470 ± 0.0004
$Mo_{0.75}Tc_{0.25}$	3.127 ± 0.001
$Mo_{0.55}Tc_{0.45}$	3.111 ± 0.001
$Mo_{0.50}Tc_{0.50}$	3.107 ± 0.001
$Mo_{0.46}Tc_{0.54}$	3.104 ± 0.001
$Mo_{0.40}Tc_{0.60}$	3.098 ± 0.002

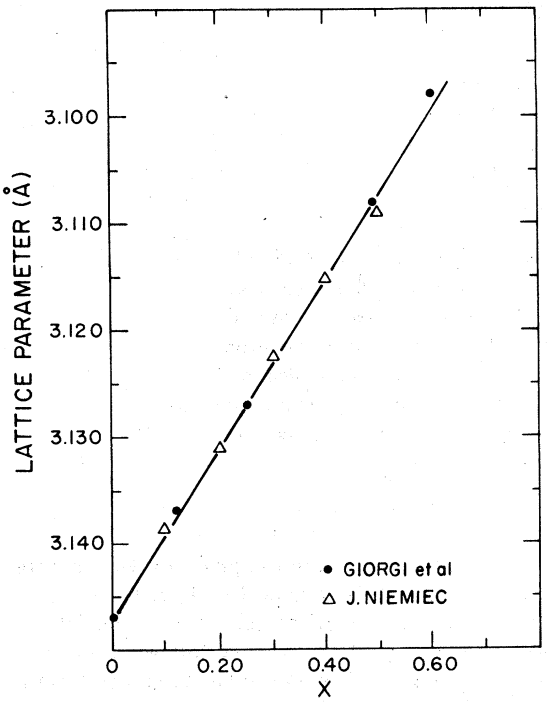

FIG. 1. Lattice parameter vs Tc content in $Mo_{1-x}Tc_x$.

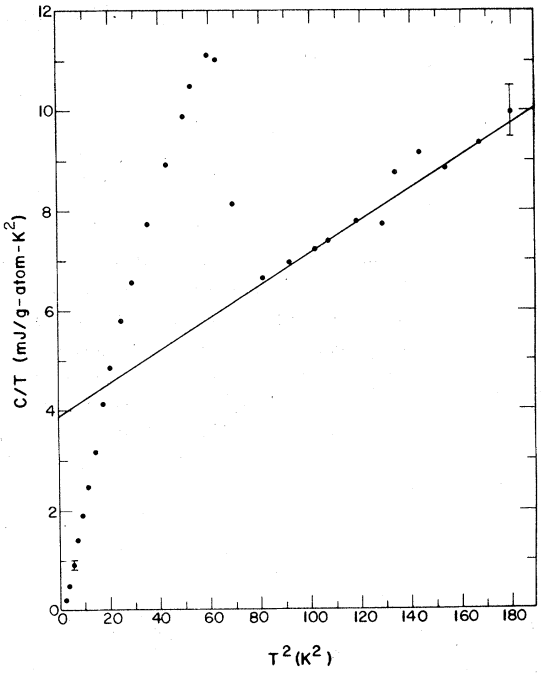

FIG. 2. Specific heat of $Mo_{0.75}Tc_{0.25}$.

110.58, and 124.03 mg, respectively. These weights are sufficiently large to give excellent accuracy to the measurements reported here. The specific-heat addenda for the three Tc-rich samples were less than 21% of the total specific heat over the entire range of measurement for each sample. For $Mo_{0.75}Tc_{0.25}$, the addenda were 21% of the total at lower temperatures, rising to 41% at the highest-temperature range of measurement. Since the addenda corrections for the calorimeter are known to approximately 5%,[1,5] the absolute errors for the specific data presented below is approximately ±4% for $Mo_{0.75}Tc_{0.25}$, and ±2% for the other three samples.

III. RESULTS

A. $\gamma+\beta$

The specific-heat data for $Mo_{0.75}Tc_{0.25}$, $Mo_{0.55}Tc_{0.45}$, $Mo_{0.50}Tc_{0.50}$, and $Mo_{0.46}Tc_{0.54}$ are given in Figs. 2-5, respectively. The normal-state specific heat C_n is given by

$$C_n = \gamma T + \beta T^3 \tag{1}$$

TABLE II. Parameters for the bcc $Mo_{1-x}Tc_x$ system.

Compound	Midpoint T_c (K)	Transition Width (K)	$\gamma\left(\frac{mJ}{g\text{-atom}K^2}\right)$	θ_D (K)	$\Delta C/\gamma T_c$	$\frac{2\Delta}{kT_c}$	λ	$H_c(0)$ (G)
Mo	0.92		2.11	470				
$Mo_{0.75}Tc_{0.25}$	8.21	0.7	3.88 ± 0.15	400 ± 6	1.37	3.85 ± 0.2	0.68	1249 ± 30
$Mo_{0.55}Tc_{0.45}$	12.1	0.8	4.4 ± 0.15	318 ± 3	1.86	5.06 ± 0.2	0.87	2185 ± 40
$Mo_{0.50}Tc_{0.50}$	12.5	0.4	4.3 ± 0.3	291 ± 6	2.34	5.2 ± 0.3	0.93	2220 ± 40
$Mo_{0.46}Tc_{0.54}$	12.8	0.3	5.57 ± 0.15	285 ± 3	2.08	6.4 ± 0.2	0.95	2800 ± 40
$Mo_{0.40}Tc_{0.60}$	12.7	0.4	6.8 ± 0.3	258 ± 3	2.1	6.2 ± 0.2	1.0	2430 ± 40
BCS					1.43	3.52		

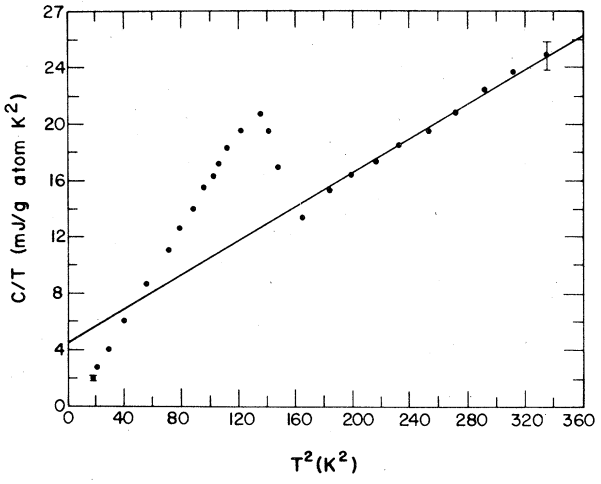

FIG. 3. Specific heat of $Mo_{0.55}Tc_{0.45}$.

in each case, without the need for an additional T^5 term to fit the data. In addition to using a least-squares-fit computer program to fit the data in Figs. 2–5 above T_c the transition temperature, the following stricture of thermodynamics may be used:

$$\int_o^{T_c} \frac{C_s}{T}\,dT = S_s(T_c) = S_n(T_c) = \int_o^{T_c} \frac{C_n}{T}\,dT\ , \quad (2)$$

where $S(T_c)$ is the entropy at T_c. Since the intercept of the straight line fitting the normal-state data gives γ, and thus $N(0)$, the electronic density of states, via

$$\gamma = \tfrac{1}{3}k^2\pi^2 N(0)(1+\lambda)\ , \quad (3)$$

the accuracy of this extrapolation is of great importance. Thus, the superconducting specific heat C_s may be used, via Eq. (2), as a check on the accuracy of the computer fit to C_n and of the extrapolation. The agreement between the two entropies, using the computer fits of the data to Eq. (1) for C_n below T_c, is 4.3%, 0.9%, 6.4%, and 2.5% for $x=0.25$, 0.45, 0.50, and 0.54, respectively. These agreements are quite good and speak well for the accuracy of the data. Table II contains values of γ and β for the four compounds, where the values have been adjusted for entropy agreement; e.g., since $S_n(T_c)$ using γ and β from the computer fit was higher than $S_s(T_c)$ by 4.3% for $Mo_{0.75}Tc_{0.25}$, the values reported in Table II for γ and β for $Mo_{0.75}Tc_{0.25}$ are each decreased by 4.3% from the computer-fitted values.

From β can be derived the Debye temperature, θ_D

$$\theta_D = (1944/\beta)^{1/3} \times 10. \quad (4)$$

These values are given in Table II and show a consistent progression across the bcc phase. Of central interest is the behavior of γ and $N(0)$, across the bcc phase. The parameter λ in Eq. (3), the electron-phonon coupling constant, is given by the McMillan formula[6]

$$\lambda = \frac{1.04 + \mu^* \ln(\theta_D/1.45T_c)}{(1-0.62\mu^*)\ln(\theta_D/1.45T_c) - 1.04}\ , \quad (5)$$

where μ^* is taken as 0.13. Both γ and $N(0)$ are plot-

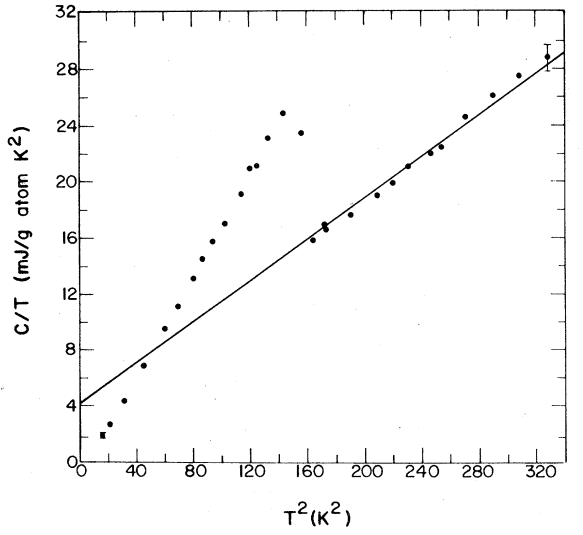

FIG. 4. Specific heat of $Mo_{0.50}Tc_{0.50}$.

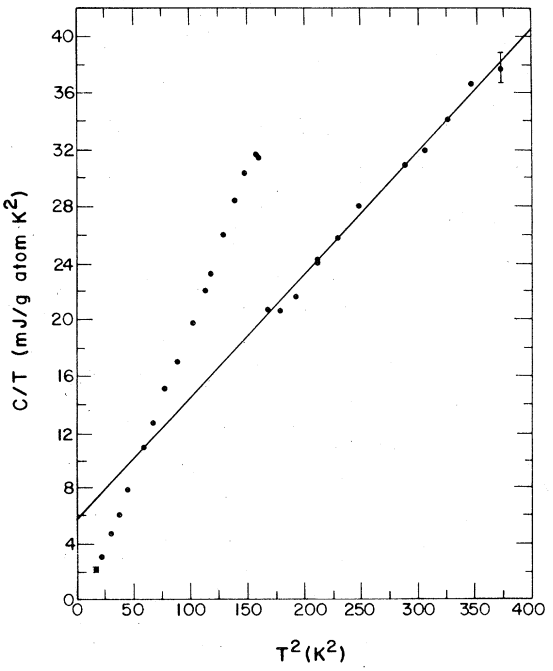

FIG. 5. Specific heat of $Mo_{0.46}Tc_{0.54}$.

ted in Fig. 6, with λ being given in Fig. 7. As may be seen, for $0 \leq x \leq 0.50$ the behavior of $N(0)$, in a rigid-band picture, is indicative of increasing population of a rather broad d band for $0 \leq x \lesssim 0.4$, until at $x \sim 0.40$ the peak in the d-band density of states is passed and $N(0)$ decreases as x is further increased to $x = 0.50$. This behavior is exactly as that found in the bcc $Mo_{1-x}Re_x$ solution, which extends only to $x = 0.4$, and in fact the γ's of both systems are within error limits of each other for the same x. Beyond $x = 0.5$ in the $Mo_{1-x}Tc_x$ system, Fig. 6 shows a radical increase in $N(0)$, indicating the onset of a very sharp d band in the band structure. This sharp rise in the density of states $N(0)$ may play a role in the strong electron-phonon coupling observed in bcc $Mo_{0.4}Tc_{0.6}$ (also observed in bcc $Mo_{1-x}Tc_x$ for x near 0.6), discussed below.

B. $2\Delta/kT_c$

One of the major questions raised by the discovery of large normalized energy gaps $2\Delta/kT_c$ in $Mo_{0.4}Tc_{0.6}$ (6.5 for the A-15 phase, 6.2 for the bcc) was how far, if at all, this strong coupling extended into the bcc phase from the phase boundary at 60% Tc. The method by which energy gaps are deduced from the superconducting specific heat C_s is based on

$$C_s = C_{es} + C_{\text{lattice}}\,, \tag{6}$$

$$C_{es} = ae^{-(\Delta/kT_c)T_c/T}\,, \tag{7}$$

where C_{es} is the electronic part of the superconducting specific heat. From the BCS formula of Eq. (7), it is seen that a semilog plot of C_{es} vs T_c/T would have a slope of $(-\Delta/kT_c)$. There are, however, complications involved with Eq. (7). The BCS prediction for ln C_{es} vs T_c/T is in fact not a straight line: it is curved with its lowest slope at $T_c/T = 1$, $\Delta/kT_c = 1.44$ for $2.5 < T_c/T < 6$, and at the lowest temperature we have $\Delta/kT_c \rightarrow 1.76$. Unfortunately, no example of this type of behavior of ln C_{es} vs T_c/T is found in experimental specific-heat results for superconductors, neither in absolute magnitude nor even in shape. Instead, the slope of such a plot typically has a maximum near $T_c/T = 1$, which then decreases at lower temperatures, i.e., the ln C_{es} vs T_c/T plot curves up (not down as in BCS) as T_c/T increases.

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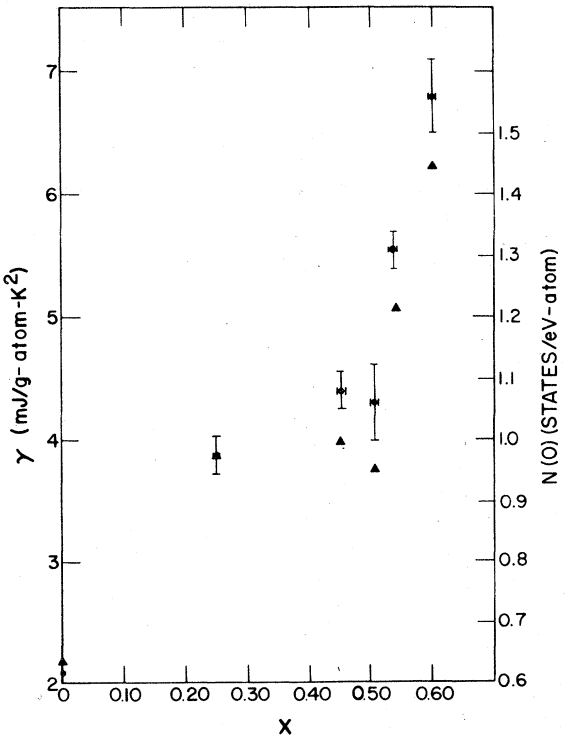

FIG. 6. γ (circles) and $N(0)$ (triangles) vs x in $Mo_{1-x}Tc_x$. Note that the points overlay at $x = 0.25$.

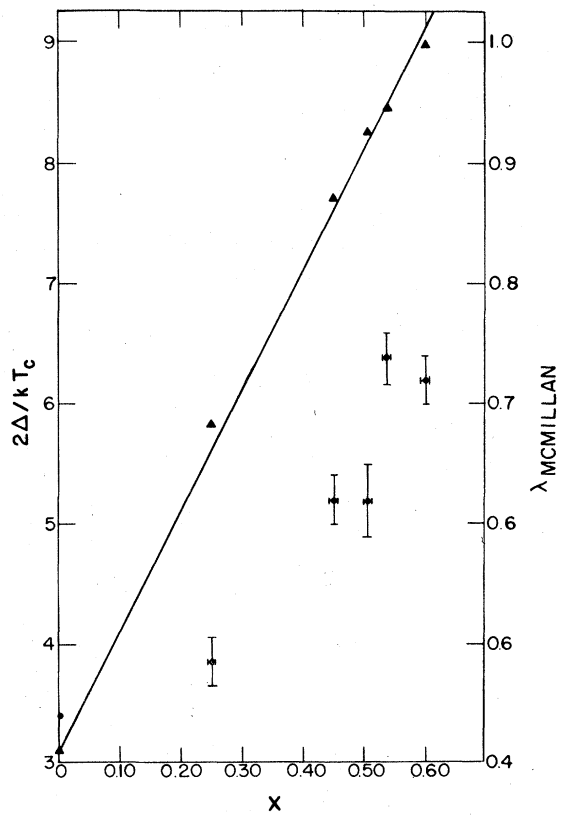

FIG. 7. $2\Delta/kT_c$ (circles) and $\lambda_{\text{McMillan}}$ (triangles) vs x in $Mo_{1-x}Tc_x$.

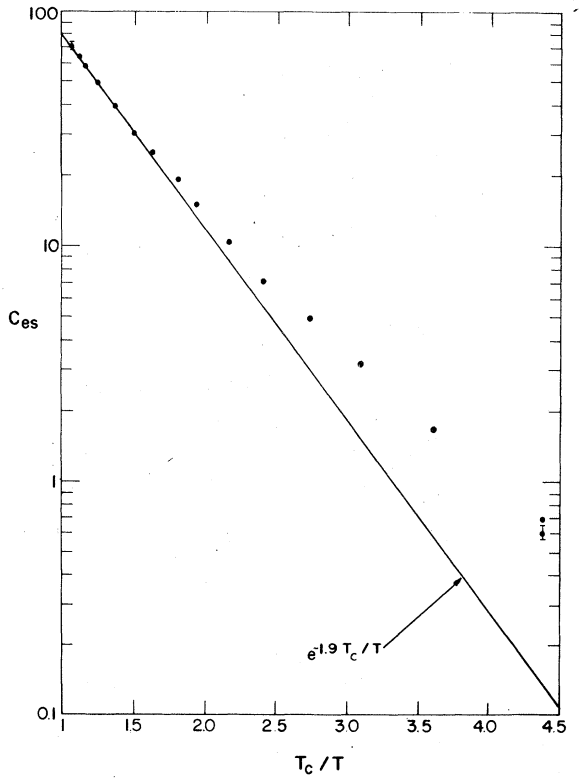

FIG. 8. Superconducting electronic specific heat in $Mo_{0.75}Tc_{0.25}$.

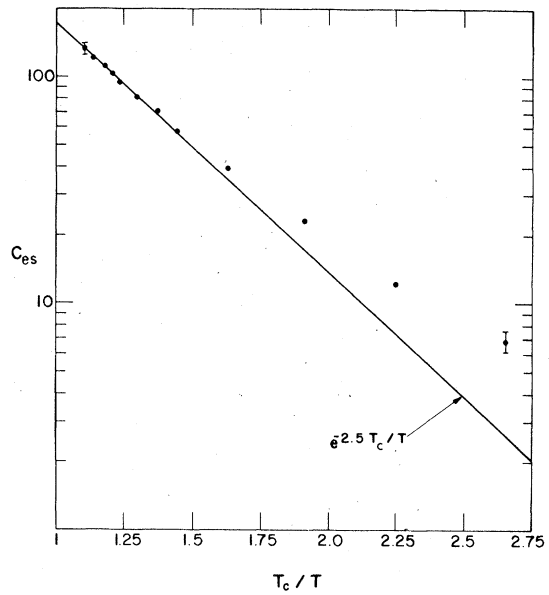

FIG. 9. Superconducting electronic specific heat in $Mo_{0.55}Tc_{0.45}$.

the slope of their ln C_{es} vs T_c/T plots for $2.5 < T_c/T \leq 6$, to the BCS value of 1.44, and then multiplied this ratio times the BCS T = 0 value of 1.76 to obtain $\Delta(T=0)/kT_c$. There are two objections to this method: (i) scaling to the BCS theory when even the shape of the BCS prediction for ln C_{es} vs T_c/T is wrong, seems unsatisfactory. (ii) In the case of Δ's significantly larger than the weak coupling BCS value of 1.76, comparisons should not be made without modifying the BCS theory for strong coupling.

There exists, however, a better method for extracting $2\Delta(T=0)/kT_c$ values from specific-heat data. As pointed out by Grunzweig-Gennosar and Revzen,[7,8] it's generally true that minus the slope of ln C_{es} vs T_c/T near T_c/T may be identified with $\Delta(0)/kT_c$. This empirical relationship bears some scrutiny. Using

TABLE III. Comparison of tunneling and specific-heat values for Δ/kT_c.

Material	$\frac{\Delta(0)}{kT_c}$ via Tunneling	(Reference)	$\frac{\Delta}{kT_c}$ via Specific-Heat[a]	(Reference)
Al	1.7	9	1.8	10
Hg	2.2	11	2.1	12
In	1.8	13	~3.4	14
Nb	1.9	15	2.0	16
Pb	2.2	15	3.1	17
Sn	1.8	18	2.0	19
Tl	1.9	20	2.2	12
Zn	1.6	21	1.7	22
Nb_3Ge	2.1	23	2.1	24
Nb_3Sn	2.2	25	2.8	26

[a]Using minus the slope of ln C_{es} vs T_c/T near T_c.

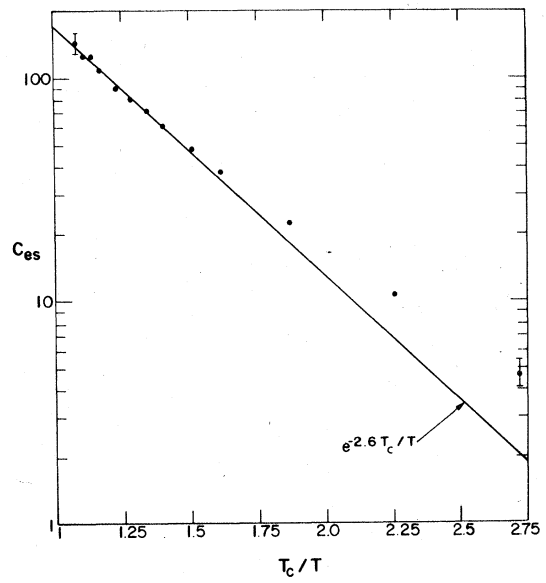

FIG. 10. Superconducting electronic specific heat in $Mo_{0.50}\,Tc_{0.50}$.

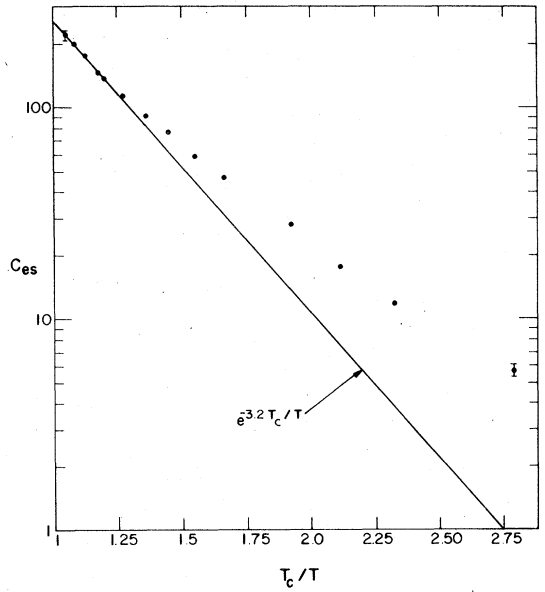

FIG. 11. Superconducting electronic specific heat in $Mo_{0.46}\,Tc_{0.54}$.

tunneling results at low temperatures as a source for $\Delta(0)$, Table III compares $\Delta(0)^{\text{tunneling}}/kT_c$ with minus the slope of ln C_{es} vs T_c/T near T_c for ten cases, where data for C_{es} and $\Delta(0)^{\text{tunneling}}$ exist. Some of the slopes given are approximate since they were taken from published graphs. As may be seen, in seven out of ten cases, the empirical relation proposed by Grunzweig-Gennosar and Revzen is borne out. In the exceptions, Pb, In, and Nb_3Sn, the disagreement is though to be real, i.e., outside experimental uncertainties.

Based on this discussion, $2\Delta/kT_c$ values are derived from ln C_{es} vs T_c/T plots (Figs. 8-11) for the $Mo_{1-x}Tc_x$ samples reported here by taking the slopes near T_c. Tunneling work is underway to verify these values. As may be seen in Figs. 8-11, the ln C_{es} data is straight for $1.0 < T_c/T \lesssim 1.5$, and then curves upward. This upward curvature may be due to anisotropy, or the onset of a second energy gap. This last interpretation is given credence by the evidence of overlapping bands as discussed above. Error bars on the C_{es} data are small since C_{lattice}[see Eq. (6)] is well known (in error by approximately the percentage difference between $S_s(T_c)$ and $S_n(T_c)$ as discussed above) and less than $\frac{1}{2}$ of C_s near T_c for all four samples, so that the error in C_{lattice} is not magnified in C_{es}.

The values for $2\Delta/kT_c$ derived from Figs. 8-11 are presented in Fig. 7, along with another indication of electron-phonon coupling strength λ, given by Eq. (5). As may be seen, $2\Delta/kT_c$ vs x appears to be a smooth, monotonic function, with values above 4 for $0.3 \lesssim x \lesssim 0.6$. Thus, the composition of samples for tunneling measurements appears not be critical, since compositions within a Δx of 0.15 of the phase boundary will give $2\Delta/kT_c$ values of greater than 5.

IV. CONCLUSIONS

The specific heat of four compositions of bcc $Mo_{1-x}Tc_x$ have been measured, where $x = 0.25$, 0.45, 0.50, and 0.54. The strong coupling previously found for bcc and A-15 $Mo_{0.4}Tc_{0.6}$ is found to extend across approximately half of the bcc phase from the phase boundary at $x = 0.6$. This broad region for finding strong coupling will simplify preparation of thin films for tunneling investigations. The behavior N(0) vs x implies the onset of a very sharp d band near the phase boundary at $x = 0.6$. This is thought to be linked to the presence of the large normalized energy gaps $2\Delta/kT_c$ observed in this system.

ACKNOWLEDGMENT

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