Superconductivity of Re-Os, Re-Ru, Ru-Os, and Re-W hcp Alloy Systems and Slightly Doped Re

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The superconducting transition temperature T_c has been measured on the hcp Re-Os, Re-Ru, Ru-Os, and Re-W alloy systems and on slightly doped Re. The T_c variation is analyzed and discussed in terms of McMillan's theory. A sharp peak is observed in the slope of the curve for T_c vs Os concentration. This is attributed to the Fermi-surface-topology change of Re due to alloying. A small addition of impurities is observed always to increase the T_c of Re. This is explained in terms of the effects of the band-structure smearing and the Fermi-surface-topology change. By invoking only the second effect near the Fermi level, we can also easily account for the unusual impurity effect on T_c of slightly doped Tl observed by other workers.

I. INTRODUCTION

Both experimental and theoretical studies[1,2] of superconductivity in transition elements and alloys have been carried out quite extensively in recent years. However, emphasis is given mainly to the bcc and the fcc phases. Little work has been done on the hcp phase in the middle of the series. Moreover, high-pressure work on superconducting Re has recently led to the proposition that the Fermi surface of Re undergoes a topological change by hydrostatic compression.[3] This implies that slightly above the Fermi level ϵ_F there exists a critical energy ϵ_k where Fermi-surface topology changes. In addition, the band-structure calculation[4] and specific-heat measurements[5] indicate that the density of states rises steeply just below ϵ_F of Re. The existence of such singularities close to ϵ_F in Re suggests the possible occurrence of anomalous behavior in the superconducting transition temperature T_c through alloying. For these reasons we have measured T_c of the Re-Os, Re-Ru, Ru-Os, and Re-W hcp alloy systems and Re slightly doped with W, Mo, Os, Ru, Rh, and Ir.

T_c of the Re-Os and Re-Ru systems passes a maximum and then drops with increase of Os or Ru concentration. For the Ru-Os system, T_c varies smoothly although more strongly with the Os content than that previously observed by Geballe.[6] No simple correlation between T_c and the band-structure density of state $N_{bs}(0)$ at the Fermi surface is observed. McMillan's strong-coupling theory[2] was used to analyze the results whenever specific-heat data were available.

A sharp peak is found in the slope of the T_c-vs-concentration plot of dilute Re-Os alloys. T_c of Re is always enhanced by small addition of impurities. These are attributed to the peculiar band structure of Re near (both above and below) ϵ_F.

II. EXPERIMENTAL

Because Re, Ru, and Os all have the hcp crystal structure and similar atomic sizes, they form complete hcp solid solutions.[7] Alloys of Re-Os, Re-Ru, and Ru-Os were prepared by the arc-melting technique from Material Research Corporation (MRC) Grade 1 99.9-wt%-purity Re, Varlacoil Chemical Company 99.8-wt%-purity Os, and MRC Grade 1 99.8-wt%-purity Ru. hcp Re-W solid solutions and slightly doped samples of Re with Mo, W, Os, Ru, Rh, and Ir (~ 99.8-wt% purity) were made similarly. The constituents of the samples with desired proportions were melted at least seven times on the water-cooled copper hearth of an arc furnace in a pure argon atmosphere. Samples of very low concentration (< 0.6 at.%) were obtained by successively diluting the next more concentrated one. Three samples of Re slightly doped with equal amounts of Os and W were made. Two of them were prepared by arc melting two binaries together, e.g., mixing $Re_{0.998}W_{0.002}$ and $Re_{0.998}Os_{0.002}$ to get $Re_{0.998}W_{0.001}Os_{0.001}$. The weight losses which occurred during melting were negligibly small. The quoted compositions were those calculated from the initial relative weights of the constituents. T_c was measured in a He^4 or He^3 cryostat depending on whether T_c > 1 K or < 1 K by an ac inductance method at ~ 150 Hz. The temperature was determined by measuring the vapor pressure of the liquid-helium bath.

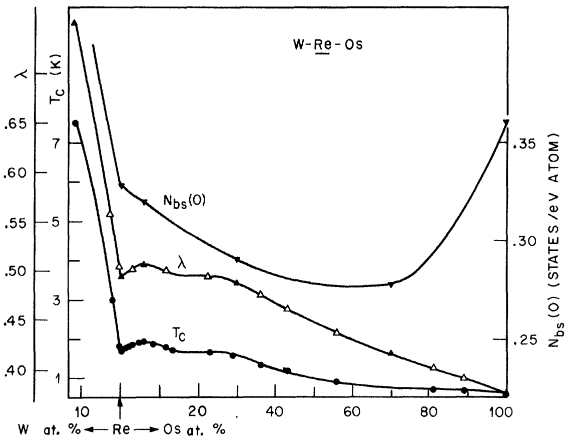

FIG. 1. T_c, λ, and $N_{bs}(0)$ vs W and Os concentration in Re.

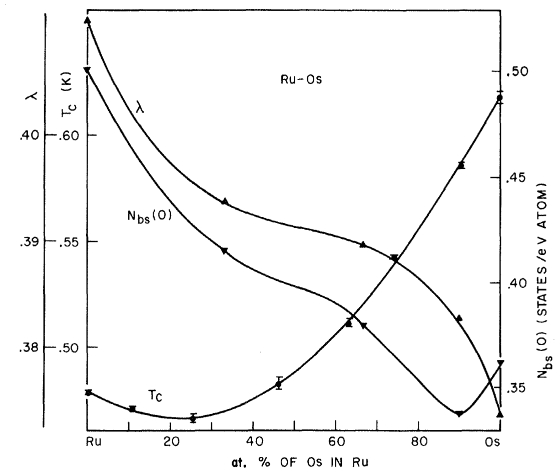

FIG. 3. T_c, λ, and $N_{bs}(0)$ vs Os concentration in Ru.

III. RESULTS

The superconducting temperatures of the binary hcp solid solutions of Re, Ru, Os, and W, and slightly doped Re are shown as a function of composition in Figs. 1–5. The following interesting features are observed:

(a) T_c increases with Os concentration C in Re and reaches a maximum (1.93 K) at 5.8-at.% Os before it finally decreases. The Re-Ru system exhibits a similar T_c variation but with a broader maximum (2.23 K) at ~ 17.5-at.% Ru. In contrast, the Sommerfeld coefficient γ of specific heat, which is usually taken as a measure of the electronic density of states N, for the Re-Os system (unavailable for the Re-Ru system) decreases smoothly from the Re rich end through a minimum and then increases with Os content. T_c and γ for the Ru-Os system were found not to vary in step, as was observed formerly by Geballe.[6]

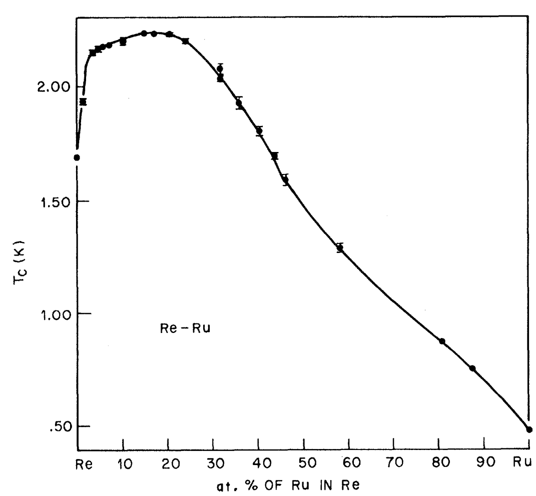

FIG. 2. T_c vs Ru concentration in Re.

(b) There exists a sharp peak in the slope of the T_c-vs-C plot at (0.27 ± 0.05)-at.% Os in Re.

(c) Small additions of Mo, W, Ru, Os, Rh, and Ir always enhance T_c of Re.

We shall discuss these features separately in Sec. IV.

IV. DISCUSSION

(a) Recently McMillan[2] calculated T_c as a function of electron-phonon coupling constant λ and the electron-electron Coulomb interaction μ^* within the framework of strong-coupling theory. The formula for T_c is given by

$$T_c = \frac{\Theta_D}{1.45} \exp\left(-\frac{1.04(1+\lambda)}{\lambda - \mu^*(1+0.62\lambda)}\right) , \qquad (1)$$

where Θ_D is the Debye temperature. Neglecting the "strong-coupling" correction $(1+0.62\lambda)/(1+\lambda)$ in Eq. (1), one can extract μ^* from the isotope-shift coefficient α of T_c according to the relation

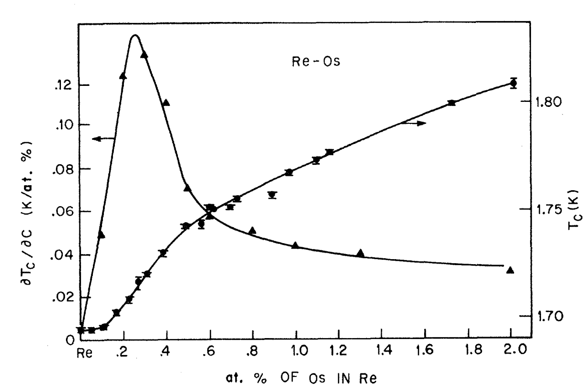

FIG. 4. T_c and $\partial T_c/\partial C$ for slightly doped Re samples.

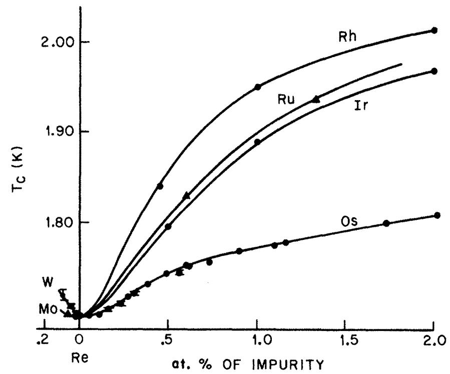

FIG. 5. T_c of Re samples slightly doped with W, Mo, Os, Ir, Ru, and Rh.

$$\mu^* = (1-2\alpha)^{1/2}/\ln(\Theta_D/1.45T_c) . \quad (2)$$

With this theoretical result he concluded that λ does not depend on the density of states but is equal to a constant divided by the ionic mass M times the average phonon frequency $\langle\omega^2\rangle$. He also showed empirically for bcc transition metals and theoretically for the polyvalent metals that this is the case.

In a similar way, λ is obtained empirically from T_c, Θ_D, and α according to Eqs. (1) and (2) for W-Re-Os and Ru-Os hcp alloy systems. The numerical values are tabulated in Table I. For alloys α was determined by linear interpolation between any two of the following values[8]: 0.21 for Re, 0.21 for Os, and 0 for Ru. λ is plotted in Figs. 1 and 3 as a function of alloy concentration. The renormalized density of states[9] $N_{bs}(0)$ at the Fermi surface found from γ using the relation

$$N_{bs}(0) = 3\gamma/2\pi^2 k_B^2 (1+\lambda) \quad (3)$$

is also shown for comparison. k_B in the above equation is the Boltzmann constant. λ scales very well with T_c of the W-Re-Os system but not at all with T_c of the Ru-Os system. And no simple $N_{bs}(0)$ dependence of λ is found for them in contrast to the case of bcc phase. Lack of knowledge of the phonon spectrum for these systems prevents us from making any quantitative check on the $1/M\langle\omega^2\rangle$ dependence of λ. However, since treating $\langle\omega^2\rangle^{1/2}$ as varying in step with Θ_D is a pretty good assumption, we have plotted, in Fig. 6, λ vs $M\Theta_D^2$. Except for the region ranging from ~30- to ~70-at.% Os in Re, λ does

TABLE I. Empirical value of λ and $N_{bs}(0)$ found from T_c, Θ_D, and γ for the hcp 5d transition-metal alloys. Values of Θ_D in parenthesis were obtained by interpolation.

Alloy	at.% second metal	T_c (K)	Θ_D (K)	γ (mJ/mole K^2)	λ	$N_{bs}(0)$ (states/eV atom)	Ref.
Re-W	12	7.5	332	3.76	0.75	0.454	a
	2.4	3.00	(402)		0.558		b
	0.6	1.84	(413)		0.505		b
Re-Os	0	1.695	417	2.31	0.494	0.328	a, b
	5.8	1.93	412	2.28	0.507	0.320	b, c
	11.5	1.79	(398)		0.500		b
	23.2	1.67	(365)		0.495		b
	30	1.54	351	2.05	0.489	0.291	a, b
	36.2	1.35	(346)		0.476		b
	43.2	1.18	(344)		0.461		b
	56	0.94	(355)		0.437		b
	70	0.80	380	1.86	0.416	0.278	a, b
	81	0.73	(413)		0.401		b
	89	0.70	(443)		0.391		b
	100	0.62	500	2.35	0.376	0.362	b, d
Ru-Os	0	0.478	505	3.35	0.411	0.501	b, e
	33.3	0.470	480	2.74	0.394	0.416	b, c, f
	66.6	0.569	448	2.5	0.390	0.380	b, c, f
	90	0.584	432	2.2	0.383	0.338	b, c, f

[a]E. Bucher, F. Heiniger, and J. Muller, in *Proceedings of the Ninth International Conference on Low Temperature Physics, New York*, 1965 (Plenum, New York, 1965), p. 1059.
[b]Present work.
[c]J. P. Maita (private communication).
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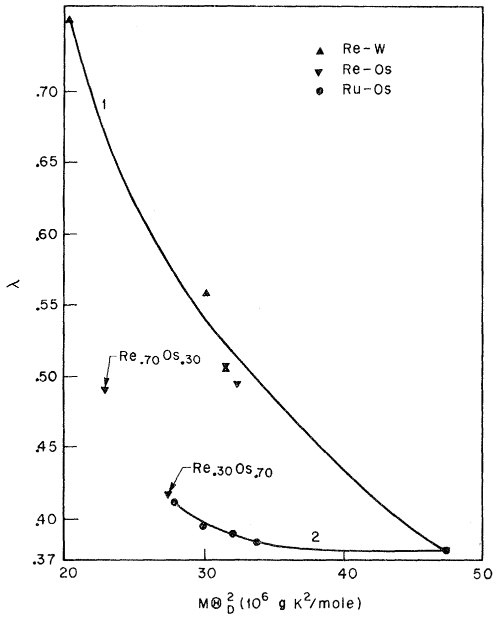

FIG. 6. λ vs $M\Theta_D^2$ for Re-W, Re-Os, and Ru-Os systems.

decrease as $M\Theta_D^2$ ($\propto$ elastic hardness) increases.

No analysis is given for the Re-Ru system because of lack of specific-heat data. But we believe that all that we have discussed for Re-Os will be true for Re-Ru.

(b) It had been shown[3,10] that a peak appears in the $\partial T_c/\partial\epsilon_F$-vs-$\epsilon_F$ curve when Fermi-surface topology of Re changes. The effect on T_c here was obtained with the BCS model through a sudden change in the density of states due to the Fermi-surface-topology variation. Although the role of density of states is overemphasized in the BCS model, the result of Makarov and Baryakhtar[10] is still considered to be qualitatively valid.[11] In Fig. 4, T_c and $\partial T_c/\partial C$ are shown as a function of C for the dilute Re-Os solid solution. Since $\partial T_c/\partial C = (\partial T_c/\partial\epsilon_F) \times(\partial\epsilon_F/\partial C)$ and $\partial\epsilon_F/\partial C$ is a slowly varying function of C, any peak occurs in $\partial T_c/\partial\epsilon_F$ while Fermi-surface topology changes will reflect in $\partial T_c/\partial C$. From Fig. 4 it is easy to find such a peak in $\partial T_c/\partial C$ at critical concentration $C_k = (0.027 \pm 0.05)$-at.% Os in Re. This means that when (0.27 ± 0.05)-at.% Os is introduced into Re, the Fermi level ϵ_F is raised so that $\epsilon_F = \epsilon_k$ where Fermi-surface topology varies. The value of C_k obtained from high-pressure T_c measurements is ~ 0.14 at.%.[3] The difference can be due to the complication, in addition to the shift of ϵ_F involved when Re is hydrostatically compressed.

(c) Various workers[12] had previously studied the effect of a small addition (when the mean free path $\lesssim$ coherence length) of nonmagnetic impurities in superconductors. They found that the small addition generates a *decrease* in T_c which is a universal function of the mean free path, independent of the nature of the specific impurity introduced. Later it was shown theoretically by Markowitz and Kadanoff[12] by considering the removal of anisotropy in electron energy spectrum which was assumed favorable for pair formation.

In Re we observed that T_c always increases with small additions of impurities (see Figs. 5 and 7) in contrast to most other superconductors.[12] The finding in the ternary system agrees with that observed by Doulat *et al.*[13] in the neutron-damage experiment on Re. The band-structure calculations[4] and the low-temperature specific-heat measurements[5] indicate that the electronic density of states increases sharply just below ϵ_F. Impurity scattering will smear out the Fermi level, increase the density of states, and thus enhance T_c. We propose this band-structure smearing due to impurity scattering as an explanation of the T_c increase in slightly doped Re (especially for samples doped with impurities with electron per atom ratio $\mathfrak{z}$ smaller than that of Re), and we examine a simple theoretical model of this effect.

We take a density of states $N_p(\epsilon)$ for pure Re as a smooth part $N_s(\epsilon)$ plus a van Hove singularity at energy ϵ_0 below ϵ_F (neglecting the other singularity at $\epsilon > \epsilon_F$ for a moment):

$$N_p(\epsilon) = N_s(\epsilon) + A(-\epsilon_0 - \epsilon)^{1/2}. \quad (4)$$

The density of states of the dirty material $N_d(\epsilon)$ is then the convolution of $N_p(\epsilon)$ with a Lorentzian

$$N_D(\epsilon) = \int d\epsilon' \frac{N_p(\epsilon')\Gamma}{\pi[(\epsilon-\epsilon')^2 + \Gamma^2]}, \quad (5)$$

where the level width Γ is of the order of $\hbar ne^2\rho/m$ and ρ is the resistivity, n the charge density, e the electronic charge, and m the electronic mass. We find for the increased density of states due to the impurity scattering near the singularity

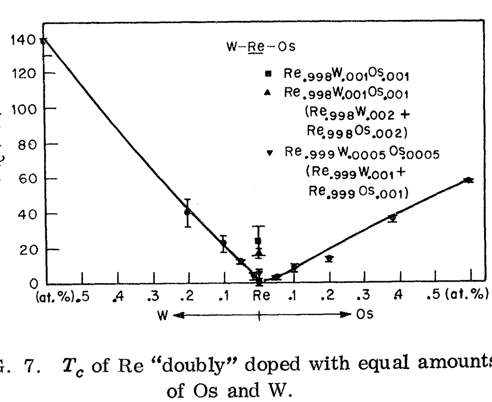

FIG. 7. T_c of Re "doubly" doped with equal amounts of Os and W.

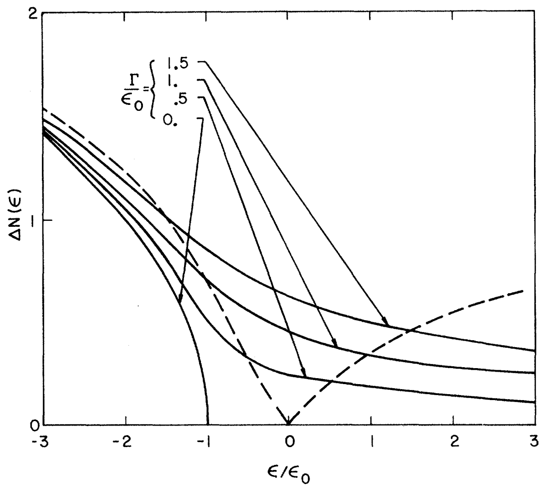

FIG. 8. Effect of band-structure smearing on the density of states.

$$\Delta N(\epsilon) = N_d(\epsilon) - N_s(\epsilon) = \frac{A\Gamma}{(\epsilon + \epsilon_0 + i\Gamma)^{1/2} + (\epsilon + \epsilon_0 - i\Gamma)^{1/2}} . \qquad (6)$$

This function is plotted in Fig. 8 for several values of Γ. The change of the density of states of a binary alloy series is shown by the dashed line of the same figure. Adding impurities of $\mathfrak{z}$ smaller (larger) than that of Re varies ϵ_F and moves one to the left (right) in Fig. 8; it also increases the resistivity and one moves up the series of curves $\Gamma/E_0 = 0$, 0.5, 1, etc. This process traces out the dashed curve.

The transition temperature is given approximately by the BCS expression

$$T_c \sim \Theta_D \exp[-1/N_d(\epsilon_F)V] , \qquad (7)$$

with V the electron-phonon interaction and the change in T_c on doping is

$$\frac{\Delta T_c}{T_c} = \frac{\Delta N(\epsilon_F)}{N_s \ln(\Theta_D/T_c)} , \qquad (8)$$

so that the T_c curve on alloying is the same shape as the dashed curve of Fig. 8. Initially T_c increases linearly with solute concentration and then flattens out. For the ternary system $Re_{1-2x}W_xOs_x$ one is increasing ρ without changing $\mathfrak{z}$ and one marches vertically up the curves in Fig. 8; this produces a linear initial increase in T_c which flattens out at higher concentration.

The study on T_c of Re and slightly doped Re at atmospheric pressure and at high pressure[3] demonstrates the existence of a critical energy (corresponding to a Fermi-surface-topology change) slightly above the Fermi level. According to Markarov and Baryakhtar,[10] Fermi-surface-topology change of this kind will also result in a rise in T_c over the critical region[1] $\epsilon_k - k_B\Theta_D \lesssim \epsilon_F \lesssim \epsilon_k + k_B\Theta_D$ as ϵ_F is shifted toward ϵ_k from below. Since $\epsilon_k - \epsilon_F \simeq 10^{-3}$ Ry and $k_B\Theta_D \simeq 2\times10^{-3}$ Ry for Re, any introduction of small amounts of nonmagnetic impurities with larger $\mathfrak{z}$ than that of Re will thus increase T_c. To differentiate this effect from the band-structure smearing mechanism in Re, more careful quantitative calculation is needed. However, the sometimes increasing and sometimes decreasing impurity effect on T_c of Tl[4,5] can be explained satisfactorily in terms only of the Fermi-surface-topology mechanism as will be shown later. This may be due to the absence of a singularity in the electron energy spectrum below ϵ_F of Tl.

Tl is the only other superconducting element which exhibits an anomalous pressure effect on its T_c. Lazarev and co-workers[14] had demonstrated that, like Re there exists an ϵ_k slightly above ϵ_F of Tl. Quinn and Budnick[15] and Lazarev *et al.*[16] found that T_c of Tl is enhanced by adding small amounts of Bi, Pb, and In but is suppressed by Hg, Cd, and Sb. The latters[16] were the first to suggest without explanation that this unusual impurity effect might be associated with the positive pressure effect (at pressure $\lesssim$ 2 kbar) on T_c of Tl. Now the reason for this correlation is clear. Small additions of Bi and Pb with more valence electrons to Tl cause ϵ_F to move up toward ϵ_k while that of Hg and Cd with less valence electrons do the opposite. Hence T_c increases for Tl doped with Bi and Pb but decreases for Tl doped with Hg and Cd. As for the case of In-doped Tl, increase of T_c can be understood in terms of the internal-pressure effect induced by In which has a smaller atomic volume than Tl. 0.1% of In in Tl is estimated to correspond to ~150 bar which is bigger than the critical pressure to induce the Fermi-surface-topology change. While for Sb-doped Tl, the combination effect of internal pressure and increase of valence electrons has raised ϵ_F above ϵ_k. Hence T_c drops.

V. CONCLUSION

(a) There is no simple direct correlation between T_c and $N_{bs}(0)$ observed in the hcp transition-metal alloys in contrast to that observed in the bcc ones. The rapid and irregular T_c variation with concentration for the hcp W-Re-Os system can be accounted for by the similar λ variation determined empirically with McMillan's formula. λ behaves with hardness ($\sim M\Theta_D^2$) the way McMillan's theory predicts at both ends of the W-Re-Os system and over the whole region of Ru-Os system. In spite of the above success the following remains puzzling: λ does not scale with $1/M\Theta_D^2$ between ~30- and ~70-at.% Os in Re. An independent method not involving T_c to determine μ^* seems to be crucial at this point.

(b) The Fermi-surface-topology change in Re by the alloy is observed as is evident by the appearance of a sharp peak in the $\partial T/\partial C$-vs-C curve. The critical concentration so determined is (0.27 ± 0.05) at.% of Os in Re.

(c) Small additions of nonmagnetic impurities to Re is found to enhance the T_c. This is explained in terms of the effects of band-structure smearing by impurity scattering near a singularity below ϵ_F and the Fermi-surface-topology change at a singularity above ϵ_F. The anomalous impurity influence on T_c of slightly doped Tl is understood by using only the Fermi-surface-topology change mechanism.

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†Part of the T_c results is taken from C. W. Chu's Ph. D. thesis, University of California, San Diego, Calif., 1968. Work at San Diego was sponsored by the Air Force Office of Scientific Research under Grant No. AF-AFOSR-631-67.

‡Also of Applied Physics and Information Science Department, University of California, San Diego, Calif. Research supported by the U. S. Atomic Energy Commission under Contract No. AT(04-3)-34.

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[9]Values of $N_{bs}(0)$ for Re, $Re_{0.88}W_{0.12}$, $Re_{0.70}Os_{0.30}$, and $Re_{0.30}Os_{0.70}$, first evaluated by McMillan in Ref. 2, are slightly different from ours because of the different α used by us.

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[11]A similar result is believed obtainable from the possible peculiar phenomenon in the phonon spectrum or in the electron-phonon interaction due to the sudden change in N. However, this anomaly in λ, if any, is not large enough to show up in our analysis.

[12]Recently J. E. Crow, M. Strongin, R. S. Thompson, and O. F. Kammerer, Phys. Letters 30A, 161 (1969) found that T_c of W, Mo, and Re films are enhanced. They attributed this to the smearing of $N(0)$ where a valley was assumed to exist. However, it is not clear both from the band-structure calculation (Ref. 4) and specific-heat measurements (Ref. 5) that this valley is in existence at ϵ_F of Mo and Re. Also see D. Markowitz and L. Kadanoff, Phys. Rev. 131, 563 (1963), and references therein.

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Thermal Conductivity of Superconducting Niobium†

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The thermal conductivity of single-crystal superconducting niobium has been measured in the temperature range 0.04–4 K. No evidence is found either for thermal transport or for phonon scattering by electrons associated with a second energy gap.

The possibility that superconducting transition metals may exhibit two distinct energy gaps was suggested by Suhl *et al.*[1] This two-band model has since been used in the analysis of data on specific heat,[2–5] critical field,[6] upper critical field,[7,8] penetration depth,[9] and tunneling.[10–13] Generally, the data for Nb are consistent with $\Delta_s/\Delta_d \simeq 10^{-1}$ and $N_s/N_d \simeq 10^{-2}$–10^{-1}, where Δ is the energy gap and N