Superconductivity in Mo-Re and Nb-Ir σ Phases*

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Superconducting transition temperatures and low-temperature specific-heat capacities were measured for well-characterized Nb-Ir and Mo-Re σ-phase alloys. The transition temperatures T_c, and the electronic specific-heat-capacity coefficients γ were found to vary only slowly with composition in these alloys. By considering data from the literature on other σ-phase alloys as well as our own data, it was concluded that no clear correlation could be made between T_c and γ [and therefore the electronic density of states at the Fermi level $N_{bs}(0)$]. Good correlation was obtained, however, between McMillan's electron-phonon coupling constant λ and T_c. This suggests that the phonon spectrum may be more important than the electronic density of states at the Fermi level in controlling T_c for σ phases. The high value of T_c (9.8 °K) reported in the literature for the Nb-40 at.% Ir σ phase is believed to be due to small quantities of a second superconducting phase.

INTRODUCTION

The σ phases, which can exist over wide ranges of composition, comprise one of the largest groups of superconducting intermediate phases. The σ phase is tetragonal $D8_b$ with 30 atoms per unit cell in five nonequivalent crystallographic positions. Detailed x-ray[1,2] and neutron-diffraction studies[3] have revealed chemical ordering on these sites with at least two basically different ordering schemes. σ phases usually occur in a transition-metal alloy system at average group numbers (AGN) of between 5.6 and 7.5.[4]

Superconductivity has been observed in many σ phases.[5] It has been suggested[6] that the σ-phase superconducting transition temperatures follow the empirical Matthias rules with a maximum transition temperature T_c near an AGN of 6.5. While there may be a statistical justification for this statement, an examination of the data[5] indicates no such clear trend.

This paper reports a study of superconductivity in Nb-Ir and Mo-Re σ phases as a function of composition. These alloys were selected for study because of the following: (i) According to the literature,[5] Nb-Ir exhibits a wide variation of T_c with composition (AGN) while the T_c of the Mo-Re σ phase varies slowly with AGN. (ii) The chemical ordering schemes in these σ phases fall into two different classes.[2] Since all of the attempts to explain T_c from extensions of the Bardeen-Cooper-Schrieffer (BCS) theory require a knowledge of the electronic specific-heat-capacity coefficient γ and the Debye temperature Θ_D, as well as T_c, the measurement of low-temperature specific-heat capacity was selected as the principal experimental technique.

PREVIOUS WORK

Superconducting transition temperatures have been reported for the Nb-Ir and Mo-Re σ phases by several investigators. Compton et al.[7] and Bucher et al.[8] found a T_c of 9.8 °K for the Nb-40 at.% Ir σ phase and Blaugher and Hulm[6] found a T_c of 7.9 °K for the Nb-37.5 at.% Ir σ phase. However, Bucher et al.[9] report a T_c of 2.4 for the Nb-37 at.% Ir σ phase. Thus, there is an apparent dramatic change in T_c with composition in this system. Values of γ of 2.78 mJ/mole deg^2 and Θ_D of 330 °K were reported for the Nb-37 at.% Ir alloy.[10]

Blaugher et al.[11] reported a nearly constant T_c of 5.7-5.9 °K from Mo-55 at.% Re to Mo-67 at.% Re for the Mo-Re σ phase. Other investigators found other values for T_c,[7,8,10] but with the exception (8.4 °K for a Mo-58 at.% Re alloy[8]) all fall in the 6-7 °K range and no marked variation with composition was noted. Values of γ of 3.31 mJ/mole deg^2 and Θ_D of 351 °K were reported for the Mo-58 at.% Re σ phase.[10] The above transition temperature values are summarized in Table I.

The chemical ordering schemes for various σ phases were summarized by Spooner and Wilson.[2] Since both the chemical nature and size of the atom influence ordering in the σ phases, the resultant

TABLE I. Values of critical temperature for Nb-Ir and Mo-Re σ phases from the literature.

Alloy	AGN	T_c (°K)	Ref.
Nb-37 at.% Ir	6.48	2.40	9
Nb-37.5 at.% Ir	6.50	7.90	6
Nb-38.5 at.% Ir	6.54	9.70	8
Nb-40 at.% Ir	6.60	9.80	7
Nb-41 at.% Ir	6.64	9.80	8
Mo-50 at.% Re	6.50	6.40	8
		7.30	7
Mo-55 at.% Re	6.55	5.90	11
Mo-58 at.% Re	6.58	6.35	10, 8
		8.40	8
Mo-62 at.% Re	6.62	5.70	11
Mo-67 at.% Re	6.67	5.80	11

schemes are complex. However, the ordering schemes are clearly different for the Nb-Ir and Mo-Re σ phases.

EXPERIMENTAL

Specimen Preparation

Specimens were prepared from starting material having a purity of better than 99.9%. Niobium dendritic powder was obtained from CIBA Ltd., iridium powder from Engelhard Industries, molybdenum rod from Fansteel Corporation, and rhenium rod from Chase Brass and Copper Corporation. The Nb-Ir alloys were prepared by pressing the mixed powders into pellets and then sintering at 1000 °C in a vacuum better than 10^{-6} Torr. After sintering, the Nb-Ir pellets were arc melted on a water-cooled copper hearth using a nonconsumable electrode in a partial pressure of purified argon. The alloys were turned and remelted at least six times. Melting losses were negligible and nominal compositions were accepted as being correct. The Mo-Re alloys were arc melted as above from weighed pieces of the as-received metal rods.

The as-cast Nb-Ir and Mo-Re alloys were homogenized *in vacua* of better than 10^{-8} Torr, at 1600 and 1800 °C, respectively. Chemical analyses for interstitial elements were performed on the homogenized alloys and the results are presented in Table II. Alloys were prepared with nominal compositions of Nb−34, −37, −38.5, −40 at.% Ir and Mo−55, −60, −65 at.% Re.

Specimen Characterization

Optical metallography was performed on small sections of the alloys which were spark machined from the ingot. The specimens were mounted in Epoxy molds and mechanically polished. The Nb-Ir alloys were etched in solutions of 25% HNO_3, 25% H_2SO_4, 25% HF, and 25% H_2O, while the Mo-Re alloys were etched in 50% H_2O_2−50% NH_4OH solutions. Repeated polish-etch cycles were required to remove surface cracks apparently caused during coarse polishing in these extremely brittle materials. Microhardness measurements were made on the metallographic samples.

X-ray patterns were taken from crushed alloy powders. Since the alloys were so brittle, annealing the powders after crushing was not necessary. The powders were placed in glass capillaries and exposed to either $Cu K\alpha$ or $Cr K\alpha$ radiation in a con-

ventional Debye-Scherrer camera. The patterns were indexed and precise lattice parameters were calculated using a computer program described previously.[12]

Low-Temperature Measurements

The specific-heat capacities were measured using techniques that have been described previously.[13] In brief, an adiabatic calorimeter was placed inside a superconducting solenoid capable of producing fields up to 40 kG. A synthetic addendum (0.1237 g) was used with carefully weighed parts (graphite resistor, manganon wire, and varnish). The addendum heat capacity was established by measurement with a copper standard specimen and this result was in close agreement with the known specific-heat capacities of the constituent parts. The value was 1−5% of the alloy-specimen specific-heat capacities in the temperature range 1−4.5 °K. The graphite resistor was calibrated against the vapor pressure of He^4 after each cooling to low temperatures and with the magnetic field applied after cooling.

The superconducting transition temperatures were determined both from the specific-heat-capacity measurements and by an ac susceptibility technique which has been described previously.[14] The transition temperature was defined at the midpoint of the respective transition.

RESULTS

Specimen Characterization

With the exception of the Nb−40 at.% Ir alloy, all the alloys prepared were single phase as deter-mined by optical metallography. X-ray diffraction confirmed that the structure was that of the σ phase and lattice parameters were determined. In agreement with previous work,[15] the lattice parameters varied slowly with composition for both the Nb-Ir and Mo-Re alloys. Microhardness measurements on the metallographic specimens gave values of about 1000 kg/mm² for the Nb-Ir alloys and 1500 kg/mm² for the Mo-Re alloys. There was little variation of hardness as a function of composition in both systems. The lattice parameter and hard-ness data are summarized in Table III.

The Nb−40 at.% Ir alloy showed small amounts of a second phase in the optical microstructure. The amount of second phase present was below the limit of detection of the x-ray diffraction patterns, but quantitative metallography was used to estimate the amount at about 2% by volume. According to the published Nb-Ir phase diagram[16] this second phase is presumably the α_1 phase which has the tetragonal AuCu-type structure.

Low-Temperature Measurements

The Nb-Ir alloys had sufficiently low T_c's that

TABLE II. Typical interstitial analyses homogenized alloys.

	H(ppm)	N(ppm)	O(ppm)	C(ppm)
Nb−37 at.% Ir	8	1	70	96
Mo−55 at.% Re	3	3	260	66

TABLE III. Lattice-parameter and microhardness data.

Alloy	a_0(Å)	c_0(Å)	c_0/a_0	Atomic volume (Å³)	Microhardness (kg/mm²)
Nb–34 at.% Ir	9.892 ± 0.001	5.072 ± 0.003	0.5127	16.54	965 ± 50
Nb–37 at.% Ir	9.869 ± 0.001	5.062 ± 0.002	0.5129	16.43	1010 ± 65
Nb–40 at.% Ir	9.842 ± 0.001	5.045 ± 0.002	0.5126	16.29	975 ± 50
Mo–55 at.% Re	9.602 ± 0.001	4.984 ± 0.002	0.5191	15.32	1500 ± 40
Mo–60 at.% Re	9.595 ± 0.001	4.984 ± 0.002	0.5194	15.29	1500 ± 50
Mo–65 at.% Re	9.588 ± 0.001	4.983 ± 0.002	0.5197	15.27	1505 ± 60

an appreciable linear range of C/T vs T^2 was obtained without applying a magnetic field to suppress the normal-to-superconducting transition. However, this was not the case for the Mo-Re alloys; therefore, the specific-heat-capacity measurements were made in an applied magnetic field of 35 kG. Typical data for each alloy system are illustrated in Fig. 1 for the Nb–37 at.% Ir alloy in zero field and the Mo–55 at.% Re alloy in a field of 35 kG.

The electronic specific-heat-capacity coefficient γ and the Debye temperature Θ_D were determined from a least-squares fit of the data, assuming the relationship $C = \gamma T + \beta(T/\Theta_D)^3$ is valid over the temperature range considered. The values determined for γ and Θ_D are listed in Table IV and are plotted along with values from the literature against AGN in Fig. 2. There is little change in γ or Θ_D vs AGN for the Nb-Ir σ-phase alloys. The Mo-Re alloys show a steady decrease in γ with increasing AGN while the Θ_D values go through a minimum near an AGN of 6.6.

The transition temperatures measured by ac susceptibility for the Mo-Re alloys are plotted along with literature values against AGN in Fig. 3. With the exception of one literature value for Mo–58 at.% Re, the present work is in reasonable agreement with the values from the literature.

The transition temperatures for Nb-Ir alloys are plotted in Fig. 4 along with the literature values from Table I. Our measurements indicate an essentially constant value of T_c across the entire

σ-phase field. For alloys near Nb–40 at.% Ir, literature values of about 9.8 °K are in contrast to our values of about 2.2 °K. Our specific-heat-capacity measurement of T_c for the Nb–40 at.% Ir specimen clearly indicated the bulk of the sample, therefore the σ phase, to have the lower transition temperature. However, transitions were detected by the ac susceptibility technique at 8.7 and 7.7 °K for two separate melts of the Nb–40 at.% Ir alloy. In each case the bulk of the specimen had the 2.2 °K transition so that we must attribute the higher transition temperatures to the second phase which was observed by optical metallography.

DISCUSSION

It was disappointing to observe that T_c, γ, and Θ_D varied only slowly in both the Nb-Ir and the Mo-Re σ phases. The dramatic changes in T_c as a function of composition for the Nb-Ir σ phase reported in the literature, which prompted its selection for this study, were not observed. The present work shows that alloys near the Nb–40 at.% Ir composition exhibit transitions near 8–9 °K because of the presence of a second superconducting phase, while the σ phase has a T_c value of 2.2 °K, nearly independent of composition.

Since the Mo-Re σ phase decomposes below 1150 °C into the bcc and α-Mn structures,[17] it is possible the single high value of T_c reported[8] for the Mo–58 at.% Re alloy of 8.4 °K is due to the α-Mn structure, which has such a value for T_c near

TABLE IV. Parameters from low-temperature measurements.

Alloy	AGN	T_c (°K)	γ (mJ/mole deg²)	Θ_D (°K)	$N_{bs}(0)$ (states/eV atom)	λ
Nb–34 at.% Ir	6.36	2.25	3.037	388	0.431	0.495
Nb–37 at.% Ir	6.48	2.23	3.043	384	0.431	0.495
Nb–38.5 at.% Ir	6.54	2.16				
Nb–40 at.% Ir	6.60	2.20	2.985	371	0.423	0.497
	Second phase	7.70				
		8.73				
Mo–55 at.% Re	6.55	6.47	3.434	388	0.444	0.639
Mo–60 at.% Re	6.60	6.49	3.200	355	0.409	0.657
Mo–65 at.% Re	6.65	5.60	3.116	386	0.409	0.614
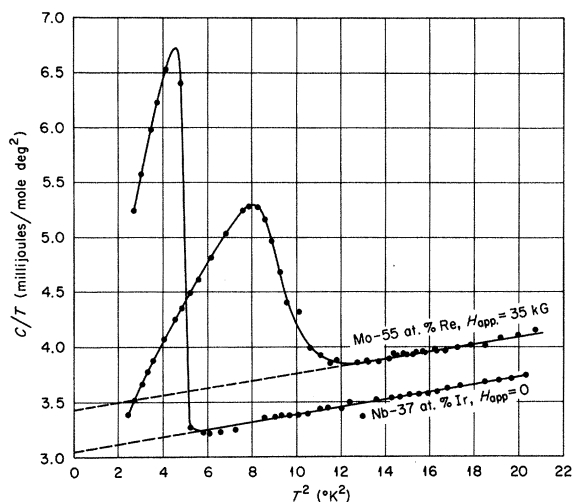
FIG. 1. Typical specific-heat-capacity data.

FIG. 3. Transition temperature T_c vs AGN for Mo-Re σ phases.

the α/σ + α-Mn phase boundary.[11]

Atomic ordering can markedly affect the T_c of A-15 compounds, as has been clearly demonstrated by Blaugher et al.[18] Changes in the complex ordering scheme for the σ phases are apparently of little significance in changing T_c, since T_c is so insensitive to composition ("stoichiometry") in most of
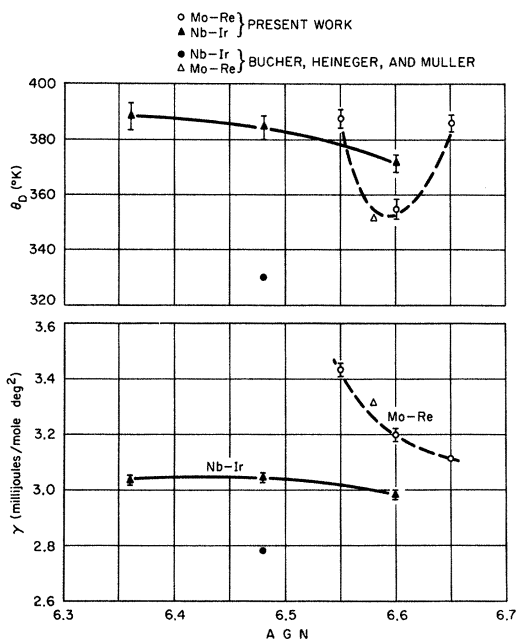

FIG. 2. Debye temperature (Θ_D) and electronic specific-heat-capacity coefficient γ vs AGN for Nb-Ir and Mo-Re σ phases.

the σ phases. A single attempt to change the chemical order by long-time low-temperature (800 °C) annealing of a Nb-37 at.% Ir alloy was unsuccessful.

Interstitial impurity level may have an effect on the T_c's of σ phases. In order to check the magnitude of such an effect, two samples which had been tested previously, were annealed in a partial pressure of air. The Nb-38.5 at.% Ir and Nb-40 at.% Ir samples were held at 1000 °C for 16 h in a vacuum of 10^{-2} Torr. The T_c of the single-phase Nb-38.5 at.% Ir alloy increased from 2.16 to 3.70 °K. The transition was broad with a "tail" extending up to 4.08 °K. Both phases in the Nb-40 at.% Ir alloy showed an increase in T_c, from 2.20 to 3.7 °K (σ phase) and from 7.70 to 8.10 °K (second phase). The breadth of the transition was presumably related to a gradient in interstitial impurity concentration. The contamination of the Nb-Ir alloys did not change their optical microstructures. Chemical analyses showed a small increase in interstitial H, N, and C, but a marked increase in O. The contamination procedure increased the over-all oxygen content of the Nb-Ir samples from 70 to 260 ppm. The local oxygen concentrations near the specimen surface were presumably appreciably higher than these average values. Increases in T_c with interstitial impurity content are consistent with previous observations on elements from group VII of the Periodic Table,[19] that is, near the AGN where σ phases occur. Both technetium and rhenium have lower T_c's when they are purified
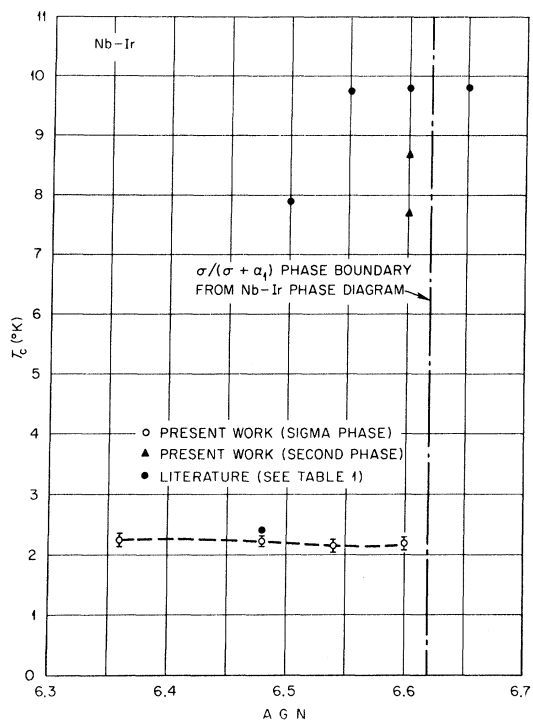
FIG. 4. Transition temperature T_c vs AGN for Nb-Ir σ phases.

known, in general, it has been calculated for a number of materials from the above equations using measured quantities of T_c, Θ_D, and γ. In particular, Morin and Maita[21] calculated V for a number of transition metals and found it to be relatively constant. Since Θ_D doesn't change dramatically, it has been assumed that the variation of T_c in the Periodic Table was due to variations in $N(0)$. This assumption has been substantiated in central ($4 \leq$ AGN < 8) transition metals and alloys,[22] since γ was found to qualitatively follow the variation of T_c with AGN. Maxima in T_c vs AGN in compound superconductors also have been rationalized as resulting from peaks in $N(0)$, although there are less specific-heat-capacity data to support these claims.[23]

We find no clear correlation of T_c with AGN or with γ for the Nb-Ir or Mo-Re σ phases. In fact, we can see no such correlations when the data for T_c (Ref. 5) and γ (Ref. 24) available from the literature are plotted vs AGN in Fig. 5. It is evident that several alloy systems show little variation in T_c with composition across the AGN of 6.5, where the peak in T_c for σ phases was proposed.[6] In particular, the W-Re σ phase shows almost constant T_c vs AGN, and since W and Re are neighbors in the Periodic Table, they would be most likely to obey any

with respect to interstitial impurities. A more extensive study of the role of interstitial contamination on σ-phase superconductivity is presently being carried out in the authors' laboratory.

The above work shows interstitial impurities can influence the transition temperatures of the σ phases. This must be kept in mind when systemizations of T_c data obtained from the literature are attempted, since in most cases the details of the chemistry and microstructure are not provided. With this warning, however, correlations will now be outlined, taking the available literature data at face value.

There have been several attempts[20,21] to systematize T_c in the transition metals using the BCS expression

$$k_B T_c = (\hbar \omega_0 / 1.45) \, e^{-1/g} \ ,$$

with the approximations

$$k_B \Theta_D \cong \hbar \omega_0, \qquad g_{BCS} = N(0) V,$$

$$N(0) = 3\gamma / 2\pi^2 k_B^2 \ ,$$

where $N(0)$ is the electronic density of states at the Fermi level, $\hbar \omega_0$ is a characteristic phonon energy, k_B is Boltzmann's constant, and V is the net interaction energy between electrons. While V is un-
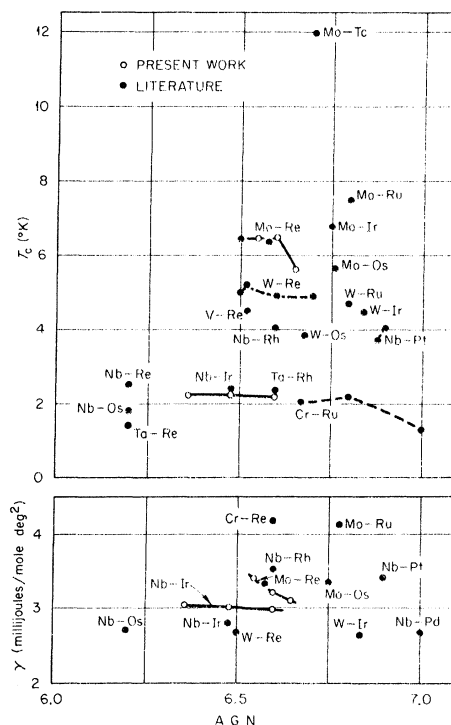

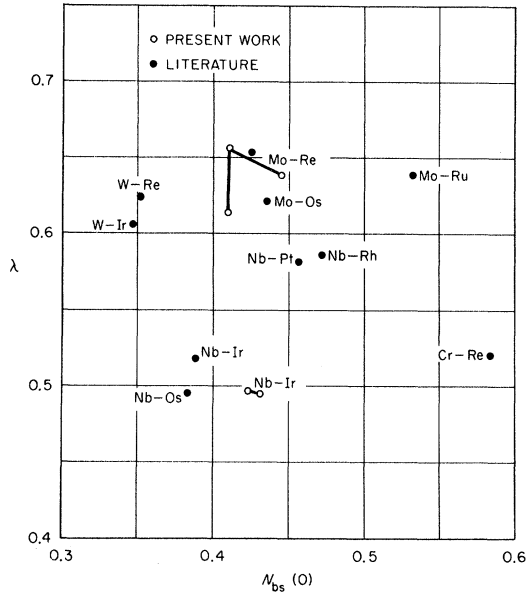FIG. 5. Transition temperature T_c and electronic specific-heat-capacity coefficient γ vs AGN for σ phases.

FIG. 6. McMillan electron-phonon coupling constant
λ vs band-structure density of electronic states $N_{bs}(0)$
for σ phases.
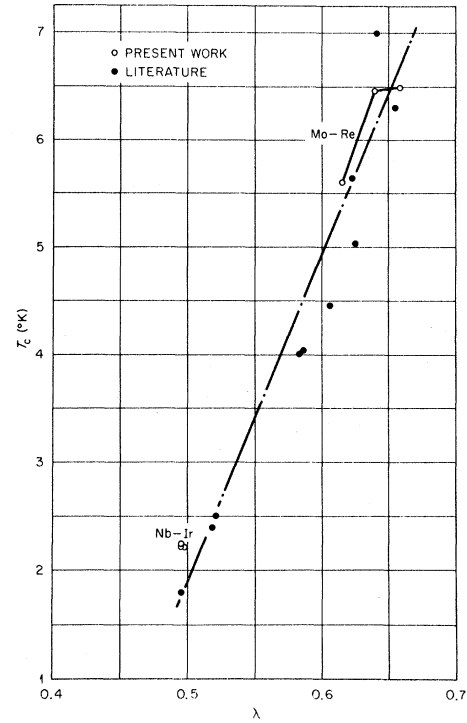
FIG. 8. Transition temperature T_c vs McMillan
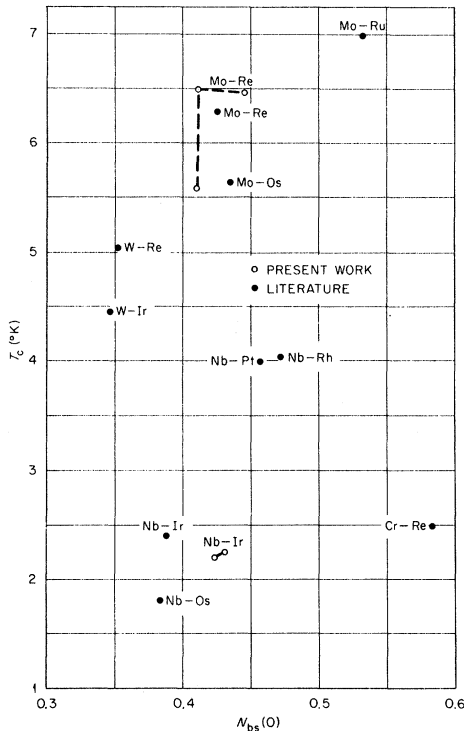electronic-phonon coupling constant λ for σ phases.

FIG. 7. Transition temperature T_c vs band-structure
density of electronic states $N_{bs}(0)$ for σ phases.

"rigid-band" scheme for a variation of $N(0)$. It was
previously shown[9] that the magnetic susceptibility
χ could not be correlated with T_c for σ phases. This
is consistent with the present work since χ is also
related to $N(0)$.

McMillan[25] has extended the BCS formulation to a
treatment more applicable to the transition metals.
He used the strong-coupled treatments of the BCS
model to calculate T_c as a function of the electron-
phonon and electron-electron coupling constants.
He derived the following relation for T_c:

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

where Θ_D is the Debye temperature, λ is the elec-
tron-phonon coupling constant, and u^* is the Coulomb
"pseudopotential" of Morel and Anderson.[26] This
equation is the result of a numerical solution as-
suming the phonon density of states of niobium. Us-
ing an "average" empirical value of $u^* = 0.13$, λ can
be calculated from Θ_D and T_c as

$$\lambda = \frac{1.04 + 0.13\,\ln(\Theta_D/1.45\,T_c)}{0.92\,\ln(\Theta_D/1.45\,T_c) - 1.04} .$$

The band-structure density of electronic states
$N_{bs}(0)$, which approximately takes out the enhance-
ment to γ of electron-phonon interactions, can be

calculated[25] by

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

McMillan[25] found that λ varied with AGN in the same manner as $N_{bs}(0)$ for a number of transition-metal alloys. Plots of λ vs $N_{bs}(0)$ gave nearly linear relationships for the $3d$, $4d$, and $5d$ transition metals, respectively. Blaugher et al.[18] observed the same sort of behavior for A-15 compounds containing V or Nb with separate lines for the V_3X and Nb_3X compounds.

No clear relationship of λ with $N_{bs}(0)$ was observed for the σ phases. Figure 6 is a plot of λ vs $N_{bs}(0)$ for the σ phases for which values of T_c, Θ_D, and γ were available in the literature[5,24] along with those obtained from the present work. With the data available, there does not appear to be a correlation of λ with $N_{bs}(0)$. We also note from Fig. 7 that there is no obvious correlation between T_c and $N_{bs}(0)$. Thus, it would appear that the density of electronic states $[N_{bs}(0)]$ is not an important factor in determining T_c for the σ phases.

However, T_c is found to be very sensitive to the electron-phonon coupling constant λ, as illustrated in Fig. 8. This is not surprising since Θ_D is relatively constant for the σ phases and there is thus a direct functional relationship between T_c and λ. In turn, λ has been found[25] to depend mainly on the phonon frequencies and is insensitive to large variations in the electronic density of states. That $N_{bs}(0)$, as long as it is relatively large, is not the major parameter of interest for systematizing T_c in the transition metals has been proposed recently by Hopfield.[27] His expression for the electron-phonon coupling constant λ is a quotient of two parameters with a short-range or "chemical" nature. One of these parameters, the mean vibrational frequency, is a characteristic of the bonding; the other is an atomic property which is essentially constant within a given type of bonding. Thus, this theoretical treatment as well as empirical observations on hardness[28] and melting points[29] indicate short-range "bonding" parameters may be controlling T_c in certain transition-metal alloys and compounds. This would appear to be the case for the σ phases.

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[1]C. G. Wilson, Acta Cryst. 16, 724 (1963).

[2]F. J. Spooner and C. G. Wilson, Acta Cryst. 17, 1533 (1964).

[3]J. S. Kasper and R. M. Waterstrat, Acta Cryst. 9, 289 (1956).

[4]M. V. Nevitt, in Electronic Structure and Alloy Chemistry of the Transition Elements, edited by P. A. Beck (Wiley, New York, 1963), pp. 106–107.

[5]B. W. Roberts, in Intermetallic Compounds, edited by J. H. Westbrook (Wiley, New York, 1967), p. 597.

[6]R. D. Blaugher and J. K. Hulm, J. Phys. Chem. Solids 19, 134 (1961).

[7]V. B. Compton, E. Corenzwit, J. P. Maita, B. T. Matthias, and F. J. Morin, Phys. Rev. 123, 1567 (1961).

[8]E. Bucher, F. Heiniger, and J. Müller, in Proceedings of the Eighth International Conference on Low Temperature Physics, London, 1962, edited by R. O. Davies (Butterworths, Washington, D. C., 1963), p. 153.

[9]E. Bucher, F. Heiniger, and J. Müller, Helv. Phys. Acta 34, 843 (1961); in Proceedings of the Eighth International Conference on Low Temperature Physics, London, 1962, edited by R. O. Davies (Butterworths, Washington, D. C., 1963), p. 153.

[10]E. Bucher, F. Heiniger, and J. Müller, Physik Kondensierten Materie 2, 210 (1964).

[11]R. D. Blaugher, A. Taylor, and J. K. Hulm, IBM J. Res. Develop. 6, 116 (1962).

[12]D. E. Williams, Ames Laboratory Report No. IS-1052 (computer program modified by H. L. Yakel, Oak Ridge National Laboratory) (unpublished).

[13]G. D. Kneip, J. O. Betterton, and J. O. Scarbrough, Phys. Rev. 130, 1687 (1963).

[14]C. C. Koch and G. R. Love, J. Appl. Phys. 40, 3582 (1969).

[15]W. B. Pearson, A Handbook of Lattice Spacings and Structures of Metals and Alloys (Pergamon, New York, 1967), Vol. 2, pp. 1097–98, 1038.

[16]B. C. Giessen, R. Koch, and N. J. Grant, Trans. AIME 230, 1268 (1964).

[17]R. P. Elliott, Constitution of Binary Alloys (McGraw-Hill, New York, 1965), Suppl. p. 629.

[18]R. D. Blaugher, R. E. Hein, J. E. Cox, and R. M. Waterstrat, J. Low-Temp. Phys. 1, 539 (1969).

[19]K. M. Ralls and J. Wulff, J. Less-Common Metals 11, 127 (1966).

[20]D. Pines, Phys. Rev. 109, 280 (1958).

[21]F. J. Morin and J. P. Maita, Phys. Rev. 129, 1115 (1963).

[22]G. Gladstone, M. A. Jensen, and J. R. Schrieffer, in Superconductivity, edited by R. D. Parks, (Dekker, New York, 1969) Vol. 2, pp. 740–744.

[23]B. W. Roberts, in Intermetallic Compounds, edited by J. H. Westbrook (Wiley, New York, 1967), pp. 588–593.

[24]F. Heiniger, E. Bucher, and J. Müller, Physik Kondensierten Materie 5, 243 (1966).

[25]W. L. McMillan, Phys. Rev. 167, 331 (1968).

[26]P. Morel and P. W. Anderson, Phys. Rev. 125, 1263 (1962).

[27]J. J. Hopfield, Phys. Rev. 186, 443 (1969).

[28]B. T. Matthias, Phys. Letters 25A, 226 (1967).

[29]B. T. Matthias, W. H. Zachariasen, G. W. Webb, and J. J. Engelhardt, Phys. Rev. Letters 18, 781 (1967).