Superconductivity and Electronic Properties of Transition Metal Alloys

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One of the basic problems of superconductivity in the transition metals concerns the expression of the critical temperature T_c as a function of parameters which may be derived from properties of the normal state. The BCS theory suggests a strong dependence of T_c on the dimensionless quantity $N(0)V$, where $N(0)$ denotes the density of states at the Fermi level and V represents an interaction energy. Therefore, T_c may be particularly influenced by appreciable variations of $N(0)$, as is the case in transition metals. On the other hand, the empirical rules of Matthias[1] have generally been successful in describing the variations of T_c in many alloy systems—at least if solid solutions of transition metals with *B*-metals are disregarded.[2] To a very rough approximation, the apparent importance of the number of valence electrons might well be linked with the fact that the rigid band model often (but not always) provides a satisfactory description of these alloys.

Extending the work of previous investigations,[3–8] we have measured the superconducting and calorimetric properties of alloys in the systems Ti–Zr, Nb–Re, Nb–Ru, Nb–Os, Nb–Rh, Nb–Ir, Nb–Pd, Nb–Pt, Cr–Re, Mo–Re, Mo–Ru, Mo–Os, W–Re, and W–Ir.[9,10,11] The low temperature specific heat data of the Ti-Zr alloys are the first, to our knowledge, representing a binary system where the components belong to the same column of the periodic table. The number of valence electrons per atom being constant, these alloys unambiguously offer a test of the correlation between the transition temperature and the electronic density of states. According to the results plotted in Fig. 1,[12,13,14] the transition temperature clearly follows (qualitatively) the variation of the electronic specific heat, which is assumed proportional to $N(0)$. If the data are used to calculate the interaction parameter with the simple BCS expression for T_c, then V is found to rise steadily from Ti to Zr. This conclusion cannot be affected significantly by deviations of the effective phonon spectrum from a true Debye spectrum.

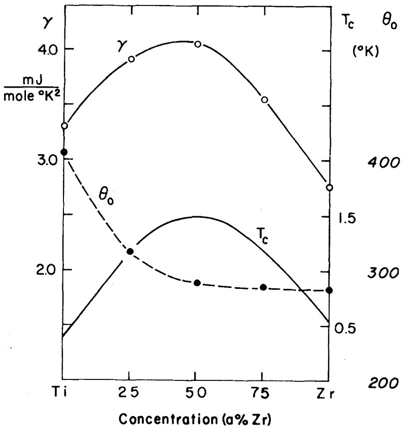

FIG. 1. Coefficient of electronic specific heat γ, Debye temperature $\theta(T = 0)$, and transition temperature T_c, of hcp Ti-Zr alloys. The curve of T_c is smoothed, using values of the following authors: present work, references 12, 13, and 14. Contrary to the behavior of the specific heat, the maximum T_c depends markedly on the heat treatment.

Most of the remaining alloys investigated in the present work belong to a class of complex binary phases, having either the σ-type (D 8_b) or the α-Mn (A 12) crystal structure. With only a few exceptions, these complex phases occur in the region of a mean number of valence electrons between 6 and 7. Within this range of electron concentration, a distinct maximum of the transition temperature has been

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[1] See e.g., B. T. Matthias, T. H. Geballe, and V. B. Compton, Rev. Mod. Phys. **35**, 1 (1963).

[2] We have found, for instance, that T_c of alloys of Vanadium within the bcc homogeneity range is always depressed by the addition of Al, Ga, Si, Ge, or Sn, in spite of the more favorable number of valence electrons than in pure V. For Nb–Sn (solid solution) see also reference 1.

[3] E. Bucher, J. Muheim, and J. Muller, *Proceedings of the Eighth International Conference on Low-Temperature Physics, London, 1962* (Butterworths Scientific Publications Ltd., London, England, to be published).

[4] E. Bucher, F. Heiniger, and J. Muller, *Proceedings of the Eighth International Conference on Low-Temperature Physics, London, 1962* (Butterworths Scientific Publications Ltd., London, England, to be published).

[5] R. D. Blaugher, J. K. Hulm, J. A. Rayne, B. W. Veal, and R. A. Hein, *Proceedings of the Eighth International Conference on Low-Temperature Physics, London, 1962* (Butterworths Scientific Publications Ltd., London, England, to be published).

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

[7] C. H. Cheng, K. P. Gupta, E. C. van Reuth, and P. A. Beck, Phys. Rev. **126**, 2030 (1962).

[8] R. R. Hake, Phys. Rev. **123**, 1986 (1961).

[9] A complete account of these measurements and a description of the experimental technique will be published elsewhere (see Refs. 10 and 11).

[10] E. Bucher, F. Heiniger, and J. Muller (to be published).

[11] J. Muheim and J. Muller (to be published).

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

[13] T. S. Smith, W. B. Gager, and J. G. Daunt, Phys. Rev. **89**, 654 (1953).

[14] T. S. Smith and J. G. Daunt, Phys. Rev. **88**, 1172 (1952).

observed.[4] In certain alloys of this class, the calorimetric determination of the electronic specific heat is complicated by appreciable variations of the Debye θ as a function of temperature, even in the vicinity of T_c. Since, with this kind of substance, no reliable measurements in the normal state below T_c could be expected by the application of available moderate magnetic fields, the data for $T > T_c$ have been completed by a careful measurement of the specific heat in the superconducting state and a calculation of the entropy at some temperature slightly above T_c. With this procedure, the γ values are correct within $\pm 2\%$. As an example, the results for three Nb–Re alloys (A 12 structure) are reproduced in Fig. 2 and 3. These alloys cover the steep rise of T_c near 6.5 electrons per atom and it is found that this again corresponds to an increase in γ.

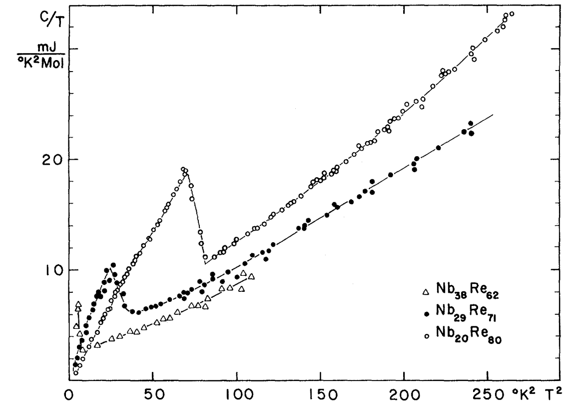

FIG. 2. Atomic specific heat of Nb–Re alloys with A12-type structure.

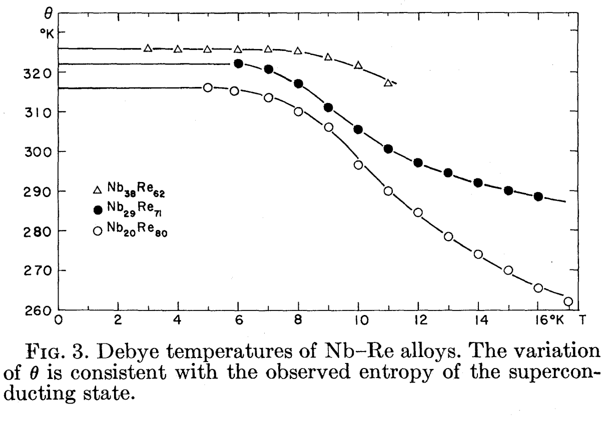

FIG. 3. Debye temperatures of Nb–Re alloys. The variation of θ is consistent with the observed entropy of the superconducting state.

The data for some alloys where a considerable homogeneity range exists are plotted in Fig. 4. It is evident that the observations cannot be accounted for by the simple BCS expression with a constant V. Certain regularities, however, appear if the position of the alloy components in the periodic table is considered. For instance, if we limit comparison to the central part of the transition metals (say from 4 to 7 electrons per atom), then, for a given value of the electronic specific heat, T_c/θ is lower if one or both components are $3d$-elements and higher if the $4d$ or $5d$-character predominates. The results for a number of complex phases[10] not shown in Fig. 4 support this general rule. A somewhat more universal representation of the experimental data is obtained if, according to Morel and Anderson[15] and Garland,[16] the effective Coulomb interaction is taken into account. To obtain a relation between the electronic specific heat and the parameter of the electron–phonon interaction, the latter may be calculated with the aid of observed values and interpolated deviations from the normal isotope effect.[10]

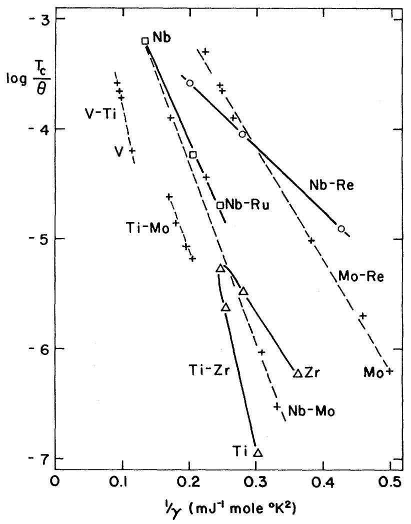

FIG. 4. Observed superconducting and calorimetric data of transition metal alloy systems. Broken lines according to the following references: V-Ti,[7] Ti-Mo,[8] Nb-Mo[5,6], Mo-Re[6].

An interesting empirical fact is noted if the electronic specific heat is analyzed in the superconducting state. The discontinuity at the transition temperature, $(C_{es}/\gamma T)_{T=T_c}$ seems to deviate appreciably from the BCS-value (2.43) if one component is taken from the last columns of the transition elements. In the sequence of the alloys $Mo_{62}Os_{38}$, $W_{72}Ir_{28}$, and $Nb_{62}Pt_{38}$, 2.50, 2.26, and 1.90 have been observed, respectively. Furthermore, the exponential in the superconducting electronic specific heat, which is related to the energy gap and its temperature dependence, is measured as 1.43 for $Mo_{62}Os_{38}$ and 1.26 for $W_{72}Ir_{28}$, to be compared with 1.44 given by BCS.

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

[16] J. W. Garland (to be published).

It would be desirable to know the corresponding figures for pure Os and Ir.

Whilst there is sufficient experimental evidence that, for similar alloys, T_c strongly correlates with the electronic specific heat, it now also seems clear, why in many cases no apparent relation exists between T_c and the observed paramagnetism.[17] In fact, it has been shown for V- and Nb-alloys[18–20] that the measured susceptibility is not indicative of the density of states. If we write

$$\chi_{\text{tot}} = \chi_{\text{ion}} + \chi_{\text{Pauli}} + \chi_{\text{L.P.}} + \chi_{\text{add}}$$

the additional term χ_{add} can be calculated from the observed χ_{tot} and the electronic specific heat (the Landau–Peierls contribution being neglected). According to Clogston *et al.*[18] the value of χ_{Pauli} obtained by the use of γ has to be corrected for attractive interaction by the factor $[1 + N(0)V]^{-1}$. For a series of Nb-alloys, we obtain the results in Table I.

TABLE I. Magnetic susceptibility of niobium alloys.

alloy	structure	electrons per atom	χ_{tot} ($\times 10^{-6}$ emu/g.at)	χ_{add} ($\times 10^{-6}$ emu/g.at)
Nb	A2	5.0	+212	+145
Nb_{90} Ru_{10}	A2	5.3	+176	+140
Nb_{60} Os_{40}	$D8_b$	6.2	+ 98	+ 77
Nb_{38} Re_{62}	A12	6.24	+ 98	+ 82
Nb_{63} Ir_{37}	$D8_b$	6.48	+ 82	+ 61
Nb_{60} Rh_{40}	$D8_b$	6.60	+ 79	+ 49
Nb_{62} Pt_{38}	$D8_b$	6.88	+ 67	+ 40
Nb_{60} Pd_{40}	$D8_b$	7.0	+ 50	+ 29

The large values of χ_{add}, which are likely to be due to the orbital paramagnetism, demonstrate that no similar variation of the transition temperature and the observed susceptibility may be expected. The figures listed for Nb-alloys would suggest that the orbital contribution decreases towards the end of the *d*-band.

A special situation with respect to the occurrence of superconductivity and antiferromagnetism arises in the chromium–rhenium system. Although superconducting Cr-alloys are known already,[21] Cr-base alloys with Re are exceptional in being superconducting within the homogeneity range of the Cr crystal structure. It is seen from Fig. 5 that the maximum transition temperature near the cubic phase boundary exceeds 5°K. The Cr–Re alloys therefore cover an antiferromagnetic and superconducting region[22] without any phase change. Baltensperger and Strässler[23] have shown that a superconducting antiferromagnet may exist, but their model is hardly applicable to the present case. The measurement of the electrical resistance anomaly in dilute Cr–Re mixed crystals has revealed a striking increase of the Néel-temperature of almost a factor of 2 in a very narrow concentration range. Specimens near the composition of 20% Re still exhibit a resistance anomaly as well as a superconducting transition, although for further conclusions, a detailed knowledge of the microstructure is required. A substantial increase of the electronic specific heat has been observed[11] just at this critical composition and is clearly correlated with the abrupt change from the magnetic to the superconducting state.

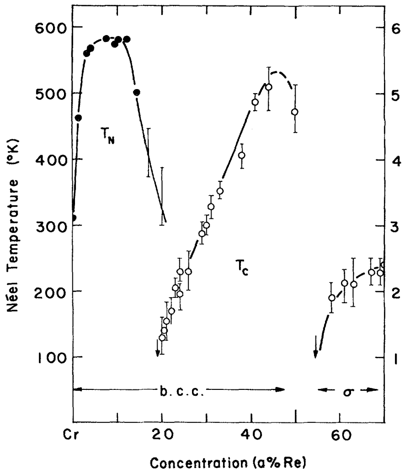

FIG. 5. Antiferromagnetic and superconducting transition temperatures of Cr–Re solid solutions.

ACKNOWLEDGMENTS

We should like to thank T. Binkert and W. Duss for their help with the measurements. This work was supported by the Schweizerische Nationalfonds and the Kredit für Arbeitsbeschaffung.

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[17] E. Bucher, F. Heiniger, and J. Muller, Helv. Phys. Acta **34**, 843 (1961).

[18] A. M. Clogston, A. C. Gossard, V. Jaccarino, and Y. Yafet, Phys. Rev. Letters **9**, 262 (1962).

[19] B. G. Childs, W. E. Gardner, and J. Penfold, Phil. Mag. **8**, 419 (1963).

[20] D. Bender, E. Bucher, and J. Muller, Phys. Kondens. Materie **1**, 225 (1963).

[21] B. T. Matthias, T. H. Geballe, V. B. Compton, E. Corenzwit, and G. W. Hull, Phys. Rev. **128**, 588 (1962).

[22] G. E. Bacon, E. Bucher, W. E. Gardner, F. Heiniger, and J. Muller (to be published).

[23] W. Baltensperger and S. Strässler, Phys. Kondens. Materie **1**, 20 (1963).

Discussion 21

HAKE: We also have made some measurements in the Ti–Zr alloy system [Bull. Am. Phys. Soc. **8**, 419, (1963)]. Our measurements were calorimetric and we measured one alloy Ti–50 at.% Zr. The gamma and the T_c were in reasonable agreement with those shown by Dr. Müller and we came to similar conclusions regarding the applicability of the BCS expression for T_c to the Ti–Zr system. An interesting facet of our work is that in this Ti–50 at.% Zr alloy, we also placed 0.2 at.% manganese. This had the effect of introducing a localized moment as indicated by Dr. Cape's susceptibility measurements. It also succeeded in nearly destroying the bulk calorimetric superconducting transition (down to 1.2°), and strongly suggested that Mn in pure hcp Ti would have a similar deleterious effect on superconductivity, as recently demonstrated by Falge (Discussion 20).

MATTHIAS: What was the transition temperature of your Ti?

HAKE: That's hard to say. We don't actually measure the transition temperature of our starting Ti, but presumably it's about as pure as one can get commercially.

MATTHIAS: I understood from Mr. Falge it was 0.14° for your Ti.

HAKE: Mr. Falge measured some Ti that we furnished, but there is variation in the magnetic impurity concentration from lot to lot in that particular material and we expect, from Falge's work, a corresponding variation in T_c.

FALGE: 0.17°K.

MATTHIAS: Well, Mr. Hake? Pure titanium becomes superconducting above 0.3°K. Yours cannot have been very pure.

E. ROLAND DOBBS, *Royal Society Mond Laboratory:* I would only like to make the point that although the Fermi surface of niobium has not yet been determined, the number of free electrons is far from 5 per atom. We estimate that the Fermi surface area is something like 25% of the free-electron surface or about 0.7 electrons per atom.

Superconductivity in the NbMo System

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INTRODUCTION

The BCS theory of superconductivity[1] with some simplifying assumptions[2] predicts that

$$T_0 = 0.855\theta_D e^{-1/N(0)V}, \qquad (1)$$

where T_0 is the superconducting transition temperature in zero magnetic field, θ_D is the Debye characteristic temperature, $N(0)$ is the density of electronic states at the Fermi surface for one spin orientation, and V is the electron–electron interaction parameter which gives rise to superconductivity.

This above relation, according to Pines,[3] should be particularly simple for the transition metals where the narrow *d* band overlaps the broader *s* band at the Fermi surface. In this case $N(0)$ is now determined almost entirely by the *d*-band state density which is much higher than the corresponding *s* band. He then argues that the most important contribution to V then arises from interactions between the *d*-band electrons, and V should be insensitive to variations in $N(0)$. Hence, for the transition metals, a "decoupling" results between $N(0)$ and V, and V becomes approximately a constant.

Measurements by Hulm and Blaugher[4] first suggested that the Group 5–Group 6 region in the iron group transition metals should furnish an ideal case for studying the predicted BCS dependence of T_0 on parameters such as the density of states and Debye temperature. Pippard[5] emphasized that an experiment evaluating this above equation would provide a critical test of the theory and Pines' suggestion of a constant interaction parameter.

The niobium–molybdenum system was chosen for detailed study due to its apparently large variation of T_0 with composition within a single crystal structure. Furthermore, previous measurements on this alloy system[6] at temperatures below 1°K, had revealed an apparent discrepancy between theory and experiment. These experiments indicated that T_0 de-

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[1] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957).

[2] B. B. Goodman, J. Hillairet, J. J. Veyssie, and L. Weil, in *Proceedings of the Seventh International Conference on Low Temperature Physics* (University of Toronto Press, Toronto, 1961), p. 350.

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

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

[5] A. B. Pippard, remarks at the IBM Conference on Superconductivity, 1961 (unpublished).

[6] J. K. Hulm, R. B. Blaugher, T. H. Geballe, and B. T. Matthias, Phys. Rev. Letters **7**, 302 (1961).