PHYSICAL REVIEW VOLUME 158, NUMBER 2 10 JUNE 1967

Far-Infrared Absorption in Superconducting Niobium Alloys*†

R. L. CAPPELLETTI‡ AND D. M. GINSBERG
Department of Physics, University of Illinois, Urbana, Illinois
AND
J. K. HULM
Westinghouse Research Laboratories, Pittsburgh, Pennsylvania

(Received 16 January 1967)

Far-infrared measurements have been made to determine the superconducting energy gap widths in bulk samples of binary alloys in the system Zr–Nb–Mo. The variation of the gap width 2Δ with concentration is qualitatively similar to the variation of the critical temperature T_c. There is a marked variation in the BCS coupling constant V. The relation between $2\Delta/kT_c$ and V is opposite to that in the simple metals.

I. INTRODUCTION

MOST superconductors have a well-defined energy gap.[1] The width of this gap 2Δ and the superconducting critical temperature T_c have a profound and fundamental effect on the thermodynamic properties and transport processes in the superconductor.[2] Nevertheless, the calculation of 2Δ and T_c from first principles is so difficult that it has been attempted only a few times,[3,4] although empirical rules have been discovered.[5] The factors which would determine these two parameters in an isotropic superconductor are thought to be the electron density of states with one direction of spin in the normal state at the Fermi level N_0, the electron-electron coupling constant V, and the phonon energy $\hbar\omega_p$.

In our experiment, we have determined the way in which 2Δ varies as zirconium or molybdenum are added to niobium. These metals are found next to each other in the periodic table in the order zirconium, niobium, molybdenum. In the concentration range of our samples, the crystal structure is constant.[6] The variation[7] of N_0 ($\sim 130\%$) is much larger than that of other parameters which might affect V and $\hbar\omega_p$, such as the molecular weight ($\sim 1\%$), the atomic volume ($\sim 20\%$), the chemical valence ($\sim 15\%$), and the Debye temperature[7] Θ_D ($\sim 30\%$). This rapid variation of N_0 against a background of more slowly varying quantities is thought to provide shifts in 2Δ which are primarily attributable to the variation of N_0. This fortunate circumstance, together with the existance of published data for T_c, N_0, and Θ_D, accounts for our choice of these alloys. It has been stated that V should be approximately constant for the transition metals[8]; our results, together with values of T_c, are used to test this.

In the interpretation of our results, we will use these relations derived in the BCS theory,[2]

$$2\Delta = 4.01\langle\hbar\omega_p\rangle \exp(-1/N_0V), \qquad (1)$$

$$kT_c = 1.14\langle\hbar\omega_p\rangle \exp(-1/N_0V), \qquad (2)$$

where k is Boltzmann's constant and $\langle\hbar\omega_p\rangle$ is some average phonon energy. The value of 2Δ in Eq. (1) is its value at a temperature $T=0°\text{K}$, but is almost exactly[1,9] the value expected for any temperature $T<0.3T_c$. Our measurements are all made at $T<0.17T_c$. These equations are derived in the weak-coupling limit, which is not strictly applicable. They make no allowance for crystalline anisotropy, and indeed there are excellent theoretical[10,11] and experimental[12,13] reasons for believing that there is very little anisotropy in the superconducting properties of alloys in which the impurity concentration is as high as in our samples. In the BCS theory, the coupling constant V which appears in Eqs. (1) and (2) is assumed to be independent of energy for electrons which are separated in energy from the Fermi surface by less than $k\Theta_D$, and zero otherwise. This approximation is crude but useful. The average phonon energy $\langle\hbar\omega_p\rangle$ is also introduced in a rough way in the theory. It is customary to use the Debye model, and to set

$$\langle\hbar\omega_p\rangle = \tfrac{3}{4}k\Theta_D. \qquad (3)$$

According to Eqs. (1) and (2), we should have

$$2\Delta/kT_c = 3.53, \qquad (4)$$

independent of the other parameters. Observed values

---

[*] Research supported in part by the National Science Foundation.

[†] Based on the Ph.D. thesis of R. L. Cappelletti, University of Illinois, 1966 (unpublished).

[‡] Present address: Physics Department, Iowa State University, Ames, Iowa.

[1] D. H. Douglass, Jr., and L. M. Falicov, in *Progress in Low-Temperature Physics*, edited by C. J. Gorter (North-Holland Publishing Company, Amsterdam, 1964), Vol. IV.

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

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

[4] J. W. Garland, Jr., Phys. Rev. Letters **11**, 114 (1963); and (to be published).

[5] B. T. Matthias, in *Progress in Low-Temperature Physics*, edited by C. J. Gorter (North-Holland Publishing Company, Amsterdam, 1957), Vol. II.

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

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

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

[9] B. Muhlschlegel, Z. Physik **155**, 313 (1959).

[10] P. W. Anderson, J. Phys. Chem. Solids **11**, 26 (1959).

[11] D. Markowitz and L. P. Kadanoff, Phys. Rev. **131**, 563 (1963).

[12] P. L. Richards, Phys. Rev. Letters **7**, 412 (1961).

[13] W. V. Budzinski and M. P. Garfunkel, Phys. Rev. Letters **17**, 24 (1966).

of this ratio range from about 3.2 to 4.6.[1,14,15] We determine whether it is approximately constant for our narrow range of alloys, which all possess the same crystal structure, and which are believed to be homogeneous.

The method we have used to determine the gap width is the measurement of the reflection of far-infrared radiation from the surface of bulk samples.[16,17] An absorption edge is observed at a photon energy which is equal to the gap width, so a rather direct measurement of 2Δ is obtained. The only other means by which such a direct measurement could be made at present would be by electron tunnelling.[1] This has been tried[18] for niobium with 25% zirconium, but the results were anomalous, so no firm estimate of the gap width can be made from them.

II. EXPERIMENTAL METHODS

A. General Remarks

The techniques which we have used were derived by slightly modifying those used previously,[17] and only the modifications will be mentioned here. All of the far-infrared measurements were made at 1.3°K at the University of Illinois, and the samples were prepared at Westinghouse.

B. Sample Preparation

The starting materials were electron-beam melted niobium, iodide crystal bar zirconium, and wrought molybdenum rod made from hydrogen-reduced and hydrogen-sintered ammonium molybdate powder. The major impurities are listed in Table I.

TABLE I. Starting material impurities (ppm).[a]

Impurity	Nb	Mo	Zr
H	5	<5	4
C	40	<50	<10
N	45	<30	<13
O	<50	<150	<100
Nb	99.9	...	...
Fe	<100	50	<100
Cu	<40	10	<25
Si	<100	50	<25
Ta	500	<10	...
Ti	<100	<20	<25
W	<200	<20	<25
Zr	<500	<20	99.9

[a] Cr, Mg, Mn, Mo, Ni, Pb, Sn, V, Zr < 20 ppm.

The preparation technique used for the $Zr_{61.8}Nb_{38.2}$ and $Nb_{95.2}Mo_{4.8}$ alloys was that by which approximately 1-lb charges were repeatedly arc melted under a partial atmosphere of argon and helium in a tungsten-electrode cold-hearth furnace. These ingots were annealed in a molybdenum susceptor vacuum induction furnace for 16 h at 1600°C and less than 7×10^{-5} Torr. The ingots were then machined so that top and bottom surfaces were flat, parallel, and smooth in preparation for rolling. The samples were subsequently cold rolled to about 98% reduction in thickness, sealed in quartz tubes at about 2.5×10^{-6} Torr, annealed at 1000°C for 1 h, water quenched, and cleaned in a solution composed of 1 part HF, 3 parts HNO_3 and 5 parts H_2SO_4.

A slightly different procedure was necessary for the $Nb_{74.7}Zr_{25.3}$ alloy owing to the great hardness of this material. The alloy was prepared as part of a 20-lb ingot which was arc melted in a consumable-electrode furnace. The ingot was hot extruded in a molybdenum container at 1550°C and air cooled. A portion of the extrusion was then machined and cold rolled to 98% reduction in thickness. The subsequent procedure was identical with that described for the other alloys.

C. Cryogenics

Each sample consisted of four thin slabs. They were held in the shape of a box, the bottom of which was formed by a brass cone and the sides by the sample slabs backed up by brass plates. Each slab was about 10 cm long, 2.2 cm wide, and 0.04 cm thick. Thermal contact between each slab and its backing plate was provided with a thin layer of Apiezon "N" grease, and moderate pressure was also applied around the edge of each slab at points which were not exposed to the far-infrared radiation. The sample holder was located inside a vacuum-tight can which was immersed in a helium bath. The thermal contact between the sample holder and the can was provided by a copper braid. The sample slabs formed a cavity, from which room-temperature radiation was excluded by a piece of black polyethylene, glued around the edge to a piece of fused quartz which was in good thermal contact with the helium bath. The top of the sample cavity was identical to that used previously.

D. Radiation Generation and Detection

The monochromator was virtually identical to those which have been used before.[16,17] The only significant change made since our last measurements[17,19] was to cover the monochromator with a Lucite box[20] which permitted us to remove practically all of the water vapor from the beam path. (Neoprene gloves provided access to the monochromator.) Air was circulated in the box through a drying agent.[21] Since this removed

---

[14] Values above 4.0 are known to be correct only for two elements, lead and mercury. In these metals, the electron-phonon coupling is unusually strong, and the BCS theory calculation does not apply quantitatively (see Ref. 15).

[15] J. C. Swihart, D. J. Scalapino, and J. Wada, Phys. Rev. Letters **14**, 106 (1965).

[16] P. L. Richards and M. Tinkham, Phys. Rev. **119**, 575 (1960).

[17] J. D. Leslie and D. M. Ginsberg, Phys. Rev. **133**, A362 (1964).

[18] I. Dietrich, Phys. Letters **9**, 221 (1964).

[19] J. D. Leslie *et al.*, Phys. Rev. **134**, A309 (1964).

[20] This was carried out by R. E. Harris.

[21] Linde molecular sieve, type 4A, from Union Carbide Company, New York, New York.

TABLE II. Sample composition and characteristics.

Sample No.	Composition	ν_g (cm^{-1})	2Δ (10^{-3} eV)	T_c (°K)	Θ_D (°K)	N_0 (eV^{-1} atom^{-1})	$2\Delta/kT_c$	p (42 cm^{-1})	K
1	$Zr_{61.8}Nb_{38.2}$	27.3±0.3	3.38±0.04	8.7±0.1	190±6	3.24±0.16	4.51±0.07	0.994	4.237
2	$Zr_{25.3}Nb_{74.7}$	30.95±0.3	3.84±0.04	11.0±0.1	205±6	2.95±0.6	4.05±0.06	0.996	5.025
3	$Nb_{95.2}Mo_{4.8}$	20.1±0.5	2.49±0.06	8.0±0.1	247±6	1.43±0.04	3.61±0.10	0.986	8.065
	Nb		3.04±0.05	9.25±0.01	238±6	1.63±0.02	3.81±0.06		

the water-vapor absorption lines, we chose a more evenly distributed set of wavelengths and radiation filters. The zero-order grating filters were chosen on the basis of calculations, and the transmission filters were chosen on the basis of observed attenuation constants. For each wavelength, filters were chosen so that the intensity of the desired wavelength was cut by a factor of about 5; and the second harmonic (at half the desired wavelength) was decreased by a factor of at least 500. The bandwidth of the radiation was 3% half-width at half-maximum.

The radiation was detected by a bolometer in the sample cavity. The bolometer was made of single-crystal gallium arsenide[22] doped with zinc (1 to 2×10^{17} atoms/cc). The bolometer size was about 9 mm long, 0.9 mm wide, and 0.25 mm thick. The bolometer was polished to a bright mirror finish to facilitate the soldering of leads onto it. The leads, No. 36 Advance wire, were soldered to the bolometer in a pure hydrogen atmosphere by means of a solder consisting of 50% In, 42% Pb, 3% Zn, and 5% Ag by weight.[23] The leads were shaped into the form of an S to provide slack for differential thermal contraction between the bolometer and the cryostat material (brass). With General Electric 7031 varnish, the free ends of the leads were glued down to a Mylar sheet, 0.001-in. thick, and this in turn was fixed to the cryostat with Apiezon "N" grease for thermal contact. The leads coming into the cryostat were thermally grounded before reaching the bolometer. The thermal contact between the bolometer and the helium bath was controlled by adjusting the pressure of helium gas in the can which contained the sample holder. In this way the thermal time constant of the bolometer could be optimized to achieve a maximum signal-to-noise ratio. The best pressure was typically in the neighborhood of 10^{-3} Torr, and a bolometer current of about 1 μA proved suitable. Transverse magnetic fields up to 26 kOe did not seem to affect the bolometer sensitivity.

E. Far-Infrared Measurements

As in previous work,[17] it was necessary to make measurements of far-infrared reflection from our samples in both the superconducting state and the "normal" state (produced by a magnetic field) so extraneous factors could be removed from the data by normalization.[24,25] The methods used to do this were nearly identical to those used previously,[17] but it was found useful to average the data in a slightly different way. In a given run, bolometer readings were determined for a series of wavelengths with the sample superconducting, and then for the same wavelengths in the same order with the sample "normal." In each case, the sample cavity signal was divided by a reference cavity signal to yield a ratio P_s or P_n for the readings with the sample superconducting or "normal," respectively.[24,25] It is useful to define

$$p = P_s/P_n. \qquad (5)$$

The numbers P_s, P_n, and p are functions of the far-infrared wave number ν. We have found it convenient to normalize our readings by defining $P(\nu)$, which is similar to the function with the same symbol in a previous article[17]:

$$P(\nu) = K[p(\nu)/p(42.0\ \mathrm{cm}^{-1}) - 1]. \qquad (6)$$

Since 42 cm^{-1} is a wave number which exceeds $2\Delta/hc$ by a considerable amount, the superconducting sample would have almost the same electromagnetic properties as the "normal" sample. This is indeed true: $p(42.0\ \mathrm{cm}^{-1})$ was close to unity (see Table II). It is impossible to rule out systematic errors of the order of 1% or 2%, and $p(42.0\ \mathrm{cm}^{-1})$ is equal to unity within this uncertainty. The normalizing factor K is introduced to make $P(\nu) = 1$ at the gap edge. This facilitates a comparison of the shapes of the absorption edges of the different samples with each other. The value of K for each sample appears in Table II. In calculating p for each ν in a given run, several readings were taken; and

---

[22] R. G. Wheeler and J. C. Hill, J. Opt. Soc. Am. **56**, 657 (1966).

[23] Suggested and supplied by C. Nuese (private communication).

[24] By "normal" we mean the state of the sample in a steady applied magnetic field of 26 kOe. This field is greater than H_{c1}, but less than H_{c2} for samples No. 1 and No. 2 (see Ref. 25). For sample No. 3, the resistive transition is complete for $H = 10$ kOe at 4.2°K, so it should be complete for $H = 26$ kOe at 1.3°K, the temperature at which our measurements were made. The data show that each "normal" sample had a far-infrared absorption curve with no sharp break in it, so that each curve of $P(\nu)$ versus ν has only one sharp break, indicating the energy gap edge for the superconductor in zero applied dc magnetic field.

[25] C. K. Jones and J. K. Hulm, Rev. Mod. Phys. **36**, 74 (1964).

averaged values of P_s and P_n were used in Eq. (5). In calculating $P(\nu)$ for each ν, the values of p which were put into Eq. (6) had been averaged over a number of runs. Standard deviations were estimated statistically from the observed scatter of the readings. In the graphs below, the "error bars" indicate plus and minus one standard deviation of the mean. The uncertainty in the value of 2Δ for each sample was estimated generously by drawing various "reasonable" curves on the graphs, and observing where the absorption edge seemed to occur on each of them.

III. EXPERIMENTAL RESULTS AND DISCUSSION

A. Absorption Curves

In Figs. 1–3 are shown the values of $P(\nu)$, defined above in Eq. (6), as a function of the far-infrared wavenumber ν. Each curve has an absorption edge which is sharply defined, within the resolution of our measurements. One expects this in a homogeneous alloy, particularly if the alloy has an electron mean free path sufficiently short so that gap anisotropy is washed out.[10]

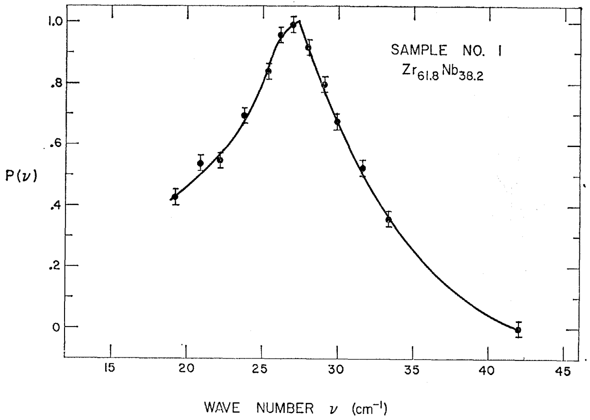

FIG. 1. Far-infrared absorption curve for sample No. 1 $P(\nu)$ is defined in Eq. (6).

B. Gap Widths and Thermodynamic Data

We wish to discuss the variation in the gap width as a function of impurity concentration. In doing this we will use Eqs. (1) and (2). We present in Table II the relevant numbers. Those measured in our experiments are of course ν_g, the width of the energy gap expressed in wave numbers. The corresponding values of 2Δ in the fourth column were calculated from them. For pure Nb we have averaged the number resulting from the tunnelling measurements of Sherill and Edwards[26] with that found in similar measurements by Townsend and Sutton,[27] and we have used the latter's estimate of the uncertainty.[28] The critical temperatures were taken from Fig. 8 of Ref. 6. The value of T_c for pure Nb was taken from the work of Finnemore, Stromberg, and Swenson[29] for a very pure sample.

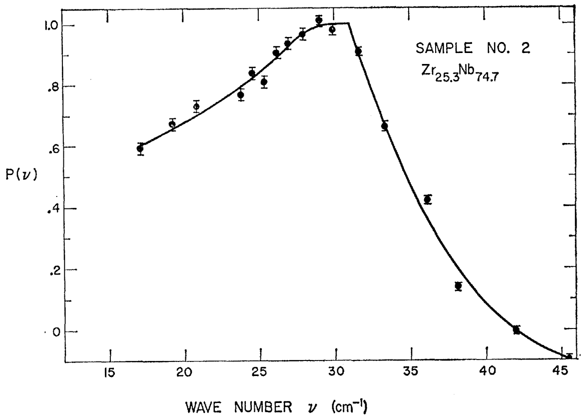

FIG. 2. Far-infrared absorption curve for sample No. 2. $P(\nu)$ is defined in Eq. (6).

We rely on the specific-heat data of Morin and Maita[7] for obtaining N_0 and Θ_D. There was some ambiguity in their results, which resulted in two sets of

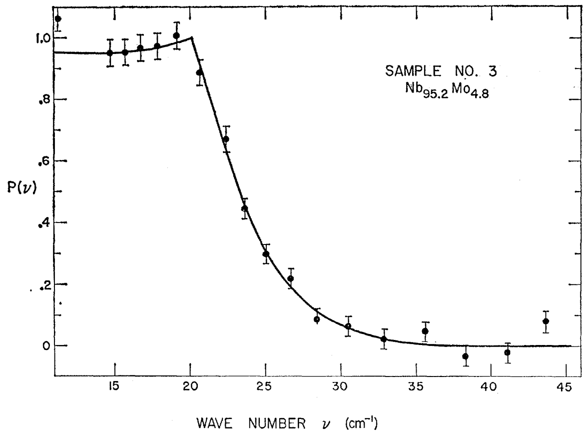

FIG. 3. Far-infrared absorption curve for sample No. 3. $P(\nu)$ is defined in Eq. (6).

---

[26] M. D. Sherrill and H. H. Edwards, Phys. Rev. Letters **6**, 460 (1961). The reduced gap $2\Delta/kT_c$ is given in this paper as 3.59, but should be 3.79, as the other numbers in the paper show.

[27] P. Townsend and J. Sutton, Phys. Rev. **128**, 591 (1962).

[28] The far-infrared measurements of Ref. 16 yielded a value of the energy gap in niobium of only $(2.8\pm0.3)kT_c$. It is possible that surface contamination is responsible for such a low value. (This would probably be a less serious problem in a niobium alloy because of its larger penetration depth.) It would be difficult to rule out a possible effect from surface contamination in the tunnelling measurements also. We have used the tunnelling results in Table II because they agree with each other very well.

[29] D. K. Finnemore, T. F. Stromberg, and C. A. Swenson, Phys. Rev. **149**, 231 (1966).

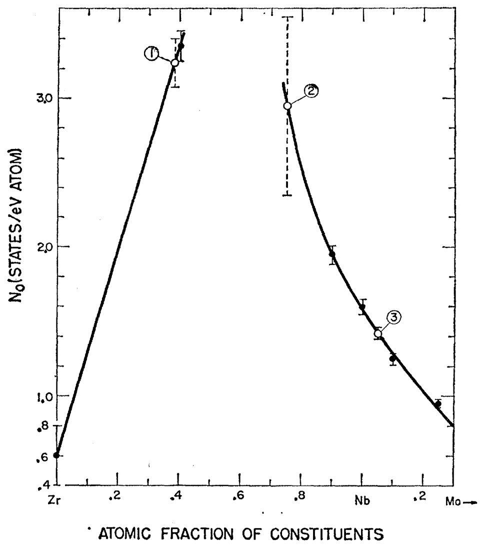

FIG. 4. The electronic density of states at the Fermi level for a single-spin orientation as a function of the composition. The points labeled 1, 2, and 3 correspond to our samples with the same numbers.

values for N_0 and Θ_D in the alloy series from $Zr_{60}Nb_{40}$ to $Nb_{62}Mo_{38}$. The difficulty came from a deviation of the specific heat from its theoretical behavior, according to the Debye model. The values of N_0 and Θ_D which Morin and Maita calculated from the measurements at their lowest temperatures are relevant to our experiment, and they agree very much better for N_0 (although slightly worse for Θ_D) with the other available data.[30–33] We therefore choose these values rather than the high-temperature values. These data are shown in Table II and in Figs. 4 and 5 with smooth curves drawn by us.

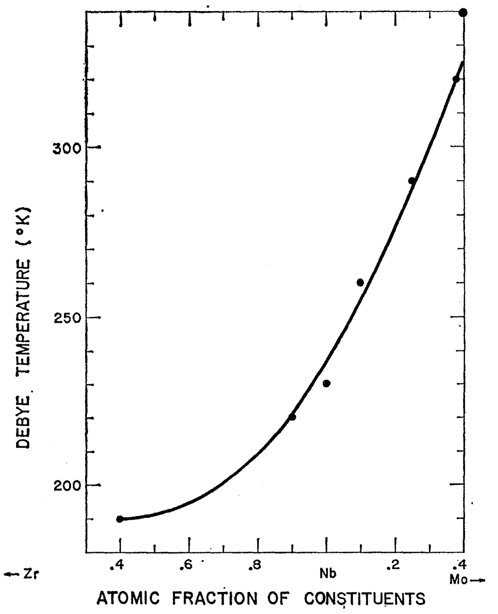

FIG. 5. The Debye temperature as a function of composition.

The uncertainty of Θ_D which is shown in Table II was estimated from the scatter of the points in Fig. 4.[34] Comparison of the value of N_0 for pure Nb in Fig. 5 with that of the other investigators[30–33] enabled us to roughly estimate the uncertainties which we have shown in Fig. 5. For pure Zr we used the value of N_0 found by Kneip *et al.*[35] In connecting the point for pure Zr to that for $Zr_{60}Nb_{40}$ by a straight line, we have assumed that the N_0 curve is similar to the T_c curve[6] in this region. This procedure is rough, especially because pure Zr has a hcp crystal structure while all the other points in Fig. 5 are for substances with a bcc structure. This introduces an uncertainty into the size of N_0 for sample No. 1, which we have estimated as shown. In our discussion below, we will use values for N_0 and Θ_D which are taken from the curves shown in Figs. 4 and 5.

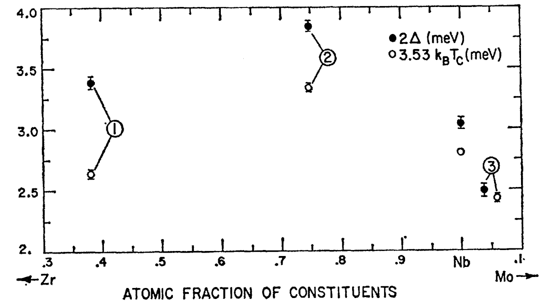

FIG. 6. 2Δ and 3.53 kT_c as a function of composition. The points labeled 1, 2, and 3 correspond to our samples with the same numbers.

C. Discussion

In Fig. 6, we show how 2Δ and 3.53 kT_c depend on composition. Since these two parameters rise and fall together, they confirm qualitatively the BCS result shown in Eq. (4). Nevertheless the reduced gap width $2\Delta/kT_c$ is considerably higher than 3.53 for two of the

---

[30] B. J. C. Van der Hoeven, Jr., and P. H. Keesom, Phys. Rev. **134**, A1320 (1964).

[31] H. A. Leupold and H. A. Boorse, Phys. Rev. **134**, A1322 (1964).

[32] R. D. Blaugher *et al.*, in *Proceedings of the Eighth International Conference on Low-Temperature Physics, London,* 1962, edited by R. O. Davies (Butterworths Scientific Publications Ltd., London, 1963), p. 147.

[33] B. W. Veal, J. K. Hulm, and R. D. Blaugher, Ann. Acad. Sci. Fennicae, Ser. A VI **210**, 108 (1966).

[34] The uncertainty in the absolute value would be larger, but we are interested here primarily in relative values for the different alloys.

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

alloys. In the simple metals a large reduced gap is generally associated with a large coupling constant V, and the theoretical reason for this is understood.[15] As shown in Fig. 7, the opposite is true in our samples: A large reduced gap is associated with a small value of V. (For the transition metals in general there seems to be no simple correlation between the reduced gap width and V.) In Fig. 7, V_Δ is the value of V calculated from Eq. (1), and V_{T_c} is the value calculated from Eq. (2), using Eq. (3) in each case to evaluate $\langle\hbar\omega_p\rangle$.

In Fig. 8 we show how V_Δ and V_{T_c} depend on composition for alloys ranging from $Zr_{60}Nb_{40}$ to Mo. It is seen that over this range V_{T_c} changes by a factor of four.[36] Perhaps the weakest link in the argument here has been our use of Eq. (3) to find the average phonon energy. As we mentioned above, the energies of the phonons which are important for creating superconductivity are comparatively large,[3] so the Debye model is not reliable for them. If we assume that V is actually independent of composition, then the data can be used with Eq. (2) to show that

$$\langle\hbar\omega_p\rangle = \alpha k\Theta_D, \tag{7}$$

where α varies with composition by a factor of at least ten in the composition range shown in Fig. 8.[37] It is difficult to see how this could be true in alloys which have the same crystal structure and such a narrow range of compositions and average atomic weights. It has also been pointed out that there is large variation of V near the ends of the regions in the periodic table which contain the transition elements.[38] There is good evidence to show that in *some* alloy systems V is approximately constant.[39,40] Apparently this is very likely not true for all alloy systems. Our present theoretical and empirical knowledge about the interaction responsible for superconductivity in the transition metals has been reviewed recently.[41]

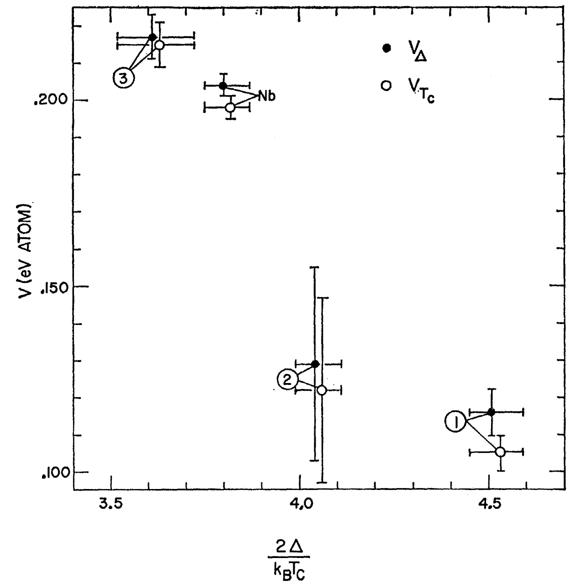

FIG. 7. The BCS coupling constant as a function of the reduced gap width $2\Delta/kT_c$. V_Δ is calculated from Eqs. (1) and (3). V_{T_c} is calculated from Eqs. (2) and (3). The circled numbers are our sample numbers. V_Δ has been shifted to the left and V_{T_c} to the right slightly to resolve the error bars.

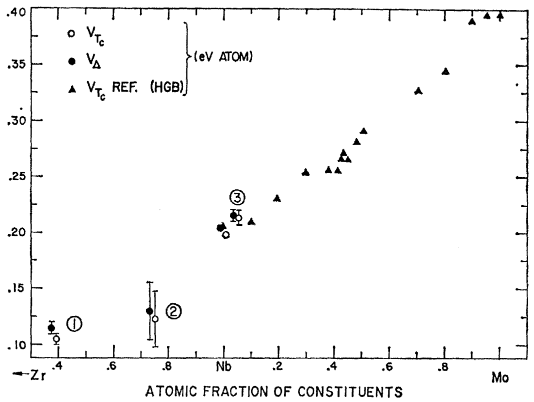

FIG. 8. The BCS coupling constant as a function of composition. V_Δ is calculated from Eqs. (1) and (3). V_{T_c} is calculated from Eqs. (2) and (3). The points labeled V_{T_c} REF. (HGB) were taken from R. A. Hein *et al.* (Ref. 36). To resolve the points and error bars, V_Δ has been shifted slightly to the left, and V_{T_c} has been shifted slightly to the right for Nb and for the points labeled 1, 2, and 3, which correspond to our samples with the same numbers.

---

[36] This type of analysis has been made previously for the Nb-Mo alloys in R. A. Hein, J. W. Gibson, and R. D. Blaugher, Rev. Mod. Phys. **36**, 149 (1964) and in Ref. 32.

[37] In this calculation the maximum value of V, that for pure Mo, yields the smallest percentage variation in α.

[38] M. A. Jensen and J. P. Maita, Phys. Rev. **149**, 409 (1966).

[39] See, for example, Refs. 7 and 41.

[40] C. H. Cheng *et al.*, Phys. Rev. **126**, 2030 (1962).

[41] E. Bucher *et al.*, in *Low-Temperature Physics LT9*, edited by J. G. Daunt *et al.* (Plenum Press, Inc., New York, 1965), Part A, p. 616.