

which may be written as

$$(\gamma_n \eta \hbar T_2)^2 \geq (\omega_n T_2)^{-1} [\eta(m/M)]^{-2} (M/m) (\gamma_n / \gamma_e).$$

With the usual assumptions, the equation is

$$(\gamma_n \eta \hbar T_2)^2 \geq 3.$$

The critical field we obtain is much larger than the field given by the usual saturation condition. With such a field all the approximations made in this Appendix are not valid.

The effect of the  $\delta m_z$  term is examined. The calculations are similar and lead to the condition

$$\alpha^2 M_z \delta m_z / C_q \geq 1 / T_{2q}.$$

We obtain

$$(\gamma_n \eta \hbar T_2)^2 \geq 8 (\omega_n T_2)^{-1} (\eta m / M)^{-2}.$$

Or with the assumptions,  $(\gamma_n \eta \hbar T_2)^2 \geq 10$ .

The conclusion is that it is impossible to reach a critical field giving rise to Suhl instability.

## Specific Heats of Transition Metal Superconductors

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Specific heats have been measured on superconducting transition metal elements, alloys and compounds which cover a wide range in  $T_c$  and a large portion of the  $d$  band. A strong dependence of  $T_c$  upon the density of states in the  $d$  band indicates that the superconducting electrons are  $d$  electrons. The electron interaction parameter,  $V$ , of the Barden-Cooper-Schrieffer theory is found to be approximately 0.4 eV for all the metals investigated. The phonon frequency involved in the electronic interaction is less than that predicted by theory and changes over a range of about a factor of 5 when the Fermi level is moved to different parts of the  $d$  band. The product  $N(0)V$  exceeds the weak coupling limit for many specimens, yet the results for these do not depart from the general behavior.

### INTRODUCTION

THE experimental investigation of transition metal elements, alloys, and compounds by Matthias and Hultm have emphasized certain regularities in the appearance of superconductivity throughout the periodic system. The connection between these regularities and the Barden-Cooper-Schrieffer theory of superconductivity<sup>1</sup> is given by the expression

$$kT_c = 1.14 \langle \hbar \omega \rangle_{av} \exp[-1/N(0)V], \quad (1)$$

where  $T_c$  is the critical temperature,  $\langle \hbar \omega \rangle_{av}$  the average energy of the phonons which scatter electrons at the Fermi surface,  $N(0)$  the density in energy of electronic states at the Fermi surface, and an adjustable parameter  $V$ , which measures the difference between the Coulomb repulsion and the phonon-induced interaction of electrons close to the Fermi surface. However, nearly all of the published data describe the behavior of  $T_c$  as a function of the average number of valence electrons per atom and, therefore, do not constitute a test of Eq. (1). If Eq. (1) is approximated by

$$T_c \approx \theta_D \exp[-1/N(0)V], \quad (2)$$

where  $\theta_D$  is the Debye temperature, one sees that a

measurement of specific heat versus temperature, which yields  $T_c$ ,  $\theta_D$ , and  $N(0)$ , will allow the behavior of  $V$  to be determined. Some specific-heat data have been published for alloys of Ti-Mo,<sup>2</sup> Ti-V-Cr,<sup>3</sup> and<sup>4</sup> Ti-V but they range over only a factor of 4 in  $T_c/\theta_D$ , not enough for any general conclusions to be drawn concerning  $V$ . In this paper we report data on elements, alloys, and compounds of the transition metals in which  $T_c/\theta_D$  is varied by a factor of 300. It is found that  $V$  is a constant, as Pines<sup>5</sup> suggested it might be for  $d$ -band metals. However, an unexpected result indicates that the phonon frequency involved in the electronic interaction is less than that predicted by theory and changes over a range of about a factor of 5 when the Fermi level is moved to different parts at the  $d$  band.

### EXPERIMENTAL

In order to test the theory, results of moderate accuracy on a large number of samples were required. For this purpose a calorimeter was developed in which heat capacity was measured by a pulse method designed for speed, small samples, and for use in an ordinary cryostat mounted between the poles of an

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<sup>1</sup> J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957).

<sup>2</sup> R. R. Hake, Phys. Rev. **123**, 1986 (1961).

<sup>3</sup> J. K. Hulm and R. D. Blaugher, Phys. Rev. **123**, 1569 (1961).

<sup>4</sup> C. H. Cheng, K. P. Gupta, E. C. van Reuth, and P. A. Beck, Phys. Rev. **126**, 2030 (1962).

<sup>5</sup> D. Pines, Phys. Rev. **109**, 280 (1958).

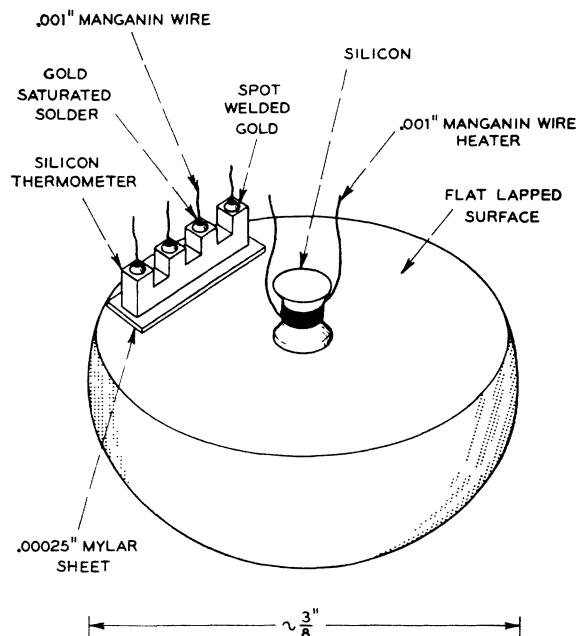


FIG. 1. Sketch showing the scale and manner of mounting thermometer and heater on a typical sample.

electromagnet capable of up to 18 kG. Usually, the sample was a hemispherical button from an arc furnace, and was prepared for the measurement as shown in Fig. 1. A heater was located near the center of mass of the sample so that the temperature rise with the heat pulse was uniform throughout the sample and gave a clear cut signal on the thermometer. Heater and thermometer were cemented to the sample with G. E. No. 7031 adhesive. The thermal capacity of the heater, thermometer, Mylar, and adhesive was measured and found to be negligible. The thermometer was cut from a silicon crystal doped with boron and compensated to  $n$  type with arsenic. The resulting electronic conduction involved both the conduction band and the impurity band, and yielded a smooth resistance-temperature curve from  $1 \Omega$  at room temperature to  $10^7 \Omega$  at  $1^\circ\text{K}$ . In the temperature region of measurement,  $20\text{--}1.5^\circ\text{K}$ ,  $\Delta R/\Delta T$  changed smoothly from 7.6 to  $9.3 \times 10^5 \Omega/^\circ\text{K}$ . The square current pulses put into the heater were about 2-sec duration and large enough to give a  $\Delta T$  of a few tenths percent of the ambient temperature. The sample was contained in an evacuated can filled with aluminum oxide powder following a procedure described by Kunzler.<sup>6</sup> Isolating the sample in this way minimized radiation loss and heating due to vibration. The powder connected the sample thermally to the refrigerant with a time constant which was much longer than that of the sample itself but short enough to allow the sample to cool from 20 to  $1.5^\circ\text{K}$  in a few hours. The cooling rate was adjusted

<sup>6</sup> J. E. Kunzler, L. R. Walker, and J. K. Galt, Phys. Rev. **119**, 1609 (1960).

by varying the composition of a mixture of 350 mesh and 600 mesh powder. Measurements were usually made during cooling but could also be made during warming. The temperature was allowed to drift and power pulses were fired as often as data were required, the power pulse, the thermometer response, and timing pulses were recorded on a multichannel recorder.

The bcc binary alloys of Nb-Mo, Mo-Tc, Mo-Pd, and Mo-Re and the compound  $\text{Mo}_3\text{Ir}$  were prepared by Corenzwit. The structure and magnetic properties of the alloys have been reported by Clogston.<sup>7</sup> The superconducting properties of the Mo-Pd alloys were discovered by Matthias.<sup>8</sup> The Zr-Nb alloy specimens were obtained from Hulm.<sup>3</sup> The compounds  $\text{V}_3\text{Ga}$ ,  $\text{V}_3\text{Si}$ ,  $\text{Nb}_3\text{Sn}$ ,  $\text{V}_3\text{Ge}$ , and  $\text{Re}_2\text{B}$  and the Mo-Ru alloys were supplied by Wernick.

## RESULTS

Below  $25^\circ\text{K}$  the heat capacity in the normal state of nearly all of the alloys and compounds investigated followed the expression

$$C = \gamma T + \beta T^3, \quad (3)$$

although for Re and its alloys a  $T^5$  term was required to fit the data. In (3)  $\gamma$  is given by

$$\gamma = 2\pi^2 N(0) k^2 t / 3, \quad (4)$$

and

$$\beta = 12\pi^4 n k (T/\theta_D)^3 / 5. \quad (5)$$

Evaluating (4) and (5)

$$N(0) = 0.0885 \gamma / t, \quad (6)$$

$$\theta_D = (4.65 \times 10^6 n / \beta)^{1/3}, \quad (7)$$

where  $N(0)$  is the number of states of one spin  $eV^{-1}$  atom $^{-1}$  at the Fermi surface,  $\gamma$  is in  $10^{-4}$  cal deg $^{-2}$

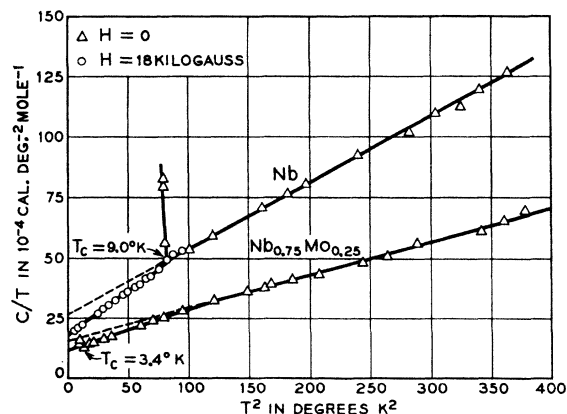


FIG. 2. A plot of heat capacity data for a sample of Nb and a sample of Nb-Mo alloy showing the change in slope which occurs at  $9.5^\circ\text{K}$  in the  $C/T$  plot.

<sup>7</sup> A. M. Clogston, B. T. Matthias, M. Peter, H. J. Williams, E. Corenzwit, and R. C. Sherwood, Phys. Rev. **125**, 541 (1962).

<sup>8</sup> B. T. Matthias (to be published).

TABLE I. Parameters determined from heat capacity measurements. The double columns for some alloys represent results from below and above the temperature at which a change in slope occurs in the  $C/T$  plot.

	$T_c$ (°K)	$\gamma$ ( $10^{-4}$ cal deg $^{-2}$ mole $^{-1}$ )		$\beta$ ( $10^{-4}$ cal deg $^{-4}$ mole $^{-1}$ )		$N(0)$ (states eV $^{-1}$ atom $^{-1}$ )		$\theta_D$ (°K)	
Zr <sub>60</sub> Nb <sub>40</sub>	8.8	38		0.66		3.35		190	
Zr <sub>10</sub> Nb <sub>90</sub>	10.5	22	34	0.45	0.36	1.95	3.00	220	230
Nb	9.0	18	28	0.37	0.27	1.60	2.50	230	260
Nb <sub>90</sub> Mo <sub>10</sub>	5.3	14	22	0.25	0.19	1.25	1.95	260	290
Nb <sub>75</sub> Mo <sub>25</sub>	3.4	10.8	16	0.19	0.14	0.95	1.40	290	320
Nb <sub>62</sub> Mo <sub>38</sub>	0.76 <sup>a</sup>	7.8	8.8	0.14	0.13	0.69	0.78	320	330
Nb <sub>60</sub> Mo <sub>40</sub>	0.50 <sup>a</sup>		7.2	0.120		0.64		340	
Nb <sub>58</sub> Mo <sub>42</sub>	0.31 <sup>a</sup>		6.4	0.122		0.57		340	
Nb <sub>50</sub> Mo <sub>50</sub>	...		4.8	0.090		0.42		380	
Nb <sub>20</sub> Mo <sub>80</sub>	...		4.0	0.070		0.35		405	
Mo	1.0 <sup>a</sup>		4.8	0.044		0.42		470	
Mo <sub>95</sub> Re <sub>5</sub>	1.5		5.2	0.051		0.46		450	
Mo <sub>90</sub> Re <sub>10</sub>	2.9		6.3	0.054		0.56		440	
Mo <sub>80</sub> Re <sub>20</sub>	8.5		9.0	0.064		0.79		420	
Mo <sub>75</sub> Re <sub>25</sub>	10.5		9.6	0.071		0.85		405	
Mo <sub>70</sub> Re <sub>30</sub>	10.8		9.8	0.075		0.87		395	
Mo <sub>60</sub> Re <sub>40</sub>	12.6		10.6	0.115		0.94		340	
Mo <sub>50</sub> Re <sub>50</sub>	11.5		10.5	0.14		0.93		320	
Re	1.7		5.9	0.069		0.52		405	
Mo <sub>50</sub> Tc <sub>50</sub>	12.6		11	0.17		0.97		300	
Mo <sub>95</sub> Ru <sub>5</sub>	2.5		7.0	0.056		0.62		435	
Mo <sub>70</sub> Ru <sub>30</sub>	6.7		9.3	0.057		0.82		435	
Mo <sub>40</sub> Pd <sub>60</sub>	2.3		7.8	0.13		0.69		330	
Mo <sub>50</sub> Pd <sub>50</sub>	4.1		9.0	0.13		0.80		330	
Mo <sub>60</sub> Pd <sub>40</sub>	4.4		8.5	0.13		0.75		330	
Ta	4.4		15	0.33		1.33		240	
Y	...		24	0.35		2.1		235	
V <sub>3</sub> Si	14.6		186	0.52		5.5		330	
V <sub>3</sub> Ga	14.6		244	0.62		7.1		310	
V <sub>3</sub> Ge	6.1		73	0.28		2.14		405	
Nb <sub>3</sub> Sn	17.3		150	0.79		4.40		290	
Mo <sub>3</sub> Ir	8.5		32	0.54		0.95		325	
R <sub>2</sub> B	4.6		15	0.21		0.66		405	

<sup>a</sup>  $T_c$  measured by T. H. Geballe.

mole $^{-1}$ ,  $\theta_D$  in °K,  $n$  the number of atoms per formula unit,  $\beta$  is in  $10^{-4}$  cal deg $^{-4}$  mole $^{-1}$ , and  $t$  in the number of transition metal atoms per formula unit.

Heat capacity was measured first in zero magnetic field from 20°K down to include the superconducting transition and then in a field of 18 kG to destroy the transition and yield the normal state down to about 1.5°K. At the transition, in all of the specimens measured,  $C/T$  was found to increase smoothly with decreasing temperature and not discontinuously as predicted by theory. The intersection of this behavior and that of the normal metal was taken to be  $T_c^2$ . Some typical data are shown in Fig. 2. The data of Fig. 2 also show a change in slope which was found to occur at  $\sim 9.5^\circ$ K in the alloy series from Zr<sub>10</sub>Nb<sub>90</sub> to Nb<sub>58</sub>Mo<sub>42</sub> inclusive. In this series  $\gamma$  and  $\theta_D$  have two possible values as shown in Table I depending upon which slope is taken to represent the lattice contribution. Although the change in slope occurs near  $T_c$  in Nb and is seen only when superconductivity has been destroyed by a magnetic field, it is connected to neither of these circumstances because it persists at  $9.5^\circ$  when  $T_c$  is changed by alloying from  $10.5^\circ$  to  $0.5^\circ$  and can be seen in zero field when  $T_c$  is well below  $9.5^\circ$  as indicated by the data in Fig. 2 for Nb<sub>75</sub>Mo<sub>25</sub>. How far

in the direction of increasing Zr content the change in slope can be found was not determined. The critical field of Zr<sub>60</sub>Nb<sub>40</sub>, the only other Zr-Nb alloy to be measured, was too high to allow the superconductivity to be destroyed. The change in slope was not found in Ta. The difference in  $\gamma$  obtained by the two extrapolations of the data decreased approximately linearly with increasing number of valence electrons per atom and could not be seen in a Nb<sub>50</sub>Mo<sub>50</sub> sample. In the summary of results, Table I, values for  $\gamma$  and  $\beta$  are quoted for both extrapolations except for Nb<sub>60</sub>Mo<sub>40</sub> and Nb<sub>58</sub>Mo<sub>42</sub> where the change in slope was evident but the data too scattered to yield a significant difference. A rapid change in  $N(0)$  with temperature seems required to explain this result. The intersection of the Fermi surface and the zone boundary at some point would cause an increase in  $N(0)$  but this model would predict that the change in slope would disappear over a narrow range of alloying. Since the Fermi level is in a region of the band where  $N(0)$  is high and changing rapidly, the most likely explanation seems to be a relative shift in band edges with temperature and a consequent redistribution of electrons.

In the region of the  $d$  band which we are considering, there are two peaks in  $N(0)$ , as shown in Fig. 3. These

appear to be the second and third peaks in the band. The point for yttrium indicates the presence of a first peak at about 3 electrons per atom. No detail concerning this peak could be obtained because Y-Zr do not form a series of solid solutions. Results on some Sc alloys and the low value of  $N(0)$  for Zr indicates that  $N(0)$  probably drops to around 0.2 between Y and Zr. The work of Budworth, Hoar, and Preston<sup>9</sup> on alloys of Rh-Pd-Ag indicates the existence of a fourth peak at about Pd or 10 electrons per atom. The location of peaks two and three correspond closely to peaks found in the  $3d$  band by Cheng, Wei, and Beck.<sup>10</sup> In the  $3d$  band, however,  $N(0)=3.5$  at the third peak compared to  $N(0)=0.95$  found here, probably because the  $3d$  wave functions are less extensive than the  $4d$  and  $5d$  and thus give rise to a narrower band. Note that  $N(0)$  is the same for  $\text{Mo}_{50}\text{Tc}_{50}$  and  $\text{Mo}_{50}\text{Re}_{50}$  indicating that in this region the  $4d$  and  $5d$  bands are alike. The second peak in Fig. 3 has been dotted in up to  $N(0)=4.0$ . This is the behavior predicted from  $T_c$  values of reference 3 and the lower line of the BCS plot in Fig. 4.

The relation between  $T_c$  and  $N(0)$  is shown in Fig. 4 where  $\log(T_c/\theta_D)$  is plotted against  $1/N(0)$  according to Eq. (2) for elements, alloys, and compounds which involve the second and third peaks of the  $4d$  and  $5d$  bands. Our data and those from the literature<sup>11-13</sup> appear to cluster about two main lines depending upon whether the Fermi level is in the second peak (lower line) or third peak (upper line) of the  $d$  band. Some points for the Nb-Mo alloys, indicated by crosses and circles, correspond to the lower choice of  $N(0)$  values and lie as shown by the dotted line. This dotted line joins the lower solid line as the change in the slope of the  $C/T$  curves disappears with alloying. The points which correspond to the higher choice of  $N(0)$  lie on or somewhat below the lower main line. This suggests the possibility that in the superconducting state the samples exist in the condition represented by the higher value of  $N(0)$ . This does not seem impossible energetically since the entropy difference between the two states represented by the higher and lower values of  $N(0)$  is only a few percent of the total entropy of the system at  $T_c$ . However, the difference between the upper dotted line and the lower main line may be real and due to the same mechanism which produces the difference in behavior connected with the two peaks in the band. The two main clusters of points indicated by the solid lines are straight to within experimental error with slopes of  $-1/V=2.70$  and  $2.35$  for the lower and higher, respectively. These results indicate

<sup>9</sup> D. W. Budworth, F. E. Hoar, and J. Preston, Proc. Roy. Soc. (London) **A257**, 250 (1960).

<sup>10</sup> C. H. Cheng, C. T. Wei, and P. A. Beck, Phys. Rev. **120**, 426 (1960).

<sup>11</sup> J. K. Hulm, R. D. Blaugher, T. H. Geballe, and B. T. Matthias, Phys. Rev. Letters **7**, 302 (1961).

<sup>12</sup> R. A. Hein, J. W. Gibson, and R. D. Blaugher, Bull. Am. Phys. Soc. **7**, 322 (1962).

<sup>13</sup> G. T. Armstrong, J. Am. Chem. Soc. **71**, 3583 (1949).

that the electron interaction parameter is essentially constant in a great many  $d$  band superconductors even when compounds are included. These two situations differ mainly in their intercepts, which suggest that the important phonon frequency changes as the Fermi level moves through the band. This may result because the symmetry of the  $d$  wave functions at the Fermi level are different. For the two peaks in the band, for example, one might expect predominantly  $t_{2g}$  states when there are less than approximately six electrons per atom and predominantly  $e_g$  states when there are more than six electrons per atom.

Some data taken from the literature and from our measurements on  $3d$  band alloys and compounds which involve the second peak in the band are plotted in Fig. 5 and compared with the results of Fig. 4 (dotted line). Although there is some scatter in the  $3d$  band data, they suggest that  $1/V$  is about the same for the  $3d$  band and that the intercept may be somewhat lower. The points which deviate the most from the general behavior are the V-Cr alloys (open circles), probably because  $V$  must change sign somewhere between vanadium and chromium. Also plotted in Fig. 5 are data for Mo-Ru and Mo-Pd alloys which involve states taken from well beyond the third peak in the band. These results are compared with the third peak data of Fig. 4 (upper dotted line). Again,  $1/V$  is about the same but the intercept is different. The fact that the compounds fall in with the elements and alloys in Figs. 4 and 5 indicates that in the compounds the states at the Fermi surface are predominately  $d$  states.

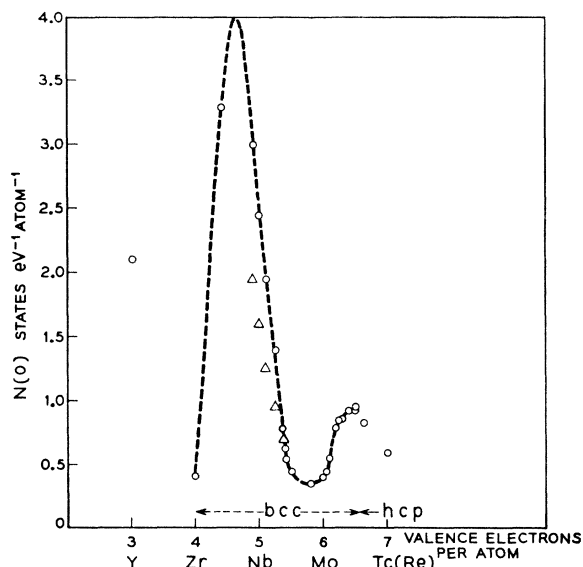


FIG. 3. A plot of  $N(0)$ , the density of states in number of states of one spin per eV per atom as a function of the number of valence electrons. The  $\Delta$  points represent  $N(0)$  obtained from  $C/T$  below the change in slope. A structure change from body-centered cubic to hexagonal close packed is indicated by the arrows. The value for Zr was obtained elsewhere [T. S. Smith and J. G. Daunt, Phys. Rev. **88**, 1172 (1952)].

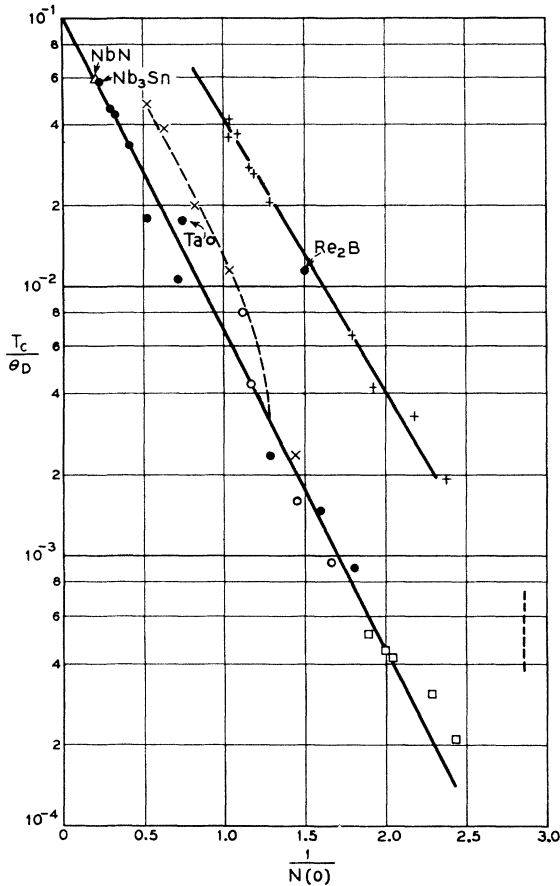


FIG. 4. Experimental results which involve the  $4d$  and  $5d$  bands plotted according to Eq. (2). Data points  $\bullet$ , for Zr-Nb-Mo alloys and  $+$ , for Mo-Tc-Re alloys are measurements reported in this paper. Points  $\times$ , represent  $C/T$  data taken below the change in slope for Zr-Nb-Mo alloys;  $\circ$ , from reference 11 and  $\square$ , from reference 12 were obtained for Nb-Mo alloys using our  $N(0)$  values; NbN is from reference 13.

It has been assumed that this is the case in calculating  $N(0)$  for the compounds by counting only the transition metal atoms per formula unit. If other than  $d$  states made a significant contribution to the band  $1/V$  would not be that found to be characteristic of particular region of the  $d$  band and the data points for the compounds would not correlate with the  $d$  band alloys. Clogston and Jaccarino,<sup>14</sup> from a study of Knight shifts in compounds such as  $V_3Ga$  which have the  $\beta$ -wolfram structure, have also concluded that predominately  $d$  states exist at the Fermi surface. A consideration of the structure shows a continuous lattice of transition metal atoms with the nontransition metal atoms imbedded in it. The  $s$  and  $p$  orbitals of these latter atoms do not contribute significantly to  $N(0)$ . However, the location of  $Mo_3Ir$  in Fig. 5 (with the Mo-Pd alloys) suggests that Ir contributes  $d$  states to the band.

<sup>14</sup> A. M. Clogston and V. Jaccarino, Phys. Rev. **121**, 1357 (1961).

## SUMMARY

We have tested the BCS theory as it relates  $T_c$  to  $N(0)$ , over a wide range in  $T_c$  and over a considerable portion of the  $d$  band. It appears from the results that  $V$  is essentially constant throughout and is close to 0.4 eV in magnitude. The strong dependence of  $T_c$  upon  $N(0)$  demonstrates that the superconducting electrons are  $d$  electrons. It seems more reasonable to assume that the shift in the intercept (at  $1/N(0)=0$ ) depends upon the location of the Fermi level in the  $d$  band rather than upon some dependence of  $V$  upon  $N(0)$ . Thus, the intercept is probably a measure of  $\langle \hbar\omega \rangle_{av}/\theta_D$  which is found to vary from  $\sim 0.08$  to  $\sim 0.5$ . These values appear to be well below that expected from BCS. In the region of high  $N(0)$ ,  $N(0)V > 1$ , which is well beyond the weak coupling limit of  $N(0)V < 0.5$ . In spite of this, the results here seem not to depart from the general behavior.

The results in Figs. 4 and 5 suggest several areas for future work. First, since it is evident that the superconducting electrons are  $d$  electrons and that electron-lattice interactions are important, measurements should be extended to include the region around Ru and Os where the absence of an isotope effect has been shown.<sup>15</sup>

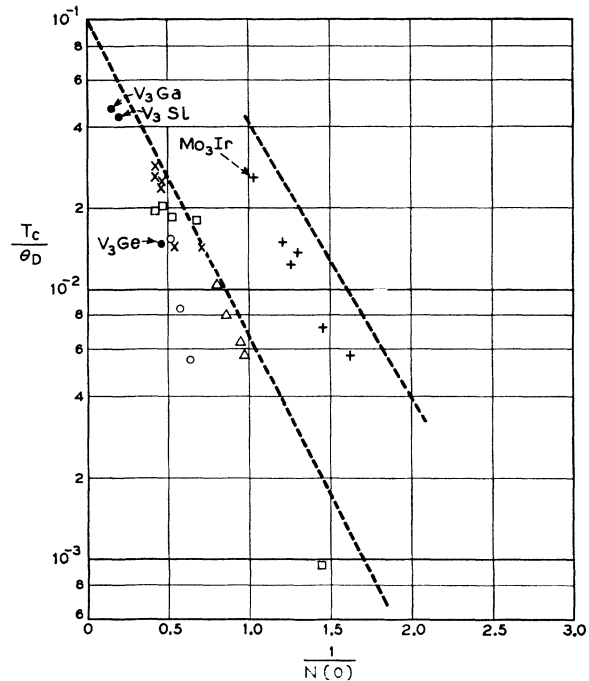


FIG. 5. Experimental results which involve the second peak in the  $3d$  band (lower set of data) and states beyond the third peak in the  $4d$  and  $5d$  bands (upper set of data) plotted according to Eq. (2). Data points  $\bullet$ , and  $+$  for Mo-Ru and Mo-Pd alloys are measurements reported in this paper;  $\square$  for Ti-V alloys reference 3,  $\Delta$  for Ti-Mo alloys reference 2,  $\circ$  for V-Cr alloys reference 3, and  $\times$  for Ti-V alloys reference 4. The dotted lines are taken from Fig. 4 for comparison.

<sup>15</sup> T. H. Geballe, B. T. Matthias, G. W. Hull, Jr., and E. Corenzwit, Phys. Rev. Letters **6**, 275 (1961).

Second, one would like to know if the two main lines are connected by Nb-Mo alloys in the region of low  $N(0)$ . The work of Geballe and Matthias<sup>16</sup> on pure Mo suggests that these alloys may also be superconducting if they can be made free from iron. The presence of a small amount of iron in the Nb-Mo samples represented by the lowest data points may have depressed  $T_c$  and obscured a trend connecting the two lines. The vertical dotted line in Fig. 4 at  $1/N(0)=2.9$  represents the probable minimum in  $N(0)$  through which a connecting line must go. It is to be noted that in this region, the  $N(0)$  for the  $s$  band is probably about one-third of the total  $N(0)$ . Therefore  $1/V$ , as well as the intercept, might be expected to change due to  $s$ - $s$  or  $s$ - $d$  interaction. Thus, superconductivity will be discontinuous in this region if these interactions cause  $V$  to change sign. A third area for investigation is the region of high  $N(0)$

<sup>16</sup> T. H. Geballe and B. T. Matthias, Phys. Rev. Letters **8**, 313 (1962).

where one finds the compounds. Since the metals on the upper line of Fig. 4 have a value of  $T_c/\theta_D$  about five times that of the lower line for a given  $N(0)$  it seems reasonable to suppose that one can move up along the upper line to very high values of  $T_c$  by appropriate compound formation. The idea is to narrow the  $d$  band by compound formation and increase  $N(0)$  while maintaining the Fermi level in the center of the third peak. The limit in  $T_c$  probably has been reached in compound formation involving the second peak because in  $V_3Ga$ ,  $N(0)=7.1$  and there are only 10 states in the band. This is far from being the case in the compounds involving the third peak.

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## X-Ray Scattering Factor of Nitrogen in $Fe_4N$ †

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A comparison of the x-ray intensities of the superlattice reflections of  $Fe_4N$  with the normal lattice reflections shows that nitrogen is negatively charged in this compound and is probably in the  $N^{3-}$  state.

THE iron nitride,  $Fe_4N$ , has been shown by x-ray<sup>1,2</sup> and neutron diffraction<sup>3</sup> to be cubic. The space group is probably  $O_h^1-Pm3m$  with

- 1 Fe at (0,0,0);  
 3 Fe at (0,1/2,1/2), (1/2,0,1/2), (1/2,1/2,0);  
 1 N at (1/2,1/2,1/2).

Guillaud<sup>4</sup> found  $Fe_4N$  to be ferromagnetic with a saturation magnetization per gram,  $\sigma=208.5$ . From this value the net number of Bohr magnetons is calculated to be 8.86 per unit cell. A magnetic structure in which the three face-centered irons donate electrons to the nitrogen in the center of the cell, making it  $N^{3-}$ , has been proposed by Zener<sup>5</sup> to account for the observed magnetism. But more recently Wiener and Berger<sup>6</sup> have

suggested a model in which electrons are either transferred in the opposite direction, making nitrogen  $N^{3+}$ , or are used in covalent bonding between the central nitrogen and the nearest iron neighbors. This model has been confirmed by the neutron diffraction work of Frazer.<sup>3</sup> The question of charge distribution in  $Fe_4N$  and similar compounds is only partially answered by these experiments, however, and an x-ray investigation of  $Fe_4N$  was undertaken in this laboratory in the hope of obtaining further information.

The x-ray powder diffraction pattern of  $Fe_4N$  contains several lines of low intensity which are due almost entirely to scattering by nitrogen.<sup>7</sup> Two of these, the (100) and (110), occur at values of  $\sin\theta/\lambda$  for which the calculated intensities are markedly dependent on the nitrogen scattering factor used in the calculation, and thus on the electronic charge. For example, the (100) reflection is roughly five times stronger if nitrogen is in the  $N^{3-}$  state than if it is in the  $N^{3+}$  state. A comparison of these weak reflections with the more intense reflec-

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<sup>1</sup> Gunnar Hägg, Z. Physik. Chem. **8b**, 455 (1930).

<sup>2</sup> K. H. Jack, Proc. Roy. Soc. (London) **A195**, 34 (1948).

<sup>3</sup> B. C. Frazer, Phys. Rev. **112**, 751 (1958).

<sup>4</sup> C. Guillaud, Compt. Rend. **222**, 1170 (1946).

<sup>5</sup> C. Zener, Phys. Rev. **85**, 324 (1952).

<sup>6</sup> G. W. Wiener and J. A. Berger, J. Metals **7**, 360 (1955).

<sup>7</sup> The contribution by iron in different oxidation states in non-equivalent sites is less than 1% of the intensity.

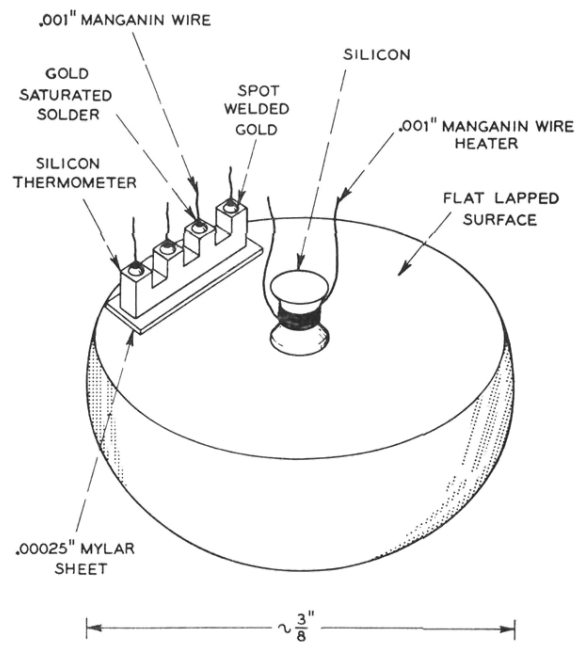


FIG. 1. Sketch showing the scale and manner of mounting thermometer and heater on a typical sample.