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Solute Size and Valence Effect in Some Superconducting Alloys of Transition Elements

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The use of the concept of an effective electron-atom ratio, N_{eff}, which contains a solute size correction (rather than the usual ratio N used in Matthias' rule), introduced earlier in correlating superconducting critical temperatures of some dilute solutions of transition elements of the 4th, 5th, and 6th columns in niobium, has been extended to include some other transition-metal solutes of columns 7, 8, 9, and 10 in niobium. The concept has also been tried on some other transition-metal solid solutions of wider range of composition. For these latter alloys the analysis reveals that peaks in the curve of T_c versus electron-atom ratio occur at $N_{\mathrm{eff}}\sim 4.4$ and ~ 6.6, whereas with the uncorrected electron-atom ratio, these peaks tend to occur near $N\sim 4.7$ and ~ 6.4. The variation of H_{c2} with N_{eff} for alloys of transition metals of columns 4 and 5 suggests that the maximum values of H_{c2} also occur near $N_{\mathrm{eff}} \approx 4.4$. Both peaks in T_c versus N_{eff} and H_{c2} versus N_{eff} seem to be independent of whether the solvent or solute atom is in the 3*d*, 4*d*, or 5*d* series.

INTRODUCTION

THE principal successful guide in describing the occurrence of superconductivity in the periodic system has been the empirical rules proposed by Matthias.[1-3] For an element, alloy or compound, a function $T(N)$ describes qualitatively variations of critical temperature T_c with average number of valence electrons per atom, N. This considers all electrons outside a filled shell. N is often referred to as an electron-atom ratio (e/a) or valence-electron concentration.

For transition elements $T(N)$ peaks when N is equal to 5 and 7;[4] while for the transition-metal alloys, the peaks, though not strictly fixed, are assumed to occur in the vicinity of N equal to approximately 4.7 and 6.4. More specifically, these latter values refer to a series of transition-metal binary alloys of columns 4, 5, 6, and 7 of the periodic table. These alloys offered the first opportunity to examine Matthias' empirical equation in systems that were primary solid solutions with a relatively wide range of solubility and with a simple body-centered cubic structure.[5] For transition metals forming complex phases with σ- or α-Mn structures,[6] the distribution of T_c as a function of electron-atom ratio appears to show a peak when the mean number of electrons is 6.6–6.8.

Attempts have been made to study and discuss these peaks in their relationship to parameters suggested by the BCS theory.[7] For example, an important comparison has been made between T_c and γ, the coeficient of the electronic specific heat related to the parameter $N(0)$, the density of states at the Fermi level.[5,6,8] Further studies to examine the strict validity of the BCS theory in describing the occurrence of superconductivity in transition metals in the periodic system are, at the present time, a subject of much interest.[9-14]

Recently, the critical temperature of some dilute solutions of transition elements of the 4th, 5th, and 6th columns in niobium (body-centered cubic structure) have been found to correlate better with an effective electron-atom ratio N_{eff} which contains a solute size-dependent correction than with the usual ratio N.[15] In this report we have extended this analysis to include some dilute solutions of transition elements of columns 7, 8, 9, and 10 in niobium. The approach has also been extended to a wider range of concentration of some binary substitutional solid solutions of groups 4, 5, 6, and 7 of the periodic table. For these transition-metal alloys, the analysis reveals that the peaks in the curve of T_c versus electron-atom ratio occur at $N_{\mathrm{eff}}\sim 4.4$ and ~ 6.6, while with the uncorrected electron-atom ratio, these peaks tend to occur near $N\sim 4.7$ and ~ 6.4. The analysis has also been tried on the variation of H_{c2} with this parameter for metals of columns 4 and 5, where it is found that H_{c2} also tends to peak near $N_{\mathrm{eff}}\sim 4.4$, similar to the peak occurrence in T_c.

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[1] B. T. Matthias, Phys. Rev. **97**, 74 (1955).

[2] B. T. Matthias, in *Progress in Low Temperature Physics*, edited by C. J. Gorter (North-Holland Publishing Company, Amsterdam, 1957), Vol. II, p. 138.

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

[4] D. C. Hamilton and M. Anthony Jensen, Phys. Rev. Letters **11**, 205 (1963).

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

[6] E. Bucher, F. Heiniger, and J. Muller, *Proceedings of the Eighth International Conference on Low-Temperature Physics, London, 1962*, edited by R. O. Davies (Butterworths Scientific Publications Ltd., London, 1963), p. 153; Physik Kondensierten Materie **2**, 210 (1964).

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

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

[9] J. W. Garland, Jr., Phys. Rev. Letters **11**, 111 (1963); *ibid.* **11** 114 (1963).

[10] B. R. Coles, Rev. Mod. Phys. **36**, 139 (1964).

[11] P. W. Anderson, Science **144**, 373 (1964).

[12] B. T. Matthias, Science **144**, 378 (1964).

[13] E. Bucher, F. Heiniger, J. Muller, and J. L. Olsen, in *Proceedings of the Ninth International Conference on Low Temperature Physics, Columbus, Ohio, 1964*, edited by J. G. Daunt, D. V. Edwards, F. J. Milford, and M. Yagub (Plenum Press, Inc., New York, 1965).

[14] M. Anthony Jensen, Bull. Am. Phys. Soc. **10**, 45 (1965).

[15] W. DeSorbo, Phys. Rev. **130**, 2177 (1963).

DISCUSSION AND RESULTS

A. Effective Electron-Atom Ratio

According to Matthias,[2,3] the relationship between T_c and $T(N)$ may be written as follows:

$$T_c \propto V^x T(N). \tag{1}$$

This approach regards the variation of T_c with volume independent of the variation with N. Recently, Harrison[16] has suggested a specific form for the volume dependence of the valence-electron concentration which takes the size of a solute atom into account. A similar suggestion had been made earlier by him in the theory of electrical resistivity; namely, that if a solute atom is larger than that of the solvent, the lattice is expanded locally and, therefore, the region behaves as if the solute had a lower valence than in the undistorted case; or if the solute atom is smaller than that of the solvent, the lattice contracts locally and, therefore, the region behaves as if the solute has a higher valence than in the undistorted case. This suggestion has been used in examining the resistivity of some nontransition-metal alloys[17,18]; and more recently it has been shown to be effective also in some transition-metal systems.[15]

Following Harrison's suggestion, we may write the effective electron-atom ratio N_{eff} for dilute homogeneous binary solid solutions

$$N_{\mathrm{eff}} = Z_0 + C_1\left[(Z - Z_0) - \left(\frac{\delta V}{V}\right) Z_0\right], \tag{2}$$

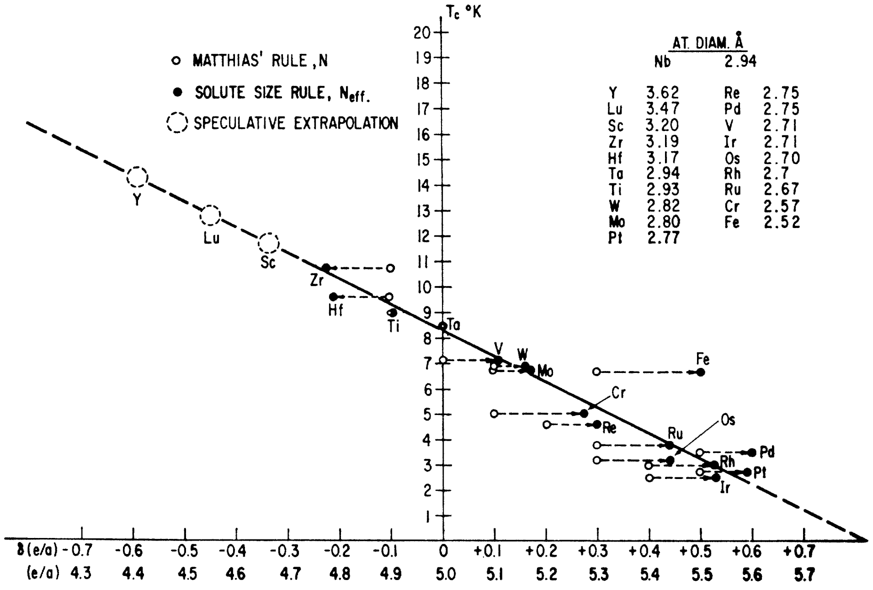
where Z_0 is the valence of the solvent, Z is the valence of the solute, δV is the local change in volume, V is the original cell volume, and C_1 is the atom fraction of the solute. The equation computes the electron-atom ratio in the solvent itself. For general ideal solutions, the expression becomes

$$N_{\mathrm{eff}} = \frac{C_0Z_0 + C_1Z_1 + C_2Z_2 \cdots C_nZ_n}{C_0 + C_1(V_1/V_0) + C_2(V_2/V_0) \cdots C_n(V_n/V_0)}, \tag{3}$$

where C_0 is the atom fraction of the solvent; $C_1, C_2 \cdots$ are the atom fractions of solutes 1, 2, respectively; Z_0 is the valence of the solvent; $Z_1, Z_2 \cdots$ are the valences of the solute atoms; V_0 is the unit cell volume of the pure metal solvent; $V_1, V_2 \cdots$ are the unit cell volumes of the solute metals. The numerator alone gives N as used in Matthias' rule.

B. N_{eff} and T_c for Some Dilute Solutions of Niobium

The change in electron-atom ratio, with and without solute size correction, compared to critical temperature for some dilute solid solutions of niobium, is illustrated in Fig. 1. In determining N_{eff}, the cell volume V and local lattice distortion δV have both been roughly approximated from the atomic diameters. The definition of atomic diameter is that assumed by Hume-Rothery[19]—namely, the closest distance of approach between atoms in a crystal of the element. A more rigorous calculation of the local change in volume and the lattice parameter change is given by Eshelby.[20]



AT. DIAM. Å

Nb	2.94		
Y	3.62	Re	2.75
Lu	3.47	Pd	2.75
Sc	3.20	V	2.71
Zr	3.19	Ir	2.71
Hf	3.17	Os	2.70
Ta	2.94	Rh	2.7
Ti	2.93	Ru	2.67
W	2.82	Cr	2.57
Mo	2.80	Fe	2.52
Pt	2.77		

FIG. 1. The change in electron-atom ratio (e/a) with and without solute size corrections, and critical temperature when 10 at. % solute is added to niobium. The dashed circles are speculative extrapolation of T_c for hypothetical alloys —$\mathrm{Nb}_{0.9}\mathrm{Sc}_{0.1}$, $\mathrm{Nb}_{0.9}\mathrm{Lu}_{0.1}$, and $\mathrm{Nb}_{0.9}\mathrm{Y}_{0.1}$.

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[16] W. A. Harrison, reported in Ref. 15.

[17] F. J. Blatt, Phys. Rev. **108**, 285 (1957).

[18] B. A. Green, Jr., Phys. Rev. **126**, 1402 (1962).

[19] W. Hume-Rothery, *Atomic Theory for Students of Metallurgy* (The Institute of Metal, London, 1960), Chap. 15, p. 121.

[20] J. D. Eshelby, J. Appl. Phys. **25**, 255 (1954).

In addition to presenting the correlation of T_c and N_{eff} of the transition metal solutes of columns 4, 5, and 6 in niobium shown earlier,[15] the correlation has been extended in Fig. 1 to include the T_c data of Geballe[21] on the alloys niobium-ruthenium, niobium-osmium, and niobium-iron (solutes of column 8) and the T_c data recently obtained[22] on niobium-rhenium (solutes of column 7), niobium-rhodium, niobium-iridium (solutes of column 9), and niobium-platinum, niobium-palladium (solutes of column 10). The solute concentration in each case is 10 at. %. In these dilute solutions of transition-metal solutes in niobium, the simple relationship between T_c and N_{eff}, first established with the solutes of columns 4, 5 and 6, seems to be appropriate also for the transition-metal solutes selected from columns 7 through 10 of the periodic table. It is to be noted that this relationship appears to be independent of whether the solute atoms are in the 3*d*, 4*d*, or 5*d* transition series. Extending the empirical relationship to include solute atoms of column 3 would indicate that the primary substitutional alloys of niobium-scandium, niobium-lutetium, and niobium-yttrium, if they could be fabricated, would perhaps be expected to have T_c well above 9°K.

It is to be noted that for the niobium-iron and the niobium-palladium systems correlation of the modified electron-atom ratio with T_c shows a larger variation from the linear relationship. This behavior would indicate an abnormal enhancement of T_c of the alloy by the solute atom. Geballe[21] has suggested that the concept of interaction through virtual states might account for such an enhancement in the niobium-iron alloy. The variation in the niobium-palladium alloy is not clear.

C. N_{eff} and Maximum T_c in Some Transition-Metal Alloys

Figure 2 illustrates the variation of T_c with N and N_{eff} evaluated both from Matthias' rule and from the effective electron-atom ratio, respectively, for four alloys. Each of these alloys has a body-centered cubic structure and a wide range of solubility.[5] The function $T(N)$ has been discussed earlier by Hulm and Blaugher.[5] Of the several alloys studied, the variation of $T(N)$ for these four alloys was considered by them to be most representative of the alloys consisting of metals of columns 4 and 5 from which an average peak value of $N\sim4.7$ was derived. However, it is seen that, when the electron-atom ratio is corrected to include an effective valence of the solute in the solvent matrix, the peaks in the function in each alloy occur at a value of approximately 4.4. In the Nb-Ti system the two functions practically coincide. This would be expected, since the disparity in atom size between the solvent and solute atom is small. In the other three alloys, where a relatively large disparity in atom size exists, the peak in each $T(N_{\mathrm{eff}})$ curve is shifted to the lower value, N_{eff} $\sim$4.4. The results are summarized in Table I.[23] From this analysis it appears that the position of the peak in $T(N_{\mathrm{eff}})$ occuring between columns 4 and 5, is not dependent on whether the solvent or solute atom is in the 3*d*, 4*d* or 5*d* series. If $T(N)$ represents a universal form of the *d* band common to the majority of transition elements in this part of the periodic table, as suggested,[5] then the correction to this band brought about by introducing the concept of effective electron-atom ratio would indicate that the peak in the band occurs at the same value, approximately 4.4 and not 4.7.

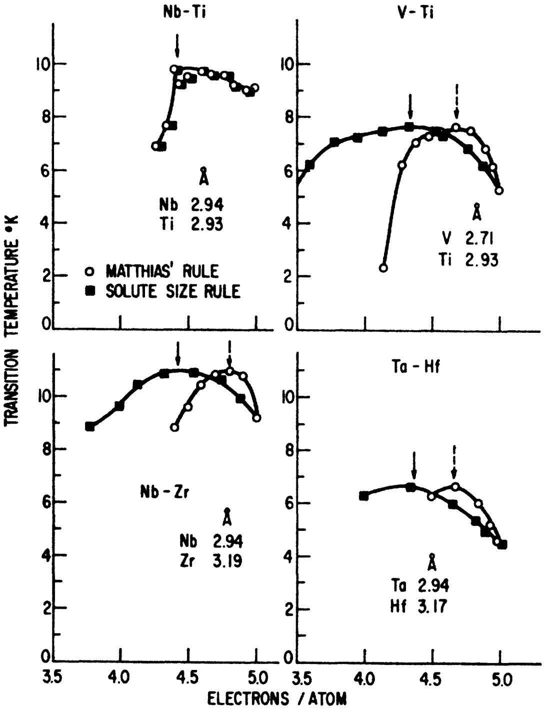

FIG. 2. The variation of T_c with N and N_{eff} evaluated both from Matthias' rule and from the effective electron-atom ratio [Eq. (3)], respectively, for four alloys having a body-centered cubic structure and a wide range of solubility.

It is also interesting to point out that the use of the effective electron-atom ratio, or the solute size valence rule, offers a simple means of accounting for the peaks observed in the T_c-composition curves of some alloy systems where ***both*** the solvent and solute atoms are from the same column of the periodic table. An example of this is the Ti-Zr system[5,24] which also is reported to exist over a wide range of solubility. For such a system the uncorrected electron-atom ratio gives a value $N=4.0$ for the composition corresponding to a maximum in T_c (see Table I); however, for the solute size valence

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[21] T. H. Geballe, Rev. Mod. Phys. **36**, 134 (1964).

[22] W. DeSorbo and W. A. Healy (unpublished).

[23] The results for the Nb-Hf system are anomalously high for either analysis (see also comments in Ref. 5).

[24] E. Bucher, F. Heiniger, J. Muheim, and J. Muller, Rev. Mod. Phys. **36**, 146 (1964).

rule, $N_{\text{eff}}\sim 4.5$, a value more consistent with that obtained for the other alloys.

The Ti-Mo system[25] consisting of transition atoms from columns 4 and 6, also reveals a peak in $T(N_{\text{eff}})$ curve at $N_{\text{eff}}\sim 4.4$ for a composition, $\text{Ti}_{0.84}\text{Mo}_{0.16}$, corresponding to maximum T_c (see Table I).

Alloy systems consisting of elements of columns 6 and 7, having a body-centered cubic structure existing over a wide range of solubility, are molybdenum-rhenium and tungsten-rhenium. The critical temperature of these systems has been studied,[5] and T_c was reported to have a maximum value at N equal to approximately 6.4. Analyzing the data in terms of an effective electron-atom ratio shows the peak in T_c to correspond more closely to a value, $N_{\text{eff}}\sim 6.6$ (see Table II). The same result is obtained when the analysis is carried out on the critical-temperature–composition data obtained by Schadler and Kouvel[26] on the Mo-Re system. The variation of the critical temperature with composition of the system Tc-Mo has also been reported.[27] The alloy found to have the maximum critical temperature has a composition $\text{Tc}_{0.75}\text{Mo}_{0.25}$. The effective electron-atom ratio corresponding to this composition has a value of approximately 6.6 although the structure of this material may not be a terminal solid solution.[28] Significantly, these alloy systems suggest the occurrence of a common peak in the $T(N_{\text{eff}})$ curve existing between columns 6 and 7 at a value $N_{\text{eff}}\sim 6.6$. The positioning of this also appears to be independent of the nature of the d-band electrons of the constituent metals, similar to the peak existing between columns 4 and 5.

It is interesting to note that in the systems, such as $\text{W}_{0.85}\text{Pt}_{0.15}$,[29] $\text{Mo}_{0.84}\text{Rh}_{0.16}$,[30] $\text{Cr}_{0.75}\text{Rh}_{0.27}$,[31] and $\text{Cr}_{0.72}\text{Ir}_{0.28}$ (hcp),[31] where the solvent atom is located in column 6 while the solute atom is in a column higher than 7, N_{eff} corresponding to peaks in T_c also has a value near 6.6 (see Table II). However, there are other systems where peaks in T_c-composition curves have been observed but upon analysis the data in terms of the effective electron-atom ratio do not show the peak to occur at $N_{\text{eff}}\sim 6.6$. Among these systems are, for example, Cr-Re,[21] Nb-Re[6] and Ti-Fe,[29] and Cr-Ir (β-W structure).[31] Whether this difference is a fundamental one or one due to experimental or structural (sample) considerations is not clear at this time.

TABLE I. Maximum critical temperature and the electron-atom ratio with and without solute size correction for some transition metal solutions of the 4th, 5th, and 6th columns of the periodic table.

Alloy	T_c(max.)°K	Electron-atom ratio N (Mathias' rule)	N_{eff} (Solute size rule)
$\text{Ta}_{0.68}\text{Hf}_{0.32}$	6.8[a]	4.68	4.33
$\text{Nb}_{0.60}\text{Ti}_{0.40}$	9.8[b]	4.40	4.43
$\text{Nb}_{0.75}\text{Zr}_{0.25}$	10.9[a]	4.75	4.40
$\text{V}_{0.75}\text{Ti}_{0.25}$	7.6[a]	4.75	4.45
$\text{Nb}_{0.85}\text{Hf}_{0.15}$	9.6[a]	4.85	4.67
$\text{Ti}_{0.5}\text{Zr}_{0.5}$	1.5[a,c]	4.00	4.50
$\text{Ti}_{0.84}\text{Mo}_{0.16}$	~4.0[d]	4.32	4.41

[a] Reference 5.
[b] This research.
[c] Reference 24.
[d] Reference 25.

TABLE II. Maximum critical temperature and the electron-atom ratio with and without solute size correction for some transition metal solutions of (a) the 6th and 7th, and (b) the 6th, 9th, and 10th columns of the periodic table.

Alloy	T_c(max.)°K	Electron-atom ratio N (Matthias' rule)	N_{eff} (Solute size rule)
(a) Columns 6 and 7			
$\text{Mo}_{0.59}\text{Re}_{0.41}$	12.3[a]	6.41	6.55
$\text{Mo}_{0.57}\text{Re}_{0.43}$	14.0[b]	6.43	6.57
$\text{W}_{0.60}\text{Re}_{0.40}$	5.2[a]	6.40	6.59
$\text{Tc}_{0.75}\text{Mo}_{0.25}$	16.4[c]	6.75	6.55
(b) Columns 6, 9, 10			
$\text{W}_{0.85}\text{Pt}_{0.15}$	2.7[d]	6.60	6.55
$\text{Mo}_{0.84}\text{Rh}_{0.16}$	7.8[e]	6.48	6.58
$\text{Cr}_{0.73}\text{Rh}_{0.27}$	1.1[f]	6.81	6.53
$\text{Cr}_{0.72}\text{Ir}_{0.28}$	0.8[f]	6.84	6.53

[a] Reference 5.
[b] H. W. Schadler and J. S. Kouvel (unpublished).
[c] Reference 27.
[d] Reference 29.
[e] Reference 30.
[f] Reference 31.

D. N_{eff} and Maximum H_{c2} in Some Transition-Metal Alloys

Berlincourt and Hake[32] have studied the upper critical field, H_{c2},[33] of some transition metal alloys from elements of columns 4 and 5 mentioned above. The

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[25] R. R. Hake, D. H. Leslie, and T. G. Berlincourt, J. Phys. Chem. Solids **20**, 177 (1961).

[26] H. W. Schadler, and J. S. Kouvel (unpublished). The author is grateful for permission to use this information prior to publication.

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

[28] J. B. Darby, Jr., and S. T. Zegler, J. Phys. Chem. Solids **23**, 1825 (1962).

[29] B. T. Matthias, *Proceedings of the Eighth International Conference on Low-Temperature Physics, London, 1962*, edited by R. O. Davies (Butterworths Scientific Publications Ltd., London, 1963), p. 135.

[30] B. T. Matthias, E. A. Wood, E. Corenzwit, and V. B. Bala, J. Phys. Chem. Solids **1**, 188 (1956).

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

[32] T. G. Berlincourt and R. R. Hake, Phys. Rev. **131**, 140 (1963).

[33] Actually, these authors measured the upper resistive critical field, H_r ($J=10$ A/cm^2), at $T=1.2$°K using a pulsed field method. In some dilute alloys of transition metals where H_{c2} was recently measured by magnetization techniques, this upper resistive critical field, H_r ($J=10$ A/cm^2), was found to be approximately 10% higher than H_{c2} when both quantities were measured at 4.2°K. [see W. DeSorbo, Rev. Mod. Phys. **36**, 90 (1964)]. More recently, the variation of H_{c2} with composition for the Nb-Ti system has been found [P. E. Lawrence, W. A. Healy, and W. DeSorbo (unpublished)] to vary at 4.2°K in a manner similar to the variation of H_r ($J=10$ A/cm^2) with composition at 1.2°K (see Ref. 32). The absolute values of H_{c2} were, as expected, lower at the higher temperature.

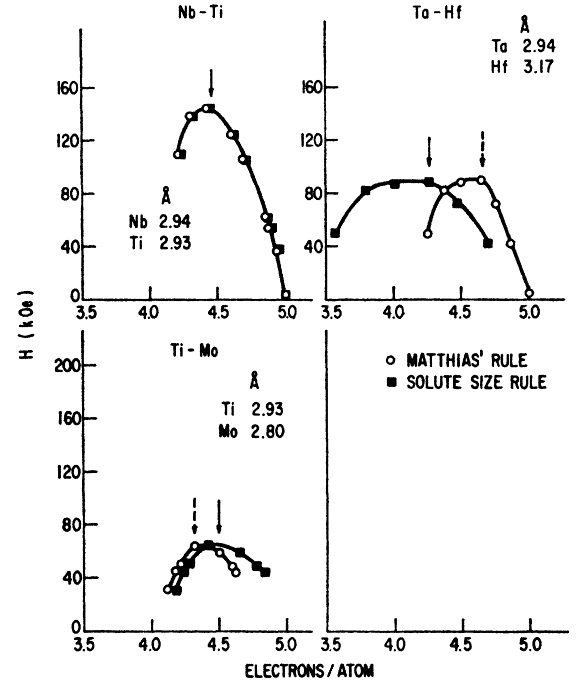

FIG. 3. H_r ($J=10$ A/cm^2, $T=1.2$°K) from Ref. 32 and electron-atom ratio with and without solute size corrections.

variation in H_{c2} with composition or with electron-atom ratio has characteristics similar to the variation observed in the T_c-composition curves.[5]

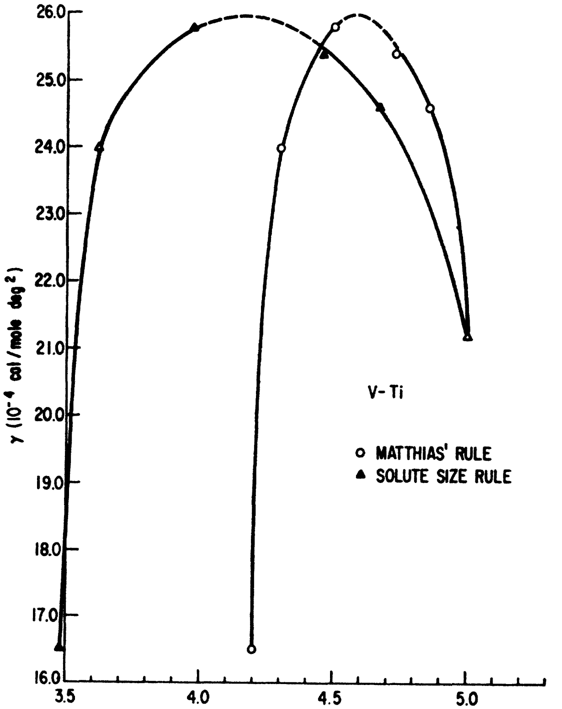

FIG. 4. The coefficient of the electronic specific-heat data of vanadium-titanium (Ref. 35) and the electron-atom ratio with and without solute size correction.

This variation in H_{c2}-composition was discussed by the authors in terms of a simplified relationship of H_{c2} with T_c, γ, and ρ_n, the resistivity in the normal state, namely:

$$H_{c2}\propto \rho_n\gamma T_c. \tag{4}$$

The equation is derived from the Ginsburg-Landau-Abrikosov-Gorkov theories. It is significant to note that in those alloys revealing smooth H_{c2}-composition curves, reflecting the presence of homogeneous solid solutions, when H_{c2} is analyzed in terms of $N_{\rm eff}$, it also appears to peak at a value of $N_{\rm eff}$ equal to 4.4.[34] This is illustrated in Fig. 3, where the H_{c2} data have been analyzed both in terms of the unmodified Matthias rule and the effective electron-atom ratio. The analysis has been carried out on an alloy where the disparity in atom size between the solvent and solute is small (Nb-Ti); where it is relatively large (Ta-Hf); and where the two atoms of different size occur in the same column of the periodic table, namely column 4 (Ti-Mo).

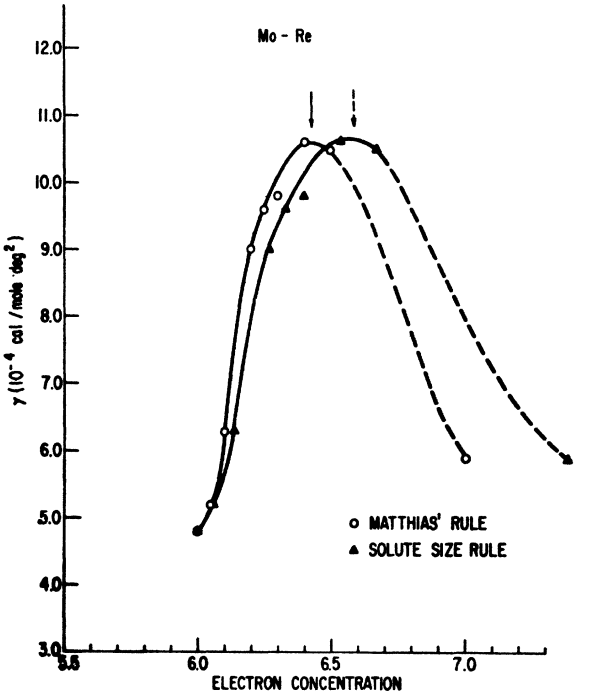

FIG. 5. The coefficient of the electronic specific-heat data of molybdenum-rhenium (Ref. 36) and the electron-atom ratio with and without solute size correction.

Accurate specific-heat data required to evaluate γ of the alloys of interest here is scarce. In Figs. 4 and 5 we show some values of γ plotted as a function of electron

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[34] An exception to this appears to be the V-Ti system. Analyses of the H_{c2}-composition data [Refs. 32 and 33; also Y. B. Kim, C. F. Hempstead, and A. F. Strnad, Phys. Rev. 139, A1163 (1965)] show the maximum in H_{c2} to appear at approximately $N_{\rm eff}=3.9$. Again, whether this is a fundamental difference or one due to experimental conditions is not clear.

concentration for the systems V-Ti[35] and Mo-Re.[36] When the data are presented in terms of an effective electron-atom ratio, there is an apparent shift in the position of the peak of the curve to a value N_{eff} less than 4.7, probably close to 4.4, for the V-Ti system; and an apparent shift in the peak from 6.4 to 6.6 for the Mo-Re system. The physical significance of this is not clear.

The influence of effective valence on resistivity of some of these transition-metal alloys has already been cited.[15]

SUMMARY

1. The change in electron-atom ratio N_{eff}, which includes a solute size correction to determine an effective valence of the solute in a transition-metal matrix such as niobium, reveals a linear relationship with T_c for dilute alloys of niobium with transition-metal solutes selected from columns 4 through 10 of the periodic table.
2. For transition-metal alloys of columns 4 and 5 and columns 6 and 7, with body-cubic centered structures, the function $T(N_{\mathrm{eff}})$ has peak values at approximately 4.4 and 6.6, respectively, whereas the unmodified functions were earlier shown to have average peak values at approximately 4.7 and 6.4.
3. In these transition-metal alloys, the influence of solute size on effective valence and on T_c appears to be independent of whether the solvent or solute are of the 3*d*, 4*d*, or 5*d* series.
4. The concept of effective electron-atom ratio offers a simple means for accounting for maxima in T_c-composition curves observed in some transition-metal alloys where both the solvent and solute metal are from the same column of the periodic table.
5. Alloys made from transition metals of columns 4, 5, and 6 with a wide range of solubility appear to show that the upper critical field H_{c2} also has a peak value near $N_{\mathrm{eff}} \sim 4.4$.

ACKNOWLEDGMENTS

The author wishes to thank W. A. Harrison for valuable discussions. Discussions with R. L. Fleischer and helpful criticism of the manuscript by B. W. Roberts are also gratefully acknowledged.

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[35] C. H. Cheng, C. T. Wei, and P. A. Beck, Phys. Rev. **120**, 426 (1960).

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

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Photomagnetoelectric Effect in Thin *p*-Type Silicon Crystals

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The photomagnetoelectric (PME) open-circuit voltage has been measured at room temperature for thin *p*-type silicon samples subjected to various surface treatments The effect was found to increase linearly with the magnetic field up to 20 kG, but for all surface treatments showed sublinear behavior with photon flux even at relatively low light intensities. This effect, which was more pronounced at shorter wavelengths, could be attributed to an accumulation layer in the space-charge region of the crystal. Toward longer wavelengths the PME voltage versus light intensity became linear and could be used for calculating an effective surface recombination velocity S^* at the border between the space-charge region and the bulk crystal.

INTRODUCTION

THE photomagnetoelectric (PME) effect in semiconductors has been measured extensively for Ge,[1–3] InSb,[4] InAs,[5,6] PbS,[7] Bi,[8] Te,[9] and theoretical treatments have been given for the case of nonpenetrating light,[10] exponential absorption profile,[11] nonlinear surface recombination rates,[12] and bulk trapping effects.[13] For silicon there exists only one qualitative measurement,[14] and a short note in which the dependence of the effect on light intensity for one wavelength and one surface treatment have been reported.[15] Since the PME effect is generally considered, in conjunction with the photoconductivity (PC), a powerful tool for the investigation of bulk lifetimes and surface recombi-

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