Superconductivity and Electron Interaction in the 3d Band

K. Andres, E. Bucher, J. P. Maita, and R. C. Sherwood

Bell Telephone Laboratories, Murray Hill, New Jersey 07974

(Received 7 May 1968; revised manuscript received 21 October 1968)

The superconducting transition temperatures, electronic specific heats, and magnetic susceptibilities have been measured for the alloy series Cr-V, Cr-Mo, V-Mo, Ru-Fe (hcp), and Ru-Mn (hcp). These data are combined within the framework of current theoretical models, and conclusions are drawn regarding the strength of the electron phonon attraction and electron-electron repulsion in the 3d band. In particular, it is deduced that the superconducting transition temperature of "paramagnetic" Cr would be $\sim 10^{-6}$°K, and that paramagnetic (hcp) Fe and Mn would not be superconducting at any temperature.

I. INTRODUCTION

IN this paper we wish to present measurements of superconducting transition temperatures, electronic specific heats, and magnetic susceptibilities for several transition-metal alloy series. By combining these data in the light of current theoretical models, it is possible to draw conclusions regarding the variation of both the electron-phonon and electron-electron interaction in the 3d band. One may also examine the possibility of superconductivity of the paramagnetic state of Cr, hcp Fe, and hcp Mn. The spirit of the investigation is much like that of Heiniger *et al.*,[1] who found by extrapolation of the electronic specific heat γ in the paramagnetic Mo-Cr alloy series that "paramagnetic" Cr would have a γ value considerably larger than that observed in the itinerant antiferromagnetic spin-density-wave state which occurs at atmospheric pressure.

II. EXPERIMENTAL

The starting materials used are listed in Table I. All samples were melted in an argon arc furnace. In Mo-Cr, Ru-Fe, and Ru-Mn, the weight loss was assumed to be due to the more volatile component only, and therefore the composition was calculated from the final wei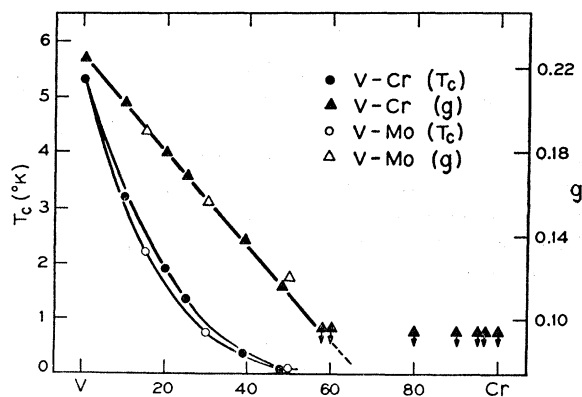ght. Superconductivity was measured with a mutual inductance method at 28 Hz. In cases where large concentration gradients in the sample had to be expected (Mo-Cr), the sample was cut or its surface ground off and etched, but no difference in transition temperature could be detected. The samples were annealed for 48 h at 1000°C at pressures below 10^{-6} torr, except Mo-Cr where segregation occurs. For the technique of the measurement of specific heat and susceptibility we refer the reader to Refs. 2 and 3, respectively.

III. RESULTS

Our new data are listed in Table II together with relevant data of other authors, as indicated. The variations of the transition temperature T_c and of the BCS parameter $g=[\ln(1.14\Theta/T_c)]^{-1}$ ($\Theta=$Debye temperature) in the V-Cr and V-Mo alloys are quite similar, as shown in Fig. 1. It should be noted that we found a much smaller drop in T_c of vanadium per atomic percent of Cr, as well as per atomic percent of other solutes like Mn, Fe, and Co, in contrast to earlier results.[4,5] Our high purity vanadium, kindly supplied by Sullivan (Bureau of Mines, Boulder City, Nevada), had a transi-
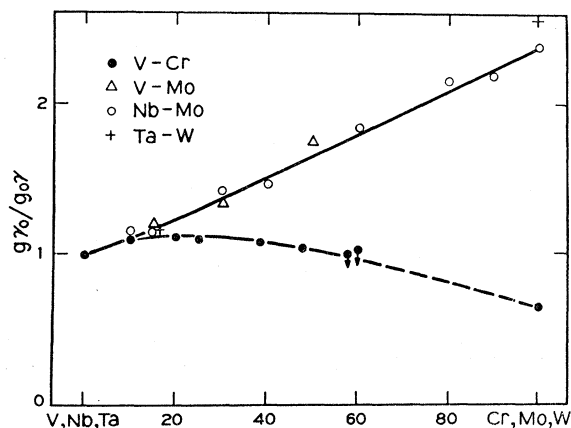

FIG. 1. Transition temperatures and $g=[\ln(1.14\Theta/T_c)]^{-1}$ in V-Cr and V-Mo alloys.

FIG. 2. Electron interaction in V-Cr, V-Mo, Nb-Mo, and Ta-W alloys.

[1] F. Heiniger, E. Bucher, and J. Muller, Phys. Letters 19, 163 (1965).

[2] F. J. Morin and J. P. Maita, Phys. Rev. 129, 1115 (1963).
[3] R. M. Bozorth, H. J. Williams, and D. E. Walsh, Phys. Rev. 103, 572 (1956).
[4] J. Muller, Helv. Phys. Acta 32, 141 (1959).
[5] J. K. Hulm and R. D. Blaugher, Phys. Rev. 123, 1569 (1961)

TABLE I. Source and purity of the elements used for the alloys.

Element	Supplier	Purity	Other characteristics
V	T. A. Sullivan, Bureau of Mines	$\geq 99.94\%$	$T_c = 5.31°K$ $RR = 500$
Cr	Battelle	$\geq 99.999\%$	
Mo	Wah-Chang	$\geq 99.99\%$	$T_c = 0.91°K$
Ru	United Mineral and Chemical Corp.	$\geq 99.999\%$	
Fe	United Mineral and Chemical Corp.	$\geq 99.999\%$	
Mn	Johnson Matthey	$\geq 99.99\%$	

tion temperature $T_c = 5.31°K$ and a residual resistivity ratio of 500. In both of these systems, this drop in T_c must be due to the decreasing electronic specific heat γ. According to the BCS theory, if renormalization is taken into account,[6] the ratio g/γ is the net average electron-electron interaction (i.e., the phonon-mediated

TABLE II. Superconducting transition temperature, electronic specific heat, Debye temperatures, and susceptibilities of alloys investigated.

Alloy	T_c (°K)	$\gamma \frac{mJ}{°K^2\,mole}$	θ (°K)	$10^6 \chi_{1.43}°$ cm³/mole	$10^6 \chi_{296}°$ cm³/mole
$V_{0.90}$ $Cr_{0.10}$	3.21	a	b		
$V_{0.80}$ $Cr_{0.20}$	1.90	a			
$V_{0.75}$ $Cr_{0.25}$	1.36	a			
$V_{0.61}$ $Cr_{0.39}$	0.37	a			
$V_{0.52}$ $Cr_{0.48}$	0.10	a			
$V_{0.42}$ $Cr_{0.58}$	<0.015	a			
$V_{0.40}$ $Cr_{0.60}$	<0.015	a			
$V_{0.20}$ $Cr_{0.80}$	<0.015				
$V_{0.10}$ $Cr_{0.90}$	<0.015				
$V_{0.08}$ $Cr_{0.92}$	<0.015				
$V_{0.055}$ $Cr_{0.945}$	<0.015				
$V_{0.85}$ $Mo_{0.15}$	2.28	6.94	395		
$V_{0.70}$ $Mo_{0.30}$	0.76	5.15	403		
$V_{0.50}$ $Mo_{0.50}$	0.11	3.02	412		
$Mo_{0.94}$ $Cr_{0.06}$	0.71	c	c		
$Mo_{0.85}$ $Cr_{0.15}$	0.50	c	c	99	104
$Mo_{0.75}$ $Cr_{0.25}$	0.155	c	c		
$Mo_{0.60}$ $Cr_{0.40}$	0.095	c	c		
$Mo_{0.525}$ $Cr_{0.475}$	0.045	c	c	131	135
$Mo_{0.43}$ $Cr_{0.57}$	0.030	c	c		
$Mo_{0.27}$ $Cr_{0.73}$	<0.015	c	c	152	155
$Mo_{0.16}$ $Cr_{0.84}$	<0.015	c	c	154	162
$Mo_{0.08}$ $Cr_{0.92}$	<0.015	c	c	155	164
Cr	<0.015			154	164.5
$Ru_{0.982}$ $Fe_{0.018}$	0.165				
$Ru_{0.969}$ $Fe_{0.031}$	0.054				
$Ru_{0.957}$ $Fe_{0.043}$	0.018				
$Ru_{0.95}$ $Fe_{0.05}$	<0.015			70	73
$Ru_{0.90}$ $Fe_{0.10}$	<0.015			97	104
$Ru_{0.75}$ $Fe_{0.25}$	<0.015	d	d	168	183
$Ru_{0.50}$ $Fe_{0.50}$	<0.015	7.78[d,e]	447[d]	249	283
$Ru_{0.30}$ $Fe_{0.70}$	<0.015	7.56	445	306	354
$Ru_{0.80}$ $Mn_{0.20}$		5.28	489	137	148
$Ru_{0.65}$ $Mn_{0.35}$				196	211
$Ru_{0.52}$ $Mn_{0.48}$				224	246

[a] T. M. Srinivasan and P. A. Beck, Ann. Acad. Sci. Fennicae 210, 163 (1966).
[b] θ linearly interpolated between V($\theta = 399°K$) and Cr($\theta = 630°K$).
[c] Reference 1.
[d] F. Heiniger, E. Bucher, and J. Muller, Phys. Kondensierten Materie 5, 243 (1966).
[e] H. Claus, J. Phys. Chem. Solids 28, 2449 (1967).

[6] J. R. Schrieffer, Theory of Superconductivity (W. A. Benjamin, Inc., New York, 1964), p. 169 ff.
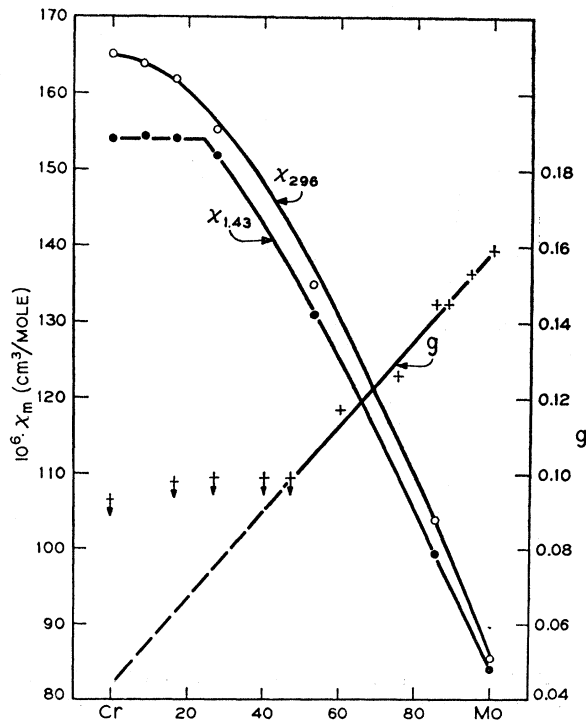

FIG. 3. Low- and room-temperature susceptibility and $g = [\ln(1.14\theta/T_c)]^{-1}$ in bcc Cr-Mo alloys.

electron-electron attraction minus the screened Coulomb repulsion divided by the enhancement factor of the bare density of states due to the electron-phonon interaction. This ratio g/γ is plotted in Fig. 2 for the two systems V-Cr and V-Mo, as well as for the isoelectronic systems Nb-Mo [7] and Ta-W.[5,8] The values are normalized to their values for the parent metal V, Nb, and Ta, respectively. As can be seen, there is a striking difference between the 3d solute Cr and the 4d and 5d solutes Mo and W. The g value of pure "paramagnetic" Cr used in Fig. 2 has been obtained by linearly extrapolating g values in the Mo-Cr system to pure Cr (see Fig. 3). The value of γ for paramagnetic Cr used in Fig. 2 is taken from the extrapolation of Heiniger et al.[1] of γ in the Cr-Mo system. According to the extrapolation in Fig. 3, paramagnetic Cr would be superconducting around 10^{-6} °K which unfortunately prevents an experimental study of the influence of spin-density waves (SDW) on superconductivity in Cr and its alloys. Figure 3 also shows the increase in susceptibility in the isoelectronic Cr-Mo system towards the Cr-rich side, which is partly due to an increase in the d-band density of states and partly due to an increase in exchange enhancement. We will show in our analysis in Sec. IV that the lack of superconductivity

[7] B. W. Veal, J. K. Hulm, and R. D. Blaugher, Ann. Acad. Sci. Fennicae 210, 108 (1966).
[8] E. Bucher, F. Heiniger, and J. Muller, in Proceedings of the Ninth International Conference on Low Temperature Physics, edited by J. G. Daunt et al. (Plenum Press, Inc., New York, 1965), p. 1059.
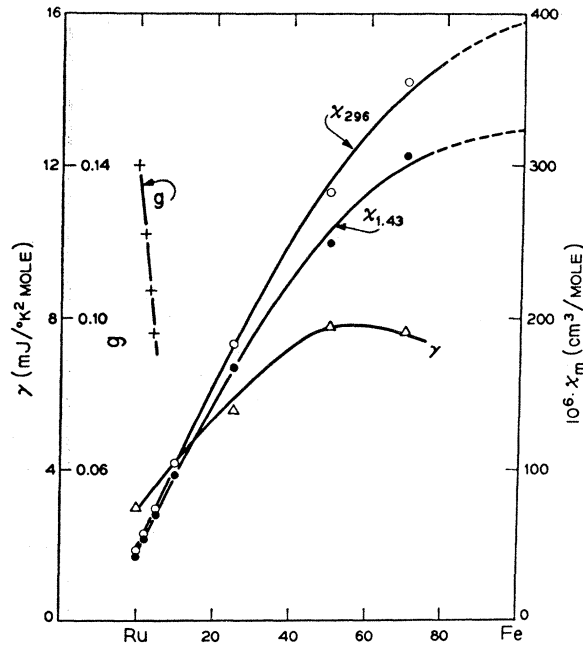
FIG. 4. Low- and room-temperature susceptibility, electronic specific heat, and $g=[\ln 1.14\theta/T_c]^{-1}$ in Ru-Fe (hcp) alloys.

in paramagnetic Cr is however not only due to an increased exchange enhancement between the d electrons but also due to a lower electron-phonon interaction in Cr compared to Mo.

In Fig. 4, the experimental results in Ru-Fe (hcp) are analyzed in a similar way. With the addition of Fe, the superconductivity of Ru vanishes surprisingly fast, although the system remains in the Pauli paramagnetic state over the whole range of the hcp phase (i.e., the Fe does not show a local moment in this phase). In Fig. 5, the electronic specific heat and the low-temperature susceptibility of the two systems Ru-Fe and Ru-Mn are compared. In both systems, the susceptibility is exchange enhanced with the addition of Fe or Mn, but it is enhanced somewhat less in the case of Mn. If Mn could be stabilized in an hcp phase (e.g., at high pressure) one would therefore expect it to be paramagnetic in analogy with hcp iron.[9]

IV. DISCUSSION

In this section we calculate the Coulomb interaction parameter μ and the electron-phonon interaction parameter λ from experimental values of T_c, θ, γ, and χ in the alloy series investigated. In doing this a uniform, rigid d-band model is assumed. It is generally accepted that this is a very good approximation especially in the middle of the d band, e.g., in the V-Cr and Nb-Mo alloys. In the alloy systems Mo-Cr, Ru-Fe, and Ru-Mn this is certainly not true. We now make use of the BCS

theory with renormalization effects taken into account, as treated by Schrieffer[6]:

$$T_c = 1.14\Theta e^{-1/g} \tag{1}$$

with

$$g = (\lambda - \mu^*)/(1+\lambda), \tag{2}$$

and

$$\mu^* = \mu/[1+\mu \ln(\epsilon_F/k\Theta)]. \tag{3}$$

In the intermediate $(\frac{1}{2}<\lambda<1)$ and strong-coupling limit $(\lambda>1)$. McMillan's formula,[10] instead of (1) and (2), is used

$$T_c = \frac{\theta}{1.45} e^{-1.04(1+\lambda)/[\lambda-\mu^*(1+0,62\lambda)]}. \tag{4}$$

λ and μ are the products of the bare density of states times an average of the electron-phonon or an electron-electron matrix element. The electronic specific heat γ is proportional to the bare density of states N_0 enhanced by a factor $1+\lambda$:

$$\gamma = \frac{2}{3}(\pi k)^2 N_0 (1+\lambda). \tag{5}$$

The Pauli spin susceptibility χ_s is also proportional to the bare density of states and enhanced by the Stoner factor $1/1-\mu$, where μ is the unscreened Coulomb repulsion:

$$\chi_s = 2\mu_B^2 N_0/(1-\mu). \tag{6}$$

The set of Eqs. (3)–(6) or (1)–(3)+(5) and (6) is sufficient to determine the unknown values; λ, μ, μ^*, and N_0, assuming we know approximate values of ϵ_F.

For V and Cr we chose $\chi_s = 160\times10^{-6}$ and 80×10^{-6} cm^3/mole [11] and $\epsilon_F = 2.0$ and 2.5 eV,[8] respectively. The uncertainty in χ_s is mostly due to our lack of knowledge of the orbital contribution to χ. Fortunately, λ does not depend critically on this choice because of Eq. (3). In the V-Cr system, μ^* was linearly interpolated and λ calculated as a function of μ^*, T_c, and θ. The values of λ in V-Cr calculated in this way are plotted in Fig. 6 together with the same parameter in the corresponding $4d$ alloy series Nb-Mo. In the latter case, however, the analysis is more straightforward because the superconducting isotope effect in Mo is well known,[12] leading directly to experimentally observable values of μ^* and λ as can be seen in the following equations:

$$T_c \sim M^{-1/2(1-\zeta)}, \tag{7}$$

$$\lambda = [g/2(1-g)^2]\{2(1-g)+\zeta g$$
$$+\zeta^{1/2}[4(1-g)+\zeta g^2]^{1/2}\}, \tag{8}$$

$$\mu^* = g[\zeta(1+\lambda)]^{1/2}. \tag{9}$$

Equations (7)–(9) are based on Eqs. (1)–(3) [McMillan's formula (4) of course would lead to two ex-

[9] D. N. Pipkorn, C. K. Edge, P. Debrunner, G. De Pasquali, H. G. Drickamer, and H. Frauenfelder, Phys. Rev. **135**, A1604, (1964).

[10] W. L. McMillan, Phys. Rev. **167**, 331 (1968).
[11] J. S. Denbigh and W. M. Lomer, Proc. Phys. Soc. (London) **82**, 156 (1963).
[12] B. T. Matthias, T. H. Geballe, E. Corenzwit, and G. W. Hull, Jr., Phys. Rev. **129**, 1025 (1963); E. Bucher and C. Palmy, Phys. Letters **24A**, 340 (1967).

pressions similar to (8) and (9)]. Expressions (7)–(9) can also be used to test various theoretical models leading to values for μ, μ^* or λ. It is now interesting to note that in the case of Mo the experimentally observed $\mu^*=0.102$ can be theoretically calculated assuming a Thomas-Fermi-type potential which leads to an expression[13]

$$\mu = \tfrac{1}{2}X \ln(1+1/X),\qquad(10)$$

with

$$X = \frac{3\pi}{4}\left(\frac{e\hbar}{\pi k}\right)^2 \frac{\gamma_0}{\epsilon_F},\qquad(11)$$

where γ_0 is the bare electronic specific heat. With $\gamma_0=0.144$ mJ/°K^2 cm^3, $\epsilon_F=5$ eV, and $m_B^*=m$, where m_B^* is the band effective mass we also find $\mu^*=0.10$. Encouraged by this agreement, we calculated μ^* first in the Nb-Mo alloy series, using (10) and (11) with $\lambda=0$ as a first approximation and correcting γ for $\lambda\neq0$ in the second iteration. For Nb we chose $\epsilon_F=4$ eV, $m_B^*=m$ and interpolated ϵ_F linearly in the Nb-Mo alloy series. λ in Nb-Mo was again calculated as a function of μ^*, T_c, and Θ. The values obtained in this way for Nb-Mo are also plotted in Fig. 6. In the narrow band limit ($X\gg1$), the Thomas-Fermi model fails since it yields a maximum value $\mu=\tfrac{1}{2}$. Vanadium appears to be such a limiting case. With the Thomas-Fermi model we find $\mu=0.48$ compared with 0.51 for our chosen X_s value. According to Fig. 6, the electron-phonon interactions in the $3d$ elements V and Cr are smaller than in the corresponding $4d$ elements Nb and Mo. Moreover, μ (and μ^*) gradually increases towards the end of the $3d$ band, leading to ferromagnetism. It is, therefore,
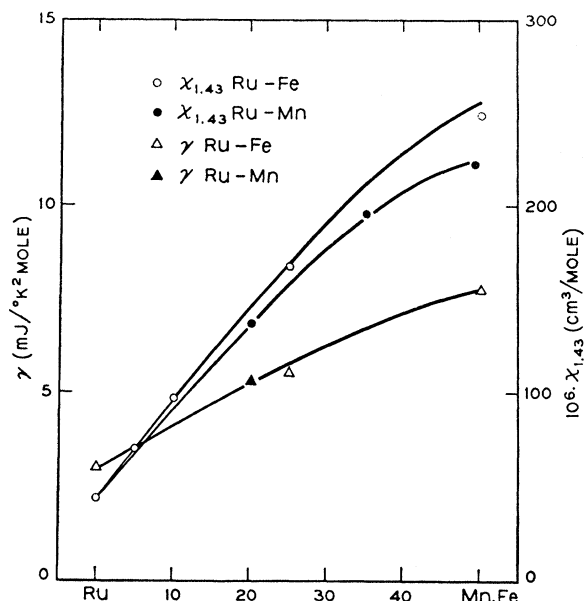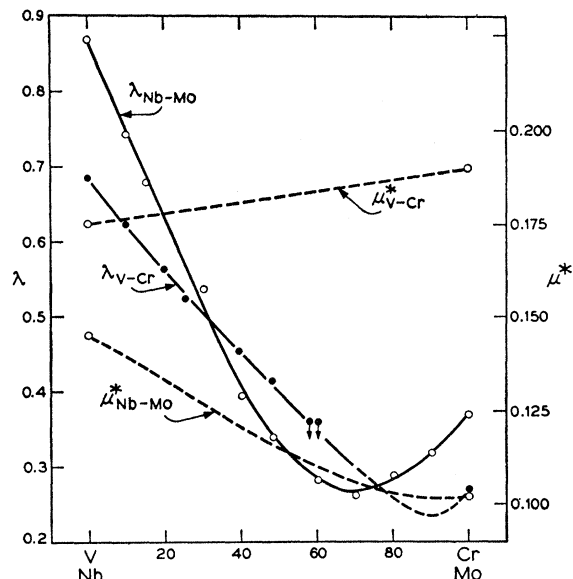

FIG. 6. Electron-phonon and screened Coulomb interaction in V-Cr and Nb-Mo alloys.

both the low value of λ and the high value of μ^* which are responsible for the extremely low transition temperature of 10^{-6} °K which we extrapolate for paramagnetic Cr and which makes the study of the influence of (SDW) on superconductivity impossible in this element. It must be emphasized that the decrease in T_c in the isoelectronic system Mo-Cr cannot be explained by ascribing this drop to an increasing μ^* only (and assuming λ to be constant). This would lead to an unreasonably high value $\mu^*=0.25$. Even in the ferromagnetic limit $\mu=1$, μ^* cannot exceed 0.21. If we compare the average electron-phonon matrix element λ/N_0 the difference between the $3d$ and $4d$ elements becomes even larger. No explanation of this fact has yet been given, but it seems almost obvious that λ and μ are somehow correlated if we compare the $3d$- with the $4d$-band values. In the Ru-Fe (hcp) system the transition temperature T_c drops very rapidly and no extrapolation of T_c is possible to the paramagnetic hcp phase of Fe. It is, however, extremely unlikely that this phase will become superconducting. Using for comparison the low-temperature susceptibility $X\approx320\times10^{-6}$ cm^3/mole for pure hcp Fe, as extrapolated from Ru-Fe alloys and the specific-heat coefficient $\gamma\approx5.9mJ/K^2$ mole,[14] we see that the enhancement in hcp Fe is only slightly lower than in pure Pd, which cannot be expected to be a superconductor.[15] If we try to apply expressions (1)–(3), (5), and (6) and make use of (7)–(9) for pure Ru($\zeta=1$)[16] one

FIG. 5. Low-temperature susceptibility and electronic specific heat in Ru-Fe (hcp) and Ru-Mn (hcp) alloys.

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

[14] G. L. Stepakoff and L. Kaufmann, Acta Met. 16, 3 (1968).
[15] K. Andres and M. A. Jensen, Phys. Rev. 165, 533 (1968).
[16] T. H. Geballe, B. T. Matthias, G. W. Hull, Jr., and E. Corenzwit, Phys. Rev. Letters 6, 275 (1961); T. H. Geballe and B. T. Matthias, IBM J. Res. Develop. 6, 256 (1962); D. K. Finnemore and D. E. Mapother, Phys. Rev. Letters 9, 288 (1962); R. A. Hein and J. W. Gibson, Phys. Rev. 131, 1105 (1963); J. W. Gibson and R. A. Hein, Phys. Rev. 141, 407 (1966).

would find an increase in μ^* in pure Ru per unit of Fe concentration of $d\mu^*/dc = 2.3 \times 10^{-3}$ (at.%)$^{-1}$ and a corresponding drop of λ of $d\lambda/dc = -1.3 \times 10^{-2}$ (at.%)$^{-1}$. This drop in λ with the addition of small portions of Fe appears to be much too large and the error must be due to our assumption of a homogeneous enhancement model of the susceptibility. The addition of Fe in Ru will introduce a locally enhanced magnetization at the Fe atom and therefore a locally varying Coulomb repulsion. In k space, the Coulomb interaction μ can no longer be considered to be constant and therefore making the screening [see Eq. (3)] less effective. At least qualitatively, it can be expected that the introduction of a local exchange enhancement will tend to increase $d\mu^*/dc$ over the value calculated above and therefore make the drop $d\lambda/dc$ less drastic. More details of course can only be obtained by solving the gap equation, which is beyond the scope of this work.

Finally, we would like to discuss another interesting problem related to the low-temperature susceptibility in Mo-Cr. From the difference $\Delta\gamma = \gamma_p - \gamma_{af}$ between the paramagnetic and antiferromagnetic state one might expect a difference $\Delta\chi$ in the low-temperature susceptibility equal to

$$\Delta\chi = \tfrac{1}{3}\alpha\Delta\gamma/(1+\lambda)(1-\mu). \qquad (12)$$

α is a conversion constant (13.7 if γ is measured in $mJ/°K^2$ mole and χ in 10^{-6} cm^3/mole). The factor $\tfrac{1}{3}$ is explained in Fedder's and Martin's paper,[17] since χ parallel to the spin direction vanishes at $T = 0$ and the value perpendicular remains unchanged.[18] (12) yields a value of 13×10^{-6} cm^3/mole in pure Cr, compared with experimentally observed values between 8 and 12. From these values we have to subtract a few units due to the temperature dependence of the chemical potential as Cr is close to a minimum in the $3d$-band density of states. Part of the discrepancy between the experimental value and the value given by Eq. (12) could be due to an error in μ. The residual discrepancy might

be explained by the possibility that the SDW state has a higher Coulomb interaction than the paramagnetic state. This possibility seems to us more likely rather than an additional paramagnetic contribution due to the magnetic energy gap as suggested by Heiniger.[19]

V. CONCLUSIONS

Combining experimental results of superconductivity, electronic specific heat and susceptibility in V-Cr, V-Mo, Mo-Cr, and Nb-Mo it is shown that the electron phonon interaction in the $3d$ band is generally much smaller than in the $4d$ and $5d$ bands. For Cr in its hypothetical paramagnetic state (which can probably be generated at very high pressure)[20] we extrapolate an extremely low transition temperature of the order 10^{-6} °K due to both a large Coulomb repulsion and a weak attractive electron-phonon interaction. Therefore the simultaneous occurrence of superconductivity and SDW cannot be studied, but probably these two phenomena are incompatible because a relatively high Coulomb repulsion is apparently needed for stabilization of the SDW state. The rapid drop of T_c in Ru-Fe cannot be explained by a uniform band model. To explain this drop the influence of local exchange enhancement has to be taken into account explicitly in the theory of superconductivity. It is very unlikely that Fe in its hcp paramagnetic state as well as a hypothetical hcp Mn phase are superconducting.

[17] P. A. Fedders and P. C. Martin, Phys. Rev. **143**, 245 (1966).
[18] We would like to thank T. M. Rice and B. I. Halperin for bringing this point to our attention.

[19] F. Heiniger, Phys. Kondensierten Materie **5**, 285 (1966).
[20] D. B. McWhan and T. M. Rice, Phys. Rev. Letters **19**, 846 (1967).