Phys. kondens. Materie 5, 243—284 (1966)

Bericht - Revue générale - Review Article

Low Temperature Specific Heat of Transition Metals and Alloys

F. HEINIGER, E. BUCHER and J. MULLER
Institut de Physique Expérimentale, University of Geneva, Switzerland

Received July 11, 1966

The article reviews experimental results on the low temperature specific heat of the transition metals and their alloys. Particularly discussed are the variations of the electronic part on the basis of a complete compilation of measurements given.

On résume les résultats expérimentaux concernant la chaleur spécifique à basse température des métaux de transition et de leurs alliages. Particulièrement, les variations de la contribution électronique sont discutées sur la base d'un recueil complet des mesures.

Die experimentellen Ergebnisse zur spezifischen Wärme der Übergangsmetalle und ihrer Legierungen bei tiefen Temperaturen sind übersichtlich dargestellt. Die Diskussion betrifft vor allem die Variationen des elektronischen Anteils und stützt sich auf eine vollständige Zusammenstellung der Meßresultate.

Contents

Introduction

Since 1956, when the review article of KEESOM and PEARLMAN [*1*] appeared, the list of low temperature specific heat data of solids has increased impressively, but no subsequent survey on this subject has been given. Most of the data has to be sought in the vast literature of the last ten years. A good picture of the actual knowledge of the electronic structure of transition metals and alloys is given in a book edited by BECK [*2*], and in an article by MOTT [*3*], but neither contains a complete compilation of known data.

At the time of the article of KEESOM and PEARLMAN [*1*] the measurements in the domain of calorimetry were mainly restricted to elements; since 1956 not only have most of the elements been measured or remeasured, but also some hundreds of binary and other alloys have been investigated. In view of the large amount of new data we have restricted the present survey to transition metals and to alloys with a major fraction composed of these elements. We have also limited ourselves to the discussion of properties in the normal state and have neglected those of main interest in superconductivity theory. Several of our own hitherto unpublished results appear in the tables given in the review.

A. Basic Results of Specific Heat Theory

In our treatment of theoretical aspects of the work we shall only mention the main results of specific heat theory and those facets of it which are of direct interest to the experimental results to be presented. For more detailed accounts we suggest further reference to the literature (e. g. [*4*—*8*]).

The Lattice Specific Heat

The lattice specific heat of a solid is determined by the total vibrational frequency distribution $\varrho(\nu)$:

$$C_l = 3\,N\,k \int\limits_0^\infty \frac{(h\,\nu/k\,T)^2 \exp(h\,\nu/k\,T)}{[\exp(h\,\nu/k\,T) - 1]^2}\,\varrho(\nu)\,d\nu\,, \tag{1}$$

with $\int\limits_0^\infty \varrho(\nu)\,d\nu = 1$. The temperature range of interest in this article only requires a knowledge of $\varrho(\nu)$ for low frequencies. For ν low enough the distribution function must be that of an elastic continuum and has the form

$$\varrho(\nu) = \alpha_2\,\nu^2 = 4\,\pi\,v_\mathrm{a} \left\langle \frac{1}{v^3} \right\rangle_{\mathrm{av}} \nu^2\,, \tag{2}$$

with the average taken over the longitudinal and transverse modes and over all directions of the lattice wave velocities v. The coefficient α_2 is determined by the elastic constants and the density of the crystal. In this way we can approximate eq. (1), and at low temperatures we obtain the well-known T^3 law:

$$C_l = \frac{12\,\pi^4}{5}\,N\,k \left(\frac{T}{\Theta_0} \right)^3. \tag{3}$$

Θ_0, the Debye characteristic temperature at low temperatures, is defined by the Debye-theory (see [*5*]) and is given by the expression

$$\Theta_0 = \sqrt[3]{\frac{3}{4\,\pi\,v_\mathrm{a}}}\;\frac{h}{k} \left\langle \frac{1}{v^3} \right\rangle_{\mathrm{av}}^{-\frac{1}{3}}, \tag{4}$$

where v_a is the atomic volume.

For a Debye spectrum ($\varrho(\nu)$ as given by (2) with cut-off at $\nu = k\,\Theta_0/h$) the error of the T^3 approximation is less than 1% for temperatures $T < \Theta_0/12$ and for the discussion of most of the specific heat data of transition metals and alloys below 20 °K is of no importance. On the other hand deviations of $\varrho(\nu)$ from a Debye spectrum due to dispersion can be considerable even at low frequencies [*4*], and these depend strongly on the crystal structure and on the forces responsible for the cohesion of the lattice. An expansion of $\varrho(\nu)$ including higher terms ($\varrho(\nu) = \alpha_2\,\nu^2 + \alpha_4\,\nu^4 + \alpha_6\,\nu^6 + \cdots$) leads to correspondingly higher terms in the formula for the specific heat: $C_l = \alpha\,T^3 + \beta\,T^5 + \delta\,T^7 + \cdots$. Such deviations of the specific heat from a simple T^3 law have to be considered for the interpretation of low temperature specific heat data for temperatures above approximately $\Theta_0/100$.

The Electronic Specific Heat

The contribution of a non-interacting, degenerate electron gas to the heat capacity of a solid at low temperatures is linear in T and is proportional to the density of electron states $N(E_F)$ at the Fermi level:

$$C_{el} = \gamma T = \frac{2}{3} \pi^2 k^2 N(E_F)\, T, \tag{5}$$

where

$$N(E_F) = \frac{1}{8\pi^3} \int\limits_{F.S.} \frac{dS}{|\mathrm{grad}_k E(\boldsymbol{k})|}. \tag{6}$$

These relations remain valid in a system of interacting electrons if the excitations can be considered as a gas of independent quasi-particles with $E(\boldsymbol{k})$ being the appropriate quasi-particle excitation spectrum. The great value in knowing the Sommerfeld coefficient γ arises from its importance in giving information about this energy spectrum near the Fermi surface (F. S.).

More particularly in a simple Sommerfeld free-electron model $N(E_F)$ is only a function of the number of electrons per unit volume. For the calculation of energy levels in a real metal, one must consider the periodic potential of the lattice consisting of the ions with filled shells, as well as the interactions of the conduction electrons with both each other and the phonons. Whilst in simple metals (as e. g. the alkalis) these effects can be described by corrections applied to the free-electron model [*9—11*], in transition metals none of them is small. For these metals the calculation of electron bands is made difficult by the large number of electrons in unfilled cores which have to be considered in a self-consistent manner [*12*]. The results of such calculations give bands with high and strongly varying densities of states (d-bands). These densities of states have to be corrected for electron-phonon interactions which raise the heat capacity of the electron system and seem to be especially important for metals with a high density of states at the Fermi level. Estimations for transition metals with a high density of states lead to enhancements by factors of 2 and more over the uncorrected value [*13, 14*].

Nuclear Specific Heats

Additional terms in the specific heat, considerable only over a restricted temperature range, can occur from the interactions of the nuclei with the electrons. For the discussion of such specific heat contributions these interactions can be described by effective magnetic or electric fields at the positions of the nuclei. These act on the magnetic dipole moment μ or the electric quadrupole moment Q of the nuclei and thereby remove the $(2I + 1)$ fold degeneracy in the absence of these effective fields (I: nuclear spin). The mentioned nuclear heat capacity is then a consequence of the temperature dependence of the distribution of the spin orientations among these Zeeman energy levels.

The hyperfine heat capacity associated with N nuclei having a spin I and a magnetic moment μ and situated in an effective magnetic field H_e is equal to:

$$C_{\mathrm{hf}} = N k \left\{ \frac{1}{3} \left\langle \frac{I+1}{I} (\mu H_e)^2 \right\rangle_{\mathrm{av}} \left(\frac{1}{kT} \right)^2 - \frac{1}{30} \times \right. \\ \left. \times \left\langle \frac{(I+1)(2I^2+2I+1)}{I^3} (\mu H_e)^4 \right\rangle_{\mathrm{av}} \left(\frac{1}{kT} \right)^4 + \cdots \right\} \tag{7}$$

for $kT \gg \mu H_e$ [*7*]. The average has to be taken over the different nuclei and the inequivalent lattice positions. Additional quadrupole interactions would contribute two further terms proportional to T^{-2} and T^{-4} and would also give rise to a T^{-3} term.

Specific Heat of Spin Waves

The determination of the thermodynamic functions for a spin wave system succeeds with certain approximations in simpler cases such as ferromagnets and two-lattice antiferromagnets (see [*8*]). In a ferromagnet with a quadratic dispersion law spin waves contribute a term proportional to $T^{3/2}$ to the specific heat (e.g. [*15, 16*]). If the energy spectrum has a gap the contribution will have an exponential behaviour. The theory of a two-lattice antiferromagnet leads to a T^3 part in the specific heat and the separation from the lattice specific heat will hardly be possible by measuring C as a function of the temperature.

Other Specific Heat Contributions

The specific heat of a system of independent spins having possible energy values $E = nh\nu_0$, with n a sufficiently large number, is equal to

$$C_{\mathrm{cl}} = B \cdot \frac{\exp(T_E/T)}{[\exp(T_E/T) - 1]^2} (T_E/T)^2 , \tag{8}$$

where $kT_E = h\nu_0$, and is *temperature-independent* for $T \gg T_E$. This situation is probably realized in some alloy-systems of the 3d-period at the critical concentration between paramagnetism and ferromagnetism. In these circumstances magnetic clusters can be formed which in a weak effective field H have energy values $E_m = E_0 + 2m\beta H$, $0 \leqq m \leqq 2n$, where n is the number of free magnetic electrons in the cluster [*17*].

Specific heat contributions magnetic in origin and which are *linear in the temperature* have been suggested by OVERHAUSER [*18*] and by MARSHALL [*19*]. In the model of OVERHAUSER [*18*] this contribution is connected with an antiferromagnetic ordering of a dilute paramagnetic solute; in the model of MARSHALL [*19*] it is the heat capacity of a sufficiently large number of spins of this solute in small effective magnetic fields.

B. Experimental Results

The greater part of the work carried out in low temperature calorimetry on transition metals and alloys has been done above all in order to determine the electronic contribution to the specific heat. The coefficient γ of the electronic heat capacity offers a very direct information on the electronic structure of a metal. The calorimetrically determined density of states is a valuable means of testing models and approximations in band theory and theories of many other properties as for instance magnetism and superconductivity.

Only to a lesser extent has the main interest laid in the other specific heat terms like the lattice heat capacity with its information on elastic properties and the phonon spectrum, or the nuclear specific heat contribution in connection with nucleus-lattice interactions.

Considering the reliability of results in low temperature calorimetry different points such as temperature scale, quality of the specimens, precision of measurements and interpretation of the determined heat capacity can be of importance:

The data compiled in the review article of KEESOM and PEARLMAN [*1*] are based on the temperature scale of 1948; this can give inaccurate specific heat values through the determination of ΔT by several percent. For later work the scales of 1955 and 1958 had generally been accepted, and the differences between these two scales are of little importance; even further refinements of the 1958 scale will be of no consequence for the precision of the present low temperature specific heat data.

That the quality of a sample affects the thermal properties is best seen by comparison of the results for the elements. The lattice specific heat of a very pure element at low temperatures is generally raised by the solution of small amounts of another element. How far internal strains, dislocations and ordering affect the lattice specific heat is not still clear, but it could be that they are responsible for the many differences observed for Θ_0-values even on very pure elements. It has been demonstrated recently that impurities can also drastically affect the linear term γT. KEESOM and RADEBAUGH [*20*] published a γ-value determined for very pure V with a resistivity ratio of 150, which was considerably higher than previous values on less pure V. On the other hand RORER et al. [*21*] investigated Mo-specimens of different impurity contents and arrived at the conclusion that earlier measured γ-values on impurer specimens were 5—20% too high. In general however, the great progress made in the purification of transition metals in the last few years would appear to have contributed to the reduced scatter observed in the specific heat data.

It has been the custom not to publish the whole specific heat function $C(T)$, but to divide it up into different parts with the aid of its temperature variation. A restricted temperature range is sometimes the reason for some ambiguity in this interpretation of the measured specific heat. In cases where C consists only of the electronic and the lattice parts, a neglect of higher terms in the expansion of the lattice specific heat can yield entirely incorrect results. If we describe such a behaviour of the lattice heat capacity by a function $\Theta(T)$ (defined by formula (3) if Θ_0 is replaced by $\Theta(T)$) then this function decreases rather generally from its value Θ_0 at the lowest temperatures towards a minimum (see e. g. Fig. 11). The determination of γ and Θ_0 by a least square fitting of $C(T)$ as measured below the Θ-minimum to $\gamma T + \alpha T^3$ means that both, γ and Θ_0, will be too low, whilst Θ_0 will be too low if obtained from results for $C(T)$ in the range of the minimum, and γ will be too high for $C(T)$ determined above the Θ-minimum. With respect to these facts some data of MORIN and MAITA [*22*] must be considered as doubtful; they expressed $C(T)$ of their metals and alloys by $\gamma T + \alpha T^3$ (with the exception of Re, where a T^5 term was included) up to 25 °K. Also the careful analysis of specific heat data for $T > 10$ °K by CLUSIUS et al. (see Sect. I) cannot yield very accurate values of γ and Θ at 0 °K. Below 10 °K and in a not too limited T-range $C(T)$ can often be fitted successfully to an expression with higher terms in T, but at least T^5 and T^7 terms will be necessary above 3 to 5 °K; these then permit adequate extrapolation to $T = 0$ °K. The most reliable method of determining γ and Θ_0 is to measure $C(T)$ at sufficiently low temperatures where the Θ-variations are still negligible. This is only possible for non-superconductors and superconductors with a low enough T_c. In metals with T_c's up to 10 °K and inconveniently high critical fields to allow the suppression of superconductivity another method is available. This has proved to be reliable in the case of Nb, and we have applied it to Nb-Zr alloys. The extrapolation of $C(T)$ in the superconducting state to 0 °K assuming an exponential behaviour of the electronic specific heat at the lowest temperatures and an equal lattice specific heat in both states yields the coefficient α of the cubic term and thus the Debye temperature Θ_0. The other three coefficients in the expansion $C(T) = \gamma T + \alpha T^3 + \beta T^5 + \delta T^7$ can then be obtained from the entropy $S(T_0) = \int_0^{T_0} \frac{C}{T} dT$ at a temperature $T_0 \gtrsim T_c$, the specific heat $C(T_0)$ and the derivative $\frac{dC}{dT}$ at T_0.

In the following sections we present a survey on the investigated elements and alloys. For the elements we shall only quote data not already included in the article of Keesom and Pearlman [1] and cite as representative results of the time before 1955 the best estimates given therein. For alloys with at least one transition metal component we hope to give a rather complete compilation.

All data in the following lists are given for one g-atom for elements and for one mole, defined by the formula $A_{1-x}B_x$, for binary alloys. The listed values γ, Θ_0 etc. should be taken above all as the coefficients of the linear, the cubic or other terms of the specific heat at constant pressure or (as $C_p - C_v$ can be neglected at low temperatures) at constant volume.

I. Elements

Table 1 represents as we believe the actually most probable values of γ and Θ_0 of the transition elements. For the choice of these values we considered the purity of the investigated specimens, the temperature range of the measurements and how the specific heats had been analysed to determine the coefficients γ and Θ_0. We think these values to be more reliable than the averaged values given in an article by Gschneidner [23]. In the following sections we list the data which we considered for the values of Table 1.

1. Sc, Y, La. The second value of γ for *Sc* in Table 2 originates from Montgomery and Pells (private communication to Anderson et al. [25]). The measurement of Lynam et al. [26] was done in order to test for the presence of a hyperfine interaction in Sc. They found no clear evidence from the specific heat for such a property.

The value of Jennings et al. [27] for *Y* is the result of an extrapolation of $C(T)$ from above 15 °K assuming the Θ-variation to be similar to that in La and Lu. The Θ_0-value of Morin and Maita [22] might be too low because the specific heat was fitted to $C = \gamma T + \alpha T^3$ at elevated temperatures.

Table 1. *Debye temperature,* Θ_0*(°K) (first number below symbol of element), and electronic specific heat,* γ*(mJ°K*$^{-2}$*mole*$^{-1}$*) (second number), for pure elements for phase stable at low temperatures. Values are best estimates from available calorimetric data. Other data for* γ*(in mJ°K*$^{-2}$*mole*$^{-1}$*): Cr (paramagnetic)* 2.9, *β-Mn* 9.7, *γ-Mn* 9.2, *δ-Mn* 9.4, *La* (*f.c.c.*) 11.5

Sc	Ti	V	Cr	Mn	Fe	Co	Ni
450	425	399	630	385	470	460	470
11.0	3.32	9.9	1.41	12.4	4.8	4.4	7.1
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd
280	290	277	460	—	550	500	270
10.2	2.78	7.8	1.83	—	3.0	4.7	9.5
La	Hf	Ta	W	Re	Os	Ir	Pt
150	252	258	390	415	500	420	235
9.4	2.16	6.0	0.90	2.3	2.3	3.2	6.5

The very low γ-value of [*1*] for *La* originates from an extrapolation from above the superconducting critical temperature, and where the Θ-variation was neglected. BERMAN et al. [*28*] give values for γ and Θ_0 which are the average over the h.c.p. and the f.c.c. phases of their sample. The samples reported in [*179*] are at least 95% pure phase.

Table 2. *Low temperature specific heat of Sc, Y and La*

Element	Range (°K)	γ (mJ°K^{-2}mole^{-1})	Θ_0 (°K)	Ref.
Sc	1.7 – 4.2	11.3	470	[*24*]
		11.1	—	[*25*]
	0.15– 3	10.9	344	[*26*]
	0.15– 3	10.2	397	[*26*]
Y	> 15	8.5	—	[*27*]
	1.7 – 4.2	10.2	300	[*24*]
	1.5 –25	10.1	235	[*22*]
	1.5 – 4	10.5	330	[*30*]
	2 –40	9.4	232	[*182*]
La		6.7	132	[*1*]
	1.6 – 6.5	10.1	142	[*28*]
	1.5 – 9	10.0	142	[*29*]
	1.5 – 4	10.0	142	[*30*]
	1.1 –10	9.4	152	[*179*]
La (f. c. c.)	1.1 –10	11.5	140	[*179*]

2. Ti, Zr, Hf. With the exception of the Θ-value in [*1*] and γ and Θ_0 of CLUSIUS and FRANZOSINI [*33*] the results of *Ti* contained in Table 3 are consistent. The three recent results for *Zr* [*34, 35, 37*] agree within their limits of error. The quite large differences in the γ-values of *Hf* could be an effect of impurities.

3. V, Nb, Ta. The reason for the relatively large scatter in the specific heat parameters of the group of metals given in Table 4 probably lies in the high sensitivity to impurities, the deviations from a T^3 law even at low temperatures and the high transition temperatures of superconductivity making the determination of the normal state parameters more difficult. The most reliable value for *V*

Table 3. *Low temperature specific heat of Ti, Zr and Hf*

Element	Range (°K)	γ (mJ°K^{-2}mole^{-1})	Θ_0 (°K)	Ref.
Ti		3.34	278	[*1*]
	4—15	3.38	421	[*31*]
	1.2—20	3.56	430	[*32*]
	>13	5.9	368	[*33*]
	1.1— 4.5	3.346	427	[*34*]
	1.1— 4.5	3.351	430	[*34*]
	1.5—16	3.3	415	[*35*]
	1.2— 4.5	3.30	429	[*36*]
	0.9—12	3.31	412	[*37*]
Zr		2.95	270	[*1*]
	1.2—20	3.04	310	[*32*]
	1.1— 4.5	2.81	292	[*34*]
	1.5—16	2.75	290	[*35*]
	0.9—12	2.77	290	[*37*]
Hf	1.2—20	2.64	261	[*32*]
	1.1— 4.5	2.159	252.3	[*34*]
	1.1— 4.5	2.167	251.5	[*34*]

Table 4. *Low temperature specific heat of V, Nb and Ta*

Element	Range (°K)	γ (mJ°K^{-2}mole^{-1})	Θ_0 (°K)	Ref.
V		8.83	273	1
	1.2—20	9.2	380	[*38*]
	1.1— 5	9.26	338	[*39*]
	>10	6.70	425	[*40*]
	2—7	8.88	315	[*41*]
	<6	9.92	399	[*20*]
		9.64	400	[*42*]
Nb		8.5	252	[*1*]
	1.5—30	7.55	256—320	[*43*]
	>10	8.59	250	[*40*]
	1.1—12	7.53	238	[*44*]
	1.4— 4.2	7.70	320	[*45*]
	1.5—25	7.54	230	[*22*]
	0.4— 4.2	7.79	275	[*46*]
		7.80	(275)	[*47*]
	1.5 —18	7.80	—	[*48*]
	1.5 —18	7.80	278	[*49*]
	0.35—25	7.79	277	[*50*]
	0.35—25	7.85	277	[*50*]
		see text	—	[*51*]
Ta		5.44	231	[*1*]
	>10	3.4	228	[*52*]
	1.2—20	5.87	245	[*38*]
	1.3—25	5.70	255	[*53*]
	1.5—25	6.28	240	[*22*]
		6.02	258.2	[*42*]

seems to be that of Keesom and Radebaugh [*20*] whose sample had a resistance ratio of 150 and a T_c of 5.37 °K. Phillips and Shen [*42*] report a resistance ratio of 13, Cheng et al. [*41*] a critical temperature of superconductivity of only 4.59 °K.

For *Nb*, the agreement between the most recent publications is very good. The first specimen of Shen et al. [*50*] had a resistance ratio of 24 and a T_c of 9.13 °K, for their second, purer specimen both the resistance ratio and T_c were higher being 110 and 9.26 °K respectively. The specific heat of very pure Nb ($T_c = 9.33$ °K) has been measured from 1.5 to 18 °K by Bucher et al. [*48*] without magnetic field. Using a careful analysis of the heat capacity in the normal and the superconducting states (see introduction to Part B) we redetermined the values of γ and Θ_0 [*49*] as presented in Table 4. Leupold and Boorse [*47*] investigated a single crystal of Nb with a T_c of about 9.19 °K and van der Hoeven and Keesom [*46*] a polycrystalline specimen down to 0.4 °K. The results reveal a considerable deviation from a T^3 behaviour even at 3 °K and explain why previous measurements had given the erroneous result suggesting that the total specific heat in the superconducting state is smaller than the lattice specific heat in the normal state. McConville and Serin [*51*] report a γ of 0.80 mJ/cm³ °K² but no value for the density of their specimens for comparison.

Morin and Maita [*22*] found a sharp change in the slope of C/T vs. T^2 at 9.5 °K and explained it on the basis of a rapid variation in the density of states as a function of T. They fitted the results to $C = \gamma T + \alpha T^3$ both above and below 9.5 °K and obtained approximate agreement with other authors for $\gamma (T < 9.5\,°\mathrm{K})$ but a much lower Θ_0. The temperature range in which this behaviour was seen has been reinvestigated by Bucher et al. [*48*]. Besides observing that the slope of the specific heat curve C/T vs. T^2 was a smooth function of temperature they also found no anomalous behaviour of the susceptibility at 9.5 °K, as would be expected if there were such a sudden variation in the density of states.

Phillips and Shen [*42*] report a residual resistivity ratio of 400 for their *Ta* - sample investigated in a super-critical magnetic field. The superconducting critical temperatures T_c of the specimens of Morin and Maita [*22*], and White et al. [*53*], were 4.4 and 4.39 °K respectively. The latter took into account a possible Θ-variation by using a numerical method for the extrapolation of $C(T)$ to 0 °K.

4. Cr, Mo, W. The comparison of the γ values with the purity of the investigated substances seems to indicate that in this group of metals (see Table 5) the linear term in the specific heat decreases with increasing purity.

The results for antiferromagnetic *Cr* are in reasonable agreement with each other with the exception of that of reference [*58*]. In Table 5 we also give a value for paramagnetic Cr which will be discussed further in the section on Cr-alloys.

The most recent measurements on 99.999% pure *Mo* reported by Heiniger et al. [*60*] and Rorer et al. [*21*] are in excellent agreement but are lower than previous values of probably impure material. The first specimen of Rorer et al. [*21*], that with the highest resistance ratio of 2700, consisted of three crystals, the other three were single crystals; the sample of Heiniger et al. [*60*] was polycrystalline.

Very pure *W* with a resistance ratio of 20,000 investigated by Maita (see Geballe [*65*]) had a lower γ than most of the previously measured samples. The temperature range responsible for providing this measurement and the limits of error are lacking. A 99.99% pure W-specimen, melted and well annealed in a high vacuum, has been investigated by Bucher et al. [*48*] and this also showed a

Table 5. *Low temperature specific heat of Cr, Mo and W*

Element	Range (°K)	γ (mJ°K^{-2}mole^{-1})	Θ_0 (°K)	Ref.
Cr (antiferromagnetic)		1.54	402	[1]
	1.2—20	1.55	585	[38]
	1.5—4.2	1.40	630	[54]
	> 14		580	[55]
	2—4	1.39	630	[56]
		1.42	606	[57]
		1.62	400	[58]
		1.45		[59]
Cr ("paramagnetic")		2.9		[60, 61]
Mo		2.14	425	[1]
	1.2—20	2.12	470	[38]
	> 10	2.10	454	[62]
	1.0—4.2	1.93	427	[63]
	1.0—4.2	1.91	458	[63]
	1.4—4.2	2.20	470	[45]
	1.5—25	2.01	470	[22]
	0.4—4	1.83	423	[21]
	0.4—4	1.81	382	[21]
	0.4—4	1.89	461	[21]
	0.4—4	1.87	456	[21]
	1.5—4	1.83	430	[60]
W		1.48	379	[1]
	1.2—20	1.21	405	[38]
	4—15	1.1	378	[64]
	> 10	1.13	380	[62]
	1.5—4.2	0.95	396	[48]
		0.84		[65]

relatively low γ. We believe that the impurity dependence of γ originates from magnetic contributions rather than from a change in the density of states.

5. *Mn, Tc, Re.* The most recent results for α-*Mn*, with the exception of that of Franzosini et al. [70] determined in the liquid hydrogen range and that of Stetsenko and Avksent'ev [58], are in good agreement (Table 6). The weak tendency towards higher values of γ by Guthrie et al. [71] could partly be explained by the error made in neglecting the hyperfine specific heat contribution. From the T^{-2} term of the heat capacity, Zych and Heer [68] determined the hyperfine field to 80—90 kOe and Scurlock and Stevens [72] to 90 kOe; this must be taken as a mean value over the different non-equivalent Mn-places.

For β-*Mn* the specific heat shows an anomaly below 15 °K (Booth et al. [66]) and an estimate of the γ value was only possible from high temperature specific heat data (Weiss and Tauer [67], Shinozaki et al. [69]).

A careful investigation of the low temperature specific heat of γ-*Mn* has been made by Ho and Phillips [74]. From the T^{-2} part they determined the hyperfine field to 65 kOe. Zimmerman and Sato [73] arrived at their γ-value by an extrapolation of its value in the f.c.c. alloy-system Mn-Cu to pure γ-Mn, the extrapolation is not very well defined however. On the other hand the variation of γ

in the Mn rich Mn-Cu alloys shows that the correction of the measured specific heat of Mn + 6 wt.-% Cu to pure γ-Mn with the γ-value of pure Cu as made by Franzosini et al. [*70*] cannot be correct.

Table 6. *Low temperature specific heat of Mn and Re*

Element	Range (°K)	γ (mJ°K^{-2}mole^{-1})	Θ_0 (°K)	Ref.
α-Mn		13.8		[*1*]
	11 –20	11.8	392	[*66*]
	1.2–20	18.0	450	[*38*]
		(10.6)	(460)	[*67*]
	0.3 – 2	11.9	—	[*68*]
	2 –20	12.6	380	[*69*]
	> 10	13.7	415	[*70*]
	0.3 – 4.0	16	418	[*58*]
	1.75– 4.2	12.8	—	[*71*]
	0.3 – 1.0	12.0	393	[*72*]
β-Mn	11–20	—	—	[*66*]
		(9.4)	(422)	[*67*]
		(10.1)	(365)	[*69*]
	> 14	—	—	[*188*]
γ-Mn		(4.7)	(355)	[*67*]
		3–6	—	[*73*]
	2–20	8.4	370	[*69*]
	> 10	10.4	373	[*70*]
	0.066–4.2	9.20	328	[*74*]
δ-Mn		(9.4)	(370)	[*67*]
Re	1.2 –20	2.45	450	[*38*]
	0.37– 4.2	2.31	417	[*75*]
	1.5 –25	2.47	405	[*22*]
	1.2 –24	2.26	407	[*76*]
	> 10	—	—	[*77*]

The values for δ-*Mn* are estimates from high temperature specific heats.

As far as *Tc* is concerned no data for the pure metal exists.

For *Re* a good agreement has been found between the data of Keesom and Bryant [*75*] and that of Blanpain [*76*], but a higher γ-value is given by Morin and Maita [*22*]. The specific heat had been represented by the latter by $C = \gamma T + \alpha T^3 + \beta T^5$ which is apparently too rough for the strong Θ-variation of Re. The contribution of the quadrupole interaction to the specific heat has been separated and discussed in the work of Keesom and Bryant [*75*].

6. Fe, Ru, Os. In the ferromagnetic metals a possible contribution to the specific heat from spin waves has to be considered. Rayne and Chandrasekhar [*80*] reanalysed the data of Cheng et al. [*79*] for *Fe* using the expansion $C = \gamma T + \alpha T^3 + \varepsilon T^{3/2}$ and obtained for γ a slightly different value (Table 7). Likewise the value of Dixon et al. [*81*] for γ of Fe originates from the same expression for C.

7. Co, Rh, Ir. The most reliable values for γ and Θ_0 of *Co* seem to be those obtained on spectral pure material by Dixon et al. [*81*] (see Table 8). From the

Table 7. *Low temperature specific heat of Fe, Ru and Os*

Element	Range (°K)	γ (mJ°K^{-2}mole^{-1})	Θ_0 (°K)	Ref.
Fe		5.0	467	[*1*]
	0.35— 0.7	4.9	—	[*78*]
	1.4 — 4.2	4.98	445	[*79*]
		4.9	477	[*80*]
	1.2 — 4.2	4.755	473	[*81*]
	1.2 — 4.2	4.762	469	[*81*]
	2 — 4	4.81	463	[*178*]
Ru	1.2 —20	3.35	600	[*38*]
	> 10	2.6	505	[*82*]
		2.98	—	[*83*]
Os	1.2 —20	2.35	500	[*38*]

Table 8. *Low temperature specific heat of Co, Rh and Ir*

Element	Range (°K)	γ (mJ°K^{-2}mole^{-1})	Θ_0 (°K)	Ref.
Co		5.0	445	[*1*]
	0.6 —3.3	4.74	443	[*84, 85*]
	1.9 —4.2	4.44	416	[*86*]
	0.35—0.7	5.6	—	[*78*]
	1.4 —4.2	4.7	469	[*79*]
	1.2 —4.2	4.38	460	[*81*]
	0.7 —2.5	4.51	—	[*87*]
Rh	> 10	4.85	450	[*88*]
	1.2—20	4.90	478	[*38*]
	1.8— 4.2	4.65	512	[*89*]
Ir	> 10	3.18	430	[*88*]
	1.2—20	3.14	420	[*38*]
		3.3	410	[*65, 186*]

Table 9. *Low temperature specific heat of Ni, Pd and Pt*

Element	Range (°K)	γ (mJ°K^{-2}mole^{-1})	Θ_0 (°K)	Ref.
Ni		7.4	456	[*1*]
	1.5—4.2	7.05	468	[*54*]
	1.9—4.2	6.7	348	[*86*]
	1.4—4.2	7.2	334	[*90*]
	1.2—4.2	7.039	477	[*81*]
	1.2—4.2	7.028	471	[*81*]
	1.5—4.2	7.16	469	[*91*]
Pd		10.7	275	[*1*]
	2 — 4.2	9.31	274	[*92*]
	1.5— 4.2	9.87	299	[*93*]
	1.5— 4.2	9.38	272	[*94*]
	1.4—100	9.42	273.6	[*95*]
	1.3— 30	9.57	267	[*96*]
		9.53	—	[*97*]
Pt		6.8	229	[*1*]
	> 10	6.6	221	[*98*]
	1.2—4.2	6.68	240	[*99*]
	1.8—4.2	6.41	235.3	[*89*]
	1.2—4.2	6.507	234.9	[*81*]

specific heat term proportional to T^{-2} they determined the H_{eff}. at the nucleus to be 223 kOe. The specimen of Cheng et al. [*79*] was of a purity of only 99.56% but their parameters agree reasonably well with those of Dixon et al. [*81*]. The coefficients of Arp et al. [*78*] have been determined in a very restricted temperature range below 1 °K. Their γ value which is considerably higher than that of Dixon et al. [*81*] may therefore be less reliable than their hyperfine term which agrees well with that of the other authors.

8. Ni, Pd, Pt. Dixon et al. [*81*] fitted the specific heat function of *Ni* to the expression $C = \gamma T + \alpha T^3 + \varepsilon T^{3/2}$. Their coefficient ε was not well defined and is smaller than that calculated by Rayne and Kemp [*54*] from magnetization data. The latter determined γ by first subtracting the spin wave term from the measured heat capacity. Nevertheless the agreement between the results in γ of these authors is excellent because ε has little effect upon the value of γ. The deviations of the other authors cannot be explained by the neglect of the $T^{3/2}$ term.

The most recent results of *Pd* are in good agreement. As both γ and Θ_0 of Rayne [*93*] seem to be slightly too large, the difference could reflect an inaccurate separation of the electronic and lattice parts of the specific heat.

For *Pt* all results agree reasonably well with each other.

II. Alloys of Two 3d-Transition Metals

The large amount of specific heat data on alloys of transition elements of the first long period is collected in Table 10a (alloys between neighbouring elements in the periodic system) and Table 10b. The coefficients γ of the specific heats of the alloys given in Table 10a are plotted as a function of the number of valence electrons per atom in Fig. 1 together with those from Cr-Fe alloys.

The variation of the electronic specific heat γ of Sc-rich Sc-Ti alloys, investigated by Montgomery and Pells (see [*25*]), has been found to explain that of the magnetic susceptibility as a function of concentration and temperature (Anderson et al. [*25*]). The γ value of h.c.p. $\mathrm{Ti}_{0.96}\mathrm{V}_{0.04}$, compared with that of b.c.c. Ti-V alloys, suggests that γ varies smoothly through the phase change from h.c.p. to b.c.c. alloys (Fig. 1). The large series of b.c.c. and f.c.c. alloys mainly investigated by Beck and coworkers has been reviewed by Gupta et al. [*116*]. Recent results on Cr-V alloys in the antiferromagnetic region appear in Table 10a; γ decreases steeply to the value for pure Cr [*61*]. For Mn-Fe and Ni-Cu of Table 10a and V-Fe and Mn-Ni of Table 10b a temperature-independent cluster contribution had to be taken into account. The γ-values of Ni-Cu by Guthrie et al. [*105*] and those of V-Fe by Cheng et al. [*79*] have been subsequently reevaluated by considering this cluster specific heat (Schröder [*17*]); for Ni-Cu the new values are given in brackets. Usually the Θ_0-values are not very reliable in such cases where C had to be separated into three or more different contributions. In order to confirm the theory of Schroeder [*17*] for the specific heat of magnetic clusters Scurlock and Wray [*109*] measured the specific heat of some V-Fe alloys between 0.4 and 4 °K and found the expected deviations from temperature independent contributions below 1 °K.

In Fe-Co and Co-Ni alloys the Co^{59} isotope makes a considerable hyperfine contribution to the specific heat (Table 19). The coefficients for Fe-Co alloys of Arp et al. [*78*] and of Cheng et al. [*79*] differ somewhat; as the former investigated

Table 10a. *Low temperature specific heat of alloys of two 3d-elements (neighbouring elements)*

Alloy-system	Conc. of the 2nd element (at.-%)	Structure	γ (mJ°K^{-2}mole^{-1})	Θ_0 (°K)	Ref.
Sc-Ti	10	h. c. p.	9.3	—	[25]
Ti-V	4	h. c. p.	4.6	365	[35]
	20—100	b. c. c.	Fig. 1	244—315	[41]
V-Cr	23—95	b. c. c.	Fig. 1	314—500	[79, 190]
	95—99	b. c. c.	Figs. 1 and 6	560—625	[61]
Cr-Mn	10	b. c. c.	2.23	467	[79]
	20	b. c. c.	< 6.7	—	[79]
	31	b. c. c.	< 12.1	—	[79]
	39	b. c. c.	< 19.7	—	[79]
	50	b. c. c.	< 23.4	—	[79]
Mn-Fe	53	f. c. c.	5.99	428	[90]
	55	f. c. c.	6.11	482	[100]
	66	f. c. c.	6.66	405	[90]
	76	f. c. c.	8.34	399	[90]
	84	f. c. c.	13.87	398	[90]
	89	f. c. c.	17.6	—	[101]
	98—99.5	—	—	—	[102, 178]
Fe-Co	0—75	b. c. c.	Fig. 1	353—476	[79]
	0— 4	—	—	—	[178]
	93	f. c. c.	5.91	436	[79]
	0—58.7	b. c. c.	see text	—	[78]
	91.5	f. c. c.	see text	—	[78]
	30	b. c. c.	1.76	465	[110]
Co-Ni	30—100	f. c. c.	Fig. 1	337—416	[86]
	40	f. c. c.	see text	—	[78]
Ni-Cu	1	f. c. c.	7.16	448	[91]
	10—55	f. c. c.	Fig. 1	321—389	[103]
	18—78	f. c. c.	Fig. 1	335—386	[104]
	57	—	—	—	[184]
	58	f. c. c.	6.2 (5.24)	—	[105, 17]
	63	f. c. c.	4.0 (3.56)	—	[105, 17]
	69	f. c. c.	2.03	375	[106]
	73	f. c. c.	2.03	385	[105]
	89	f. c. c.	1.05	343	[105]

Table 10b. *Low temperature specific heat of alloys of two 3d-elements (elements with valence difference of 2 or more)*

Alloy-system	Conc. of the 2nd element (at.-%)	Structure	γ (mJ°K^{-2}mole^{-1})	Θ_0 (°K)	Ref.
Ti-Cr	2.5	h. c. p.	4.1	370	[107]
Ti-Mn	0.17—1.7	h. c. p.	—	—	[36]
	2.0	h. c. p.	—	—	[107]
	14	b. c. c.	5.53	372	[36]
Ti-Fe	1.0	h. c. p.	3.3	380	[107]
	1.5	h. c. p.	3.4	370	[107]
	8	b. c. c.	6.1	295	[107]
	50	CsCl, ord.	0 ± 0.8	495	[108]
	98—99.5	—	—	—	[102, 178]

Table 10 b (continued)

Alloy-system	Conc. of the 2nd element (at.-%)	Structure	γ (mJ°K^{-2}mole^{-1})	Θ_0 (°K)	Ref.
Ti-Co	50	CsCl, ord.	10.5	325	[*108*]
V-Fe	4.4	b. c. c.	—	—	[*112*]
	13.8	b. c. c.	—	—	[*112*]
	8—67	b. c. c.	Fig. 7	369—509	[*79, 17*]
	22	b. c. c.	3.58	(390)	[*109*]
	26	b. c. c.	3.81	(390)	[*109*]
	31	b. c. c.	6.75	(390)	[*109*]
	67	b. c. c.	3.71	341	[*110*]
	90	b. c. c.	3.38	404	[*111*]
	98—99.5	—	—	—	[*102, 178*]
V-Ni	0—8	b. c. c.	—	—	[*190*]
	60	f. c. c.	4.82	419	[*90*]
	65	f. c. c.	4.48	422	[*90*]
	72	f. c. c.	4.27	388	[*90*]
	82	f. c. c.	3.98	479	[*90*]
	91	f. c. c.	8.09	398	[*90*]
Cr-Fe	2—100	b. c. c.	Fig. 1	—	[*79*]
	55.9	b. c. c.	5.02	400	[*113*]
	55.9	σ	(26.8)	—	[*113*]
	98—99.5	—	—	—	[*102, 178*]
Mn-Ni	25	f. c. c.	6.66	307	[*90*]
	40	f. c. c.	4.15	311	[*90*]
	60	f. c. c.	3.35	312	[*90*]
	70	f. c. c.	7.00	356	[*90*]
	75	f. c. c. ord.	4.9	—	[*114*]
	75	f. c. c. disord.	9.4	—	[*114*]
	75	f. c. c.	7.58—9.68	261—329	[*90*]
	80	f. c. c.	9.25	373	[*90*]
Mn-Cu	3	f. c. c.	7 ± 2	—	[*73*]
	5	f. c. c.	9.4	—	[*73*]
	9	f. c. c.	11.6	—	[*73*]
	18	f. c. c.	11.8	—	[*73*]
	27	f. c. c.	11.4	—	[*73*]
	42	f. c. c.	6.9	—	[*73*]
	57	f. c. c.	3.8	—	[*73*]
	76	f. c. c.	(2.8)	—	[*73*]
	87	—	—	—	[*184*]
Fe-Ni	0—4	—	—	—	[*178*]
	28	f. c. c.	13.2	309	[*90*]
	35.3	—	11.9	(341)	[*115*]
	37	f. c. c.	5.28	323	[*90*]
	40	f. c. c.	7.12	326	[*90*]
	45	f. c. c.	5.53	383	[*90*]
	48	f. c. c.	5.1	358	[*104*]
	55	f. c. c.	4.32	418	[*90*]
	68	f. c. c.	4.15	425	[*90*]
	80	f. c. c.	4.5	407	[*104*]
	84	f. c. c.	4.9	409	[*104*]
	95	f. c. c.	6.54	390	[*90*]
	97	f. c. c.	6.95	391	[*90*]
	99	f. c. c.	7.01	435	[*91*]

only the temperature range between 0.35 and 0.7 °K those γ-values are probably less reliable and the hyperfine specific heats more reliable than the data of Cheng et al. [*79*] who measured above 1 °K.

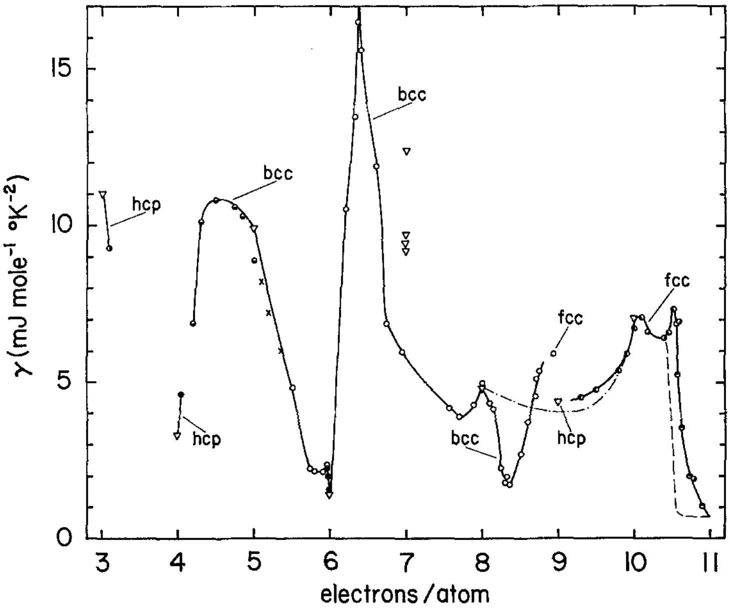

Fig. 1. Specific heat coefficient γ vs. number of valence electrons per atom in 3d-alloys. ▽ elements (from Table 1), ◑ Anderson et al. [*25*], ● Heiniger and Muller [*35*], and Heiniger [*61*], ◒ Cheng et al. [*41*], X Gupta et al. [*116*], ○ Cheng et al. [*79*], ◐ Walling and Bunn [*86*], ⊘ Gupta et al. [*103*], ◕ Keesom and Kurrelmeyer [*104*], ◓ Guthrie et al. [*105*], (—.—.—.—) electronic specific heat in f. c. c. alloys (Gupta et al. [*90*]), (– – – – – – –) electronic specific heat in f. c. c. Ni-Cu (Gupta et al. [*103*])

The curve of Fig. 1 which shows the coefficients γ as a function of the number of electrons per atom outside the filled cores has been adjusted so that the points for the pure elements correspond to the values in Table 1. Several authors have already discussed the variations of γ in b.c.c. alloys assuming a more or less rigid 3d-band where the position of the Fermi level and thus the density of states is determined by the number of valence electrons (Gupta et al. [*116*], Shimizu and Katsuki [*117*], Berger [*118*]). Under these assumptions an unequivocal determination of the density of states is only possible for paramagnetic elements and alloys, as are those of Fig. 1 with 4 to 5.95 electrons per atom. For antiferromagnetic or ferromagnetic metals the model must explain both the specific heat and the magnetic properties at the same time. In the case of antiferromagnetic Chromium and its alloys it now seems to be probable that a certain fraction of the conduction electrons (in pure Cr about 50%) are condensed in an antiferromagnetic state and do not contribute to the specific heat at temperatures far below the Néel temperature (Heiniger [*61*], see also Section VII).

The ferromagnetism in the Cr-Fe system is explained by Gupta et al. [*116*] assuming that γ between about 5.8 and 8.2 electrons per atom represents the density of states of a sub-band containing only electrons with one spin direction and above 8.2 electrons per atom that of another sub-band with the other spin direction. The magnetization of this model shows a linear increase with the number of valence electrons up to 8.2 electrons per atom and a linear decrease above 8.2 electrons per atom in good agreement with the experimental data of FALLOT [*119*] for Fe-Cr and of WEISS and FORRER [*120*] for Fe-Co.

Another band model of ferromagnetism has been discussed by SHIMIZU and KATSUKI [*117*]. They used the above mentioned magnetization data for Fe-Cr and Fe-Co and some of the γ-values of CHENG et al. [*79*] of the b.c.c. 3d-alloys neglecting those they believed to include other than electronic contributions to the specific heat, as e. g. the data of Fe-Cr-alloys with less than 30 at.-% Fe. With the assumption of an exchange energy proportional to the square of the magnetization: $E_{\text{ex.}} = -\frac{1}{2}\alpha M^2$ and with the condition that $E(M)$ must be a minimum they arrived at a density of states curve which differed from that of GUPTA et al. [*116*] by a reduced peak above 6 electrons/atom and which was more suitable in explaining the experimental results for Fe. To the neglect of some data of the Fe-Cr system it might be objected that even at high temperatures a marked maximum in the specific heat has been found by SCHROEDER [*121*] at 19 at.-% Fe in Cr, and that the high value of CHENG et al. [*79*] is probably not enhancement by some hidden magnetic contribution.

Assuming an exchange energy $-J$ between any two electrons of the same spin orientation, BERGER [*118*] found in his model that the paramagnetic state is unstable if $N(E_{\text{F}})$, the density of states at the Fermi surface, is larger than $N_{\text{crit}} = 1/J$ and that the ferromagnetic state with different positions of the Fermi energy for the two spin directions will have a lower energy. The experimental data of magnetization and electronic specific heat can be obtained quite well by two different band forms proposed by this author. The sharp decrease of the electronic specific heat in the Cr-Fe system above the peak seen at about 6.3 el./atom is a direct consequence of the onset of ferromagnetism. The case of TiCo in the ternary system (TiFe)-(TiCo) (see Table 17 and Fig. 7), which is similarly disposed with respect to the corresponding peak, has to be explained differently; in this case no localized moments have been found [*122*].

Above about 7.5 electrons per atom where the f.c.c. structure becomes more stable than the b.c.c. structure, γ is correlated with the number of electrons only in nonmagnetic and in strongly ferro- or antiferromagnetic alloys. GUPTA et al. [*90*] who discussed these alloys in detail believe that for many of these alloys the measured linear specific heat is the electronic part enhanced by magnetic contributions explained by the theory of MARSHALL [*19*]. In Fig. 1 we reproduce only their curve which they consider as the most probable function for the electronic specific heat (chain-line in Fig. 1).

At the upper end of the 3d-band the magnetization and the linear term of the specific heat are in contradiction if γ is considered as pure electronic. GUPTA et al. [*103*] investigated the effect of a magnetic field on γ of Ni-Cu alloys and found a marked dependence indicating that a magnetic contribution to the specific heat must be present. It is possible that the conditions for a contribution linear in T as explained by MARSHALL [*19*] are fulfilled. The broken line in Fig. 1 shows the electronic specific heat γ they expect from a simple band model explaining at the same time the saturation magnetization data.

Until now we have discussed the behaviour of the 3d-alloys with the model of a rigid band, and Fig. 1 which contains only alloys between elements with a valence difference of one or two is in this approximation a picture of the sum of the 3d- and the 4s-bands. Surprisingly enough this approximation even describes the qualitative behaviour of some alloys between elements with a larger valence difference as e. g. V-Fe (Fig. 7) and also that of ternary alloys such as (TiFe)-(TiCo) and (TiCo)-(TiNi) (Table 17, Fig. 7). Nevertheless it must be kept in mind that for a quantitative model with a thorough consideration of the electron-interactions the rigid band picture cannot be very realistic.

III. Alloys of Two 4d-Transition Metals

The number of investigated alloys between two 4d-elements (Table 11) is smaller than for the 3d-alloys, but on the other hand there seems to be less uncertainty in the interpretation of the measured specific heat because any magnetic contribution can probably be excluded. In the alloy-system Zr-Nb (Table 11) we find large differences between our results [49] and those of MORIN and MAITA [22], and BINDARI and LITVAK [123], which were evaluated by different procedures. The determination of γ and Θ_0 by fitting the experimental specific heat above the critical temperature T_c of superconductivity to the function $C = \gamma T + \alpha T^3$ as done by the latter authors [22, 123] yields values for γ and α which are not consistent with the condition that the entropy above T_c must be the same whether determined from the normal or superconducting state specific heat data. On the other hand we determined our values considering this condition by the method described in the introduction to the experimental part of the present article.

Table 11. *Low temperature specific heat of alloys of two 4d-elements*

Alloy-system	Conc. of the 2nd element (at.-%)	Structure	γ (mJ°K^{-2}mole^{-1})	Θ_0 (°K)	Ref.
Zr-Nb	40	b. c. c.	15.9	190	[22]
	50	b. c. c.	8.3 ± 0.4	238±5	[49]
	75	b. c. c.	8.9 ± 0.4	246±7	[49]
	75	b. c. c.	10.9	200	[123]
	90	b. c. c.	9.2	220	[22]
Nb-Mo	0—100	b. c. c.	Fig. 2	230—470	[22]
	0—100	b. c. c.	Fig. 2	320—470	[45, 181]
	15	b. c. c.	6.3 ± 0.3	265±4	[49]
Mo-Tc	50	b. c. c.	4.6	300	[22]
Rh-Pd	0—100	f. c. c.	Fig. 2	259—512	[89]
Pd-Ag	0—100	f. c. c.	Fig. 2	231—313	[92]
Zr-Rh	0—8	see text	Fig. 2	192—290	[37]
Nb-Ru	10—38	b. c. c.	Fig. 7	305—405	[124]
Nb-Rh	40	σ	3.52	329	[125]
Nb-Pd	40	σ	2.66	293	[125]
Mo-Ru	5	b. c. c.	2.94	435	[22]
	30	b. c. c.	3.90	435	[22]
	39	σ	4.11	418	[125]
Mo-Pd	40	see text	3.56	330	[22]
	50	see text	3.77	330	[22]
	60	see text	3.27	330	[22]

In the system Nb-Mo where the superconducting critical temperatures are lower the data of the different authors agree reasonably well. The Zr-Rh alloys (Table 11) with less than 3 at.-% Rh are probably heterogenous and only the results of alloys with 3 and more at.-% Rh with the b.c.c. structure are included in Fig. 2. After a recent phase diagram of the alloy-system Mo-Pd, published by Savitzkii et al. [*126*], the solubility of Pd in b.c.c. Mo is much lower than 40 at.-%, and we wonder if the specimens of Morin and Maita [*22*] had consisted of one phase. Otherwise their results have to be taken as an average for two alloys of different concentrations.

In Fig. 2, we report primary γ-values of alloys between neighbouring elements in the periodic system. The heavy line which adopts the new values [*49*] for the Zr-Nb alloys now shows a very similar behaviour to the curve for the 3d-alloys in Fig. 1. The criticized values of references [*22*] and [*123*] are given by a broken line. We believe that the heavy curve of Fig. 2 gives at least a rough picture of the 4d-band. It is surprising that even the recent results for Zr-Rh alloys containing very differing elements, and represented in Fig. 2 by a chain line, provide a smooth continuation of this curve.

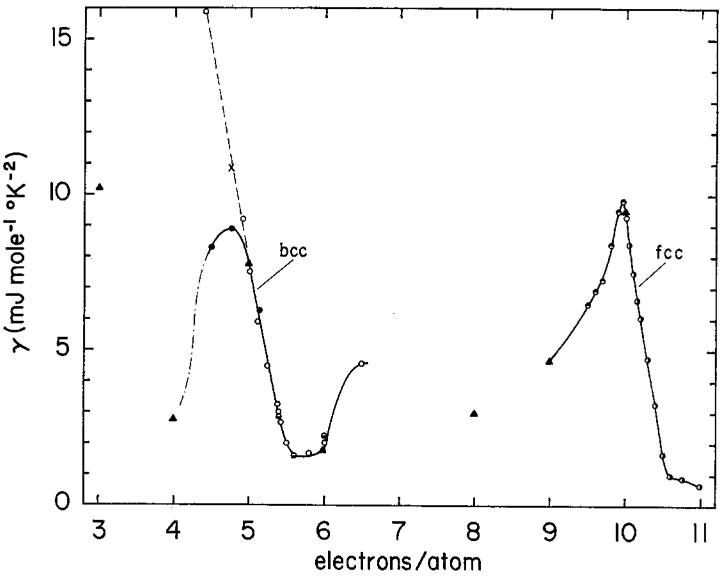

Fig. 2. Specific heat coefficient γ vs. number of valence electrons per atom in 4d-alloys. ▲ elements (from Table 1), ● Heiniger et al. [*49*], (– – –○– – –) Morin and Maita [*22*], × Bindari and Litvak [*123*], ◒ Blaugher et al. [*45*], ◓ Budworth et al. [*89*], ◑ Hoare and Yates [*92*], (–.–.–.–) Zr-Rh by Dummer [*37*]

IV. Alloys of Two 5d-Transition Metals

In order to compare the 3d- and 4d-alloy series with alloys of 5d-metals we investigated a large number of b.c.c. and h.c.p. alloys in the range of 4.7 to 7.7 electrons per atom [*48*] (Table 12). In addition some γ-values can be found in a figure in an article of Geballe [65] for f.c.c. Os-Ir alloys, and a series of values for the f.c.c. Pt-Au system are given by a publication of Budworth et al. [89]. The alloy $W_{0.09}Pt_{0.91}$ has been investigated by Ho and Phillips [128] with regard to the possible application to calorimetry below 0.1 °K.

Table 12. *Low temperature specific heat of alloys of two 5d-elements*

Alloy-system	Conc. of the 2nd element (at.-%)	Structure	γ (mJ°K^{-2}mole^{-1})	Θ_0 (°K)	Ref.
Hf-Ta	70	b. c. c.	8.30	209	[48]
Ta-W	16—100	b. c. c.	Fig. 3	265—396	[48]
W-Re	0—25	b. c. c.	Fig. 3	396—351	[48]
	50	σ	2.69	327	[125]
	88	h. c. p.	3.76	332	[48]
Re-Os	30	h. c. p.	2.05	351	[48]
	70	h. c. p.	1.86	382	[48]
Os-Ir	65—100	f. c. c.	Fig. 3	410	[65]
Ir-Pt	90—100	f. c. c.	Fig. 3	237—273	[127]
Pt-Au	0—4	f. c. c.	Fig. 3	237—252	[127]
	0—100	f. c. c.	Fig. 3	167—235	[89]
W-Ir	28	σ	2.62	322	[125]
W-Pt	91	f. c. c.	3.42	193	[128]

Fig. 3 represents the γ-values for these alloys as a function of the number of electrons per atom and shows, corresponding to Figs. 1 and 2, an approximative picture of the 5d-band.

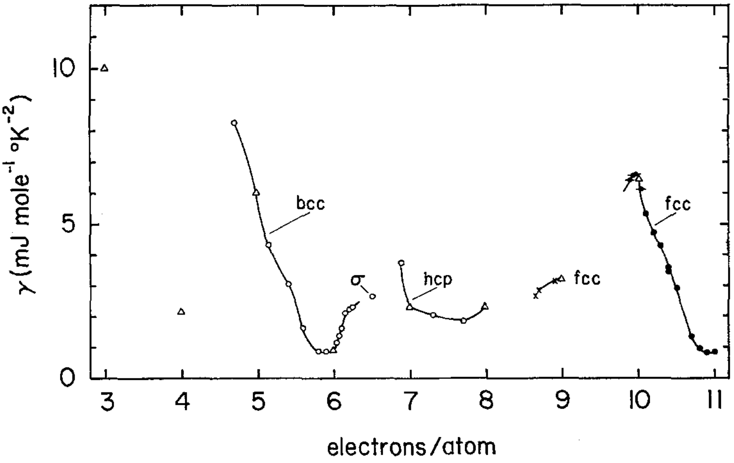

Fig. 3. Specific heat coefficient γ vs. number of valence electrons per atom in 5d-alloys. △ elements (from Table 1), ○ Bucher et al. [48], × Geballe [65], -●- Dixon et al. [127], ● Budworth et al. [89]

V. Comparison of 3d-, 4d- and 5d-Alloys

Fig. 4 representing the reproduced curves of Figs. 1—3 facilitates a comparison of the γ-variations in 3d-, 4d- and 5d-alloys. A very similar behaviour is found in all three series of b.c.c. alloys with less than 5.95 valence electrons per atom, all of them being paramagnetic. A depression in the specific heat linear in T of the 3d-series above 5.95 electrons per atom, where antiferromagnetism sets in, is the first marked difference between the behaviour of this series and the other alloys.

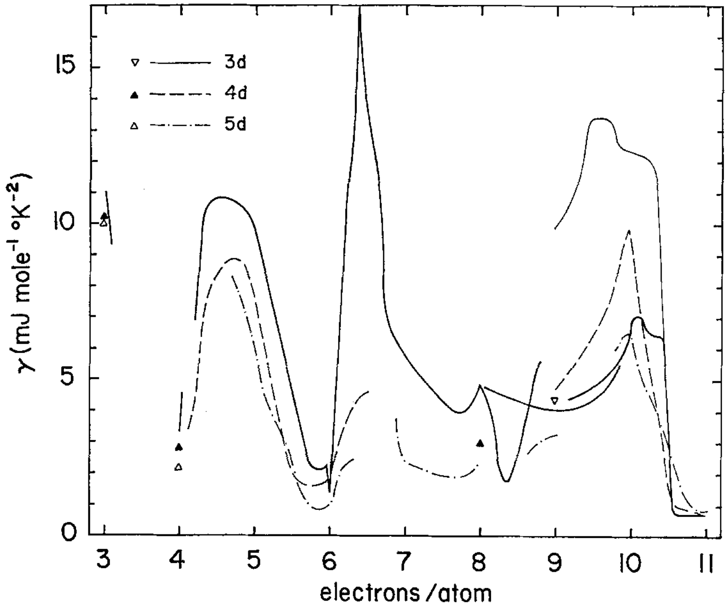

Fig. 4. Comparison of specific heat coefficient γ vs. number of valence electrons per atom in 3d-, 4d- and 5d-alloys. Light curve above 9 el./atom shows the probable density of states for both spin orientations (see text)

In the b.c.c. region above 6 electrons per atom the agreement between the 3 curves is only qualitative even for the paramagnetic 4d- and 5d-series. The coefficient γ shows maxima at about the same electron number but the absolute values of these maxima decrease strongly in the sequence of 3d-, 4d- and 5d-alloys. The difference between the three series is most marked just above 6 electrons per atom. The high maximum of the 3d-alloys differs from the corresponding maxima in the 4d- and 5d-series by its height and sharpness. With the model of Berger [*118*] the latter property could be explained by a rounded density of states curve, similar to those of the 4d- and 5d-alloys, but it would still be necessary to have a high density of states.

In the region between 7 and 9 electrons per atom where the solid solubilities are very restricted the lack of data prevents a comparison between the 3 series. In the f.c.c. range from 9 to 11 electrons per atom we find similar maxima at about 10 electrons per atom in all three series[1]. In the case of this maximum it seems clear that the γ-values for the Ni-alloys originate mainly from one spin direction. A density of states for both spin directions, as traced in Fig. 4, with a light line, could explain the measured γ-values as well as the magnetization data

---

[1] In the light of recent work of Berk and Schrieffer [*189*] it is questionable whether these peaks even qualitatively reflect the band shapes. These authors consider the influence of spin fluctuations in Pd and find a large enhancement of the electronic specific heats.

of Ahern et al. [*129*]. The maxima to be compared then would again decrease in the sequence of 3d-, 4d- and 5d-alloys. In the model of a rigid band for every one of the three series this would mean that the 3d-, 4d- and 5d-bands are very similar but that the width is smallest for the 3d- and largest for the 5d-band.

VI. Alloys of Two Isoelectronic Transition Elements

In the approximation of a rigid band model no drastic variation of the density of states would be expected in paramagnetic alloys between elements with the same number of valence electrons per atom. Nevertheless strong variations of the linear term of the specific heat, γ, are found in many of the investigated alloys (Fig. 5).

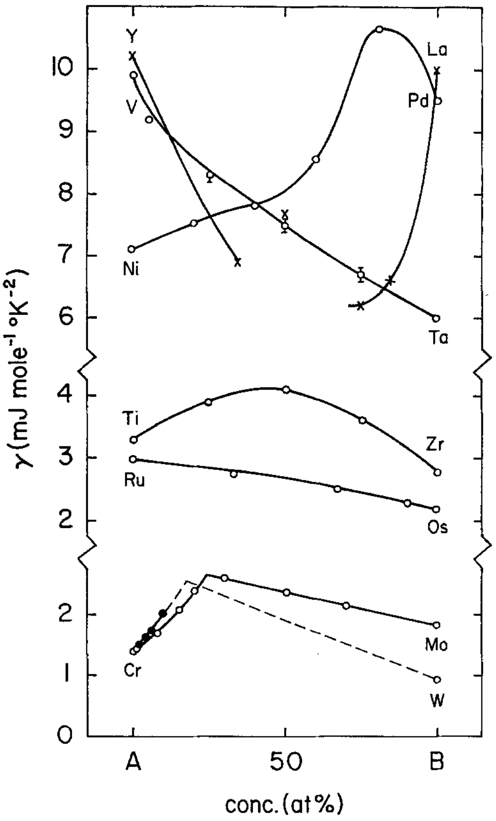

Fig. 5. Specific heat coefficient γ vs. concentration of the components in alloys of two isoelectronic transition elements

In the alloy system Y-La γ decreases from the high values of the elements to those of the alloys [*130*]. Another marked variation has been found in the Ti-Zr alloys (Table 13, Fig. 5) which also explains the maximum in the superconducting critical temperature at about 50 at.-% Zr (Bucher et al. [*133*]). The coefficient seems to vary almost linearly in Ti-Hf and to go through a minimum in the Zr-Hf system.

The decrease of γ from the value of pure Nb to that of $V_{0.12}Nb_{0.88}$ is accompanied by a decrease in the critical temperature of superconductivity to 5.7 °K. For V-Ta we believe that alloys with V of the same purity would lead to an almost straight line for γ as a function of concentration. We did not find any lattice constants in the literature for these alloys and therefore added in Table 13 our values for the lattice constant a. The superconducting critical temperatures of the same specimens were 2.80 °K, 2.35 °K and 2.65 °K for the alloys with 25, 50 and 75 at.-% of Ta respectively.

Table 13. *Low temperature specific heat of binary alloys of isoelectronic transition elements*

Alloy-system	Conc. of the 2nd element (at.-%)	Structure	γ (mJ°K^{-2}mole^{-1})	Θ_0 (°K)	Ref.
Y-La	15	h. c. p.	8.3	245	[*130*]
	35	h. c. p.	7.1	205	[*130*]
	48	Sm-h. c. p.	7.1	192	[*130*]
	60	La-h. c. p.	5.8	175	[*130*]
	75	La-h. c. p.	6.2	170	[*130*]
	85	La-h. c. p.	6.6	162	[*130*]
Ti-Zr	25	h. c. p.	3.9 ± 0.1	323 ± 5	[*49*]
	50	h. c. p.	4.1 ± 0.1	294 ± 3	[*49*]
	50	h. c. p.	4.21	304	[*36*]
	50	h. c. p.	4.16	295	[*37*]
	75	h. c. p.	3.6 ± 0.2	292 ± 5	[*49*]
Ti-Hf	50	h. c. p.	2.5 ± 0.2	252 ± 5	[*49*]
Zr-Hf	50	h. c. p.	2.0 ± 0.1	240 ± 6	[*49*]
V-Nb	88	b. c. c.	7.05 ± 0.10	268 ± 3	[*49*]
V-Ta	5	b. c. c.	9.20	357	[*131*]
	25	b. c. c. a = 3.111 Å	8.3 ± 0.1	285 ± 4	[*49*]
	50	b. c. c. a = 3.182 Å	7.5 ± 0.1	264 ± 4	[*49*]
	75	b. c. c. a = 3.254 Å	6.7 ± 0.1	250 ± 4	[*49*]
Cr-Mo	0.8—100	b. c. c.	Fig. 5	425—580	[*61*]
Cr-W	2—10	b. c. c.	Fig. 5	495—560	[*61*]
Fe-Ru	50	h. c. p.	8.35 ± 0.1	430 ± 40	[*49*]
	75	h. c. p.	5.6 ± 0.1	460 ± 50	[*49*]
Ru-Os	33—100	h. c. p.	Fig. 5	—	[*65*]
Ni-Pd	20—100	f. c. c.	Fig. 5	272—388	[*94*]
Ni-Pt	99.5	f. c. c.	—	—	[*132*]

The Cr-Mo and Cr-W alloys will be discussed in the following section. An almost linear variation of the electronic specific heat has been found in the Ru-Os system (GEBALLE [*65*]). A strong dependence of γ upon concentration is seen in alloys between the ferromagnetic Ni and the paramagnetic Pd, which has been discussed by MACKLIET and SCHINDLER [*94*]. They propose a band model which is in agreement with both specific heat and magnetization data but does not explain for example the γ-values in Ni-Cu alloys. We do not believe that it is realistic to use the same density of states curve of Pd and Ni. In order to decide if the marked maximum in the γ-function is related with a maximum in the density of states curve or if it is rather an effect of the transition from ferromagnetism to paramagnetism it will be necessary to obtain more information about the specific heat and the magnetization in the Pd-rich range of concentrations.

VII. Binary Chromium Alloys

On the basis of a series of low temperature specific heat results obtained from Cr-based solid solutions with other transition metals, HEINIGER [*61*] estimated the effect of antiferromagnetic ordering on the density of states of these alloys. The experimental data in question is summarized in Table 14 and reported in Figs. 5 (Cr-Mo, Cr-W) and 6 (Cr-Re, Cr-Ru, Cr-Os).

Table 14. *Low temperature specific heat of alloys of Chromium with other transition metals*

Alloy-system	Conc. of the 2nd element (at.-%)	Structure	γ (mJ°K^{-2}mole^{-1})	Θ_0 (°K)	Ref.
Cr-(Ti, V, Fe)		see table 10			
Cr-(Mo, W)		see table 13			
Cr-Ru	7—14	b. c. c.	Fig. 6	505—530	[*61*]
Cr-Re	0—38	b. c. c.	Fig. 6	410—630	[*56*]
	60	σ	4.18	335	[*125*]
Cr-Os	5—20	b. c. c.	Fig. 6	430—510	[*61*]
Cr-Nb	0—2	b. c. c.	—	—	[*61*]
Cr-Ta	0—1	b. c. c.	—	—	[*61*]

For Cr-Mo alloys (Fig. 5) γ varies almost linearly in the paramagnetic ($>$ 24 at.-% Mo) and antiferromagnetic regions ($<$ 24 at.-% Mo) but shows sharp discontinuity in slope at the border between them. An even steeper rise than in Cr-Mo alloys is found in Cr-rich Cr-W alloys (Fig. 5) which leads to a value of 2.55 mJ °K^{-2}mole^{-1} for the concentration of 16 at.-% W where the Néel temperature T_N reaches 0 °K [*134*]. An investigation of paramagnetic Cr-W alloys was prevented by a miscibility gap, but it is reasonable to expect again, as in Cr-Mo, an almost linear variation of γ between the values for pure W (Table 1) and for $Cr_{0.84}W_{0.16}$ (dashed line in Fig. 5). For both alloy-systems, Cr-Mo and Cr-W, an extrapolation of the electronic specific heats for paramagnetic alloys leads to a γ_p-value of 2.9 mJ °K^{-2}mole^{-1} for pure paramagnetic Chromium which should exist at high enough pressure (see ref. [*61*]).

A γ_p-value of about 2.9 mJ °K^{-2}mole^{-1} is also obtained by a smooth interpolation of γ for paramagnetic alloys of the systems V-Cr-Re and V-Cr-Os (dashed line 1 in Fig. 6). By considering these interpolations as representative of the specific heat of paramagnetic alloys, we notice that they look very similar to those of the analogous systems Nb-Mo-Re and Ta-W-Re (Fig. 6, curves 2 and 3), whilst any irregularities for Cr-alloys, as discussed in a recent article (BUCHER et al. [*48*]) have disappeared.

HEINIGER [*61*] also determined the difference γ' between γ_p for the paramagnetic and γ_a for the antiferromagnetic state as a function of the solute concentration, γ' was found to reach values corresponding to more than 50% of the total paramagnetic density of states and to vary similarly as the Néel temperature

T_N and the average magnetic moment $\bar{\mu}$. The reduction of γ in the antiferromagnetic state was explained assuming a truncation of the Fermi surface by magnetic energy-gaps and the resulting diminution of $N(E_F)$ in (6).

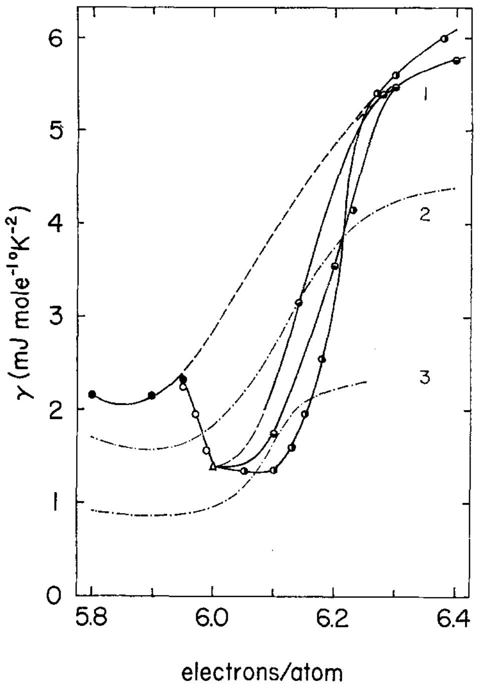

Fig. 6. Specific heat coefficient γ in V-Cr, Cr-Re, Cr-Os and Cr-Ru alloys. Dashed line (1) smooth interpolation of γ for paramagnetic V-Cr and Cr-Re or Cr-Os alloys, chain-lines (2) and (3) γ for the analogous systems Nb-Mo-Re and Ta-W-Re respectively. ● V-Cr (Cheng et al. [*79*]), ○ V-Cr (Heiniger [*61*]), ◑ Cr-Re (Muheim and Müller [*56*]), ◒ Cr-Os (Heiniger [*61*]), ◕ Cr-Ru (Heiniger [*61*])

VIII. Other Alloys of Two Transition Elements

Table 15 contains in alphabetic order the remaining data on binary alloys between two transition elements not yet mentioned in any of the preceding tables.

For Pd containing approximately 0.1 at.-% Co Boerstoel et al. [*96*] found a maximum in the specific heat at about 1.9 °K and below 0.5 °K a magnetic contribution linear in T. The investigations of Tsiovkin and Volkenshtein [*132*] concerned the influence of 0.5 at.-% solid solutions of Cr, Mn, Fe, Ni and Gd in Pt, and they analysed the specific heat by the three-term formula $C = \gamma T + \alpha T^3 + A T^{-2}$. They found no T^{-2} contribution and only a slight increase of γ in Pt-Ni. For the solid solutions with Cr, Fe and Mn these authors report an almost constant α and a large increase of γ. They explained this behaviour by an increase of the density of states near the Fermi surface by additional impurity states. The analysis seems somewhat uncertain and we suspect that the increase of the specific heat may at the least be partly caused by an increase of α.

Effective hyperfine fields have been determined from the specific heat at very low temperatures by Kogan et al. [*135*] in Fe alloyed with Ir and Re, by Ho and Phillips [*137*] in Fe alloyed with Os and Pt and also in Fe-Re by Lounasmaa et al. [*136*] (see also Table 19). The investigations of Morin and Maita [*22*] and of

Table 15. *Low temperature specific heat of binary alloys of transition metals*

Alloy-system	Conc. of the 2nd element (at.-%)	Structure	γ (mJ°K^{-2}mole^{-1})	Θ_0 (°K)	Ref.
Co-Pd	5—99.5	—	—	—	[*183*]
	99.9	f. c. c.	—	—	[*96*]
Co-Pt	96.5—99	—	—	—	[*183*]
Cr-Pt	99.5	f. c. c.	10	—	[*132*]
Fe-Ir	6.1—9.0		see text	—	[*135*]
	95—99		—	—	[*186*]
Fe-Mo	0—2		—	—	[*178*]
Fe-Nb	0—1		—	—	[*178*]
Fe-Re	0.15		see text	—	[*135*]
	10	b. c. c.	4.35	413	[*136*]
Fe-Os	0.75		4.76	—	[*137*]
Fe-Pd	98.48—100	f. c. c.	—	—	[*95*]
Fe-Pt	3.21		4.98	—	[*137*]
	99.5	f. c. c.	12	—	[*132*]
Fe-Rh	99		—	—	[*186*]
Fe-W	0—1		—	—	[*178*]
Ir-Mo	75	β-W	3.35	325	[*22*]
Ir-Nb	63	σ	2.78	330	[*125*]
Mn-Pt	99.5	f. c. c.	11	—	[*132*]
Mo-Os	38	σ	3.32	371	[*125*]
Mo-Re	0—50	b. c. c.	Fig. 7	320—470	[*22*]
	58	σ	3.31	351	[*125*]
	77	α-Mn	3.80	272	[*125*]
Mo-Ti	91.4	b. c. c.	5.88	310	[*138*]
	92.5	b. c. c.	5.56	337	[*138*]
	93.5	b. c. c.	5.06	354	[*138*]
	93.7	b. c. c.	4.90	364	[*138*]
	97.5	h. c. p.	3.8	360	[*107*]
Nb-Os	40	σ	2.70	310	[*125*]
Nb-Pt	38	σ	3.40	336	[*125*]
Nb-Re	62	α-Mn	2.35	326	[*125*]
	71	α-Mn	3.58	322	[*125*]
	80	α-Mn	5.00	316	[*125*]
Nb-Ti	96	h. c. p.	4.3	340	[*35*]
Ni-Pt	99.5	f. c. c.	see text	—	[*132*]
Re-V	8	h. c. p.	3.7 ± 0.1	—	[*49*]
Ru-V	55	CsCl	7.40 ± 0.1	413 ± 20	[*49*]
	65	CsCl	1.93 ± 0.1	460 ± 20	[*49*]
	75	b. c. c.	1.93 ± 0.1	460 ± 20	[*49*]
	85	b. c. c.	3.95 ± 0.1	351 ± 20	[*49*]
Sc-Zr	20		7.4	330	[*139*]
	50		4.5	325	[*139*]
	75		2.6	321	[*139*]
	90		2.4	309	[*139*]
	95		2.5	311	[*139*]

HAKE [*138*] on cubic alloys and those of BUCHER et al. [*125*] on complex structures revealed not only a correlation of γ with the number of valence electrons per atom but also with the critical temperature T_c of superconductivity.

We also present in Table 15 new results on $Re_{0.92}V_{0.08}$ and on Ru-V alloys. The increase of T_c up to 6.8 °K by alloying of Re with 8 at.-% V is accompanied by an increase of γ to (3.7 ± 0.1) mJ °K^{-2}mole^{-1}. The Θ-variation of Re-alloys is still important below that T_c, and the total entropy at T_c had to be considered for the determination of γ. A large variation of γ has been found in Ru-V alloys

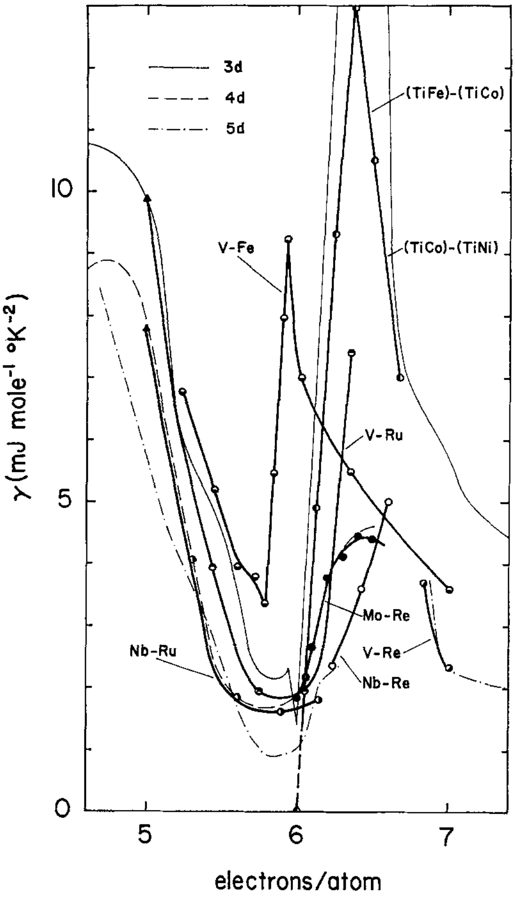

Fig. 7. Specific heat coefficient γ vs. number of electrons per atom for alloys of transition elements which have 5 to 7 electrons per atom. Light lines representing pure 3d-, 4d- and 5d-alloys are taken from Fig. 4

(Fig. 7 and 13). Only in the alloy with the highest γ, $Ru_{0.45}V_{0.55}$, could superconductivity be detected above 1.1 °K, and this had a T_c of 4.0 °K. The variations of the density of states in Ru-V alloys are so large that we believe them to be reflected in the behaviour of the Debye-temperatures (see Section XI). Other hitherto unpublished works are the results on Sc-Zr alloys due to Maita and are quoted in reference [*139*].

In addition to the γ-values for the alloys Mo-Re, Nb-Re, V-Re and V-Ru of Table 15 we also report in Fig. 7 the coefficient γ for the ternary alloys (TiFe)-(TiCo) and (TiCo)-(TiNi) and for binary alloys of the preceding sections which have 5—7 valence electrons per atom. A very similar feature for all of the different alloys is the deep minimum in γ slightly below 6 electrons per atom. In extreme cases γ reaches minimum values corresponding to those of the monovalent noble metals. Furthermore the height of the maxima in γ between 6 and 7 electrons per atom for different alloy-systems again seems to decrease with increasing average atomic mass.

IX. Binary Alloys of Transition Metals with Non-Transition Elements

The major part of the data in Table 16a originates from Beck and coworkers who investigated the influence of non-transition elements dissolved in 3d-metals and alloys. The results for b.c.c. alloys are discussed in detail in an article by Beck [*144*] and show that the thermal and magnetic properties of these alloys can hardly be understood in terms of filling a rigid or semi-rigid band as proposed e.g. by Shimizu and Wohlfahrt [*145*] for Fe-Al alloys. The comparison of the behaviour of the calorimetric density of states with the number of electrons per atom for b.c.c. 3d-metals and alloys with that for the same alloys containing 10 at.-% Al (Fig. 8) shows no apparent shift of the maxima or minima by alloying and gives no justification for such simple models.

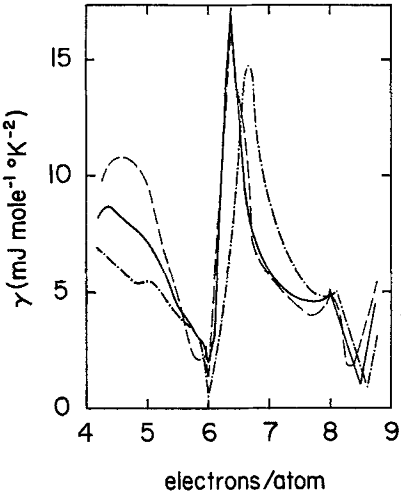

Fig. 8. Specific heat coefficient γ vs. number of electrons per transition metal atom for 3d-metals and alloys (broken line) and for the same alloys but containing 10 at.-% Al (heavy line) and 20 at.-% Al (chain line) respectively (fromPessall et al. [*57*] and Srinivasan et al. [*146*])

The electronic specific heat γ of V is lowered by the solution of Al, Sn and Sb (Fig. 9). For 10—30 at.-% Al in Cr (Fig. 9) the variation of γ seems to be similarly related with the Néel temperature T_N (Koester et al. [*147*]) as described in Section VII for other Cr-alloys, but we do not know T_N between 0 and 10 at.-% Al in Cr so cannot make a more thorough comparison. B.c.c. solid solutions of Fe

Table 16a

Low temperature specific heat of alloys of 3d-elements with non-transition metals

Alloy-system	Conc. of the 2nd element (at.-%)	Structure	γ (mJ°K^{-2}mole^{-1})	Θ_0 (°K)	Ref.
V-Au	25	β-W	9.6	—	[*140*]
	25	β-W	9.8 ± 0.2	350±20	[*49*]
V-Al	10—40	b. c. c.	Fig. 9	323—487	[*57*]
V-Ga	25	β-W	25.6	310	[*22*]
V-C	50	—	—	—	[*180*]
V-Si	25	β-W	19.5	330	[*22, 176*]
V-Ge	25	β-W	7.6	405	[*22*]
V-Sn	2—6	b. c. c.	Fig. 9	315—393	[*57*]

Table 16 a (continued)

Alloy-system	Conc. of the 2nd element (at.-%)	Structure	γ (mJ°K^{-2}mole^{-1})	Θ_0 (°K)	Ref.
V-Sb	1—3	b. c. c.	Fig. 9	319—352	[*57*]
Cr-Al	0—30	b. c. c.	Fig. 9	425—606	[*57*]
Mn-Cu			see Table 10b		
Mn-Au	50	CsCl, tetr.	1.05	—	[*141*]
Fe-Al	0—50	b. c. c.	Fig. 9	240—540	[*142*]
	1—2		—	—	[*178*]
Fe-Si	1—2		—	—	]*178*]
	4—25	b. c. c.	Fig. 9	397—450	[*143*]
Fe-Ge	4—12	b. c. c.	Fig. 9	363—474	[*143*]
Fe-Sn	4—8	b. c. c.	Fig. 9	344—487	[*143*]
Fe-Sb	5.4	b. c. c.	5.45	411	[*136*]
Ni-Cu			see Table 10a		
Ni-Al	10	f. c. c.	6.83	338	[*103*]
Ni-Si	4—8	f. c. c.	Fig. 9	345—366	[*103*]
Ni-Sb	4—8	f. c. c.	Fig. 9	287—318	[*103*]
Ni-Zn	9—26	f. c. c.	Fig. 9	317—387	[*103*]

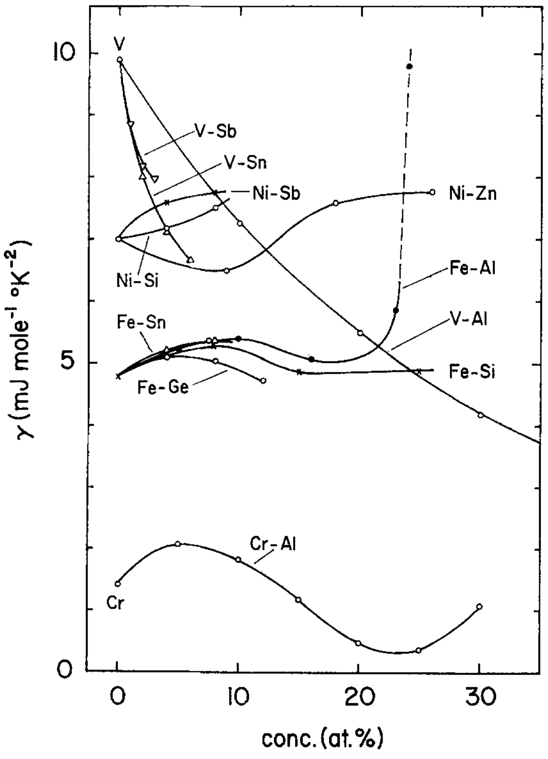

Fig. 9. Specific heat coefficient γ vs. solute concentration for solid solutions of transition elements with non-transition elements

Table 16b

Low temperature specific heat of alloys of 4d- and 5d-elements with non-transition metals

Alloy-system	Conc. of the 2nd element (at.-%)	Structure	γ (mJ°K^{-2}mole^{-1})	Θ_0 (°K)	Ref.
Y-Si	65.5	b. c. tetrag.	0.655	400	[*30, 130*]
Y-Ge	61.8	b. c. tetrag.	1.53	354	[*30, 130*]
Y-Gd	0— 6		—	—	[*182*]
Zr-Ag	0— 5.66	h. c. p.	$2.81+0.01303x$	$291-2.492x$	[*148*]*
Zr-Cd	0— 8.15	h. c. p.	$2.81+0.03778x$	$291-1.766x$	[*148*]*
Zr-In	0—11.26	h. c. p.	$2.81+0.04882x$	$291-0.8795x$	[*148*]*
Zr-Sn	0—9.06	h. c. p.	$2.81+0.06811x$	$291-1.881x$	[*148*]*
Zr-Sb	0— 1.85	h. c. p.	$2.81+0.1016x$	$291-4.037x$	[*148*]*
Nb-Au	25	β-W	7.5	—	[*140*]
	25	β-W	10.0±0.3	280±20	[*49*]
Nb-B	67		—	—	[*180*]
Nb-C	35—50	NaCl	—	—	[*149*]
	42.8		1.19	500	[*150*]
	48.7		1.33	492	[*150*]
	49.5		1.33	464	[*150*]
Nb-N	45.6		1.64	331	[*150*]
	47.6		1.38	307	[*150*]
Nb-Sn	25	β-W	15.7	290	[*22*]
Nb-S	67		—	—	[*180*]
Nb-U	74.1	b. c. c.	16.0	138.8	[*151*]
Mo-S	66.7	—	—	—	[*152*]
Mo-U	70.4	b. c. c.	14.2	147.3	[*151*]
	74.7	b. c. c.	14.7	137.3	[*151*]
	78.4	b. c. c.	14.9	134.5	[*151*]
	82.2	b. c. c.	15.1	127.5	[*151*]
	86.3	b. c. c.	16.9	128.6	[*151*]
Ru-Th	33	cub.	6.40	—	[*140*]
Pd-H	36—47		—	—	[*185*]
Pd-Ag			see Table 11		
Pd-Te	50	hex.	2.83	277	[*153*]
	51	hex.	2.04	239	[*153*]
Pd-Th	1	f. c. c.	8.8	—	[*97*]
	2	f. c. c.	8.0	—	[*97*]
	5	f. c. c.	5.8	—	[*97*]
	10	f. c. c.	2.2	—	[*97*]
Pd-Gd	0.36—0.85		—	—	[*183*]
La-Si	66.7	b. c. tetrag.	1.93	365	[*30, 130*]
La-Ge	66.7	b. c. tetrag.	2.03	222	[*30, 130*]
La-Gd	0—2		—	—	[*182*]
Re-B	33		2.1	405	[*22*]
Os-Th	33	cub.	1.34	—	[*140*]
Ir-Th	31—33	cub.	7.5—12.6	—	[*140*]
Pt-Cu	50	rhombohedral:			
		-ordered	0.530	385	[*154*]
		-disordered	0.825	357	[*154*]
Pt-Au			see Table 12		
Pt-Gd	0.5	f. c. c.	—	—	[*132*]

---

* *x:* concentration of the 2nd element in at.-%

with Al, Si, Ge and Sn exhibit maxima in γ vs. concentration at low solute concentrations (Fig. 9). The large increase in γ for more than 20 at.-% Al in Fe is interpreted by CHENG et al. [*142*] with the aid of a magnetic contribution to the linear term of the specific heat. The interpretation of the data of f.c.c. solid solutions of Ni with Al, Si and Sb is at present not clear (Fig. 9).

Very high γ-values are found for the compounds V_3Ga, V_3Si, V_3Au, Nb_3Sn and Nb_3Au and are given in Tables 16a and 16b per mole, defined by the formula $T_{0.75}B_{0.25}$. Calculating an average number of electrons per atom as for alloys of two transition elements and taking into account 4 electrons per atom for Si and Ge, 3 for Ga and 1 for Au then γ of V_3Ga, V_3Si, V_3Ge and Nb_3Sn would coincide with the maximum of the density of states curve between 4 and 5 electrons per atom but the high values observed in V_3Au and Nb_3Au would correspond to the minimum at 4 electrons per atom. A pronounced decrease of the heat capacity of V_3Si with stress has been found by KUNZLER et al. [*176*] at temperatures below 25 °K.

KNEIP et al. [*148*] found an increase of γ proportional to the concentration and linear in the valence of the solute metal for solid solutions of Ag, Cd, In, Sn and Sb in Zr (Table 16b). They discussed these γ-variations in terms of a model with a rigid d-band for Zr and a common s-band for Zr and the solute metal; this included both the cases with and without a concentration dependent shift of the two bands relative to each other. The high density of states and residual resistivity found in the b.c.c. alloys of U (Table 16b) suggest a band structure similar to that of transition metals to be present. In reference [*97*] BATES and UNSTEAD compare MONTGOMERY's unpublished specific heat data on Pd-Th alloys (Table 16b) with their magnetic susceptibilities.

X. Ternary Alloys

The addition of 10 at.-% Al to Ti-V and V-rich V-Cr alloys causes a considerable decrease in the electronic specific heat (Fig. 8) which could partly be explained by a decrease in the number of states in the d-band. γ of Cr-rich V-Cr alloys increases on doing this, and in the ferromagnetic alloys with more than 6 electrons per atom γ remains essentially constant (Fig. 8). On the other hand a considerable shift of the prominent features of the specific heat curve vs. electron concentration for alloys containing 20 at.-% Al is found above 6 electrons/atom [*146*] (Fig. 8). As already mentioned in Section IX, this behaviour can hardly be explained by a simple band model.

By contrast the ternary alloy systems (TiFe)-(TiCo) and (TiCo)-(TiNi), which have an ordered CsCl-structure, have specific heats which behave similarly with the electron number as do those of the binary 3d-alloys (Fig. 7).

If a rigid band model were applicable to the ternary system Ni-Cu-Zn then we should expect no change in γ for alloys with a constant number of electrons per atom as in $Ni_xZn_xCu_{1-2x}$. In contradiction to this, the data of GUTHRIE [*155*] show rather large variations of γ which can be explained by adding up the effects of Zn and Ni on Cu separately (Table 17).

Table 17. *Low temperature specific heat of ternary alloys*

Alloy-system	Conc.	Structure	γ (mJ°K^{-2}mole^{-1})	Θ_0 (°K)	Ref.
(3d-alloys)-Al	10 at.% Al	b. c. c.	Fig. 8	—	[*57*]
	20 at.% Al	b. c. c.	Fig. 8	—	[*146*]
$(TiFe)_x$-$(TiCo)_{1-x}$	$x = 0 - 1$	CsCl, ord.	Fig. 7	325—502	[*108*]
$(TiCo)_x$-$(TiNi)_{1-x}$	$x = 0.75$	CsCl, ord.	7.0	282	[*108*]
$Ni_xZn_xCu_{1-2x}$	$x = 0$	f. c. c.	0.691	349.1	[*155*]
	$x = 0.03$	f. c. c.	0.850	349.6	[*155*]
	$x = 0.08$	f. c. c.	0.993	344	[*155*]
Ti-Zr-Mn	$Ti_{0.499}Zr_{0.499}Mn_{0.002}$	h. c. p.			[*36*]
$(Nb_{0.75}Au_{0.25})_x$-$(V_{0.75}Au_{0.25})_{1-x}$	$x = 0$	β-W	9.8±0.2	350±20	[*49*]
	$x = 0.1$	β-W	9.1±0.2	320±20	[*49*]
	$x = 0.25$	β-W	7.5±0.2	305±20	[*49*]
	$x = 0.5$	β-W	6.3±0.2	280±20	[*49*]
	$x = 0.75$	β-W	5.2±0.3	280±20	[*49*]
	$x = 0.9$	β-W	7.6±0.3	280±20	[*49*]
	$x = 1.0$	β-W	10.0±0.3	280±20	[*49*]
NbN-Cr	1—3 at.-% Cr		—	—	[*150*]
$Nb_{0.50}C_{0.15}N_{0.35}$			1.63	351	[*150*]
$Fe_{0.75-x}Ni_xMn_{0.25}$	$x = 0.15$	f. c. c.	10.5	359	[*177*]
	$x = 0.30$	f. c. c.	13.0	177	[*177*]
	$x = 0.45$	f. c. c.	11.7	222	[*177*]
	$x = 0.60$	f. c. c.	5.9	224	[*177*]
$(TiFe_2)$-$(ZrFe_2)$					[*187*]

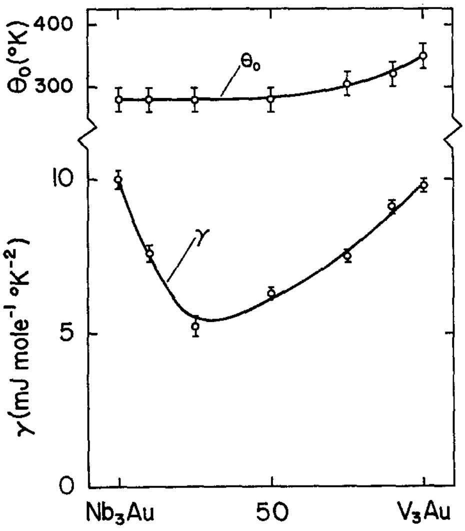

Fig. 10. Specific heat coefficient γ and Debye temperature, Θ_0, in continuous series of solid solution (Nb_3Au)-(V_3Au)

The specific heat of h.c.p. $Ti_{0.499}Zr_{0.499}Mn_{0.002}$ shows an anomaly at the lowest temperatures similar to the h.c.p. solid solutions of Mn in Ti. Probably related with the higher density of states in $Ti_{0.5}Zr_{0.5}$ than in Ti is the appearance in the former of a smaller localized moment of Mn.

A strong variation of γ has been found in the alloy-system $(Nb_3Au)_x$-$(V_3Au)_{1-x}$ which forms a continuous series of solid solutions in the β-W structure (Table 17, Fig. 10). For $x = 1.0$, 0.9 and 0.75 the critical temperatures of superconductivity, T_c, were 10.75, 7.8 and 4.9 °K respectively and were in fair agreement with earlier results of Bucher et al. [*156*]. T_c varies with x in a similar fashion as γ for $x \geqq 0.75$ but for $x < 0.75$ it remains below 1 °K even in alloys with a high γ.

XI. Miscellaneous Results

Electronic Specific Heat

In the preceding sections we observed that for many alloy-systems the behaviour of γ as a function of the number of electrons per atom in the unfilled shells is very similar. Little conclusive information is available about the dependence of the density of states on properties of the lattice such as structure, degree of order, crystal potentials or atomic numbers.

A large difference between the γ-values for the b.c.c. and the σ-modification of $Cr_{0.441}Fe_{0.559}$ (Table 10b) has been found by Hoare and Matthews [*113*]. It is possible that the large enhancement of the linear specific heat of this σ-phase is a magnetic contribution; a systematic investigation of the specific heat in σ-phases by Bucher et al. [*125*] did not confirm that they are especially favorable for high densities of states at the Fermi level.

A strong variation of γ with the degree of order has been reported by Roessler and Rayne [*154*] in CuPt (Table 16b) and by Goldman [*114*] in Ni_3Mn (Table 10b) in contrast with a constant γ in Cu_3Au found by Rayne [*157*]. It cannot be decided if these effects are due to either a change of the Brillouin-zone structure by superlattice formation or magnetic contributions to γ in the ordered state or other effects.

Changes in the atomic masses or atomic numbers are much less instrumental in changing γ than are variations in the number of valence electrons per atom; for equal numbers of valence electrons per atom, γ is rather lower for higher atomic numbers.

To take an extreme approach to transition metals is to neglect any dependence of γ other than on the mean number of conduction electrons per atom and even to suppose an identical conduction band $N(E)$ for alloys of the same row in the periodic system. With this rigid-band model Shimizu and coworkers explained in a series of papers (for references see [*158*]) the temperature dependence of the electronic specific heat and the magnetic susceptibility of transition metals and alloys. It is questionable how far such a model of independent electrons is realistic as electron-interactions can considerably affect the density of states $N(E)$ in a way depending on the position of the Fermi-level. Moreover these interactions have different effects upon γ and the spin susceptibility.

Debye Temperatures

The lattice part of the specific heat of transition metals is usually small compared with the electronic specific heat at temperatures where the T^3-law is valid; it is therefore determined with rather poor precision so that many of the published Θ_0-values are not very reliable. The large amount of calorimetric data nevertheless permits some conclusions to be drawn.

In Table 18 we collected Θ-values determined from the elastic constants at low temperatures for comparison with those from calorimetric data. Although the elastic constants had been obtained at frequencies several orders of magnitude lower than those important to the specific heat in the liquid helium temperature range, no disagreement can be detected up to the accuracy of the measurements. This means that any dispersion effects at frequencies lower than $\nu = 10^{10}$ c/s must be small.

Table 18. *Comparison of the characteristic constants* $\Theta_{\text{cal.}}$ *and* $\Theta_{\text{elast.}}$ *determined calorimetrically or calculated from low temperature elastic constants respectively*

Element	$\Theta_{\text{cal.}}$ (°K)	$\Theta_{\text{elast.}}$ (°K)	Ref.
Y	280	256.4	[*159, 160*]
Ti	425	425.7	[*161*]
Zr	290	296.0	[*161*]
Hf	252	256.3	[*161*]
V	399	399.3	[*162*]
Nb	277	273	[*163, 164, 165*]
Ta	258	261.9	[*166*]
Mo	460	474.2	[*166*]
W	390	384.3	[*166*]
Re	415	416.2	[*167*]
Fe	470	477	[*168*]
Ir	420	436	[*169*]
Ni	470	472	[*170*]
Pd	270	275	[*171*]
Pt	235	237.8	[*172*]

On the other hand the temperature where a considerable Θ-variation sets in can vary drastically. Fig. 11 shows $\Theta(T)$ for Ti, Zr and Nb. This function has been determined by subtracting from the measured specific heat (Heiniger [*49*] (Ti, Zr), Bucher et al. [*48*] (Nb)) a normal state electronic specific heat $C_{\text{el}} = \gamma T$, γ taken as constant (see eq. (3), Θ_0 replaced by $\Theta(T)$). In Nb $\Theta(T)$ varies with temperature even at $\Theta_0/100$ and goes sharply to a minimum at $\Theta_0/30$ whilst in the two hexagonal metals Ti and Zr the Θ-minimum lies at considerably higher temperatures.

For alloys no elastic data are available for a direct comparison. Considering the large amount of data for binary alloys the most striking features are the following:

Quite generally the Debye temperature Θ_0 is rather high for an element and is lowered by alloying with even small quantities of other elements. Thus, in contrast to the electronic specific heat coefficient γ, which varies smoothly with the number of electrons (e/a) per atom for the continuous alloy series $A - B$ and $B - C$ at the position of the element B, the curve $\Theta_0(e/a)$ shows peaks at the positions of the

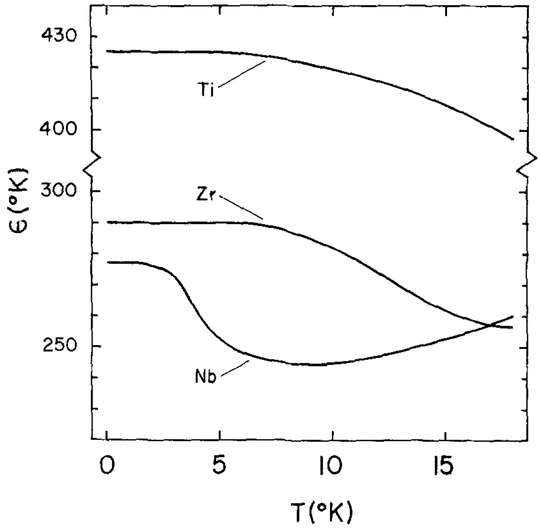

Fig. 11. Variation of Debye temperature Θ as a function of temperature in the h. c. p. metals Ti and Zr and the b.c.c. Nb

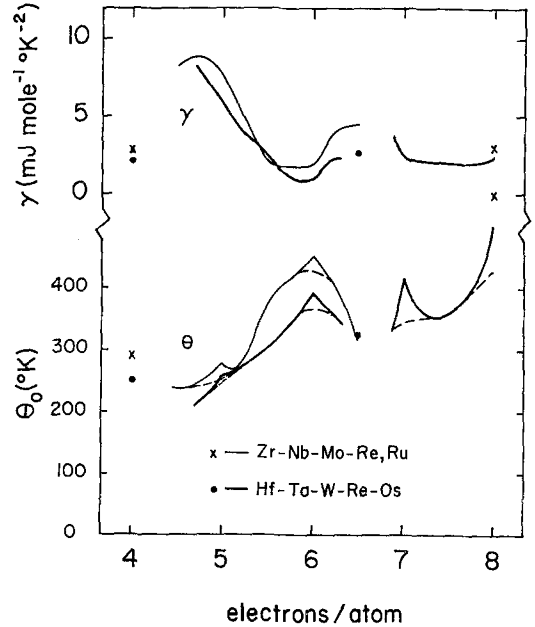

Fig. 12. Comparison of specific heat coefficient γ and Debye temperature Θ_0 of 4d- and 5d-alloys

elements (Fig. 12). This must be related with a decrease in the stiffness constants by dilute alloying as has been observed in some non-transition metals (HUNTINGTON [*173*]).

Superimposed upon this effect is a variation of Θ correlating most obviously with that of the electronic specific heat coefficient γ both being opposite to each other. $\Theta(e/a)$ in Fig. 12 shows maxima for that electron number corresponding to a minimum in the density of states provided that we do not consider the peaks for dilute alloys but rather the curve smoothed by a broken line. The effect is very drastic in the system V-Ru shown in Fig. 13. Qualitatively, we even expect that the onset of CsCl-ordering, which happens near the Θ-maximum of V-Ru, partly counteracts [*154, 157*] the decrease at higher electron concentrations.

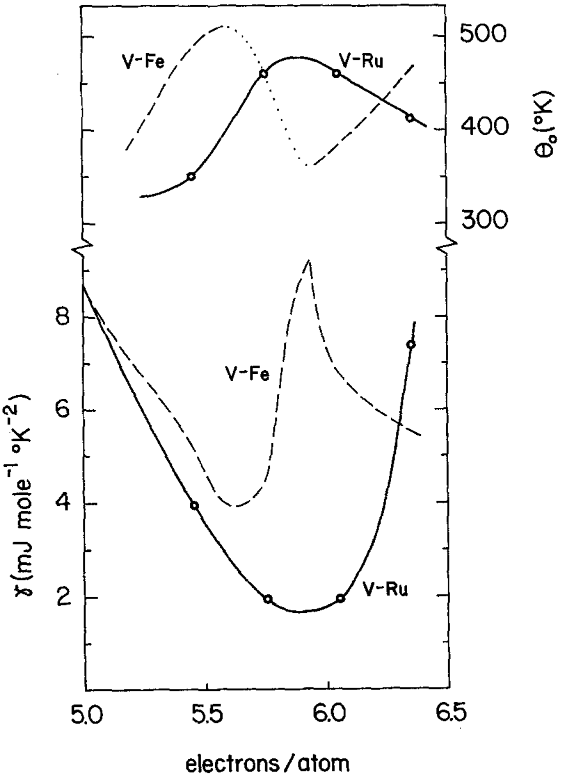

Fig. 13. Comparison of specific heat coefficient γ and Debye temperature Θ_0 of the V-Ru and V-Fe systems (from Bucher et al. [*48*])

The effect of the presence of conduction electrons on lattice vibrations in a metal has been investigated in several ways (for references see e. g. Krebs [*174*]). Earlier models considered the contribution of the electrons to the bulk moduli of the crystal thereby increasing the longitudinal component of the lattice wave velocities. In a simple band model due to Rayne [*171*] the bulk modulus of the electron gas is expected to be inversely proportional to the density of states, leading qualitatively to a high Θ_0 for a low γ. But quantitative estimates show that the large variations of Θ_0 with γ can hardly be fully explained in this way. Other theories consider the effect of the electrons on lattice vibrations through the screening of the Coulomb interaction between the ions. From the Thomas-Fermi model we expect a high density of electron states to give a low Θ_0. As the densities of states of transition metals primarily originate from d-electrons they must, despite their localized character, provide substantial screening of the deformation potential.

Nuclear Specific Heats

From formula (7) we see that in cases where electron-nuclear interactions are mainly magnetic the determination of the T^{-2} specific heat contribution permits an evaluation of the effective hyperfine fields H_e. A compilation of hyperfine fields of transition metals as determined by this method is given in Table 19.

Table 19

Effective hyperfine fields as determined by low temperature specific heat measurements

Alloy-system	Conc. of the 2nd element (at.-%)	Structure	Nuclei	$H_{\mathrm{eff.}}$ (kOe)	Ref.
Cr	—	b. c. c.	Cr^{53}	~ 0	[59]
Cr	—	b. c. c.	Cr^{53}	150	[58]
Mn	—	—	Mn^{55}	100	[58]
Mn	—	cub.	Mn^{55}	90	[72]
Mn	—	f. c. tetrag.	Mn^{55}	65	[74]
Mn-Au	50	CsCl, tetr.	Mn^{55}	320	[141]
Fe-V	4.4	b. c. c.	V^{51}	78	[112]
	10	b. c. c.	V^{51}	80	[111]
	13.8	b. c. c.	V^{51}	58	[112]
	33	b. c. c.	V^{51}	<61	[110]
Fe-Co	4.8	b. c. c.	Co^{59}	314	[78]
	17.2	b. c. c.	Co^{59}	293	[78]
	30	b. c. c.	Co^{59}	312	[110]
	58.7	b. c. c.	Co^{59}	256	[78]
	91.5	f. c. c.	Co^{59}	223	[78]
	10–75	b. c. c.	Co^{59}	395–227	[79]
	93	f. c. c.	Co^{59}	236	[79]
(Fe-Co) + + 10 at.-% Al	9–63	b. c. c.	Co^{59}	347–225	[57]
Fe-Sb	5.4	b. c. c.	Sb^{121,123}	169	[136]
Fe-Re	0.15	b. c. c.	Re^{185,187}	670	[135]
	10	b. c. c.	Re^{185,187}	610	[136]
Fe-Os	0.75	b. c. c.	Os^{187,189}	1400	[137]
Fe-Ir	6.1	—	Ir^{191,193}	~ 1350	[135]
	9.0	—	Ir^{191,193}	~ 1350	[135]
Fe-Pt	3.21	b. c. c.	Pt^{195}	1390	[137]
Co	—	h. c. p.	Co^{59}	183	[84, 85]
Co	—	h. c. p.	Co^{59}	219	[78]
Co	—	h. c. p.	Co^{59}	225	[79]
Co	—	h. c. p.	Co^{59}	−225.2	[87]
Co-Ni	40	f. c. c.	Co^{59}	161	[78]

The results for Cr are contradictory: Stetsenko and Avksent'ev [58] report an effective magnetic field of 150 kOe whilst the specific heat of Cr measured by Phillips and Ho [59] with a better precision shows no T^{-2} term. The effective fields in Mn could be overestimated by the neglect of the electric quadrupole splitting but the absence of a measurable T^{-3} term of the specific heat limits the error to less than 8% (Ho and Phillips [74]). Arp et al. [78] found an approximately linear variation of H_e with the number of electrons per atom in the alloys Fe-Co and Co-Ni. The variation is almost independent of the changing crystal structure and behaves similarly to the magnetic moments in these alloys (see Crangle [*175*]). Proctor et al. [*87*] measured the hyperfine specific heat in strong external magnetic fields and determined in such a way the sign of H_e to be negative. For the results of Cheng et al. [*79*] and of Pessall et al. [*57*] we refer to the original papers.

A specific heat term proportional to T^{-2} has been found in pure Re at very low temperatures by Keesom and Bryant [*75*]. This is explained by a quadrupole splitting of the 6 levels of the two Re-isotopes with spin $I = 5/2$ in 3 doubly degenerated pairs.

We restrict ourselves here to the presentation of these specific heat results without comparing them with the very numerous data on hyperfine interactions obtained by other methods and without entering on the origin of the observed effective fields. The subject of hyperfine interactions has been treated extensively by Freeman and Watson [*7*].

Acknowledgements. The authors wish to thank Prof. C. P. Enz and Prof. M. Peter for valuable discussions. We are also grateful to Dr. R. Burton for a critical review of the manuscript. This work has been supported by the Fonds National Suisse and the Commission Fédérale pour l'encouragement de la recherche scientifique.

References

[*1*] Keesom, P. H., and N. Pearlman: In: Encyclopedia of Physics, ed. by S. Flügge. Vol. **14**, 282 (1956).
[*2*] Beck, P. A.: Electronic Structure and Alloy Chemistry of the Transition Elements. New York-London: Interscience Publishers John Wiley and Sons 1963.
[*3*] Mott, N. F.: Advanc. Phys. **13**, 325 (1964).
[*4*] Blackman, M.: In: Encyclopedia of Physics, ed. by S. Flügge, Vol. **7**, Part 1, 325 (1955).
[*5*] de Launay, J.: In: Solid State Physics, ed. by F. Seitz and D. Turnbull. New York-London: Academic Press Inc. 1956, Vol. **2**, p. 220.
[*6*] Wilson, A. H.: The Theory of Metals. Cambridge: University Press 1954.
[*7*] Freeman, A. J., and R. E. Watson: In: Magnetism, ed. by T. Rado and H. Suhl. New York-London: Academic Press 1965, Vol. II, Part A, p. 167.
[*8*] Walker, L. R.: In: Magnetism, ed. by T. Rado and H. Suhl. New York-London: Academic Press 1963, Vol. I, p. 299.
[*9*] Martin, D. L.: Phys. Rev. **139**, A 150 (1965).
[*10*] Ashcroft, N. W., and J. W. Wilkins: Phys. Letters **14**, 285 (1965).
[*11*] Silverstein, S. D.: Phys. Rev. **128**, 631 (1962).
[*12*] Callaway, J.: Energy Band Theory. New York-London: Academic Press 1964.
[*13*] Clogston, A. M.: Phys. Rev. **136**, A 8 (1964).
[*14*] Krebs, K.: Phys. Letters **6**, 31 (1963).
[*15*] Shinozaki, S. S.: Phys. Rev. **122**, 388 (1963).
[*16*] Dixon, M., F. E. Hoare, and T. M. Holden: Phys. Letters **14**, 184 (1965).
[*17*] Schröder, K.: J. Appl. Phys. **32**, 880 (1961).
[*18*] Overhauser, A. W.: J. Phys. Chem. Solids **13**, 71 (1960).
[*19*] Marshall, W.: Phys. Rev. **118**, 1519 (1960).
[*20*] Keesom, P. H., and R. Radebaugh: Phys. Rev. Letters **13**, 685 (1964).
[*21*] Rorer, D. C., D. G. Onn, and H. Meyer: Phys. Rev. **138**, A 1661 (1965).
[*22*] Morin, F. J., and J. P. Maita: Phys. Rev. **129**, 1115 (1963).
[*23*] Gschneidner, K. A., Jr.: In: Solid State Physics, ed. by F. Seitz and D. Turnbull. New York-London: Academic Press Inc. 1964, Vol. **16**, p. 275.

[*24*] Montgomery, H., and G. P. Pells: Proc. Phys. Soc. A **78**, 622 (1961).

[*25*] Anderson, R. A., W. E. Gardner, and J. Penfold: Proc. Int. Conf. on Magnetism, Nottingham, London: Inst. Phys. and Phys. Soc. 1964, p. 186.

[*26*] Lynam, P., R. G. Scurlock, and E. M. Wray: Proc. LT 9. New York: Plenum Press 1965, p. 905.

[*27*] Jennings, L. D., R. E. Miller, and F. H. Spedding: J. Chem. Phys. **33**, 1849 (1960).

[*28*] Berman, A., M. W. Zemansky, and H. A. Boorse: Phys. Rev. **109**, 70 (1958).

[*29*] Finnemore, D. K., D. L. Johnson, J. E. Ostenson, F. H. Spedding, and B. J. Beaudry: Phys. Rev. **137**, A 550 (1965).

[*30*] Satoh, T., and T. Ohtsuka: Phys. Letters **20**, 565 (1966).

[*31*] Aven, M. H., R. S. Craig, T. R. Waite, and W. E. Wallace: Phys. Rev. **102**, 1263 (1956).

[*32*] Wolcott, N. M.: Phil. Mag. **2**, 1246 (1956).

[*33*] Clusius, K., and P. Franzosini: Z. Phys. Chem. Neue Folge **16**, 3—6, p. 194 (1958).

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

[*35*] Heiniger, F., and J. Muller: Phys. Rev. **134**, A 1407 (1964).

[*36*] Hake, R. R., and J. A. Cape: Phys. Rev. **135**, A 1151 (1964).

[*37*] Dummer, G.: Z. Phys. **186**, 249 (1965).

[*38*] Wolcott, N. M.: Proc. LT 5. Paris: Inst. Intern. du Froid 1956, p. 286.

[*39*] Corak, W. S., B. B. Goodman, C. B. Satterthwaite, and A. Wexler: Phys. Rev. **102**, 656 (1956).

[*40*] Clusius, K., P. Franzosini u. U. Piesbergen: Z. Naturforsch. **15a**, 728 (1960).

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

[*42*] Phillips, N. E., and L. Y. L. Shen: Private communication.

[*43*] Chou, C., D. White, and H. L. Johnston: Phys. Rev. **109**, 788 (1958).

[*44*] Hirshfeld, A. T., H. A. Leupold, and H. A. Boorse: Phys. Rev. **127**, 1501 (1962).

[*45*] Blaugher, R. D., J. K. Hulm, J. A. Rayne, B. W. Veal, and R. A. Hein: Proc. LT 8. London: Butterworths 1963, p. 147.

[*46*] van der Hoeven, B. J. C., and P. H. Keesom: Phys. Rev. **134**, A 1320 (1964).

[*47*] Leupold, H. A., and H. A. Boorse: Phys. Rev. **134**, A 1322 (1964).

[*48*] Bucher, E., F. Heiniger, and J. Muller: Proc. LT 9. New York: Plenum Press 1965, p. 1059.

[*49*] Heiniger, F.: Unpublished.

[*50*] Shen, L. Y. L., N. M. Senozan, and N. E. Phillips: Phys. Rev. Letters **14**, 1025 (1965).

[*51*] McConville, T., and B. Serin: Phys. Rev. **140**, A 1169 (1965).

[*52*] Clusius, K., u. C. G. Losa: Z. Naturforsch. **10a**, 939 (1955).

[*53*] White, D., C. Chou, and H. L. Johnston: Phys. Rev. **109**, 797 (1958).

[*54*] Rayne, J. A., and W. R. G. Kemp: Phil. Mag. **1**, 918 (1956).

[*55*] Clusius, K., and P. Franzosini: Z. Naturforsch. **17a**, 522 (1962).

[*56*] Muheim, J., u. J. Muller: Phys. kondens. Materie **2**, 377 (1964).

[*57*] Pessall, N., K. P. Gupta, C. H. Cheng, and P. A. Beck: J. Phys. Chem. Solids **25**, 993 (1964).

[*58*] Stetsenko, P. N., and Y. I. Avksent'ev: Soviet Phys.-JETP **20**, 539 (1965).

[*59*] Phillips, N. E., and J. C. Ho: Private communication.

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

[*61*] — Phys. kondens. Materie **5**, 285 (1966).

[*62*] Clusius, K., u. P. Franzosini: Z. Naturforsch. **14a**, 99 (1959).

[*63*] Bryant, C. A., and P. H. Keesom: J. Chem. Phys. **35**, 1149 (1961).

[*64*] Waite, T. R., R. S. Craig, and W. E. Wallace: Phys. Rev. **104**, 1240 (1956).

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

[*66*] Booth, G. L., F. E. Hoare, and B. T. Murphy: Proc. Phys. Soc. B **68**, 830 (1955).

[*67*] Weiss, R. J., and K. J. Tauer: J. Phys. Chem. Solids **4**, 135 (1958).

[*68*] Zych, D. A., and C. V. Heer: Bull. Amer. Phys. Soc. 8, 420 (1963).

[*69*] Shinozaki, S., A. Arrott, H. Sato, and J. E. Zimmerman: Bull. Amer. Phys. Soc. 8, 66 (1963).

[*70*] Franzosini, P., C. G. Losa and K. Clusius: Z. Naturforsch. **19a**, 1348 (1964).

[*71*] Guthrie, G. L., S. A. Friedberg, and J. E. Goldman: Phys. Rev. **139**, A 1200 (1965).
[*72*] Scurlock, R. G., and W. N. R. Stevens: Proc. Phys. Soc. **86**, 331 (1965).
[*73*] Zimmerman, J. E., and H. Sato: J. Phys. Chem. Solids **21**, 71 (1961).
[*74*] Ho, J. C., and N. E. Phillips: Phys. Letters **10**, 34 (1964).
[*75*] Keesom, P. H., and C. A. Bryant: Phys. Rev. Letters **2**, 260 (1959).
[*76*] Blanpain, R.: Bull. Classe Sci. Acad. Roy. Belg. **47**, 750 (1961).
[*77*] Piesbergen, U.: Z. Naturforsch. **19 a**, 1075 (1964).
[*78*] Arp, V., D. Edmonds, and R. Petersen: Phys. Rev. Letters **3**, 212 (1959).
[*79*] Cheng, C. H., C. T. Wei, and P. A. Beck: Phys. Rev. **120**, 426 (1960).
[*80*] Rayne, J. A., and B. S. Chandrasekhar: Phys. Rev. **122**, 1714 (1961).
[*81*] Dixon, M., F. E. Hoare, T. M. Holden, and D. E. Moody: Proc. Roy. Soc. A **285**, 561 (1965).
[*82*] Clusius, K., and U. Piesbergen: Z. Naturforsch. **14 a**, 23 (1959).
[*83*] Phillips, N. E., and R. H. Batt: Private communication.
[*84*] Heer, C. V., and R. A. Erickson: Phys. Rev. **108**, 896 (1957).
[*85*] — Physica **24**, Suppl. S **155** (1958).
[*86*] Walling, J. C., and P. B. Bunn: Proc. Phys. Soc. **74**, 417 (1959).
[*87*] Proctor, W., R. G. Scurlock, and E. M. Wray: Phys. Letters **20**, 621 (1966).
[*88*] Clusius, K., u. C. G. Losa: Z. Naturforsch. **10 a**, 545 (1955).
[*89*] Budworth, D. W., F. E. Hoare, and J. Preston: Proc. Roy. Soc. **257**, 250 (1960).
[*90*] Gupta, K. P., C. H. Cheng, and P. A. Beck: J. Phys. Chem. Solids **25**, 73 (1964).
[*91*] Ehrat, R., and D. Rivier: Helv. Phys. Acta **38**, 643 (1965).
[*92*] Hoare, F. E., and B. Yates: Proc. Roy. Soc. A **240**, 42 (1957).
[*93*] Rayne, J. A.: Phys. Rev. **107**, 669 (1957).
[*94*] Mackliet, C. A., and A. I. Schindler: J. Phys. Chem. Solids **24**, 1639 (1963).
[*95*] Veal, B. W., and J. A. Rayne: Phys. Rev. **135**, A 442 (1964).
[*96*] Boerstoel, B. M., F. J. du Chatenier, and G. J. van den Berg: Proc. LT 9. New York: Plenum Press 1965, p. 1071.
[*97*] Bates, L. F., and P. B. Unstead: Proc. Int. Conf. Magnetism, Nottingham, p. 188. London: Inst. Phys. and Phys. Soc. 1964.
[*98*] Clusius, K., C. G. Losa, and P. Franzosini: Z. Naturforsch. **12 a**, 34 (1957).
[*99*] Ramanathan, K. G., and T. M. Srinivasan: Proc. Indian Acad. Sci. A **49**, 55 (1959).
[*100*] Wei, C. T., C. H. Cheng, and P. A. Beck: Phys. Rev. **112**, 696 (1958).
[*101*] Goldman, J. E., and G. L. Guthrie: Bull. Am. Phys. Soc. Ser. II, Vol. **1**, 148 (1956).
[*102*] Shinozaki, S., and A. Arrott: Proc. LT 9. New York: Plenum Press 1965, p. 1066.
[*103*] Gupta, K. P., C. H. Cheng, and P. A. Beck: Phys. Rev. **133**, A 203 (1964).
[*104*] Keesom, W. H., and B. Kurrelmeyer: Physica **7**, 1003 (1940).
[*105*] Guthrie, G. L., S. A. Friedberg, and J. E. Goldman: Phys. Rev. **113**, 45 (1959).
[*106*] Manchester, F. D.: Can. J. Phys. **37**, 989 (1959).
[*107*] Bucher, E., F. Heiniger, and J. Muller: Proc. LT 9. New York: Plenum Press 1965, p. 482.
[*108*] Starke, E. A., C. H. Cheng, and P. A. Beck: Phys. Rev. **126**, 1746 (1962).
[*109*] Scurlock, R. G., and E. M. Wray: Phys. Letters **6**, 28 (1963).
[*110*] Wei, C. T., C. H. Cheng, and P. A. Beck: Phys. Rev. **122**, 1129 (1961).
[*111*] Brewer, D. W., D. R. Howe, and B. G. Turrell: Phys. Letters **13**, 204 (1964).
[*112*] Nikitin, L. P., A. V. Kogan, V. D. Kulkov, and I. P. Shiryapov: Zh. Eksp. Teor. Fiz. **49**, 1028 (1965).
[*113*] Hoare, F. E., and J. C. Matthews: Proc. Phys. Soc. A **71**, 220 (1958).
[*114*] Goldman, J. E.: Rev. Mod. Phys. **25**, 108 (1953).
[*115*] Burford, J. C., and G. M. Graham: Can. J. Phys. **43**, 1915 (1965).
[*116*] Gupta, K. P., C. H. Cheng, and P. A. Beck: J. Phys. Radium **23**, 721 (1962).
[*117*] Shimizu, M., and A. Katsuki: Proc. Int. Conf. Magnetism, Nottingham, p. 182. London: Inst. Phys. and Phys. Soc. 1964.
[*118*] Berger, L.: Phys. Rev. **137**, A 220 (1965).
[*119*] Fallot, M.: Ann. Phys. **6**, 305 (1936).
[*120*] Weiss, P., and R. Forrer: Ann. Phys. **12**, 279 (1929).
[*121*] Schröder, K.: Phys. Rev. **125**, 1209 (1962).

[*122*] Nevitt, M. V.: J. Appl. Phys. **31**, 155 (1960).

[*123*] Bindari, A. E., and M. M. Litvak: J. Appl. Phys. **34**, 2913 (1963).

[*124*] Bender, D., E. Bucher u. J. Muller: Phys. kondens. Materie **2**, 225 (1963).

[*125*] Bucher, E., F. Heiniger u. J. Muller: Phys. kondens. Materie **2**, 210 (1964).

[*126*] Savitzkii, E. M., M. A. Tylkina, and O. Kamidov: Zhur. Neorg. Khim. **9**, 2738 (1964).

[*127*] Dixon, M., F. E. Hoare, T. M. Holden, and D. E. Moody: Conf. on Electronic Structure of Alloys, Sheffield (1963), paper 1.5.

[*128*] Ho, J. C., and N. E. Phillips: Rev. Sci. Instr. **36**, 1382 (1965).

[*129*] Ahern, S. A., M. J. C. Martin. and W. Sucksmith: Proc. Roy. Soc. A **248**, 145 (1958).

[*130*] Ohtsuka, T., and T. Satoh: Ann. Acad. Sci. Fennicae A VI, **210**, 92 (1966).

[*131*] Hake, R. R., and W. G. Brammer: Phys. Rev. **133**, A 719 (1964).

[*132*] Tsiovkin, Y. N., and N. V. Volkenshtein: Soviet Phys.-Solid State **7**, 432 (1965).

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

[*134*] Butylenko, A. K., and V. N. Gridnyev: Ukr. Fiz. Zh. **9**, 325 (1964).

[*135*] Kogan, A. V., V. D. Kul'kov, L. P. Nikitin, N. M. Reinov, and M. F. Stel'makh: Soviet Phys.-JETP **18**, 1 (1964).

[*136*] Lounasmaa, O. V., C. H. Cheng, and P. A. Beck: Phys. Rev. **128**, 2153 (1962).

[*137*] Ho, J. C., and N. E. Phillips: Phys. Rev. **140**, A 648 (1965).

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

[*139*] Jensen, A.: Ph. D. Thesis, University of California, San Diego (1965), unpublished.

[*140*] Geballe, T. H., B. T. Matthias, J. P. Maita, V. B. Compton, K. Andres, and E. Corenzwit: Bull. Amer. Phys. Soc. **10**, 579 (1965).

[*141*] Ho, J. C., and W. Bindloss: Phys. Letters **20**, 459 (1966).

[*142*] Cheng, C. H., K. P. Gupta, C. T. Wei, and P. A. Beck: J. Phys. Chem. Solids **25**, 759 (1964).

[*143*] Gupta, K. P., C. H. Cheng, and P. A. Beck: J. Phys. Chem. Solids **25**, 1147 (1964).

[*144*] Beck, P. A.: Proc. Int. Conf. on Magnetism, Nottingham, Inst. Phys. and Phys. Soc. London (1964), p. 178.

[*145*] Shimizu, M., and E. P. Wohlfahrt: Phys. Letters **11**, 108 (1964).

[*146*] Srinivasan, T. M., H. Claus, R. Viswanathan, P. A. Beck, and D. I. Bardos: Battelle Colloquium on "The Thermodynamic Stability of Metallic Phases". Geneva, Villars, 1966.
— — To be published.

[*147*] Köster, W., E. Wachtel, and K. Grube: Z. für Metallkunde **54**, 393 (1963).

[*148*] Kneip, G. D., Jr., J. O. Betterton, Jr., and J. O. Scarbrough: Phys. Rev. **131**, 2425 (1963).

[*149*] Sandenaw, T. A., and E. K. Storms: J. Phys. Chem. Solids **27**, 217 (1966).

[*150*] Geballe, T. H., B. T. Matthias, J. P. Remeika, A. M. Clogston, V. B. Compton, J. P. Maita, and H. J. Williams: Physics **2**, 293 (1966).

[*151*] Goodman, B. B., J. Hillairet, J. J. Veyssie, and L. Weil: Proc. LT 7. Toronto: University of Toronto Press (1961), p. 350.

[*152*] Westrum, E. F., Jr., and J. J. McBride: Phys. Rev. **98**, 270 (1955).

[*153*] Raub, Ch. J., V. B. Compton, T. H. Geballe, B. T. Matthias, J. P. Maita, and G. W. Hull, Jr.: J. Phys. Chem. Solids **26**, 2051 (1965).

[*154*] Roessler, B., and J. A. Rayne: Phys. Rev. **136**, A 1380 (1964).

[*155*] Guthrie, G. L.: Phys. Rev. **113**, 793 (1959).

[*156*] Bucher, E., F. Laves, J. Muller, and H. von Philipsborn: Phys. Letters **8**, 27 (1964).

[*157*] Rayne, J. A.: Phys. Rev. **108**, 649 (1957).

[*158*] Katsuki, A., and M. Shimizu: J. Phys. Soc. Japan **21**, 279 (1966).

[*159*] Alers, G. A.: In: Physical Acoustics, Academic Press (W. P. Mason, Editor), to be published.

[*160*] Smith, J. F., and J. A. Gjevre: J. Appl. Phys. **31**, 645 (1960).

[*161*] Fisher, E. S., and C. J. Renken: Phys. Rev. **135**, A 482 (1964).

[*162*] ALERS, G. A.: Phys. Rev. **119**, 1532 (1960).
[*163*] —, and D. L. WALDORF: Phys. Rev. Letters **6**, 677 (1961).
[*164*] WEBER, R.: Phys. Rev. **133**, A 1487 (1964).
[*165*] CARROLL, K. J.: J. Appl. Phys. **36**, 3689 (1965).
[*166*] FEATHERSTON, F. H., and J. R. NEIGHBOURS: Phys. Rev. **130**, 1324 (1963).
[*167*] SHEPARD, M. L., and J. F. SMITH: J. Appl. Phys. **36**, 1447 (1965).
[*168*] RAYNE, J. A., and B. S. CHANDRASEKHAR: Phys. Rev. **122**, 1714 (1961).
[*169*] MACFARLANE, R. E., J. A. RAYNE, and C. K. JONES: Phys. Letters **20**, 234 (1966).
[*170*] ALERS, G. A., J. R. NEIGHBOURS, and H. SATO: J. Phys. Chem. Solids **13**, 40 (1960).
[*171*] RAYNE, J. A.: Phys. Rev. **118**, 1545 (1960).
[*172*] MACFARLANE, R. E., J. A. RAYNE, and C. K. JONES: Phys. Letters **18**, 91 (1965).
[*173*] HUNTINGTON, H. B.: In: Solid State Physics, ed. by F. SEITZ and D. TURNBULL. New York-London: Academic Press Inc. 1958, Vol. **7**, p. 213.
[*174*] KREBS, K.: Phys. Rev. **138**, A 143 (1965).
[*175*] CRANGLE, J.: In ref. [*2*] p. 51.
[*176*] KUNZLER, J. E., J. P. MAITA, H. J. LEVINSTEIN, and E. J. RYDER: Phys. Rev. **143**, 390 (1966).
[*177*] WATANABE, H., K. EHARA, T. FUKUROI, Y. MUTO, and H. YAMAMOTO: Sci. Rep. Res. Insts. Tohoku Univ., Series A, **17**, 300 (1965).
[*178*] ARROTT, A., and S. S. SHINOZAKI: Ann. Acad. Sci. Fennicae A. VI, **210**, 31 (1966).
[*179*] FINNEMORE, D. K., and D. L. JOHNSON: Ann. Acad. Sci. Fennicae A. VI, **210**, 85 (1966).
[*180*] UKEI, K., and E. KANDA: Ann. Acad. Sci. Fennicae A. VI, **210**, 104 (1966).
[*181*] VEAL, B. W., J. K. HULM, and R. D. BLAUGHER: Ann. Acad. Sci. Fennicae A. VI, **210**, 108 (1966).
[*182*] BONNEROT, J., B. CAROLI, and B. COQBLIN: Ann. Acad. Sci. Fennicae A. VI, **210**, 120 (1966).
[*183*] HOARE, F. E., and J. C. G. WHEELER: Ann. Acad. Sci. Fennicae A. VI. **210**, 157 (1966).
[*184*] HO, J. C., H. R. O'NEAL, and N. E. PHILLIPS: Rev. Sci. Instr. **34**, 782 (1963).
[*185*] MACKLIET, C. A., and A. I. SCHINDLER: Phys. Rev. **146**, 463 (1966).
[*186*] GEBALLE, T. H., B. T. MATTHIAS, A. M. CLOGSTON, H. J. WILLIAMS, R. C. SHERWOOD, and J. P. MAITA: J. Appl. Phys. **37**, 1181 (1966).
[*187*] MASSENA, C. W.: Diss. Abstr. **24**/5, 63—7523, p. 1851 (1963).
[*188*] BUTERA, R. A., and R. S. CRAIG: J. Chem. Eng. Data **10**, 38 (1965).
[*189*] BERK, N. F., and J. R. SCHRIEFFER: Phys. Rev. Letters **17**, 433 (1966).
[*190*] SRINIVASAN, T. M., and P. A. BECK: Ann. Acad. Sci. Fennicae A. VI, **210**, 163 (1966).