A simple model for alloys

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II. The influence of ionicity on the stability and other physical properties of alloys

Introduction

In the first part of this article [*] it was shown that a very satisfactory description of the energy effects encountered in the alloying of transition metals can be obtained from a model in which the basic starting point is the idea that the metal atoms in an alloy remain very similar to those in the pure metals. The heat of formation of the alloy arises because on one hand the chemical potential of electrons must become equal for both kinds of atomic cells, while on the other hand the discontinuity in the electron density (in electrons per cm³) that appears at the boundary of dissimilar atoms has to be smoothed out. This gives:

$$\Delta H = f(c) \left[- Pe(\Delta \Phi^*)^2 + Q(\Delta n_{WS})^2 \right]. \quad (1)$$

Here ΔH is the formation enthalpy of the alloy, $f(c)$ is a symmetrical function of the concentration of one of the metals and $\Delta \Phi^*$ and Δn_{WS} represent the discontinuity in electronegativity Φ^* and electron density n_{WS} at the boundary between dissimilar atomic cells; e is the electronic charge and P and Q are constants. Equation (1) describes the alloying behaviour of transition metals with one another and of transition metals with Cu, Ag, Au, Li, Ca and Sr. If transition metals are alloyed with trivalent or polyvalent non-transition metals, an extra negative contribution to the heat of formation appears, which is independent of which particular transition metal is alloyed with which particular p electron metal from the group Al, Ga, In, Tl, Sn, Pb, Sb and Bi:

$$\Delta H = f(c) \left[- Pe(\Delta \Phi^*)^2 + Q(\Delta n_{WS})^2 - R \right]. \quad (2)$$

The validity of this equation was demonstrated in Part I, and it was explained there how the parameters Φ^* and n_{WS} can be obtained. Values for the ratios Q/P and R/P of the constants in various cases can also be obtained from the analysis of the sign of the heat of formation.

In this second part we shall first be concerned with the absolute values of ΔH, that is to say we determine $f(c)$ and the value of P, quantities that can be used to

calculate the heat of formation for any alloy of a transition metal. This is followed by a discussion of the heat of mixing of liquid metals, from which it can be concluded that equation (1) is also valid for (liquid) alloys of two *non*-transition metals.

Finally, the significance of charge transfer for the physical properties of alloys is examined. In the case of the heat of formation it was essential that the chemical potential of the electrons was made the same for the different atomic cells in an alloy. The transport properties, which are largely determined by the contribution of the d electrons to the conduction band, are strongly affected by this transfer of charge, particularly in the transition metals. In the present context these properties are of interest both in themselves, and also because they provide the information from which the quantitative relation between difference in electronegativity and charge transfer can be derived.

Absolute values of ΔH

In equations (1) and (2) another unknown apart from the constants P, Q and R is the dependence of ΔH on the concentration c. In addition, although values for Q/P and R/P were found in Part I, no value was found for P.

Let us start with $f(c)$. For solid solutions the function would be expected to be $f(c) = c(1 - c)$ if c is the concentration of one of the two metals, and size mismatch, Brillouin-zone effects and short-range order do not come into play. In ordered compounds no difference from statistical solid solutions would be expected provided that the concentration of one of the metals was small (again assuming that elastic energies associated with a difference in atomic size are relatively small; this is in fact almost always so if $|\Delta H|$ is fairly large — i.e. if $\Delta \Phi^*$ is large). This means that the heat of formation of ordered alloys in *fig. 14* should lie between curve *1*, which is the parabola $c(1 - c)$ for solid solutions, and the curves *2*, the tangents to the parabola at $c = 0$ and $c = 1$. An impression of the shape of $f(c)$ can be obtained by comparing the heat of ordering with the total heat of formation for say 50/50 alloys possessing an

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ordering temperature. These results suggest that on average the heat of ordering contributes about 30% of the total negative heat of formation.

It is also possible to estimate $f(c)$ from experimental values of ΔH, provided that for a particular system there are a large number of ordered structures for which ΔH has been measured. These results have been plotted in fig. 14 for Ni-Al, Co-Al, Cd-Mg, Cu-Zn and the Pd-Al system, all systems whose measured ΔH values lie fairly symmetrically about the vertical $c = 0.5$. The results have been normalized with respect to the parabola $c(1 - c)$ by ensuring that at low concentrations the correct derivative is obtained. Close to the concentration 0.5 the difference between the solid curve and the parabola is about 30% of $f(c)$; this agrees with the values for the relative magnitudes of the ordering energies.

In principle it is now possible to determine the parameter P by comparing experimental values for the heat of formation of alloys (and not just the sign) with equation (1) or (2), since the ratios Q/P and R/P have already been found. Little experimental information is available about the absolute value of ΔH for cases in which $\Delta \Phi^*$ or Δn_{WS}, and hence ΔH, are large. *Fig. 15* shows all the ΔH values that clearly differ from zero and are related to the groups discussed earlier (two transition metals, transition metals with p metals and hydrides). To find P, ΔH is plotted against the quantity $f(c)\,[-e(\Delta \Phi^*)^2 + (Q/P)\,(\Delta n_{WS})^2 - R/P]$, making use of the values found earlier for Q/P and R/P; R is of course put equal to zero for the hydrides and alloys of two transition metals. The amount of data available is too small to be able to determine whether P has a different value for the three groups of alloys. When all the results are taken together the mean straight line corresponds to $P = 0.85 \text{ V}^{-1}$. A detailed table has been shown elsewhere [9] in which the ΔH values calculated with this value of P for all the alloys quoted have been compared with experiment.

Alloys of two non-transition metals. Liquid metals

To what extent do the model, and with it equation (1), also describe the alloying behaviour of non-transition metals? It is known that for example in the compounds or elements with the diamond-type structure (GaSb, InAs, Si, Ge) a large contribution to the energy originates from Brillouin-zone effects. The presence of eight valence electrons per unit cell makes these 'metals' semiconductors. The relatively large energy gap at the Fermi surface causes a fairly large decrease in energy. An impression of the magnitude of this energy contribution can be obtained from the latent heat of fusion, which is considerably larger for the four semiconduc-
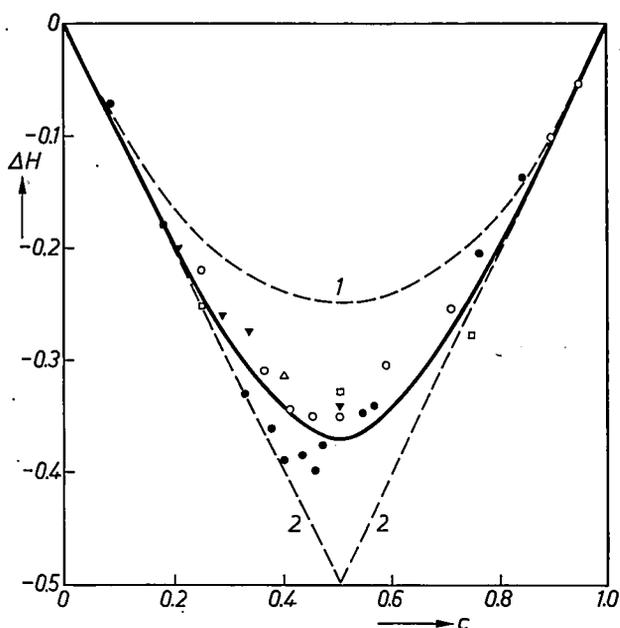

Fig. 14. The heat of formation ΔH of an ordered alloy (or compound) of two metals as a function of the atomic concentration c. Curve *1* represents the parabola that would be expected for solutions in which the metal atoms are statistically distributed over the lattice sites. The curves *2* give a lower limit for the factor $f(c)$ of equation (1) in ordered alloys. O Ni-Al, □ Cd-Mg. ▼ Co-Al, △ Cu-Zn, ● Pd-Al. The data have been taken from the publications of notes [16] and [17].
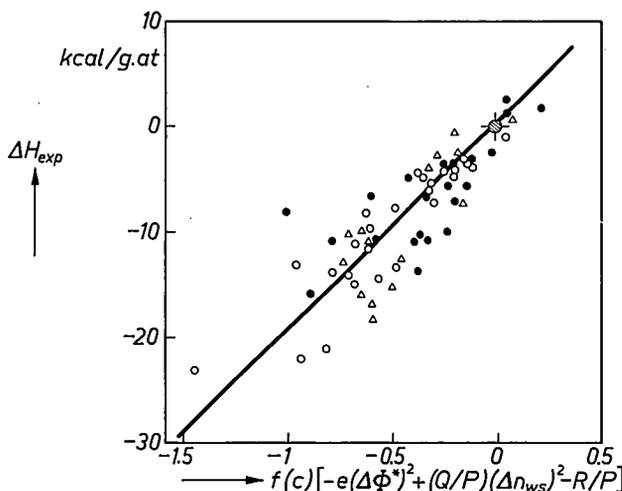

Fig. 15. Determination of the parameter P in the ionic energy contribution $-Pe(\Delta\Phi^*)^2$. The value of P can be derived from the slope of the straight line through the origin giving the best fit to the plotted points. ● Alloys of two transition metals. O Alloys of transition metals with non-transition metals of valency greater than 2. △ Hydrides of transition metals.

[*] A. R. Miedema, A simple model for alloys, I. Rules for the alloying behaviour of transition metals, Philips tech. Rev. 33, 149-160, 1973 (No. 6).

[16] R. Hultgren, R. L. Orr, P. D. Anderson and K. K. Kelley, Selected values of thermodynamic properties of metals and alloys, Wiley, New York 1963.

[17] M. Ettenberg, K. L. Komarek and E. Miller, Metallurg. Trans. 2, 1173, 1971.

tors mentioned above than for ordinary metals, whose latent heats of fusion are usually all very similar. The contribution of Brillouin effects to the heat of formation can be estimated from the unusually large latent heat of fusion. It is clear that this contribution only becomes comparable in magnitude with the terms of equation (1) for crystals with the ZnS or NaCl structure.

In liquid alloys there should in principle be no Brillouin-zone effects. The equation

$$\Delta H = c(1 - c) \left[-Pe(\Delta \Phi^*)^2 + Q(\Delta n_{\mathrm{WS}})^2 \right] \quad (1')$$

would therefore be expected to apply for two non-transition metals.

In the first article of note [9], which presented an analysis of liquid metals with $\Phi^* = \Phi$, this relation has already been fairly clearly established. It is interesting to note that (1') is very similar to the equation used by N. F. Mott to predict (to an accuracy of 80%) whether two liquid metals were miscible. Mott used the electronegativity X, which we know to be approximately proportional to Φ^*, and a positive term proportional to $[\Delta(E_v/V_m)^{\frac{1}{2}}]^2$, where E_v is the latent heat of evaporation of a metal. The parameter n_{WS} used here represents $[\Delta(KV_m)^{-\frac{1}{2}}]$, and since the compressibility K is approximately inversely proportional to the latent heat of evaporation this means that Mott's equation is almost identical with equation (1'). Comparing the absolute values found with the two equations shows that for liquid metals Q is relatively a little higher than we found for the solid transition metals. The conclusion is that the difference in electronegativity and in electron density are also responsible for the greater part of the heat of mixing in non-transition metals. The size mismatch between the atoms of an alloy also contributes to some extent to the positive terms in ΔH (which can lead to decomposition in the liquid phase), but this contribution is considerably smaller than has recently been suggested by B. Predel and H. Sandig [18]. It is perhaps fairly obvious that energy effects depending on a difference in atomic size could be confused, for disordered solid and liquid alloys, with effects due to difference in density. Metals that differ considerably in electron density at the boundary of the atom will in general also differ considerably in atomic radius.

Magnetic properties and charge transfer

In the model presented here it is of essential importance that the negative term in the heat of formation of alloys is concerned with the transfer of electrons, and hence with ionicity. How large is the charge transfer in a particular case, expressed for example in numbers of electronic charges per atom? It is also interesting to

consider to what extent charge transfer affects other properties of alloys besides the heat of formation.

In our model, in which the negative part of ΔH is determined by f(c) and $\Delta \Phi^*$, the charge transfer per atom will also be a function of only c and $\Delta \Phi^*$. If Φ^* does indeed represent the value of the chemical potential for electrons in the correct units, then the ionic contribution contained in ΔH is equal on one hand to $-P$ f(c) $(\Delta \Phi^*)^2$, but we also have:

$$\Delta H = -c_A e \, \Delta Z_A \, \Delta \Phi^*/2. \quad (3)$$

The quantities c_A and ΔZ_A represent the concentration of metal A and the charge per atom A in the alloy. The equation states in fact that the total charge displaced, $c_A e \Delta Z_A$, is on average transferred over the half potential difference, $\Delta \Phi^*/2$. (During the transfer of charge this potential difference is gradually reduced from $\Delta \Phi^*$ to zero; the average potential difference was $\Delta \Phi^*/2$.) From the above it follows that

$$\Delta Z_A = 2 \, \Delta \Phi^* \, \mathrm{f}(c) \, P'/c_A. \quad (4)$$

We now distinguish between P' and P, since it is not certain that the Φ^* scale does in fact give the chemical potential in the correct units. We do know that our scale is a good relative measure of the chemical potential, but in the procedure selected it is by definition normalized to the scale of the work function Φ. If however there is a proportionality constant relating Φ and Φ^*, then it will also apply to the quantities P and P'.

For solid solutions f(c) is equal to $c_A(1 - c_A)$, and (4) therefore becomes:

$$\Delta Z_A = 2 \, \Delta \Phi^* (1 - c_A) P'. \quad (5)$$

The value of P' can be derived from experiments in which ΔZ_A manifests itself in some other way than a reduction of energy. An example for the transition metals is given by the *magnetic* properties.

In fig. 7 (Part I) the three groups of the 3d, 4d and 5d transition metals were quoted together, with the appropriate values of Φ^*. The partially filled d shell indicates that for these metals the d levels make a considerable contribution to the density of states at the Fermi surface. This is associated with a relatively large contribution to the linear term in the specific heat of metals and a large contribution to the temperature-independent (Pauli paramagnetic) susceptibility (for 4d, 5d and some 3d metals) or the ferromagnetic behaviour (for other 3d metals).

The charge-transfer effect can have a considerable effect on the magnetic behaviour of alloys. In the alloy Pd$_3$Y — formed from the last and the first transition metal of the 4d series — the difference in Φ^* is very large. The Y gives up electrons, the Pd receives electrons. The effect is as if Y displaces itself to the left in

the periodic system, thus losing its transition-metal character. The Pd displaces itself to the right, the d levels become completely filled and Pd becomes diamagnetic, like Ag. As a result the alloy Pd_3Zr does not have the properties of a transition metal (the high susceptibility). This change in properties when the number of d electrons becomes very small or is increased to ten allows an estimate of charge transfer to be made. The magnetic susceptibility of solutions of Zr in Pd decreases sharply with increasing Zr concentration and appears to go to a 'diamagnetic' value for 12.5 at. % Zr (the compounds Pd_4Zr and Pd_3Zr are also diamagnetic). From equation (5), and assuming that pure Pd metal has a number of 0.35 holes in its d level then it follows from the diamagnetic nature of $Pd_{87.5}Zr_{12.5}$ that $P' = 0.55$ V^{-1}. Comparable values for P' also follow from the magnetic properties of alloys of Co and Ni with the transition metals of the first two columns, if again it is assumed that the absence of ferromagnetism in intermetallic compounds of Co and Ni at $T = 0$ indicates an almost completely filled d level. On average we find that $P' \simeq 0.6$ V^{-1} (see note [9]).

Charge transfer can also be estimated from experiments on X-ray fluorescence (A. Wenger et al. [19]). Wenger obtained a value for the change in the number of d electrons at the Fe and Co sites in compounds with Al. The value of P' in this case is again in the region of 0.6 V^{-1}.

Note that the value found for P' corresponds to a relatively large charge transfer. In a disordered AB compound with $\Delta\Phi^* = 1$ V equation (5) shows that the charge is given by $A^{-0.6}B^{+0.6}$; here it should not be forgotten that on one hand still greater values of $\Delta\Phi^*$ can be found in practice, while on the other hand ΔZ is larger by a factor of 1.5 in ordered AB alloys (i.e. compounds).

The value found in this subsection for P' (0.6 V^{-1}) differs from the value found for P (0.85 V^{-1}) when the calculation is based on energy data alone. As was noted earlier, this does not necessarily mean that the model is 'wrong', but it can be taken as an indication that the scale of Φ^* ought really to be stretched by a factor of 1.4 to enable the internal chemical potential to be expressed in the correct units. On further consideration this result suggests that a proportionality exists between the work function Φ of a metal, the discontinuity D in potential that is present because there is an electric-dipole layer at the surface of a metal, and the chemical potential Φ^*, which relates to the interior of a metal. The difference between P and P' suggests that

$$\Phi : D : \Phi^* = 1 : 0.4 : 1.4$$

could be a general relation for all metallic elements.

Ionicity and the physical properties of alloys

In the previous section the initial assumption in seeking quantitative data for the relation between the charge transfer per atom and the difference in electronegativity was that it was possible to derive information about the ionicity not only from the energy effects but also from the magnetic properties of alloys, for example. In fact, a basic assumption is involved here. In the model, as it was used in considering heats of formation, it was assumed that the distribution of charge (electrons) in the crystal lattice of an alloy could be found by first taking the charge distribution for the two kinds of pure metal and then applying an important correction (making Φ^* equal) to this distribution. In the description of magnetic properties we have gone much further. Here it has been assumed, for example in the case of the Pd-Zr alloys, that in the resulting distribution obtained for the alloy the original metals would still be clearly distinguishable. To give a picture of the situation it is assumed that the electron states (wave functions) of the alloy can be represented to a good approximation as a combination of Pd-like states and Zr-like states. In the alloy, in this explanation of the diamagnetic nature of $Pd_{87.5}Zr_{12.5}$, Pd has obtained a completely filled d level while that of Zr has become completely empty, so that the resulting metal has lost its transition-metal nature.

It is by no means obvious that electron states in an alloy can be obtained by adding metal A-like states and metal B-like states together, although this picture has been fairly widely used in descriptions of magnetic properties of Pd, Ni or Co alloys. No theoretical justification for this has been given; a possible qualitative explanation could be that the 'overlapping' of electron states of neighbouring atoms is relatively small in a lattice of transition-metal atoms, i.e. n_{WS} is small compared with the average density of d electrons in het atomic cell. A metal can be thought of as being made up from a number of free atoms that are first located a long way apart and then gradually approach one another. In this picture transition metals are metals in which the original free atoms have not yet come very close together. The 'overlap' still remains small; on this basis it might be expected that the properties of free atoms (and in alloys those of the *differing* atoms) could be recognized in the metal. In non-transition metals, on the other hand, n_{WS} is not small compared with the average d electron density and the atomic nature is lost.

In spite of the doubt, for theoretical reasons, about an atomic description of the physical properties of

[18] B. Predel and H. Sandig, Z. Metallk. **60**, 208, 1969.
[19] A. Wenger, G. Bürri and S. Steinemann, Solid State Comm. **9**, 1125, 1971.

alloys of transition metals, this kind of description has been found to give surprisingly good results in practice. For example, it has been found possible to give a simple formula for the specific heat at low temperature γ — which is a measure of the density of electron states at the Fermi surface — for solid solutions of transition metals. It is assumed in the first place that γ is atomic in nature for transition metals: γ is mainly determined by Z, the number of valence electrons per atom. For an alloy of two metals A and B it is assumed in the second place that

$$\gamma_{all} = c_A \gamma_A + c_B \gamma_B. \tag{7}$$

Here γ_A is the γ value for the A atoms in the alloy, and γ_B is the γ value for the B atoms; γ_A and γ_B depend on the number of valence electrons possessed by A and B in the alloy. This number is found for each type from the number Z_0 that applies for the pure metal, and the electron transfer ΔZ in the alloy:

$$Z = Z_0 + \Delta Z. \tag{8}$$

For Ti, Zr and Hf Z_0 is equal to 4, for V, Nb and Ta Z_0 is equal to 5, for Cr, Mo and W Z_0 is equal to 6, etc. (fig. 7, Part I). The value of ΔZ follows from equation (5) with $P' = 0.6 \, V^{-1}$. Before we can use the formula, we still need to know the relation between γ and Z. This is given in *fig. 16*. The curve goes through the points for the pure elements, and is drawn in such a way that all the known data for paramagnetic transition metals are well reproduced. *Fig. 17* shows that with the simple formula a good agreement is obtained between calculated and measured values for a large number of alloys.

A similar atomic description also serves for the transition temperature for superconductivity in solid solutions of two transition metals. The assumption that electron states of metal A and of metal B can be added together corresponds to the addition of $[\ln(T_c/\Theta_D)]^{-1}$ for those metals in the theory of superconductivity. The transition temperature T_c is measured with respect to the Debye temperature (Θ_D) for the lattice vibrations. Equation (7) now becomes:

$$\left[\ln(T_c/\Theta_D)\right]_{all}^{-1} = c_A \left[\ln(T_c/\Theta_D)\right]_A^{-1} + c_B \left[\ln(T_c/\Theta_D)\right]_B^{-1}. \tag{9}$$

The characteristic function that represents the dependence of T_c/Θ_D on Z is shown in *fig. 18*, in which T_c/Θ_D is plotted to give a linear curve for $\ln(T_c/\Theta_D)^{-1}$. Although equation (9) is slightly more difficult to use than equation (7), the 'recipe' for finding the T_c of alloys of transition metals is really quite simple. The results obtained on comparing the calculated and measured values are again surprisingly good [9]. A
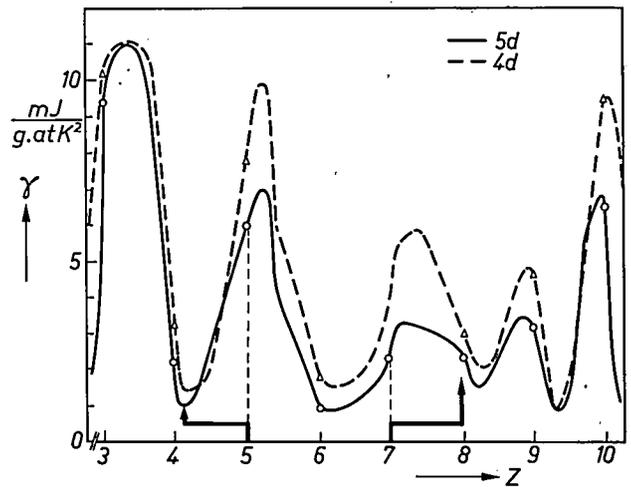

Fig. 16. The coefficient γ of the linear term in the specific heat of metals, plotted against the number of valence electrons per atom Z for the 4d and 5d metals. To give an example of the way in which equation (7) is applied the figure shows the Z values for Ta and Re in an alloy $Ta_{50}Re_{50}$ that does not in fact exist as a solid solution. The value Z_0 of Z for the metals in the pure state is 5 for Ta and 7 for Re.

simple demonstration of the applicability of the atomic curve for T_c/Θ_D as a function of Z shown in fig. 18 can be found in the change in T_c of Nb in alloys with small quantities of a second metal. As fig. 18 shows, pure Nb, for which $Z_0 = 5$, lies at a point of the curve at which the derivative of T_c/Θ_D with respect to Z has a high value. If a metal is dissolved in Nb, then it is relatively unimportant that the second metal gives a characteristic contribution to $[\ln(T_c/\Theta_D)]^{-1}$ different from that
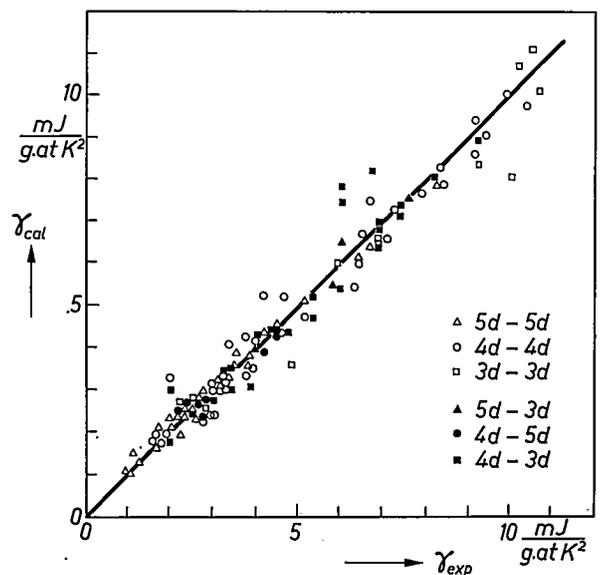

Fig. 17. Comparison of experimental data on γ for solid solutions of two transition metals with the values γ_{cal}, calculated from equation (7). The points lie close to a straight line of slope 1. The figure shows which types of alloy the various kinds of points in the figure refer to.
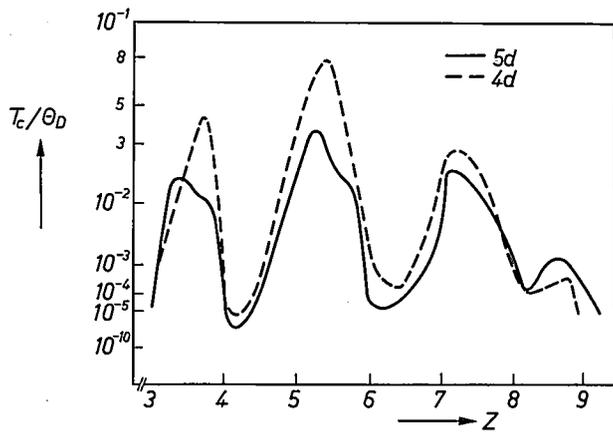
Fig. 18. The ratio T_c/Θ_D of the temperature at which a transition metal becomes superconducting and its Debye temperature, plotted against Z, the number of valence electrons per atom. The solid curves apply for 5d metals, and the other curves for 4d metals.

given by pure Nb. However, it is important that the dissolved metal can change the Z of the Nb. If the dissolved metal takes up electrons from the Nb (if it is more strongly electronegative than Nb, higher Φ^*) then T_c/Θ_D will decrease; if the dissolved metal gives up electrons, then T_c will be able to increase because of the high value of the derivative of T_c/Θ_D with respect to Z at the location of Nb on the curve. In this argument it would be expected that the change in T_c for niobium on the solution of small concentrations of a second metal would chiefly be determined by $\Delta\Phi^*$ between Nb and this metal. The truth of this prediction is shown in
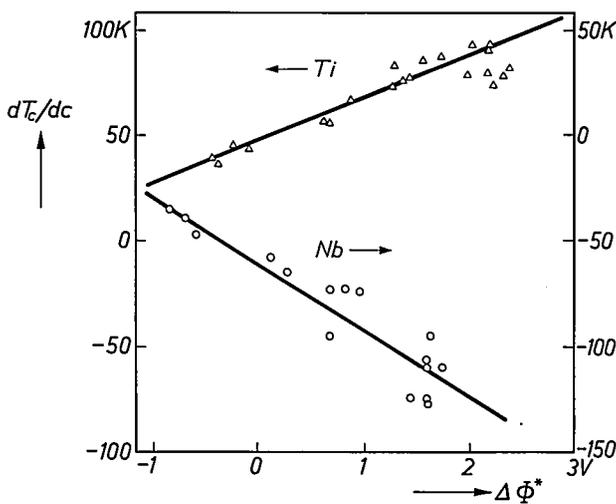
fig. 19, in which dT_c/dc, the change in T_c with the concentration of metal added, is plotted against $\Delta\Phi^*$. The metals with the higher values of Φ^* reduce T_c very noticeably; the relation between dT_c/dc and $\Delta\Phi^*$ can be approximated quite well by a straight line. Fig. 19 also shows the change in T_c for Ti in alloys, plotted against $\Delta\Phi^*$ for the dissolved element. The slope of the curve of T_c/Θ_D as a function of Z is also relatively large for Ti ($Z_0 = 4$), but the sign is different.

As was noted at the beginning of this section, there is no obvious reason for using an atomic description for alloys of non-transition metals; we can only say that it does appear to describe energy effects. It is consequently more difficult to justify the use of Wigner-Seitz cells for these alloys. A definition that appears reasonable for the boundary between neighbouring atomic cells in a transition metal is the minimum in the electron density as a function of location. This is no longer possible in non-transition metals, and it will be obvious that it is difficult to speak of the transfer of electrons while it is not in fact possible to define the location of the boundary between atoms A and atoms B. It is also much less obvious which physical properties will be affected by the transfer of charge. Whether $Na^{+0.5}K^{-0.5}$ or $Na^{-0.5}K^{+0.5}$ is written as the formula for an Na-K alloy does not affect the metallic properties at all. Similarly, it makes no obvious difference to the semiconductor properties of GaSb whether we are dealing with Ga^+Sb^-, GaSb or Ga^-Sb^+. However, the existence of charge transfer can be observed indirectly in the change in total volume on the alloying of two non-transition metals, from the appearance of electric-field gradients (which can for example be studied at the locations of atomic nuclei in nuclear-resonance experiments), or from measurements of the isomer shift in Mössbauer-effect experiments. Let us consider Ag and Au in such an alloy of two non-transition metals. The two metals both have the f.c.c. structure and very nearly the same atomic volume. Nevertheless, a fairly large isomer shift is found in Mössbauer experiments on Ag-Au alloys. This shift is a direct measure of the probability of s electrons arriving at the location of the nucleus of Au. While it is true that it is not (yet) possible to convert a change in isomer shift into a transfer of charge, it is indeed possible to see that the ionicity does have consequences for the physical properties, and not only for the transition metals.

To summarize quickly the results of the second part of this article, we see that in alloys of two transition metals the negative contribution to the heat of formation is almost entirely determined by the difference in electronegativity $\Delta\Phi^*$. Difference in electronegativity

Fig. 19. The derivative of the transition temperature for superconduction T_c with respect to the concentration c, plotted against the difference in electronegativity $\Delta\Phi^*$ for diluted Nb [11] and Ti alloys [20]. (The Ti alloys had 5% of Rh added to stabilize the b.c.c. structure.) For each of these alloys the points lie very nearly on a straight line; the line for the Ti alloys rises for increasing $\Delta\Phi^*$, the other one falls.

[20] Ch. J. Raub, Z. Physik 178, 216, 1964.

signifies transfer of charge. This is large: ΔZ is proportional to $\Delta\Phi^*$, and for solid solutions the proportionality constant is given by $1.2\,(1-c)$. Physical properties of transition metals can be particularly sensitive to electron transfer, as has been shown in this article for the contribution of the electrons to the specific heat and the transition temperature T_c for superconduction.

Summary. This part of the article first treats the influence of the concentration on the heat of formation of alloys and the value of the coefficient of the electronegativity contribution, from which the absolute value of the heat of formation can be calculated. It is found that the relation derived in I for the heat of formation of alloys of two transition metals is also valid for liquid alloys of two non-transition metals. Difference in electronegativity signifies transfer of charge, to which the physical properties of transition metals can be very sensitive; this is demonstrated for the electron contribution to the specific heat and for the temperature at which the alloy becomes superconducting.