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ENTHALPIES OF FORMATION OF SOLID NICKEL–GALLIUM AND NICKEL–GERMANIUM ALLOYS

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ABSTRACT

Tin solution calorimetry has been used to measure the enthalpies of formation of the solid phases of the nickel–gallium system at 300 K and of the nickel–germanium system at 330 K. Values are reported for the two nickel-rich binary solid solutions and for the intermediate phases Ni_3Ga, Ni_2Ga, Ni_3Ga_2, NiGa, Ni_2Ga_3, Ni_3Ga_7, Ni_3Ge, Ni_2Ge and NiGe. These and previously determined enthalpies of formation of related palladium alloy compounds are compared and factors affecting the bonding mechanisms are discussed; a dependence of intercomponent transfer upon electron concentration and electronegativity differences is suggested by a re-examination of the intermediate phase data.

INTRODUCTION

Systematic studies of alloys of Pd with B-sub-group elements[1–4] have begun to provide understanding of the major factors influencing the enthalpies and entropies of formation of the solid solutions and intermediate phases of such transition-metal systems. While similar effects are likely in equivalent Ni-based alloys, significant differences may be expected between the thermodynamic properties of the First and Second Long Period systems. Thermodynamic data for alloys of Ni with B-sub-group elements are sparse. Previous investigations of complete systems are mostly e.m.f. or vapour pressure studies and provide reliable data only for free energies of formation[5–8]. Calorimetric studies have been made throughout the continuous Ni–Cu solid-solutions[5], but otherwise such measurements on Ni-alloys are mainly confined to limited studies of particular compounds[5,9,10]. Since enthalpies of formation provide valuable indications of bonding character, the establishment of good calorimetrically-measured values for these continues to be of interest. The present studies of the binary alloys of Ni with the Group III and IV elements, Ga and Ge, were undertaken to provide particular comparison with the previously examined Pd–In[3] and Pd–Sn[1] systems.

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EXPERIMENTAL

Enthalpies of formation have been measured by tin-solution calorimetry, using an isoperibol calorimeter and operating procedures which have been described in earlier publications[1,3,11]. In the present case, tin-bath temperatures of approximately 770 K (Ni–Ga alloys) and 840 K (Ni–Ge alloys) provide optimum experimental conditions and samples were dropped from initial reference temperatures of 300 K (Ni–Ga alloys) and 360 K (Ni–Ge alloys). Alloys were prepared from 99.999% pure elements by H. F. melting under argon in sealed silica capsules and annealed, again sealed under argon, until equilibrium structures were obtained. Ni–Ga alloys containing 0–60 at. % Ga were annealed at 1000°C, to provide maximum ranges of the α- and β-phases, and at 650°C to yield samples containing the intermediate compounds Ni_2Ga, Ni_3Ga_2 and Ni_2Ga_3. Alloys containing 70% or more of Ga were aged at room temperature for 2 months to obtain structures containing Ni_3Ga_7. In the case of Ni–Ge alloys, annealing temperatures of 920–950°C were employed with Ni-rich (0–35 at. % Ge) and 750°C for those of higher Ge content. All samples were water-quenched from the annealing temperatures to retain the high temperature phase equilibria. Checks on composition were maintained by weighing and by chemical analysis and phase equilibria were confirmed by metallographic and X-ray examination. The specimens for solution calorimetry were prepared by filing or, in the case of Ge-rich alloys, by crushing and the resulting powders were enclosed in small thin-walled capsules of pure tin to provide suitable samples for introduction into the calorimeter via the dispensers. The calorimeter was calibrated at frequent intervals, by the drop technique, using pure tin samples; heat content values for this element, for calibration and for the calculation of the capsule corrections, were taken from Hultgren's[12] assessed data.

RESULTS

Heats of solution of elements

In preparation for the alloy studies the heats of solution of Ni, Ga and Ge in liquid tin were first measured. For the purpose of comparison with other measurements of these quantities, the present results for these elements are here reported as isothermal heats of solution at the tin-bath temperatures. The changes of heat content between initial and solution temperatures were calculated using Hultgren's[12] data for the elements.

Nickel. Heats of solution of Ni were measured at the two bath temperatures of 773 and 832 K used for the Ni–Ga and Ni–Ge alloy studies, respectively. The mean values obtained were:

773 K $\Delta\bar{H}_{Ni} = -10.21$ kcal* g-at.$^{-1}$
(standard deviation 140 cal g-at.$^{-1}$ on 8 experiments)

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*Note: throughout this paper 1 cal = 4.184 J.

and 832 K $\Delta\bar{H}_{Ni} = -10.72$ kcal g-at.$^{-1}$
(standard deviation 250 cal g-at.$^{-1}$ on 6 experiments)

The values obtained are in very satisfactory agreement with other studies at similar temperatures (−11.85 kcal g-at.$^{-1}$, 743 K[13]; −10.47 kcal g-at.$^{-1}$, 741 K[14]) but no significance is attached to the temperature dependence which appears to be contrary to the general trend suggested if all previous studies are examined.

Gallium. The heat of solution of Ga in tin was measured at 778 K. The average value obtained at this temperature and expressed relative to pure liquid gallium is:

778 K $\Delta\bar{H}_{Ga} = +720$ cal g-at.$^{-1}$
(standard deviation 50 cal g-at.$^{-1}$ on 10 experiments)

This value is also in satisfactory agreement with previous measurements[15,16] for this element of which the heat of solution in tin varies very little with temperature.

Germanium. Present measurements of the heat of solution of Ge in liquid tin were made at 836 K and the average value obtained was:

836 K $\Delta\bar{H}_{Ge} = +9370$ cal g-at.$^{-1}$
(standard deviation 230 cal g-at.$^{-1}$ on 7 experiments)

This value interpolates excellently between values reported at higher and lower solution temperatures[17].

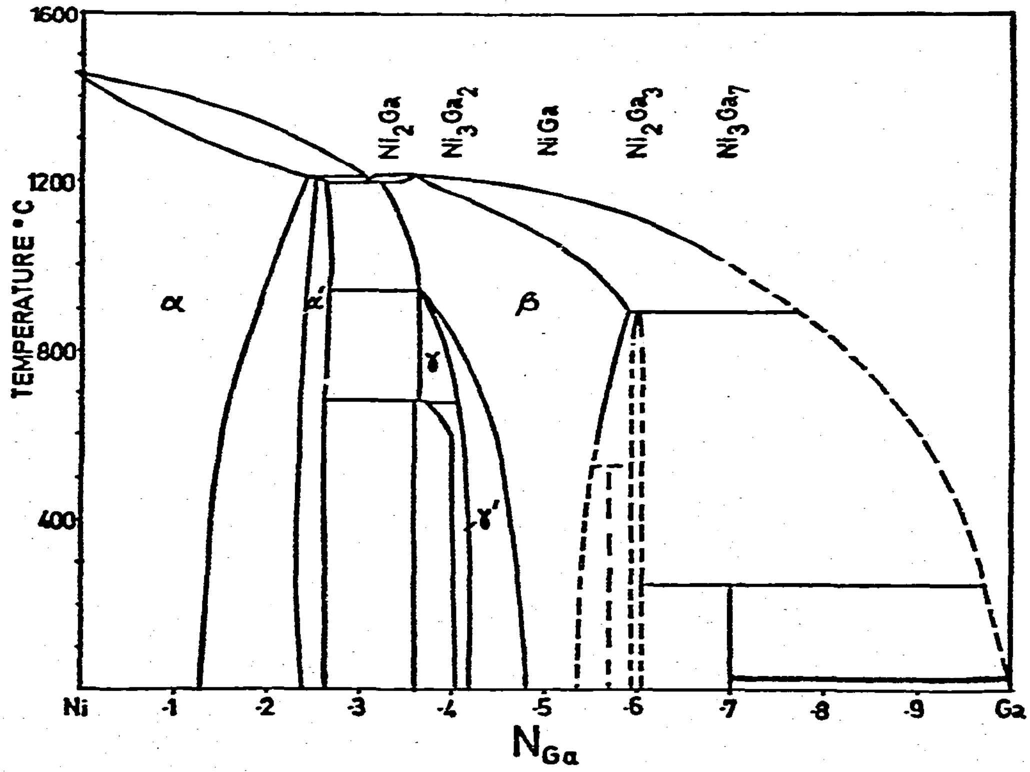

Fig. 1. The Ni–Ga equilibrium diagram.

Heats of formation of nickel–gallium alloys

The Ni–Ga phase diagram, based mainly on that of Hellner[18] but modified in the light of investigations by Schubert[19], is shown in Fig. 1. From the present calorimetric study, extending over the complete composition range, enthalpies of formation have been obtained for the f.c.c. α-solid-solutions and for the intermediate phases Ni_3Ga, Ni_2Ga, Ni_3Ga_2, NiGa, Ni_2Ga_3 and Ni_3Ga_7. The experimental integral heats of formation at 300 K, referred to the pure solids as the standard states, are assembled in Table 1. The data are also presented in Fig. 2, to show the values corresponding to the sequence of phases existing at the higher annealing temperature (1273 K), and in Fig. 3 where, except for the inclusion of Ni_3Ga_7, they are plotted in a manner consistent with the reported phases boundaries at the lower annealing temperature (923 K).

The heat of formation of the compound "Ni_2Ga" (36 at. % Ga) has been obtained by extrapolation from the data for the limiting α′ (27 at. % Ga) and two phase α′+Ni_2Ga (31 at. % Ga) alloys. The results for the 55 at. % Ga alloy (Fig. 3) are anomalous and incompatible with the high-temperature equilibrium; the observations are, however, consistent with the separation during quenching of the low-temperature phase reported by Schubert[19] at 57 at. % Ga. Values for the b.c.c. "NiGa" phase are slightly less exothermic than those given by Jacobi[10], but the variation is believed to reflect the different reference temperatures (300 and 1023 K)

TABLE 1

HEATS OF FORMATION OF Ni–Ga ALLOYS AT 300 K

Reference states: Ni(s) and Ga(s).

N_{Ga}	ΔH ($cal\ g\text{-}at.^{-1}$)	σ	*Phase*
0.06	−1430	±130	α
0.11	−2400	±230	α
0.20	−4390	±180	α
0.25	−5610	±170	Ni_3Ga
0.27	−5920	±550	Ni_3Ga
0.31	−6370	±240	Ni_2Ga+Ni_3Ga
0.34	−6800[a]		Ni_2Ga
0.38	−7500	±190	Ni_3Ga_2
0.40	−8560	±180	Ni_3Ga_2
0.41	−9580	±200	Ni_3Ga_2
0.44	−9060	±350	NiGa
0.50	−9120	±170	NiGa
0.52	−8580	±130	NiGa
0.55	−10120	±300	[b]
0.60	−10760	±100	Ni_2Ga_3
0.70	−8060	±110	Ni_3Ga_7
0.80	−5300	±100	$Ga+Ni_3Ga_7$
0.90	−2760	±120	$Ga+Ni_3Ga_7$
0.95	−1400	±100	$Ga+Ni_3Ga_7$

[a] Interpolated. [b] Non-equilibrium alloy; possible precipitation of Ni_3Ga_4.

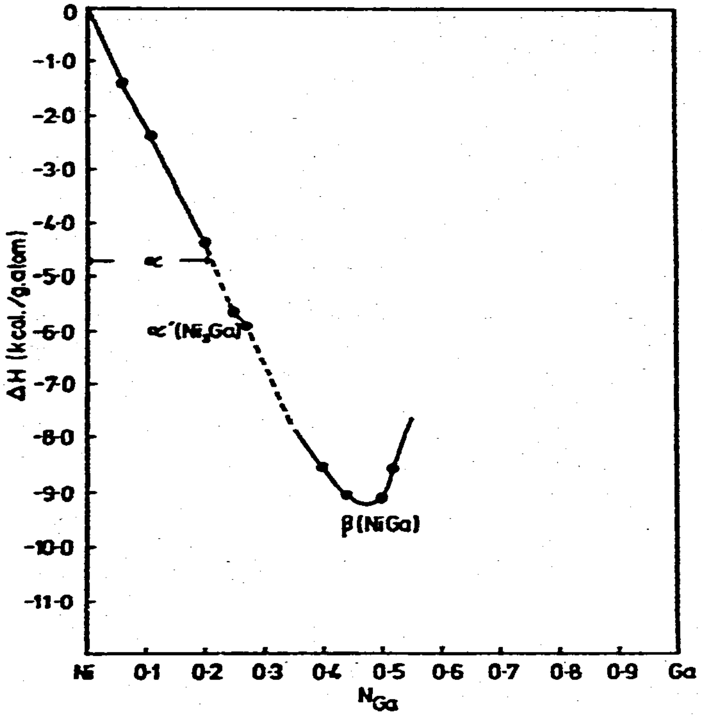

Fig. 2. Enthalpies of formation of Ni-Ga alloys at 300 K (1273 K anneal).

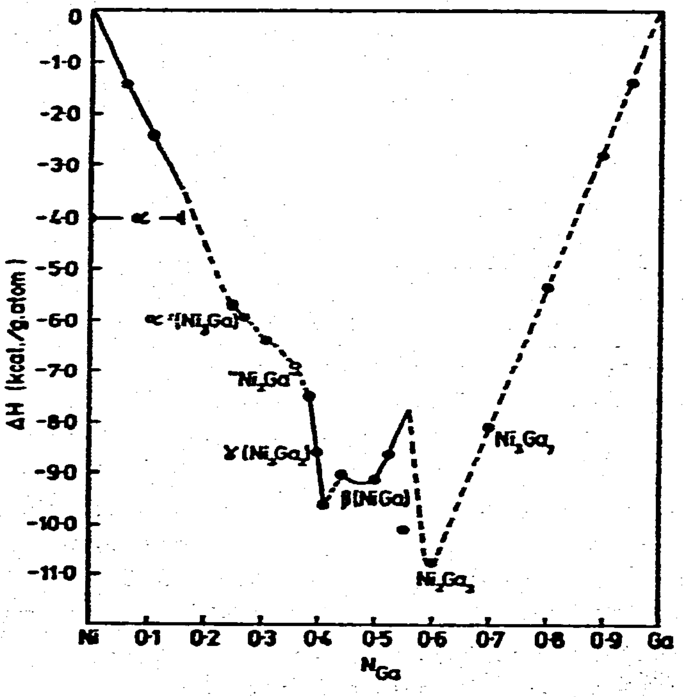

Fig. 3. Enthalpies of formation of Ni–Ga alloys at 300 K (923 K and room temperature anneals).

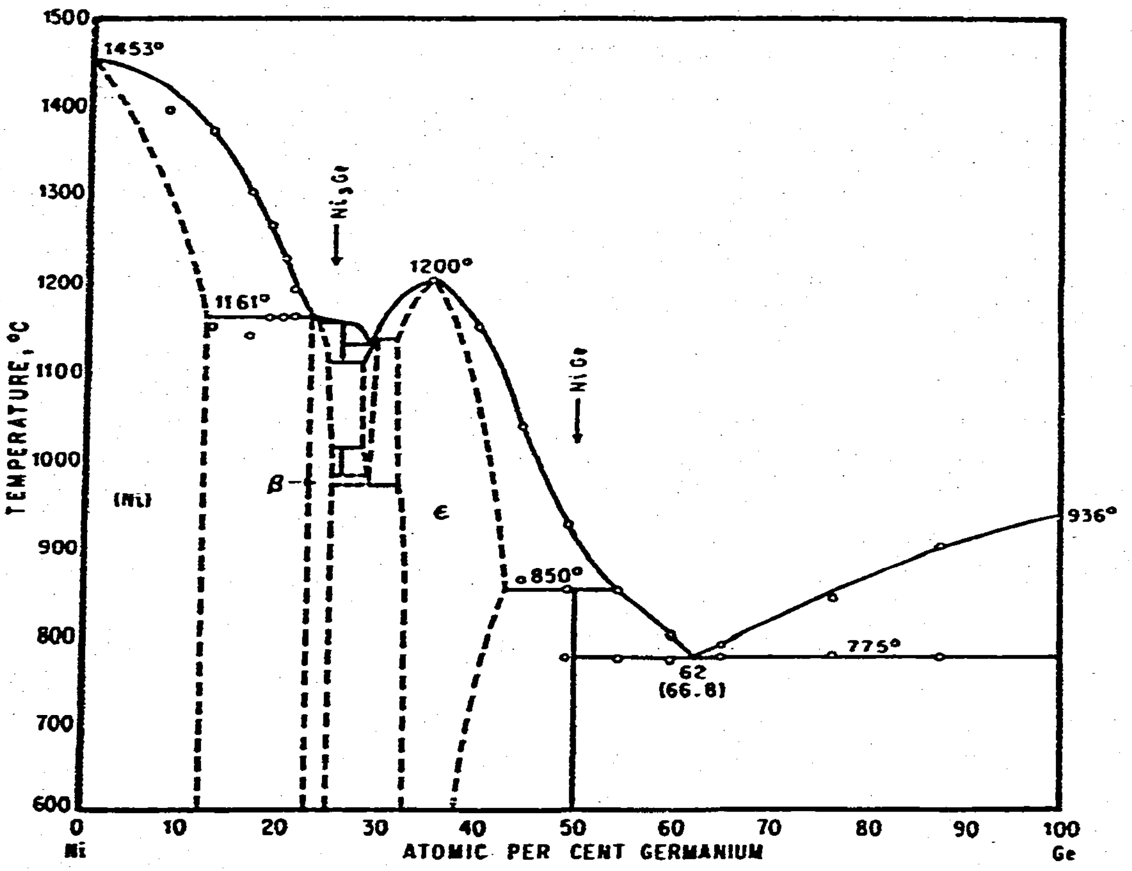

Fig. 4. The Ni–Ge equilibrium diagram.

TABLE 2

HEATS OF FORMATION OF Ni–Ge ALLOYS AT 330 K

Reference states: Ni(s) and Ge(s).

N_{Ge}	ΔH (cal g-at.$^{-1}$)	σ	*Phase*
0.06	−1970	±260	α
0.10	−3140	±270	α
0.20	−4620	±260	$\alpha+\beta$
0.24	−5930	±260	β
0.27	−6470	±400	$\beta+\varepsilon$
0.35	−7510	±360	ε
0.40	−7820	±210	NiGe+ε
0.45	−7660	±330	NiGe+ε
0.50	−7600	±350	NiGe
0.60	−6600	±460	Ge+NiGe
0.70	−3300	±200	Ge+NiGe
0.80	−3710	±270	Ge+NiGe
0.90	−920	±220	Ge+NiGe

and suggests negative deviations from Neumann–Kopp behaviour. A similar composition dependence of the heats of formation of the "NiGa" intermediate phase is indicated in both calorimetric studies.

Heats of formation of nickel–germanium alloys

The equilibrium diagram of the Ni–Ge system, according to Hansen and Anderko[20], is shown in Fig. 4. A series of 13 compositions have been examined in the present study in order to establish the heats of formation of the Ni-rich solid solutions and of the intermediate phases β(Ni_3Ge), ε(Ni_2Ge) and NiGe. The results obtained are presented in Table 2 and also shown diagramatically in Fig. 5, which has been constructed in a manner consistent with the tentative phase boundaries at 925 C (0–35 at. % Ge) and 750 C (35–100 at. % Ge) given in Fig. 4; all data are, however, referred to a uniform reference temperature of 330 K and to the pure solid elements as standard states. The results are generally very satisfactory, but variable solution behaviour gave persistently scattered data for the two-phase (NiGe+Ge) alloys. The value for NiGe itself is, however, well established by measurements on the single-phase alloys and the (NiGe+Ge) two-phase data line is therefore plotted by reference to this.

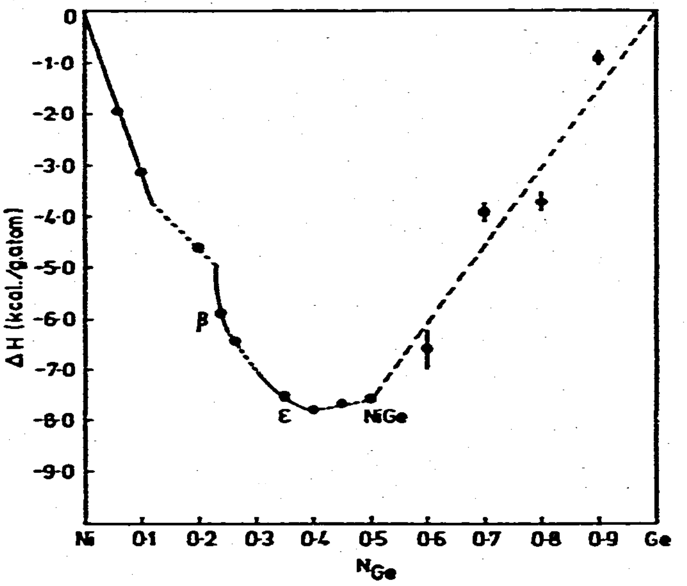

Fig. 5. Enthalpies of formation of Ni–Ge alloys at 330 K.

The only other known thermodynamic study of this system is a calorimetric measurement of the heat of formation of the phase Ni_2Ge by Predel and Ruge[9]. They have reported a value of 8770 (±440) cal g-at.$^{-1}$; this is slightly more exothermic than the present result, but allowing for experimental uncertainties, the two investigations are in satisfactory agreement.

DISCUSSION

The solid solutions

Although smaller in magnitude than those of the Pd-based examples[1–3], the present enthalpies of formation of the Ni–Ga and Ni–Ge α-solid solutions show exothermic characteristics similar to those typifying the later Period alloys. Examination of the data for the solutions of Ge, Ga and Zn[5] in Ni reveals a clear dependence on electron concentration akin to that shown by the solutions of Cd, In, Sn and Sb in Pd[2] and comparison with the magnetic properties of the Ni-based alloys[21] again suggests a correlation between the enthalpies of formation of the α-solid-solutions and the rate of filling of their *d*-electron levels. The close coincidence of the enthalpies of formation, viewed as a function of electron concentration, suggests that, as with the Pd-based solutions, a solute-induced modification of the 4*s*–3*d* electron distribution of the solvent Ni, rather than intercomponent transfer, is involved.

Intermediate phases

Intercomponent electron transfer has been invoked, however, as a predominant factor in stabilising intermediate phases of Pd–B-sub-group-element alloy systems[1,3]. This suggestion is based on the observation, demonstrated in Fig. 6, that their enthalpies of formation show a strong dependence on the number of electron-absorbing *d*-states present, i.e., on the likely degree of heteropolarity of the phase. Similar, but less uniform, behaviour is shown by the intermediate phases of the Ni–Ga and Ni–Ge systems, but an alternative examination of these, together with the Pd-phases, now gives some indication of probable variations in intercomponent transfer.

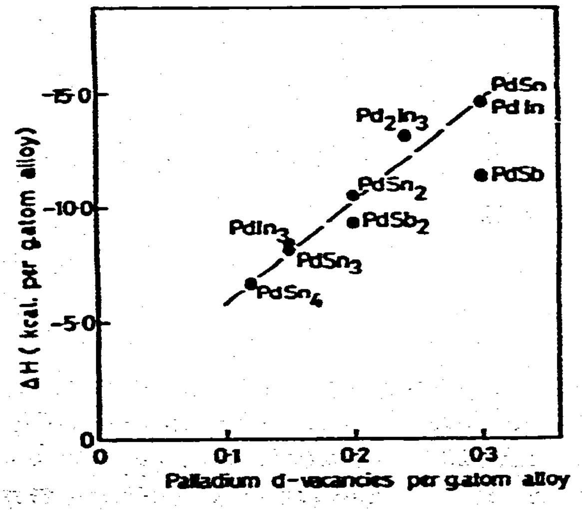

Fig. 6. The *d*-state dependence of the enthalpies of formation of palladium-alloy intermediate phases.

Differences in behaviour are more clearly revealed by re-expressing the enthalpy of formation of the phases *per g-at. transition metal* and examining these as a function of outer electron concentration (or average group number). The results of this modified analysis are shown in Fig. 7. In this diagram, an increase of ΔH g-at.$^{-1}$ transition metal is considered to indicate a higher degree of *d*-state filling, due to either increased local $s \rightarrow d$ transfer (solid solutions) or additional intercomponent transfer (intermediate phases). On the other hand, establishment of essentially constant values for this function is consistent with the "saturation" of the Pd or Ni *d*-states, so that intercomponent transfer and enthalpy of formation per mole of alloy falls in direct proportion to the decreasing transition metal content.

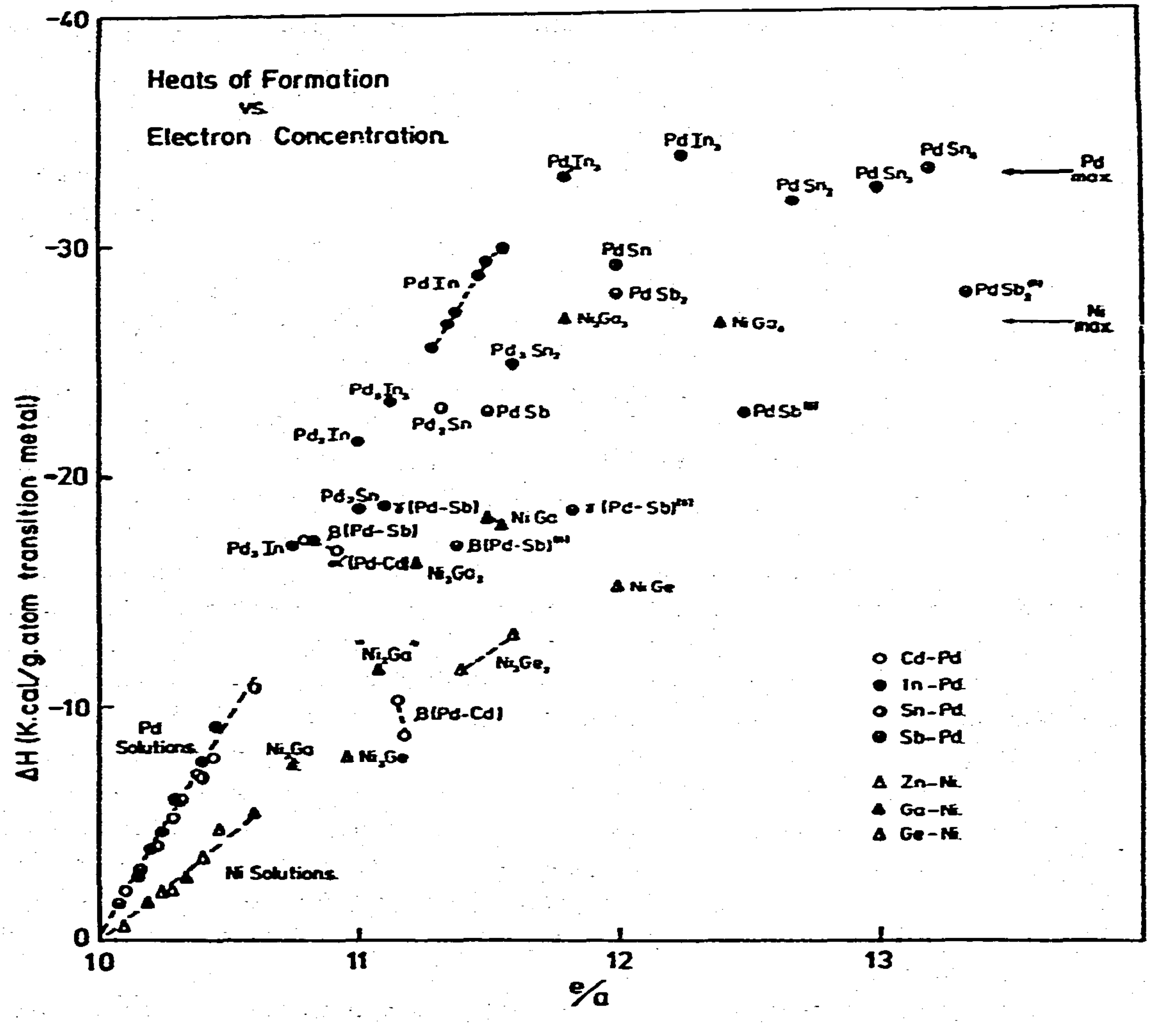

Fig. 7. A comparison of nickel-alloy and palladium-alloy enthalpies of formation.

The data so plotted show that while the enthalpies of formation of the solid solutions depend only on the solvent metal and the electron concentration, the behaviour of the intermediate phases varies also according to the B-group element involved. The suggested difference in electronic mechanisms for the solid solutions and intermediate phases is thus clearly displayed.

Consideration of the available intermediate phase values indicates that the extent of intercomponent transfer increases regularly with electron concentration until saturation of the transition metal *d*-shells is achieved and that the maximum effect of this (per g-at. transition metal) is greater with Pd than with Ni. The difference in behaviour between the individual Pd alloys and between the Ni–Ga and Ni–Ge systems also appears to reflect the varying electronegativity factors. It is noted that as the electronegativity difference between components is reduced, a higher electron concentration is required to reach similar heats, i.e., presumably to reach an equivalent degree of intercomponent electron transfer. Thus, for example, in the Pd–In and Ni–Ga systems, transfer appears almost complete in Pd_2In_3 and Ni_2Ga_3, with an outer electron concentration of 11.8 per atom. By comparison, a slower development of transfer is implied for Pd–Sn alloys, where maximum values are only approached at electron concentrations of ca. 13 per atom, while for the lowest electronegativity difference systems, Pb–Sb (5-valent) and Ni–Ge, the data suggest that "saturation" transfer may well not be achieved even in the most electron-rich intermediate phases ($PdSb_2$ and NiGe). The latter behaviour is consistent with the existence of zero electronegativity difference between Ni and Ge and the small electronegativity difference between Pd and pentavalent Sb. Strictly, however, the behaviour of Sb is ambiguous and the data for the Pd–Sb intermediate phases are therefore plotted in two forms, assuming either tri- or penta-valent (superscript 5) valency for Sb. For the α-solid solutions the heats of formation and magnetic properties have been most consistent with the behaviour of Sb as a tri-valent solute[2]; if this state should persist in the compounds, then the dependence of the heats on electron concentration becomes close to that of the Pd–Sn compounds, as might be expected in view of the similarity of the electronegativities of 4-valent Sn and 3-valent Sb. An exception to the above general hypothesis is the Pd–Cd system for which, despite a high electrochemical factor, compound heats decline rapidly with increasing Cd without approaching the high maximum values characteristic of other Pd systems.

Turning to the individual nickel-alloy phases, it is first noted that Ni_3Ga and Ni_3Ge, like several of the corresponding Pd-based phases, possess the Cu_3Au structure and are thus closely related to the α-solid-solutions; the present re-examination nevertheless indicates that some intercomponent transfer, dependent on solute character, is beginning at these compositions.

The ε("Ni_2Ge") phase is isomorphous with $\gamma(Ni_3Ga_2)$ and both possess partly-filled NiAs (B8) structures. The difference between the enthalpies of formation of these (Ni_2Ge, -7.1 to -7.8 kcal g-at.$^{-1}$; Ni_3Ga_2, -7.5 to -9.6 kcal g-at.$^{-1}$) and the more rapid variation with composition and narrower stability range of

$\gamma(Ni_3Ga_2)$ are all attributable to a higher heteropolar bonding in the latter phase. Both phases exhibit enthalpies of formation which increase as the occupation of the NiAs trigonal interstitial sites, by excess transition metal atoms, is reduced. Such behaviour has been suggested by Predel[9] to be a general characteristic of filled-NiAs-type phases. In the present instance the increasing heats are to be associated with the continuing development of heteropolar bonding as the phase field is crossed.

The phase "NiGa" has the CsCl (B2) structure, exists over a range of composition and shows enthalpies of formation which are asymmetric about the equiatomic ratio. This latter feature is attributable to the change from anti-structure substitution to the creation of Ni-sub-lattice vacancies, as the predominant defect mechanism, on moving from the Ni-rich to the Ga-rich ranges of non-stoichiometry[22–25]. The Ni_2Al_3-type phase Ni_2Ga_3 is considerably more exothermic than its CsCl neighbour, but this may be seen as a consequence of the continuing development of electron transfer heterpolarity at these compositions in the Ni–Ga case.

The phase NiGe is of fixed stoichiometry and exhibits the MnP (B31)-type structure, following the behaviour found in the alloys of Pd with its higher-valent partners, such as Sn or Sb. It appears that this structure, rather than the CsCl form, is favoured by high solute valencies combined with comparatively low electronegativity differences. The present limited number of examples—PdSn (-14.6 kcal g-at.$^{-1}$), PdSb (-11.4 kcal g-at.$^{-1}$) and NiGe (-7.6 kcal g-at.$^{-1}$)—suggest that the enthalpies of formation increase with electronegativity difference and with electron concentration.

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