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ON THE ENTHALPIES AND ENTROPIES OF FORMATION OF SOLID NICKEL—ZINC ALLOYS

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ABSTRACT

The enthalpies of formation of solid nickel—zinc alloys have been measured at 355 K using an isoperibol calorimeter and the technique of tin-solution calorimetry, and values have been obtained for the nickel-rich α-solid solutions and for the β_1, γ, γ_1 and δ intermediate phases. Exothermic values have been observed throughout and these have been compared with the results obtained in previous free energy studies and with those suggested by the empirical model of Miedema. The existing free energy data have been re-assessed at 900 K and the results combined with the present calorimetric enthalpies to derive entropies of formation. The possible contributions to the entropies of the phases are discussed and their Debye temperatures are estimated.

INTRODUCTION

The present study of the nickel-zinc system is one of a continuing series of investigations [1—4] of alloys of transition metals with B-sub-group elements aimed at examining the influence of various alloying factors upon the thermodynamic properties of alloy phases. The equilibrium diagram of the system, as assessed by Hansen and Anderko [5], is shown in Fig. 1. It is generally well established except for some uncertainties regarding the true extent of the nickel-rich solution and the possibility of a low-temperature transformation existing within this phase [6—9]; the suggestion that γ and γ_1 are parts of a single phase field has also been made recently [10].

Numerous previous thermodynamic studies, employing either vapour pressure or galvanic cell techniques, have been made of the nickel—zinc system and the nature and scope of these are summarised in Table 1. While there is conflict between the results of some of these investigations, most of the more recent vapour pressure studies are in general agreement with respect to the activities and free energies of formation. Characteristic features are marked negative deviations from ideality throughout, very strong ordering tendencies in β' and β_1 and the absence of any similar stoichiometric effects

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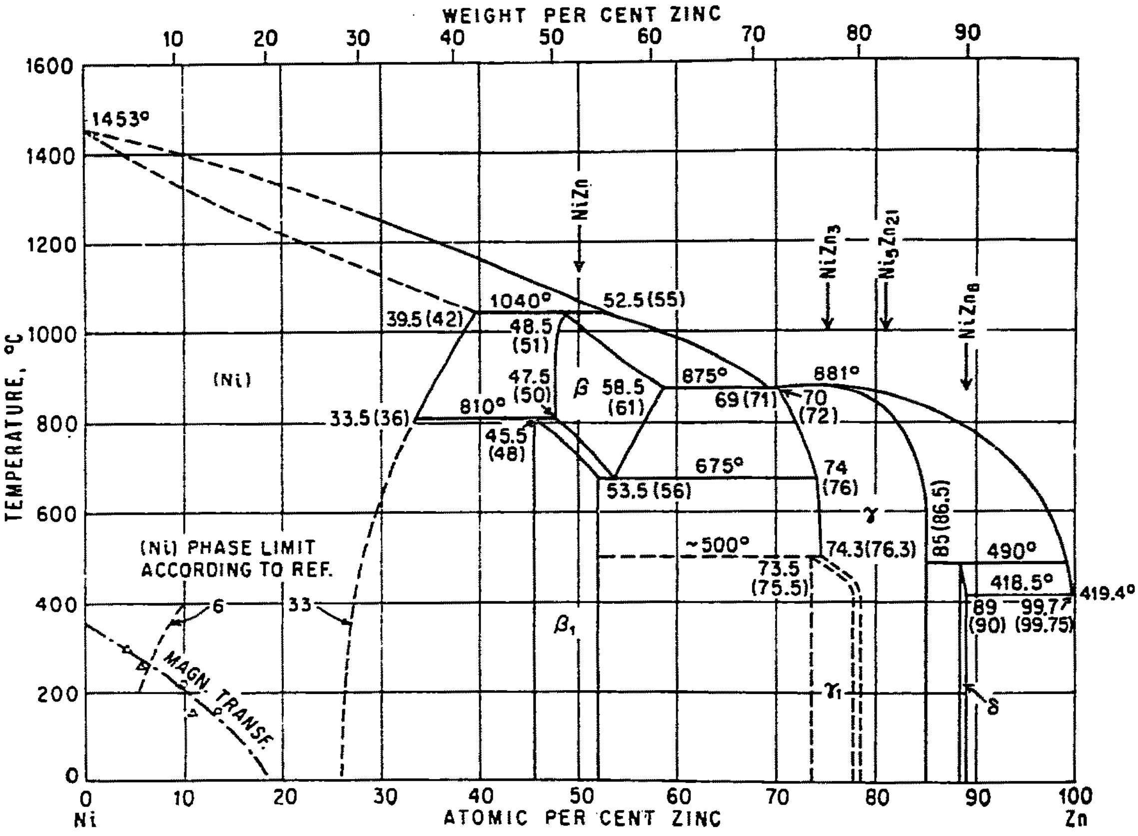

Fig. 1. The nickel—zinc equilibrium diagram (Hansen and Anderko [5]).

in the γ phase. Most authors have attempted to derive second law entropies and heats of formation from their data, but there is considerable variation in the values so obtained for these properties. Because of this, and since no calorimetric study had been reported, measurements on solid nickel—zinc alloys, by means of tin-solution calorimetry, were undertaken in order to resolve the existing uncertainties regarding the heats of formation and also to permit the derivation of improved values for the entropies of formation.

EXPERIMENTAL DETAILS

Alloy preparation

The alloys were prepared directly from 99.999% pure nickel (International Nickel Co. Ltd.) and 99.995% pure zinc (Imperial Smelting Co. Ltd.) using various procedures to circumvent evaporation losses and other problems presented by the large difference in melting points of the components and the high vapour pressure of zinc. In all cases, weighed, chemically cleaned and dried quantities of the pure metals were sealed in silica capsules which were evacuated and back-filled with argon to a pressure of approxi-

TABLE 1

Previous thermodynamic investigations of the free energies of formation of the Ni—Zn system

Authors	Measurement technique	Composition range (at. % Zn)	Temp. range (K)	Phase
Clougherty and Kaufman [11]	Dew point	4.78—32.42	1164—1395	α
Chart et al. [12]	Dew point	9.1—25.7, 42.5, 48.8, 67.0 and 76.0	1100	α, $\alpha + \beta$, β, $\beta + \gamma$ and γ
Chang et al. [8]	Isopiestic	2.83—33.95	772—1200	α
Liang et al. [13]	Dew point	48.0—52.0	1050—1150	β
Lau et al. [14]	Dew point	48.0—56.0	1042—1159	β
Liang et al. [15]	Dew point	47.0—52.0	789—1022	β_1
Anantatmula and Masson [16]	Atomic absorption spectroscopy	5.07—29.79, 45.75 —52.0 and 79.0 85.0	728—925, 605 817 and 613—742	α, β_1 and γ
Ali and Geidrikh [9]	EMF	0—84.5	693—873	α, $\alpha + \beta_1$, β_1, $\beta + \gamma$, γ
Lyazgin et al. [17]	EMF	2.7—94.7	950—1120	Whole system
Budurov et al. [18]	Isopiestic	6.9—30.7 and 4.9—28.3	1067 and 1296	α
Budurov and Wassilew [19]	Dew point	49.4—55.4 and 74.0—84.7	1071—1113 and 973—1158	$\beta(\beta_1)$ and γ
Cunat et al. [20]	Torsion-effusion	27—96	613—952	α, β_1, γ and δ

mately 0.5 atm. With the higher melting point alloys (α, $\alpha + \beta$ and β regions), these capsules were in turn similarly encapsulated as a further precaution against capsule failure occasionally encountered during treatment. Using a small resistance furnace the double-walled capsules were then heated slowly up to approximately 900°C and held for 1 h; the temperature was then gradually raised to 1000°C and maintained for a further similar period. This preliminary treatment proved necessary and sufficient to absorb free zinc so that alloying could then be completed without difficulty by high-frequency induction melting of the pre-annealed samples. Alloys containing a higher proportion of zinc ($\beta + \gamma_1$, γ_1, γ and δ regions) were prepared in single-walled capsules using simple resistance heating. A sequence of gradual heating was again employed to prevent the development of explosive zinc pressures. The encapsulated materials were first heated to just above the melting point of zinc for 48 h. Temperatures were then raised to approximately 50° below the corresponding liquidus of the alloy for 72 h and finally to about 50° higher than the liquidus where they were held for 25—100 h, depending on the nickel content of the alloy. Samples were shaken vigorously during alloying to ensure rapid and complete mixing.

After melting by either technique the liquid alloys were quenched into cold water to give fine-grained samples and minimise segregation. The resulting ingots were then homogenised at as high a temperature as possible, consistent with the desired phase structure; argon encapsulation was again employed. α-Phase alloys were cold-worked before annealing at near liquidus temperatures for at least 2 weeks, while alloys in the $\alpha + \beta_1$, β_1, $\beta_1 + \gamma_1$, γ_1, γ and δ phase fields were equilibrated at 600°C for 1 week. Attempts to obtain samples of the high-temperature β phase by rapidly quenching from 830° were unsuccessful owing to the impossibility of preventing the $\beta \rightarrow \beta_1$ transformation. There was no evidence of alloy contamination or reaction with capsules and, although some minor zinc losses occurred, compositions were monitored by careful weighing at each stage. Phase structures and sample homogeneity were confirmed by metallography and Debye—Scherrer X-ray examination. In the case of the single phase alloys the compositions of the final alloys were also checked by comparison of the measured lattice parameters with previously established values [21].

Calorimetry

Measurements were made using an isoperibol calorimeter and operating procedures which have been described in previous publications [1—4]. The heats of formation of the alloys were obtained in the usual manner from difference in heats of dissolution in molten tin of the alloys and of the individual pure components. In the present work a tin-bath temperature of approximately 745 K provided optimum conditions for the rapid solution of samples and return to equilibrium. Solution times varied from 1.5 to 8 min, depending on alloy composition, but were less than 3 min for the majority. Samples were dropped from 355 K (the ambient temperature of the main dispenser) which is thus the reference temperature for the resulting heats of formation. Finely-divided forms of the annealed alloys were prepared by filing or crushing and approximately 0.1—0.2 g quantities of these were enclosed in small thin-walled capsules of pure tin to provide convenient calorimeter samples. Corrections for the thermal effects of the capsules were calculated using assessed enthalpy data for tin [22]. These data also formed the basis for the calibration of the calorimeter, which was effected by observing drops with pure tin samples.

RESULTS

Heats of solution of pure nickel and zinc were measured as a necessary preliminary to the alloy studies. For ease of comparison with previous published values, these are most usefully reported as isothermal heats of solution at the bath temperature (745 K); the enthalpy changes of the elements between 355 and 745 K were again calculated from the appropriate assessed data [22]. Values obtained in the present experiments for the infinite dilution heats of solution of the elements in liquid tin at 745 K were:

$$\Delta\bar{H}^0_{\mathrm{Ni}} = -42890\ (\pm\ 1090)\ \mathrm{J\ mole^{-1}}$$
$$\Delta\bar{H}^0_{\mathrm{Zn}} = +10335\ (\pm\ 160)\ \mathrm{J\ mole^{-1}}$$

These are in satisfactory agreement with previous work [23].

In the course of the alloy studies 20 different compositions were investi-

TABLE 2

Calorimetric heats of formation of solid nickel + zinc alloys at 355 K [reference states: Ni(s) and Zn(s)]

Atomic fraction of zinc	ΔH formation of alloys (J mole^{-1})	Phase
0.043	—3540 (±1100)	α
0.075	—4730 (±1000)	α
0.095	—5420 (±1000)	α
0.138	—6350 (± 980)	α
0.142	—6660 (± 970)	α
0.188	—7560 (± 950)	α
0.258	—8490 (± 900)	α
0.304	—9650 (± 800)	$\alpha + \beta_1$
0.402	—12 560 (± 670)	$\alpha + \beta_1$
0.460	—16 610 (± 680)	β_1
0.484	—18 120 (± 620)	β_1
0.496	—18 740 (± 640)	β_1
0.618	—17 250 (± 560)	$\beta_1 + \gamma_1$
0.697	—16 530 (± 600)	$\beta_1 + \gamma_1$
0.746	—15 940 (± 650)	γ_1
0.783	—15 130 (± 480)	γ
0.805	—14 540 (± 500)	γ
0.818	—14 240 (± 430)	γ
0.832	—13 950 (± 390)	γ
0.884	—6350 (± 300)	δ

gated, yielding heat of formation data for the α (f.c.c. solid solution), β_1 (f.c. tetragonal $L1_0$), γ_1 and γ(γ-brass $D8_2$) and δ (hexagonal distorted γ) phases and related two-phase alloys. The values obtained at the experimental alloy compositions, referred to a temperature of 355 K and to the solid elements as standard states are presented numerically in Table 2. The results represent averages of four to six measurements at each composition.

DISCUSSION

The heats of formation are plotted in Fig. 2; they are exothermic in accord with previous indications and, although somewhat asymmetric with respect to composition, are most exothermic around equiatomic compositions. The magnitudes are greater than observed for similar non-transition metal systems (e.g. Cu—Zn) [22], but smaller than found for equivalent alloys of nickel with higher valent B-sub-group elements (e.g. Ga [4], Ge [4], Sn [24]), suggesting that electronic effects involving the unfilled transition metal *d*-band are significant in these alloys.

Since no other calorimetrically-determined heats of formation are available, the present results have been compared with those derived from free energy studies. The values indicated by the various investigations, converted to refer to the solid reference states are assembled in Table 3. It will be seen that the calorimetric values generally reveal slightly less exothermic behaviour than suggested by previous EMF and vapour pressure measurements, but, remembering the difference in experimental temperatures, there is satisfactory agreement with those reported between 15 and 52 at. % zinc by Chang et al. [8,13—15].

It is also of interest to compare the calorimetric heats of formation with those which would be predicted by the model of Miedema et al. [25,26],

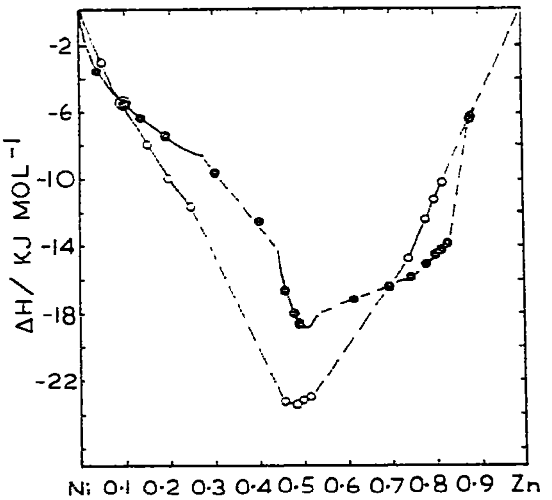

Fig. 2. Comparison of calorimetrically determined and calculated enthalpies of formation of solid nickel—zinc alloys [reference states: Ni(s) and Zn(s)]. ●, Tin-solution calorimetry (present work); ○, calculated (Miedema model).

TABLE 3

Comparison of experimental heats of formation of solid nickel—zinc alloys (J mole^{-1}) [reference states: Ni (f.c.c.) and Zn (c.p.h.)]

x_{Zn}	Phase	Present work (355 K)	Chang et al. [8] (1200 and 900 K)	Anantatmula and Masson [16] (773 K)	Chart et al. [12] (1100 K)	Clougherty [11] and Kaufman (1200 K)	Ali and Geiderikh [9] (753 K)	Lyazgin et al. [17] (973 K)	Cunat et al. [20] (623—673 K)
0.05	α	—3800	—1940	—3040		—2200	+1450		—2340
0.10	α	—5500	—3810	—6070	—6860	—5900		—8000	—5160
0.15	α	—6750	—5590	—8900	—9870	—9300			—7970
0.20	α	—7750	—7240	—11 660	—12 220	—13 300		—16 000	—10 780
0.25	α	—8450	—8770	—14 180	—14 210	—17 300			—13 440
0.46	β_1	—16 600	—17 740	—24 900			—20 100	—28 600	—24 220
0.48	β_1	—18 050	—18 980	—24 270			—21 300		—25 000
0.50	β_1	—18 800	—19 820	—26 500			—22 300	—26 400	—25 000
0.52	β_1	—18 300	—19 300	—26 000					—24 600
0.74	γ_1	—16 100		—21 500			—19 000		—23 440
0.78	γ	—15 200		—21 160			—18 300		—23 130
0.80	γ	—14 700		—20 800			—18 100	—18 000	—22 800
0.82	γ	—14 200		—20 370			—17 800	—17 400	—22 500
0.884	δ	—6000							—17 890

TABLE 4

Comparison of experimental (present work) and calculated (Miedema model) heats of formation of Ni—Zn alloys [Reference states: Ni (f.c.c.) and Zn (c.p.h.)]

x_{Zn}	$\Delta H_{exp.}$ (present work) (J mole^{-1})	$\Delta H_{calc.}$ (J mole^{-1})	Phase
0.05	—3800	—3010	α
0.10	—5500	—5710	α
0.15	—6750	—8090	α
0.20	—7750	—10 100	α
0.25	—8450	—11 800	α
0.46	—16 600	—23 290	β_1
0.48	—18 050	—23 390	β_1
0.50	—18 800	—23 250	β_1
0.52	—18 300	—23 050	β_1
0.74	—16 100	—14 690	γ_1
0.78	—15 200	—12 430	γ
0.80	—14 700	—11 280	γ
0.82	—14 200	—10 180	γ
0.884	—6000	—6560	δ

which utilises empirical relationships involving the Wigner—Seitz cell electron densities and the work functions of the elements. Comparison of the two sets of values is made in Table 4 and Fig. 2. This suggests that for the Ni—Zn system the agreement between experimental and model values is less good overall than has been found with other nickel- and palladium-based systems. Possibly this reflects the sensitivity of the model to the relative magnitudes of $\Delta\phi^*$ (the difference in work functions of the elements) and Δn_{ws} (the difference in Wigner—Seitz cell electron densities); for predictions to be of accuracy comparable with experiment it is desirable that $2.4 > (\Delta\phi^*/\Delta n_{ws}^{1/2}) > 3.7$. Thus, since the corresponding value for the Ni—Zn system is 2.56, accurate prediction should perhaps not be expected. Nevertheless the discrepancies between experimental and calculated values are less than 25% accuracy normally claimed for the model.

Entropies of formation have been derived previously from temperature coefficient measurements in most of the free energy investigations. While they generally agree that the system is characterised by negative excesses, there is considerable variation in the values reported. Improved definition of the entropies of formation may, however, now be provided by combination of the present heats of formation with existing free energy data. To this end the calorimetric enthalpies of formation have been converted to Ni (f.c.c.) and Zn (liquid) reference states most relevant to the temperatures of the free energy studies. The resulting values have been combined with free energies of formation derived at the constant temperature of 900 K from a critical re-examination of all published free energy studies. In the absence of heat capacity data, temperature independence of the enthalpies of formation has been assumed. Smoothed values of the integral thermodynamic properties found for the α, β_1, γ and δ phases are assembled in Table 5. The entropies

TABLE 5

Heats, free energies and entropies of formation of solid nickel—zinc alloys [reference states: Ni (f.c.c.) and Zn (liq.)]

x_{Zn}	Phase	ΔH (355 K) ($J\ mole^{-1}$)	ΔG (900 K) ($J\ mole^{-1}$)	ΔS ($J\ K^{-1}\ mole^{-1}$)
0.10	α	—6110	—6260	+0.17
0.15	α	—7660	—8690	+1.14
0.20	α	—8960	—10 800	+2.04
0.25	α	—9970	—12 620	+2.94
0.46	β_1	—19 390	—18 890	—0.56
0.47	β_1	—20 300	—19 140	—1.29
0.48	β_1	—20 960	—19 330	—1.81
0.49	β_1	—21 470	—19 450	—2.24
0.50	β_1	—21 830	—19 470	—2.62
0.51	β_1	—21 790	—19 390	—2.67
0.52	β_1	—21 700	—19 240	—2.73
0.79	γ	—19 740	—13 900	—6.49
0.81	γ	—19 360	—13 160	—6.89
0.884	δ	—11 360	—9430 *	—2.14

* Value for metastable δ derived from ref. 20 data.

of formation confirm the negative excess character throughout but suggest slightly less negative values than indicated by free energy measurements alone.

Third law calculation of the entropies of this system is precluded by the lack of thermal data. Some indication of their validity and insight into their origins may, however, be obtained by using the structural, magnetic and heat capacity data which are available to estimate configurational, electronic and magnetic contributions and hence deriving Debye temperatures from the balance of vibrational and dilational entropy remaining. The analysis has been made at the arbitrarily chosen temperature of 900 K, the total entropies of the phases being derived by combining present entropies of formation with entropies of the elements at this temperature given by Hultgren et al. [22].

Low temperature heat capacity studies of three nickel-rich solid solutions have been made by Gupta et al. [27]. While the presence of magnetic effects prevented the unambiguous estimation of Debye temperatures, values of the low temperature electronic specific heat coefficients (γ_0) were less sensitive to the data analysis procedure employed. The γ_0 values obtained by these authors' use of a two-term analysis have been used to calculate the electronic entropies of the x_{Zn} = 0.1 and 0.2 alloys from the relation $S_{elec} = \int_0^T \gamma_0 dT$. The γ_0 values have been treated as constants throughout, although it is to be expected that the high γ_0 values of the α-phase alloys with unfilled d-bands will decrease with increasing temperature; attempts to correct for this using an approximate Stoner treatment proved unfruitful. Electronic entropies for the intermediate phases have been similarly calculated. The values of γ_0 for the β_1 examples have themselves been obtained using the free electron approximation, whence they are given by the relation $\gamma_0 = 9.62 \times 10^{-5}$

$(V_A/n)^{2/3}$ J K^{-2} $mole^{-1}$, where V_A is the atomic volume and n is the number of free electrons per atom. Atomic volumes were calculated using the lattice parameter values reported for β_1 (Ni—Zn) by Schramm [28]. Valencies of zero for nickel and two for zinc were assumed in calculating the electron concentrations for this phase and for the γ (Ni—Zn) phase discussed below. The composition and structure ($D8_2$) show the latter to be a typical 21/13 electron compound of the γ-brass family, and since first contact of the Fermi surface with the complex {330} {411} Brillouin zone of this structure occurs at an electron to atom ratio of 1.537, most compositions of this phase, having electron concentrations exceeding this, will have electronic heat capacities lower than the free electron values. This was demonstrated for the Cu—Zn γ-brass phase by Veal and Rayne [29], who further showed that the electronic heat capacities for immediate post-contact alloys were consistent with the density of states of a still spherical, but segmented, Fermi surface advancing into the zone corners. Since analogous behaviour may be anticipated for the Ni—Zn case, the electronic heat capacity coefficients for the $x_{Zn} = 0.79$ and 0.81 examples of γ(Ni—Zn) were calculated on this basis starting from the free electron value calculated at 1.537 electrons per atoms ($x_{Zn} = 0.768$). Lattice parameters for the γ-phase used in the calculations were taken from the work of Anantatmula and Masson [16].

At 900 K the nickel-rich solid solutions are in the paramagnetic condition and thus have entropy contributions arising from the randomised ferromagnetic spins. These magnetic entropies have been calculated using the standard half integral spin model, i.e. $S_{mag} = R\ln(2\bar{S} + 1) = \mu_{alloy}R\ln 2$; the magnetic moments of the solid solutions were taken from Crangle and Martin's assessment [30] of the work of Sadron [31] and Marian [32]. Negligible magnetic entropies are to be expected in the β_1 and γ phases since Schramm [33] has shown them to be weakly paramagnetic and diamagnetic, respectively.

The contribution of configurational terms to entropies of the phases under discussion varies considerably. The α-solid solutions may be expected to be fully disordered at the temperature in question (900 K) and random mixing entropies have therefore been assigned. Careful theoretical analysis by Chang and co-workers [14,15] of the experimental partial thermodynamic properties of β_1 has, however, shown that this superlattice phase is characterised by very low intrinsic disorder and simple anti-structure substitutional defects at non-stoichiometric compositions. Chang and co-worker's results yield the small configurational entropies shown (Table 6) for the β_1 examples. A greater uncertainty attaches to the exact configurational state of the γ phase. The unit cell of the $D8_2$ structure comprises four sub-lattices with 8, 12, 8 and 24 sites per cell, respectively, and the X-ray and neutron diffraction studies by Johansson et al. [34] suggest that γ(Ni—Zn) is based on the stoichiometry Ni_4Zn_{22}, where Ni atoms occupy the single sublattice of outer tetrahedral positions (eight per cell); however, they were unable to establish the probable atomic distributions at non-stoichiometric compositions. The configurational entropies have therefore been estimated by assuming that occupation of the outer octahedral sublattice by nickel remains complete while the balance of nickel and zinc are randomly distributed on all the other lattice sites.

TABLE 6

Analysis of the entropies of solid Ni—Zn alloys at 900 K (entropy units = J K^{-1} $mole^{-1}$)

x_{Zn}	0.1(α)	0.2(α)	0.48(β_1)	0.5(β_1)	0.52(β_1)	0.79(γ)	0.81(γ)
S_{900} (elements)	65.45	67.42	72.95	73.35	73.74	79.08	79.47
S_{900} (alloy)	65.62	69.46	71.14	70.73	71.01	72.59	72.58
$S_{config.}$	2.70	4.16	0.80	0.25	0.75	1.72	1.24
$S_{elec.}$	6.21	7.14	0.47	0.46	0.44	0.30	0.23
S_{mag}	2.25	1.05	0	0	0	0	0
$S_{vib.}$ + dil.	54.46	57.11	69.87	70.02	69.82	70.57	71.11
θ (K)	415	373	225	223	225	218	214

After deducting the above contributions from the total entropies, Debye temperatures have been derived from the remainder by assuming that the vibrational contribution may be described by the Debye entropy function, $\{S_D(T) - S_D(0)\}$, whilst the small dilatational component is well approximated by $10^{-4} \times \{U_D(T) - U_D(0)\}$, the Debye internal energy function. Analyses of the entropies of examples of the α, β_1 and γ phases are given in Table 6. The results for the face-centred-cubic solid solutions show that the Debye temperatures vary with composition. Values obtained differ from those suggested by the previous analyses of low temperature C_p data, but they are consistent with those derived from X-ray intensity values; they confirm that the Debye temperature at first increases slightly on alloying nickel with zinc, but falls with increasing solute contents when these exceed approximately 10 at. %. Essentially constant values of approximately 225 and 216 K, respectively, are indicated for the β_1 and γ phases. However, it should be noted that the value obtained for the latter is particularly sensitive to the exact configurational state assumed. The maximum degree of order would be achieved if excess Ni atoms were confined to a second single (inner tetrahedral) sublattice and the characteristic temperature would then become approximately 210 K. At the other extreme, in the unlikely event of a completely random atomic distribution on the γ-brass structure, the indicated Debye temperature would be raised to about 240 K.

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