PREDICTIVE APPROACH TO THERMODYNAMIC PROPERTIES OF Co NITRIDES AND PHASE-STABILITY IN THE Co-N SYSTEM

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ABSTRACT

The thermodynamic properties of the Co-N system are poorly known from experiments, and there is a need of information on the stability of its various phases and the Co-N phase diagram. This kind of information has been obtained by us. Our approach combines the methods of thermodynamic modelling developed in the so-called CALPHAD (i.e. CALculation of PHAse Diagrams) work with predictions of unknown thermodynamic quantities. The predictions of entropy and enthalpy of formation for nitrides are based on regularities in bonding properties and vibrational entropy of 3d-transition metal compounds. The excess Gibbs energy parameters for the cubic and hexagonal nitride phase are determined by interpolation, relying on trends in the data for 3d-transition metal-nitrogen systems. The properties of the liquid phase are evaluated from experiments and tested in calculations of N-solubility in the ternary systems Co-Cr-N, Co-Fe-N and Co-Ni-N. The Gibbs energy functions obtained by us are used as input information in the Hillert-Staffansson "Two-Sublattice" phenomenological model to calculate the Co-N phase diagram. Our results are compared with information on the Fe-N and Ni-N systems, and with the predictions of Miedema's formula.

1. INTRODUCTION

The study of the thermodynamic properties of transition metal systems is a matter of great theoretical and practical interest. Accurate thermodynamic information forms the basis of the so-called CALPHAD approach (i.e. the Computer Coupling of Phase Diagrams and Thermochemistry) to phase-stability in alloys. In this approach, pioneered by Kaufman[1,2] one searches for a consistent description of the thermodynamics of a system, based on constructing the Gibbs energy (G) of its various phases, making use of descriptions of the lower-order systems, e.g. binaries and ternaries. Since the experimental information on the binary systems may sometimes be uncertain, scarce or lacking, there is a strong interest in the development of methods for predicting thermodynamic quantities, and judging available estimates.

Miedema's formula[3] has been very successful in accounting for the enthalpy of formation of various groups of compounds, but it does not treat the entropy part of G, which is necessary in a study of the high-temperature phase-equilibria. The problem of estimating G at high temperatures led Fernández Guillermet and Grimvall[4] to a systematic study of the thermodynamic properties of various 3d-transition metal compounds. They have reported various correlations which allowed the estimation of e.g. the room-temperature entropy and the enthalpy of formation of various carbides, nitrides and oxides. Later, those correlations were combined with thermodynamic calculations of phase diagrams in order to study the stability of the metastable CrC(cF8)[5] and Cr_3C(oP16)[6] carbides of the Cr-C system, various metastable carbides of Mn and V in the Mn-V-C system[7], and in binary Me-C systems with Me=Sc, Ti, V, Cr, Mn, Fe, Co and Ni[8]. Finally, the

combination of predictions and thermodynamic calculations was used to study the properties of a metal-nitrogen system which is poorly known from experiments, the Ni-N system[9].

In the present work we combine the predictive methods developed in[4-9] with thermodynamic calculations to gain information on the thermodynamic properties and the phase diagram of a system which is poorly known from direct measurements, the Co-N system. The purpose of our study is to obtain a description of that system that can be used in thermodynamic modelling of higher-order phase diagrams based on Co-N. The outline of the present paper is as follows. In Section 2 we present the models for the Gibbs energy of the various phases in the Co-N system, and in Section 3 we explain the procedure for evaluation of the model parameters. Sections 4 and 5 are devoted to the analysis of the Gibbs energy of formation of nitrides and excess Gibbs energies of solution phases, respectively, and in Section 6 we present our predictions for the Co-N system.

2. THERMODYNAMIC MODELLING

2.1. Phases and Structures

The Co-N phase diagram is not known from experiments. Early studies[10] indicated that the solubility of N in Co is very low up to 1473K. X-ray analysis[11] of Co powder nitrided with NH_3 at 653K revealed two nitride phases, an hexagonal phase which was represented by the formula Co_3N, and a phase denoted by the formula Co_2N, the structure of which was described as an orthorhombic distortion of an hexagonal packing. The "Co_2N" phase was later shown[12] to be isomorphous with the orthorhombic

Co_2C(oP6) carbide which had been detected in the Co-C system. An electron-diffraction study[14] of Co films nitrided with NH_3 confirmed the existence of the hexagonal "Co_3N" phase and revealed another hexagonal structure, which was referred to as Co_xN ($x<3$). In addition, a cubic Co_4N nitride was detected[14], isomorphous with the compounds Ni_4N(cP5) and Fe_4N(cP5) of the Ni-N[15] and Fe-N[16] system, respectively, but the orthorhombic Co_2C phase was not observed. In more recent work[17] based on X-ray diffractometry, SEM observation and chemical analysis of Co-N films prepared by a sputtering technique, the nitrides "Co_2N", "Co_3N" and "Co_4N" were formed, but appreciable deviations from the ideal formulae were observed.

In the present study of the Co-N system we treat the dilute interstitial solutions of N in fcc (cF4) and hcp (hP2) Co and two N-richer nitride phases. The first nitride is the hexagonal phase early referred to using the ideal formula Co_3N. Its range of homogeneity is not known from experiments, but we study it here by using thermodynamic model calculations. The second nitride is the cubic phase Co_4N(cP5). It is treated by us as a stoichiometric compound, in line with previous analyses of the Fe-N[18] and Ni-N[9] systems. Because of the lack of experimental information, the orthorhomic Co_2N(oP6) phase is excluded from the present study.

2.2. Non-Magnetic Gibbs Energy of Solid Solution Phases

The Gibbs energy of all the solid phases was described by resolving it into a magnetic (ΔG_m^{mg}) and a non-magnetic contribution. The magnetic contribution was described by Hillert and Jarl's[19] modification of the model proposed by Inden[20], whereas the non-magnetic contribution was described by a

two-sublattice model[21].

Co atoms were assumed to occupy the first sublattice, whereas N atoms and vacant (Va) interstitial sites were assumed to substitute for each other in the second one. In the solutions based on the fcc and hcp structure of Co, the Gibbs energy per mole of formula units, $(Co)_1 (N,Va)_c$, was represented by the expression

$$G_m^{\phi} = y_N {}^{\circ}G_{Co:N}^{\phi} + y_{Va} {}^{\circ}G_{Co:Va}^{\phi} + cRT\,(y_N \ln y_N + y_{Va} \ln y_{Va}) + \Delta G_m^{mg,\phi} + {}^{E}G_m^{\phi} \qquad (1)$$

The variable y_i (i=N, Va) is the so-called[22] site fraction of the component "i" in its sublattice. The parameter ${}^{\circ}G_{Co:Va}^{\phi}$ (ϕ=fcc, hcp) is the Gibbs energy of Co in a non-magnetic state with the structure ϕ, and ${}^{\circ}G_{Co:N}^{\phi}$ (ϕ=fcc, hcp) is the Gibbs energy of a non-magnetic state where all interstitial sites are filled with N. The symbol c denotes the number of interstitial sites per metallic atom.

All the ${}^{\circ}G^{\phi}$ values were referred to the enthalpy of a special standard state recommended by the SGTE (Scientific Group Thermodata Europe) organization[23]. This state, denoted by the superscript SER (Stable Element Reference) is defined as the stable state at 298.15K and 0.1 MPa.

The term ${}^{E}G_m^{\phi}$ (ϕ=fcc, hcp) represents the excess Gibbs energy. It was treated using the regular-solution approximation

$$ {}^{E}G_m^{\phi} = y_N y_{Va} \cdot L_{Co:N,Va}^{\phi} \qquad (2)$$

In eqs. (1-2) the comma separates components that interact in the same sublattice, and the colon separates components in different sublattices. The phenomenological regular solution interaction parameter L^{ϕ} is independent of composition, but it was allowed to vary with temperature according to

$$L^{\phi}_{Co:N,Va} = A^{\phi}_{Co:N,Va} + B^{\phi}_{Co:N,Va} \cdot T \qquad (3)$$

When treating the fcc phase eq.(3) was simplified by setting $B^{fcc}_{Co:N,Va}$ equal to zero. The determination of $A^{fcc}_{Co:N,Va}$ and $L^{hcp}_{Co:N,Va}$ (= $A^{hcp}_{Co:N,Va} + B^{hcp}_{Co:N,Va} \cdot T$) is discussed in Sections 4.3.2 and 5.1, respectively.

2.3. The Magnetic Contribution

The second last term in eq.(1), which is the magnetic contribution to the Gibbs energy, is given by the expression

$$\Delta G^{mg,\phi}_{m} = RT \ln (\beta^{\phi}+1).f^{\phi}(\tau) \qquad (4)$$

where β^{ϕ} is a composition-dependent parameter related to the total magnetic entropy, i.e. the quantity $\Delta S^{mg,\phi}_{m}(\infty)-\Delta S^{mg,\phi}_{m}(0)$, as follows

$$\Delta S^{mg,\phi}_{m}(\infty) - \Delta S^{mg,\phi}_{m}(0) = R \ln(\beta^{\phi}+1) \qquad (5)$$

τ is defined as T/T^{ϕ}_{C}, where T^{ϕ}_{C} is the critical temperature for magnetic ordering of the structure ϕ at a given composition, i.e. the Curie temperature for ferromagnetic ordering and the Néel temperature (T_N) for antiferromagnetic ordering, and $f^{\phi}(\tau)$

represents the polynomial proposed by Hillert and Jarl[19], which is presented in Table I.

When applying the model to alloys, the composition dependence of the quantities T_C^{ϕ} and β^{ϕ} has to be accounted for. This was done by adopting the following phenomenological expressions, previously used to treat the Co-C system[24]

$$T_C^{\phi} = y_N {}^{\circ}T_{C_{Co:N}}^{\phi} + y_{Va} {}^{\circ}T_{C_{Co:Va}}^{\phi} + y_N y_{Va} T_{C_{Co:N,Va}}^{\phi} \qquad (6)$$

$$\beta^{\phi} = y_N {}^{\circ}\beta_{Co:N}^{\phi} + y_{Va} {}^{\circ}\beta_{Co:Va}^{\phi} + y_N y_{Va} \beta_{Co:N,Va}^{\phi} \qquad (7)$$

The quantities ${}^{\circ}T_{C_{Co:Va}}^{\phi}$ and ${}^{\circ}\beta_{Co:Va}^{\phi}$ (ϕ=fcc, hcp), which correspond to pure Co, have been determined by Fernández Guillermet[25] as follows

$${}^{\circ}T_{C_{Co:Va}}^{fcc} = {}^{\circ}T_{C_{Co:Va}}^{hcp} = 1396K \qquad (8)$$

$${}^{\circ}\beta_{Co:Va}^{fcc} = {}^{\circ}\beta_{Co:Va}^{hcp} = 1.35 \qquad (9)$$

His results were accepted in the present work. The quantities ${}^{\circ}T_{C_{Co:N}}^{\phi}$ and ${}^{\circ}\beta_{Co:N}^{\phi}$ (ϕ=fcc, hcp) correspond to the nitrides obtained by filling up with N atoms all octahedral interstitial sites of fcc and hcp Co, respectively, the properties of which are not known from experiments. Following an approximation used in the treatment of the related quantities ${}^{\circ}T_{C_{Co:C}}^{\phi}$ and ${}^{\circ}\beta_{Co:C}^{\phi}$ of the Co-C system[24] we set those quantities equal to zero,

$$ {}^{o}T_{C_{Co:N}}^{fcc} = {}^{o}T_{C_{Co:N}}^{hcp} = 0 \qquad (10) $$

$$ {}^{o}\beta_{Co:N}^{fcc} = {}^{o}\beta_{Co:N}^{hcp} = 0 \qquad (11) $$

Finally, the parameters $T_{C_{Co:N,Va}}^{\phi}$ and $\beta_{Co:N,Va}^{\phi}$ (ϕ=fcc,hcp) give a measure of the extent to which the properties of a nitride $(Co)_1(N,Va)_c$ based on the fcc and hcp metallic structure, respectively, deviate from the linear interpolation between the values for pure Co and for the Co_1N_C nitride, in T_C vs. y_N and β_C vs. y_N plots. Lacking experimental information we relied on the linear interpolation, i.e. we assumed that

$$ T_{C_{Co:N,Va}}^{fcc} = T_{C_{Co:N,Va}}^{hcp} = 0 \qquad (12) $$

$$ \beta_{Co:N,Va}^{fcc} = \beta_{Co:N,Va}^{hcp} = 0 \qquad (13) $$

In summary, the present treatment of the magnetic properties of the fcc and hcp interstitial phases is based on assuming that T_C^{ϕ} and β^{ϕ} (ϕ=fcc,hcp) decrease with the increase in the N content, and become zero at $y_N^{\phi} = 1$. In particular, the quantities T_C^{ϕ} and β^{ϕ} of the Co-N system are treated as linearly dependent upon the site fraction y_N^{ϕ}, relying on the results of an analysis of their composition dependence in the related system Co-C[24].

2.4. Fcc Interstitial Solution and the CoN(cF8) Nitride

For the interstitial solution of N in fcc(cF4) Co we have c=1 and the two-sublattice model will be $(Co)_1(N,Va)_1$. In this case eq. (1) involves the parameters ${}^{o}G_{Co:Va}^{fcc}$ and ${}^{o}G_{Co:N}^{fcc}$, which

were treated as follows. ${}^{o}G^{fcc}_{Co:Va}$, the non-magnetic Gibbs energy of fcc Co, was taken from the study by Fernández Guillermet[25]. ${}^{o}G^{fcc}_{Co:N}$ represents the Gibbs energy of a non-magnetic nitride obtained by filling up with N atoms all octahedral interstitial sites of the fcc(cF4) phase of Co. Such a nitride would have the formula CoN and the (cF8) NaCl structure. As a consequence, the problem of determining the ${}^{o}G^{fcc}_{Co:N}$ parameter for the fcc interstitial phase was considered by us to be equivalent to evaluating the Gibbs energy of an NaCl structure phase in the Co-N system, i.e. the kind of problem that has been discussed in recent works[4,5,8,9]. ${}^{o}G^{fcc}_{Co:N}$ was expressed in terms of the enthalpy of the elements in their reference states as

$$ {}^{o}G^{fcc}_{Co:N} = H^{SER}_{Co} + H^{SER}_{N} + \Delta^{o}G^{fcc}_{Co:N} \qquad (14) $$

and the temperature-dependent quantity $\Delta^{o}G^{fcc}_{Co:N}$ was determined in the way described in Section 4. The information on the properties of N that is necessary for applying eq. (14) was taken from a paper by Frisk[28].

2.5. Hcp Interstitial Solution and the Hexagonal (ε) Nitride Phase

The range of stability of the hexagonal nitride phase in the Co-N system is not known, and this phase has previously[14] been referred to using the formula Co_3N. The phase diagrams of other 3d transition metal-nitrogen systems show an appreciable range of homogeneity for the hexagonal phase. In particular, that range increases[18] when moving from the Cr-N to the Fe-N system, and it seems natural to expect a certain range of homogeneity in the Co-N system as well. In the present work an attempt was made to

predict that homogeneity range, based on adopting for the hexagonal (ε) nitride in the Co-N system the same model as used for the hexagonal nitride in the Cr-N and Fe-N systems, which is as follows[18].

The metal atom arrangement of the hexagonal nitride is close packed hexagonal, and there is one octahedral interstitial site per atom. However, it was assumed that two neighbouring interstitial sites in the hexagonal c-direction are never simultaneously occupied. This phase was thus approximated with the model $(Co)_1(N,Va)_{0.5}$, and its Gibbs energy was described with eq.(1) with c=0.5. The model parameter ${}^{o}G^{hcp}_{Co:Va}$ represents the non-magnetic Gibbs energy of hcp Co. It was taken from the study by Fernández Guillermet[25]. ${}^{o}G^{hcp}_{Co:N}$ represents the Gibbs energy of a non-magnetic nitride with formula $CoN_{0.5}$ based on an hexagonal packing of the metallic atoms. This type of nitride is observed in the Fe-N[27] system and other Me-N systems where Me is a metal of the 3d-transition series[28,29]. The parameter ${}^{o}G^{hcp}_{Co:N}$ was expressed as

$$ {}^{o}G^{hcp}_{Co:N} = H^{SER}_{Co} + 0.5\, H^{SER}_{N} + \Delta^{o}G^{hcp}_{Co:N} \qquad (15) $$

and the temperature-dependent quantity $\Delta^{o}G^{hcp}_{Co:N}$ was determined in the way described in Section 4.

2.6. The Co_4N (cP5) Nitride

The Co_4N(cP5) nitride may be considered as derived from the fcc(cF4) structure of Co by filling up with N atoms one quarter of the available octahedral interstitial sites. This type of nitride has been found in other Me-N systems formed by Me metals of the

3d-transition series[28]. In the Fe-N system it shows a narrow range of homogeneity and in the thermodynamic analysis of the Fe-N phase diagram by Frisk[18] it was treated as a stoichiometric compound with formula Fe_4N. A similar approximation was adopted when treating the Ni-N system[8], and was also applied by us in the present work. The (cP5) structure in the Co-N system was thus treated as a stoichiometric compound with the ideal formula Co_4N, and its Gibbs energy was expressed as

$$ {}^{\circ}G^{Co_4N}_{Co:N} = 4H^{SER}_{Co} + H^{SER}_{N} + \Delta^{\circ}G^{Co_4N}_{Co:N} \qquad (16) $$

The evaluation of the temperature-dependent quantity $\Delta^{\circ}G^{Co_4N}_{Co:N}$ is discussed in Section 4.

2.7. Liquid Phase

The Gibbs energy of the liquid phase was described by adopting a substitutional solution model, as follows

$$ G^{liq}_{m} = x_{Co}\,{}^{\circ}G^{liq}_{Co} + x_{N}\,{}^{\circ}G^{liq}_{N} + RT(x_{Co} \ln x_{Co} + x_{N} \ln x_{N}) + x_{Co}x_{N}L^{liq}_{Co,N} \qquad (17) $$

where x_i (i=Co,N) is the atomic fraction of the component i in the liquid phase. ${}^{\circ}G^{liq}_{Co}$ and ${}^{\circ}G^{liq}_{N}$ was taken from refs. (25) and (18), respectively. The phenomenological interaction parameter $L^{liq}_{Co,N}$ was treated as a constant and it was evaluated from experimental data, as discussed in Section 5.2.

2.8. The Gaseous Phase

The gaseous phase, was treated using the ideal-gas model, and

the following gas species were considered Co_1, N_1, N_2, and N_3. Their properties were taken from the SGTE substance data base[30] which is based upon the JANAF Tables.[31]

3. PARAMETER EVALUATION PROCEDURE

Six thermodynamic model-parameters were determined in the present work. Three of them, $\Delta^oG^{fcc}_{Co:N}$, $\Delta^oG^{hcp}_{Co;N}$ and $\Delta^oG^{Co_4N}_{Co:N}$, are related to the Gibbs energy of the nitrides CoN, $CoN_{0.5}$ and Co_4N but are not known from direct measurements. They were determined in the present work by combining estimates of the high temperature entropy of CoN, $CoN_{0.5}$ and Co_4N, based on the methods introduced in refs. (4-9), with estimations of their enthalpy of formation, as will be discussed in Section 4. The remaining model-parameters determined in the present work, $L^{fcc}_{Co:N,Va}$, $L^{hcp}_{Co:N,Va}$ and $L^{liq}_{Co,N}$ describe the excess Gibbs energy of the solid-solution and liquid-solution phases in the regular-solution approximation. $L^{liq}_{Co,N}$ was evaluated from experimental information (Section 5.2) whereas $L^{fcc}_{Co:N,Va}$ and $L^{hcp}_{Co:N,Va}$ were estimated from a consideration of the trends in regular-solution parameters for Me-N systems formed by Me metals of the 3d-transition series. All fits to experimental or estimated information reported here were performed using a computer program for the optimization of thermodynamic model parameters developed by Jansson[32].

4. ANALYSIS OF GIBBS ENERGIES OF FORMATION

4.1. General Considerations

Fernández Guillermet and Grimvall[4] have reported on various

correlations between quantities related to the strength of chemical bonding in 3d-transition metal carbides and nitrides and the average number of valence electrons per atom, n_e. Of particular relevance for the present study is the correlation between the room-temperature enthalpy of formation per atom (Δ^oH) and n_e, and the correlation involving the characteristic energy E_S. This quantity , introduced in ref. (4) is defined as

$$E_S \text{ (J/atom)} = k_S . \Omega^{2/3} \qquad (18)$$

where Ω is the average volume per atom, and k_S is a quantity with the dimension of a force constant, (i.e. force per length), which is related to the vibrational properties of the compound as follows

$$k_S = M_{eff} \, (k_B \theta_S / \hbar)^2 \qquad (19)$$

M_{eff} is the logarithmic average of the atomic masses. For a nitride $Co_a N_b$ we have

$$M_{eff}(Co_a N_b) = (M_{Co})^{a/a+b} . \, (M_N)^{b/a+b} \qquad (20)$$

where M_{Co} and M_N are the atomic masses of Co and N. k_B is the Boltzmann constant, $\hbar = h/2\pi$ where h is Planck's constant, and θ_S is an "entropy Debye temperature", defined[33,34] as the θ value that reproduces the experimental vibrational entropy per mole of atoms, S_{vib}, when inserted in the Debye model expression for the entropy, S_D

$$S_{vib}(T) = S_D(\theta_S/T) \qquad (21)$$

Previous analysis based on k_S of the vibrational entropy of transition metals[35] and their combinations with C,N and B[33,36] revealed remarkable regularities. The new correlations involving $\Delta^\circ H$ (kJ/mol of atoms) and E_S(J/atom) for 3d transition metal carbides and nitrides are given in Fig. 1 and Fig. 2, respectively. References to the sources of enthalpy and entropy data, and a discussion of the data points for Mn compounds, which deviate from the general trend in Figs. 1(b) and 2(b) have been given in ref. (4) and will not be repeated here. The experimental data points in Fig. 2(a) are too few to firmly establish the E_S vs. n_e relation at large n_e, which corresponds to nitrides of complex structures. However, the better founded and analogous trends of other plots and the general relationship observed in the E_S vs. n_e and $-\Delta^\circ H$ vs. n_e plots lend support to the tentative, dashed line in Fig. 2(a).

4.2. Estimation of θ_S and Entropy of Co Nitrides

The correlation in Fig. 2(a) was applied to predict the properties of the nitrides CoN, $CoN_{0.5}$ and Co_4N. Our procedure is as follows. From the number of valence electrons of Co, $n_e^{Co} = 9$ e/atom, and N, $n_e^N = 5$ e/atom, we calculate n_e. For a nitride Co_aN_b we find $n_e = (a\ n_e^{Co} + b\ n_e^N)/(a+b)$. Then, from the correlation in Fig. 2(a) we get E_S. From E_S and the experimental Ω we get k_S (eq.(18)) and θ_S (eq. (19)). If experimental information on Ω of a compound is not available we estimate it by relying on interpolations in Ω vs. n_e plots of experimental data for compounds with the same formula, as explained in refs. (4) and

(8). The Ω values adopted in the present work are given in Table II.

The Ω value for Co_4N (cP5), $\Omega = 10.446 \cdot 10^{-30} m^3$/atom, is experimental, due to Terao[14]. Combined with the n_e value for Co_4N, $n_e = 8.2$ e/atom, it gives $(n_e/\Omega) = 0.79 \cdot 10^{30}$ e/m^3, which is in line with an average $(n_e/\Omega)_{av} = 0.80\ (\pm 0.01) \cdot 10^{30}$ e/m^3 for the carbides and nitrides of Co[4]. A more recent value for the lattice parameter of Co_4N (cP5) reported by Oda et al.[17] gives $\Omega = 9.223 \cdot 10^{-30}$ m^3/atom and $(n_e/\Omega) = 0.89 \cdot 10^{30}$ e/m^3 which is larger than $(n_e/\Omega)_{av}$. Therefore the Ω value from Oda et al.[17] was considered too low and not used in the present work.

The Ω value for the hexagonal nitride $CoN_{0.5}$ has not been measured, but there are lattice-parameter data[12] for an orthorhombic (oP6) Co-nitride with the same formula. The lattice-parameter data for other 3d-transition elements shows small differences between the Ω values for their hexagonal and orthorhombic $MeN_{0.5}$ nitrides. Compare, for instance, $\Omega = 9.786 \cdot 10^{-30}$ m^3/atom for $FeN_{0.5}$(oP6)[37] with $\Omega = 9.86 \cdot 10^{-30}$ m^3/atom for $FeN_{0.5}$(hP3)[38] and $\Omega = 10.52 \cdot 10^{-30}$ m^3/atom for $MnN_{0.5}$ (oP12)[37] with $\Omega = 10.38 \cdot 10^{-30}$ m^3/atom for $Mn\ N_{0.5}$(hP3)[37]. In line with this trend we estimated the Ω value for the hexagonal nitride $CoN_{0.5}$ by assuming that it is the same as for $CoN_{0.5}$ (oP6), $\Omega = 9.515 \cdot 10^{-30}$ m^3/atom according to ref. (37). There are reports on the preparation of a nitride with formula CoN by decomposing $Co(NH_2)_3$ [39] and $[Co(NH_3)_6](N_3)_3$ [40], and values for its lattice-parameter have been presented. According to ref. (39) the nitride has the (cF8) NaCl structure, whereas in ref. (40) it is given the zinc blend structure. Those results were not used by us. Instead, our Ω value for the NaCl structure CoN(cF8) nitride

was estimated by interpolating in Ω vs. n_e plots for Me-nitrides where Me = Cr, Mn, Fe, Co and Ni. We obtained $\Omega = 8.6 \cdot 10^{-30}$ m^3/atom, which corresponds to a lattice parameter about 4% smaller than given in refs. (39,40).

In Table II we give the θ_s values obtained by combining Ω with estimated E_s values (see above). E_s for Co_4N (n_e = 8.2 e/atom) and $CoN_{0.5}$ (n_e = 7.67 e/atom) were estimated by relying on the dashed part of the curve in Fig. 2(a), which represents the expected behavior[4] for nitrides of complex structures. Experimental information on (cF8)NaCl structure nitrides is available only for $n_e \leq 5.5$ e/atom, (i.e. the full-drawn part of the curve in Fig. 2(a)) and the question has previously been considered[4] how the properties of this phase should be estimated at larger n_e, where this structure is metastable. The study of this problem for CoN (n_e = 7 e/atom) is hampered by the lack of entropy information. Therefore we relied, as an approximation, on the dashed line in Fig. 2(a) when estimating E_s for CoN(cF8), Table II. If, as suggested in[4], the E_s vs. n_e curve for NaCl structure nitrides at large n_e falls under that for complex nitrides (i.e. the dashed line in Fig. 2(a)), we are overestimating E_s and θ_s for CoN(cF8), i.e. underestimating its entropy.

The θ_s values obtained from the correlations presented in ref. (4) correspond, in principle to a temperature $T \approx \theta_s$. At higher temperatures θ_s shows a smooth decrease with increasing T, caused by anharmonic softening of the lattice-vibrations. When the vibrational entropy at high temperatures was needed in the study reported in refs. (5) and (6) one allowed θ_s to decrease with T, relying on the known behavior of the temperature dependence of

θ_s for similar compounds. We have neglected such correction. We also neglected non-vibrational contributions, and approximated the total entropy at high temperatures of CoN, $CoN_{0.5}$ and Co_4N by the $S_{vib}(T)$ values obtained by inserting in eq. (21) the θ_s values presented in Table II.

4.3. Estimation of $\Delta^\circ H$ for Co Nitrides

4.3.1. The hexagonal $CoN_{0.5}$ nitride and Co_4N(cP5)

The solid line in Fig. 2(b) gives a reasonably good description of the average variation with n_e of the (negative) enthalpy of formation of 3d-transition metal nitrides at 298.15K. Relying on that correlation it has previously[4,9] been possible to estimate $\Delta^\circ H$ values for the Ni nitrides Ni_3N(hP8), Ni_4N(cP5). Using that line we estimated for $CoN_{0.5}$ (n_e = 7.67 e/atom) a value of $\Delta^\circ H$ = -1 (±2) kJ/mol of atoms, and for Co_4N (n_e = 8.2 e/atom) a value of $\Delta^\circ H$ = 0.5(±2) kJ/mol of atoms. Miedema's formula[3] gives $\Delta^\circ H$ = 3 kJ/mol of atoms for $CoN_{0.5}$, and $\Delta^\circ H$ = 1 kJ/mol of atoms for Co_4N, in reasonable agreement with the present results.

4.3.2. The NaCl Structure CoN(cF8) Nitride

Enthalpy of formation data for NaCl structure (cF8) nitrides are only available for $n_e \leq 5.5$ e/atom, i.e. the linear part of the solid line in Fig. 2(b), and the question has previously been discussed[4] how to estimate $\Delta^\circ H$ for nitrides of this structure at larger n_e, where the NaCl structure is metastable. Some information on carbides suggested a linear extrapolation[4,5] (e.g. the dashed line in Fig. 1(b)) but more recent work[8] on (cF8) carbides at larger n_e led to non-linear plots with a positive

deviation.

As explained in Section 2.4 the properties of a NaCl structure MeN(cF8) nitride are involved in the two-sublattice[21] model when applied to the interstitial solution of N in the fcc(cF4) structure of the metal Me. By analysing experimental information on the fcc phase of the Fe-N and Ni-N systems it has been possible to derive numbers for the nitrides FeN(cF8) and NiN(cF8) which are metastable. In particular, one has obtained $\Delta^{\circ}H$ = 3.8(±3) kJ/mol of atoms for FeN[41] and $\Delta^{\circ}H$ = 21.6(±10)kJ/mol of atoms for NiN[9]. Those values fall under the $(-\Delta^{\circ}H)$ vs. n_e curve in Fig. 2(b), but above the line obtained by a linear extrapolation of the behavior from the range $n_e \leq 5.5$ e/atom, where the NaCl structure nitrides are stable. Lacking direct experimental information on the fcc phase of the Co-N system, $\Delta^{\circ}H$ for the CoN(cF8) nitride has preliminarily[42] been estimated as $\Delta^{\circ}H$ = 14.3(±8) kJ/mol of atoms, by a smooth interpolation between the values for FeN(cF8) and NiN(cF8). Fortunately, some experimental data on the properties of Co-rich fcc phase of the Co-Fe-N system were found, and we used those data to refine the preliminary[42] value of $\Delta^{\circ}H$ for CoN. Our procedure was as follows.

In the first place we described the properties of the fcc phase of the Co-Fe-N system using the two-sublattice model[21], which gives

$$G_m^{fcc} = y_{Co}y_N {}^{o}G_{Co:N}^{fcc} + y_{Fe}y_N {}^{o}G_{Fe:N}^{fcc} + y_{Co}y_{Va} {}^{o}G_{Co:Va}^{fcc} + y_{Fe}y_{Va} {}^{o}G_{Fe:Va}^{fcc}$$

$$+ RT\,(y_{Co}\ln y_{Co} + y_{Fe}\ln y_{Fe}) + RT\,(y_N \ln y_N + y_{Va}\ln y_{Va}) +$$

$$+ \Delta G_m^{mg,fcc} + {}^{E}G_m^{fcc} \qquad (22)$$

where the excess Gibbs energy term ${}^{E}G_m^{fcc}$ was represented by

$$ {}^{E}G_m^{fcc} = y_{Co}y_{Fe}(y_N L^{fcc}_{Co,Fe:N} + y_{Va} L^{fcc}_{Co,Fe:Va}) + y_N y_{Va}(y_{Co} L^{fcc}_{Co:N,Va} $$

$$ + y_{Fe} L^{fcc}_{Fe:N,Va}) \qquad (23)$$

The magnetic Gibbs energy term $\Delta G_m^{mg,fcc}$ was treated using the Hillert-Jarl[18] model, and its composition dependence was described with the ternary parameters T_C^{fcc} and β^{fcc} using the same type of expressions as used recently[43] to model the fcc phase of the Co-Fe-C system. Most of the quantities in eqs. (22) and (23) were known from previous work. The parameter ${}^{o}G^{fcc}_{Fe:Va}$ from[44], ${}^{o}G^{fcc}_{Co:Va}$ from[25], ${}^{o}G^{fcc}_{Fe:N}$ and $L^{fcc}_{Fe:N,Va}$ from[18], $L^{fcc}_{Co,Fe:Va}$ from[45] and the same sources for the parameters describing the magnetic contribution. Three quantities remained to be determined. The binary parameter ${}^{o}G^{fcc}_{Co:N}$ was expressed using eq. (14), with the function $\Delta^{o}G^{fcc}_{Co:N}$ described as

$$\Delta^{o}G^{fcc}_{Co:N} = a + b\,T + c\,T\,\ln T + d\,T^{-1} + e\,T^{2} \qquad (24)$$

The parameters b, c, d and e, describe the temperature dependence of ${}^{o}G^{fcc}_{Co:N}$ and were evaluated to fit the entropy as calculated from θ_s, obtained in Section 4.2.. Next, the parameter a in eq. (24), which is related to the enthalpy of formation of CoN(cF8), was studied in a series of fits to ternary experimental information where the binary interaction parameter ${}^{o}L^{fcc}_{Co:N,Va}$ was given various values. In those fits, the parameter $L^{fcc}_{Co,Fe:N}$, that measures the

deviation from the ideal behavior of the mixture between Fe and Co in the metallic sublattice of the NaCl structure nitride $(Co,Fe)_1(N)_1$, was set equal to zero. This approximation is in line with the small deviations from the ideal behavior shown by the mixture of Co and Fe in the $(Co,Fe)_1(C)_1$ phase of the related system Co-Fe-C[43]. The Co-Fe-N information considered by us comprised measurements of the solubility of N in Fe-rich Co-Fe fcc solutions with up to 20wt%Co at various temperatures due to Schenck et al.[46], and in Co-rich Co-Fe solutions with up to about 80 wt%Co due to Mori and Ichise[47]. Lacking direct information on the binary parameter $L^{fcc}_{Co:N,Va}$ we determined a range of probable values by examining the sequence of $L^{fcc}_{Me:N,Va}$ parameters obtained in analyses of Me-N systems where Me=Cr, Fe, Ni[9,18]. In Fig. 3(a) we plot $L^{fcc}_{Me:N,Va}$ as a function of the position of Me in the Periodic Table. These results suggest that $L^{fcc}_{Co:N,Va} \leq 0$, and we adopted as a probable lower limit the value L^{fcc}=-13 kJ/mol given by a linear interpolation between $L^{fcc}_{Fe:N,Va}$ and $L^{fcc}_{Ni:N,Va}$, i.e. we assume that -13 kJ/mol $\leq L^{fcc}_{Co:N,Va} \leq$ 0 kJ/mol. Experimental N solubility data for the Co-richest solutions studied in refs. (46) and (47) were analysed by us in a series of fits where $L^{fcc}_{Co:N,Va}$ was given the values 0, -6.5 and -13 kJ/mol, in agreement with the probable range selected above, and the quantity a in eq.(24) was determined by minimizing the square-sum of the differences between experimental and calculated N-solubility values. The resulting $\Delta^{\circ}H$ values for CoN(cF8), which can be calculated from eq. (24), will be refered to as the optimum $\Delta^{\circ}H$. They are given in Table III. The optimum $\Delta^{\circ}H$ obtained by extrapolation from the ternary Co-Fe-N system increases with the decrease in $L^{fcc}_{Co:N,Va}$, and we find that the probable range -13

kJ/mol $\leq L^{fcc}_{Co:N,Va} \leq 0$ kJ/mol corresponds to 21.9kJ/mol of atoms $\geq \Delta^{\circ}H \geq$ 15.4 kJ/mol of atoms, i.e. the present study favours the largest values compatible with the preliminary[42] estimate $\Delta^{\circ}H$ = 14.3(±8) kJ/mol of atoms (see above). Lacking information to sharpen our results further we adopted the mean value $\Delta^{\circ}H$ = 18.7(±3) kJ/mol of atoms, corresponding to $L^{fcc}_{Co:N,Va}$ = -6.5(±6.5) kJ/mol, see symbol with error bars in Fig. 3(a). As a comparison, Miedema's formula[3] gives for a CoN compound of unspecified structure a larger value, $\Delta^{\circ}H$ = 27 kJ/mol of atoms.

4.3.3. Representation of Gibbs Energies

The enthalpy of formation values for the Co nitrides in Table II were combined with entropy values calculated by inserting the estimated θ_s (Table II) in eq. (21) and the Gibbs energy functions ${}^{\circ}G^{fcc}_{Co:N}$ (eq.(14)), ${}^{\circ}G^{hcp}_{Co:N}$ (eq.(15)) and ${}^{\circ}G^{Co_4N}_{Co:N}$ (eq.(16)) were determined by fitting the temperature dependent quantities $\Delta^{\circ}G^{fcc}_{Co:N}$(eq.(14)), $\Delta^{\circ}G^{hcp}_{Co:N}$ (eq.(15)) and $\Delta^{\circ}G^{Co_4N}_{Co:N}$ (eq.(16)) to the five-parameter function of T as given in eq. (24) for fcc. The Gibbs energy parameters for nitrides obtained in the present work are given in Table I. In order to calculate the Co-N phase diagram it is necessary to determine the excess Gibbs energy of the hexagonal and liquid phases, which is discussed in the following section.

5. ANALYSIS OF EXCESS GIBBS ENERGIES

5.1. Hcp solution and ε Nitride Phase

Our treatment of the fcc phase involved the estimation of a probable value for the $L^{fcc}_{Co:N,Va}$ parameter, based on trends in

$L^{fcc}_{Me:N,Va}$ for Me-N systems formed by 3d-transition Me metals. In Section 4.3.2. we found that such procedure led to properties for the CoN(cF8) phase which compare well with what was expected from information on the related NaCl structure nitrides FeN and NiN. Lacking experimental information on the properties of the hexagonal phase we relied on a similar interpolation procedure to determine the $L^{hcp}_{Co:N,Va}$ parameter, which was expressed in Section 2.2. (eq.(3)) as $A^{hcp}_{Co:N,Va} + B^{hcp}_{Co:N,Va}\,T$. In Fig. 3 we plot the $A^{hcp}_{Me:N,Va}$ (Fig.3.(b)) and $B^{hcp}_{Co:N,Va}$ (Fig.3(c)) values corresponding to the regular solution $L^{hcp}_{Me:N,Va}$ parameters obtained in analyses of Me-N systems with Me = Cr, Fe and Ni[9,18]. Those data suggest for the hcp phase in the Co-N system a positive $A^{hcp}_{Co:N,Va}$ and a negative $B^{hcp}_{Co:N,Va}$ parameter. $A^{hcp}_{Me:N,Va}$ decreases smoothly when Me changes in the sequence Cr → Fe → Ni and relying on a linear interpolation we estimated for the Co-N system $A^{hcp}_{Co:N,Va}$ = 5(±5)kJ/mol. The variation of the $B^{hcp}_{Me:N,Va}$ parameters is less regular and proceeding as in Section 4.3.2. we identified the probable range of B^{hcp} values for the Co-N system as -10 J/K.mol ≤ $B^{hcp}_{Co:N,Va}$ ≤ 0 J/K.mol, and adopted the mean value $B^{hcp}_{Co:N,Va}$ = -5(±5) J/K.mol to describe the temperature dependence of $L^{hcp}_{Co:N,Va}$.

5.2. Liquid Phase

The excess Gibbs energy of the liquid phase was described using the regular-solution approximation (eq.(17)) and a constant phenomenological interaction parameter was evaluated from measurements[48,49] of the solubility of N in liquid Co. The solubility values calculated using our assessed $L^{liq}_{Co,N}$ parameter reproduce well the experimental data used in the optimization.

This is demonstrated in Fig. 4. In Fig. 5 we compare N solubility values calculated using the present description with experimental data from refs. [50-53], which were not used by us. The calculated line falls within the experimental scatter band. As a further check that our description for the Co-N liquid phase is reasonable we considered information from binary and ternary systems formed by metals of the 3d-transition series, as follows. In Fig. 6 we plot versus the position of Me in the Periodic Table the $L^{liq}_{Me,N}$ values obtained in analyses of Me-N systems where Me = Cr, Fe, Ni[9,18]. When $L^{liq}_{Me,N}$ was reported as a function of temperature we plot the value corresponding to 2000K. The $L^{liq}_{Co,N}$ parameter obtained by us fits smoothly the trend of the values for the other Me-N systems, which lends additional support to the interpolation procedure applied above to L parameters in fcc and hcp solutions. Next we considered information on the solubility of N in liquid Co-Me-N systems where Me=Cr,Fe and Ni and analysed it in terms of the following expression for G^{liq}_m

$$G^{liq}_m = x_{Co}\,{}^oG^{liq}_{Co} + x_{Me}\,{}^oG^{liq}_{Me} + x_N\,{}^oG^{liq}_N + RT(x_{Co}\ln x_{Co} + x_{Me}\ln x_{Me} + x_N\ln x_N)$$

$$+ x_{Co}x_{Me}L^{liq}_{Co,Me} + x_{Co}x_NL^{liq}_{Co,N} + x_{Me}x_N\,L^{liq}_{Me,N} + x_{Co}x_{Me}x_N\,L^{liq}_{Co,Me,N} \qquad (25)$$

Then we evaluated the ternary interaction parameter $L^{liq}_{Co,Me,N}$ by applying the optimization procedure described in Section 3. In those calculations we used the information on ${}^oG^{liq}_{Co}$ and ${}^oG^{liq}_N$ referred to in Section 2.7., and the $L^{liq}_{Co,N}$ parameter obtained by us. The sources of the remaining parameters are as follows ${}^oG^{liq\ 54)}_{Cr}$, ${}^oG^{liq\ 44)}_{Fe}$, ${}^oG^{liq\ 55)}_{Ni}$, $L^{liq\ 56)}_{Co,Cr}$, $L^{liq\ 18)}_{Cr,N}$, $L^{liq\ 57)}_{Co,Ni}$ $L^{liq\ 45)}_{Co,Fe}$, $L^{liq\ 18)}_{Fe,N}$, and $L^{liq\ 9)}_{Ni,N}$. In Figs. 7,8, and 9 we compare

the solubility of N calculated using eq. (25) with experimental information on the Co-Cr-N[48-53], Co-Fe-N[48-53,58-60] and Co-Ni-N[48-53,61-64] systems, respectively. Those data are well accounted for by the calculated lines, that are based on the present $L^{liq}_{Co,N}$ parameter and the values $L^{liq}_{Co,Cr,N}$ = -14kJ/mol, $L^{liq}_{Co,Fe,N}$=-4kJ/mol and $L^{liq}_{Co,Ni,N}$=-10kJ/mol, respectively. Those ternary parameters are reasonably small, and we conclude that the present description of the liquid Co-N phase can be combined with existing information on other binary systems to account for the observed properties of Co-Me-N liquid solutions without recourse to large ternary corrections.

6. THERMODYNAMIC PREDICTIONS FOR THE Co-N SYSTEM

6.1. The Phase Diagram

A summary of the thermodynamic parameters for the Co-N system arrived at in the present work is presented in Table I, and we used that thermodynamic description to construct, by calculation, the Co-N phase diagram. The result of a calculation using the Thermo-Calc system[65] is presented in Fig. 10. The dashed line labelled T_C^{hcp} describes the composition dependence of the Curie temperature in the ε nitride phase based on the hcp structure. The intercept of the calculated ε/fcc+ε boundary with the Curie temperature line is reflected in a kink. Between 1167 and 1142K the present calculation predicts the existence in the ε phase of the kind of miscibility gap recently discussed by Nishizawa et al. 66), and predicted by calculation in other Co-based systems e.g. Co-W[67], Co-Cr[58], and Co-Mn[68]. It has the form of a sharp horn protruding along the Curie temperature line, and separates

two compositions of the ε phase, a Co-rich ferromagnetic one, ε(f), and a N-rich paramagnetic one, ε(p). At lower temperatures the miscibility gap becomes metastable, and we have indicated it in Fig. 10 using dashed lines.

Our treatment predicts that the Co_4N(cP5) is stable in the Co-N system for temperatures up to 1335K, where it transforms congruently into ε. The calculation predicts two invariant equilibria involving fcc and Co_4N. One involves the dilute interstitial solution of N in hcp Co (denoted in Fig.10 as hcp), and occurs at 794K. The second three-phase equilibrium occurs at 980K, and involves the ε nitride phase.We may compare these features with those shown by the Fe-N phase diagram assessed by Frisk[18] from experiments, which is reproduced in Fig. 11. There we find a congruent $Fe_4N \rightarrow \varepsilon$ transformation at 970K, and an fcc+ε+Fe_4N three-phase equilibrium at 923K. A relevant difference between the calculated phase diagrams for the Fe-N and Co-N systems is the extension of the one-phase field for the fcc structure, which decreases when moving from Fe-N to Co-N. A similar trend is observed when comparing the phase diagrams for the related systems Fe-C[69] and Co-C[70]. Finally, we compare the Co-N phase diagram obtained by us with that calculated in ref. (9) for the Ni-N system, which is reproduced in Fig. 12. When moving from Co-N to Ni-N[9] the Me_4N(cP5) nitride, which is related to the fcc structure (cf. Section 2.6), becomes metastable relative to the ε nitride phase. The calculated phase diagrams for the Fe-N[18] (Fig. 11) and Ni-N[9] (Fig. 12) systems also suggest that there is an increase in the solid/liquid equilibrium temperatures for the Me-N ε nitride phase when Me changes from Fe to Ni. The congruent melting temperature for the ε nitride phase obtained by

us in the Co-N system fits that trend.

6.2. The Thermodynamic Properties of Co_3N(hP8)

Early work on the Co-N system referred to the hexagonal nitride phase using the ideal formula Co_3N. In the present work a nitride with the equivalent formula $CoN_{1/3}$ falls inside the homogeneity range of the (ε)CoN_x hexagonal nitride, the properties of which were treated by us for $0 \leq x \leq 0.5$. Since the thermodynamic properties of the hexagonal phase are not known from experiments, we shall examine the predictions of the present treatment for $CoN_{1/3}$. The total entropy at 298.15K obtained by us, $^{\circ}S$ = 34.3 J/K.mol of atoms, is larger than the estimate $^{\circ}S$ = 24.7(±1.6)J/Kmol of atoms due to Kubaschewski and Alcock[71], but compares well with $^{\circ}S$ = 33.5 J/K.mol of atoms, estimated by Yatsimirski et al[72]. Our entropy value involves a small contribution from the entropy of mixing of N and Va in the interstitial sites. We estimated that entropy by assuming random mixing in the interstitial sublattice, and obtained for the non-configurational entropy S^{nconf}=32.5 J/K.mol of atoms. A previous[4] estimate, based on the E_s vs. n_e correlation in Fig. 2(a) and the experimental[37] Ω=9.981·10^{-30} m^3/atom for Co_3N, gave[4] 34(±1)J/K.mol of atoms, i.e. a reasonably close value. According to the present description the enthalpy of formation of $CoN_{1/3}$ at 298.15K is $\Delta^{\circ}H$ = 1.4 kJ/mol of atoms. This value is bracketed by the estimate $\Delta^{\circ}H$ = 2 kJ/mol of atoms by Hahn and Konrad[73] and $\Delta^{\circ}H$ = 1 kJ/mol of atoms, given by Miedema's formula[3].

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TABLE I: Summary of parameters describing the thermodynamic properties of the Co-N system. Values are given in SI units, and correspond to one mol of formula units.

fcc and "CoN"

$${}^{o}G^{fcc}_{Co:N} - H^{SER}_{Co} - H^{SER}_{N} = 21028+284.763T - 50.261\ T\ln T + 198552T^{-1}$$

$${}^{o}G^{fcc}_{Co:Va} - H^{SER}_{Co} = 427.59 - 0.615248T + GHSERCO$$

$$L^{fcc}_{Co:N,Va} = -6500$$

hcp and ε

$${}^{o}G^{hcp}_{Co:N} - H^{SER}_{Co} - 0.5H^{SER}_{N} = -13140+198.577\ T -36.621\ T\ln T + 96383T^{-1} -8.42\ 10^{-4}\ T^{2}$$

$${}^{o}G^{hcp}_{Co:Va} - H^{SER}_{Co} = GHSERCO$$

$$L^{hcp}_{Co:N,Va} = 5000 - 5T$$

Co_4N

$${}^{o}G^{Co_4N}_{Co:N} - 4H^{SER}_{Co} - H^{SER}_{N} = -35381 + 632.579T - 120.379\ T\ln T + 237512T^{-1} - 4.466\ 10^{-3}\ T^{2}$$

Liquid

$298.15 < T < 1768.00$

$${}^{o}G^{liq}_{Co} - H^{SER}_{Co} = 15085.037 - 8.931932\ T - 2.19801\cdot 10^{-21}\ T^{7} + GHSERCO$$

$1768 < T < 6000.00$

$${}^{o}G^{liq}_{Co} - H^{SER}_{Co} = 16351.056 - 9.683796\ T - 9.3488\ 10^{30}\ T^{-9} + GHSERCO$$

$298.25 < T < 6000.00$

$${}^{o}G^{liq}_{N} - H^{SER}_{N} = 29950 + 59.02T + GHSERN$$

$$L^{liq}_{Co,N} = -7700$$

Gas Phase

Constituents: Co_1, N_1, N_2 and N_3

$$G^{g}_{Co} - H^{SER}_{Co} = GASCo1 + RT \ln P$$

$$G^{g}_{N} - H^{SER}_{N} = GASN1 + RT \ln P$$

$$G^{g}_{N2} - 2H^{SER}_{N} = GASN2 + RT \ln P$$

$$G^{g}_{N3} - 3H^{SER}_{N} = GASN3 + RT \ln P$$

where:

GHSERCo

$298.15<T<1768.00$: $309.575 + 133.36601T - 25.0861\ T\ln T - 0.002654739T^2 - 1.7348\ 10^{-7}\ T^3 + 72527\ T^{-1}$

$1768.00<T<6000.00$: $-17198.332 + 253.28374T - 40.5\ T\ln T + 9.3488\ 10^{30}T^{-9}$

GASCo1

$298.15<T<600.00$: $418357.591 + 21057.6536\ T^{-1} - 56.0526293T - 17.3222621\ T\ln T - 0.0134474178\ T^2 + 3.44982655\ 10^{-8}\ T^3$

$600.00<T<1600.00$: $416135.824 + 84845.244\ T^{-1} - 2.76030084T - 26.1536401\ T\ln T - 1.61658045\ 10^{-4}T^2 - 6.62772796\ 10^{-9}T^3$

$1600.00<T<3800.00$: $403240.513 + 3232830.36T^{-1} + 69.2075196T - 35.5393981\ T\ln T + 0.99260728052\ T^2 - 1.32555396\ 10^{-7}T^3$

$3800.00<T<6000.00$: $467728.964 - 29464564.8T^{-1} - 129.063931T - 11.669971\ T\ln T - 0.00132479875\ T^2 - 1.0865848\ 10^{-8}T^3$

GASN1

$298.15<T<2950.00$: $466446.153 + 2788.78662T^{-1} - 13.2660528T - 20.8939295\ T\ln T + 8.4552092\ 10^{-5}T^2 - 1.00186856\ 10^{-8}T^3$

$2950.00<T<6000.00$: $481259.023 - 7559107.28T^{-1} - 52.4348889T - 16.3761342T\ln T - 2.28373808\ 10^{-4}T^2 - 2.7899720910^{-8}T^3$

GASN2

298.15<T<800.00: $-8000.12601 - 38326.6952T^{-1} - 8.70687347T$

$-27.2233215T\ln T - 0.00125991746T^2 - 5.39381057\ 10^{-7}T^3$

800.00<T<2200.00: $-10569.6428+416969.072T^{-1} + 2.88463409T$

$-28.4238366T\ln T - 0.00318927492T^2 + 2.06637997\ 10^{-7}\ T^3$

2200.00<T<6000.00: $-22468.6452+3427511.88T^{-1} + 71.9269909T$

$-37.5501448\ T\ln T - 6.15899444\ 10^{-6}\ T^2 - 4.22547041\ 10^{-9}T^3$

GASN3

298.15<T<800.00: $403075.636 + 55714.144\ T^{-1} - 14.3245228T$

$-29.5595416T\ln T - 0.02413122T^2 + 3.6156036\ 10^{-6}\ T^3$

800.00<T<2000.00: $388937.207 + 1536448.48T^{-1} + 158.809275T$

$-55.404528T\ln T - 0.0026570492T^2 + 1.9365644\ 10^{-7}T^3$

2000.00<T<6000.00: $380898.006 + 3336949.2T^{-1} + 210.207464T$

$-62.295576T\ln T + 6.5726456\ 10^{-6}\ T^2 - 7.868012\ 10^{-10}\ T^3$

The magnetic contribution to Gibbs energy is described by $\Delta G_m^{mg,\phi} = RT\ \ln(\beta^{\phi}+1)\ f^{\phi}(\tau)$, $\tau = T/T_C^{\phi}$ and ϕ=fcc, hcp.

For $\tau<1$,

$$f(\tau)=1 -[\frac{79\tau^{-1}}{140p} + \frac{474}{497}(\frac{1}{p}-1)(\frac{\tau^3}{6} + \frac{\tau^9}{135} + \frac{\tau^{15}}{600})]/A,$$

and for $\tau>1$

$$f(\tau) = -(\frac{\tau^{-5}}{10} + \frac{\tau^{-15}}{315} + \frac{\tau^{-25}}{1500})/A$$

where

$A = (\frac{518}{1125}) + (\frac{11692}{15975})[(\frac{1}{p}) - 1]$ and p depends on the structure. For fcc and hcp we have p = 0.28. T_C^{ϕ} and β^{ϕ} vary with composition according to Eqs. (6) and (7), with parameter values given in Eqs. (8) to (13).

TABLE II: PROPERTIES OF Co NITRIDES

Compound	Structure (Pearson-Symbol	n_e ($e/_{atom}$	Ω ($10^{-30} m^3$/ atom	E_s (10^{-18} J/ atom	k_s (N/m)	θ_s (K)	$\Delta^\circ H$ (kJ/mol of atoms
CoN	(cF8)	7.00	8.6[a]	5.457[b]	130[c]	399[d]	18.7(±3)[e]
$CoN_{0.5}$	hexagonal	7.67	9.515[f]	4.805[b]	170[c]	321[d]	-1(±2)[g]
Co_4N	(cP5)	8.20	10.446[h]	4.587[b]	96[c]	276[d]	0.5(±2)[g]

[a] Estimated value, Section 4.2

[b] From the correlation in Fig.2(a)

[c] From Eq. 18, see also ref. 4)

[d] From Eq.19, see also ref. 4)

[e] Discussed in Section 4.3.2.

[f] Estimated value, Section 4.2.

[g] From the correlation in Fig.2(b)

[h] Experimental value, from ref. (14

TABLE III

$L^{fcc}_{Co:N,Va}$ kJ/mol	$\Delta^{\circ}H$ for "CoN" kJ/mol of atoms	COMMENTS
0	15.4	
-6.5	18.7	Adopted in the Present work
-13.0	21.9	
-	27.0	$\Delta^{\circ}H$ for a "CoN" compound of unspecified structure according to Miedema's formula[3]

The parameter $L^{fcc}_{Co:N,Va}$ describing the excess Gibbs energy of the fcc nitride phase, and the room-temperature enthalpy of formation of the (cF8) NaCl structure nitride CoN optimized in the present work as described in Section 4.3. The enthalpy value for a "CoN" compound (unspecified structure) according to Miedema's formula[3] is also given.

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FIGURE CAPTIONS

Fig. 1(a) The caracteristic energy E_s defined by eq. (18), and (b) the enthalpy of formation at 298.15K, $\Delta^\circ H$ of 3d-transition metal carbides as functions of the average number of valence electrons per atom, n_e. The numbers refer to ScC(1), TiC(2), VC(3), Cr_3C_2(4), Cr_7C_3(5), $Cr_{23}C_6$(6), Mn_7C_3(7), Mn_5C_2(8), Mn_3C(9), $Mn_{23}C_6$(10), Fe_3C(11), Co_3C(12), Ni_3C(13), Sc_2C(14) and Sc_4C_3(15). The dashed lines refer to the (cF8) NaCl structure. From Fernández Guillermet and Grimvall[4].

Fig. 2(a) E_s and (b) $\Delta^\circ H$ of 3d-transition metal nitrides, as in Fig. 1. The numbers refer to TiN(1), VN(2), CrN(3), Cr_2N(4), Mn_5N_2(5), Mn_4N(6), Fe_2N(7), Fe_4N(8) and Ni_3N(9). The E_s vs. n_e relation is only tentative. From Fernández Guillermet and Grimvall[4].

Fig. 3(a) The regular-solution parameter for the fcc phase, $L^{fcc}_{Me:N,Va}$ and the parameters describing the excess Gibbs energy of the hexagonal nitride phase based on the hcp structure of Me in Me-N systems, viz. b) $A^{hcp}_{Me:N,Va}$ and c) $B^{hcp}_{Me:N,Va}$ as a function of the position of Me in the 3d-transition metal series. Filled symbols for Me=Cr, Fe and Ni represent values from refs. (9) and (18). Empty symbols with error bars represent our estimates, which are discussed in the text.

Fig. 4 The N content in liquid Co-N solutions in equilibrium with a gas-phase at 1873K as a function of the square-root of the partial pressure of N_2(g). Data points represent experimental

values from Blossey and Pehlke[48,49], and the line is calculated using the description presented in Table I.

Fig.5 The temperature dependence of the N-solubility in liquid Co according to various sources of information. The solid line was calculated using the description presented in Table I.

Fig. 6 The regular-solution parameter $L^{liq}_{Me,N}$ describing the excess Gibbs energy of the liquid phase in Me-N systems as a function of the position of Me in the 3d-transition metal series. Filled symbols for Me=Cr, Fe, and Ni represent values from refs. (9) and (18). The value for $L^{liq}_{Co,N}$ has been evaluated by us from experimental data, as discussed in Section 5.2.

Fig. 7 The solubility of N in Co-rich Co-Cr liquid solutions according to various sources of information. The solid lines were calculated by combining the present description of the Co-N system with information on the Co-Cr and Cr-N liquid phase, and a ternary interaction parameter $L^{liq}_{Co,Cr,N}$ = -14kJ/mol, obtained in Section 5.2.

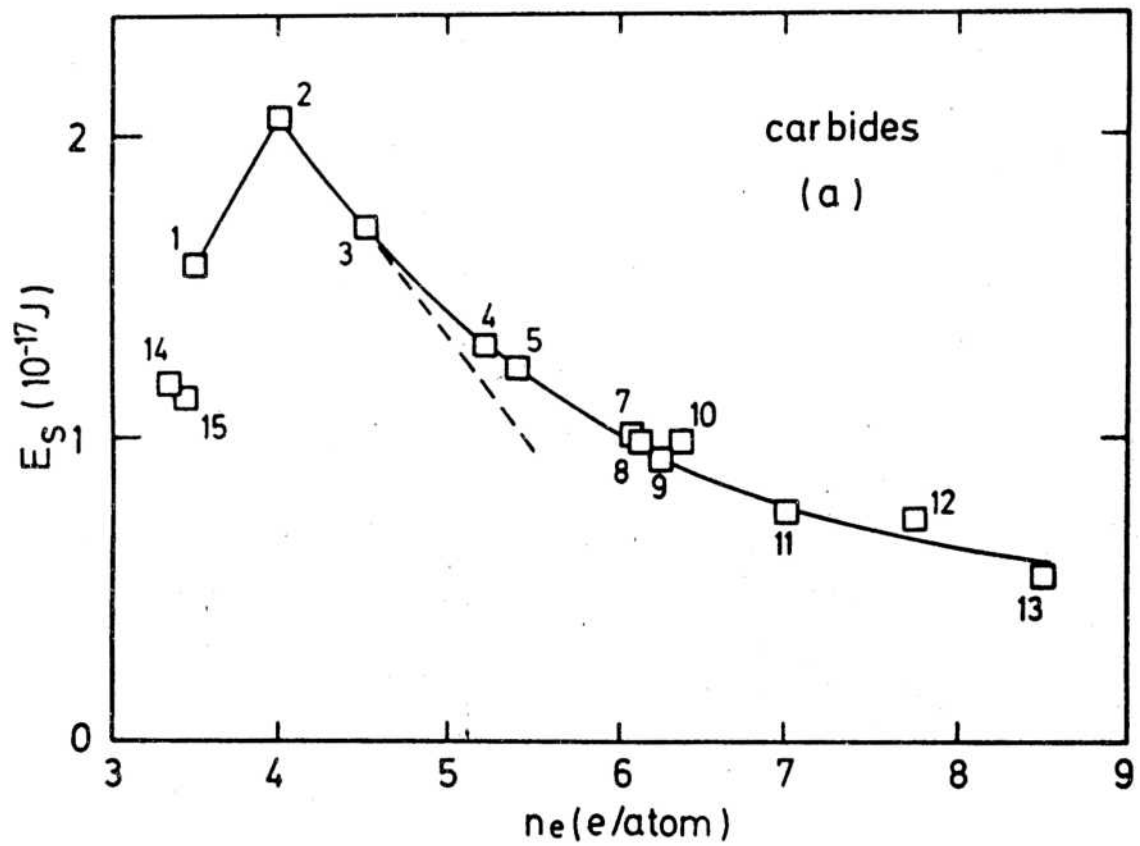
Fig. 8 The solubility of N in liquid Co-Fe solutions according to various sources of information. The solid line was calculated by combining the present description of the Co-N system with information on the Fe-Co and Fe-N liquid phase, and a ternary interaction parameter $L^{liq}_{Co,Fe,N}$ = -4kJ/mol, obtained in Section 5.2.

Fig. 9 The solubility of N in liquid Co-Ni solutions according to various sources of information. The solid line was calculated by combining the present description for the Co-N system with information on the Co-Ni and Ni-N liquid phase, and a ternary interaction parameter $L^{liq}_{Co,N,Ni}$ = -10kJ/mol, obtained in Section 5.2.

Fig. 10 The Co-N phase diagram calculated using the termodynamic description arrived at in the present work, Table I. The dashed line labelled T_C^{hcp} represent the composition dependence of the Curie temperature of the hexagonal nitride phase based on the hcp structure of Co. ε(f) and ε(p) denote ferromagnetic and paramagnetic states of that phase, respectively. The present calculation predicts a miscibility gap in the ε nitride phase. The ε(f) + ε(p) two phase equilibrium is stable between 1167 and 1142K, and becomes metastable at lower temperatures, which is represented using dashed lines.

Fig. 11 The Fe-N phase diagram calculated using the thermodynamic description assessed by Frisk[18].

Fig. 12 The Ni-N phase diagram calculated using the thermodynamic description obtained by Fernández Guillermet and Frisk[9].


carbides
(a)
E_S (10^{-17} J)
n_e (e/atom)
0
1
2
3
4
5
6
7
8
9
1
2
3
4
5
7
8
9
10
11
12
13
14
15

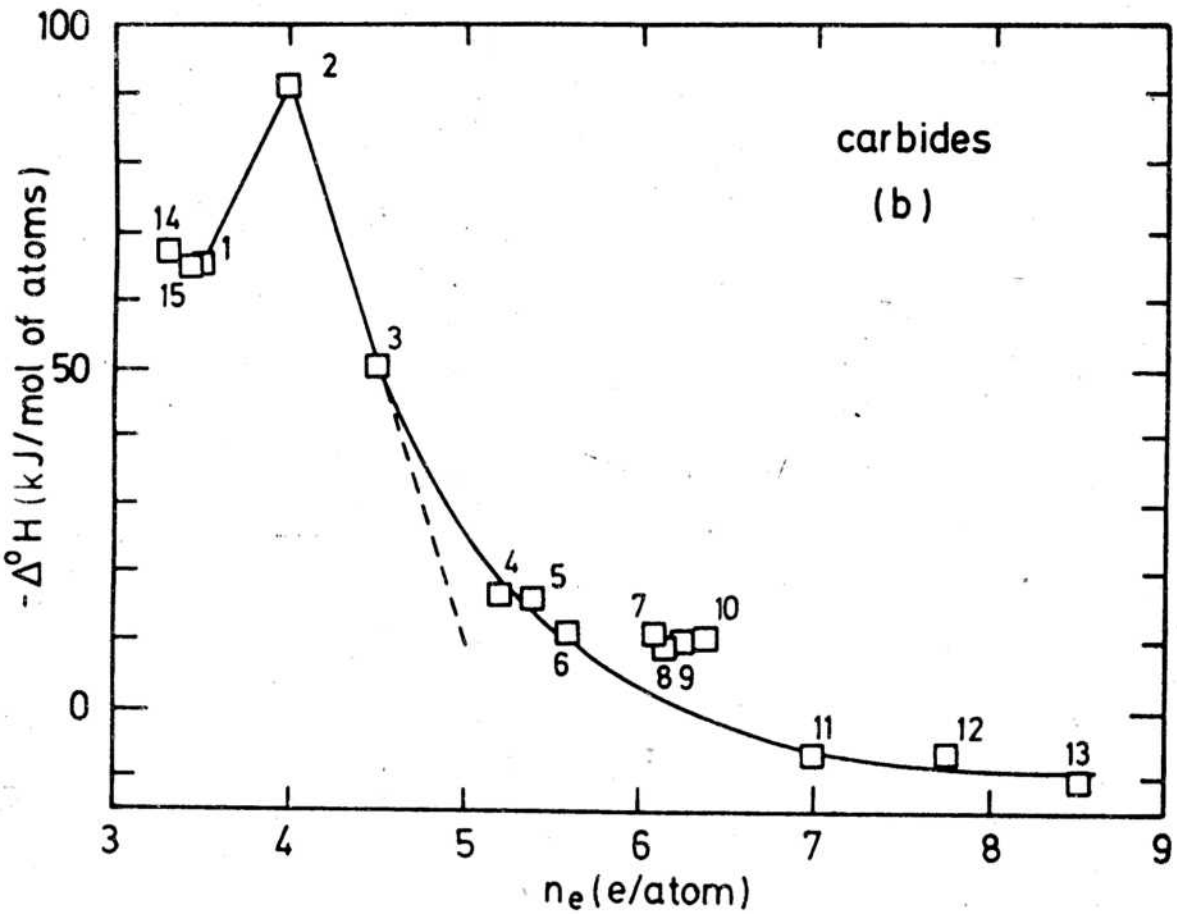
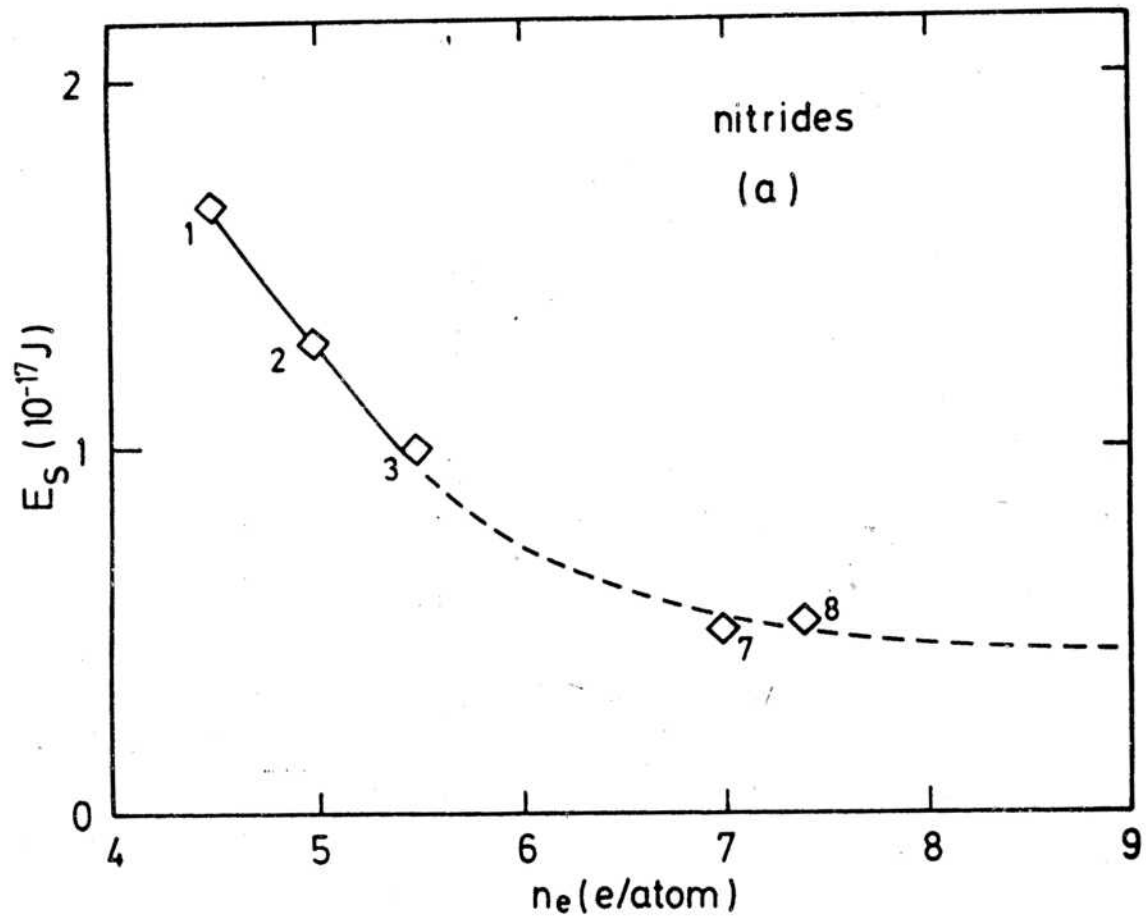

carbides
(b)
$-\Delta^{\circ}H$ (kJ/mol of atoms)
n_e (e/atom)
0
50
100
3
4
5
6
7
8
9
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15

Fig.1


nitrides
(a)
E_S (10^{-17} J)
n_e (e/atom)
0
1
2
4
5
6
7
8
9
1
2
3
7
8

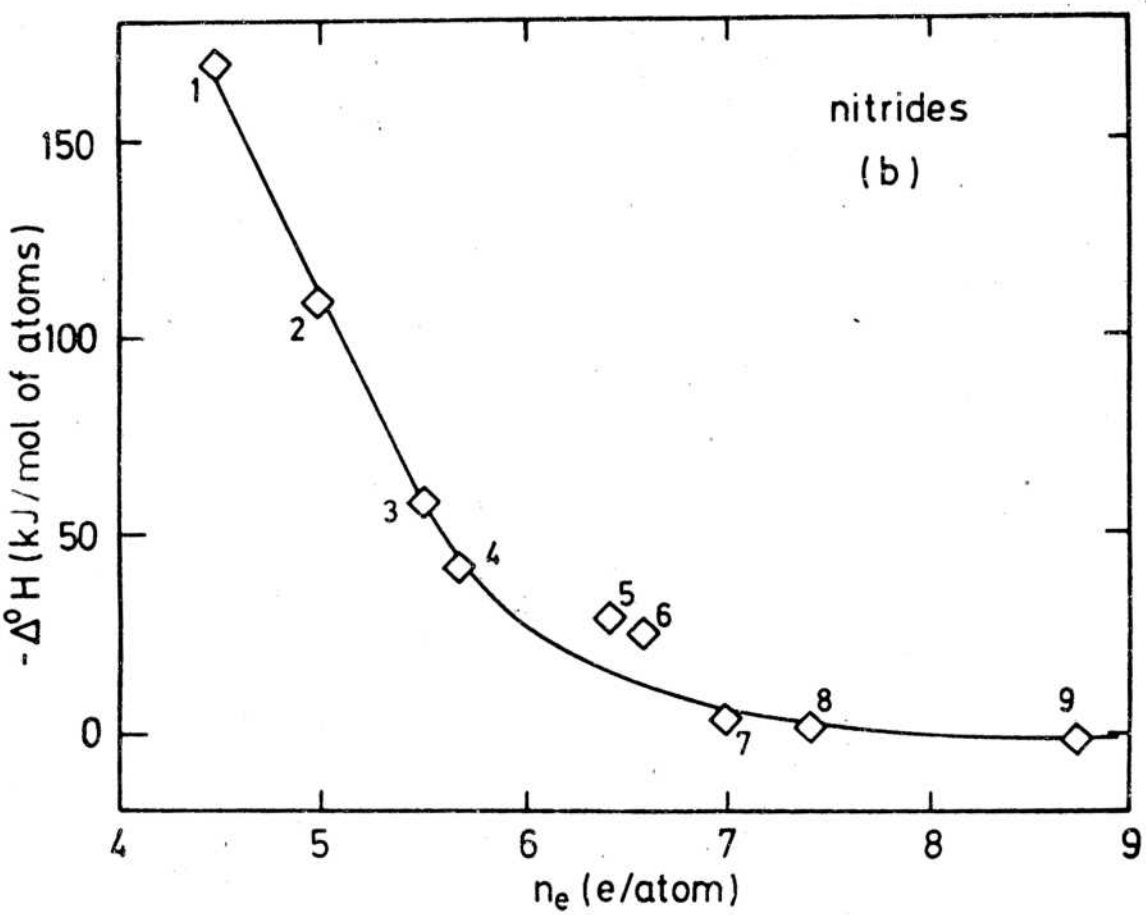

nitrides
(b)
$-\Delta^0 H$ (kJ/mol of atoms)
n_e (e/atom)
0
50
100
150
4
5
6
7
8
9
1
2
3
4
5
6
7
8
9

Fig.2

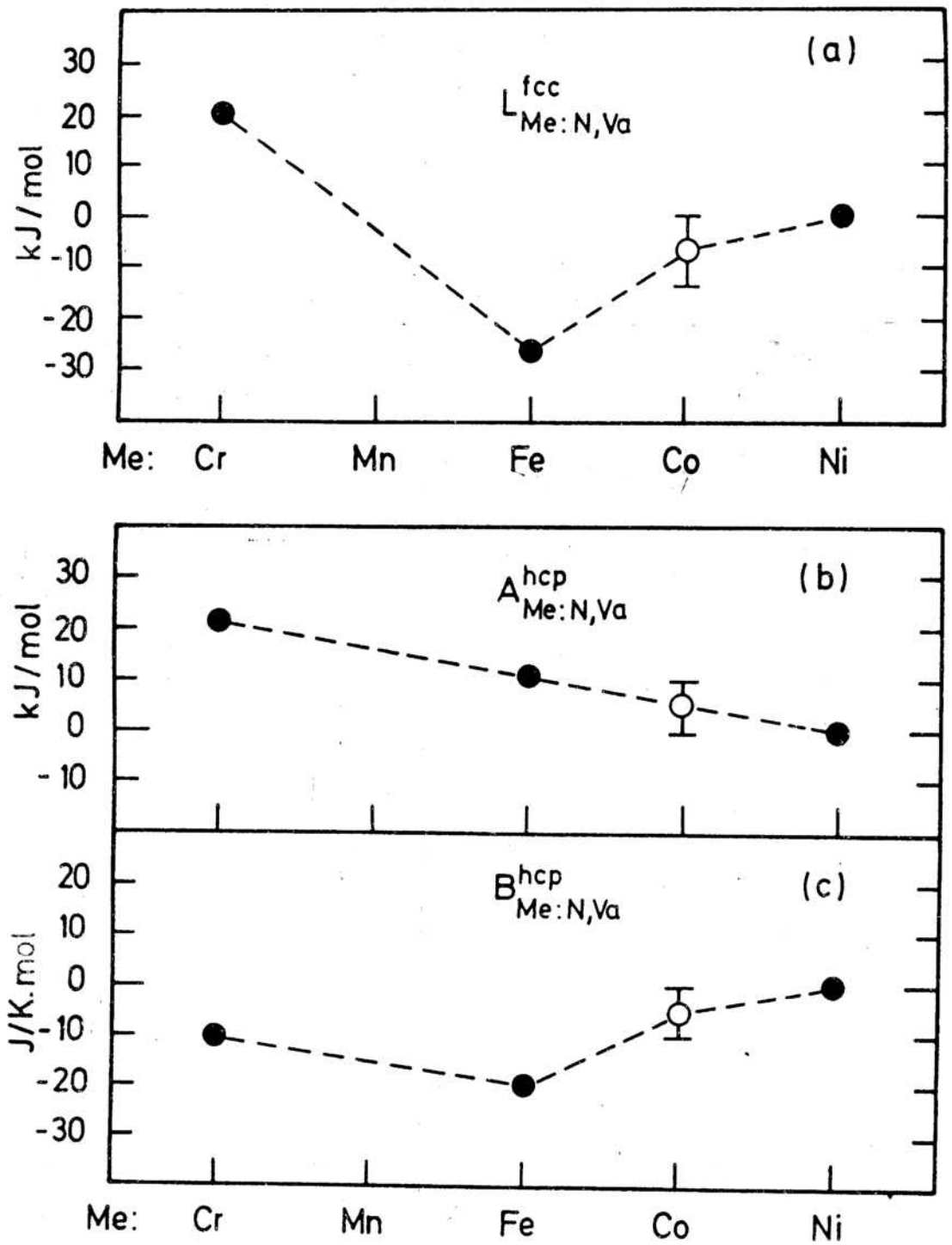

(a)
$L^{fcc}_{Me:N,Va}$
kJ/mol
30
20
10
0
-10
-20
-30
Me: Cr Mn Fe Co Ni
(b)
$A^{hcp}_{Me:N,Va}$
kJ/mol
30
20
10
0
-10
(c)
$B^{hcp}_{Me:N,Va}$
J/K.mol
20
10
0
-10
-20
-30
Me: Cr Mn Fe Co Ni

Fig.3

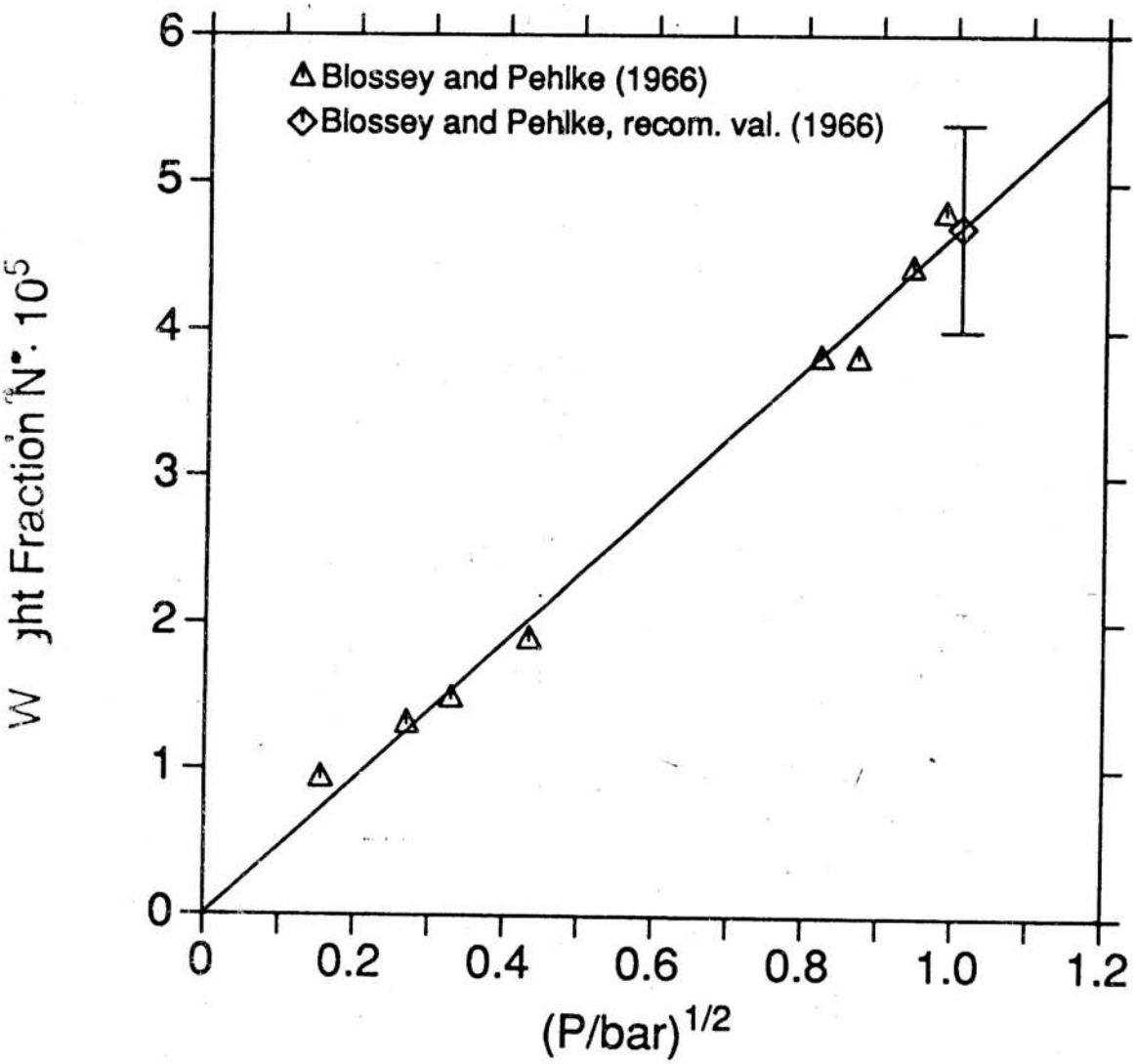

Blossey and Pehlke (1966)
Blossey and Pehlke, recom. val. (1966)
W ght Fraction N • 10^5
(P/bar)^1/2
0
1
2
3
4
5
6
0
0.2
0.4
0.6
0.8
1.0
1.2

Fig.4

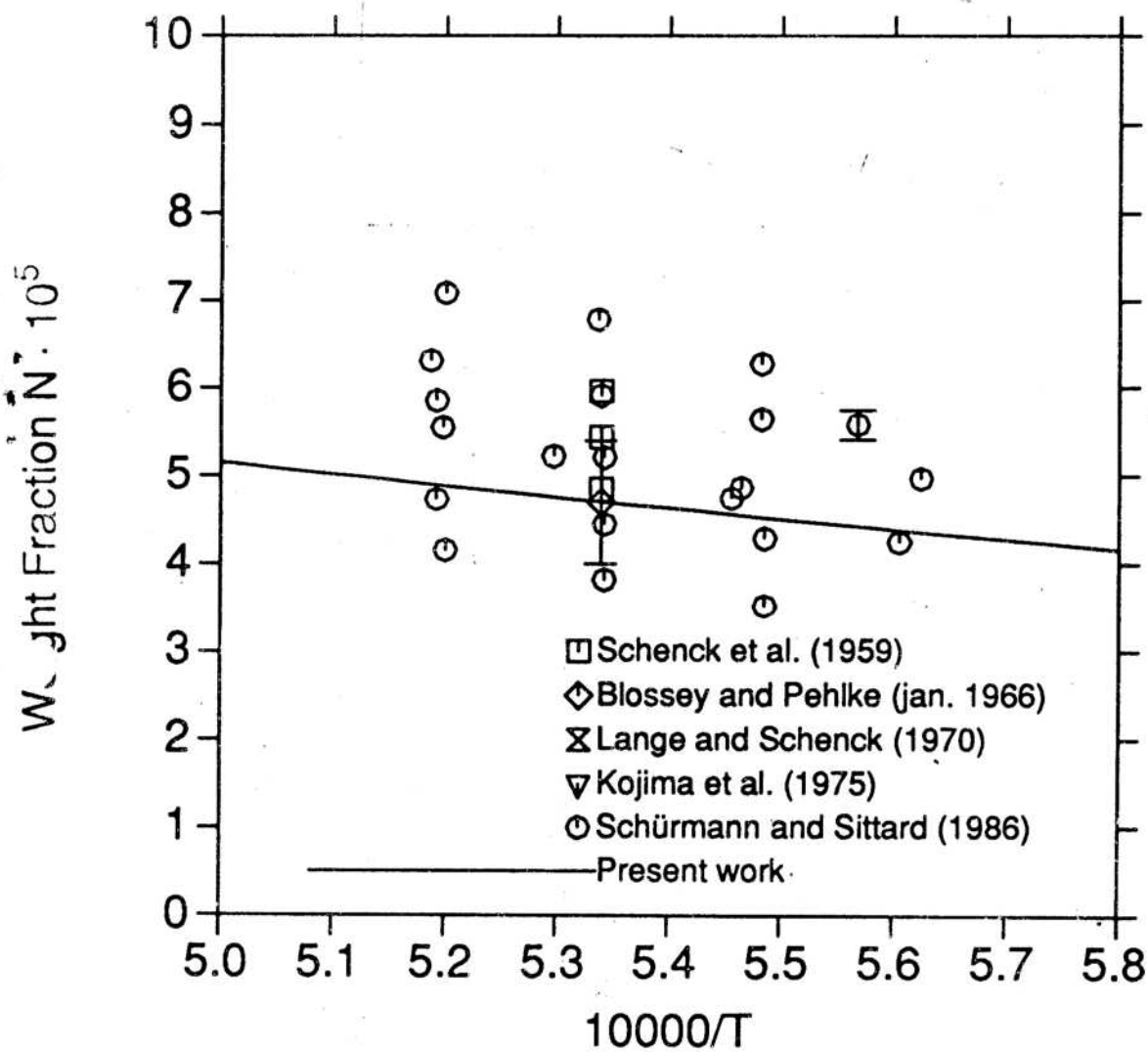

W. ght Fraction N · 10^5
10
9
8
7
6
5
4
3
2
1
0
5.0
5.1
5.2
5.3
5.4
5.5
5.6
5.7
5.8
10000/T
Schenck et al. (1959)
Blossey and Pehlke (jan. 1966)
Lange and Schenck (1970)
Kojima et al. (1975)
Schürmann and Sittard (1986)
Present work

Fig.5

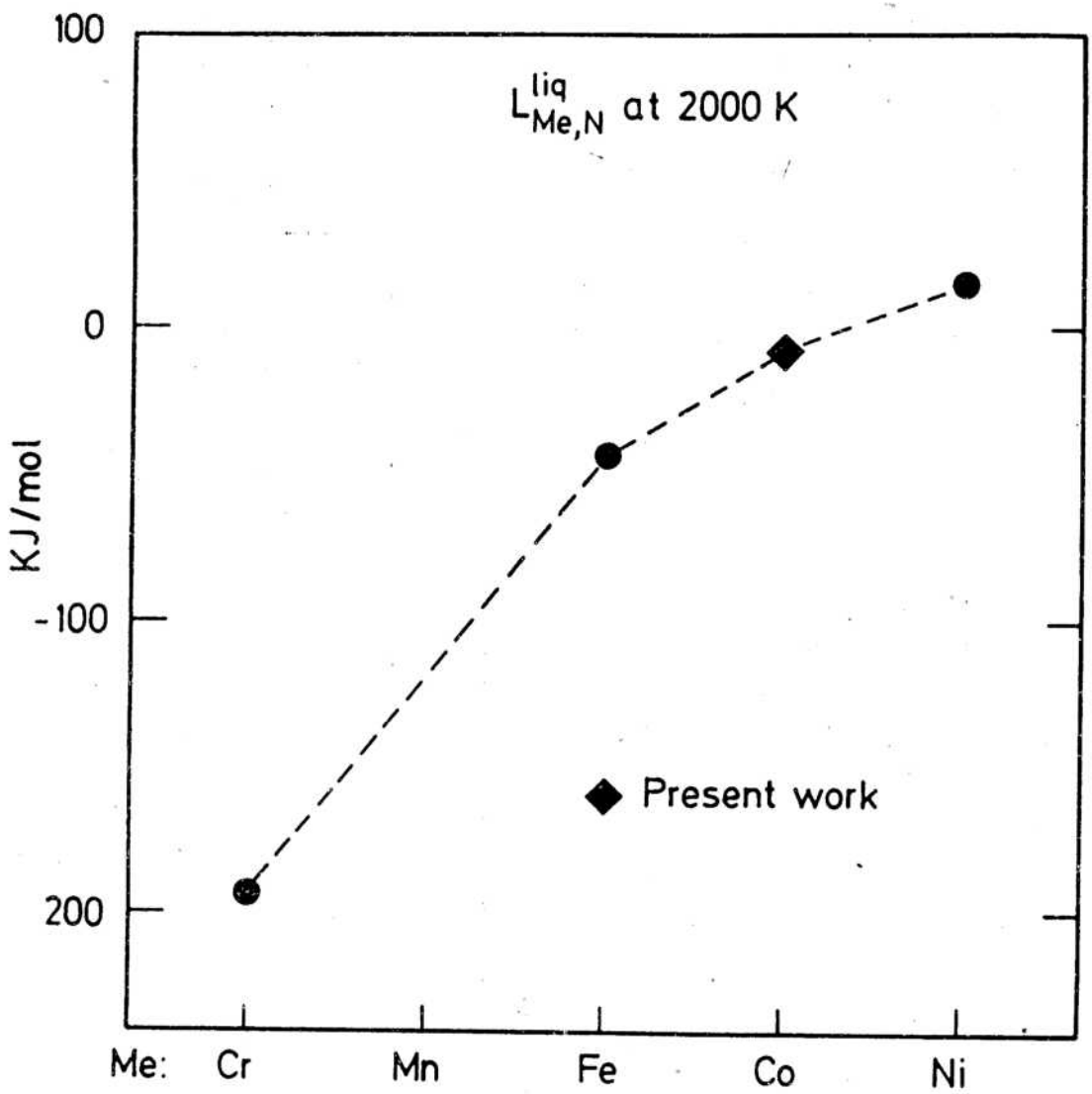

100
0
-100
200
KJ/mol
$L^{liq}_{Me,N}$ at 2000 K
Present work
Me:
Cr
Mn
Fe
Co
Ni

Fig.6

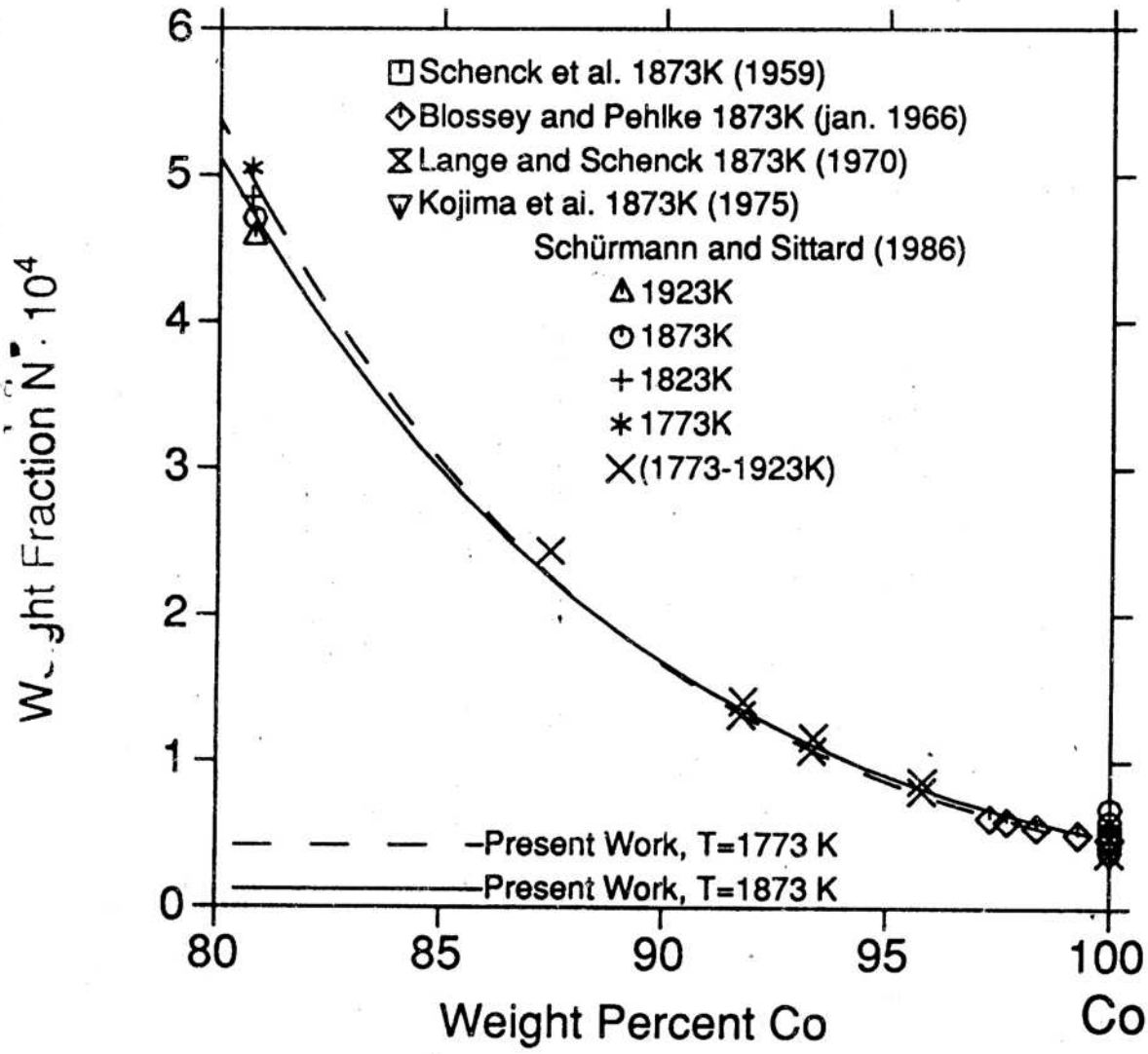

Schenck et al. 1873K (1959)
Blossey and Pehlke 1873K (jan. 1966)
Lange and Schenck 1873K (1970)
Kojima et ai. 1873K (1975)
Schürmann and Sittard (1986)
1923K
1873K
1823K
1773K
(1773-1923K)
–Present Work, T=1773 K
Present Work, T=1873 K
Weight Fraction N · 10^4
Weight Percent Co
Co
0
1
2
3
4
5
6
80
85
90
95
100

Fig.7

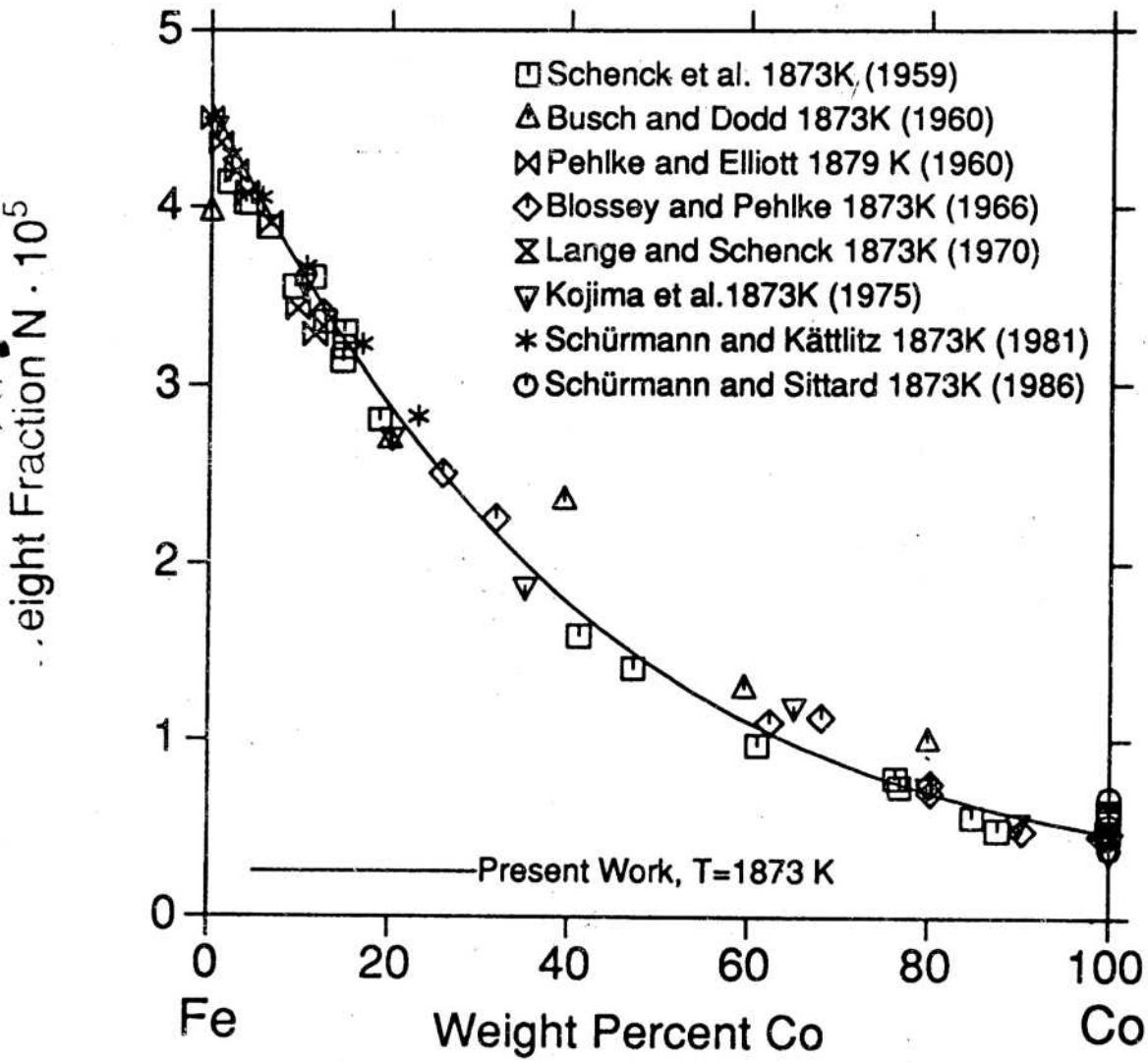

Weight Fraction N · 10^5
5
4
3
2
1
0
Schenck et al. 1873K (1959)
Busch and Dodd 1873K (1960)
Pehlke and Elliott 1879 K (1960)
Blossey and Pehlke 1873K (1966)
Lange and Schenck 1873K (1970)
Kojima et al.1873K (1975)
Schürmann and Kättlitz 1873K (1981)
Schürmann and Sittard 1873K (1986)
Present Work, T=1873 K
0
20
40
60
80
100
Fe
Weight Percent Co
Co

Fig.8

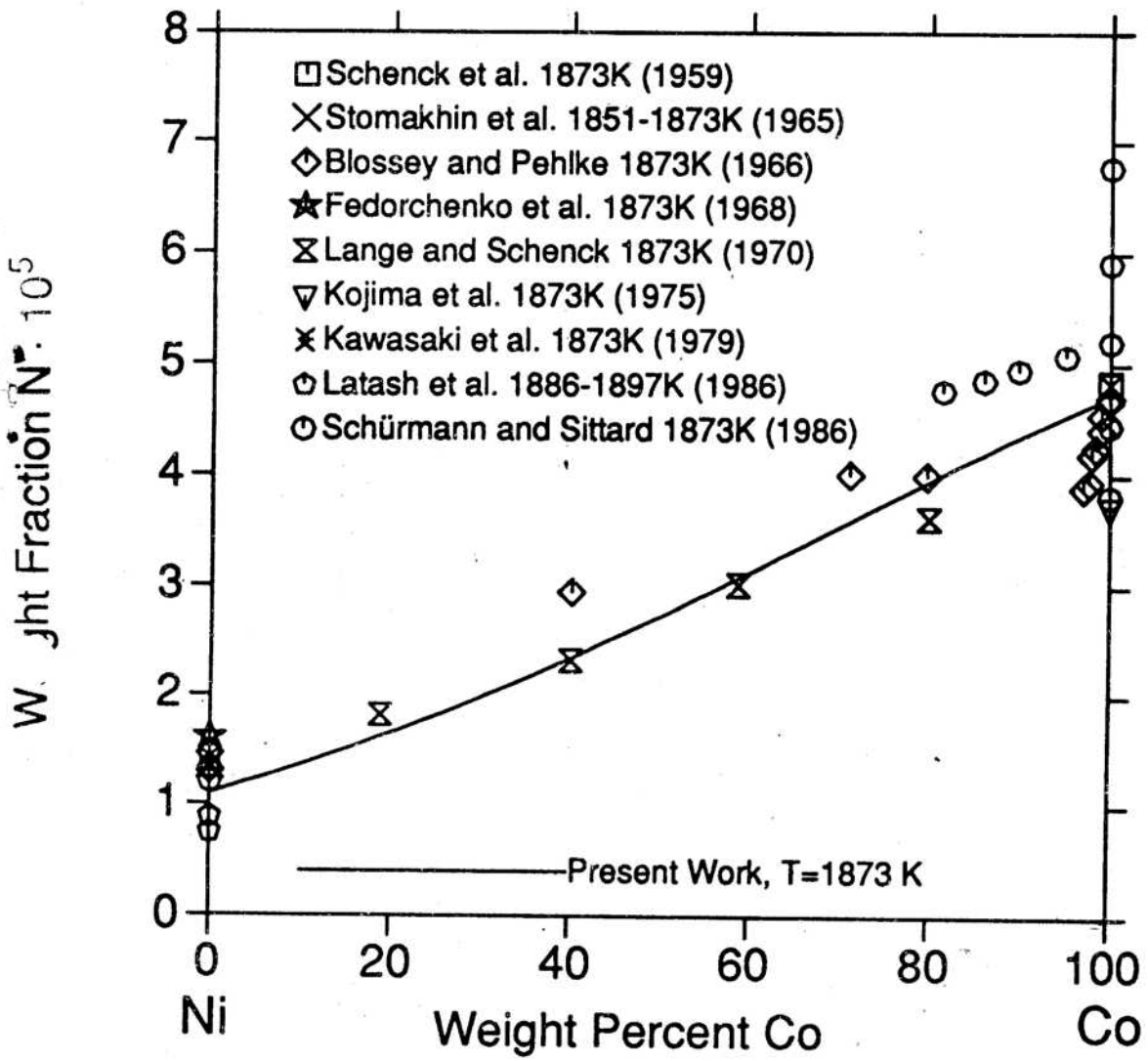

W. ght Fraction N: 10^5
8
7
6
5
4
3
2
1
0
Schenck et al. 1873K (1959)
Stomakhin et al. 1851-1873K (1965)
Blossey and Pehlke 1873K (1966)
Fedorchenko et al. 1873K (1968)
Lange and Schenck 1873K (1970)
Kojima et al. 1873K (1975)
Kawasaki et al. 1873K (1979)
Latash et al. 1886-1897K (1986)
Schürmann and Sittard 1873K (1986)
Present Work, T=1873 K
0
20
40
60
80
100
Ni
Weight Percent Co
Co

Fig.9

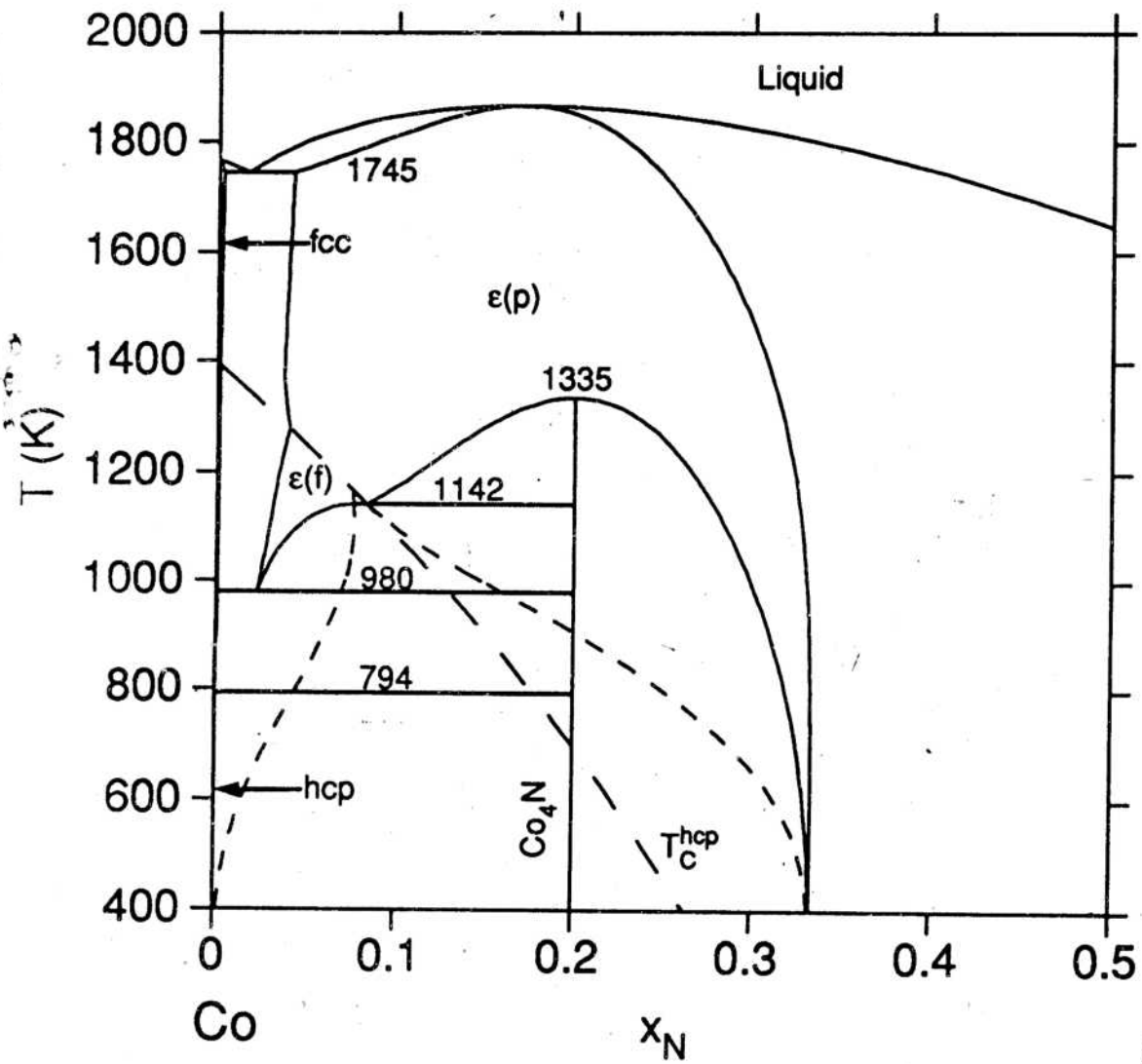

2000
1800
1600
1400
1200
1000
800
600
400
T (K)
Liquid
1745
fcc
ε(p)
1335
ε(f)
1142
980
794
hcp
Co_4N
T_C^{hcp}
0
0.1
0.2
0.3
0.4
0.5
Co
x_N

Fig.10

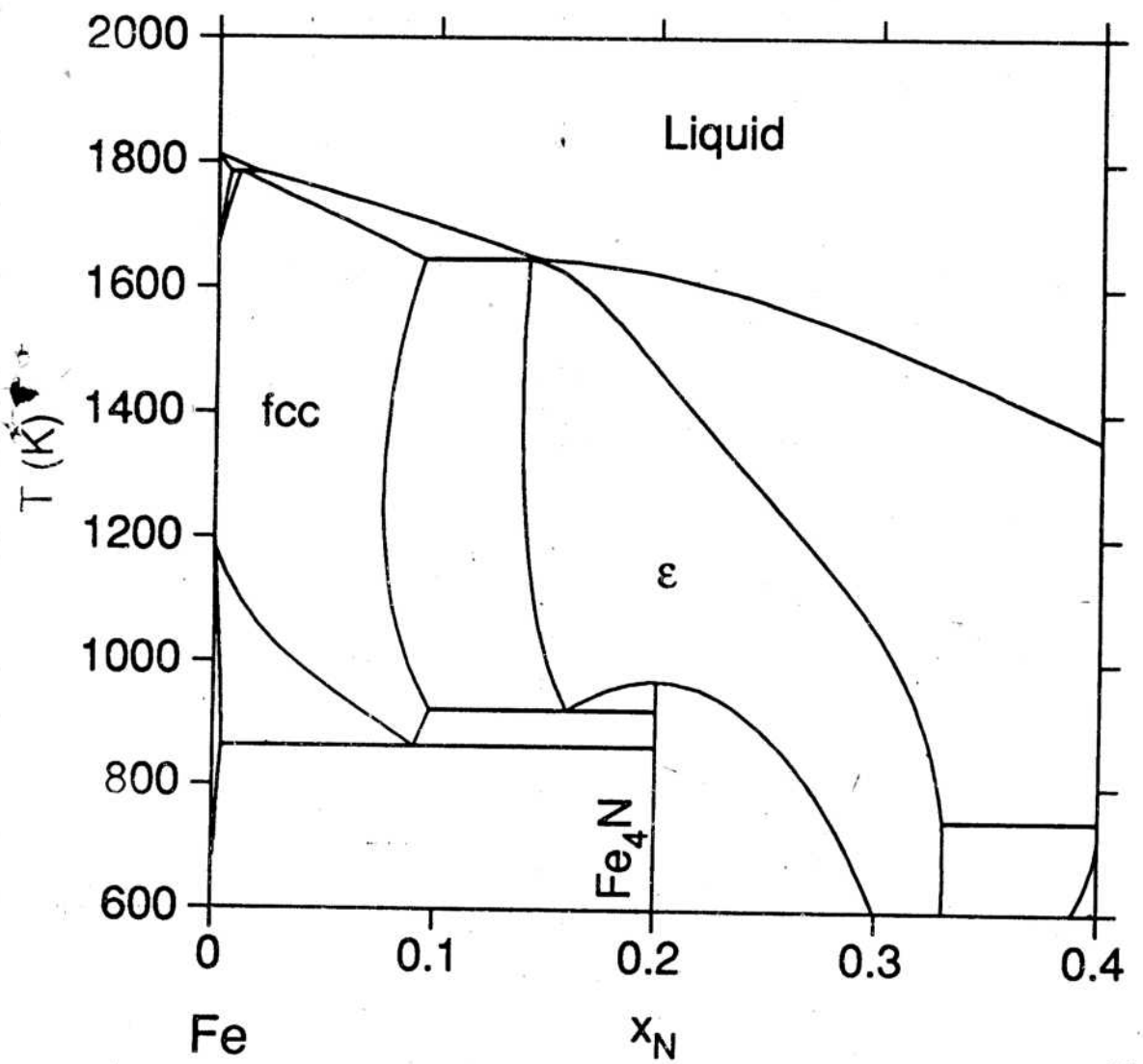

2000
1800
1600
1400
1200
1000
800
600
T (K)
Liquid
fcc
ε
Fe_4N
0
0.1
0.2
0.3
0.4
Fe
x_N

Fig.11

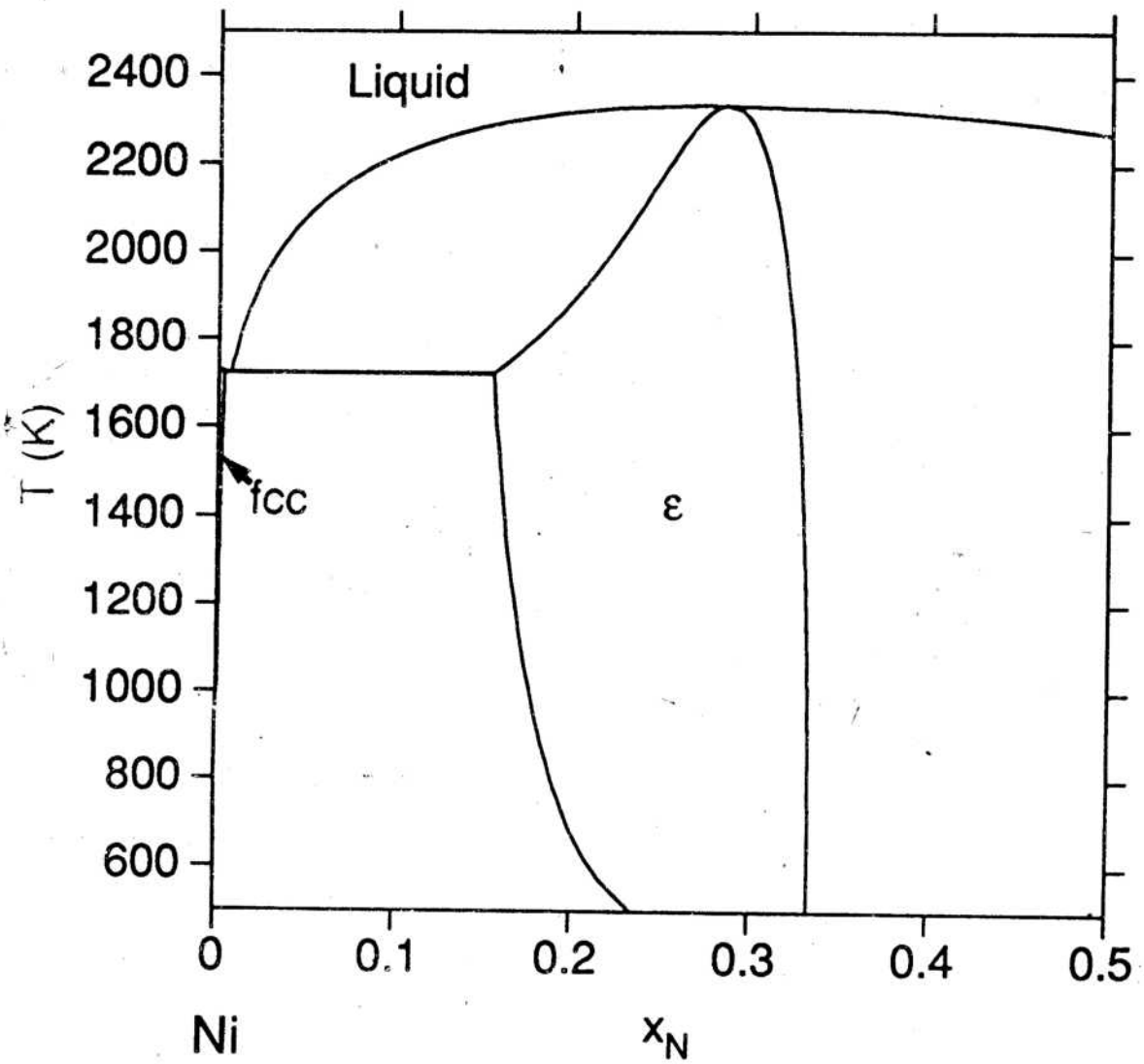

Liquid
fcc
ε
T (K)
2400
2200
2000
1800
1600
1400
1200
1000
800
600
0
0.1
0.2
0.3
0.4
0.5
Ni
x_N

Fig.12