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Thermochemical assessment and systematics of bonding strengths in solid and liquid "MeN" 3d transition metal nitrides

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Abstract

Thermodynamic data provide a kind of information on the cohesive properties of materials which is appropriate for the analysis of regularities and trends across the periodic table. This approach has been applied to the study of bonding trends in solid and liquid MeN nitride phases with Me being Sc, Ti, V, Cr, Mn, Fe, Co or Ni. The bonding strength is characterized by using a quantity introduced by us which measures the energy gained when forming the substance from the elements. This quantity, called the bonding enthalpy, is evaluated for both stable and metastable solid MeN phases with the (cF8) NaCl-type structure. Stable phases are treated by relying on calorimetric data, while the properties of metastable phases are obtained from calculations based on the compound energy model (CEM) for interstitial solutions. This analysis is complemented with a study of the bonding enthalpy of MeN liquid nitrides, which are considered in a special ordered state that is comparable with the (cF8) structure. Information about these liquid phases is obtained from the interaction energies that are involved in the nearest-neighbour bond energy model (NN-BEM) for condensed mixtures. A complete account is given of the use of the CEM and NN-BEM in a thermochemical characterization of bonding strengths. The bonding enthalpies arrived at in this work are used in establishing trends across the 3d transition series which are considered in the light of recent studies of the electronic structure of NaCl-type structure carbides and nitrides. In addition, a detailed comparison is performed with the approach to cohesion in alloys developed by Miedema and coworkers. Our analysis reveals significant systematic discrepancies. Finally, the information obtained by us is applied in examining theoretical and empirical generalizations about the predominance of chemical bonding effects in the heat of formation of compounds.

1. Introduction

Thermodynamic quantities provide a kind of information on the bonding behaviour of materials which is well adapted for systematic studies of trends and regularities. For instance, trends in the interatomic forces of the elements have often [1] been discussed by plotting the property of interest (*e.g.* bulk modulus, low temperature Debye temperature or cohesive energy) as a function of the position of the element in the periodic table. When studying binary alloys and compounds, there are various possible choices. In this paper we shall focus on the energy gained when forming a substance from the elements. For many stable phases this energy change, which we shall measure using a quantity called the bonding enthalpy, can be obtained directly from standard measurements of the heat of formation. However, a complete systematic study of a class of substances (*e.g.* those formed by metals from the same row of the periodic table) will have to deal with systems which are poorly known from experiments and with metastable phases. In those cases one needs methods to extract enthalpy-of-formation values from other type of data. The main purpose of the present paper is to present a possible approach to this problem which is based on models for the thermochemical properties of condensed phases. We shall discuss in detail the use of these models to obtain information on bonding strength and apply the results to transition metal alloys.

This work continues a line of research where thermodynamic data [2–4] and band structure calculations [5–7] were used to establish and explain trends in the bonding properties of compounds formed by metals of the 3d [2–5], 4d [3, 6] and 5d transition metal series [3, 7]. Previous studies on stable and metastable MeC

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transition metal carbides with the (cF8) NaCl-type structure demonstrated the existence of a well-defined pattern in the variation of the enthalpy of formation and other cohesive properties when studied as a function of the average number of valence electrons per atom in the compound. A similar pattern has been observed in a study of complex 3d transition metal carbides [4], which encourages a systematic study of the transition metal nitrides. In this paper we consider MeN phases with the (cF8) NaCl-type structure. The experimental information about these nitrides of the 3d transition metals is restricted, because the NaCl-type structure does not appear as a stable phase in the phase diagram of the Me–N systems with Me≡Mn, Fe, Co or Ni. However, recent work [4, 8–11] has shown that enthalpy-of-formation values for metastable MeX(cF8) compounds (with X≡C or N) can be extracted from experimental data on the phase diagram and thermochemical properties of Me–X systems by applying a particular thermodynamic model for the Gibbs energy of interstitial phases, namely the compound energy model (CEM) [12, 13]. In the present work thermodynamic values obtained by applying the CEM to the Mn–N, Fe–N, Co–N and Ni–N systems will be combined with direct measurements for the remaining systems in a study of the enthalpy of formation and bonding enthalpy of MeN(cF8) nitrides formed by Sc, Ti, V, Cr, Mn, Fe, Co and Ni.

When searching for a reliable description of trends across the periodic table, it is convenient to examine various quantities and assess the input information until a consistent picture is achieved. By applying this procedure to transition metals [14], their carbides [2, 4] and diborides [3, 15], it has been possible to detect a strong covariation of the bonding properties which has proven very useful in systematizing the available information and in predicting unknown thermodynamic values. Looking for analogous correlations, we shall introduce an additional measure of bonding strength in nitrides which is extracted from information on the liquid phase. A natural candidate to compare with a (cF8) nitride is a liquid solution with composition MeN, but liquids with such a high N content are not stable in the systems of interest here. However, we find that useful information can be obtained by applying the nearest-neighbour bond energy model (NN-BEM) [16]. More specifically, we rely on the NN-BEM and obtain enthalpies of formation for certain ordered liquid phases with formula MeN which are used in establishing trends for condensed nitrides.

Much of this work focuses on the estimation of thermodynamic properties for alloys and compounds and a pertinent question is the relation between the present values and the predictions of the scheme developed by Miedema and coworkers [17]. Their approach to the enthalpy of formation has been very successful in accounting for the experimental information on stable compounds. Besides, Miedema and coworkers [17] recently presented values for solutions of N in all liquid transition metals. With the information on condensed nitride phases obtained in the present work we perform a detailed comparison with Miedema's predictions which includes metastable MeN(cF8) nitrides and dilute solutions of N in liquid 3d transition metals.

2. Definitions

Experimental values for the enthalpy of formation of the stable (cF8) NaCl-type structure MeN compounds, $\Delta^0H[\mathrm{MeN(cF8)}]^{(\mathrm{st})}$, refer to the reaction

$$\mathrm{Me(st)} + \tfrac{1}{2}\mathrm{N_2(g)} = \mathrm{MeN(cF8)} \tag{1}$$

at $T_0 = 298.15$ K and $P_0 = 101\,325$ Pa. Here "st" denotes the modification of Me which is stable at T_0 and P_0. The stable structures of the elements change along the 3d transition series, so in order to study the contribution to Δ^0H due to variations in the bonding strength of the nitride, it is convenient to consider the formation of the compounds from all Me elements in the same crystal structure. In principle, one could choose as a reference any one of the common metallic structures. The present choice was guided by the following structural considerations. The (cF8) NaCl-type structure may be described as two interpenetrating f.c.c.(cF4) sublattices, one formed by the Me atoms and the other by filling up with N atoms all octahedral interstitial sites of the metallic sublattice. Therefore one could regard the formation of MeN(cF8) as the process of adding N to an f.c.c. metallic structure, in which case it is natural to refer the enthalpy of formation of this nitride to the f.c.c.(cF4) structure of Me. This is expressed by the reaction

$$\mathrm{Me(cF4)} + \tfrac{1}{2}\mathrm{N_2(g)} = \mathrm{MeN(cF8)} \tag{2}$$

The corresponding enthalpy difference, *with a sign change*, will be referred to as the bonding enthalpy for MeN(cF8) and will be represented by $\Delta[\mathrm{MeN(cF8)}]$. This quantity is obtained from the experimental (or estimated) $\Delta^0H[\mathrm{MeN(cF8)}]^{(\mathrm{st})}$ of eqn. (1) as

$$\Delta[\mathrm{MeN(cF8)}] = -\{\Delta^0H[\mathrm{MeN(cF8)}]^{(\mathrm{st})} + \Delta^0H(\mathrm{Me})^{(\mathrm{st/fcc})}\} \tag{3}$$

The second term in eqn. (3) is defined by

$$\Delta^0H(\mathrm{Me})^{(\mathrm{st/fcc})} = {}^0H[\mathrm{Me(st)}] - {}^0H[\mathrm{Me(fcc)}] \tag{4}$$

i.e. it is the enthalpy difference between the stable and f.c.c. structures of the Me metal at T_0 and P_0.

We remark that there are other possible definitions of the bonding enthalpy. For instance, one may wish to separate out from Δ[MeN(cF8)] the expansion energy due to the insertion of the nitrogen atom in the metallic lattice of Me(cF4). However, the application of such a separation requires additional information on f.c.c. Me which is not available from experiments in cases where the f.c.c. structure is not a stable modification of the Me metal (see Section 3.4.). Another reason why we accepted the previous definition of bonding enthalpy is that a recent *ab initio* study [18] of transition metal carbides and nitrides based on linear muffin tin orbitals (LMTO) band structure calculations indicates that the variations in what we have called Δ[MeN(cF8)] across the periodic table are dominated by the change in chemical bonding energy. Therefore we expect Δ[MeN(cF8)] to be appropriate for a study of bonding trends.

The bonding enthalpy introduced above refers to a structure where the nearest neighbours of an atom are atoms of the other kind. Besides, eqn. (2) describes the case where the arrangement of atoms in the Me phase and in the metallic sublattice of MeN is the same. In principle, it is possible to conceive an analogous reaction involving Me and MeN *in the liquid state* and a key idea of the present study was to gain information on the bonding strength from the thermodynamics of such a reaction. In Section 4 we show that application of the NN-BEM to an Me–N mixture leads to values of the enthalpy change $\Delta^0H[\mathrm{MeN(liq)}]^{(\mathrm{liq})}$ for the reaction

$$\mathrm{Me(liq)} + \mathrm{N(liq)} = \mathrm{MeN(liq)} \qquad (5)$$

Here MeN(liq) refers to an ordered liquid mixture where all nearest-neighbour bonds are between atoms of different kinds. In order to emphasize the analogy with the formation of MeN(cF8), we shall focus on the formation of MeN(liq) from Me(liq) and N_2(g), *i.e.*

$$\mathrm{Me(liq)} + \tfrac{1}{2}\mathrm{N_2(g)} = \mathrm{MeN(liq)} \qquad (6)$$

This reaction resembles eqn. (2), with the obvious difference that the atomic arrangement in Me(liq) and in the metallic sublattice of MeN(liq) is not necessarily the same. Nevertheless, it is reasonable to expect that the variations in Δ^0H for eqn. (6) across the 3d transition series will be dominated by the variations in bonding strength of MeN(liq). In line with this expectation, the enthalpy difference of eqn. (6), *with a sign change*, Δ[MeN(liq)], will be referred to as the bonding enthalpy of MeN(liq). This quantity will be obtained from the $\Delta^0H[\mathrm{MeN(liq)}]^{(\mathrm{liq})}$ value for eqn. (5) by using the relation

$$\Delta[\mathrm{MeN(liq)}] = -\{\Delta^0H[\mathrm{MeN(liq)}]^{(\mathrm{liq})} + \Delta^0H(\mathrm{N})^{(\mathrm{liq/gas})}\} \qquad (7)$$

where

$$\Delta^0H(\mathrm{N})^{(\mathrm{liq/gas})} = {}^0H[\mathrm{N(liq)}] - \tfrac{1}{2}{}^0H[\mathrm{N_2(g)}] \qquad (8)$$

In Sections 3 and 4 we explain in detail how the quantities introduced by us can be evaluated from thermodynamic data. In Section 5 we proceed to establish trends and to study the quantitative relation between Δ[MeN(cF8)] and Δ[MeN(liq)].

3. Thermodynamic analysis of solid nitrides

3.1. Stable MeN(cF8) compounds

Stable nitrides with the NaCl-type structure have been reported in the Sc–N, Ti–N, V–N and Cr–N systems and experimental values of the enthalpy of formation for the corresponding stoichiometric MeN(cF8) phases are available for Me≡Ti, V and Cr. The $\Delta^0H[\mathrm{MeN(cF8)}]^{(\mathrm{st})}$ values for TiN, VN and CrN recommended in the JANAF tables [19] were adopted in the present evaluation. Lacking direct measurements of the enthalpy of formation of ScN(cF8), we relied on a recent estimate by Fernández Guillermet and Grimvall [2].

3.2. Gibbs energy of metastable compounds

The phase diagram of the Me–N systems with Me≡Mn, Fe, Co or Ni does not show a stable NaCl-type structure nitride phase and we refer to the corresponding MeN(cF8) phases as metastable. The estimation method for the enthalpy of formation of these compounds, which has previously been applied to carbides [4, 20–22], combines information on two properties of the material, namely the molar Gibbs energy and the entropy at high temperatures. The treatment of the Gibbs energy is considered here and the estimation of the entropy is discussed in Section 3.3.

The Gibbs energy of the metastable MeN nitrides was obtained by analysing phase diagram information on the Me–N systems (Me≡Mn, Fe, Co or Ni) by means of a two-sublattice [13] version of the CEM [12] for interstitial solutions. In this model a non-stoichiometric NaCl-type structure nitride is treated by considering the two sublattices referred to in Section 2. In particular, one can describe the composition range between the stoichiometric MeN(cF8) phase and pure Me metal with the f.c.c.(cF4) structure by accounting for the existence in the non-metallic sublattice of a mixture of N atoms and vacant (Va) interstitial sites. Accordingly, a non-stoichiometric interstitial phase based on the f.c.c. arrangement of metallic Me atoms is represented in the two-sublattice model [13] as $(Me)_1(N,Va)_1$. It is treated with the following expression of the Gibbs energy (G_m) per mole of formula units:

$$\begin{aligned} G_m &= y_{Me}{}^0G_{Me:N} + y_{Va}{}^0G_{Me:Va} \\ &\quad + RT(y_N \ln y_N + y_{Va} \ln y_{Va}) \\ &\quad + \Delta G_m^{mg} + y_N y_{Va} L_{Me:N,Va} \end{aligned} \tag{9}$$

The variable y_i (i=N or Va) measures the fraction of available sites occupied by component i. The quantity ${}^0G_{Me:Va}$ is the Gibbs energy of pure Me with the f.c.c. structure in a non-magnetic state. ${}^0G_{Me:N}$ is the Gibbs energy of a non-magnetic nitride obtained by filling up with N atoms all available octahedral interstitial sites of the f.c.c.(cF4) structure of Me. That nitride has the formula MeN and the (cF8) NaCl-type structure, which means that the ${}^0G_{Me:N}$ parameter of eqn. (9) contains the information on the Gibbs energy of the metastable MeN(cF8) phase that we are searching for. The penultimate term in eqn. (9) represents the magnetic contribution to the Gibbs energy of the phase. This contribution, which is of less relevance for the present analysis. It can be described by using the phenomenological approach due to Inden [23] and Hillert and Jarl [24]. Detailed descriptions of the modelling of ΔG_m^{mg} in Me–N systems have been presented elsewhere [9–11] and will not be repeated. Finally, the parameter $L_{Me:N,Va}$ in eqn. (9) accounts phenomenologically for the interaction between N atoms and vacant interstitial sites.

Thermodynamic data on the interstitial solution of N in Me(cF4) provide Gibbs energy information. It follows from eqn. (9) that one could use these data to evaluate ${}^0G_{Me:N}$, if ${}^0G_{Me:Va}$ and $L_{Me:N,Va}$ are known. ${}^0G_{Me:Va}$ is available from assessments of the thermodynamics of Mn [25], Fe [26], Co [27] and Ni [28]. The quantities ${}^0G_{Me:N}$ and $L_{Me:N,Va}$ were obtained by analysing experimental data on the phase diagram and thermochemical properties of the Mn–N, Fe–N, Co–N and Ni–N systems. In these evaluations, which are discussed in refs. 10, 11, 9 and 8 respectively, the parameters of the CEM were determined by searching for the best fit to the input data via the computer optimization techniques [29] that are usually adopted in the so-called CALPHAD assessments of alloy phase diagrams [30]. However, we remark that an evaluation based on eqn. (9) gives, in principle, information only on the Gibbs energy function ($G=H-TS$) for the MeN(cF8) phase. In order to obtain the enthalpy part (*i.e.* the enthalpy of formation), it is necessary to know the entropy contribution. This contribution was accounted for by including predicted entropy values in the CALPHAD optimizations.

3.3. Entropy predictions for metastable compounds

The estimation procedures for the entropy of compounds have been reviewed in a recent article [31]. Here we summarize only the main points.

The temperature-dependent part of ${}^0G_{Me:N}$ is usually dominated by the lattice vibrations, which may be described by a properly defined Debye temperature. Following Grimvall and Rosén [32, 33], we use an entropy Debye temperature Θ_S. This is obtained from the $\Theta_S(T)$ function that reproduces the vibrational entropy per mole of atoms in the compound, $S_{vib}(T)$, if $\Theta_S(T)$ is inserted in the expression for entropy in the Debye model, S_D:

$$S_{vib}(T) = S_D\left(\frac{\Theta_S(T)}{T}\right) \tag{10}$$

At low temperatures ($T \ll \Theta_S$) $\Theta_S(T)$ varies with T, because the true vibrational spectrum of the compound is not of the Debye form; at high temperatures ($T > \Theta_S$) it shows a smooth decrease with increasing T, caused by the anharmonic softening of the lattice vibrations. To obtain a stable value for Θ_S, we evaluate Θ_S at $T=\Theta_S$ and denote this Θ_S by Θ_S^0. The estimation procedure for the high temperature entropy of MeN(cF8) nitrides was based on constructing a probable $\Theta_S(T)$ function. This was done in two steps. First the Θ_S^0 value was estimated and then one accounted for the decrease in Θ_S with increasing T for $T > \Theta_S^0$. The estimation of Θ_S^0 relied on information about related systems, but Θ_S^0 is not directly suitable for such comparison because it contains the contributions of the atomic masses. However, at high temperatures ($T > \Theta_S/2$) Θ_S essentially measures a logarithmic average of the phonon frequencies and in that particular average the masses separate from the interatomic forces [32]. Therefore one can define a quantity k_S, with the dimension of a force constant (*i.e.* force per length), by

$$\Theta_S^0 = \frac{\hbar}{k_B}\left(\frac{k_S}{M_{eff}}\right)^{1/2} \tag{11}$$

Here M_{eff} is the logarithmic average of the atomic masses, k_B is the Boltzmann constant and $\hbar = 2\pi h$ is the Planck constant. The parameter k_S, which has been referred to as the effective force constant [14], gives a measure of the average interatomic forces in the compound. Recent analyses of transition metal compounds have focused on the quantity E_S, with the dimension of energy, defined as

$$E_S = k_S \Omega^{2/3} \tag{12}$$

Here Ω is the average volume per atom, which is available from X-ray measurements on stable compounds and can be estimated for metastable compounds. The work on 3d transition metal carbides [2, 4] and nitrides [2] and 3d, 4d and 5d transition metal diborides [3, 15] has shown a large degree of regularity in the variation in E_S with the average number of valence electrons per atom, n_e. These regularities and the observed covariation of E_S and other bonding properties have allowed the estimation of E_S (and therefrom Θ_S^0) of a substance from the E_S value of a related substance. This approach has been used to obtain $\Theta_S(T)$ and estimates of the high temperature entropy for MnN [10], FeN [11], CoN [9] and NiN [8], which finally led to their enthalpy of formation at 298.15 K.

3.4. *Calculation of $\Delta[\mathrm{MeN(cF8)}]$*

The $\Delta^0H[\mathrm{MeN(cF8)}]^{(\mathrm{st})}$ values for MeN(cF8) compounds relied upon by us are given in Table 1, but before one can use these values to calculate bonding enthalpies through eqn. (3), it is necessary to know the structural enthalpy difference $\Delta^0H(\mathrm{Me})^{(\mathrm{st/fcc})}$ defined by eqn. (4). Ni is stable in the f.c.c. structure at all temperatures at P_0 and thus we have $\Delta^0H(\mathrm{Ni})^{(\mathrm{st/fcc})}=0$, but the remaining elements of the 3d transition series show other stable structures at T_0 and their $\Delta^0H(\mathrm{Me})^{(\mathrm{st/fcc})}$ values cannot be obtained from experimental data without applying some extrapolation procedure. Mn, Fe and Co show a stable f.c.c. phase at high temperatures and $\Delta^0H(\mathrm{Me})^{(\mathrm{st/fcc})}$ was estimated by extrapolating the description of high temperature properties obtained in thermodynamic assessments of these elements in refs. 25, 26 and 27 respectively. Ti, V and Cr do not show a stable f.c.c. phase at any temperature at $P=P_0$, but estimated values for the enthalpy difference $\Delta^0H(\mathrm{Me})^{(\mathrm{st/fcc})}$ have been obtained from the so-called CALPHAD approach [34], *i.e.* by combining the study of trends across the periodic table with extrapolations in phase diagrams. The structural enthalpy differences selected in the present analysis for Ti [35], V [36] and Cr [37] are listed in Table 1. Lacking information on $\Delta^0H(\mathrm{Sc})^{(\mathrm{st/fcc})}$, we tentatively adopted for Sc the same structural enthalpy difference which has been suggested for Ti [35]. The bonding enthalpy values for all MeN(cF8) nitrides arrived at by using eqn. (3) are presented in Table 1.

TABLE 1. Enthalpies of formation of MeN(cF8) at $T_0=298.15$ K and $P_0=101\,325$ Pa, $\Delta^0H[\mathrm{MeN(cF8)}]^{(\mathrm{st})}$ (eqn. (1)), structural enthalpy differences $\Delta^0H(\mathrm{Me})^{(\mathrm{st/fcc})}$ (eqn. (4)) and bonding enthalpies $\Delta[\mathrm{MeN(cF8)}]$ (eqn. (3)) for Me metals of the 3d transition series

Element (Me)	$\Delta^0H[\mathrm{MeN(cF8)}]^{(\mathrm{st})}$ (kJ (mol MeN)$^{-1}$)	$\Delta^0H(\mathrm{Me})^{(\mathrm{st/fcc})}$ (kJ mol^{-1})	$\Delta[\mathrm{MeN(cF8)}]$ (kJ (mol MeN)$^{-1}$)
Sc	-440^{a}	-6.0^{b}	446
Ti	-337.65^{c}	-6.0^{d}	343.65
V	-217.15^{c}	-7.50^{e}	224.65
Cr	-117.15^{c}	-7.28^{f}	124.43
Mn	-59.16^{g}	-3.11^{h}	62.27
Fe	6.43^{i}	-7.97^{j}	-1.54
Co	37.40^{k}	-0.43^{l}	-36.97
Ni	43.20^{m}	0.0	-43.20

[a] Ref. 2. [b] Present estimate. [c] Ref. 19. [d] Ref. 35. [e] Ref. 36. [f] Ref. 37. [g] Ref. 10. [h] Ref. 25. [i] Ref. 11. [j] Ref. 26. [k] Ref. 9. [l] Ref. 27. [m] Ref. 8.

4. Thermodynamic analysis of liquid nitrides

4.1. *$\Delta^0H[\mathrm{MeN(liq)}]^{(\mathrm{liq})}$ from the bond energy model*

In the nearest-neighbour bond energy model [16] one assumes that the enthalpy H of the binary phase formed *e.g.* by Me and N atoms can be expressed as the sum of the enthalpies associated with the various interatomic bonds, *i.e.*

$$H=H_{\mathrm{Me-Me}}n_{\mathrm{Me-Me}}+H_{\mathrm{Me-N}}n_{\mathrm{Me-N}}+H_{\mathrm{N-N}}n_{\mathrm{N-N}} \qquad (13)$$

where $n_{i\text{-}j}$ represents the number of i-j bonds and $H_{i\text{-}j}$ is the enthalpy of an i-j bond. Equation (13) can be rearranged by taking into account the following relations between the numbers of bonds of various types:

$$n_{\mathrm{Me-Me}}=\tfrac{1}{2}(Zn_{\mathrm{Me}}-n_{\mathrm{Me-N}}) \qquad (14a)$$

$$n_{\mathrm{N-N}}=\tfrac{1}{2}(Zn_{\mathrm{N}}-n_{\mathrm{Me-N}}) \qquad (14b)$$

In eqns. (14a) and (14b) Z is the coordination number and n_i (with $i=\mathrm{Me}$ or N) is the number of atoms of component i in the mixture. By combining eqns. (13), (14a) and (14b) with the assumption that the enthalpy of a bond is independent of the composition of the mixture and the local composition, one can derive the following expression for the enthalpy of formation, ΔH, of the phase:

$$\Delta H=n_{\mathrm{Me-N}}[H_{\mathrm{Me-N}}-\tfrac{1}{2}(H_{\mathrm{Me-Me}}+H_{\mathrm{N-N}})] \qquad (15)$$

The relations considered so far do not involve any assumption about the randomness of the system or the numbers of the various i-j bonds. Thus they should apply, in particular, to a mixture where all nearest-neighbour bonds are between atoms of different kinds. This is the case of the MeN(liq) phase referred to in Section 2. The value of $n_{\mathrm{Me-N}}$ for this phase is obtained by setting $n_{\mathrm{Me-Me}}=n_{\mathrm{N-N}}=0$ in eqns. (14a) and (14b), which yields $n_{\mathrm{Me-N}}=Zn_{\mathrm{Me}}=Zn_{\mathrm{N}}$. If we now take $n_{\mathrm{Me}}=n_{\mathrm{N}}=N_{\mathrm{A}}$, with N_{A} being the Avogadro number, we obtain the enthalpy of formation of MeN(liq) from Me(liq) and N(liq) expressed per mole of formula units of the nitride. This result coincides with the enthalpy difference for eqn. (5), $\Delta^0H[\mathrm{MeN(liq)}]^{(\mathrm{liq})}$, and we can write

$$\Delta^0H[\mathrm{MeN(liq)}]^{(\mathrm{liq})}=ZN_{\mathrm{A}}[H_{\mathrm{Me-N}}-\tfrac{1}{2}(H_{\mathrm{Me-Me}}+H_{\mathrm{N-N}})] \qquad (16)$$

A connection between the quantities on the right-hand side of eqn. (16) and the measured properties of Me–N liquid phases is provided by a particular form of the NN-BEM which is known as the regular solution approximation.

In the substitutional regular solution approximation (SRSA) of the NN-BEM one assumes that the atoms mix at random in the same sublattice, which allows the number of Me–N bonds in eqn. (15) to be calculated from the atomic fractions of Me (x_{Me}) and N (x_{N}). In this way one obtains the enthalpy of formation of one mole of atoms of the mixture as

$$\Delta^{\mathrm{M}}H = x_{\mathrm{Me}}x_{\mathrm{N}}\,{}^{0}L_{\mathrm{Me,N}} \tag{17}$$

Here ${}^{0}L_{\mathrm{Me,N}}$ is the so-called interaction parameter of the SRSA, which is related to the quantities in eqn. (15) by

$${}^{0}L_{\mathrm{Me,N}} = ZN_{\mathrm{A}}[H_{\mathrm{Me-N}} - \tfrac{1}{2}(H_{\mathrm{Me-Me}} + H_{\mathrm{N-N}})] \tag{18}$$

A comparison of eqns. (16) and (18) shows that the interaction parameter ${}^{0}L_{\mathrm{Me,N}}$ of the SRSA directly measures the enthalpy change $\Delta^{0}H[\mathrm{MeN(liq)}]^{(\mathrm{liq})}$ which enters into eqn. (7) for the bonding enthalpy of MeN(liq).

In the remainder of this evaluation we shall deal with $\Delta^{0}H[\mathrm{MeN(liq)}]^{(\mathrm{liq})}$ values extracted from two sources of information about ${}^{0}L_{\mathrm{Me,N}}$. One source consists of measurements of the N activity in Me–N solutions and the N solubility in liquid Me metals of the 3d transition series. These experimental data concern the Gibbs energy of the Me–N solutions and will be treated with the SRSA in Sections 4.2. and 4.3. The other source of information about ${}^{0}L_{\mathrm{Me,N}}$ consists of enthalpy-of-formation values for infinitely dilute solutions of N in Me, $\Delta^{\mathrm{M}}H_{\mathrm{N}}^{\infty}$, predicted by Miedema and coworkers [17]. These values will be treated according to the SRSA by applying the well-known relation for the partial enthalpy of mixing of N,

$$\Delta^{\mathrm{M}}H_{\mathrm{N}} = {}^{0}L_{\mathrm{Me,N}}(1 - x_{\mathrm{N}})^{2} \tag{19}$$

in the limiting case of $x_{\mathrm{N}} = 0$, and then combining this with the previous result for the relation between ${}^{0}L_{\mathrm{Me,N}}$ and $\Delta^{0}H[\mathrm{MeN(liq)}]^{(\mathrm{liq})}$. This procedure yields

$$\Delta^{\mathrm{M}}H_{\mathrm{N}}^{\infty} = {}^{0}L_{\mathrm{Me,N}} = \Delta^{0}H[\mathrm{MeN(liq)}]^{(\mathrm{liq})} \tag{20}$$

By combining Miedema's predictions with eqn. (20), we obtained bonding enthalpies for MeN(liq) phases which can be compared with the values we extract from experiments in the following two subsections.

4.2. Gibbs energy of Me–N solutions in the SRSA

By relying on the SRSA, we express the Gibbs energy per mole of atoms of an Me–N liquid solution as

$$G_{\mathrm{m}}^{\mathrm{liq}} = x_{\mathrm{Me}}\,{}^{0}G_{\mathrm{Me}}^{\mathrm{liq}} + x_{\mathrm{N}}\,{}^{0}G_{\mathrm{N}}^{\mathrm{liq}} + RT(x_{\mathrm{Me}}\ln x_{\mathrm{Me}} + x_{\mathrm{N}}\ln x_{\mathrm{N}}) + x_{\mathrm{Me}}x_{\mathrm{N}}\,{}^{0}L_{\mathrm{Me,N}} \tag{21}$$

where ${}^{0}G_{\mathrm{Me}}^{\mathrm{liq}}$ and ${}^{0}G_{\mathrm{N}}^{\mathrm{liq}}$ are the Gibbs energies for Me and N respectively, which must be known before eqn. (21) can be used to obtain information on ${}^{0}L_{\mathrm{Me,N}}$. ${}^{0}G_{\mathrm{Me}}^{\mathrm{liq}}$ is available from thermodynamic assessments of the liquid phase in Me metals of the 3d transition series [25–28], but ${}^{0}G_{\mathrm{N}}^{\mathrm{liq}}$ refers to a state of N which is not accessible to experiments. Therefore we shall use values of ${}^{0}G_{\mathrm{N}}^{\mathrm{liq}}$ which have been obtained previously [38] by extrapolation of liquid solution data on various Me–N systems of the 3d and 4d transition series. When performing such extrapolation [38], one must account for possible small deviations from the regular solution behaviour. This was done phenomenologically by letting the coefficient of the $x_{\mathrm{Me}}x_{\mathrm{N}}$ term of eqn. (21) vary with composition according to the so-called Redlich–Kister [39] power series. The last term in eqn. (21) was then replaced by

$$x_{\mathrm{Me}}x_{\mathrm{N}}[{}^{0}L_{\mathrm{Me,N}} + {}^{1}L_{\mathrm{Me,N}}(x_{\mathrm{Me}} - x_{\mathrm{N}}) + {}^{2}L_{\mathrm{Me,N}}(x_{\mathrm{Me}} - x_{\mathrm{N}})^{2} + \ldots] \tag{22}$$

where the composition-independent ${}^{i}L$ parameters are in general allowed to vary with temperature according to

$${}^{i}L = {}^{i}A + {}^{i}BT \tag{23}$$

with A and B being constants. In ref. 38 thermodynamic information on the liquid phase of the Fe–N, Cr–N and Mo–N systems was treated simultaneously by using at most two terms of the Redlich–Kister expansion and an expression was obtained for the difference between ${}^{0}G_{\mathrm{N}}^{\mathrm{liq}}$ and the Gibbs energy of gaseous diatomic N, namely

$${}^{0}G_{\mathrm{N}}^{\mathrm{liq}} - \tfrac{1}{2}\,{}^{0}G_{\mathrm{N_2}}^{\mathrm{gas}} = \Delta^{0}H(\mathrm{N})^{(\mathrm{liq/gas})} - T\Delta^{0}S(\mathrm{N})^{(\mathrm{liq/gas})} \tag{24a}$$

$$= 29950 + 59.02T\ (\mathrm{J\ mol^{-1}}) \tag{24b}$$

More recent analyses have shown that combination of eqn. (24b) with the Redlich–Kister expansion leads to a good account of the available information about the liquid phase in other Me–N systems [8–11, 40, 41]. This lends support to the extrapolation procedure for ${}^{0}G_{\mathrm{N}}^{\mathrm{liq}}$ adopted in ref. 38 and encourages the use of eqn. (21) in our evaluation of ${}^{0}L_{\mathrm{Me,N}}$.

4.3. Assessment of ${}^{0}L_{\mathrm{Me,N}}$ and Δ[MeN(liq)]

The evaluation of the bonding enthalpy for the MeN(liq) phase was based on eqn. (7), with $\Delta^{0}H(\mathrm{N})^{(\mathrm{liq/gas})}$ given by the temperature-independent term in eqn. (24b) and with $\Delta^{0}H[\mathrm{MeN(liq)}]^{(\mathrm{liq})}$ obtained from the relation

$$\Delta^{0}H[\mathrm{MeN(liq)}]^{(\mathrm{liq})} = {}^{0}L_{\mathrm{Me,N}} \tag{25}$$

which follows from eqns. (16) and (18). It is evident from the previous discussion of eqn. (22) that the $^{0}L_{\mathrm{Me,N}}$ values which are significant in the present study are those extracted from experimental data obtained in the dilute solution range. The $^{0}L_{\mathrm{Me,N}}$ parameters for Me ≡ Fe, Co and Ni are available from thermodynamic assessments of the Fe–N, Co–N and Ni–N systems and the reader is referred to refs. 38, 9 and 8 respectively for a survey of the data used in the evaluations. Analogous assessments have been performed of the Ti–N [40], V–N [41], Cr–N [38] and Mn–N [10] systems, but they are based on keeping two or more Redlich–Kister terms and therefore cannot be used here. The following procedure was then adopted. The $^{0}L_{\mathrm{Me,N}}$ parameters for Me ≡ V, Cr and Mn were determined by reanalysing in terms of eqn. (21) the experimental data selected in refs. 41, 38 and 10 respectively and disregarding the data for high N contents that cannot be accounted for by using only one Redlich–Kister term. When the information covered a large temperature range, it was necessary to let the parameter $^{0}L_{\mathrm{Me,N}}$ vary linearly with T as in eqn. (23), in which case $\Delta^{0}H[\mathrm{MeN(liq)}]^{(\mathrm{liq})}$ was evaluated by applying eqn. (25) to the enthalpy part of ^{0}L, *i.e.*

$$\Delta^{0}H[\mathrm{MeN(liq)}]^{(\mathrm{liq})}={}^{0}A \tag{26}$$

The information on liquid Ti–N [40] solutions comes from alloys with relatively large N contents and a temperature-dependent regular solution fit to these experiments gives an average interaction energy which does not represent the dilute solution range. Therefore $\Delta^{0}H[\mathrm{TiN(liq)}]^{(\mathrm{liq})}$ was estimated by using the method applied in Section 4.1 to Miedema's predictions of $\Delta^{\mathrm{M}}H_{\mathrm{N}}^{\infty}$. $\Delta^{\mathrm{M}}H_{\mathrm{N}}^{\infty}$ for N in Ti(liq) was extracted from the coefficients of a two-term Redlich–Kister fit to experiments. By applying the formulae [42] for partial quantities in the Redlich–Kister model to the enthalpy part of these ^{0}L and ^{1}L parameters, we found

$$\Delta^{\mathrm{M}}H_{\mathrm{N}}^{\infty}={}^{0}A-{}^{1}A \tag{27}$$

and finally we combined eqn. (27) with eqn. (20) to obtain $\Delta^{0}H[\mathrm{TiN(liq)}]^{(\mathrm{liq})}$. In Section 5 we shall show that this procedure leads to satisfactory results for TiN(liq).

The $\Delta^{0}H[\mathrm{MeN(liq)}]^{(\mathrm{liq})}$ values obtained by us for Me ≡ Ti, V, Cr, Mn, Fe, Co and Ni and the corresponding bonding enthalpies Δ[MeN(liq)] are given in Table 2. Because of the lack of experimental data, it was not possible to assess the properties of ScN(liq).

TABLE 2. Enthalpies of formation at T_0=298.15 K and P_0=101 325 Pa, $\Delta^{0}H[\mathrm{MeN(liq)}]^{(\mathrm{liq})}$ (eqn. (5)), and bonding enthalpies Δ[MeN(liq)] (eqn. (7)) of ordered liquid phases MeN(liq) formed by Me metals of the 3d transition series

Element (Me)	$\Delta^{0}H[\mathrm{MeN(liq)}]^{(\mathrm{liq})}$ (kJ (mol MeN)$^{-1}$)	Δ[MeN(liq)] (kJ (mol MeN)$^{-1}$)
Sc		
Ti	−387.99^{a}	358.04
V	−238.54^{a}	208.59
Cr	−141.97^{a}	112.02
Mn	−95.63^{a}	65.68
Fe	−19.93^{b}	−10.02
Co	−7.70^{c}	−22.25
Ni	14.98^{d}	−44.93

^{a}From $^{0}L_{\mathrm{Me,N}}$ assessed in present work, Section 4. ^{b}From $^{0}L_{\mathrm{Fe,N}}$ assessed in ref. 38. ^{c}From $^{0}L_{\mathrm{Co,N}}$ assessed in ref. 9. ^{d}From $^{0}L_{\mathrm{Ni,N}}$ assessed in ref. 8.

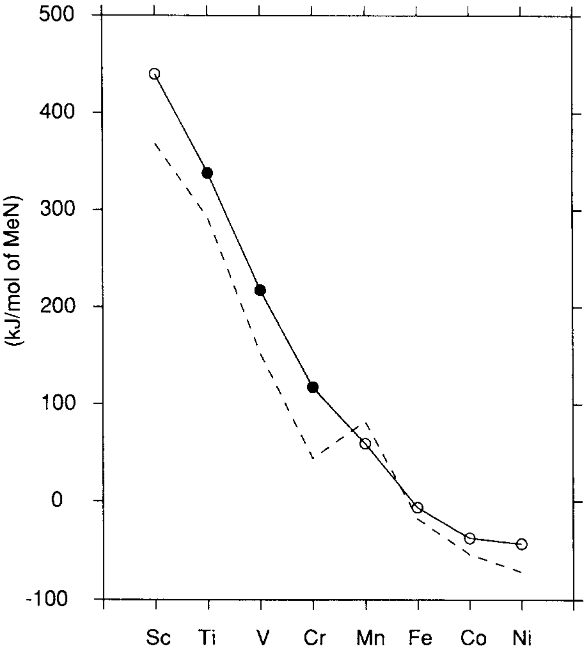

Fig. 1. Negative enthalpies of formation of (cF8) NaCl-type structure nitrides at 298.15 K and 101 325 Pa, $\Delta^{0}H[\mathrm{MeN(cF8)}]^{(\mathrm{st})}$, corresponding to eqn. (1), as a function of the position of the metal Me in the periodic table. Filled symbols connected by a solid curve represent values for stable nitrides obtained from calorimetric measurements. Empty symbols are used to represent an estimate for ScN and the values for the metastable (cF8) nitrides of Mn, Fe, Co and Ni obtained in Section 3. The dashed curve represents the predictions of Miedema and coworkers [17].

5. Results and discussion

5.1. *Trends in the enthalpy of formation of MeN(cF8)*

In Fig. 1 we plot the enthalpy-of-formation values for MeN(cF8) compounds at T_0=298.15 K and P_0=101 325 Pa, with a sign change, $-\Delta^{0}H[\mathrm{MeN(cF8)}]^{(\mathrm{st})}$, as a function of the position of Me in the periodic table. Filled symbols refer to values obtained directly from calorimetric measurements and open symbols refer to estimates and extrapolations. The dashed curve represents the predictions of Miedema's method [17], which are discussed in Section 6. According to Fig. 1, the enthalpy change due to the formation of MeN(cF8) phases becomes less negative on moving to the right of the 3d transition series. This trend, which was suggested by experiments on TiN, VN and CrN, is now observed even in the region where the MeN(cF8) compounds are metastable, *i.e.* for MnN, FeN, CoN and NiN. The values for these metastable compounds have been obtained from extrapolations of experimental data using the CEM [12, 13] and indicate a smooth variation in Δ^0H[MeN(cF8)] with the average number of valence electrons per atom, n_e. This kind of behaviour is in agreement with what is found in theoretical studies of the electron structure, which we refer to later on. Therefore we take the regular variation in the solid curve in Fig. 1 as an indication that the method of analysis applied in Section 3 leads to reliable values for metastable nitrides.

The general pattern of variation in Δ^0H[MeN(cF8)]$^{(st)}$ with n_e in Fig. 1 resembles that obtained for the MeC(cF8) carbides of the 3d transition metal series, which was discussed recently [18] in terms of information [2, 18, 43–45] about the electron structure of carbides and nitrides. Thus it is interesting to examine Fig. 1 in the light of the picture of bonding emerging from that work [18], which may be summarized as follows. At low values of n_e the chemical bonding in the MeX compounds is dominated by the hybridization of metallic d electron states with the p electron states from the non-metal atoms. These p–d hybridized states are of bonding or antibonding character. A maximum in bonding strength of MeX compounds is observed at the beginning of the 3d series (*i.e.* for TiC and ScN), which is ascribed to the filling of bonding states [2, 18, 43–45]. Increasing n_e involves the progressive filling of antibonding p–d hybridized states and a decrease in the bonding strength. At sufficiently large n_e values the electronic density of states at the Fermi level is dominated by the d electron states of the metal. In that region the enthalpy of formation of MeC carbides of the 3d transition series shows smaller variations with n_e and a tendency to reach a constant value. Therefore the electronic states at large n_e have been described as non-bonding [18]. From the results in Fig. 1 we conclude that this picture of variation in bonding strength, which has mainly been tested against thermodynamic data for carbides, accounts very well for the enthalpy trends in nitrides established in this work.

5.2. *Correlation of bonding enthalpies for MeN phases*

A significant finding of recent theoretical work [18] is that variations in the Δ^0H *vs.* n_e curve for MeX(cF8) compounds (X≡C or N) are dominated by changes in the chemical bonding energy contribution and that other contributions, *e.g.* expansion energy (see Section 2), are less important. In addition, a recent analysis of data for complex carbides with the formula MeC_x [4] indicates a qualitatively similar variation in Δ^0H with n_e. Some quantitative differences between Δ^0H for the various MeC_x carbides are noted, which have been ascribed [18] to differences in the number of bonds between metal and non-metal atoms, *i.e.* to differences in the Me:X ratio in the compound. In order to test this picture of bonding, one should compare phases with the same formula and different structures, but experimental information on such cases seems to be generally lacking. In view of this fact, we have in this work considered a metastable ordered liquid phase with the same number of Me–N bonds as MeN(cF8) and studied its enthalpy of formation. Besides, we have introduced a measure of the bonding strength which accounts for the difference between the reference states for Δ^0H of solid and liquid nitrides and we can now make a systematic analysis of the bonding strength of these two condensed phases.

A comparison between Δ[MeN(cF8)] (solid curve) and Δ[MeN(liq)] (dashed curve) is given in Fig. 2. It is remarkable how close these two quantities are for the 3d transition metals. Various conclusions can be drawn. A first conclusion concerns the predominance of chemical bonding effects on the enthalpy of formation of this class of substances. Indeed, Fig. 2 shows that it is possible to approximate Δ^0H of a perfectly ordered (cF8) structure by looking at another condensed phase

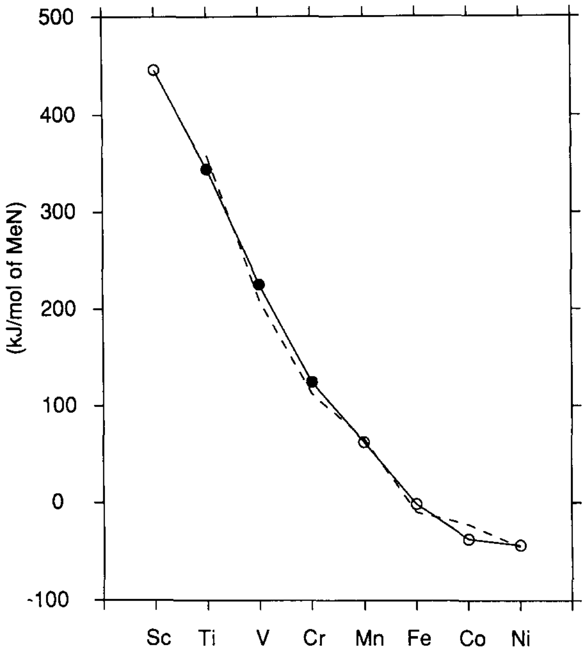

Fig. 2. Bonding enthalpies of MeN(cF8) nitrides, Δ[MeN(cF8)] (symbols connected by a solid curve), and of ordered liquid phases MeN(liq), Δ[MeN(liq)] (dashed curve), as a function of the position of Me in the periodic table. Filled symbols represent values from calorimetric measurements. Empty symbols represent values based on estimates (ScN) and thermodynamic extrapolations (MnN, FeN, CoN and NiN).

of unspecified structure but with the same number of bonds between metal and non-metal atoms per formula unit. This result supports the general conclusions from the work [18] on (cF8) and complex [4] carbides. Further, Fig. 2 demonstrates how well we can approximate the experimental bonding enthalpies for the (cF8) structure by using a model which extracts the pair interaction energies from the infinitely dilute solution range. Qualitatively, this is related to the fact that in both cases all nearest neighbours of an N atom are metallic atoms. In addition, Fig. 2 suggests that these two situations can be described with effective pair interaction energies which are fairly similar, in spite of the differences in the next-nearest-neighbour coordination shell. It is interesting to note that this result is compatible with the qualitative picture behind Miedema's model [17], where the enthalpy of formation of a compound is viewed as determined by the amount and strength of the "contacts" between an atom and its nearest neighbours. This encourages a quantitative comparison between the predictions of Miedema and coworkers [17] and the present results, which we give in Section 6.

5.3. *Applicability of thermochemical models for alloys*

Turning now to the assessment procedure applied here, we emphasize that the results in Fig. 2 help us to answer two main questions of the present study. The first question is whether it is possible to combine information on solid and liquid phases in assessing bonding trends. Indeed, as far as the pattern of variation is concerned, the quantities Δ[MeN(cF8)] and Δ[MeN(liq)] provide equivalent information. The second question concerns the possibility of combining two models, the CEM [12, 13] and the NN-BEM [16], which provide complementary approaches to two condensed phases. This leads now to a discussion of some features of these models which are relevant for their application in this study.

The CEM is based on the concept of sublattice, which allowed a simple connection between the arrangement of metallic atoms in MeN(cF8) and in the f.c.c.(cF8) form of Me. A similar comparison between MeN(liq) and Me(liq) cannot be made in the NN-BEM, because in this model a phase is characterized only by the number of nearest-neighbours, Z. This is a basic difference between the two condensed phases involved in eqns. (2) and (6), but a study of the effect upon the bonding enthalpies is beyond what is permitted by the accuracy of the experimental information. From the results in Fig. 2 one could conclude that this effect is probably small.

Another significant feature of this evaluation is that the liquid phases are treated as a substitutional mixture by using eqn. (21), whereas the dissolution of N in solid Me is described as an interstitial solution, eqn. (9). A treatment of the liquid phase based on the SRSA was justified in Section 4 by showing that it leads to interaction parameters which can be interpreted directly as enthalpies of bonding. Furthermore, we have emphasized that the effective interaction energies were extracted from information corresponding to the very dilute solution range. This is important, because for the limiting case of an N atom surrounded by Me atoms the substitutional and interstitial descriptions are indistinguishable and thus should give the same answer. Certainly, the equivalence of these two descriptions will not hold with increasing N content and one should not expect the simple SRSA, which is introduced in eqn. (21), to account very well for experiments at very large N contents. In fact, it is known from studies of the related Me–C liquid solutions [46] that forcing a substitutional model to fit the observed properties of concentrated solutions leads to a stronger composition dependence of the excess Gibbs energy and the need for several Redlich–Kister terms. However, we emphasize that the present treatment does not depend upon the applicability of eqn. (21) to concentrated Me–N solutions. Actually, the properties of these solutions are not known from experiments. The fact that the quantity ${}^0G_N^{liq}$ is involved in eqn. (21) simply expresses the possibility of introducing a hypothetical state of pure N, the Gibbs energy of which can be obtained by extrapolating to $x_N = 1$ the substitutional, essentially regular solution behaviour which accounts well for the experimental data in the dilute solution range.

6. Comparison with Miedema's approach to cohesion in alloys

6.1. *General considerations*

In the "macroscopic atom" model developed by Miedema and coworkers [17] the enthalpy change due to the formation of a binary phase A–B where an atom A is completely surrounded by atoms of B, $\Delta H^{(\mathrm{Mied})}$, is proportional to the weighted sum of the differences $\Delta\phi$ and $\Delta n_{ws}^{1/3}$ between quantities characterizing the elements A and B, *i.e.*

$$\Delta H^{(\mathrm{Mied})} \alpha -P(\Delta\phi)^2 + Q(\Delta n_{ws}^{1/3})^2 \tag{28}$$

Here ϕ and n_{ws} are adjustable parameters which are related to the work function and the electron density at the boundary of the Wigner–Seitz cell in the elements respectively and P and Q are constants. The quantity $\Delta H^{(\mathrm{Mied})}$ is used to treat the enthalpy of formation of compounds (*e.g.* with formula AB) and the enthalpy of formation of infinitely dilute solutions of A in B. Miedema and coworkers [17] have shown that information on these properties in systems formed either by two transition metals or by two non-transition metals can be reasonably well accounted for by eqn. (28) with similar values of the P and Q parameters. In contrast with this, eqn. (28) fails to account for experimental information on alloys and compounds formed by one transition metal and one polyvalent non-transition metal. The discrepancy suggested the existence of an additional negative contribution to the enthalpy of formation. Lacking information about the origin of this contribution, Miedema and coworkers [17] accounted phenomenologically for its effect by simply adding an extra term to eqn. (28). Solid compounds were thus treated using

$$\Delta H^{(\mathrm{Mied})} \propto -P(\Delta\phi)^2+Q(\Delta n_{\mathrm{ws}}^{1/3})^2-R_{\mathrm{sol}} \qquad (29)$$

As a difference from P and Q, which play the role of "universal" parameters, R_{sol} was found to vary with the positions of the elements in the periodic table. In particular, the R_{sol} values obtained by Miedema and coworkers increase with the number of p electrons in the non-transition metal atom. The analysis of liquid alloys suggested a similar effect and an empirical correction term R_{liq} was obtained which is comparable with R_{sol}. More precisely, it was found [17] that

$$R_{\mathrm{liq}}=0.73R_{\mathrm{sol}} \qquad (30)$$

This procedure led to a better description of the information about the sign of the enthalpy of formation for alloys of transition metals with non-transition metals, but the accuracy of the predictions for Me–N systems could be tested only in the few cases where sufficient thermochemical data were available. Since the database for nitrides has been considerably expanded in the present work, it is now possible to perform a detailed test of Miedema's description of stable and metastable MeN phase of the 3d transition metals.

6.2. Accuracy of the predictions for MeN phases

A comparison of the enthalpies of formation of MeN compounds is given in Fig. 1. The general trend in the variation in Miedema's $\Delta^0H[\mathrm{MeN(cF8)}]^{(\mathrm{st})}$ with the position of Me in the periodic table agrees with that established by us, except for the abrupt increase in the magnitude of the predicted enthalpy on going from CrN to MnN. A similar increase has recently been noted for the MnC(cF8) carbide [4], which suggests that this feature might originate from Miedema's description of Mn. In order to test this possibility, we examined the variation in the first two terms in eqn. (29) across the 3d transition series and found that the variation in $(\Delta\phi)^2$ with the position of Me in the periodic table indeed accounts for the trends in the dashed curve presented in Fig. 1. In addition, we note that a plot of Miedema's ϕ parameter *vs.* the position of Me in the 3d transition series shows a dip for Mn. Therefore we suggest that the cause of the peak in Miedema's values of $\Delta^0H[\mathrm{MnN(cF8)}]^{(\mathrm{st})}$ (Fig. 1) is the coupling between the enthalpy of formation and the quantity ϕ, which is an empirical parameter but varies across the periodic table according to the experimental work functions for the elements and thus shows an anomalous decrease for Mn [47].

In addition to the anomaly for MnN(cF8), Fig. 1 shows systematic discrepancies between the predictions of Miedema and coworkers [17] and the present results. Their predictions for $\Delta^0H[\mathrm{MeN(cF8)}]^{(\mathrm{st})}$ are less negative than the values measured calorimetrically for the stable nitrides of Ti, V and Cr as well as the values for the metastable FeN, CoN and NiN obtained in Section 3. The sign of the discrepancy suggests that the additional negative contribution detected by them [17] for p–d bonded compounds is not well accounted for. In addition, Fig. 1 demonstrates that the discrepancy changes along the 3d transition series, decreasing from an average of 61±15 kJ (mol MeN)$^{-1}$ for the three stable nitrides to 19±9 kJ (mol atoms)$^{-1}$ for the metastable nitrides of Fe, Co and Ni. We conclude that an accurate correction to eqn. (29) for MeN(cF8) nitrides of the 3d transition metals should be more negative and should decrease in magnitude with increasing number of valence electrons per atom, n_e, in the compound. The fact that increasing n_e is followed by a decrease in the contribution of p–d hybridization to the cohesive energy of MeN compounds lends some

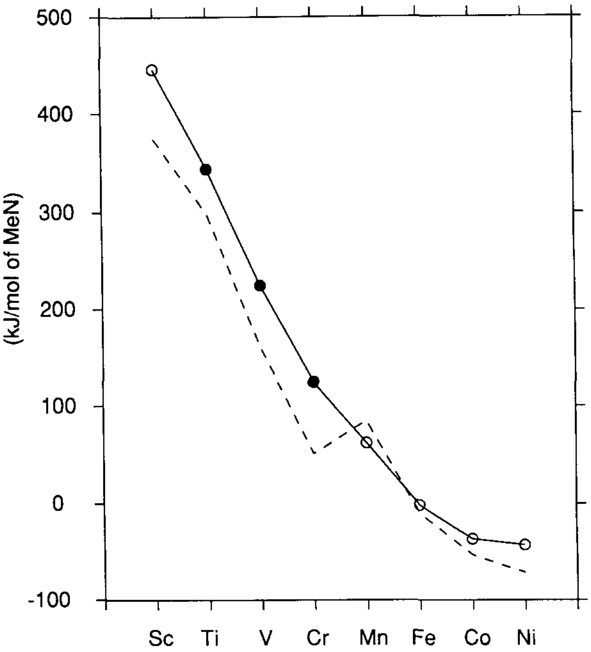

Fig. 3. Bonding enthalpies of MeN(cF8) nitrides, Δ[MeN(cF8)], according to the present study (symbols connected by a solid curve) and obtained from the enthalpy-of-formation values predicted by Miedema and coworkers [17] (dashed curve). Empty symbols represent values based on estimates (ScN) and thermodynamic extrapolations (MnN, FeN, CoN and NiN).

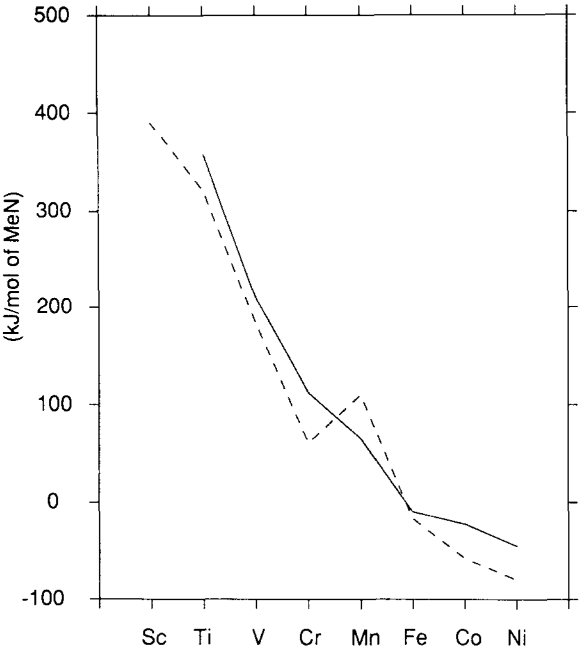

Fig. 4. Bonding enthalpies of ordered liquid phases MeN(liq), Δ[MeN(liq)], according to the present study (solid curve) and obtained from the $\Delta^{M}H_{N}^{\infty}$ values predicted by Miedema and coworkers [17] (dashed curve).

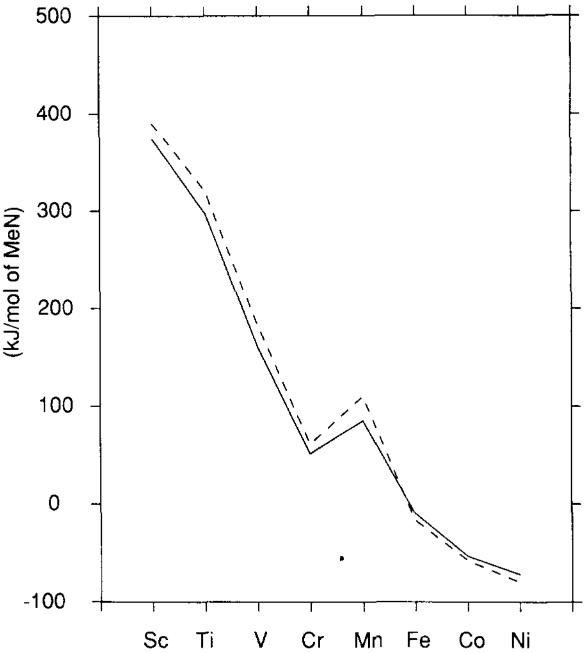

Fig. 5. Bonding enthalpies of MeN(cF8) nitrides, Δ[MeN(cF8)] (solid curve), and of ordered liquid phases MeN(liq), Δ[MeN(liq)] (dashed curve), obtained from the predictions of Miedema and coworkers [17] for $\Delta^{0}H[\mathrm{MeN(cF8)}]^{(\mathrm{st})}$ and $\Delta^{M}H_{N}^{\infty}$ respectively.

support to the early suggestion by Miedema and coworkers [17] that the R term in eqn. (29) accounts for hybridization effects. However, Miedema [48] has recently pointed out that this interpretation is not supported by information on the Mössbauer isomer shift in alloys. The present results should be useful when testing new hypotheses about the origin of this additional contribution to the heat of formation of transition metal alloys.

In Fig. 3 we compare the present results for the bonding enthalpy Δ[MeN(cF8)] with the values obtained by using enthalpy-of-formation values from ref. 17. The results in this figure can be well understood by reference to the previous discussion of Fig. 1, because $\Delta^{0}H[\mathrm{MeN(cF8)}]^{(\mathrm{st})}$ is the main contribution to Δ[MeN(cF8)] (see Table 1). The comparison is extended to Δ[MeN(liq)] in Fig. 4. Since the values represented by the dashed curve originate from the $\Delta^{M}H_{N}^{\infty}$ values reported by Miedema and coworkers, one can take Fig. 4 as a test of the accuracy of their predictions for dilute solutions of N in liquid 3d transition metals.

6.3. Bonding strengths in solid and liquid nitrides

The qualitative variation in Δ[MeN(liq)] from Miedema's values across the 3d transition series resembles the behaviour of the solid nitrides, which is natural because in their model the ϕ and n_{ws} parameters for the elements and the P and Q parameters for the liquid alloys are the same as for the solid compounds. As a difference, the correction term R_{liq} was treated as another adjustable parameter to be determined from experimental data. The resulting R_{liq} value turned out to be similar to R_{sol}, eqn. (30), which was considered in accord with Miedema's general assumption [17] that enthalpies of formation for condensed phases are essentially independent of structure. In this work we have found that the phases MeN(cF8) and MeN(liq) have almost the same bonding enthalpy and thus it is interesting to see how accurately this feature of nitride phases is accounted for by the parameters of Miedema and coworkers [17]. A comparison between Δ[MeN(cF8)] and Δ[MeN(liq)] obtained from their enthalpy predictions is presented in Fig. 5. We conclude that the model of Miedema accounts reasonably well for the relation between bonding enthalpies for the MeN(cF8) and MeN(liq) phases.

In comparing our results with Miedema's approach and other empirical generalizations, one should realize that the correlation in Fig. 2 does not imply that the strength of the individual interatomic bonds in these two ordered phases is absolutely independent of structure. Indeed, they might change *e.g.* on melting, but the correlation in Fig. 2 indicates that the expected variations are such that the difference $^{0}H[\mathrm{MeN(liq)}] - {}^{0}H[\mathrm{MeN(cF8)}]$ will be close to the difference $^{0}H[\mathrm{Me(liq)}] - {}^{0}H[\mathrm{Me(cF4)}]$. In other words, when forming the ordered liquid phase MeN(liq) from MeN(cF8), there will be no dramatic changes in the nature or strength of the chemical bonding and thus one should expect only energy effects comparable with the enthalpy of melting of the f.c.c. structure in the 3d transition series.

7. Summary and concluding remarks

Thermodynamic quantities provide a way of characterizing the bonding strength of materials which is very useful for systematic studies of trends across the periodic table. However, such studies are often hampered by the lack of direct measurements of the quantity chosen as a measure of bonding strength and there is a need for methods to extract and assess the necessary information from experimental data of various kinds. This paper has been concerned with the assessment of bonding properties for stable and metastable phases by using models for the thermochemical behaviour of condensed systems. The present characterization of bonding strength relies on the enthalpy of formation of the substance and a particular choice of reference states for the metallic elements. In this way information from both solid and liquid states can be used in establishing bonding trends. This procedure is applied to MeN condensed nitride phases of the 3d transition metals, which are chosen as an example of theoretically and practically interesting materials that have been poorly known from direct thermodynamic measurements. The assessment procedure applied by us leads to a reliable picture of the bonding trends in these substances which is appropriate for comparisons with the results of *ab initio* studies of the cohesive properties and the predictions from semiempirical models. The general consistency of our results also adds to the credibility of the thermodynamic descriptions for transition metals and their alloys with N which form the basis of our analysis. As an instructive application of the kind of insight provided by our methods, we have studied the predictions of Miedema and coworkers [17]. By comparing their results with the trends established in this work, we were able to detect two significant systematic deviations in their values. Finally, we found that our correlations support theoretical [18] and empirical [17] generalizations about the predominance of chemical bonding energy contributions to the heat of formation of compounds.

Acknowledgments

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