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Miedema's model revisited: The parameter ϕ^* for Ti, Zr, and Hf

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Abstract

Failures of Miedema's model to predict enthalpies of formation for binary Zr-based compounds are attributed to the original choice of the parameter for electronegativity, $\phi^* = 3.45$ V, for Zr. By refinement procedures based on (1) ab initio enthalpies of formation, (2) reliable calorimetric data for the compounds, and (3) data for elemental metallic Zr we suggest that $\phi^* = 3.62$ V is a reasonable choice. With this refined value, the revised enthalpies of formation for Zr-based compounds obtained by the Miedema model are substantially improved. The procedures applied possibly open up a new avenue for improving the reliability of Miedema's model by critically assessing the parameter ϕ^* also for other problematic cases, and without changing the original model.

Keywords: Thermodynamics; Enthalpies of formation; First-principles calculations; Computational modeling

The heat of formation of a compound is a very important thermodynamical quantity. Its experimental and theoretical determination is therefore of particular interest for technological applications. Traditionally in the more applied fields, the enthalpy of formation ΔH of binary compounds is calculated by means of Miedema's model [1] although it is not predictive (e.g. Ref. [2]). Nevertheless, one expects at least trends of ΔH for related compounds such as Ti-, Zr-, and Hf-based binaries to be described correctly. Studying binary Laves phases [3–5], we realized that Miedema's model is very unsatisfactory for Zr-based compounds (Fig. 1) for which the present study suggests a substantial improvement. Instead of manipulating Miedema's model itself [6,7] we focused our attention on the original parameters of the original model, and on their values derived and applied by Miedema about 30 years ago.

In Fig. 1 reliable calorimetric data ΔH_{exp} are compared to results $\Delta H^0_{\mathrm{Mie}}$ obtained from Miedema's original model for intermetallic compounds TM (T = Ti, Zr, Hf and M = Cu, Co, Ni, Ir, Ru, Rh, Pt, Pd). The figure reveals the general problem for all Zr-based compounds that $\Delta H^0_{\mathrm{Mie}}$ is far too negative, and that even its trend strongly disagrees with that of the experimental data. In contrast to those for Zr, the values of $\Delta H^0_{\mathrm{Mie}}$ for T = Ti, Hf seem to be reasonably accurate. These findings led us to the conclusion that Zr is a special case, and the corresponding parameters of Miedema's model need to be critically assessed.

The enthalpy of formation of a binary compound A_xB_{1-x} is estimated from Miedema's model [1] according to

$$\Delta H_{\mathrm{Mie}} = f_B^A \frac{2xV_A^{2/3}\{-P(\phi_A^* - \phi_B^*)^2 + Q[(n_{\mathrm{WS}}^{1/3})_A - (n_{\mathrm{WS}}^{1/3})_B]^2 - R\}}{(n_{\mathrm{WS}}^{-1/3})_A + (n_{\mathrm{WS}}^{-1/3})_B}. \quad (1)$$

In this equation, f_A^B indicates the degree to which one type of atom (A) is surrounded by dissimilar neighbouring atoms (B), and P, Q, and R are proportionality constants determined empirically. Miedema's model (Eq. (1)) requires three basic parameters for each of the elements of a binary compound: the molar volume V, the electronic density at the Wigner–Seitz boundary n_{WS}, and the electronegativity ϕ^*. The molar volume is well defined, directly measurable and calculable; the density n_{WS} is proposed to be proportional to the ratio of $(B/V)^{1/2}$ including the bulk modulus B, which is also well defined. Therefore, V and n_{WS} are easily accessible, well defined physical parameters, in contrast to the third parameter: the electronegativity ϕ^*. Originally, ϕ^* was directly related to

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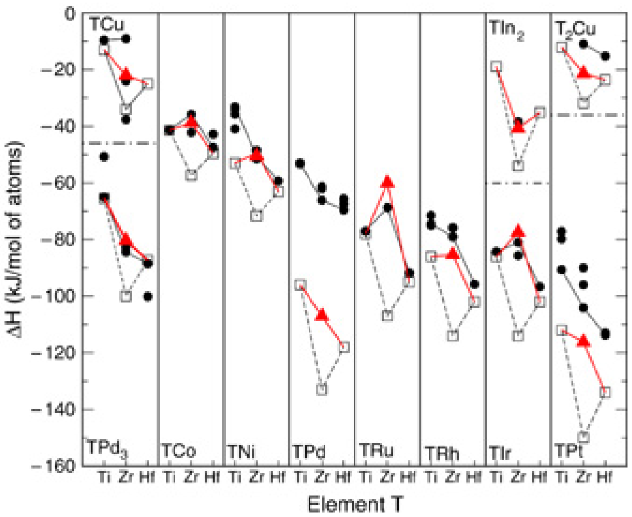

Fig. 1. (Color online). Enthalpies of formation ΔH for compounds TM (T = Ti, Zr, Hf; M = Cu, Co, Ni, Ir, Ru, Rh, Pt, Pd). Calorimetric data ΔH_{exp} [11] (filled circles), values derived by Miedema's model with original parameters ΔH^0_{Mie} (open squares), and results from applying Miedema's model with $\phi^* = 3.62$ V for Zr $\Delta H^{\text{rev}}_{\text{Mie}}$ (triangles).

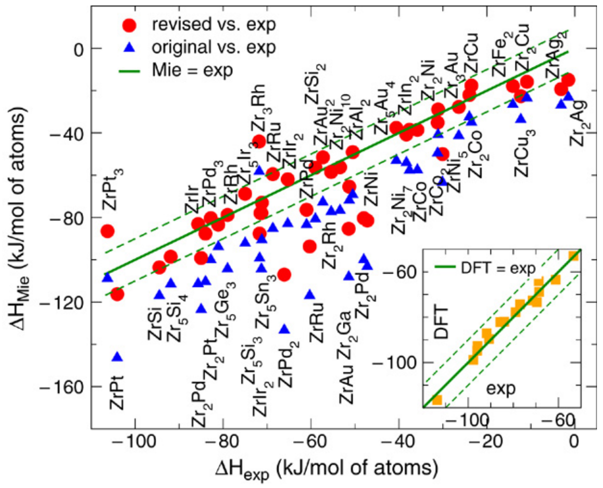

Fig. 2. (Color online). For Zr-based compounds, the experimental heats of formation ΔH_{exp} [11,13,15] are compared to the results ΔH_{Mie} of Miedema's model applied with the original (triangles) and revised (circles) parameter ϕ^* for Zr. Error acceptance data zone (dashed lines) defined by $\Delta H_{\text{exp}} \pm 10$ kJ (mol of atoms)$^{-1}$. The inset compares ab initio DFT and calorimetric data for the sixteen TM compounds as described in the text.

Table 1

Ab initio enthalpies of formation ΔH_{DFT} for compounds TM (T = Ti, Hf, Zr; M = Ru, Rh, Ir, Pt) and their ground state structures compared to the results ΔH^0_{Mie} from Miedema's model with the original parameters, and the refined values ϕ^*_{DFT} (in volts) for Ti, Zr, and Hf, as obtained from adjusting ΔH^0_{Mie} to ΔH_{DFT} (procedure (1); see the text)

	ΔH_{DFT}	Structure	ΔH^0_{Mie}	ϕ^*_{DFT}
TiRu	−74.3	B2	−64.3	3.72
TiRh	−72.6	L1$_0$	−77.4	3.84
TiIr	−82.0	L1$_0$	−85.1	3.82
TiPt	−89.6	B19	−111.2	3.95
Average				Ti: 3.83
ZrRu	−64.1	B2	−85.1	3.59
ZrRh	−77.8	B33	−104.2	3.63
ZrIr	−82.2	B33	−111.3	3.63
ZrPt	−106.2	B33	−110.4	3.68
Average				Zr: 3.63
HfRu	−87.1	B2	−75.3	3.57
HfRh	−92.7	B33	−92.4	3.60
HfIr	−98.8	B33	−99.6	3.60
HfPt	−117.9	B33	−131.7	3.64
Average				Hf: 3.60

All energies in kJ (mol of atoms)$^{-1}$.

the (average) work function ϕ [8], and interestingly, for Zr the deviation between these two quantities is the largest with Miedema's choice for Zr of $\phi^*_{\text{Zr}} = 3.45$ V [1] and the experimental work function $\phi_{\text{Zr}} = 4.05$ V [8] published in 1978. Although it is well known that results of such old measurements of work functions are rather doubtful, the large deviations between ϕ^*_{Zr} and ϕ_{Zr} for Zr indicate that the parameter ϕ^*_{Zr} should be critically investigated on the basis of reliable state-of-the-art experimental and theoretical data. On the other hand, for Ti and Hf the corresponding parameters ϕ^* seem to be reasonable (see Fig. 1). Consequently, we searched for physically sound refining techniques which correct ϕ^*_{Zr} without modifying significantly ϕ^* for Ti and Hf.

Our refinement procedure (1) consists in the application of an ab initio density functional theory (DFT) approach [9] by which the enthalpies of formation ΔH_{DFT} for binary compounds [10] TM (T = Ti, Zr, Hf; M = Ru, Rh, Ir, Pt) were calculated. These compounds were chosen because well defined experimental structural information is available for them. All the calculated results are compared to calorimetric data ΔH_{exp} (inset of Fig. 2), showing the very good agreement between DFT and experiment. Table 1 compares ΔH_{DFT} to ΔH^0_{Mie} showing a reasonable agreement for TiM and HfM compounds. However, for ZrM compounds the data for ΔH^0_{Mie} are far too negative. On the basis of the data set of ΔH_{DFT} values, the results from Miedema's model were optimized by varying ϕ^* by keeping the remaining parameters (molar volume V and electronic density n_{WS}) fixed. By this procedure, the (averaged) electronegativity parameter for elemental Zr was derived as $\phi^*_{\text{Zr}} = 3.63$ V with which Miedema's model reproduces quite well the ab initio data. The change of ϕ^*_{Zr} is considerable having in mind the original choice of $\phi^*_{\text{Zr}} = 3.45$ V. The same procedure applied for TiM and HfM leads to refined values of $\phi^*_{\text{Ti}} = 3.83$ and $\phi^*_{\text{Hf}} = 3.60$ V, as listed in Table 1. In contrast to that for Zr, the refinement for Ti and Hf is very small or negligible when compared to the original values of $\phi^*_{\text{Ti}} = 3.80$ and $\phi^*_{\text{Hf}} = 3.60$ V.

In procedure (2), we refined the parameter ϕ^* on the basis of reliable calorimetric data for Zr-, Ti-, and Hf-based binary compounds (see Tables 2 and 3). The selection was done requiring that the measured enthalpies of formation published in different papers agree reasonably well with each other, or the calorimetric data agree with ab initio results. For instance, for ZrRh three calorimetric data were reported which we consider to be sufficiently close to each other. In contrast, for ZrCu three significantly different results were published, namely −9.05 ± 1.2 [11], −37.6 ± 3.7 [12], and −24 ±