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Attachment No. 11:

Habilitation thesis reviewer's report

Masaryk University	
Faculty	Of Science
Field of study	Physical chemistry
Applicant	***Jana Pavlů, Mgr., Ph.D.***
Unit	Department of Chemistry
Habilitation thesis (title)	***Ab initio and semiempirical modelling of intermetallic phases***
Reviewer	Prof. Klaus Richter
Unit	Universität Wien

Reviewer's report

The habilitation thesis of Dr. Pavlů is based on 13 peer reviewed publications concerning various aspects of theoretical modelling of materials. The methods employed for her studies are ranging from ab initio electronic calculations using different approximations to macroscopic thermodynamic modelling using the semi-empirical CALPHAD approach. These model approaches are interconnected by the use of ab initio data (in particular ground state energies) as input data for the thermodynamic models in the framework of the Compound Energy Formalism (CEF). The studies are focused on two different material classes: 1) superaustenitic steels that may contain the intermetallic σ phase (investigated in Fe-Cr-Ni as well as in Mo- and W- containing systems) and 2) the very common Laves phases (Strukturberichts-designation C14, C15) represented by the systems Cr-Zr, Cr-Hf, Cr-Ti and V-Zr.

Although the ab initio approach does not rely on adjustable parameters, the approximations and potentials used in the calculations have to be adapted to the problem. Dr. Pavlů carefully addressed this point in her work. Her results are manifold, ranging from ground state energy calculations including fully relaxed structure optimization, spin polarized calculations allowing the analysis of the magnetic arrangement in the studied complex intermetallics, to the analysis of elastic constants for the Laves phases. Energy calculations were performed for both classes of structures, σ- and Laves phases, as well as for the respective pure elements in their stable element reference (SER) configuration. From these data the energies of formation at 0K were derived for various experimentally inaccessible metastable compounds: the pure elements in the structure of the intermetallic compound ("lattice stability") and the intermetallic compounds in various hypothetical ordered site occupancy configurations ("end member"). These values are extremely important as input data for CALPHAD calculations. The obtained energies are generally in good agreement with available experimental data and theoretical results by other authors. The variation of crystallographic parameters with the composition (comparison of different end members) are almost linear (e.g. for the V-Zr Laves phase [XVII]). Energy calculations for all 32 endmembers of the σ- phase suggest considerable site preferences [X] in Cr-Fe and Cr-Co. In another work, Dr. Pavlů calculated ground state energies for various binary shape memory compounds for direct comparison with calorimetric data [XIII]. This study included also the calculation of magnetic moments which are in good agreement with available experimental data. The calculation of magnetic

properties was also of particular interest for various end members of the σ- phase. It was shown that the magnetic moments at independent sites show relatively large differences which could be correlated with the local coordination number. Interestingly, a considerable magnetic moment for Cr was found for some of the mixed end members with Fe and Co [X].

Thermodynamic optimizations were performed for various systems containing the σ- phase, e.g. Cr-Fe [I], Cr-Co [II]. Given the large number of possible end members for the structurally complex σ- phase (5 independent sites yielding 32 possible end members), a pragmatic approach was used for the thermodynamic modelling of the phase. Instead of the reduction of endmembers by chemical constraints or the combination of several crystallographic sites to one sublattice, a (1 1) two sublattice model was applied to model the thermodynamic properties of the σ- phase. Thus, only ab initio energies for the pure endmembers were used in the CEF model. The approach was quite successful for phase diagram modelling, yielding an excellent agreement with experimental data with a reduced set of adjustable parameters. The model also successfully applied in the ternary systems Fe-Ni-Cr [III] and Cr-Fe-W [VII]. Modelling in systems containing the structurally less complex Laves phase, e.g. Cr-Zr [IX] and Cr-Ti,Hf [XI] was performed mostly with the two sublattice model $(A,B)_2(A,B)$ employing the respective end member energies obtained by ab initio calculations. For the C14 phase also the full three sublattice model was applied. A particular highlight of the presented work is the thermodynamic modelling of the pure elements in the low temperature regime employing the Einstein model for the temperature dependence of the heat capacity. This work [XIV] addresses a long-term problem of the SGTE data set, i.e. the unphysical extrapolation of the classical SGTE polynoms to low temperatures. New low temperature descriptions were adapted to complement the classical SGTE descriptions of many element descriptions at the low temperature side, and the same concept was also used for the re-modelling of the low temperature behaviour of V_2Zr [XVII].

The scientific work presented in this thesis is of high quality, using up to date theoretical tools and contributing significantly to the field of computational thermodynamics through the integration of ab initio approach with the CALPHAD methods. The studies were performed in technologically important material systems and were published in the most important international journals in the field. I therefore recommend Dr. Pavlů for habilitation in the field of physical chemistry.

Reviewer's questions for the habilitation thesis defence

The approach to model the Fe-Cr and related σ-phases with a (1 1) two sublattice model is for sure justified in the current case where it is very difficult to receive experimental data on site preferences. On the other hand some hints for site preferences were found in the author's own DFT calculations. Other authors, for example Crivello et al. [1], also found significant site preferences for the σ-phase in Cr-Mo-Re that would allow a reduction of sublattices. I wonder if – in the light of new experimental and DTF results – there is a chance to suggest a unified two or three sublattice model consistent with the site multiplicities. Or does the author believe that (1 1) two sublattice model should be the model of choice for all σ-phases?

[1] J.C. Crivello, M. Palumbo, T. Abe, J.M. Joubert, Ab initio ternary sigma-phase diagram The Cr-Mo-Re system, CALPHAD, 34 (2010) 487-494.

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Conclusion

The habilitation thesis submitted by Jana Pavlů, Mgr., Ph.D., entitled "Ab initio and semiempirical modelling of intermetallic phases" meets the requirements applicable to habilitation theses in the field of physical chemistry.

In Vienna on September 21. 2016