DOE/ER/45363-1/Final

FINAL REPORT

DE-FG02-88ER45363

HIGH-TEMPERATURE THERMOCHEMISTRY OF TRANSITION METAL BORIDES, SILICIDES AND RELATED COMPOUNDS

1. INTRODUCTION

For about 20 years our calorimetric work on high-temperature materials has been almost continuously supported by NSF under grants entitled "High Temperature Calorimetry of Refractory Systems." The present grant in this series is DMR 97-26699 which provides funding for 3 years from April 1, 1998 to March 31, 2001.

Since July 1, 1988 we have also received support from the Department of Energy for a research program which originally was entitled "High-Temperature Thermochemistry of Transition Metal Borides and Silicides." However, six years ago the title of this project was changed to "High-Temperature Thermochemistry of Transition Metal Borides, Silicides and Related Compounds." This change reflected the fact that while a significant part of our effort under this grant has been devoted to borides and silicides, our work was extended to the thermochemistry of compounds which are closely related to borides and silicides, such as e.g. transition metal carbides, germanides and stannides as well as aluminides and, most recently, also compounds of transition metals with gallium. A major part of the funds received under this grant have been used to pay the salary of a post-doctoral Research Scientist working in the area described by the title.

Since 1990 this position has been held by Dr. Susan V. Meschel who has co-authored most of the publications which have resulted from the scientific work supported by this grant.

The principal objective of our research under this grant has been to develop a systematic picture of the thermochemistry of transition metal and rare earth borides, silicides and related compounds. These investigations have been made possible by our development, somewhat more than 10 years ago, of a new high-temperature reaction calorimeter capable of continuous operation at temperatures up to about 1500K (O.J. Kleppa and L. Topor, Thermochim. Acta 139, 291-297 (1989))

2. ACCOMPLISHMENTS Under Grant DE-FG02-88ER45363.

During the past 12 years our research supported by DE-FG02-88ER45363 have contributed to the completion of 45 scientific publications. These publications are listed here:

DISCLAIMER

1. Standard Enthalpy of Formation of Sc_5Si_3, L. Topor and O. J. Kleppa, Met. Trans. **20B**, 879 (1989).

2. Standard Enthalpies of Formation of Me_5Ge_3 (Me = Ti, V, Mn, Fe, Co, Ni) by High Temperature Calorimetry, O. J. Kleppa and W.-G. Jung, High Temp. Sci. **29**, 109 (1990).

3. Standard Enthalpies of Formation of Me_5Si_3 (Me = Y, Lu, Zr) and of Hf_3Si_2, L. Topor and O. J. Kleppa, J. Less-Common Metals **167**, 91-99 (1990).

4. Standard Enthalpies of Formation of Me_5Ge_3(Me = Sc, Y, La) by High-Temperature Calorimetry, W.-G. Jung and O.J. Kleppa, J. Less-Common Metals **169**, 85-92 (1991).

5. Standard Molar Enthalpies of Formation of Me_5Ge_3(Me = Ru, Rh, Pd) and Pd_2Ge by High-Temperature Calorimetry, W.-G. Jung and O.J. Kleppa, J. Less-Common Metals **169**, 93-103 (1991).

6. Enthalpies of Formation of Refractory Borides by High-Temperature Direct Synthesis Calorimetry: $RuB_{1.1}$ and $RhB_{1.1}$, S.V. Meschel and O.J. Kleppa, Metallurgical Transaction **22A**, 1680-83 (1991).

7. Standard Molar Enthalpies of Formation of PdAl, PtAl, $ScAl_{1.78}$, YAl_2, and $LaAl_2$, W.-G. Jung, O.J. Kleppa and L. Topor, J. Alloys and Compounds **176**, 309-318 (1991).

8. Note on the Enthalpies of Formation of Cu_3Si and Cu_3Ge, S.V. Meschel and O.J. Kleppa, Metallurgical Transactions **22A**, 2162-2165 (1991).

9. Enthalpies of Formation of Refractory Borides of 5d Elements by High-Temperature Direct Synthesis Calorimetry. I. $IrB_{1.35}$ and $OsB_{2.5}$, S.V. Meschel and O.J. Kleppa, J. Alloys and Compounds **177**, 159-166 (1991).

10. Standard Molar Enthalpies of Formation of Hf_3Ge_2, MeGe (Me = Ir, Pt) and Pt_2Ge, W.-G. Jung and O.J. Kleppa, J. Alloys and Compounds **176**, 301-308 (1991).

11. Standard Molar Enthalpies of Formation of MeAl (Me = Ru, Rh, Os, Ir), W.-G. Jung and O.J. Kleppa, Metallurgical Transactions **23B**, 53-56 (1992).

12. Standard Enthalpies of Formation of Some Refractory Borides of 4d and 5d Elements from High-Temperature Direct Synthesis Calorimetry, S.V. Meschel and O.J. Kleppa, Journal de Chimie Physique **90**, 349 (1993).

13. Standard Enthalpies of Formation of 4d Aluminides by Direct Synthesis Calorimetry, S.V. Meschel and O.J. Kleppa, J. Alloys and Compounds **191**, 111-116 (1993).

14. Standard Enthalpies of Formation of NbB_2, MoB and ReB_2 by High-Temperature Direct Synthesis Calorimetry, S.V. Meschel and O.J. Kleppa, Metall. Trans. **24A**, 947-50 (1993).

15. Standard Enthalpies of Formation of 5d Aluminides by High-Temperature Direct Synthesis Calorimetry, S.V. Meschel and O.J. Kleppa, J. Alloys and Compounds **197**, 75-81 (1993).

16. The Standard Enthalpies of Formation of Some 3d Transition Metal Aluminides by High-Temperature Direct Synthesis Calorimetry, S.V. Meschel and O.J. Kleppa in *Metallic* Alloys: E*xperimental and Theoretical Perspectives*, J.S. Faulkner, and R.G. Jordan Eds., Kluwer Academic Publishers, Dordrecht, The Netherlands, (1994).

17. Standard Enthalpies of Formation of Some Rare Earth Carbides by Direct Synthesis Calorimetry, S.V. Meschel and O.J. Kleppa, J. Alloys and Compounds, **205**, 165-168 (1994).

18. Systematic Aspects of the High-Temperature Thermochemistry of Binary Alloys and Related Compounds, O.J. Kleppa, J. Phase Equilibria **15**, 240-263 (1994).

19. Standard Enthalpies of Formation of Some Carbides, Silicides and Germanides of Cerium and Praseodymium, S.V. Meschel and O.J. Kleppa, J. Alloys and Compounds **220**, 88-93 (1995).

20. Note on the standard enthalpies of formation of Ta_5Ge_3 and $OsGe_2$ by direct synthesis calorimetry, S.V. Meschel and O.J. Kleppa, J. Alloys and Compounds **216**, L13-L15 (1994).

21. Standard Enthalpies of Formation of Some Neodymium and Gadolinium Carbides, Silicides and Germanides by High-Temperature Direct Synthesis Calorimetry, S.V. Meschel and O.J. Kleppa, J. Alloys and Compounds **217**, 235-239 (1995).

22. Standard Enthalpies of Formation of Some Borides of Ce, Pr, Nd and Gd by High-Temperature Reaction Calorimetry. S.V. Meschel and O.J. Kleppa, J. Alloys and Compounds **221**, 37-41 (1995).

23. Recent Work in High-Temperature Reaction Calorimetry of Intermetallic Compounds and Related Phases. O.J. Kleppa, Q. Guo and S.V. Meschel *in Applications of Thermodynamics in the Synthesis and Processing of Materials.*, P. Nash and B. Sundman, Eds., TMS, 1995, pp. 285-302.

24. Standard Enthalpies of Formation of Some Lutetium Alloys by High-Temperature Direct Synthesis Calorimetry. S.V. Meschel and O.J. Kleppa. J. Alloys and Compounds **224**, 345-350 (1995).

25. Standard Enthalpies of Formation of AlB_{12} and Al_4C_3 by High-Temperature Direct Synthesis Calorimetry, S.V. Meschel and O.J. Kleppa, J. Alloys and Compounds **227**, 93-96 (1995).

26. Standard Enthalpies of Formation of Some Carbides, Silicides, Germanides, Stannides and Borides of Terbium Determined by High Temperature Direct Synthesis Calorimetry, S.V. Meschel and O. J. Kleppa , J. Alloys and Compounds **234**, 137-142 (1996).

27. Standard Enthalpies of Formation of Some Carbides, Silicides, Germanides, Stannides and Borides of Dysprosium by High Temperature Direct Synthesis Calorimetry, S.V. Meschel and O.J. Kleppa, J. Alloys and Compounds **233**, 272-278 (1996).

28. Standard Enthalpies of Formation of Some Rare Earth Stannides by High Temperature Direct Synthesis Calorimetry, S.V. Meschel and O.J. Kleppa, J. Alloys and Compounds **238**, 180-6 (1996).

29. Direct Synthesis Calorimetry of Some Binary Alloys in the Systems Si-As, Ge-As and Sn-As, K. Fitzner and O.J. Kleppa, J. Alloys and Compounds **247**, 52-56 (1997).

30. Standard Enthalpies of Formation of Some Carbides, Silicides, Germanides and Borides of Holmium by High Temperature Direct Synthesis Calorimetry, S.V. Meschel and O.J. Kleppa, J. Alloys and Compounds **243**, 186-193 (1996).

31. Redetermination of the Standard Enthalpy of Formation of Lu_5Ge_3 by High Temperature, Direct Synthesis Calorimetry, S.V. Meschel and O.J. Kleppa, Journal of Alloys and Compounds **245**, L28-L29 (1996).

32. Note on the Determination of the Standard Enthalpies of Formation of PdGa and Pd_2Ga by High Temperature Direct Synthesis Calorimetry, S.V. Meschel and O.J. Kleppa, Thermochimica Acta **292**, 13-17 (1996).

33. High-Temperature Direct Synthesis Calorimetry of Refractory Materials, OJ.Kleppa, Q. Guo and S.V. Meschel, In *Thermodynamics of Alloys Formation*, Y.A. Chang and F. Sommer, Eds. TMS, 1997, pp. 43-58.

34. Recent Thermochemical Studies of the Binary Alloys of Er with Group IVB Elements by High Temperature Direct Synthesis Calorimetry, S.V. Meschel and O.J. Kleppa, J. Chim. Phys. **94**, 928-938 (1997)

35. Standard Enthalpies of Formation of Some 3d, 4d and 5d Transition Metal Stannides by Direct Synthesis Calorimetry, S.V. Meschel and O.J. Kleppa, Thermochimica Acta **314**, 205-212 (1998).

36. Standard Enthalpies of Formation of Some 3d Transition Metal Silicides by High Temperature Direct Synthesis Calorimetry, S. V. Meschel and O.J. Kleppa, J. Alloys and Compounds **267**, 128-135 (1998).

37. Standard Enthalpies of Formation of Some 4d Transition Metal Silicides by High Temperature Direct Synthesis Calorimetry, S. V. Meschel and O.J. Kleppa, Journal of Alloys and Compounds **274**, 193-200 (1998)

38. Standard Enthalpies of Formation of Some 5d Transition Metal Silicides by High Temperature Direct Synthesis Calorimetry , S.V. Meschel and O.J. Kleppa, J. Alloys and Compounds **280**, 231-239 (1998)

39. Standard Enthalpies of Formation of Some Thulium Alloys by High Temperature Direct Synthesis Calorimetry, S.V. Meschel and O.J. Kleppa, Journal of Alloys and Compounds **285**, 179-184 (1999).

40. Standard Enthalpies of Formation of Some 3d Transition Metal Gallides by High Temperature Direct Synthesis Calorimetry, S.V. Meschel and O.J. Kleppa, Journal of Alloys and Compounds **290**, 150-156 (1999).

41. Standard Enthalpies of Formation of Some 4d Transition Metal Gallides by High Temperature Direct Synthesis Calorimetry, S. V. Meschel and O.J. Kleppa, Journal of Alloys and Compounds **297**, 162-167 (2000).

42. Evolution and Application of High-Temperature Reaction Calorimetry at the University of Chicago from 1952 to 2000, O.J. Kleppa, TMS Mtg. Nashville, TN, J. of Alloys and Compounds Spec. Issue (Submitted 2000)

43. Thermochemistry of Alloys of Transition Metals and Lanthanide Metals with Some IIIB and IVB Elements in the Periodic Table, S.V. Meschel and O.J. Kleppa, TMS Mtg. Nashville, TN, J. of Alloys and Compounds Spec. Issue (Submitted 2000)

44. High-Temperature Reaction Calorimetry of Alloys and Related Materials, O.J. Kleppa, Susan V. Meschel and Q. Guo, in *The Science of Alloys for the 21st Century: A Hume-Rothery Symposium Celebration* P. Turchi, Ed. TMS, (in press, 2000).

45. Standard Enthalpies of Formation of Some 5d Transition Metal Gallides by High Temperature Direct Synthesis Calorimetry, Susan V. Meschel and O.J. Kleppa, J. of Alloys and Compounds (in press, 2000).

Among the 45 scientific papers in this list there are 5 which are review papers (#18, 23 and 33, 42, and 44); these papers summarize work supported both by DOE and by NSF. The remaining 40 publications report on experiments supported by DOE alone.

3. DE-FG02-88ER45363; SUMMARY

Earlier this year in collaboration with Dr. Susan V. Meschel we prepared a major review paper which gives a comprehensive summary of what our laboratory has accomplished with support from DOE. This paper is #43 in the List of Publications given above. It was presented to TMS at its National Meeting in Nashville, TN last March. A copy of the manuscript of this paper was recently mailed to DOE. It has been submitted for publication in Journal of Alloys and Compounds.

This review paper summarizes our observed trends in the enthalpies of formation of TR-X and RE-X compounds (where X is a IIIB or IVB element) in their dependence of the atomic number of the transition metal (TR) and the lanthanide metal (RE). In this paper our measured enthalpies of formation for each alloy family are compared for the 3d, 4d and 5d transition metal elements. We also compare our experimental results with predicted values based on Miedema's semi-empirical model.

Data are presented for the carbides, silicides, germanides and stannides in Group IVB, and for the borides and aluminides in Group IIIB. During the past year (1999-2000) we have extended our work to compounds of the 3d, 4d and 5d elements with gallium (see papers #40, #41, and #45 in the List of Publications). Fig. 1 (taken from #45) presents a systematic picture of our experimental values for the most exothermic gallide compounds formed with the transition elements. This figure is characteristic of the other systematic pictures which we have found for the two other IIIB elements which we have studied and for the four IVB elements. These figures are all presented in Ref. #43. A copy of this reference is attached to this report.

This paper also illustrates how the enthalpy of formation of compounds of the IIIB and IVB elements with the lanthanide elements (with the exception of Pm, Eu and Yb) depend on the atomic number of RE. Finally our results for the RE-X compounds are compared with the predictions of Gschneidner (K.A. Gschneidner, Jr., J. Less Common Metals **17**, 1-12 (1969)) Sometimes the agreement is good, sometimes not.

Prepared by O.J. Kleppa
September 1, 2000

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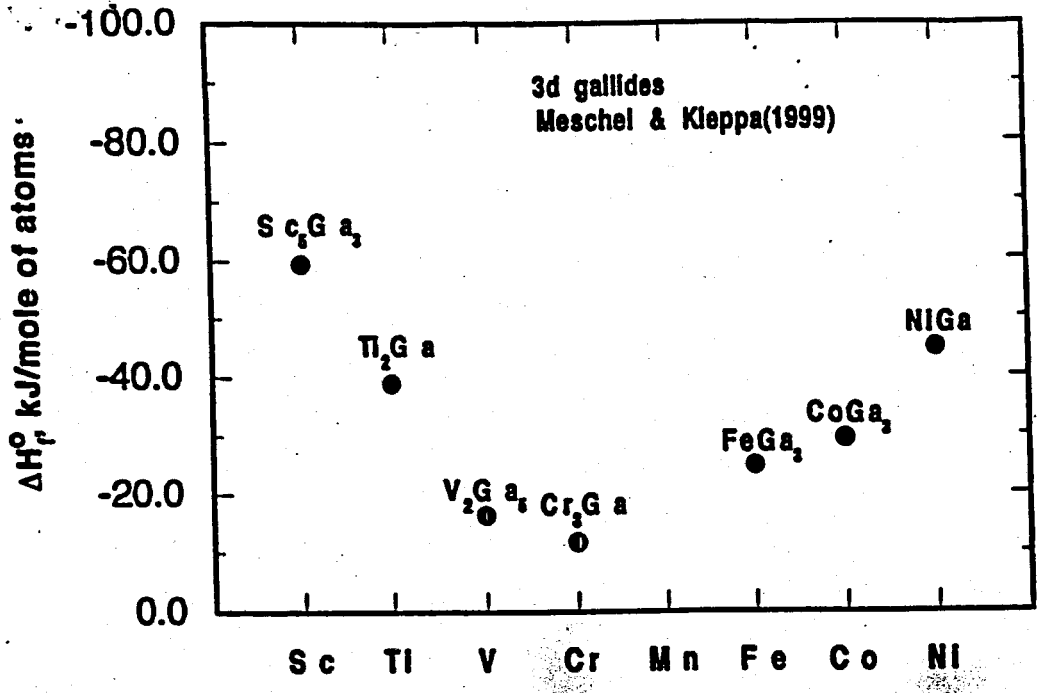
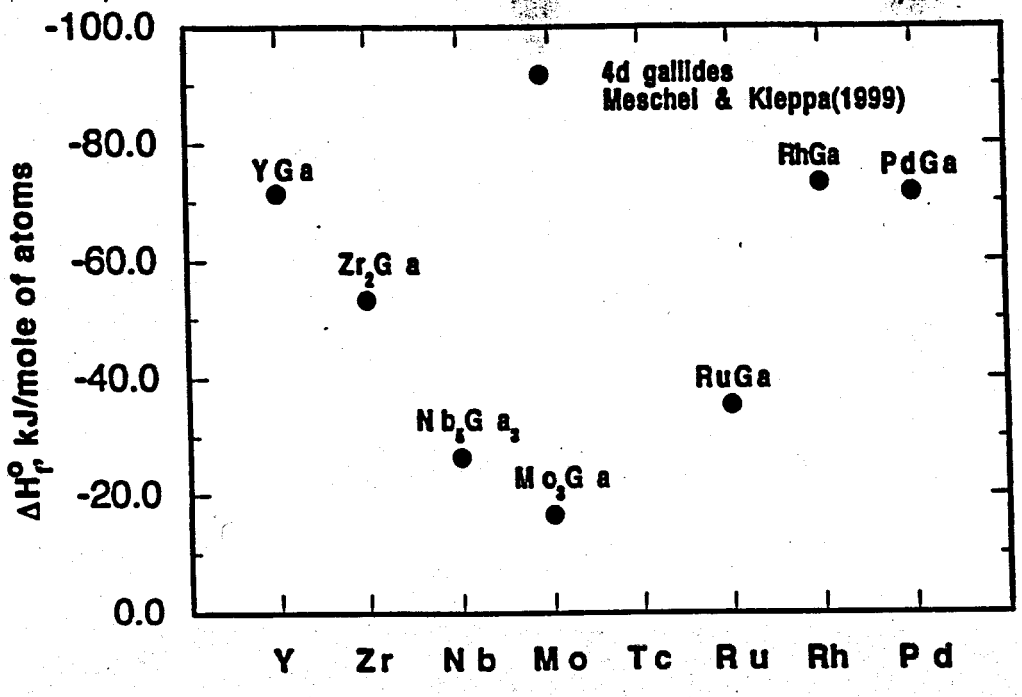
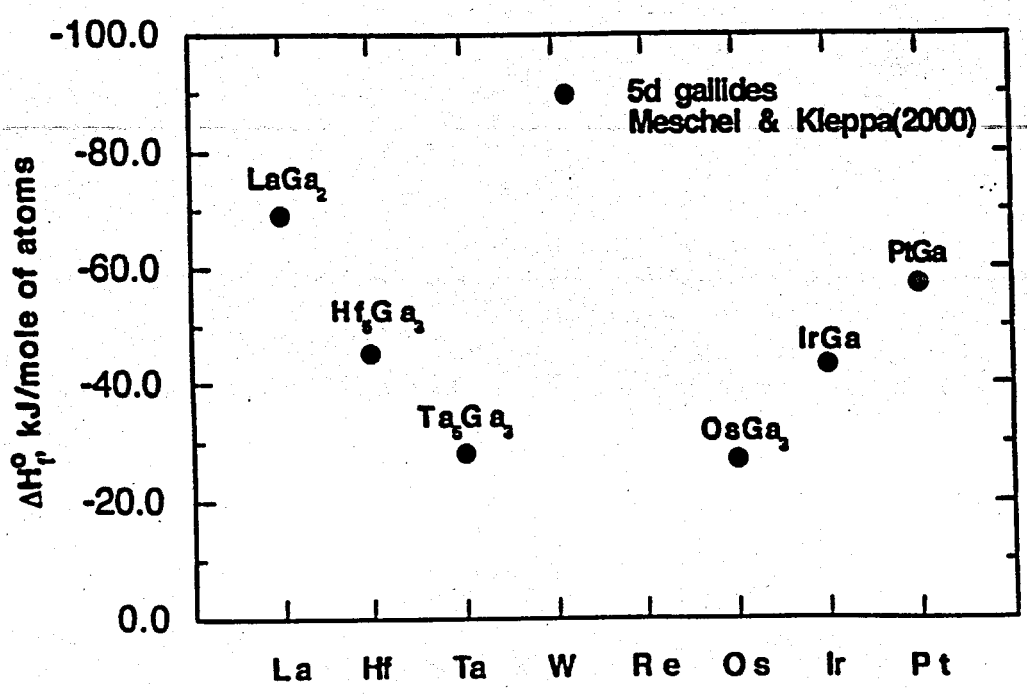
Fig 1


3d gallides
Meschel & Kleppa(1999)
ΔH_f^o kJ/mole of atoms
-100.0
-80.0
-60.0
-40.0
-20.0
0.0
Sc_5Ga_3
Ti_2Ga
V_2Ga_5
Cr_2Ga
$FeGa_3$
$CoGa_3$
NiGa
Sc Ti V Cr Mn Fe Co Ni


4d gallides
Meschel & Kleppa(1999)
ΔH_f^o kJ/mole of atoms
-100.0
-80.0
-60.0
-40.0
-20.0
0.0
YGa
Zr_2Ga
Nb_5Ga_3
Mo_3Ga
RuGa
RhGa
PdGa
Y Zr Nb Mo Tc Ru Rh Pd


5d gallides
Meschel & Kleppa(2000)
ΔH_f^o kJ/mole of atoms
-100.0
-80.0
-60.0
-40.0
-20.0
0.0
$LaGa_2$
Hf_5Ga_3
Ta_5Ga_3
$OsGa_3$
IrGa
PtGa
La Hf Ta W Re Os Ir Pt