

Thermodynamics of MgB₂—by Calorimetry and Knudsen Thermogravimetry

L. P. Cook, R. Klein, W. Wong-Ng, Q. Huang, R. A. Ribeiro, and P. C. Canfield

Abstract—The vapor pressure of MgB₂, corresponding to the reaction, $2 \text{MgB}_2(\text{cr}) \rightarrow \text{MgB}_4(\text{cr}) + \text{Mg}(\text{g})$, has been measured by Knudsen effusion vacuum thermogravimetry. The vapor pressure over the range 600°C–850°C can be expressed as: $\log p_{\text{Mg}}(\text{Pa}) = -1.129141 (10000/T) + 7.328161$, where T is the temperature in Kelvin. By extrapolation, the 0.1 MPa decomposition temperature of MgB₂ is estimated to be 1268°C. In a separate calorimetric investigation on the same material, using the isoperibol solution method, we measured the enthalpy of formation of MgB₂, $\Delta_f H_{\text{MgB}_2}^\circ (298.15)$, to be $-(155.9 \pm 14.2) \text{ kJ} \cdot \text{mol}^{-1}$. By combining the vapor pressure data and the enthalpy data, the Mg-rich part of the Mg-B phase diagram can be calculated. The measured vapor pressures are approximately an order of magnitude higher than those derived from published thermodynamic data. The lower limit of Mg pressures for the deposition of high-purity MgB₂ thin films at any given temperature may therefore be at a higher value than previously thought.

Index Terms—Enthalpy of formation, MgB₂, phase diagram, thermodynamics, vapor pressure.

I. INTRODUCTION

THE MgB₂ superconductor, with a nominal 39 K onset T_c [1], offers promise because of reduced weak link behavior [2] and the possibility of relatively low-cost wire production by a powder-in-(Fe)tube method [3]. Various dopants are being explored to improve the flux pinning characteristics [4]. As a basis for further investigations of this type, it is helpful to have detailed knowledge of the intrinsic properties of undoped MgB₂, including thermodynamic properties. Vapor pressure and enthalpy of formation are two of the most basic properties, and have direct application to the physical vapor deposition of MgB₂ thin films, and to the construction of an equilibrium Mg-B phase diagram.

II. PREVIOUS WORK AND GOAL OF PRESENT STUDY

To date, White [5] has apparently made the sole determination of the enthalpy of formation of MgB₂. As the description of the experimental procedures and the original data were not

available to us, it was not possible to accurately assess the data from [5]. Therefore, one of the goals of the present study is to make a measurement of the enthalpy of formation of MgB₂(cr), $\Delta_f H_{\text{MgB}_2}^\circ (298.15)$, for comparison with this early work.

An Mg-B phase diagram, with estimated fields of stability for MgB₂, MgB₄ and MgB₇ was published in [6]. More recently Liu *et al.* [7] calculated an Mg-B phase diagram using available thermodynamic data, and also estimated a $\log p_{\text{Mg}}$ —temperature stability field for MgB₂. As these calculations were based in part on the early thermodynamic data mentioned above, a second goal of the present study is to directly measure the vapor pressure of MgB₂, for purposes of comparison.

III. EXPERIMENTAL PROCEDURES¹

The MgB₂ sample investigated in this study was prepared by combining elemental Mg and isotopically pure ¹¹B in a sealed Ta capsule and heating to produce Mg vapor, which completely reacted with the B to produce MgB₂ [8]. The material was removed from the Ta capsule in an Ar-filled glovebox (<1 ppm contaminants), comminuted, and loaded into containers for calorimetry and thermogravimetry in the glovebox. The X-ray pattern of this material indicated its single phase nature, which was substantiated by neutron Rietveld refinement. There was no indication in the neutron refinement of nonstoichiometry or of oxygen in solid solution.

The vapor pressure of MgB₂ was determined by the Knudsen effusion method [9] using a MgO cell with a 0.5 mm orifice. Rates of mass loss as a function of temperature were determined thermogravimetrically using a Mettler TA1 thermoanalyzer with Anatech instrumental control firmware and data acquisition electronics. Uncertainty in mass loss rates was < ±1% (standard error of estimate). During the experiments, background pressure was maintained at ≈2.7 mPa by dual diffusion pumps and a liquid nitrogen cold trap. The thermoanalyzer thermocouple was calibrated against the melting point of Au; reported temperatures have < ±5°C uncertainty (standard error of estimate). The operation of the Knudsen effusion cell apparatus was checked using Mg metal, and the vapor pressures obtained over the temperature range 350°C to 550°C agreed within experimental error with vapor pressures calculated from generally accepted thermodynamic data for Mg [10].

¹Certain commercial equipment, instruments, or materials are identified in this paper to foster understanding. Such identification does not imply recommendation or endorsement by NIST, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

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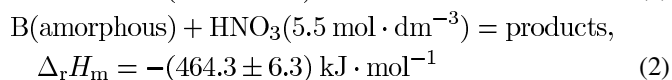
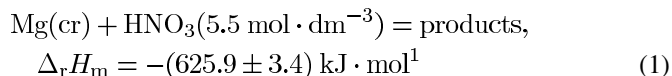
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The enthalpy of formation of $\text{MgB}_2(\text{cr})$ was determined by isoperibol solution calorimetry, using an LKB 8700 calorimeter, as described in [11]. The calorimeter accuracy was checked by measuring the enthalpy of reaction of tris(hydroxymethyl) aminomethane, NIST standard reference material 724a, with 0.1N HCl. The value obtained was in excellent agreement with the certified value. Calorimetric measurements of the enthalpy of reaction of $\text{Mg}(\text{cr})$, $\text{B}(\text{amorphous})$, and $\text{MgB}_2(\text{cr})$ with $5.5 \text{ dm}^{-3} \text{ HNO}_3$ were combined via a Hess cycle to establish the value of $\Delta_f H_{\text{MgB}_2}^\circ$ (298.15). Literature data for the conversion of $\text{B}(\text{amorphous})$ to $\text{B}(\text{cr})$ [10] was used to complete the Hess cycle.

IV. RESULTS

The measured vapor pressures of MgB_2 are shown in Fig. 1, where they have been fit by the following expression: $\log p_{\text{mg}}(\text{Pa}) = -1.129141(10000/T) + 7.328161$, where T is the temperature in Kelvin. While there is some scatter, the fit is reasonably good, with $R^2 = 0.98$. The scatter may be due in part to the fact that data were collected on both increasing and decreasing temperature steps, with temperatures selected in semi-random fashion, in order to average out thermally-induced kinetic effects associated with the vaporization process. There does not appear to be any indication in the data of a compositional effect, i.e., as the vaporization process continued, it generated pressures described by the fitted curve of Fig. 1, even as the composition became progressively depleted in Mg. If there were solid solution present in MgB_2 , then it would be expected that the data in Fig. 1 would have a broader spread, and could be best fit by several semi-parallel lines, each corresponding to a different solid solution composition produced by progressive Mg loss. However no such grouping of the data according to amount of Mg lost was observed. The vaporization process was terminated after a mass loss of 17%, which would correspond to a product with 2% (mole fraction) $\text{MgB}_2 + 98\%$ (mole fraction) MgB_4 . X-ray powder diffraction of the product showed it to be a mixture of predominantly MgB_4 and minor MgB_2 , with no other phases detected, indicating that the vaporization process occurred according to the equilibrium reaction: $2 \text{MgB}_2(\text{cr}) \rightarrow \text{MgB}_4(\text{cr}) + \text{Mg}(\text{g})$. In other samples, including some obtained commercially, presence of MgO among the vaporization products is thought to indicate entry of oxygen into the MgB_2 during its synthesis. Results of vapor pressure measurements on these materials will be published elsewhere [12].

Our experimental calorimetric data² for the reaction of $\text{Mg}(\text{cr})$, $\text{B}(\text{amorphous})$, and $\text{MgB}_2(\text{cr})$ with HNO_3 were combined with literature data for the amorphous/crystalline transition in B according to the reactions below, where $\Delta_r H_m$ designates the enthalpy per mole of solid reactant:



²Measurement uncertainties are expressed as \pm one standard deviation of the mean.

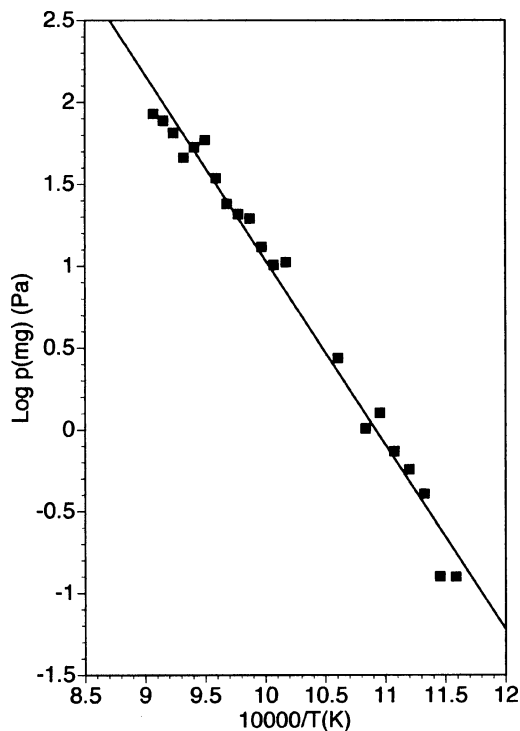
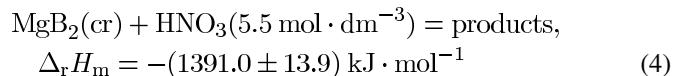
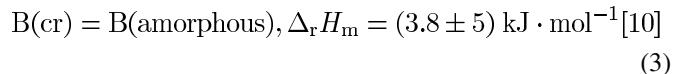


Fig. 1. Vapor pressure of MgB_2 , as measured by Knudsen effusion vacuum thermogravimetry.



These reactions define the enthalpy of formation of $\text{MgB}_2(\text{cr})$, by application of the appropriate Hess cycle: $-\Delta_r H_m(4) + 2\Delta_r H_m(2) + 2\Delta_r H_m(3) + \Delta_r H_m(1) = \Delta_f H_{\text{MgB}_2}^\circ(298.15) = -(155.9 \pm 14.2) \text{ kJ} \cdot \text{mol}^{-1}$. A more complete data set will be published elsewhere [13], together with measurements on other samples with lesser purity.

V. DISCUSSION

The vapor pressure data can be combined with the measurement of $\Delta_f H_{\text{MgB}_2}^\circ(298.15)$ to produce a calculated phase diagram [14] at 0.1 MPa for the Mg-rich part of the Mg-B phase diagram, as shown in Fig. 2. This diagram indicates a decomposition temperature of 1268°C for MgB_2 , significantly lower than that estimated in [6] and calculated in [7]. Calculation of Fig. 2 has required adjustments in the thermodynamic properties of MgB_4 as published in the literature [10], to allow production of a diagram consistent with our data for MgB_2 . Our value of $\Delta_f H_{\text{MgB}_2}^\circ(298.15)$, $-(155.9 \pm 14.2) \text{ kJ} \cdot \text{mol}^{-1}$, is more than twice the literature value of $-(74.8 \pm 3.8) \text{ kJ} \cdot \text{mol}^{-1}$ [5], [10]. Without access to a complete description of the earlier work, a full explanation of the difference is not possible. However, based on our calculation of Fig. 2, it is also likely that the enthalpy of formation of MgB_4 is significantly more negative than reported in the literature. Fig. 2 was calculated assuming negligible solubility of MgB_2 in the Mg/ MgB_2 eutectic. This

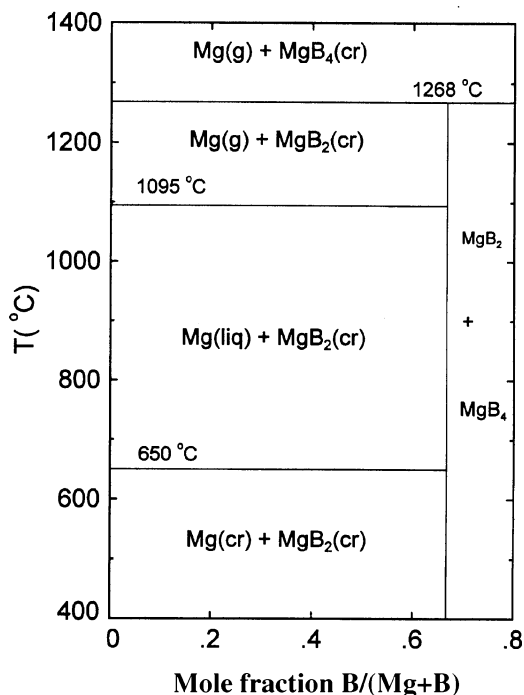


Fig. 2. Calculated phase diagram for the Mg-rich part of the Mg-B system at 0.1 MPa total pressure.

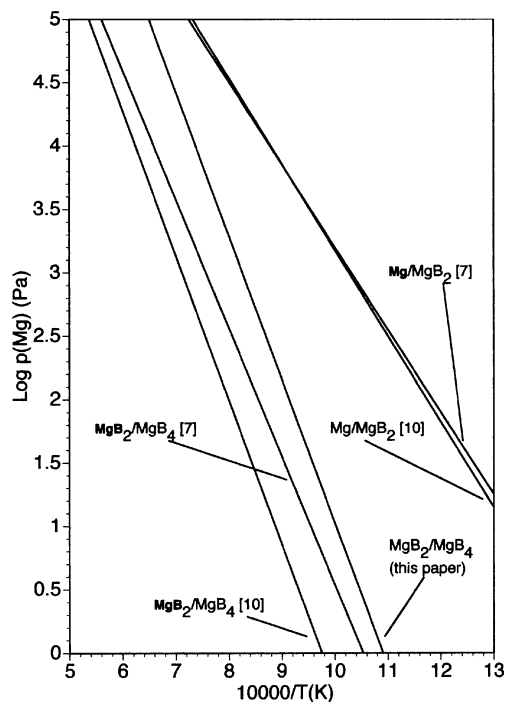


Fig. 3. Comparison of literature data on MgB_2 stability with the present study.

assumption was supported by our observation that there was no detectable lowering of the melting point of Mg in the presence of MgB_2 .

Our measured vapor pressure curve is plotted together with literature data in Fig. 3, where it can be seen that our data are approximately an order of magnitude higher than the curve calculated from the literature data [10] for the $\text{MgB}_2/\text{MgB}_4$ equi-

librium. Our measurements are also significantly higher than the calculated curve of [7]. The practical implication is that, for production of high purity MgB_2 , higher Mg pressures must be employed than would be suggested by the literature data. However, if less pure MgB_2 is desired, as is currently sought for some applications requiring improved flux pinning, then it is possible that successful processing may be achieved at lower Mg pressures than the curve in Fig. 1, in the presence of suitable dopants.

VI. SUMMARY

Using well-characterized, stoichiometric MgB_2 , with no detectable oxygen impurities, we have measured the Mg pressure over $\text{MgB}_2(\text{cr})$ as a function of temperature over the range 600°C to 850°C. From this data, we have developed an expression that can be extrapolated to give an MgB_2 decomposition temperature of 1268°C at 0.1 MPa. We have performed calorimetric studies on the same material, resulting in a new determination of $\Delta_f H_{\text{MgB}_2}^\circ$ (298.15), which differs significantly from the literature value. The thermodynamic properties of other Mg-borides will require reevaluation before a reliable phase diagram can be constructed for the complete range of Mg-B compositions.

REFERENCES

- [1] J. Nagamatsu, N. Nakagawa, T. Muranaka, Y. Zenitani, and J. Akimitsu, "Superconductivity at 39 K in magnesium diboride," *Nature*, vol. 410, pp. 63–64, 2001.
- [2] D. C. Larbalestier, L. D. Cooley, M. O. Rikel, A. A. Polyanskii, J. Jiang, S. Patnaik, X. Y. Cai, D. M. Feldmann, A. Gurevich, A. Squitieri, M. T. Naus, C. B. Eom, E. E. Hellstrom, R. J. Cava, K. A. Regan, N. Rogado, M. A. Hayward, T. He, J. S. Slusky, P. Halifah, K. Inumaru, and M. Hass, "Strongly linked current flow in polycrystalline forms of the superconductor MgB_2 ," *Nature*, vol. 410, pp. 186–189, 2001.
- [3] R. Flukiger, H. L. Suo, N. Musolino, C. Beneduce, P. Toulemonde, and P. Lezza, "Superconducting properties of MgB_2 tapes and wires," *Physica C*, vol. 385, pp. 286–305, 2003.
- [4] X. L. Wang, S. Soltanian, M. James, M. J. Qin, J. Horvat, Q. W. Yao, H. K. Liu, and S. X. Dou, "Significant enhancement of critical current density and flux pinning in MgB_2 with Nano- SiC, Si, and C doping," *Physica C*, vol. 408–10, pp. 63–67, 2004.
- [5] D. White, Olin Mathieson Chemical Corporation, Technical Research Report MCC-1023-TR-222, 1956.
- [6] T. B. Massalski, Ed., *Binary Alloy Phase Diagrams*, 2nd ed. Materials Park, OH: ASM International, 1992, vol. 1, p. 498.
- [7] Z.-K. Liu, D. G. Schlom, Q. Li, and X. X. Xi, "Thermodynamics of the Mg-B system: implications for the deposition of MgB_2 thin films," *Appl. Phys. Lett.*, vol. 78, pp. 3678–3680, 2001.
- [8] S. L. Bud'ko, G. Lapertot, C. Petrovic, C. E. Cunningham, N. Anderson, and P. C. Canfield, "Boron isotope effect in superconducting MgB_2 ," *Phys. Rev. Lett.*, vol. 86, pp. 1877–1880, 2001.
- [9] K. D. Carlson, "The Knudsen effusion method," in *The Characterization of High-Temperature Vapors*, J. L. Margrave, Ed. New York: Wiley, 1967, pp. 115–129.
- [10] M. W. Chase Jr., "NIST-JANAF thermochemical tables, 4th edition," *J. Phys. Chem. Ref. Data*, Monograph no. 9, 1952 pp., 1998.
- [11] R. Klein, L. P. Cook, and W. Wong-Ng, "Enthalpies of formation of SrPbO_3 and Sr_2PbO_4 ," *J. Chem. Thermod.*, vol. 34, pp. 2083–2092, 2002.
- [12] L. P. Cook, R. Klein, W. Wong-Ng, Q. Huang, R. A. Ribeiro, and P. C. Canfield, "Knudsen effusion thermogravimetry of MgB_2 ," *Thermochim. Acta*, submitted for publication.
- [13] R. Klein, L. P. Cook, W. Wong-Ng, Q. Huang, R. A. Ribeiro, and P. C. Canfield, "Enthalpy of formation of MgB_2 ," *J. Chem. Thermod.*, submitted for publication.
- [14] C. W. Bale, P. Chartrand, S. A. Degterov, K. Hack, R. Ben Mahfoud, J. Melancon, A. D. Pelton, and S. Petersen, "FactSage thermochemical software and databases," *CalPhad*, vol. 26, pp. 189–228, 2002.