HIGH-RESOLUTION ADIABATIC SCANNING CALORIMETRY ON THE MELTING TRANSITION OF GALLIUM

INTRODUCTION

Scanning calorimetric techniques allow to obtain continuously the evolution of the heat capacity at constant pressure $C_p(T)$ in terms of the power P and the rate dT/dt.

$$C_p = \frac{dQ}{dT} = \frac{dQ/dt}{dT/dt} = \frac{P}{\dot{T}}$$

Adiabatic Scanning Calorimetry (ASC) : A constant power P is supplied to the sample and the resulting change in temperature $T(t)$ is measured as a function of time from which the rate dT/dt can be calculated. Combining the rate with the constant power results in $C_p(T)$. Moreover, the enthalpy $H(T)$ is easily obtained from the product of the power P and the time laps between the start of the run at t_0 and the time at which $T(t)$ was reached.

$$H(T) = P\left[t(T) - t(T_0)\right]$$

Differential Scanning Calorimetry (DSC) : A constant rate dT/dt is imposed via a constant power P_{ref} imposed on a known reference material. The power $P_s = dQ/dt$ on the sample has to be adjusted to follow the constant rate (of the reference). This becomes very difficult at very sharp transitions because large power changes have to be provided, which quite often results in time lags and temperature differences between the real and the detected transition. The enthalpy $H(T)$ has to be derived from the integration of the $C_p(T)$ data.

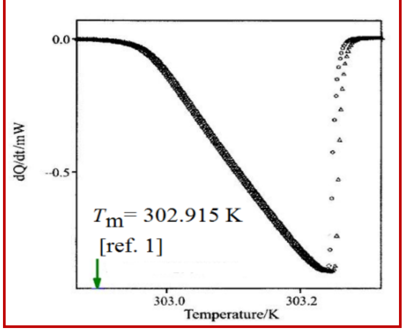
$$H(T) = \int_{T_0}^{T} C_p \, dT$$

RESULTS

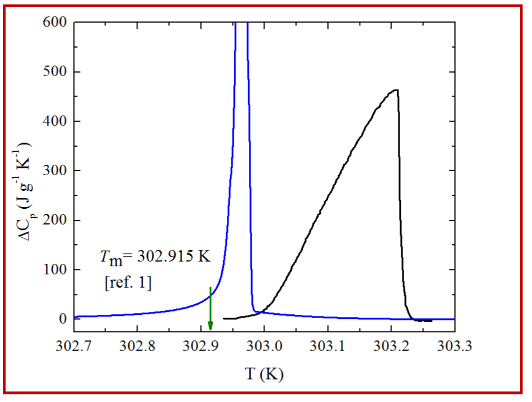
Sample measured **Gallium (assay 99.9995%) was purchased from Aldrich (203319) and it was measured as received without further treatment or purification.**

- **Melting transition temperature T_m = 302.915 K [1]**
- **Heat of fusion = 80.07 J g^{-1} [1]**

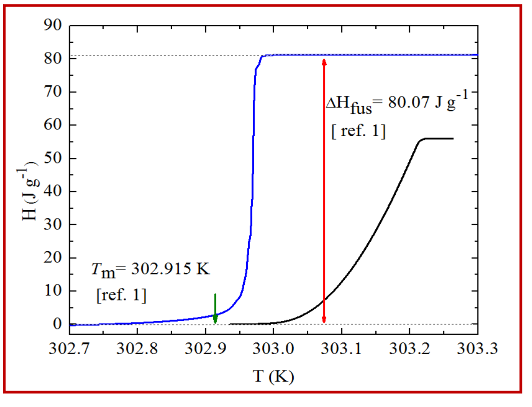
Measurement **A heating run with constant power of P = 150 µW in a Peltier-based ASC calorimeter on a 24.3 mg sample.**



DSC power data from ref [2]. Run on 2.01 mg of gallium using a constant rate of 1 mK/s [2].



Heat capacity ΔC_p. Black solid line: DSC data derived from *dQ/dt* data in the top figure from ref [2]. Blue solid line: ASC data from this work.



Enthalpy of fusion of gallium. Black solid line: DSC data derived from *dQ/dt* data in the top figure from ref [2]. Blue solid line: ASC data from this work.

CONCLUSIONS

- **The melting transition temperature agrees with the literature value within the accuracy of the temperature calibration of the calorimeter (± 30 mK).**
- **Excellent agreement with the value of heat of fusion quoted in the literature, which was obtained by step calorimetry on a very large sample of 32 g [1].**
- **The melting transition takes place in a more than 10 times narrower temperature interval (~20 mK) than the one quoted in DSC measurements (~0.25 K). During an ASC run the temperature of the sample is freely (i.e., at a first order phase transition, slowly) evolving, based on the supplied power and on its enthalpy, without any enforcement due to the instrument.**

REFERENCES

[1] D. G. Archer, The enthalpy of fusion of gallium, J. Chem. Eng. Data 47 (2002) 304.

[2] M. Minohara, K. Tozaki, H. Hayashi, and H. Inaba, Effect of the magnetic field on the melting transition of Ga and In by nW-stabilized DSC, J. Therm. Anal. Cal. 86 (2006) 833.