LOW-TEMPERATURE HEAT CAPACITY OF ILVAITE FROM SERIPHOS (GREECE): A TEST CASE FOR THE QUANTUM DESIGN® MICROCALORIMETER

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The heat capacity of natural ilvaite from Seriphos (Greece) was measured between 5 and 300 K with the Quantum Design® microcalorimeter (QDM), newly established at the Department of Mineralogy, Salzburg University (financed by FWF project P15880-NO3, which is gratefully acknowledged). This device allows the measurement on milligram-sized samples and is based on a relaxation-time calorimetric method [1]. Ilvaite from Seriphos was chosen, because low-temperature heat capacities have already been obtained for this substance by adiabatic and differential scanning calorimetry [2, 3] and a sound sample characterisation is available [3]. The natural ilvaite used has a composition close to the end-member formula [3]: $Ca_{0.992}(Fe^{2+}{}_{1.935}Fe^{3+}{}_{0.968}Mg_{0.022}Mn_{0.018}Al_{0.053})[Si_{2.003}O_7O(OH)_{0.998}]$. Its unit cell parameters are [3]: a_o = 13.011(2) Å, b_o = 8.801(2) Å, c_o = 5.851(1) Å, β = 90.05(1)°. For the QDM-measurement, a 4 x 4 mm-shaped 0.3 mm thick ilvaite plate weighing 17.73 mg was placed on the sample platform of the microcalorimeter and heat capacities were collected at 40 setpoints linearly spaced between 5 and 300 K (Figure 1, dots; each setpoint represents the mean of three separate measurements). A complete measurement lasts around 20 hours compared to several weeks required in adiabatic calorimetry. The amount of sample material for the adiabatic technique is in the order of grams, general a severe limitation for applying this method to synthetic samples. The agreement between QDM- and adiabatic heat capacities is satisfactory (Figure 1). Below 100 K the QDM-data are somewhat higher (maximal 4 % around 50 K), above 100 K at maximum 2 % lower than the adiabatic data reported by [2].

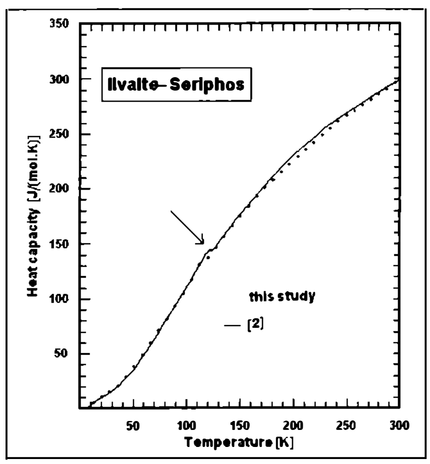

Figure 1
Low-temperature heat capacity of ilvaite from Seriphos, obtained by the Quantum Design® microcalorimeter on a 17.73 mg sample (dots, this study), compared to adiabatic calorimetry data using 408.794 g sample material (line, [2]). Arrow indicates a antiferromagnetic phase transition occuring around 120 K.

A close-up of the heat capacities is shown in Figure 2 for the temperature region 0–40 K and around 120 K, where a antiferromagnetic phase transition is known to occur. Worth mentioning is that our QDM-data show this transition at a 7 K lower temperature (113 K) compared to 120 K from adiabatic calorimetry [2]. The reason for this discrepancy is unclear but may be related to slightly different Fe^{2+}/Fe^{3+}-ratios in the samples investigated.

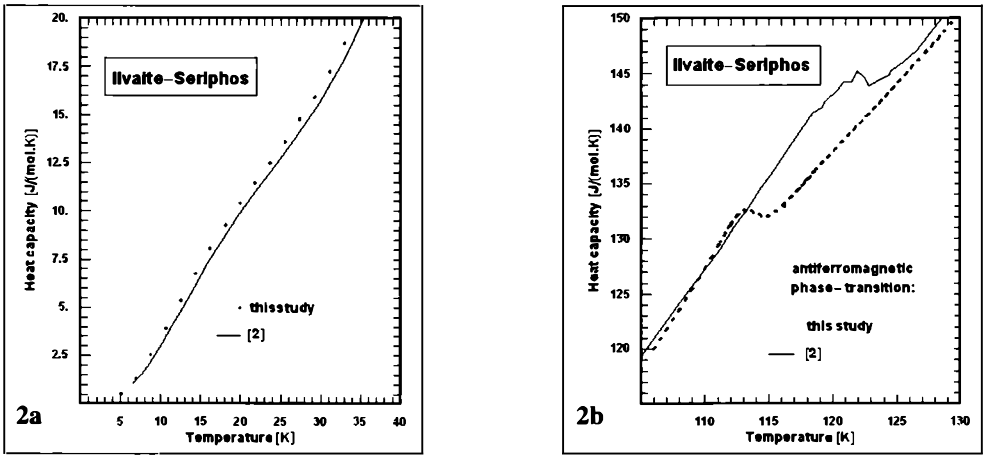

Figure 2

Close-up of ilvaite heat capacities versus temperature. a) temperature region 0–40 K: the concave curvature visible in both data sets is attributed to a mixumum in the magnetic susceptibility in this temperature interval by [2]. The QDM-data are at maximum 4 % higher than the adiabatic data.
b) temperature region 105–130 K: the QDM-measurements on our ilvaite sample, collected in 0.33 K intervalls, indicate that the antiferromagnetic phase transition occurs around 113 K, whereas the adiabatic data show this transition at 120 K.

Numerically integrating our QDM-data yields a standard entropy for ilvaite from Seriphos of 291.7 [J/(mol.K)], which agrees within error with 292.3 ± 0.6 [J/(mol.K)] calculated by [2].

Further measurements with QDM on single-crystals and powders of various substances, whose low-temperature heat capacities are known from adiabatic calorimetry, will be undertaken to further test the reliability of this technique. QDM will then be used to measure low-temperature heat capacities of various synthetic samples and to determine standard entropies for a number of important rock-forming mineral end-members from these data.

References

[1] BACHMANN, R. ET AL. (1972): Heat capacity measurements on small samples at low temperatures. - Review of Scientific Instruments 43/2: 205-214.

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[3] BERTOLDI, CH. ET AL. (2002): The heat capacity of ilvaite. - Beih. Eur. J. Mineral. 14,(2002):19.