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Heat capacities of nanostructured wurtzite and rock salt ZnO: challenges of ZnO nano-phase diagram

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Abstract: Low-temperature heat capacities (C_p) of nanostructured rock salt (rs-ZnO) and wurtzite (w-ZnO) polymorphs of zinc oxide were measured in the 2–315 K temperature range. No significant influence of nanostructuring on C_p of w-ZnO has been observed. The measured C_p of rock salt ZnO is lower than that of wurtzite ZnO below 100 K and is higher above this temperature. Using available thermodynamic data, we established that the equilibrium pressure between nanocrystalline w-ZnO and rs-ZnO is close to 4.6 GPa at 300 K (half as much as the onset pressure of direct phase transformation) and slightly changes with temperature up to 1000 K.

Keywords: zinc oxide; heat capacity; nanostructure; phase diagram; high pressure.

1. Introduction

The low-temperature heat capacity measurements are required for understanding the phase transformations and construction of low-temperature regions of the equilibrium pressure – temperature (p - T) phase diagrams of elements and compounds, especially those important for mineralogy and explorative materials science (e.g. search for new materials under high pressure). At the same time there are a number of problems that arise during the heat capacity measurements for analysis of equilibria at low temperatures and high pressures, such as

(1) the direct (adiabatic) measurements at ambient pressure are time-consuming, costly and most importantly require a significant amount of pure compound (typically hundreds of μg), which makes explorative studies and study of phases recovered from very high pressures difficult (the pressure achievable in the laboratory is inversely proportional to the reaction volume);

(2) the results of typical Physical Property Measurement System (PPMS) measurements are limited in temperature (~ 350 K) and can be influenced by systematic errors due to either poor thermal contact between the sample and the heater-thermometry platform; and/or between the grains in a polycrystalline sample (porosity, bad sintering, reduced inter-grain contacts, etc.);

(3) systematic errors can also arise due to the water present in two forms – (i) bound into crystal structure during the sample synthesis and (ii) absorbed from air due to the porosity of the sample;

(4) low thermal stability of some high-pressure phases (such as rs-ZnO) can limit possible measurements to low temperatures, while the data of interest may lay at much higher temperatures, so the reliable extrapolation procedures are required; and finally,

46 (5) heat capacity data collection at high pressure remains rather exotic, very time-consuming,
47 available in arbitrary units and accessible only in a very narrow p - T domain.

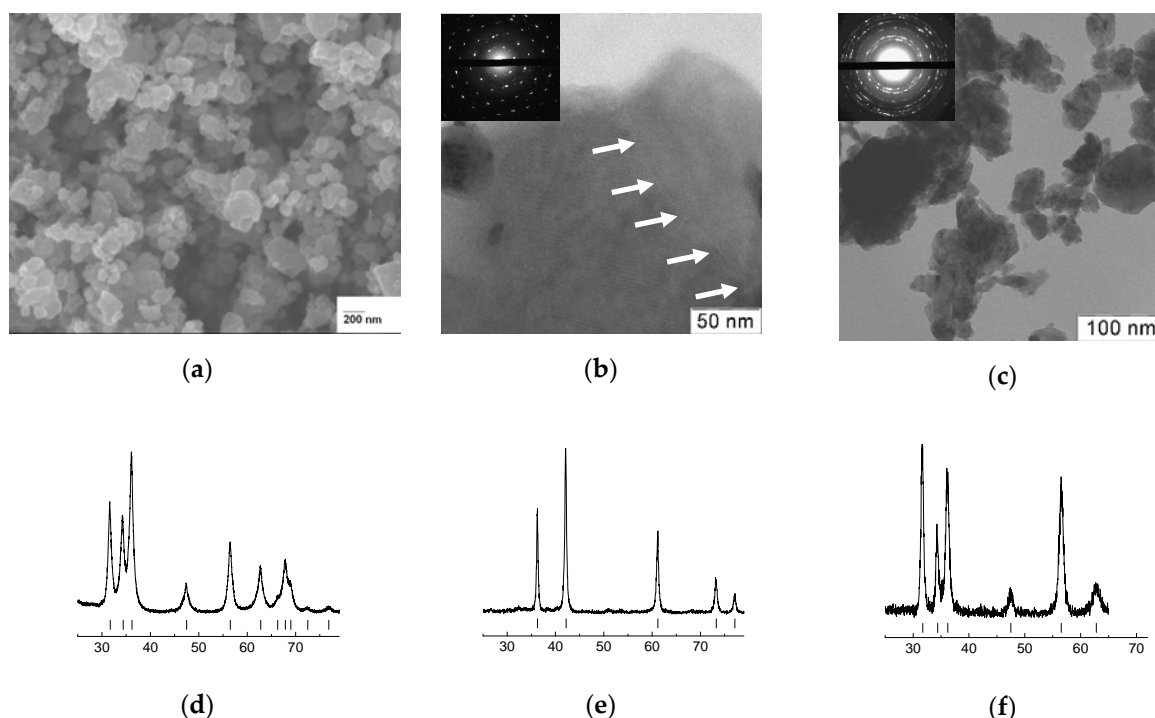
48 Usually the construction of the phase diagrams at high enough temperatures (subject to the
49 material and the pressure) is not considered be of an importance once the reversible transitions
50 between phases are observed. However, in some cases even at high temperature the crystallization
51 of a new allotrope/polymorph is not reversible and, moreover, may occur outside the domain of
52 thermodynamic stability (e.g. in the case of boron [1] or boron oxide [2]). The fundamental question
53 of low-temperature stability can be hardly resolved without reliable low-temperature heat capacity
54 data. Thus, the convincing thermodynamic analysis of materials at extended p - T regions of the
55 phase diagram is hardly possible without low-temperature data on C_p at ambient pressure and the
56 methods of its extrapolation to high temperatures and high pressures.

57 Zinc oxide ZnO is a functional material that can be used both in industrial applications and for
58 basic research in common w-ZnO form [3], as well as in high-pressure rs-ZnO form that is a
59 material of interest for bright blue luminescence [4]. rs-ZnO can be recovered at ambient conditions
60 as individual (nanostructured) phase, up to the volume of ~ 100 mm³ per individual high-pressure
61 synthesis experiment [4,5]. The recovery of such a substantial sample volume allowed conducting
62 the measurements of a wide range of physical properties - previously unavailable - such as, for
63 example, the standard enthalpy of the w-ZnO-to-rs-ZnO phase transformation $\Delta H(298.15 \text{ K}) =$
64 $11.7 \pm 0.3 \text{ kJ mol}^{-1}$ [6]. At the same time, the reported data should be taken with precaution, since the
65 bulk samples with micro-sized grains are available only for w-ZnO. Recent advances in the diverse
66 synthetic routes of rs-ZnO materials [4] allowed us to obtain samples of chemical purity for reliable
67 measurements of the heat capacities of both polymorphs for consistent side-by-side comparison.

68 Here we report low-temperature heat capacities for both nanostructured ZnO polymorphs,
69 consistent with observable phase transformation between polymorphs at high temperature (when
70 pressure hysteresis between direct and inverse transformations become negligible). We established
71 that the nanostructured samples contain the absorbed water (problem (3) of the list above) which is
72 the major source of measurement errors that can be quite significant and should be considered
73 when physical property measurements are conducted. Accounting for the exact amount of
74 absorbed water (by using thermal gravimetric analysis) allowed us to obtain the accurate estimate
75 of heat capacities and to evaluate the equilibrium pressure between w-ZnO and rs-ZnO
76 polymorphs at high pressure and room temperature. No significant impact of nanostructuring on
77 heat capacity has been observed for w-ZnO.

78 2. Experimental Section

79 The rs-ZnO sample purity was of primary concern for our work. In fact, rs-ZnO can be
80 recovered at ambient conditions only when nanopowders of w-ZnO are used as precursors [4].
81 Preparation of starting w-ZnO nanopowders by methods of solution chemistry [4] does not allow
82 synthesis of ZnO nanoparticles free of surface chemical groups that can strongly impact the heat
83 capacity measurements and subsequent free energy calculations. Milling techniques also does not
84 allow obtaining the samples of high crystal perfection for measurements of sufficient
85 thermodynamic quality. To avoid any organic or inorganic impurity - except small amount of
86 absorbed water - we synthesized w-ZnO nanopowder "precursor" by thermal decomposition of
87 zinc peroxide ZnO₂ (Prolabo, 70% of Zn in the form of ZnO₂) in a muffle furnace in air at 570 K (120
88 min.). Nanoparticles with grain size of 10-50 nm can be clearly seen on the SEM image (Figure 1a).
89 X-ray diffraction pattern of the initial w-ZnO powder shows lines broadening due to
90 nanocrystallinity (Figure 1d). No diffraction peaks from ZnO₂ or other crystalline impurities were
91 detected.
92



93

94 **Figure 1.** (a) SEM image of w-ZnO particles obtained by thermal decomposition of ZnO₂ that show
 95 morphology typical for nanopowders. (b) TEM image of rs-ZnO nanoparticles quenched from high
 96 pressure. Inset shows SAED pattern of rock salt structure. Arrows point to grain boundary. (c) TEM
 97 image of w-ZnO nanoparticles prepared by thermal decomposition of rs-ZnO. Inset shows SAED
 98 pattern of wurtzite structure. (d-f) X-ray diffraction patterns (CuK α radiation) of pristine w-ZnO
 99 nanopowder (d), synthesized rs-ZnO (e), and w-ZnO obtained by reverse phase transformation (f).
 100 Vertical bars indicate the Bragg peaks positions.

101 Single-phase nanocrystalline bulk (pellet ~1 mm thickness and 4.5 mm in diameter) rs-ZnO has
 102 been synthesized from w-ZnO nanopowder (grain size of ~9 nm) at 7.7 GPa & 800 K and
 103 subsequent rapid quenching (Figure 1b & e). The details of high-pressure synthesis and
 104 characterization of the recovered samples are described earlier [4, 5, 7]. Nanocrystalline bulk
 105 w-ZnO obtained by reverse (from rs-ZnO to w-ZnO) phase transformation was used as reference
 106 sample (Figure 1c & f). This eliminates the potential influence of grain size and possible surface
 107 contribution to the heat capacity. Before and after the calorimetric measurement X-ray powder
 108 diffraction verified that the samples were single-phases without any impurity. As one can see on
 109 the upper right part of the photo (Figure 1b) between rs-ZnO nanograins exist intergrain
 110 boundaries that could contain water molecules absorbed on the w-ZnO surface before the high-
 111 pressure synthesis. As follows from Ref. [4], this water probably plays the role of “glue” and helps
 112 to stabilize metastable rock salt phase at ambient pressure. Elimination of these water molecules
 113 will inevitably lead to reverse transformation to wurtzite phase.

114 w-ZnO samples for C_p measurements were obtained via reverse phase transformation of the
 115 corresponding rs-ZnO bulks by linear heating (5 or 10 K/min) at controlled conditions in a DSC-131
 116 evo scanning calorimeter (SETARAM Instrumentation).

117 Heat capacity of rs-ZnO and w-ZnO bulk samples was measured between 310 and 2 K (Figure
 118 2a, open symbols) using calibrated heater-thermometer platforms in Physical Property
 119 Measurement System apparatus by Quantum Design. Data at 40 different temperature points (two
 120 measurements per point) have been collected at constant helium pressure ($35\text{-}60 \times 10^{-2}$ Pa) and in
 121 constant magnetic field (0.187 Oe) (Figure 2a). Before measurements, one side of each ZnO ingot
 122 was polished into a flat surface. Most of measurements were performed on two cubic-shaped
 123 samples with 4.90 mg (rs-ZnO) and 13.80 mg (w-ZnO) weight. The ZnO molar weight of
 124 81.38 g/mole was used to molar C_p calculation according to the 2011 IUPAC recommendation [8].

125 Recently it has been shown that PPMS can precisely measure the low-temperature C_p for samples of
 126 milligram size [9]. Thus, the low-temperature C_p measurements of high-pressure phases, which
 127 were almost impossible to achieve previously, now can be carried out using this technique. The
 128 accuracy of C_p measurement in our experiments was estimated to be better than 1% between 4.2 K
 129 and 315 K, and 4% at temperatures below 4.2 K.

130 Heat capacity measurements in the 294-331 K range (Figure 2a, solid symbols) were performed
 131 by heat flux calorimetry using micro DSC-7 evo Calvet calorimeter (SETARAM Instrumentation).
 132 Dynamic calibration for heat generation was carried out by the Joule effect using a E.J.3 calibration
 133 unit. Temperature calibration of the instrument was performed with standard substances (gallium,
 134 indium, etc.) according to the IUPAC recommendations. Calisto program package (v 1.086, AKTS
 135 AG) was applied for running the experiment, data collection and initial data processing. Stepwise
 136 heating mode was used as recommended for precise thermodynamic measurements [10]. The
 137 accuracy of C_p measurements was estimated to be better than 0.25%.

138 Thermogravimetry measurements (Labsys evo TG/DSC thermal analyzer, SETARAM
 139 Instrumentation) were used for evaluation of the amount of absorbed water in the samples.
 140 Typically, the H₂O loss was in the range of 2-4 wt%. These values can be considered as an
 141 underestimate, while the heat capacity contribution shows the water amount of ~5 wt% (this value
 142 should be taken with precaution since C_p of absorbed water is higher than that of bulk water [11]).
 143 The correction to heat capacity has been made using the reference data for water in the 2–273 K and
 144 273-310 K temperature ranges [12]:

$$145 \quad H_2O C_p \quad (J \quad mol^{-1} \quad K^{-1}) = 18 \times (7.73 \times 10^{-3} \times T \times (1 - \exp(-1.263 \times 10^{-3} \times T^2)) - 7.59 \times 10^{-3} + 2.509 \times 10^{-3} \times T$$

$$146 \quad - 1.472 \times 10^{-5} \times T^2 - 1.617 \times 10^{-9} \times T^3 + 8.406 \times 10^{-11} \times T^4).$$

148 3. Results & Discussion

149 rs-ZnO samples available at ambient pressure are always nanostructured, and can survive only
 150 at quite moderate temperatures. Previous reports suggest possible impact of nanostructuring on
 151 ZnO heat capacity values. Our experiments, however, indicate that to the accuracy of the
 152 measurements, no difference between nanostructured w-ZnO (obtained by reverse transformation
 153 of rs-ZnO upon heating) and bulk w-ZnO is observed. At the same time, samples exposed to air
 154 may show higher heat capacity, if absorbed water correction is not made. Typically, 3-5 wt% of
 155 water was found as the equilibrium value for nano-rs-ZnO, and both nano- and micro-w-ZnO.
 156 Corrected values for rs-ZnO and w-ZnO are shown in Figure 2a. No distinction between nano- and
 157 micro- samples will be made in the following discussion.

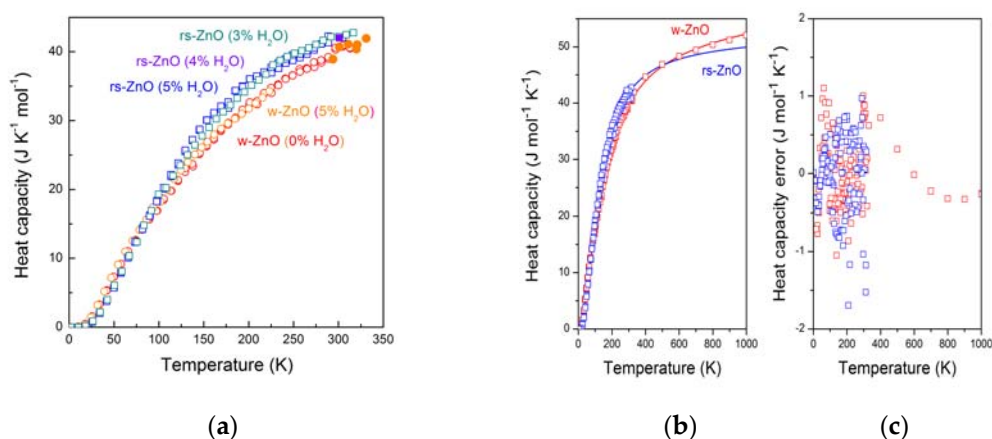
158 The experimental values of the heat capacity for w-ZnO and rs-ZnO nanostructured samples
 159 (Figure 2b) were fitted to the adaptive pseudo-Debye model proposed by Holtzapfel (explicitly
 160 formulated in Ref. [13]) that gives analytical expression for C_p as

$$161 \quad c_p = 3R\tau^3 \frac{4C_0 + 3C_1\tau + 2C_2\tau^2 + C_3\tau^3}{(C_0 + C_1\tau + C_2\tau^2 + C_3\tau^3)^2} \left[1 + A \frac{\tau^4}{(a + \tau)^3} \right], \quad (1)$$

162 where $\tau = T/\theta_h$; θ_h is Debye temperature in the high-temperature region; C_1 , C_2 and A are parameters
 163 to be fitted; $C_3 = 1$; a characterizes non-harmonicity; R is gas constant. Parameter C_0 has been chosen
 164 as $C_0 = (5 \theta^3)/(\pi^4 \theta_h^3)$, with θ and θ_h Debye temperatures in the low- and high-temperature regions,
 165 respectively, in order to obtain these values directly as fitting parameters.

166 The fitting of the experimental data to Eq. 1 was performed using the simplex method using
 167 the MATLAB software. The uniqueness and stability of the solution (i.e. a set of mentioned above
 168 parameters determining theoretical curve) of inverse problem have been tested by multiple
 169 minimization procedures from various sets of starting parameters. To improve the solution quality
 170 and obtain the parameters allowing high-temperature extrapolation, we added the available data
 171 on

172



173

174 **Figure 2.** (a) Experimental heat capacities of nanostructured rs-ZnO (squares) and w-ZnO (circles).
 175 Open symbols correspond to PPMS measurements, while solid symbols – to SETARAM calorimeter
 176 measurements. The size of symbols corresponds to the error estimate. (b) Heat capacity data fitted
 177 to Holtzapfel equation (1). High-temperature extrapolation for rs-ZnO has been made using
 178 regularized fitting procedure described in the text. Red and blue solid lines represent the calculated
 179 C_p curves for w-ZnO and rs-ZnO, respectively. Solid squares of the same color show experimental
 180 data. The size of squares corresponds to the error estimate. (c) Discrepancy between experimental
 181 and calculated values of heat capacities. Most of the data points are in within ± 0.5 J mol⁻¹ K⁻¹.

182 C_p of w-ZnO up to 1250 K (this allowed obtaining the reliable values of θ_h , A and a). It was possible
 183 to exclude the mutual compensation of fitting parameters only in the case of w-ZnO: the number
 184 and quality of the initial data combined with the a value constrained to be positive and with taking
 185 into account the additional high-temperature data. In order to avoid occasional non-physical
 186 solutions for rs-ZnO, we used the w-ZnO parameters as the initial approximation. For both phases
 187 non-harmonicity parameter a was found to be zero.

188 The fitting gave the following sets of parameters:

189 (1) for w-ZnO : $\theta_h = 256$ K, $\theta_l = 132$ K, $C_0 = 0.0070$, $C_1 = 0.4490$, $C_2 = 0.9942$, $A = 0.0208$, $a = 0$;

190 and

191 (2) for rs-ZnO : $\theta_h = 226$ K, $\theta_l = 335$ K, $C_0 = 0.1663$, $C_1 = 0.3864$, $C_2 = 0.9755$, $A = 0.0055$, $a = 0$.

192

193

194 One can see that the high-temperature limits of Debye temperature θ_D are close, while the low-
 195 temperature values are in agreement with the general rule that the higher density corresponds to
 196 higher Debye temperature. At the same time, our θ -values are noticeably lower than the previously
 197 reported Debye temperatures (~ 400 K) for w-ZnO [14]. Such discrepancy can be explained, from
 198 one side, by nanostructuring of our samples, and, from the other side, by the experimental errors
 199 that allow treating the θ_l values as fitting parameters. Only rigorous study of fully water-free
 200 samples could reveal whether nanostructuring impacts Debye temperature or not.

201

202 In the case of the nanostructured w-ZnO obtained by reverse transformation from rs-ZnO at
 203 523 K, the heat capacity is quasi-indistinguishable from the large-grain samples. This is indicative of
 204 essentially zero surface entropy of our nano-w-ZnO, similar to previous observations for nano-w-
 205 ZnO obtained by chemical decomposition of zinc nitrate at 573 K [11]. Such closeness can be
 attributed to the thermal cure of the surface.

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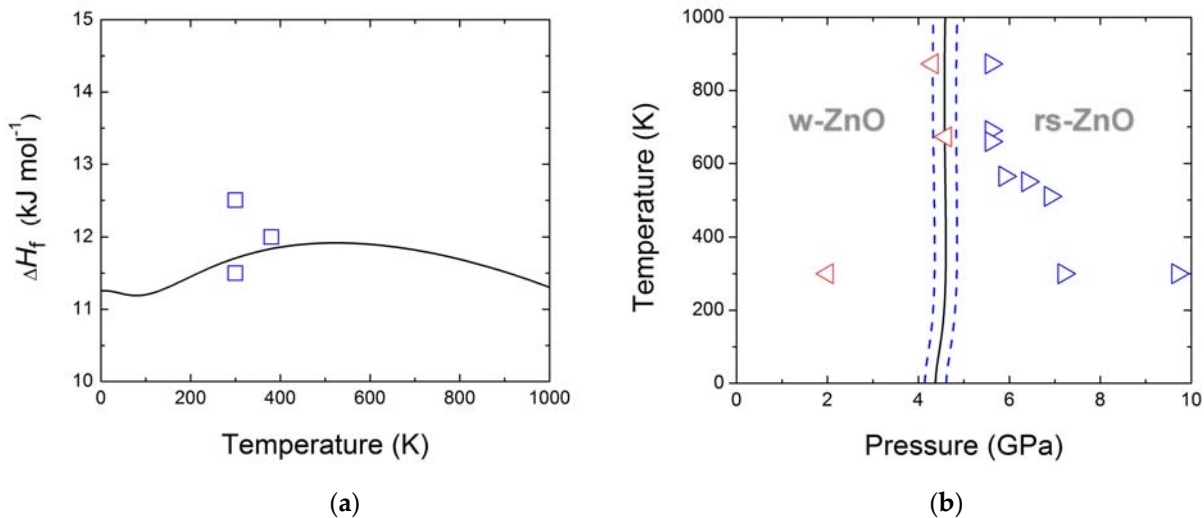
207 **Figure 3a** shows the formation enthalpy ΔH_f calculated using the fitted values of heat capacities
 208 and experimental value of ΔH_f (298.15 K) = 11.7 ± 0.3 kJ mol⁻¹ [6]. One can observe only weak
 209 temperature dependence of ΔH_f . The minimum and maximum on the curve are due to the double
 210 intersection of heat capacity curves of w-ZnO and rs-ZnO nanostructured phases. These values
 differ by a factor of two from the results of indirect measurements at high temperatures (e.g. by

211 EFM measurements [15]), which can be explained by the 1100-1300 K experimental range that is out
 212 of rs-ZnO stability region, as well as by the nanocrystallinity of our samples. It is also interesting to
 213 compare ΔH_f values with the *ab initio* predictions (at 0 K) that show a large dispersion (from 15 to 30
 214 kJ mol⁻¹) of calculated values, e.g. 21.230 and 28.950 kJ mol⁻¹ (by LDA and GGA, respectively) in
 215 Ref. [16] and 15.247 and 22.871 kJ mol⁻¹ (by LDA and GGA, respectively) in Ref. [17]. The variation
 216 of the calculated values by a factor of two does not allow making any reliable evaluation of
 217 thermodynamic stabilities of bulk phases at low temperatures. At the same time, the *ab initio*
 218 simulations of structural transition in ZnO nanowires at high pressures (calculations using the
 219 SIESTA code) indicated that passage from bulk crystal to nanograins reduces ΔH_f (0 K) from
 220 23 kJ mol⁻¹ down to 10 kJ mol⁻¹ [18]. This result is consistent with the data in Ref. [6] and imply the
 221 difference between bulk- and nano-phase diagrams of ZnO.

222 Nano-phase diagram of zinc oxide has been calculated using the fitted experimental heat
 223 capacity values, directly-measured ΔH_f [6] and thermoelastic p - V - T data on rs-ZnO [5,19] and w-
 224 ZnO [20]. The experimental data on direct and inverse transformations in ZnO at high (above
 225 500 K) temperatures are in satisfactory agreement [7,19]. At lower temperatures, where the
 226 transformation hysteresis is pronounced, the application of the estimated p_{eq} for the equilibrium
 227 pressure as

$$228 \quad p_{eq} \approx 0.5 \times (p_{direct} + p_{inverse}) \quad (2)$$

229 results in the p_{eq} value of 5 ± 3 GPa at 300 K [19,21]. The uncertainties have an order of magnitude of
 230 the yield stress accumulated during the transformation [22]. Here we should note that the use of the
 231 hypothesis that $p_{eq} \approx p_{direct}$ is methodologically incorrect. In fact, both direct and inverse
 232 transformations were observed experimentally at finite pressure, which is in agreement with
 233 Landau character of 2nd-order transformation driven by the lattice strain as order parameter. Such
 234 model requires the onset pressure of ~ 9.4 GPa [22] above the equilibrium corresponding to the
 235 formal requirement of $\Delta G_{rs/w}(p, T) = 0$.
 236



237

238 **Figure 3.** Calculated difference of formation enthalpies of ZnO polymorphs $\Delta H_f(T)$ at 0.1 MPa, and
 239 p - T phase diagram (i.e. $\Delta G_{rs/w}(p, T) = 0$) vs experimental and *ab initio* data. (a) Black solid line is ΔH_f as
 240 a function of temperature extrapolated to 1000 K using regularized procedure described in the text;
 241 blue open squares are experimental data from Ref. [6]; (b) Nano-phase diagram of ZnO representing
 242 equilibria between nanostructured phases. Isopotential curve corresponds to $\Delta G_{rs/w}(p, T) = 0$
 243 (equilibrium between w-ZnO and rs-ZnO; black solid line) with the estimated error of ± 0.3 kJ mol⁻¹
 244 for ΔH_f [6] (the dashed blue lines). Symbols represent experimental p, T -points on direct (right-
 245 oriented red triangles) and inverse (left-oriented blue triangles) transformations observed by *in situ*
 246 X-ray diffraction [7,19].

247 5. Conclusions

248 The low-temperature (2–310 K) isobaric heat capacities of rock salt ZnO, metastable high-
 249 pressure phase, and wurtzite ZnO have been experimentally studied using the thermal relaxation
 250 PPMS calorimetry. Measurements of low-temperature heat capacities of nanostructured ZnO
 251 polymorphs and analysis of the equation-of-state data allowed us to resolve the ambiguities of the
 252 equilibrium p - T phase diagram of ZnO. A set of proposed thermo-physical data is well consistent
 253 with the observed direct and inverse phase transformations in nanostructured ZnO up to 1000 K. In
 254 this temperature range the equilibrium pressure is close to 4.6 GPa, which is lower than the *ab initio*
 255 prediction for bulk ZnO, but in a good agreement with simulations made for nanoparticles.

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 257 K.V.K., P.S.S., A.N.B., F.Y.Sh. and V.L.S.; data curation, K.V.K., A.C. and V.L.S.; writing—original draft
 258 preparation, A.C.; writing—review and editing, V.L.S.; visualization, A.C.; supervision, V.L.S.; funding
 259 acquisition, V.L.S. All authors have read and agreed to the published version of the manuscript.

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265 **Conflicts of Interest:** The authors declare no conflict of interest.

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