Tepelné kapacity pevných látek

Jindřich Leitner & David Sedmidubský

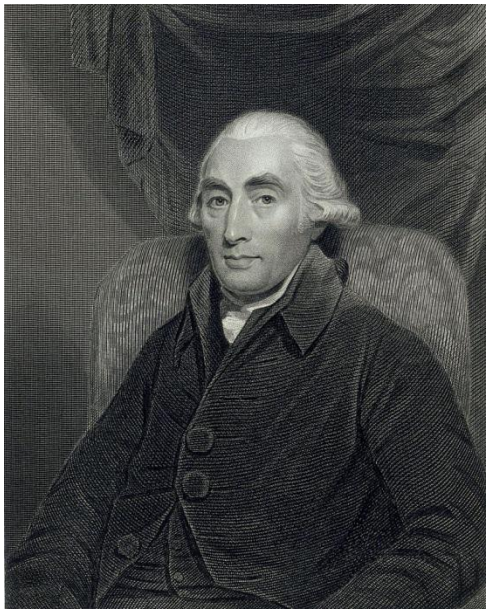
VYSOKÁ ŠKOLA
CHEMICKO-TECHNOLOGICKÁ
V PRAZE

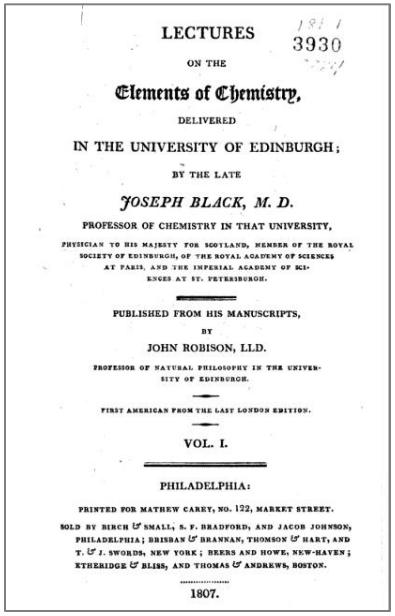
Obsah přednášky

1. Úvod – trocha historie
2. Teoretický popis tepelných kapacit pevných látek
3. Experimentální stanovení tepelných kapacit pevných látek
4. Empirické odhadové metody pro predikci tepelných kapacit pevných látek
5. Závěr

Joseph Black (1728 – 1799)

Teplo vs. teplota, koncept specifického tepla (Fahrenheitovy experimenty) a latentního tepla tání/vypařování





LECTURES
3930
ON THE
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DELIVERED
IN THE UNIVERSITY OF EDINBURGH;
BY THE LATE
JOSEPH BLACK, M. D.
PROFESSOR OF CHEMISTRY IN THAT UNIVERSITY,
PHYSICIAN TO HIS MAJESTY FOR SCOTLAND, MEMBER OF THE ROYAL SOCIETY OF EDINBURGH, OF THE ROYAL ACADEMY OF SCIENCES AT PARIS, AND THE IMPERIAL ACADEMY OF SCIENCES AT ST. PETERSBURGH.
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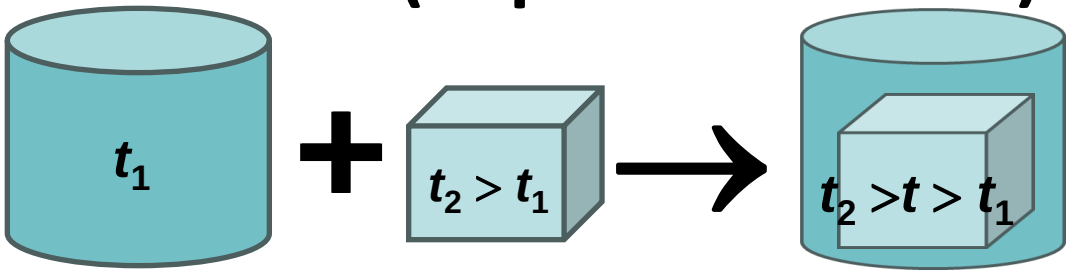
1807.

Johan Carl Wilcke (1732 – 1796)

Antoine Lavoisier (1743 – 1794)

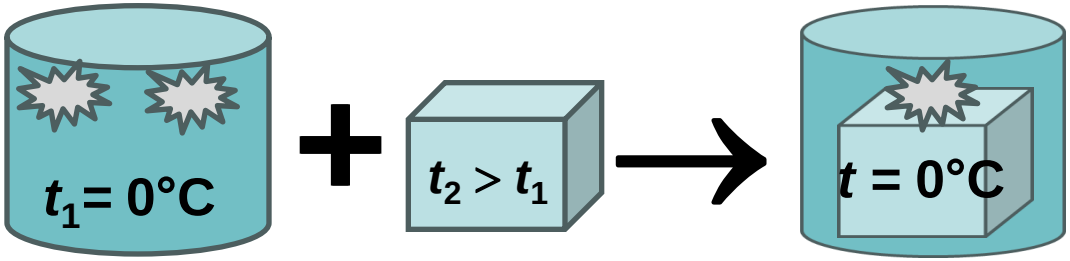
Ice calorimeter (1783)

Směšování (1. pol. 18. století)



$$Q_1 = c_1 m_1 (t - t_1) = Q_2 = c_2 m_2 (t_2 - t)$$

Tání ledu (Lavoisier-Laplace, 1783)



$$Q_1 = m_1 \Delta h_{\text{fus}} = Q_2 = c_2 m_2 (t_2 - t)$$

Pierre Louis Dulong (1785 – 1838)

Alexis Théres Petit (1791 – 1820)

Dulongův-Petitův zákon (1819)

Specifická tepla pevných prvků vynásobená atomární hmotností jsou při pokojové teplotě cca 6 cal/mol/°C

Franz Ernst Neumann (1798 – 1895)

Hermann Franz Moritz Kopp (1817 – 1892)

Neumannovo-Koppovo pravidlo (1831)

Každý chemický prvek má stejnou tepelnou kapacitu jak volný, tak ve slitinách či sloučeninách

Tepelná kapacita *C* je množství tepla, které je potřeba dané látce dodat, aby se její teplota zvýšila o jeden stupeň.

$$C_x = \lim_{\Delta T \to 0} \left(\frac{Q}{\Delta T} \right)_x$$

Důležité:

- za jakých podmínek

- jaké „množství“ látky (.../g, .../mol, .../cm³)

Látka	*M* (g/mol)	*N* (at/f.u.)	*ρ* (g/cm³)	C_{pm} (J/K/mol)	C_{pm} (J/K/mol-at)	c_p (J/K/g)	*S* (J/K/cm³)
Li	6,91	1	0,53	24,62	24,62	3,56	1,87
W	183,84	1	19,25	24,30	24,30	0,13	2,50
NaCl	58,44	2	2,16	50,50	25,25	0,86	1,86
Al_2O_3	101,96	5	3,99	79,04	15,81	0,78	3,11
$C_8H_{10}N_4O_2$ Kofein	194,19	24	1,23	227,84	9,49	1,17	1,44
$C_{27}H_{46}O$ Cholesterol	386,65	74	1,05	597,01	8,07	1,54	1,62

Příspěvky k tepelné kapacitě

Vibrace krystalové mříže - fonony

$$C_v = R \int_0^{\omega_{\max}} \left(\frac{\hbar\omega}{k_B T} \right)^2 \frac{\exp(\hbar\omega / k_B T)}{\left[\exp(\hbar\omega / k_B T) - 1\right]^2} g(\omega) d\omega$$

Vodivostní elektrony

$$C_{el} = R \frac{\pi^2 k_B}{3} N(E_F) T = \gamma T$$

Schottkyho anomálie

– přechody mezi lokalizovanými el. stavy

– rozpořádání poruch

$$C_{sh} = \frac{\Delta^2}{k_B T^2} \frac{e^{-\Delta / k_B T}}{\left(e^{-\Delta / k_B T} + 1\right)^2}$$

Magnetický příspěvek

– magnony

– magnetický fázový přechod

Fonony - harmonická aproximace

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Debyeův model

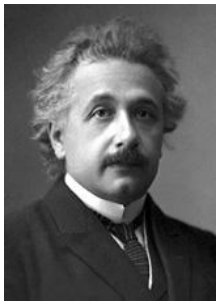
$$g(\nu) = \frac{9N}{\nu_D^3}\nu^2 \qquad \Theta_D = \frac{h\nu_D}{k_B}$$

$$U = U_0 + \frac{9}{8}Nk_B\Theta_D + \frac{9Nk_BT}{x_D^3}\int_0^{x_D}\frac{x^3}{e^x - 1}\,dx$$

$$C_{vib(D)} = \left(\frac{\partial U}{\partial T}\right)_V = \frac{9Nk_B}{x_D^3}\int_0^{x_D}\frac{x^4 e^x}{\left(e^x - 1\right)^2}\,dx$$

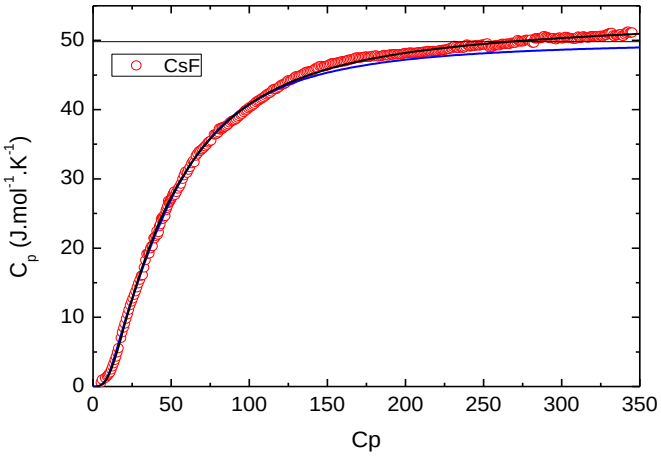
Einsteinův model

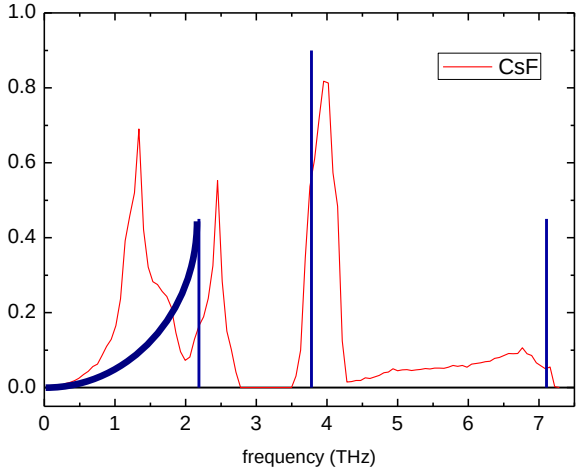
$$E_n = \left(n + \frac{1}{2}\right)h\nu_E$$



$$U = U_0 + \frac{3}{2}Nk_B\Theta_E + 3Nk_BT\frac{\Theta_E/T}{e^{\Theta_E/T} - 1}, \qquad \Theta_E = \frac{h\nu_E}{k_B}$$

$$C_{vib(E)} = \left(\frac{\partial U}{\partial T}\right)_V = 3Nk_B\left(\frac{\Theta_E}{T}\right)^2\frac{e^{\Theta_E/T}}{\left(e^{\Theta_E/T} - 1\right)^2}$$





Fonony - harmonická aproximace

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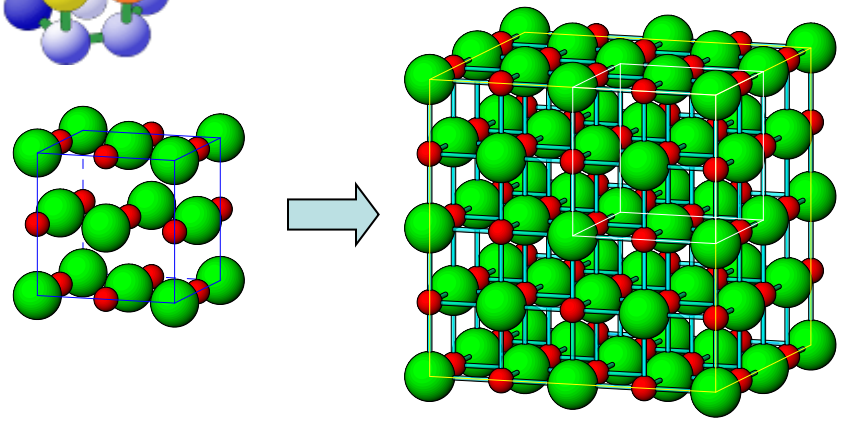


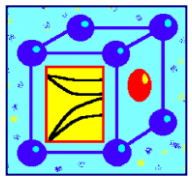
- superbuňka
- výchylky atomů
- výpočet elektronové struktury (DFT)
- Hellmann-Feynmanovy síly

- Hellmann-Feynmanovy síly
- silové konstanty
- dynamická matice
- vlastní hodnoty – frekvence fononů
- hustota stavů fononů

$$F(n) = -\sum_m \Phi(n, m)\, u(m)$$

$$D(k) = 1/M \sum_m \Phi(0, m)\ \exp[-ik(R(0)-R(m))]$$

$$\omega^2(k)\, e(k) = D(k)\, e(k)$$



program Phonon – K.Parlinski

MgO - Fononové spektrum a C_V

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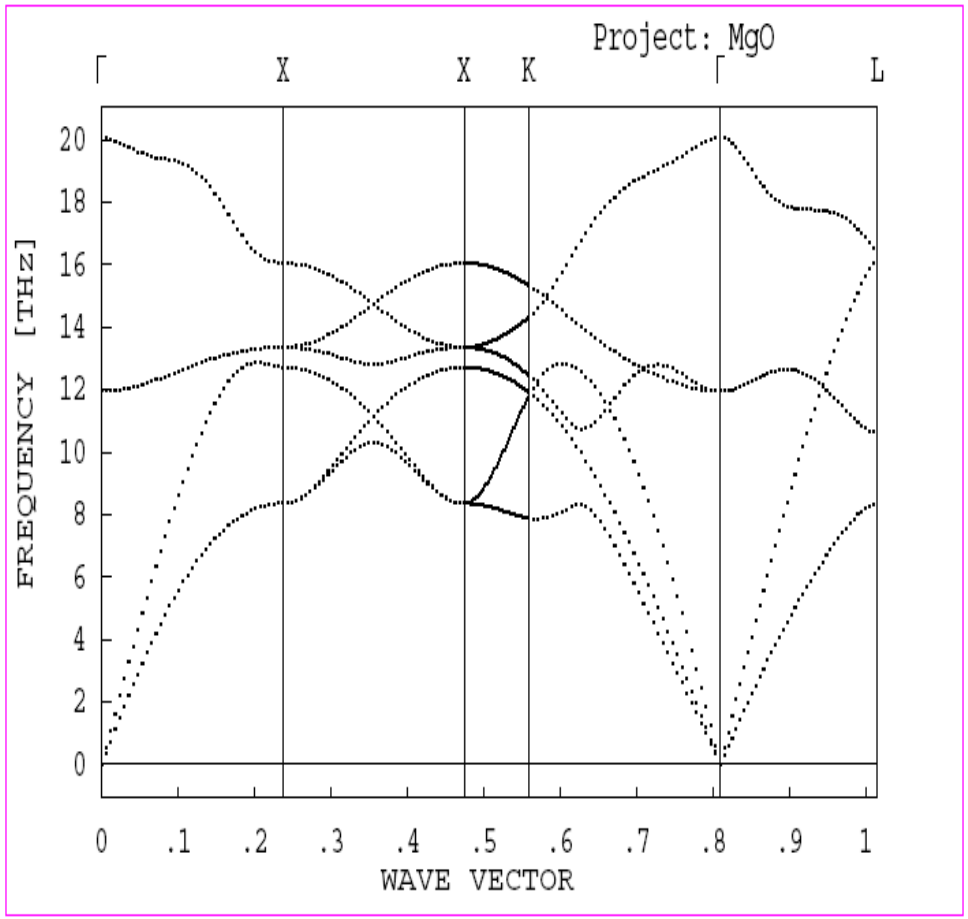

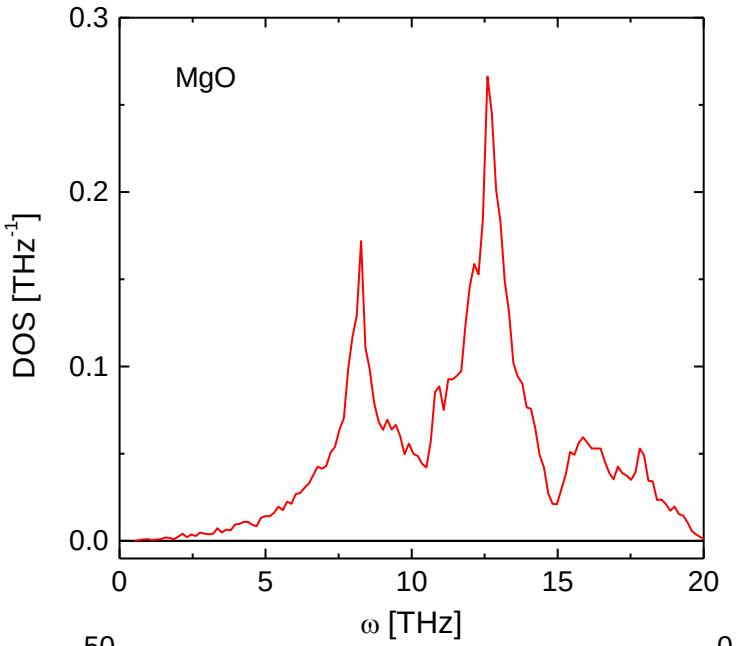

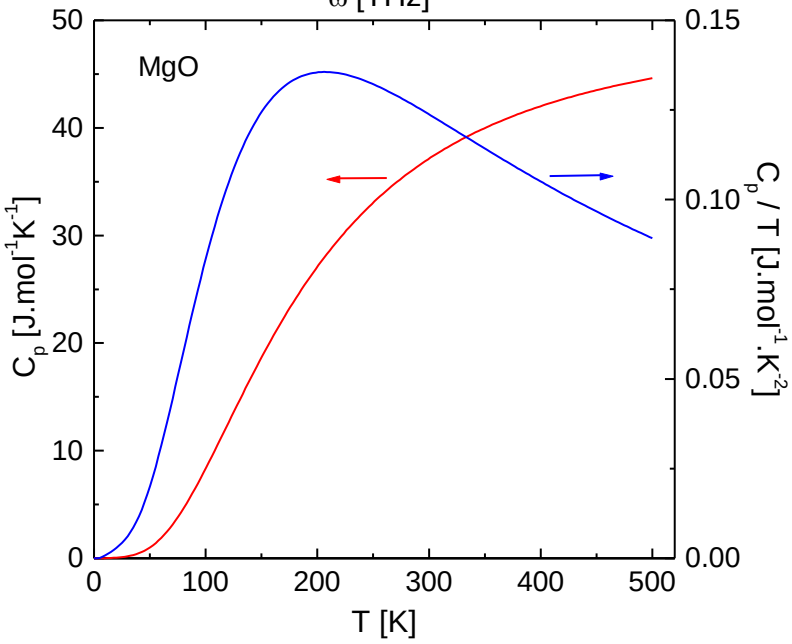

S_{298} výpočet 27.7 J/mol/K

experiment 26.9

Entropie a C_V - vliv hmotnosti a silových konstant

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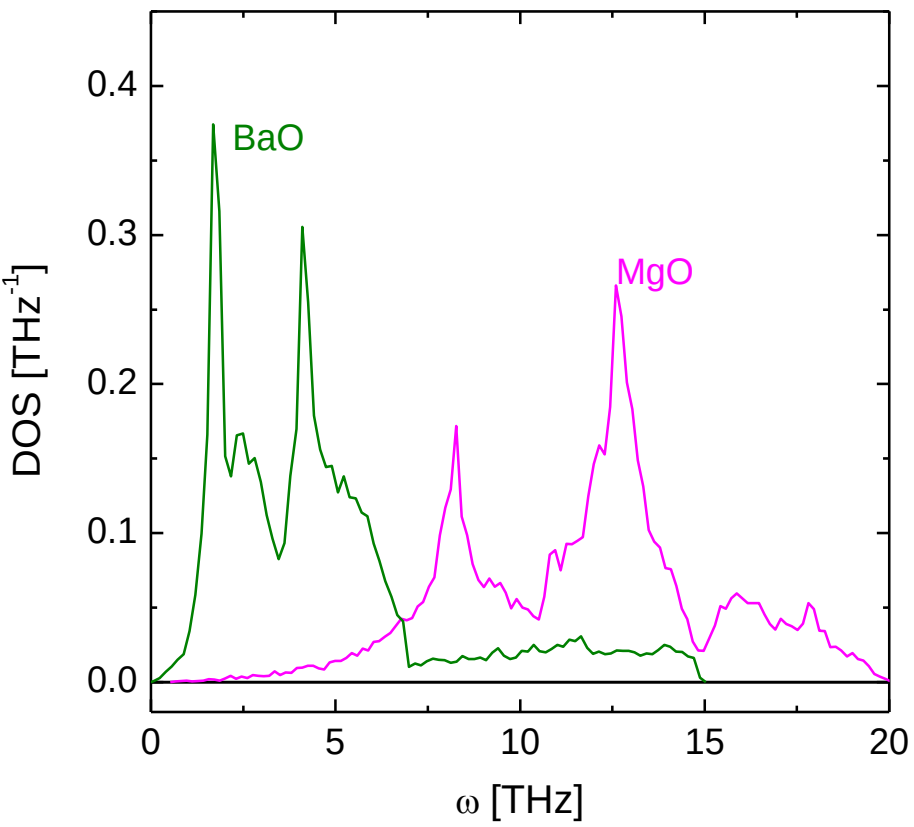

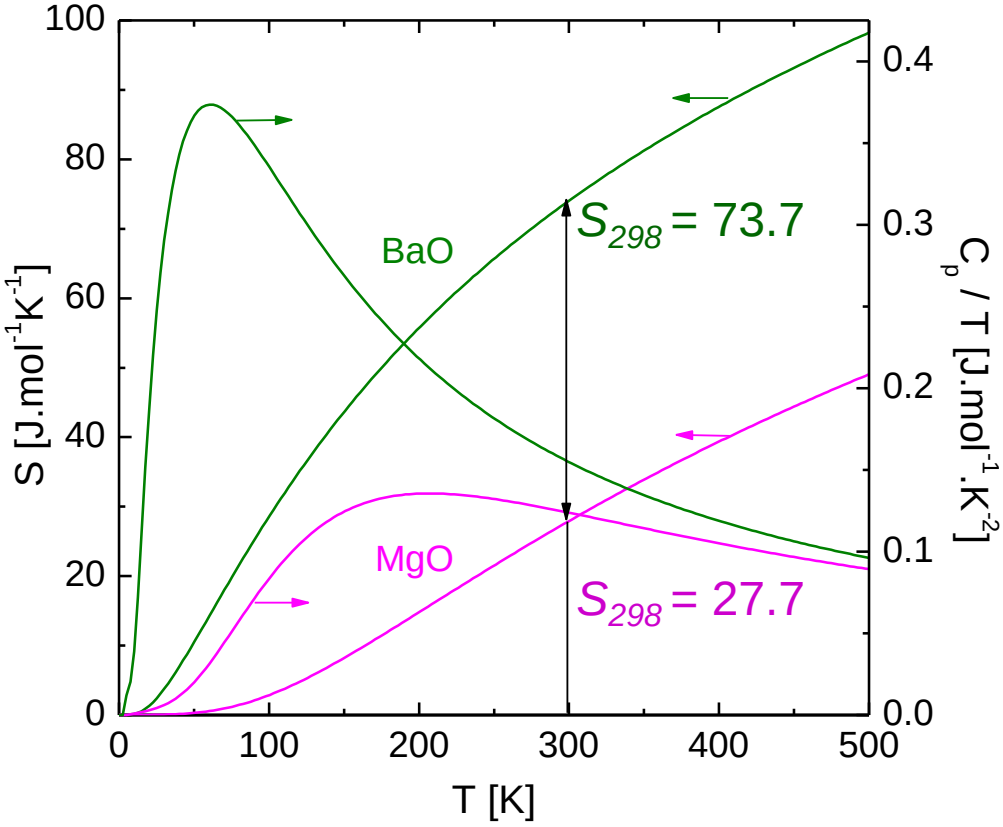

Anharmonický příspěvek a C_p- C_V

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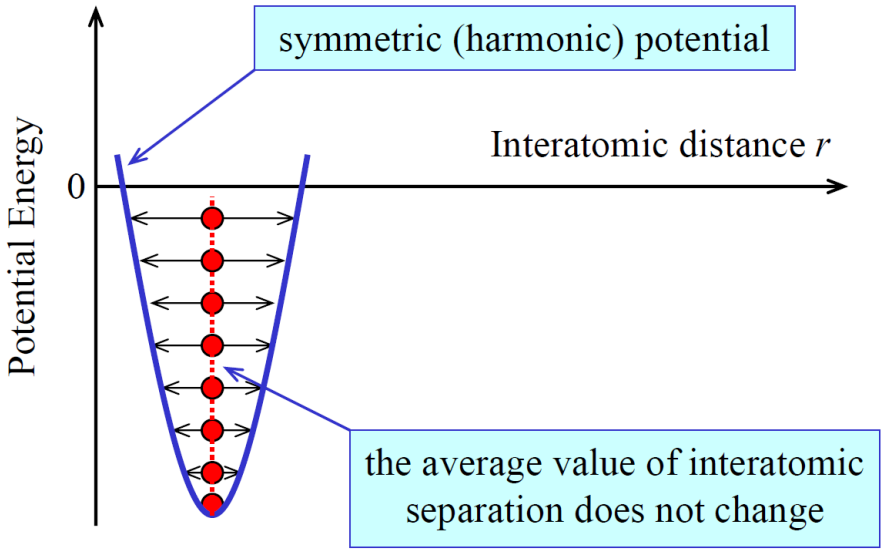

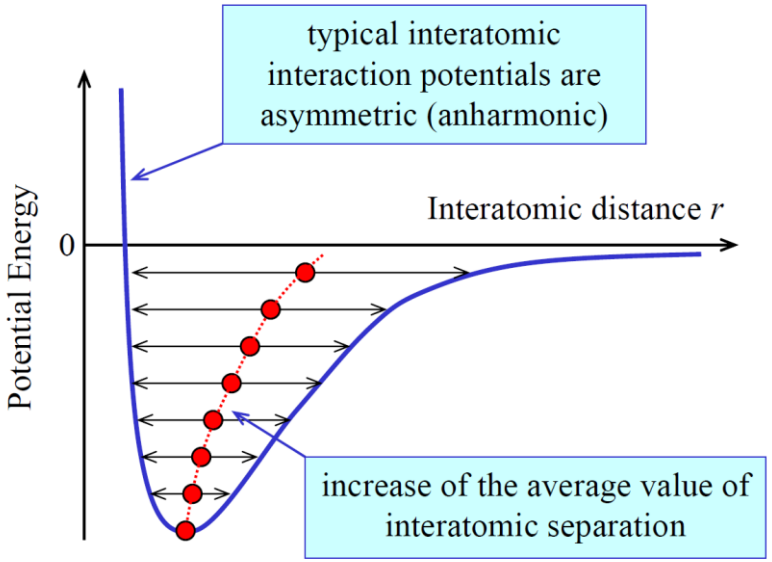

$$C_{\mathrm{dil}} = C_{p\mathrm{m}} - C_{V\mathrm{m}} = \frac{TV_{\mathrm{m}}\alpha_V^2}{\kappa_T} = TV_{\mathrm{m}}B_T\alpha_V^2, \qquad B_T = \frac{1}{\kappa_T}$$

$$\gamma_{\mathrm{G}} = \frac{\alpha_V V}{\kappa_T C_V} = \frac{\alpha_V B_T V}{C_V}$$ ... Grüneisenův parametr

$$C_{\mathrm{dil}} = C_{p\mathrm{m}} - C_{V\mathrm{m}} = T\alpha_V\gamma_{\mathrm{G}}C_{V\mathrm{m}}$$

C_V - Kvaziharmonická aproximace x C_p

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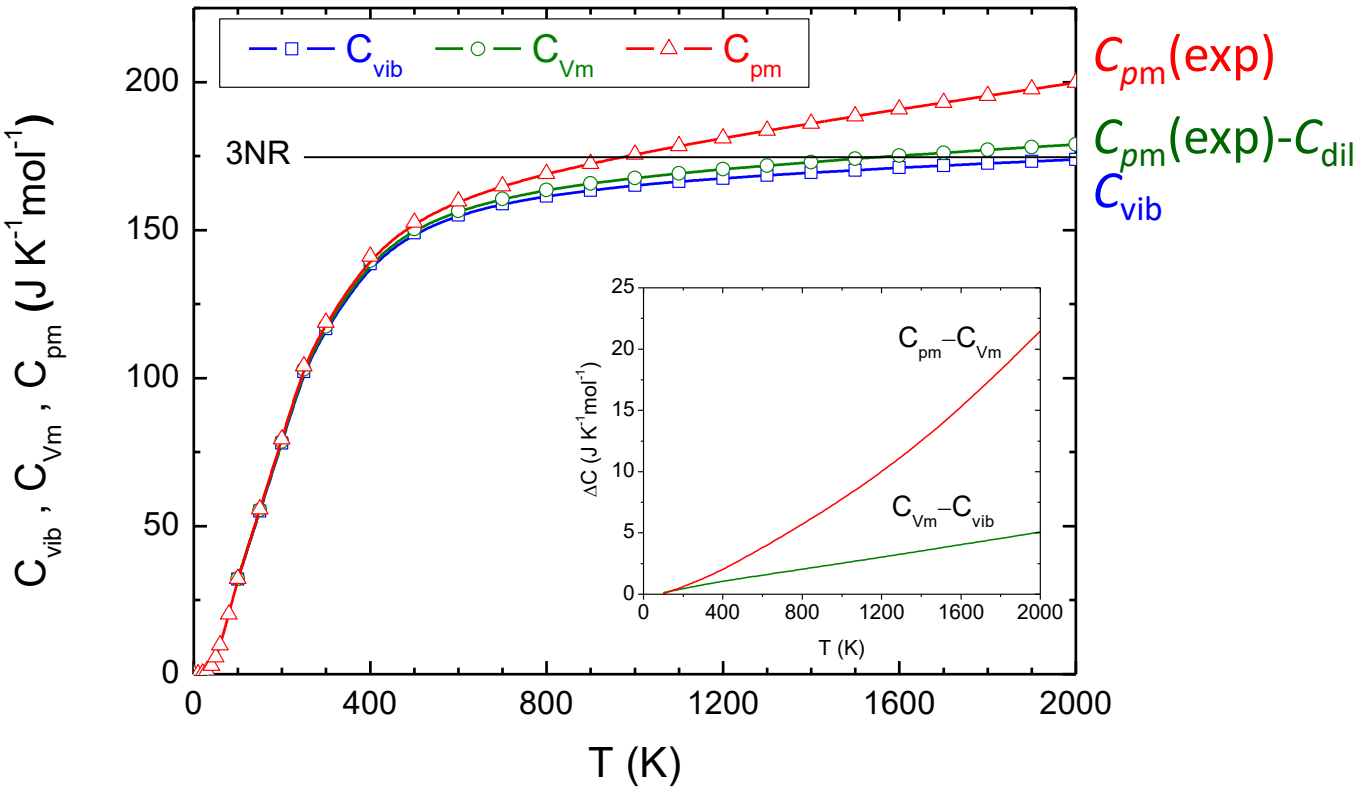
$$C_{Vm} \neq C_{vib(E)}, C_{vib(D)}$$

Mg_2SiO_4



C_{pm}(exp)

C_{pm}(exp)-C_{dil}

C_{vib}

Mg_2SiO_4 - Kvaziharmonická aproximace

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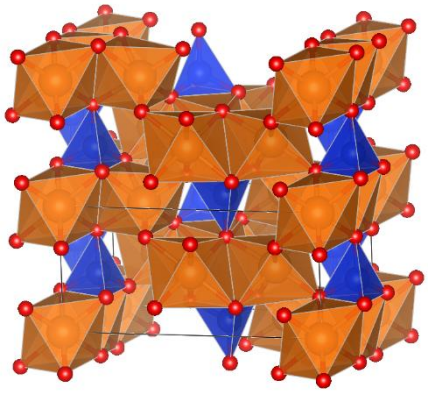
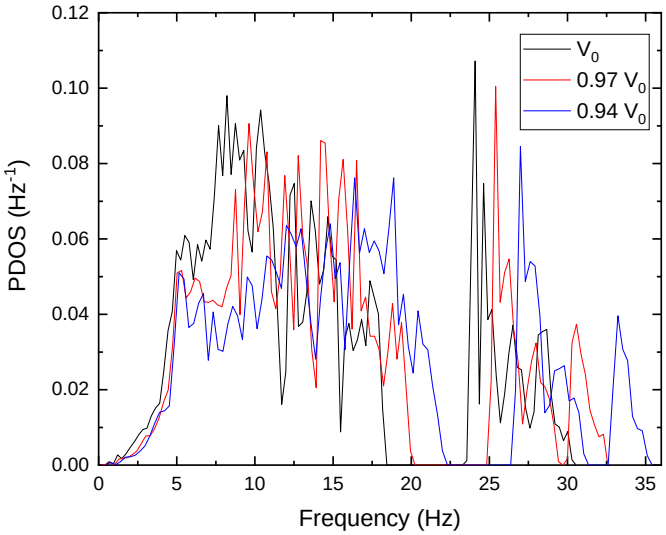
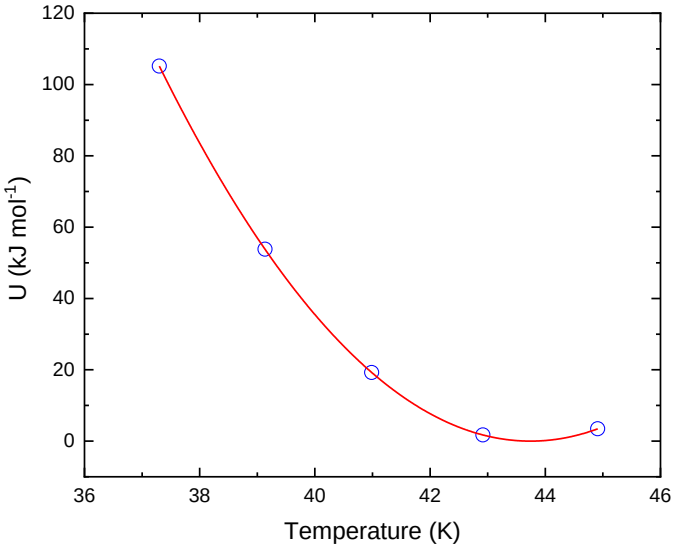
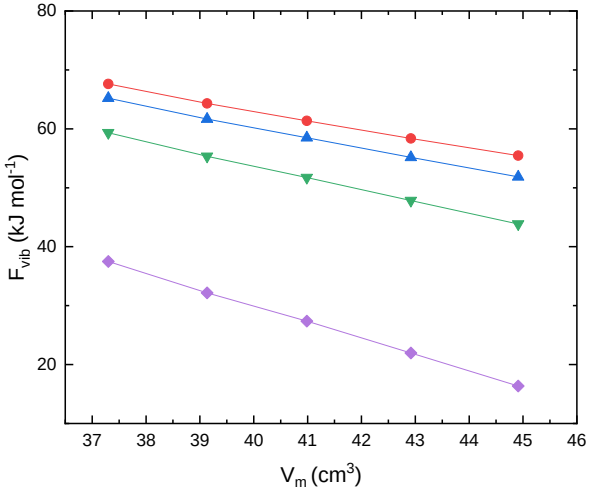
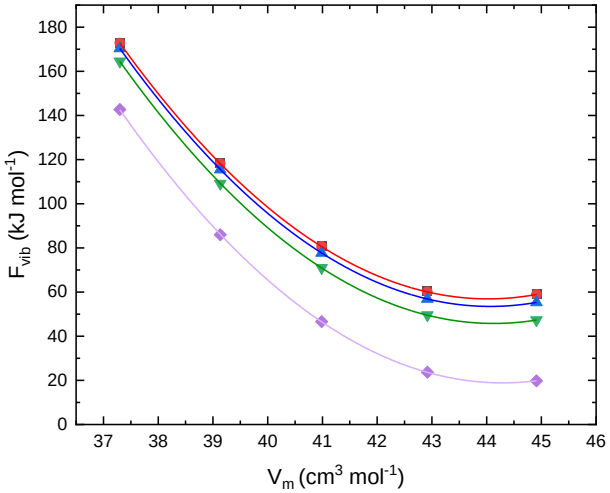


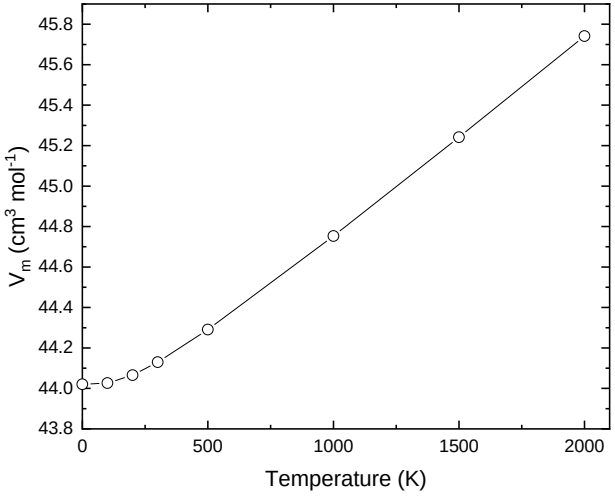
olivine











Mg_2SiO_4 - Kvaziharmonická aproximace

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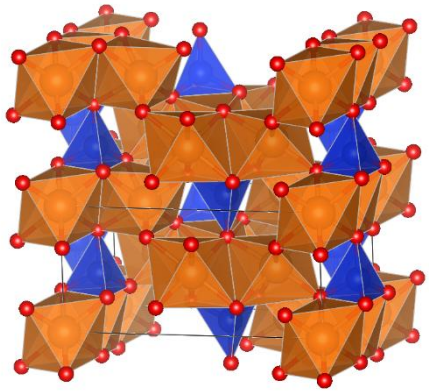
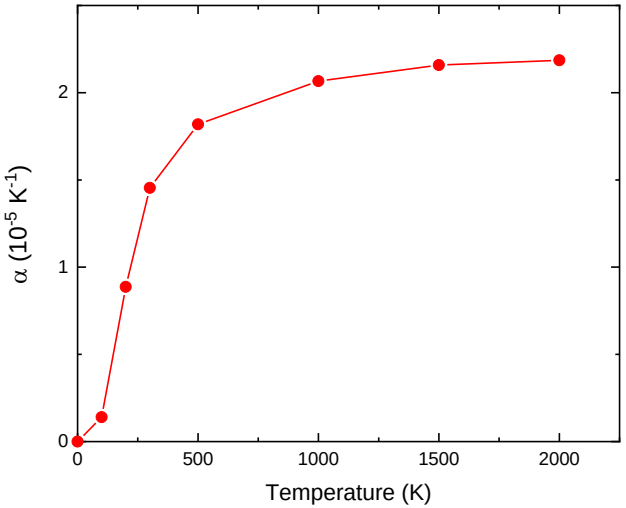
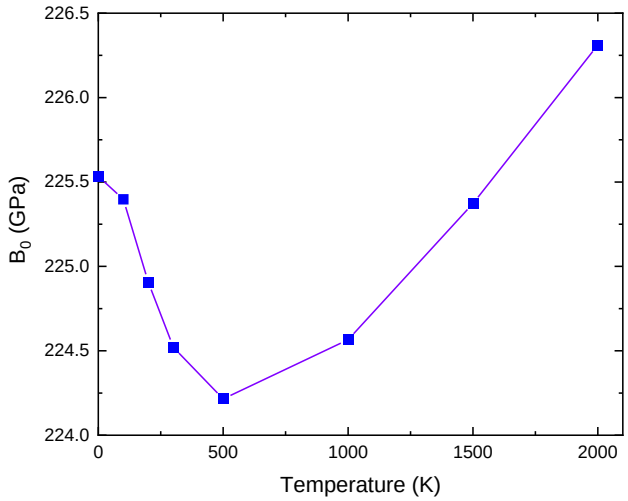
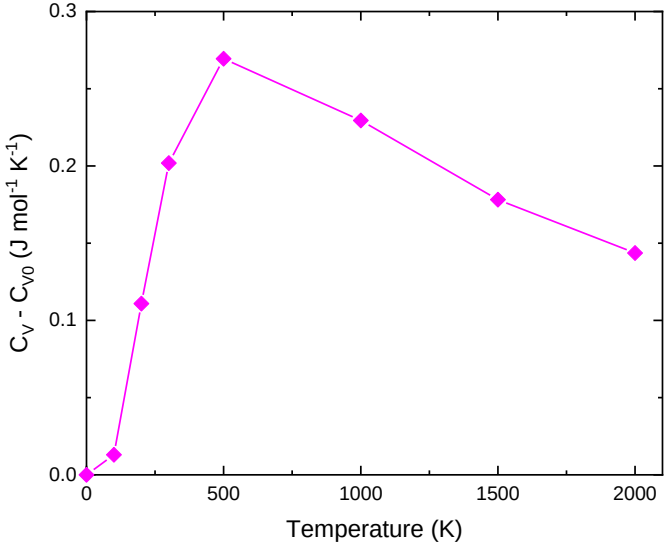
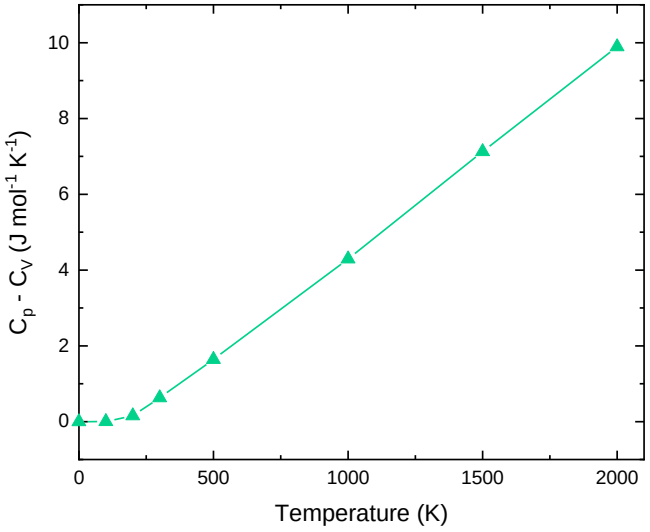


olivine









Tepelná kapacita magnonů

feromagnet

$$\omega = \alpha_{FM}\frac{2Jsa^2}{\hbar}q^2 \qquad q = \sqrt{\frac{\hbar}{\alpha_{FM}2Jsa^2}}\sqrt{\omega}$$

$$\frac{dq}{d\omega} = \sqrt{\frac{\hbar}{\alpha_{FM}8Jsa^2}}\frac{1}{\sqrt{\omega}}$$

3D

$$N(\omega) = \frac{V}{(2\pi)^3}4\pi q^2\frac{dq}{d\omega} = \frac{V}{4\pi^2}\left(\frac{\hbar}{\alpha_{FM}2Jsa^2}\right)^{3/2}\sqrt{\omega}$$

$$U = \int_0 \frac{\hbar\omega N(\omega)}{e^{\hbar\omega/kT}-1}d\omega \qquad C_m = c_{FM}R\left(\frac{kT}{2Js}\right)^{3/2}$$

1D

$$C_m \propto T^{1/2}$$

2D

$$C_m \propto T$$

antiferomagnet

$$\omega = \alpha_{AF}\frac{2Jsa^2}{\hbar}q \qquad q = \frac{\hbar}{\alpha_{AF}2Jsa^2}\omega$$

$$\frac{dq}{d\omega} = \frac{\hbar}{\alpha_{FM}2Jsa^2}$$

$$N(\omega) = \frac{V}{2\pi^2}\left(\frac{\hbar}{\alpha_{AF}2Jsa^2}\right)^3\omega^2$$

$$C_m = c_{Af}R\left(\frac{kT}{2Js}\right)^3$$

$$C_m \propto T^{5/2}$$

$$C_m \propto T^2$$

Tepelná kapacita v okolí mag. přechodu

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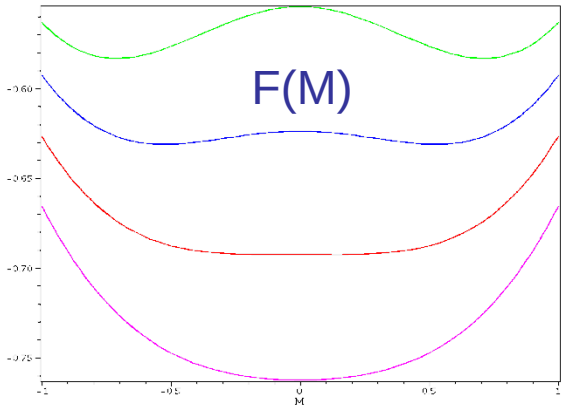
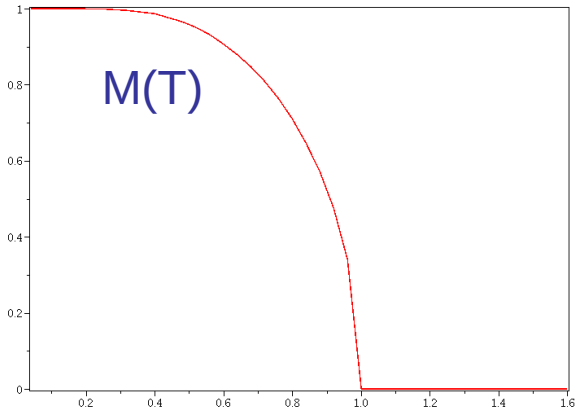
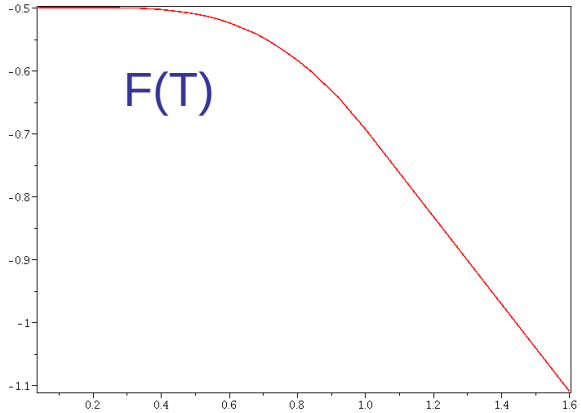
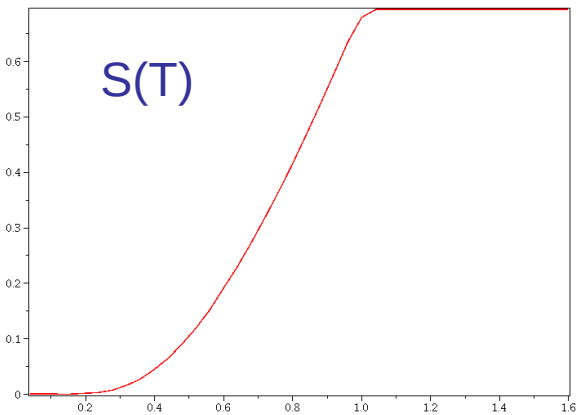
$$M = \tanh\left(\frac{J_0 M}{RT}\right)$$

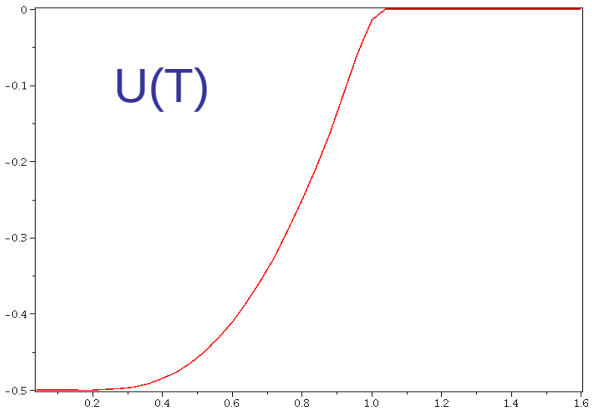
$$F = \frac{J_0 M^2}{2} - RT \ln\left(2\cosh\left(\frac{J_0 M}{RT}\right)\right)$$

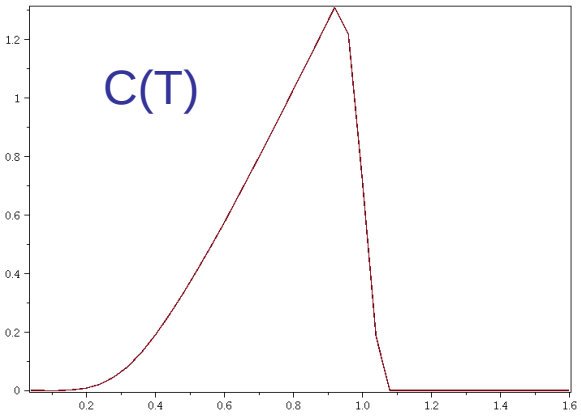










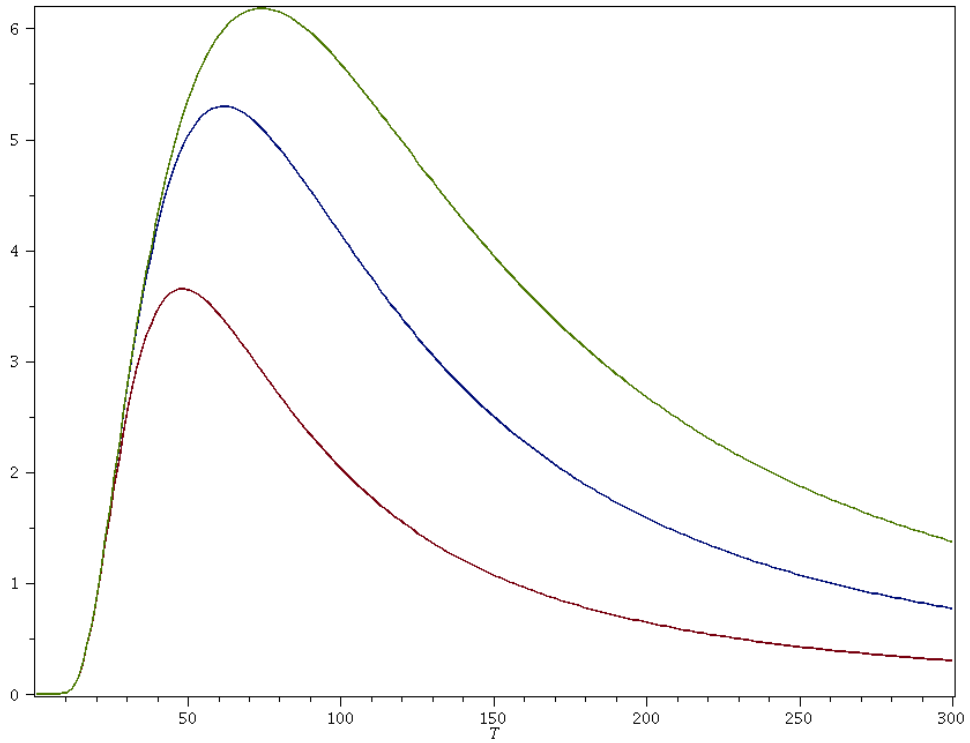


Schottkyho anomálie

$$U_{Sch} = \frac{N\sum_{n=0}^{m} \varepsilon_n g_n e^{-\varepsilon_n / kT}}{\sum_{n=0}^{m} g_n e^{-\varepsilon_n / kT}}$$

$$U_{Sch} = \frac{g_1 \Delta e^{-\Delta / kT}}{g_0 + g_1 e^{-\Delta / kT}}$$

$$C_{Sch} = R\left(\frac{\Delta}{k_B T}\right)^2 \frac{g_0}{g_1} \frac{e^{-\Delta / k_B T}}{\left((g_0/g_1)e^{-\Delta / k_B T} + 1\right)^2}$$



Příspěvek intrinsických poruch

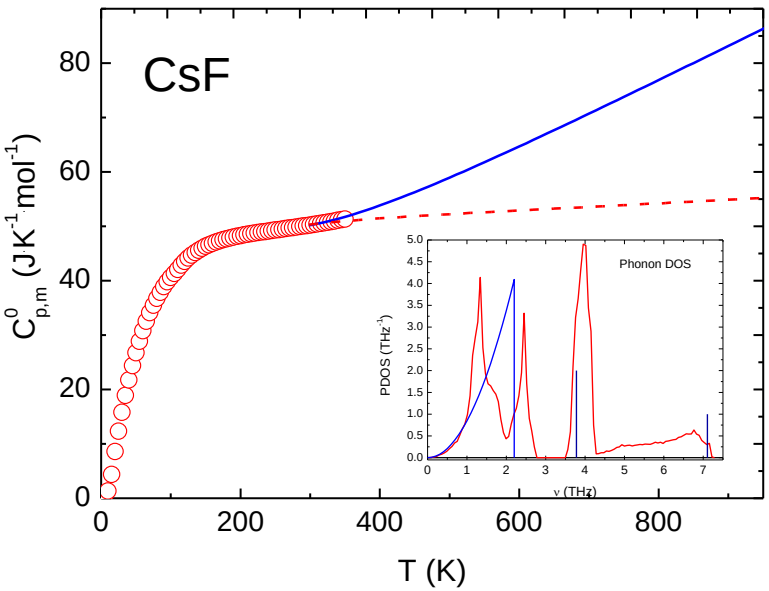
Intrinzické poruchy: Schottkyho poruchy, Frenkelovy páry

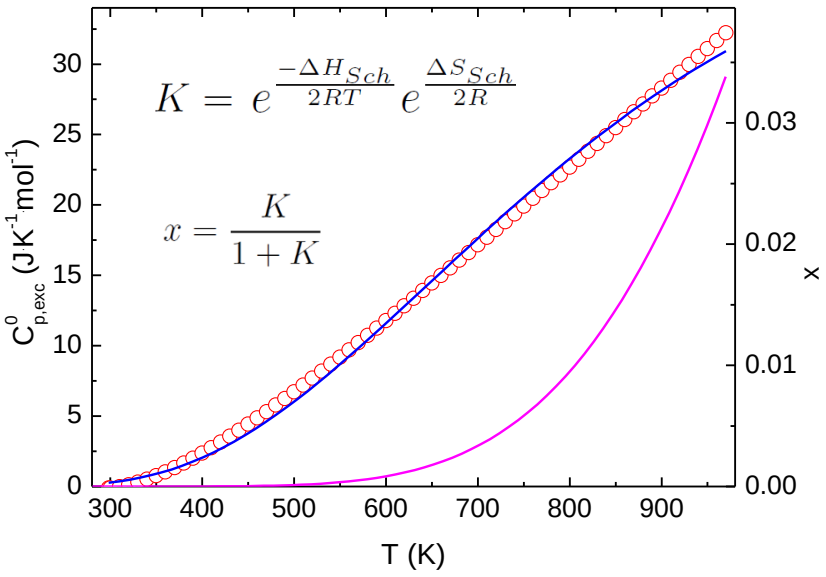
$$G = \sum \mu_j n_j = \sum (\mu^o_j + RT \ln a_j)\, n_j$$

$$n_j = \nu_{jo} + \sum \nu_{jr} . \lambda_r$$

$$(\partial G/\partial \lambda_r)_{\delta,T,P} = \sum_j \nu_{jr} (\mu^o_j + RT \ln a_j) = \Delta G^o_r + RT \ln K_r = 0 \quad \Rightarrow \quad \lambda_r^{eq} = A_r \exp(-\Delta H^o_r/RT)$$

$$\Delta_r C_P = \Delta H^o_r (\partial \lambda_r^{eq}/\partial T) = A_r (\Delta H^o_r{}^2/RT^2) \exp(-\Delta H^o_r/RT)$$





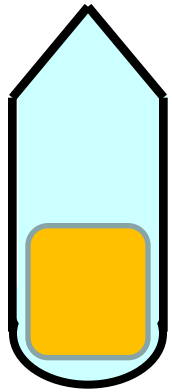
O. Beneš , R.J.M. Konings , D. Sedmidubský , M. Beilmann, O. S. Valu, E. Capelli, M. Salanne, S. Nichenko, A comprehensive study of the heat capacity of CsF from 5 K to 1400 K, Journal of Chemical Thermodynamics 57 (2013) 92-10

$$C_{p,exc} = \frac{\partial [x/(1-x)]}{\partial T} \Delta H_{Sch} = \frac{\partial K}{\partial T} \Delta H_{Sch} = \frac{\Delta H^2_{Sch}}{2\mathbf{R}T^2} K$$

Nestechiometrie a izodynamická kapacita

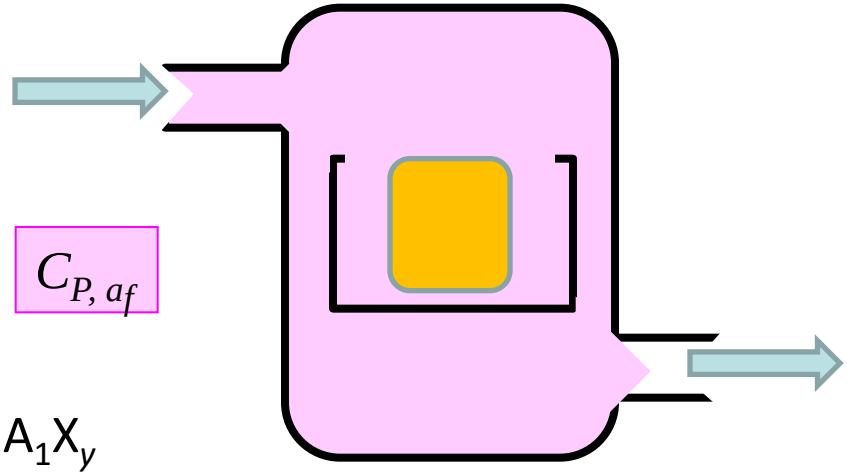
Kalsem 2025

Izopletní:

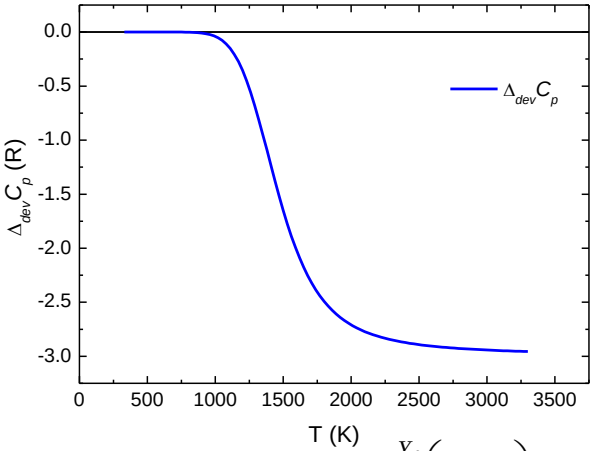


$C_{P,\,Y_f}$

Izodynamická: konstantní aktivita volné složky



$C_{P,\,a_f}$



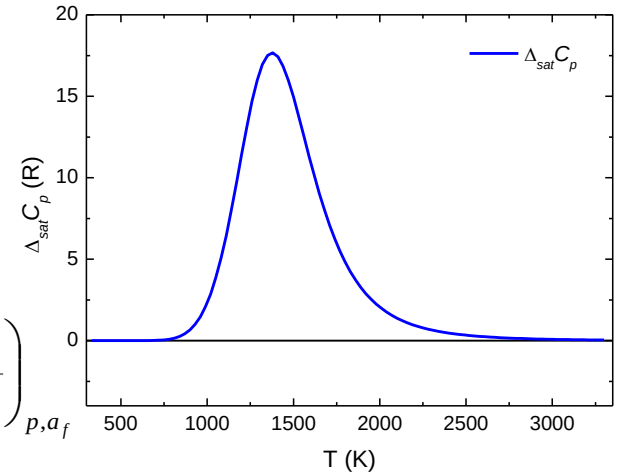
$A_nX_{m+\delta} = n\ A_1X_y$

$Y_f = (m+\delta)/n = y$

$a_f = p_f/p^o_f$

$$C_{p,a_f} = C_{p,Y_f} + \Delta_{sat}C_p$$

$$\Delta_{dev}C_p = C_{p,Y_f} - C_{p,Y_f^\circ} = \int_{Y_f^\circ}^{Y_f}\left(\frac{\partial C_p}{\partial Y_f}\right)dY_f = \int_{Y_f^\circ}^{Y_f}\left(\frac{\partial H_f}{\partial T}\right)dY_f$$



$$\Delta_{sat}C_p = -H_f\left(\frac{\partial Y_f}{\partial T}\right)_{p,a_f} = -\left(H_f^\circ + \Delta H_f\right)\left(\frac{\partial Y_f}{\partial T}\right)_{p,a_f}$$

Kalorimetr je zařízení ke stanovení množství tepla doprovázejícího proces, který v kalorimetru probíhá.

Klasifikace kalorimetrů je obtížná
velký počet různých typů kalorimetrů (více než 100)
různá klasifikační schémata a kritéria

- ***Princip měření*** (kompenzace tepla, akumulace tepla, výměna tepla)
- ***Podmínky měření*** (izotermní, adiabatické, isoperibolické ve statickém či dynamické modu)
- ***Konstrukce kalorimetru*** (jednoduchý, zdvojený/diferenční)

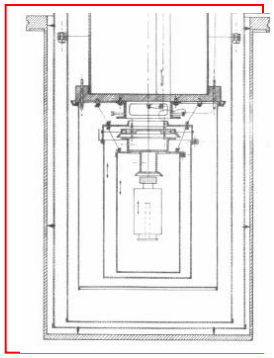
$$\dot{Q}_{\text{total}} = \frac{\mathrm{d}Q_{\text{accumulation}}}{\mathrm{d}t} + \frac{\mathrm{d}Q_{\text{exchange}}}{\mathrm{d}t} = \frac{C_{\text{total}}\mathrm{d}T_{\text{cal}}}{\mathrm{d}t} + K\left(T_{\text{cal}} - T_{\text{surr}}\right)$$

Adiabatická kalorimetrie, $Q_{ex} = 0$
A. Eucken (1909) W. Nernst (1910)

Kalorimetry *home-made*, obor teplot 4-90 K, ..., 400-1700 K

Tan Z. et al.: A fully automated adiabatic calorimeter for heat capacity measurement between 80 and 400 K. Journal of Thermal Analysis and Calorimetry, 92(2), 367-374 (2008).

- pasivní AC kalorimetry (dobrá izolace kalorimetru – vakuum 10^{-3} až 10^{-4} Pa)
- aktivní AC kalorimetry (temperace tepelného stínění mezi kalorimetrem a okolím)

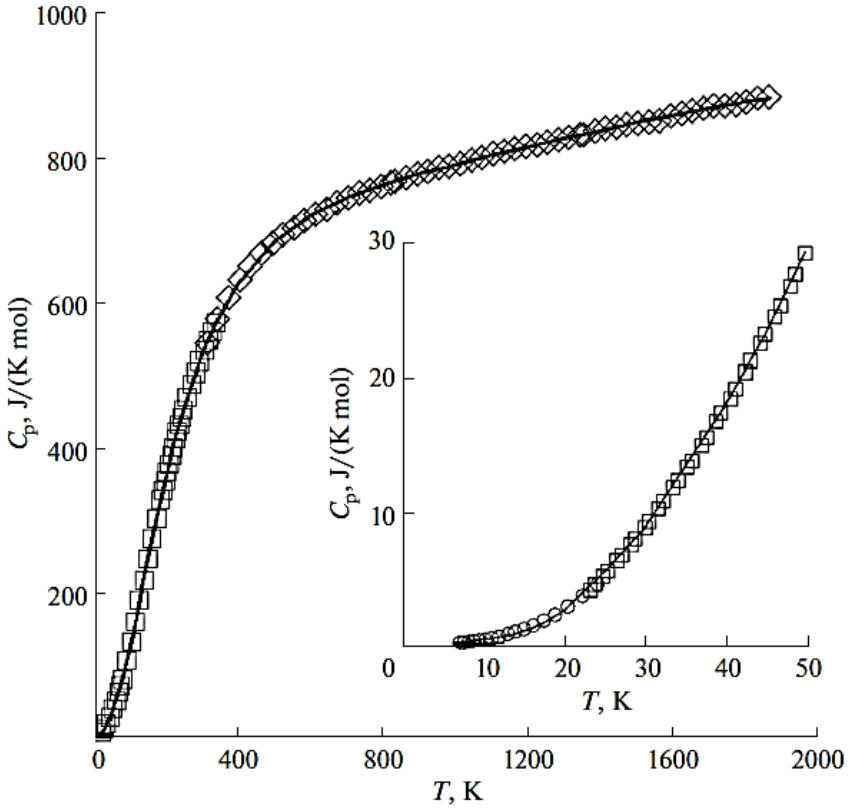


$$C_{\text{total}} = \frac{Q}{\Delta T} = \frac{RI^2 t}{\Delta T}$$

$$C_{pm} = \left(c_{\text{sample}} - c_{\text{blank}} \right) \frac{M_{\text{sample}}}{m_{\text{sample}}}$$

Adiabatická kalorimetrie

Gagarin P. G. et al.: Heat Capacity and Thermal Expansion of $LaMgAl_{11}O_{19}$
Russian Journal of Inorganic Chemistry, 69, 879-774 (2024).

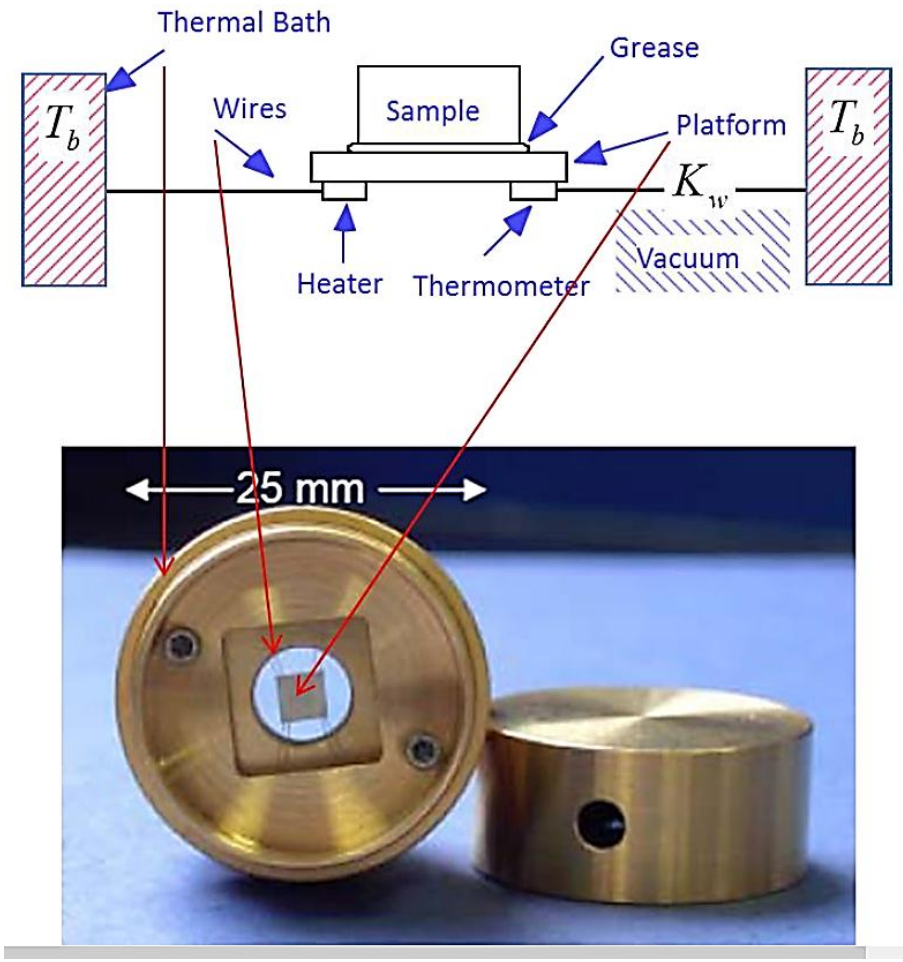


RTC 7,3-40,7 K (PPMS, QD)
ADC 23,4-347,9 K (BKT-3, …)
DSC 315-1865 K (404F-Pegasus, Netzsch)

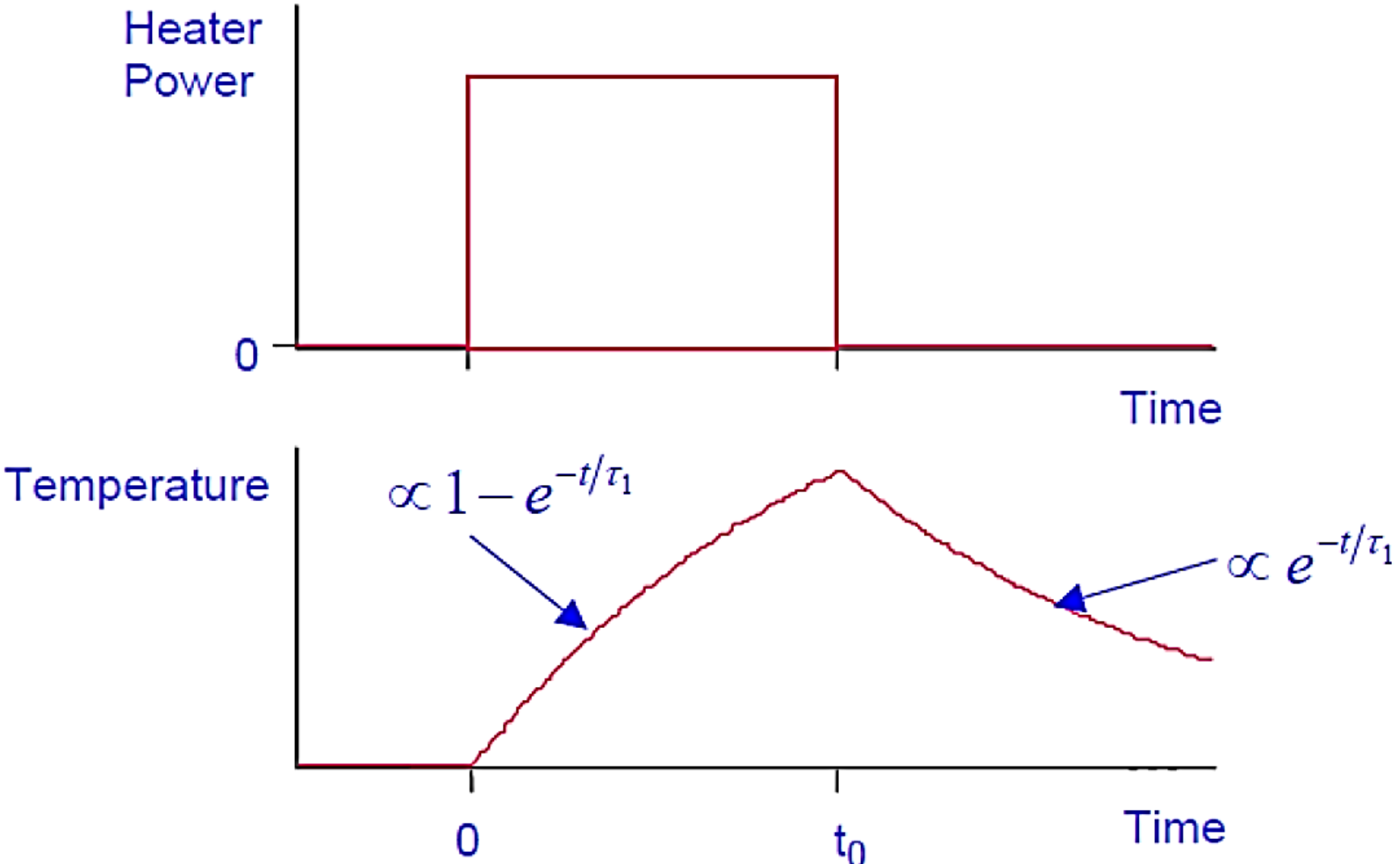
Fig. 3. Consistent dependences of the heat capacity of $LaMgAl_{11}O_{19}$ determined by relaxation (○), adiabatic (□), and differential scanning calorimetry (◇) methods.

Tepelně pulzní kalorimetrie, Q_{ex} = f(t)
A.G. Cole et al. (1960)

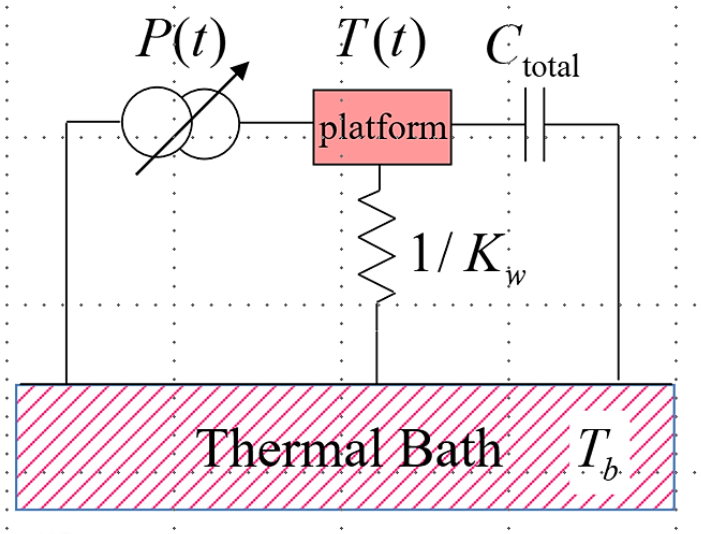
PPMS, Quantum Design



Tepelně pulzní kalorimetrie



Tepelně pulzní kalorimetrie



$$P(t) = C_{\text{total}} \frac{\mathrm{d}T(t)}{\mathrm{d}t} + K_{\text{w}} \left(T(t) - T_{\text{b}} \right)$$

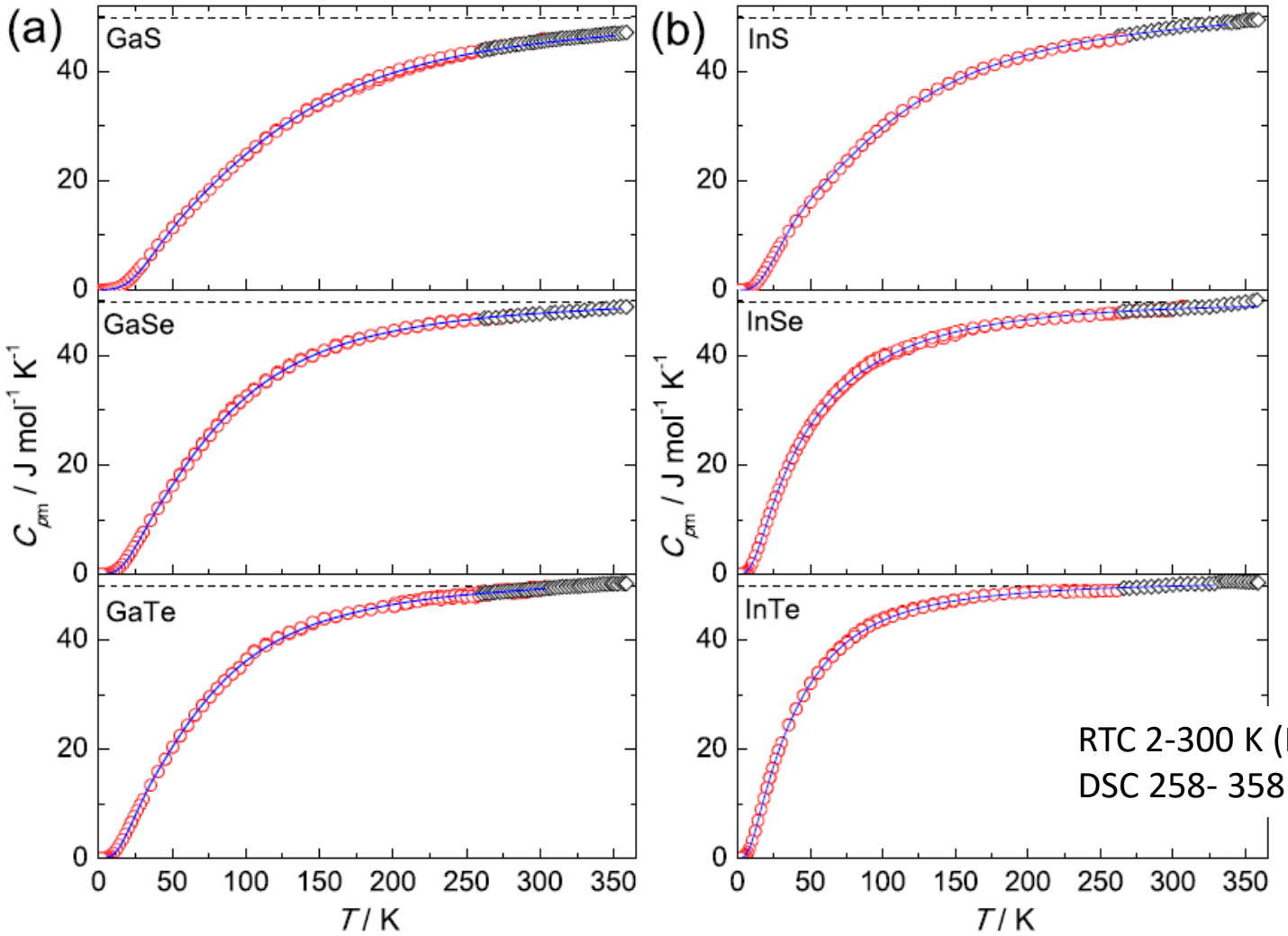
$$\left(T(t) - T_{\text{b}} \right) = \Delta T\left(t \right) = \Delta T_{\text{max}} \exp\left(-\frac{t}{\tau_1} \right), \quad \tau_1 = \frac{C_{\text{total}}}{K_{\text{w}}}$$

$$C_{\text{total}} = \frac{Q}{\Delta T} = \frac{RI^2\tau_1}{\Delta T_{\text{max}}}$$

$$C_{p\text{m}} = \left(c_{\text{platform/sample}} - c_{\text{platform}} \right) \frac{M_{\text{sample}}}{m_{\text{sample}}}$$

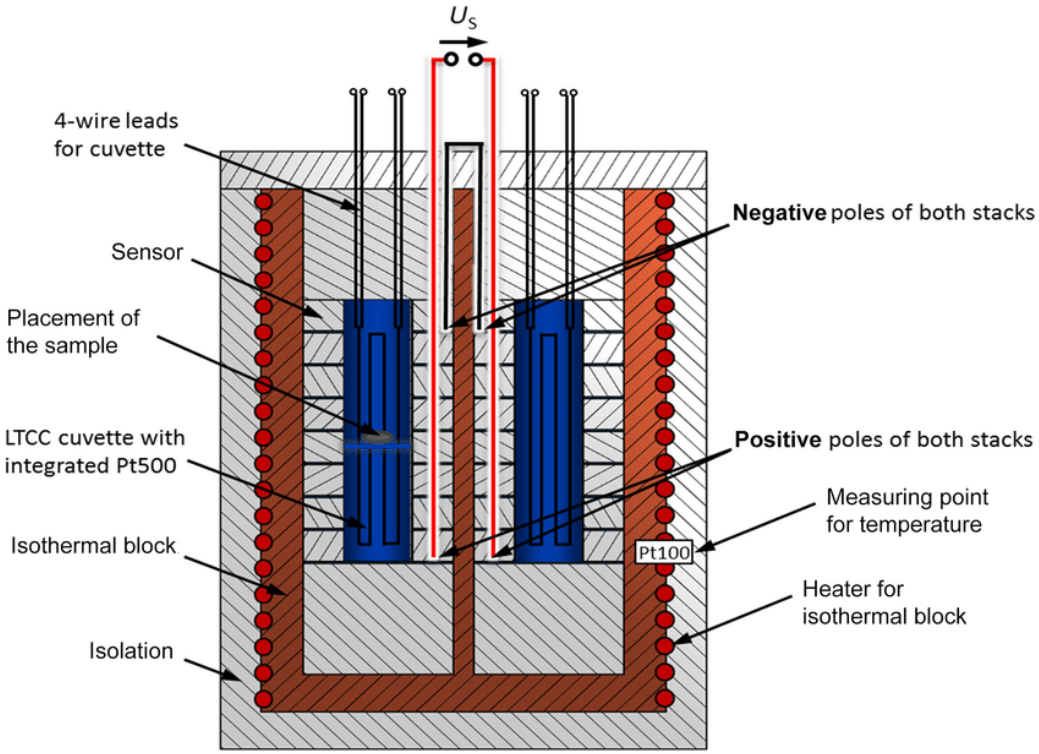
Tepelně pulzní kalorimetrie

Sedmidubský D. et al.: Chemical bonding and thermodynamic properties of gallium and indium monochalcogenides. The Journal of Chemical Thermodynamics, 128, 97-102 (2019).



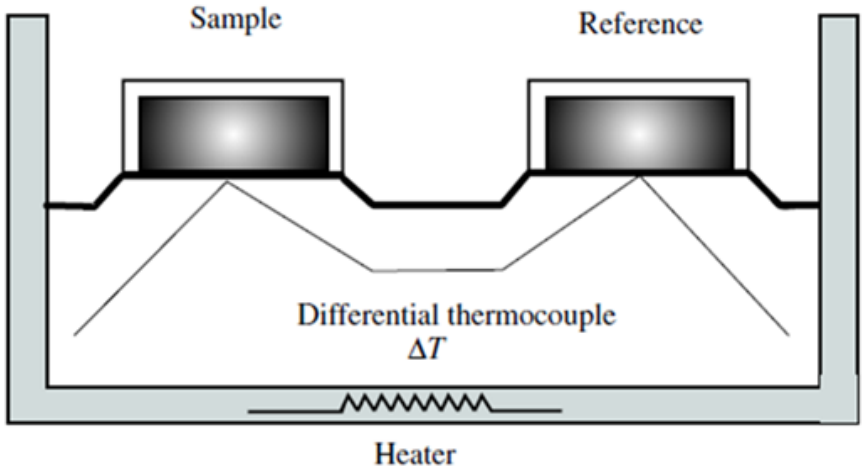
RTC 2-300 K (PPMS, QD)
DSC 258- 358 K (μ-DSC III, Setaram)

Differenční skenovací kalorimetrie, Q_{ex} = f(t) alt. Q_{ex} = 0
A. Tian and E. Calvet (1922)

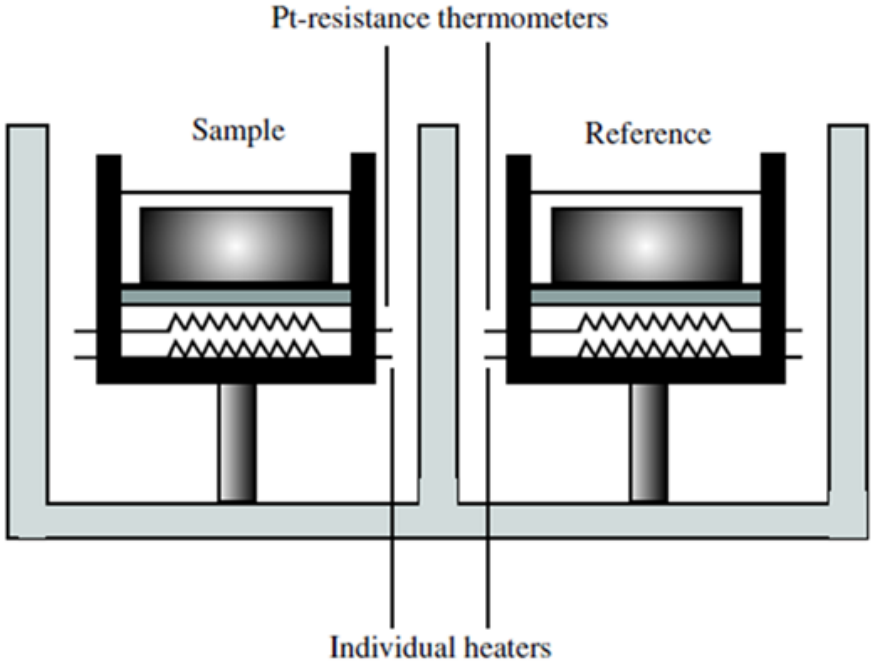


Schubert F. et al: Optimization of a sensor for a Tian–Calvet calorimeter with LTCC-based sensor discs. Journal of Sensors and Sensor Systems, 5, 381-388 (2016).

Differenční skenovací kalorimetrie, Q_{ex} = f(t) alt. Q_{ex} = 0
E. S. Watson and M. J. O'Neill (1962)



Obr. 9a
Heat flux DSC



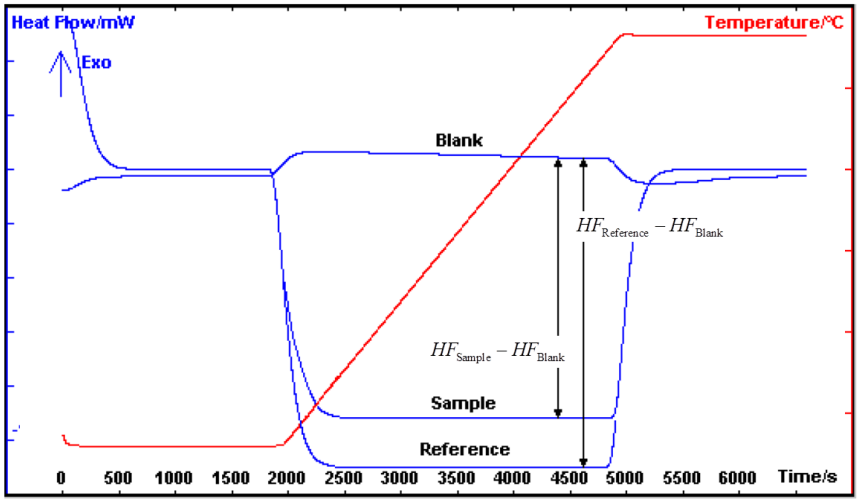
Obr. 9b
Power compensating DSC

Základní teplotní programy pro stanovení tepelných kapacit

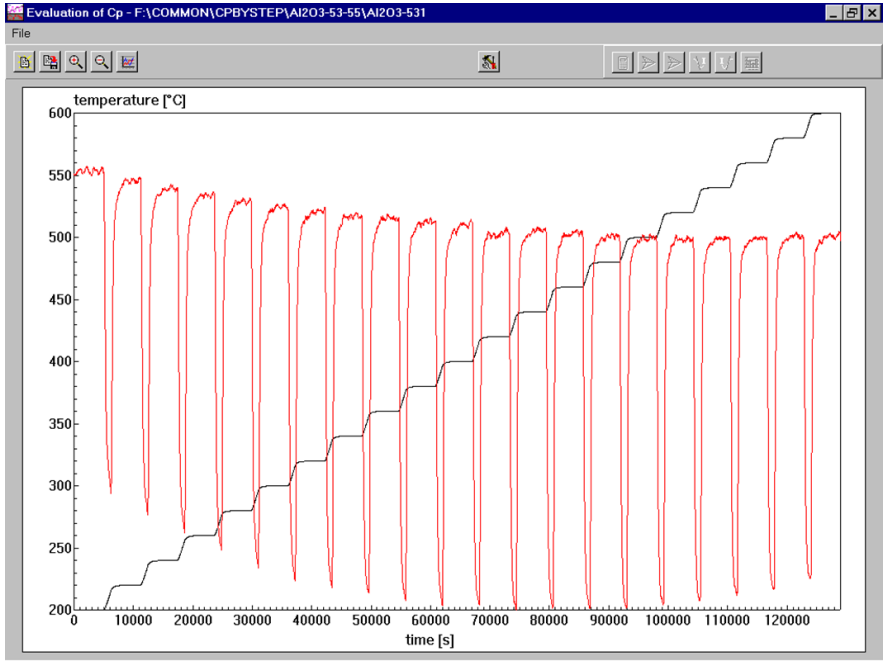
- Continuous heating (kontinuální ohřev, $T_1 \rightarrow T_2$)

- Step-by step heating (krokový ohřev, ΔT_i = 5-10 °C)

Differenční skenovací kalorimetrie



$$c_{Sample}(T) = c_{Reference}(T)\frac{\left(HF_{Sample} - HF_{Blank}\right)(T)}{\left(HF_{Reference} - HF_{Blank}\right)(T)}\frac{m_{Reference}}{m_{Sample}}$$



$$c_{Sample}(T) = c_{Reference}(T)\frac{\left(A_{Sample} - A_{Blank}\right)(T)}{\left(A_{Reference} - A_{Blank}\right)(T)}\frac{m_{Reference}}{m_{Sample}}$$

Vhazovací kalorimetrie

R. Bunsen (1870) – *ice calorimeter* ($T \rightarrow T_0$, T_0 = 0°C)

P. A. Giguere et al. (1955) – difenylether ($T \rightarrow T_0$, T_0 = 27°C)

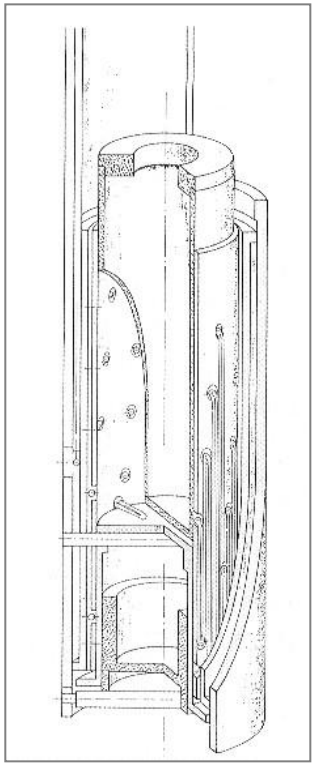
SETARAM (1974) – *invers drop calorimetry* ($T_0 \rightarrow T$)

$$H_{\mathrm{m,Sample}}(T_0) - H_{\mathrm{m,Sample}}(T_{\mathrm{ref}}) = m_{\mathrm{Ice}} \Delta_{\mathrm{fus}} h_{\mathrm{Ice}} \frac{M_{\mathrm{Sample}}}{m_{\mathrm{Sample}}}$$

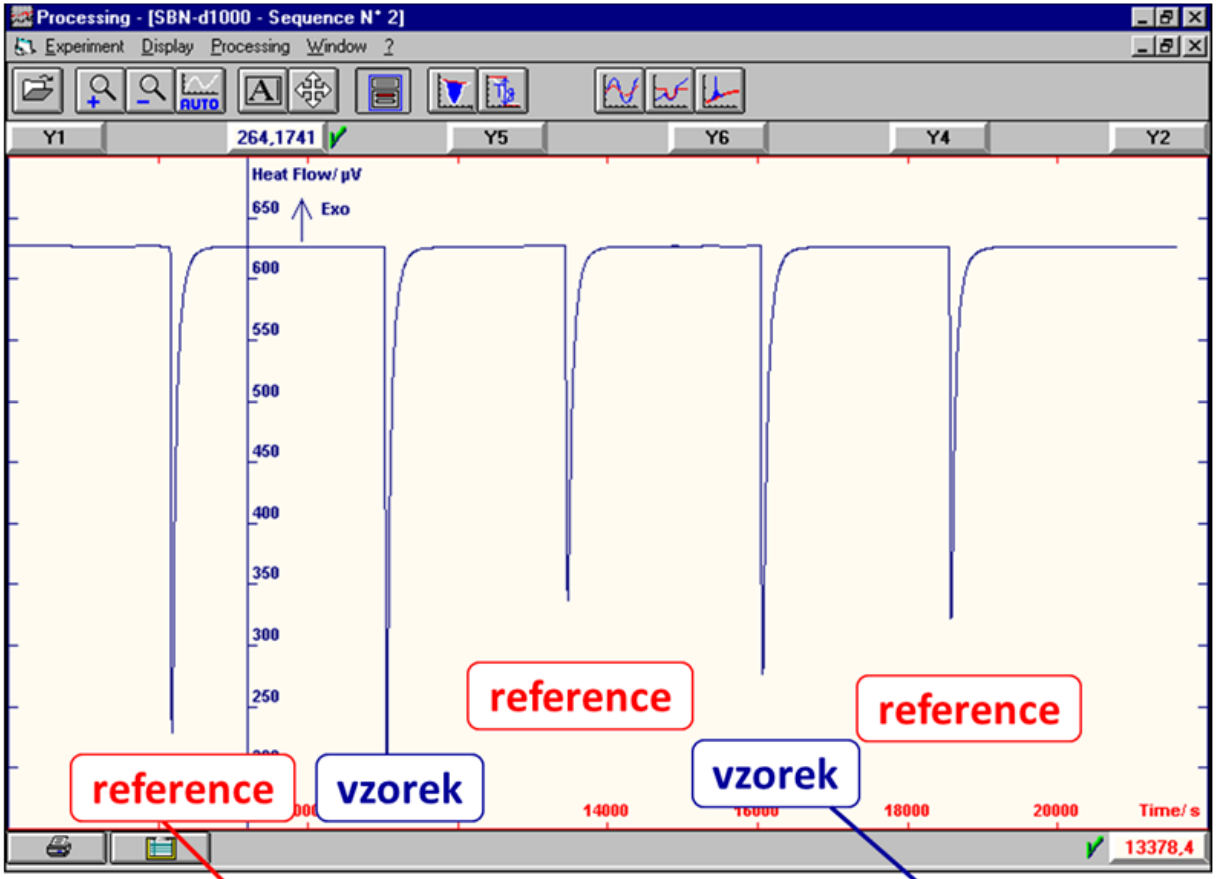
$$H_{\mathrm{m,Sample}}(T_{\mathrm{cal}}) - H_{\mathrm{m,Sample}}(T_0) = \int_{T_{\mathrm{ref}}}^{T_0} C_{p\mathrm{m,Sample}} \mathrm{d}T$$

Vhazovací kalorimetrie

Multi HTC-96, Setaram



Vhazovací kalorimetrie



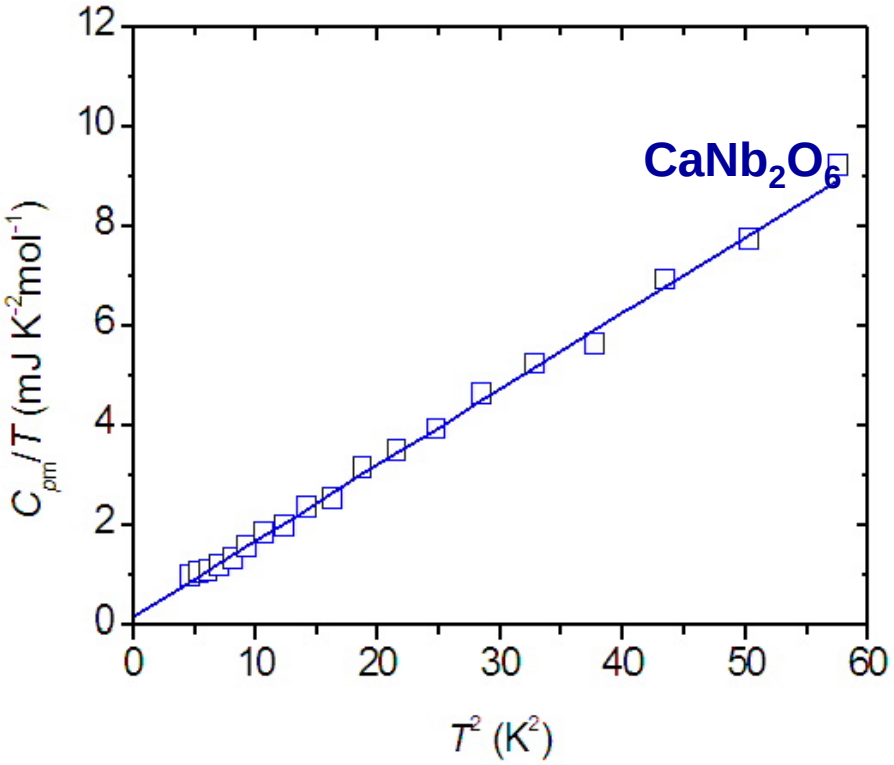
- Oblast velmi nízkých teplot (do cca 10 K)
- Oblast nízkých teplot (10 – 350 K)
- Oblast středních a vysokých teplot (nad 350 K)

Leitner, J. et al.: Heat capacity, enthalpy and entropy of calcium niobates. Journal of Thermal Analysis and Calorimetry 95, 397-402 (2009).

Experimentální C_p data, $T < 10$ K

$$C_{pm} = C_{\mathrm{el}} + C_{\mathrm{ph}} = \gamma_{\mathrm{el}} T + \beta T^3, \quad \beta \approx \Theta_{\mathrm{D}}^{-3}$$

$$C_{pm}/T = \gamma_{\mathrm{el}} + cT^2$$



$$\gamma_{\mathrm{el}} \approx 0$$

$$\Theta_{\mathrm{D}} = 234 \text{ K}$$

Experimentální C_p data, T = 10-350 K

$$C_{\mathrm{ph}} = C_{\mathrm{phD}} + \sum_{i=1}^{3n-3} C_{\mathrm{phE}i}$$

$$C_{\mathrm{phD}} = \frac{1}{1-\alpha_{\mathrm{D}}T}\left(\frac{9R}{x_{\mathrm{D}}}\right)^3 \int_0^{x_{\mathrm{D}}} \frac{x_{\mathrm{D}}^4 \exp(x_{\mathrm{D}})}{\left(\exp(x_{\mathrm{D}})-1\right)^2}\,\mathrm{d}x$$

$$C_{\mathrm{phE}i} = \frac{1}{1-\alpha_{\mathrm{E}i}T} \cdot R\, x_{\mathrm{E}i}^2 \frac{\exp(x_{\mathrm{E}i})}{\left(\exp(x_{\mathrm{E}i})-1\right)^2}$$

$$\frac{1}{1-\alpha_{\mathrm{D}}T}, \quad \frac{1}{1-\alpha_{\mathrm{E}i}T} \quad \ldots$$

Empirická korekce na anharmonicitu vibrací

Martin C. A.: Simple treatment of anharmonic effects on the specific heat. *Journal of Physics: Condensed Matter 3*, 5967 (1991).

Metoda trial-and-error + optimalizace (simplex) ⇒ Θ_{E} α_{E} α_{D}

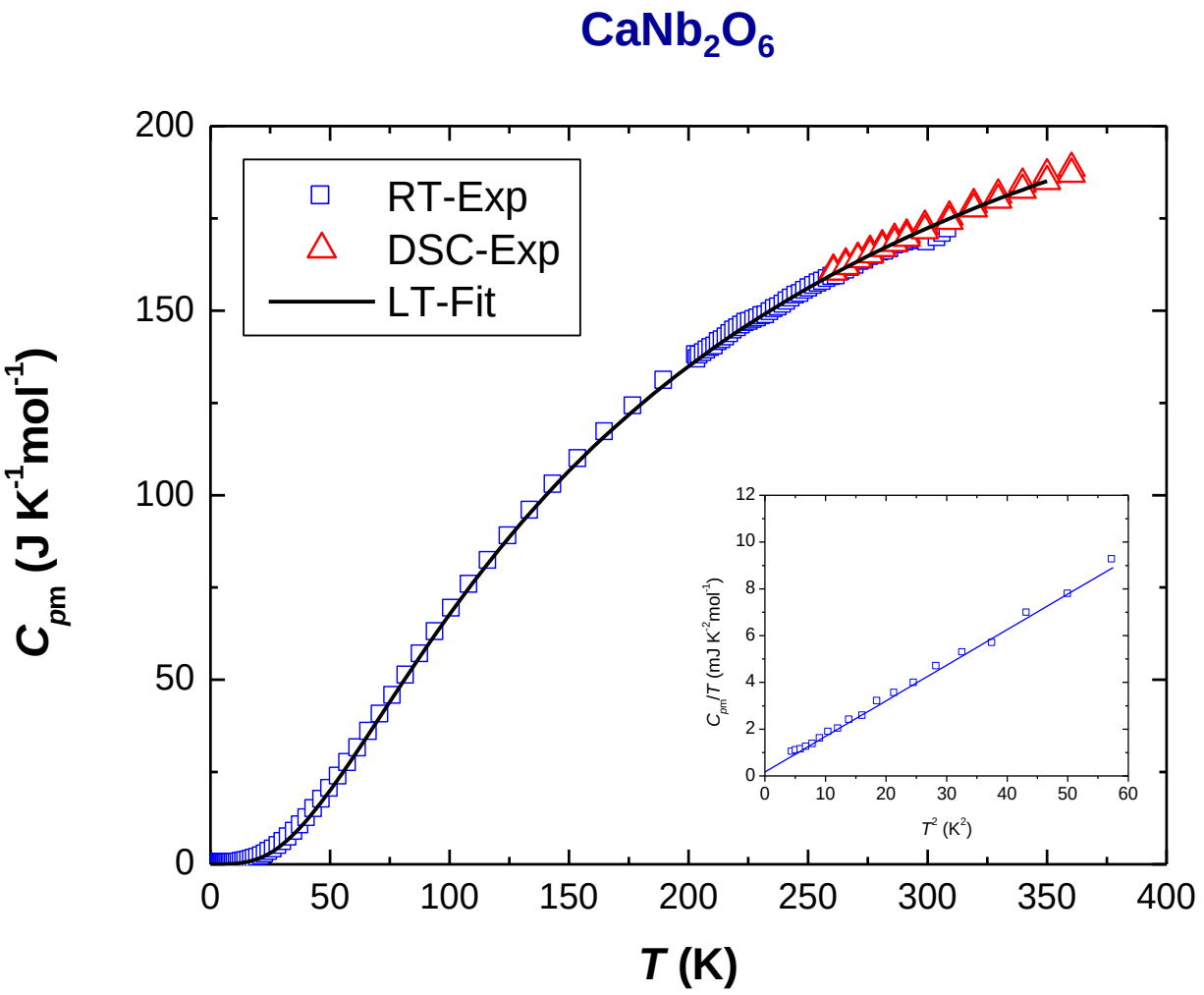
$C_{pm}(298{,}15)$, $H_{\mathrm{m}}(298{,}15) - H_{\mathrm{m}}(0)$, $S_{\mathrm{m}}(298{,}15)$

Experimentální C_p data, T = 10-350 K

Tabulka 5

Parametry pro popis teplotní závislosti tepelné kapacity C_{pm} $CaNb_2O_6$ v oblasti teplot 0–350 K

Vibrační mody (celkový počet)	Degenerace	Θ_D resp. Θ_{Ei} (K)	α_D resp. α_{Ei} (K^{-1})
Akustické (3)	3	234 ± 1	$3{,}0.10^{-4}$
Optické (24)	1	148 ± 1	$2{,}5.10^{-4}$
	7	303 ± 1	$1{,}4.10^{-4}$
	8	502 ± 1	$0{,}8.10^{-4}$
	5	903 ± 1	$0{,}5.10^{-4}$
	3	1332 ± 6	$0{,}3.10^{-4}$


CaNb2O6
RT-Exp
DSC-Exp
LT-Fit
Cpm (J K-1mol-1)
T (K)
0
50
100
150
200
250
300
350
400
Cpm/T (mJ K-2mol-1)
T2 (K2)
0
2
4
6
8
10
12
20
30
40
50
60

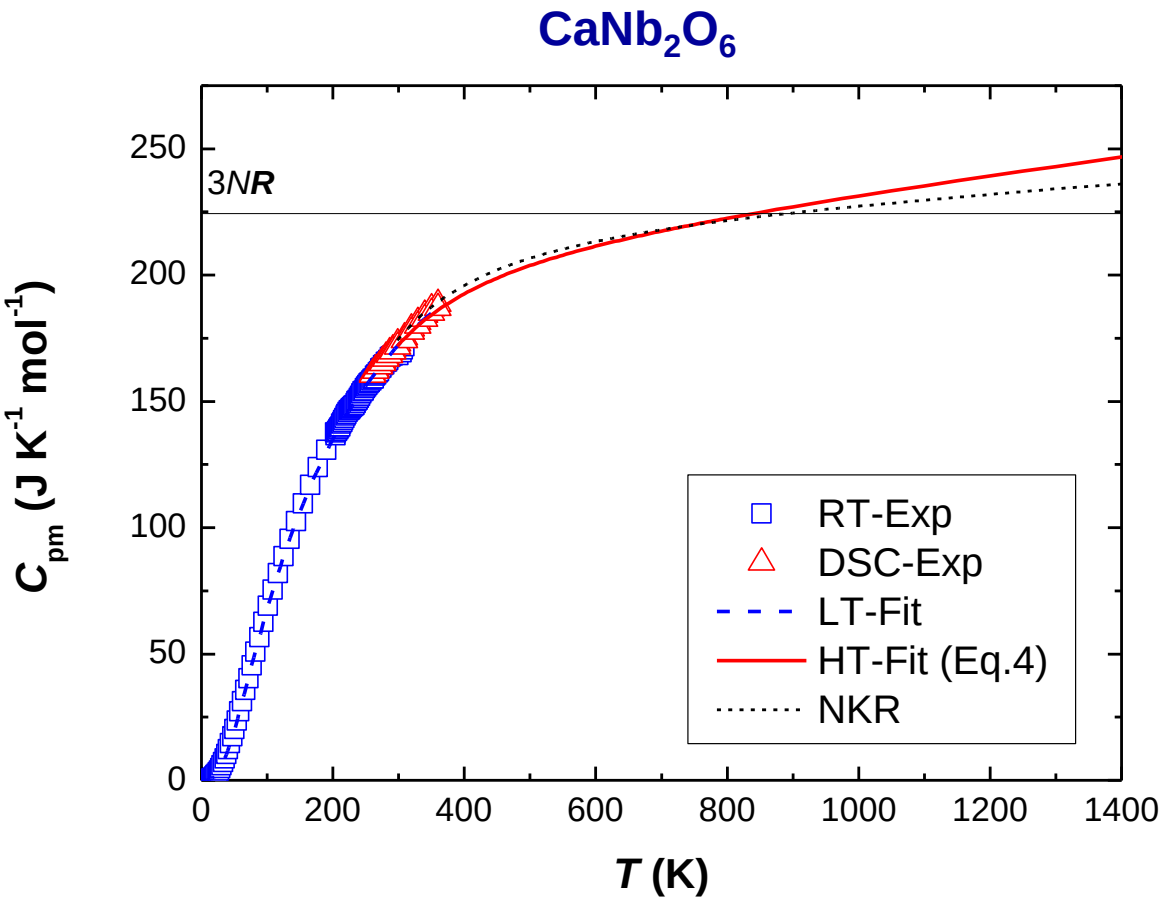
Experimentální data C_p + ΔH, T > 298 K

$$C_{p\mathrm{m}} = \mathrm{A} + \mathrm{B}\cdot T + \frac{\mathrm{C}}{T^2}$$

$$\Delta_T H_{\mathrm{m}} = H_{\mathrm{m}}(T) - H_{\mathrm{m}}(298) = \mathrm{A}\left(\mathrm{T\text{-}298}\right) + \frac{\mathrm{B}}{2}\left(T^2 - 298^2\right) - \mathrm{C}\left(\frac{1}{T} - \frac{1}{298}\right)$$

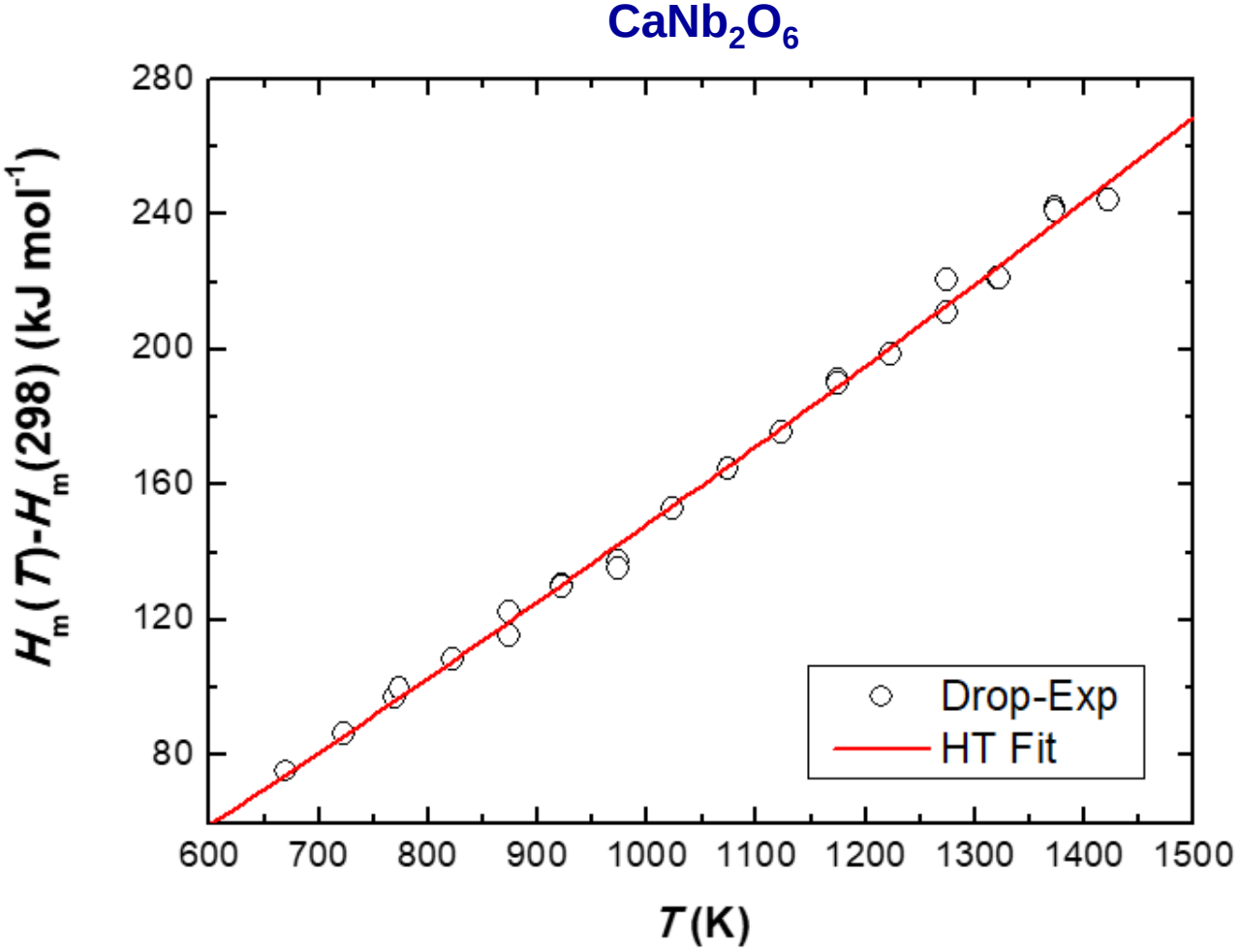
$$F(A,B,C) = \sum_i^{N_{C_p}} \frac{1}{\sigma^2_{C_{p,i}}}\left(C_{p\mathrm{m,exp}} - C_{p\mathrm{m,calc}}\right)_i^2 + \sum_i^{N_{\Delta H}} \frac{1}{\sigma^2_{\Delta H_{m,i}}}\left(\Delta H_{m,\mathrm{exp}} - \Delta H_{m,\mathrm{calc}}\right)_i^2 \rightarrow \min$$

Experimentální data C_p + ΔH, T > 298 K



$$C_{pm} = 200,4 + 0,0343T - \frac{3,450 \times 10^6}{T^2}$$

Experimentální data C_p + ΔH, T > 298 K



Metody příspěvkové

$$C_{p\mathrm{m}} = \sum C_{p\mathrm{m},i}$$

Příspěvky $C_{p\mathrm{m},i}$ – atomární, iontové, strukrurní, ... (NKR).

Metody korelační

$$C_{p\mathrm{m}} = f\left(X\right)$$

Fyzikální vlasnost X – např. molární objem, ...

Neumannovo-Koppovo pravidlo

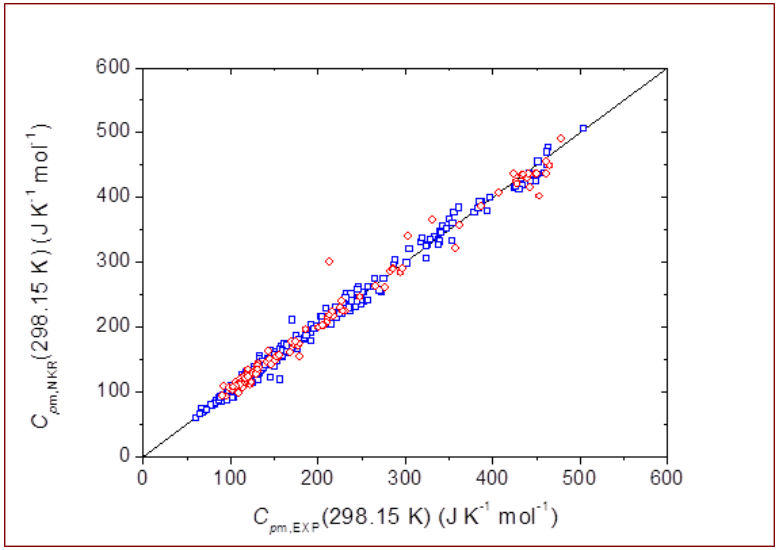
„Each element (in the solid state) has essentially the same specific or atomic heat in compounds as it has in the free state.“

Kopp H.: *Investigations of the heat capacity of solid bodies,*
Phil. Trans. Royal Soc. London 155 (1865) 71-202.

$$C_{pm}(VSi_2) = C_{pm}(V) + 2C_{pm}(V) =$$
$$24,93 + 2 \times 19,96 = 64,85 \text{ J/K/mol } (64,34)$$

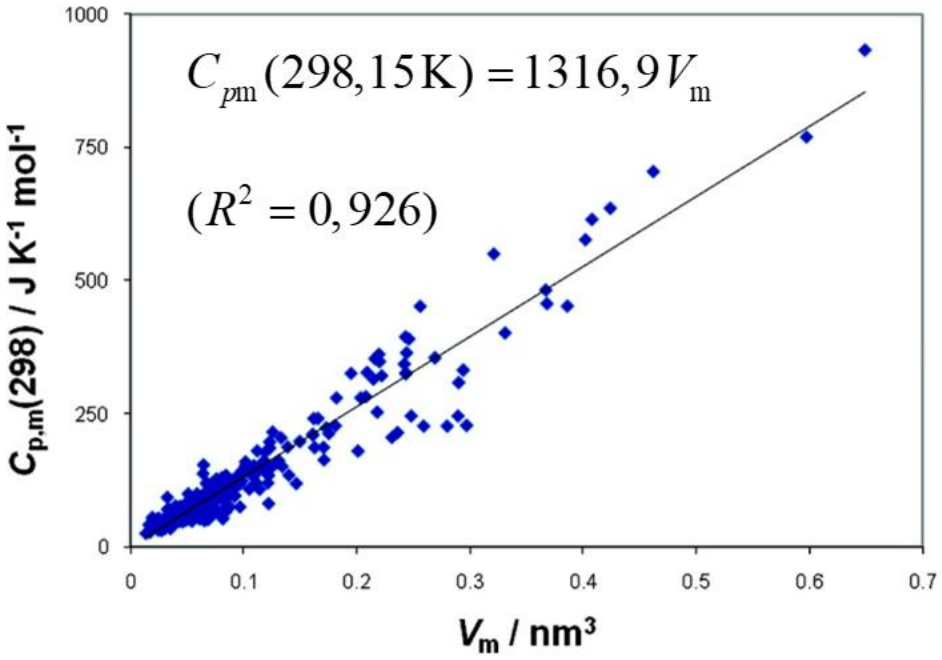
$$C_{pm}(Mg_2SiO_4) = 2C_{pm}(MgO) + C_{pm}(SiO_2) =$$
$$2 \times 37,26 + 44,43 = 118,95 \text{ J/K/mol } (118,42)$$

Zdroj	Počet	Chyba	Do 2%	Nad 5%
TCA (2003)	295	3,3%	135 (46%)	65 (22%)
Aktualizace	421	3,3%	184 (44%)	91 (22%)



Korelace C_{pm} *vs.* V_m

Glasser L., Jenkins H.D.B.: *Ambient Isobaric Heat Capacities, Cpm, for ionic solids and liquids: an Application of Volume-Based Thermodynamics (VBT).*
Inorganic Chemistry, 50(17), 8565-8569 (2011)



Korelace molární tepelné kapacity (C_{pm}) při teplotě 298,15 K na objemu vztaženém na vzorcovou jednotku dané pevné látky ($V_m = V_{cell}(nm^3)/Z_{cell}$, Z_{cell} je počet vzorcových jednotek připadajících na elementární buňku)

Děkujeme za pozornost