Ab initio study of thermophysical and mechanical properties of Ni-X (X=In,Sn) intermetallic compounds

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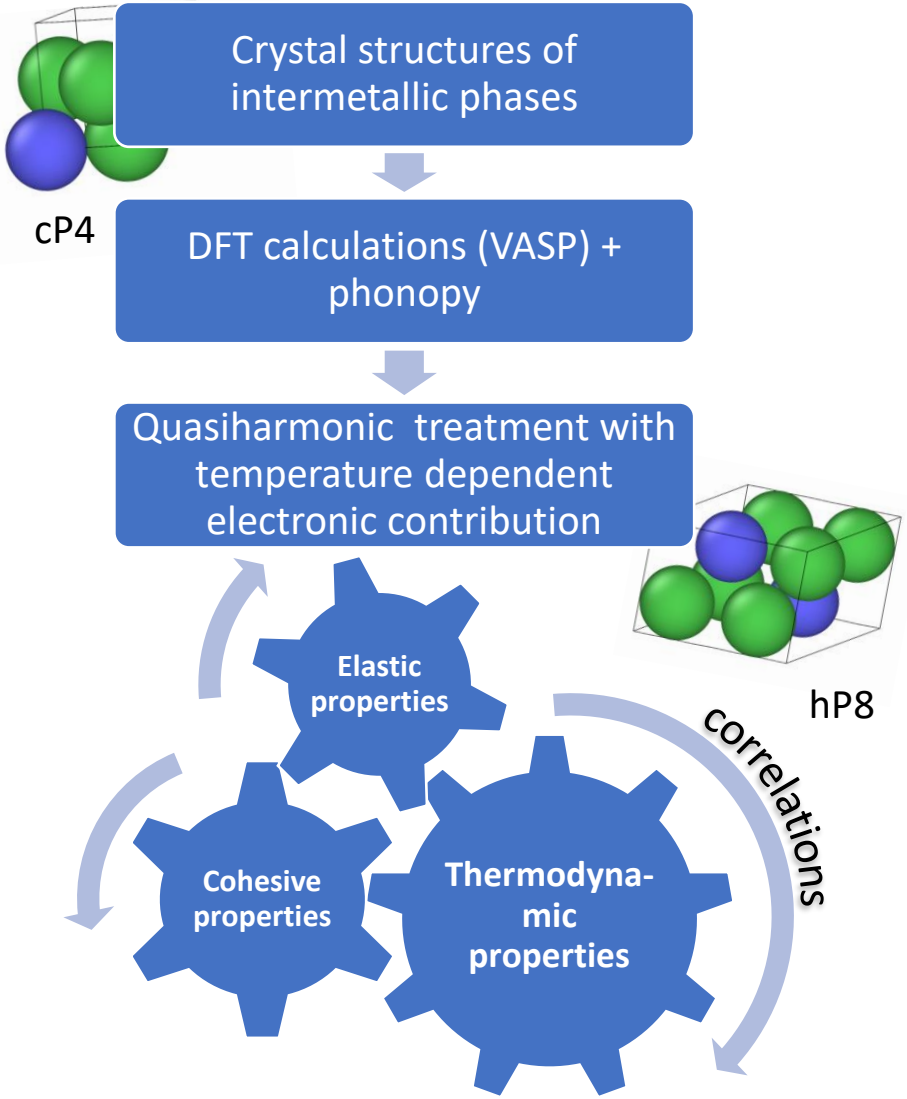


Motivation

- Intermetallic compounds (ICs) of the Ni-In and Ni-Sn systems in relation to the In-Sn solder alloys and their use in lead free micro-soldering processes, with Ni as the contact material.

Objetives

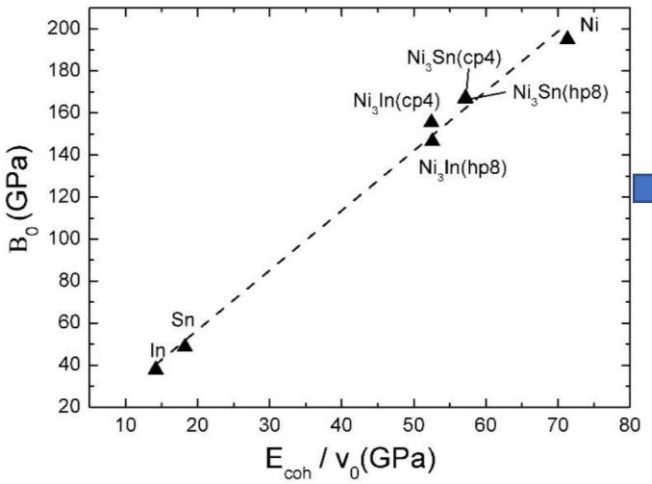
- Extend previous T = 0 K ab initio database [Bertoldi et al., JPED 2017] to include thermal properties.
- Characterize the cohesive, elastic and thermodynamic properties of the Ni_3X (X =In,Sn) compounds, for the low temperature hP8 stable phase, and the cP4 phase, present at high pressure.
- Establish interrelations and correlations between cohesive, elastic and vibrational properties.

Methodology

- DFT-PAW-GGA (XC:PW91) calculations + quasi-harmonic approximation (QHA) to predict: VDOS, Debye temperatures, Gibbs energy and heat capacities.
- Include temperature dependent electronic contribution to the free energy.
- Codes: VASP [Kresse et al., Comput. Mat. Science, 1996] and PHONOPY [Togo et al. PRB, 2008]

Zero-Kelvin calculations

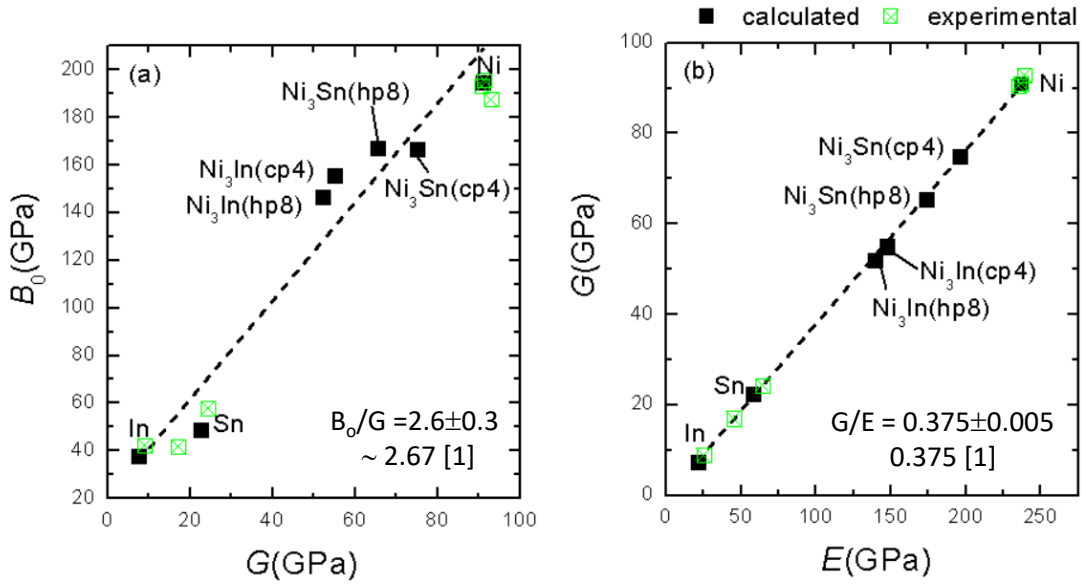
Energy and elastic modulus



Isothermal bulk modulus (B_0) vs cohesive energy density (E_{coh}/v_0) for the elemental solids and the Ni_3X compounds.

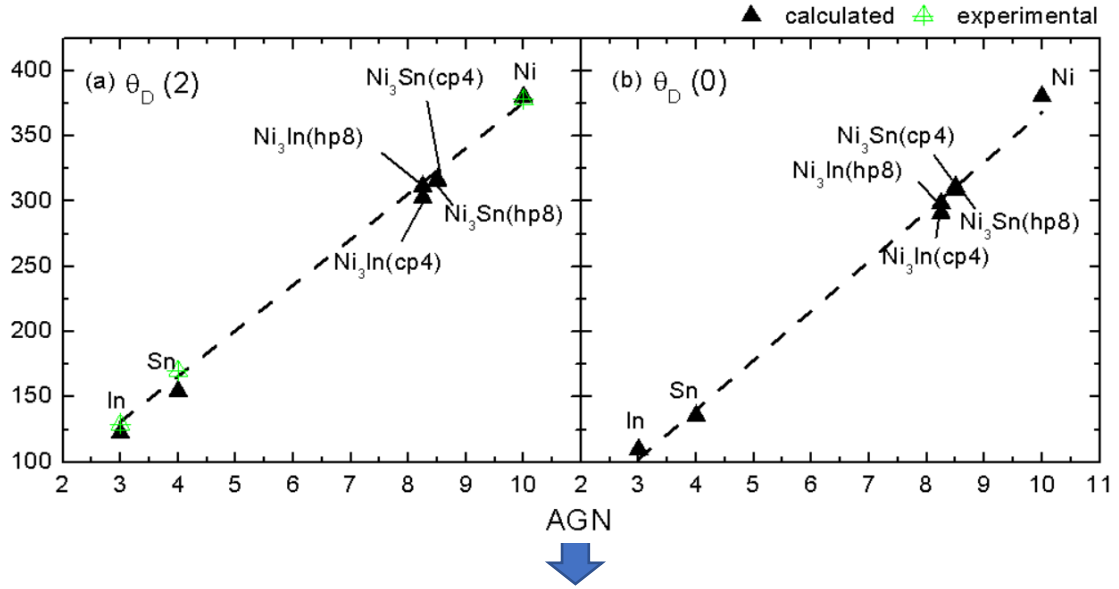
Bertoldi *et al.,* Calphad 71, (2020)

Correlations: B_0, shear (G) and Young (E) modulus



[1] Köster and Franz, Metal. Rev., (1961)

Debye temperatures



Debye temperatures $\theta_D(2)$ and $\theta_D(0)$ (in K) as functions of the average group number (AGN):

$$\theta_D(0) = \frac{\hbar}{k_B} e^{1/3} . \exp\left[\frac{\int_0^{\omega_{max}} \ln\omega \; D(\omega)\, d\omega}{\int_0^{\omega_{max}} D(\omega)\, d\omega}\right]$$

$$\theta_D(2) = \frac{\hbar}{k_B}\left[\frac{5}{3}\frac{\int_0^{\omega_{max}} \omega^2 \; D(\omega)\, d\omega}{\int_0^{\omega_{max}} D(\omega)\, d\omega}\right]^{1/2}$$

AGN: weighted average of the number of valence electrons for the elements Ni, In and Sn: Ni($3d^8\,4s^2$), In ($5s^2\,5p^1$), Sn ($5s^2\,5p^2$).

High temperature calculations

$$F = F^{vib}(T,V) + F^{el}(T,V)$$

Vibrational contribution

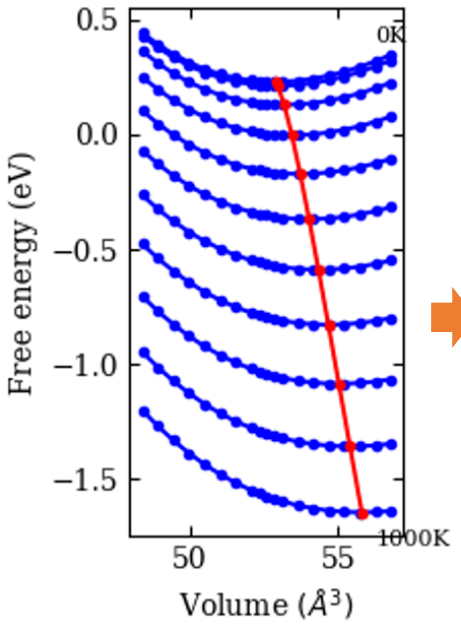
Electronic contribution

$$F^{vib}(T,V) = \frac{1}{2}\sum_{q,j}\hbar\omega_{q.j}(V) + +k_BT\sum_{q,j}\ln\left(1-e^{\hbar\omega_{q.j}(V)/k_BT}\right)$$

QHA

QHA

$$F^{el}(T,V) = \sum_j f_j\left(\varepsilon_j(V),T\right)\varepsilon_j(V) + k_BT\sum_j\left[f_j\left(\varepsilon_j(V),T\right)\ln\left(f_j\left(\varepsilon_j(V),T\right)\right) + \left(1-f_j\left(\varepsilon_j(V),T\right)\right)\ln\left(1-f_j\left(\varepsilon_j(V),T\right)\right)\right]$$



$\varepsilon_j(V)$: 1-electron eigenvalues of the KS equations

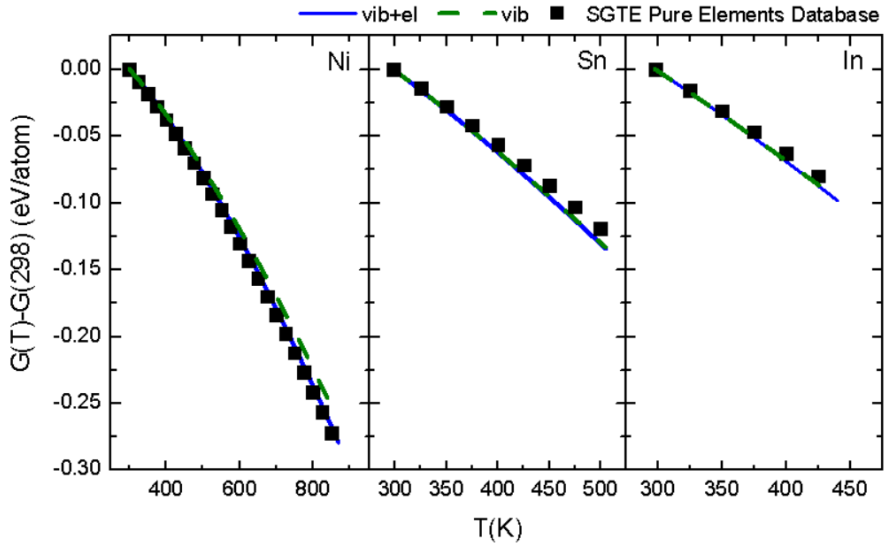
$f_j\left(\varepsilon_j,T\right)$: Fermi-Dirac occupation function in thermal equilibrium at temperature T

$$G(T,P) = min_V[F(T,V)+PV]$$

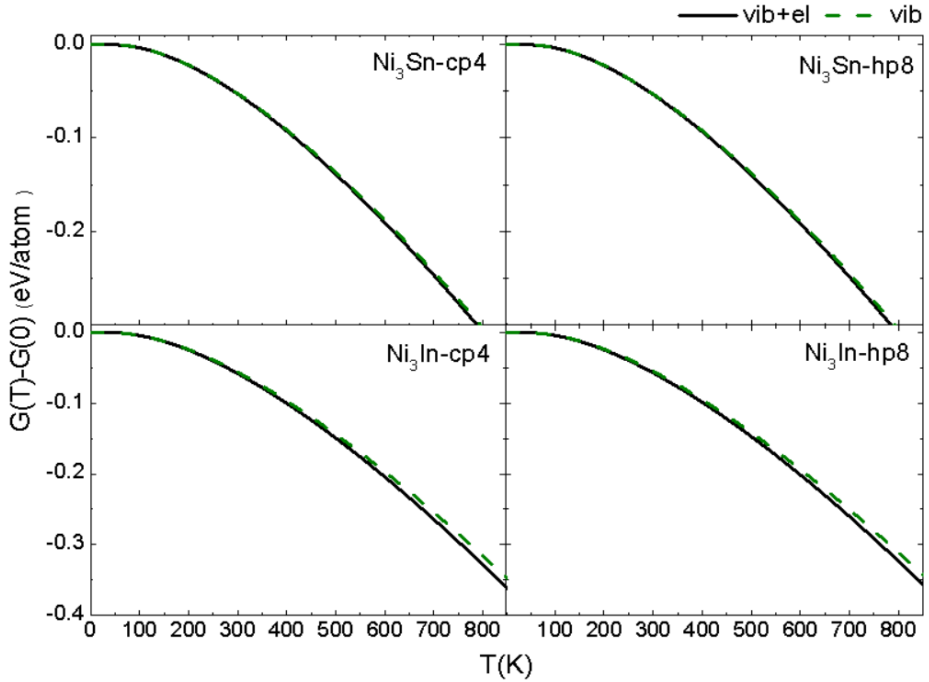
$$C_p(T,P) = -T\frac{\partial^2 G(T,P)}{\partial T^2}$$

Guillan, J. Phys.: Cond. Matter **1** 689, (1989)

Gibbs energy



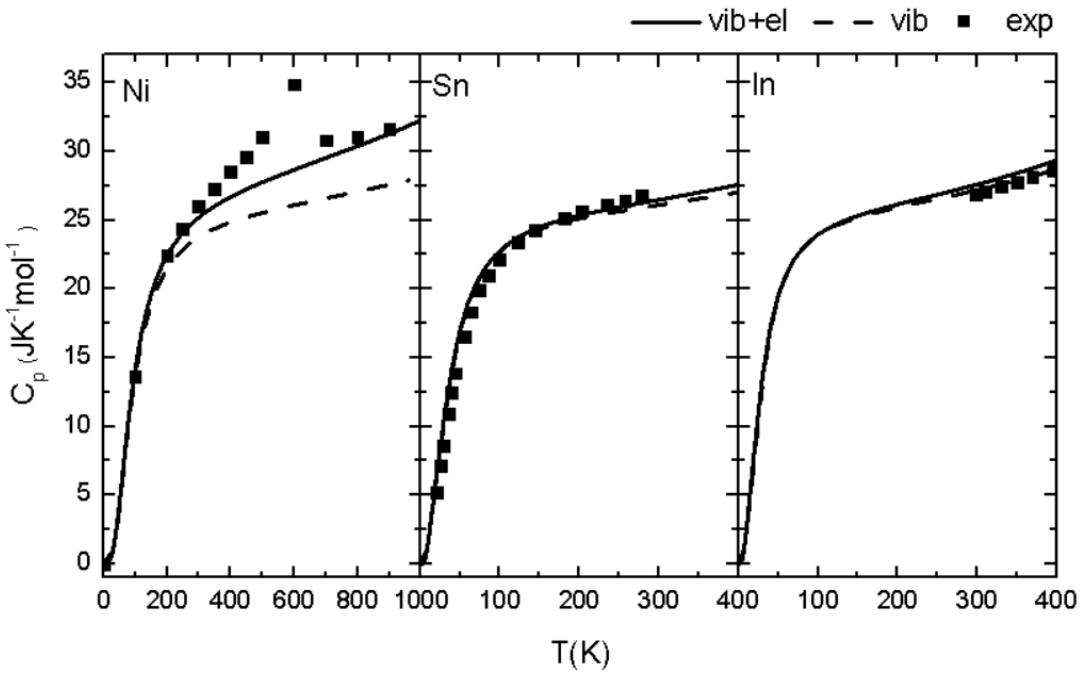
Temperature dependence of the Gibbs energy (G) for the pure elements, with and without electronic (el) contribution. SGTE Pure Elements Database: Dinsdale, Calphad, (1991)



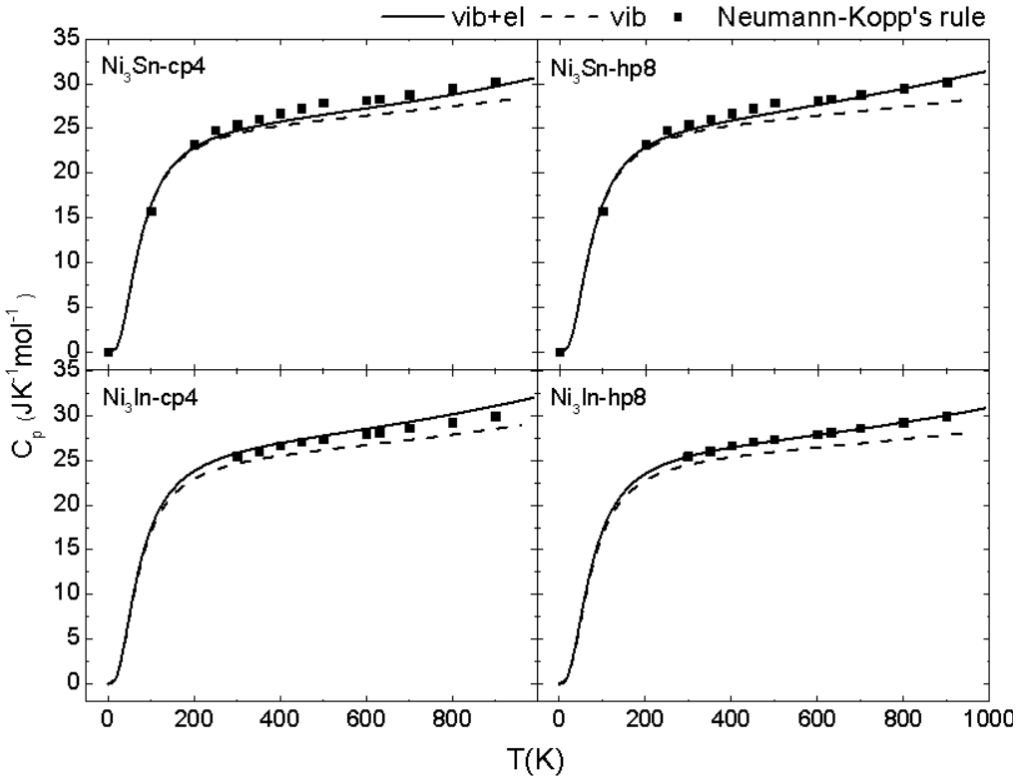
Temperature dependence of the Gibbs energy for the Ni_3X compounds, with and without electronic contribution.

Heat capacity

Heat capacity (C_P) at P=0 for the pure elements, with and without the temperature dependent electronic free energy contribution. Experimental data: Ni [1], Sn [2], In [3]



Heat capacity at P=0 for the Ni_3X compounds in comparison with values obtained with Neumann-Kopp's rule and the pure elements SGTE results: $C_p = \sum_{i=1}^{N} X_i \, . \, C_{p,i}$



[1] Chase Jr, M., J. Phys. Chem. Ref. Data, Monograph 9 (1998), [2] Khvan, A. V. et al., Calphad 65 (2019), [3] Grønvold F., J. Therm. Anal. Calorim. 13 (1978)

Conclusions

- For the elements and the Ni_3X (X= In,Sn) ICs linear correlations have been established: (i) between the B_0 and E_{coh}/V_0, and (ii) between EEMs: B_0 vs G, and for G vs E.
- The inclusion of a temperature dependent electronic free energy contribution in general improves the agreement with the experimental data of the thermal properties evaluated in the QHA.
- For the compounds the results obtained for C_p agree with Neumann-Kopp´s rule.