# Chromium and iron based zeta phases - lattice dynamics from first-principles

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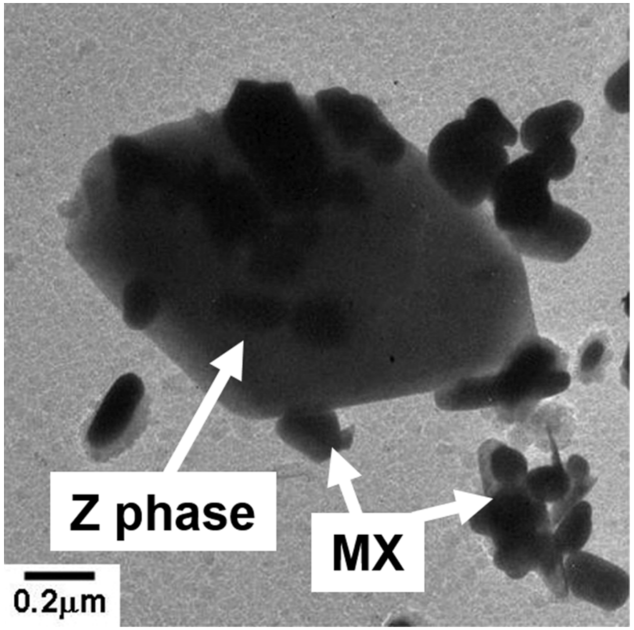
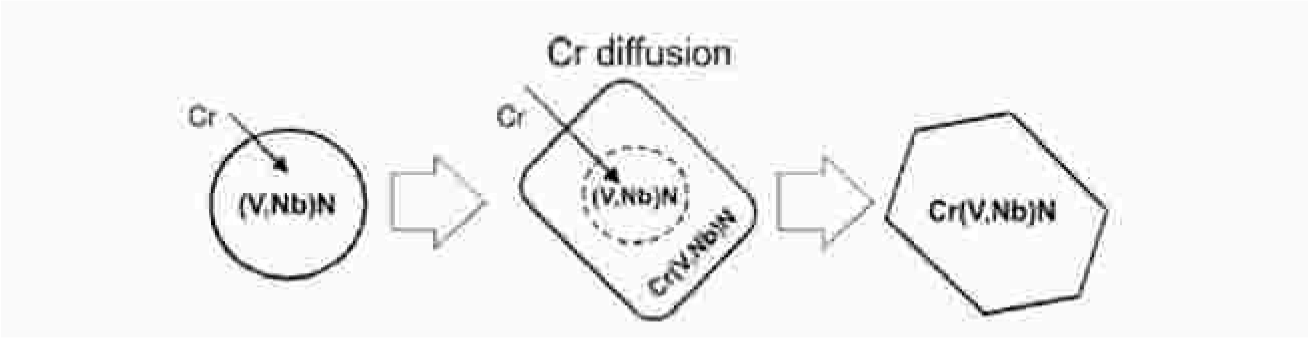
# The Z-phase

- Precipitates in Cr rich steel (9-12%)
- Dissolving beneficial MX particles (V,Nb)(N,C)
- Decreasing the creep strength
- Responsible for the failure of Cr rich steels in long time test




Abe F 2016 J. Pressure Vessel Technol. 138(4)




L. Cipolla. H. K. Danilesen. D. Venditti, P. E. Di Nunzio, J. Hald, M. A. J. Somers,(2010) 669-679.

# Calculation

- VASP, PHONOPY[6], PHONOPY-QHA
- K-mesh 28 28 12 unitcell

  14 14 6 supercell 2x2x2

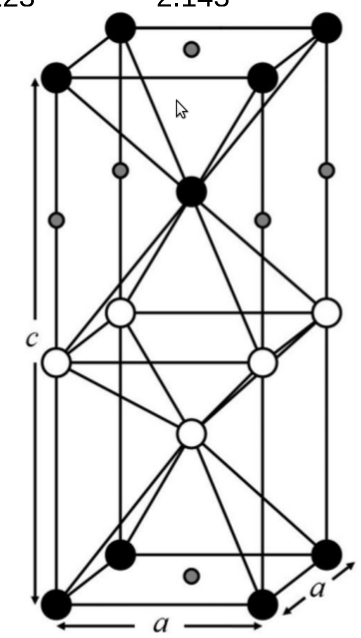
- POTCAR PAW_PBE
- ENCUT = 600 eV
- EDIFF = 1E-08
- SIGMA = 0.2

[6] Atsushi Togo and Isao Tanaka, Scr. Mater., 108, 1-5 (2015)

# Structure specification

| c | CrNbN | Cr-NbV-N | CrVN | CrMoN | FeNbN | Fe-NbV-N | FeVN | FeMoN |
|---|---|---|---|---|---|---|---|---|
| Magnetism | NO | NO | NO | NO | YES | YES | YES | YES |
| Volume (Å$^3$) | 68 | 64 | 58 | 64 | 68 | 64 | 58 | 63 |
| a (Å) | 3.037 | 2.963 | 2.855 | 2.975 | 3.053 | 2.982 | 2.858 | 2.98 |
| c (Å) | 7.383 | 7.239 | 7.126 | 7.271 | 7.297 | 7.162 | 7.121 | 7.101 |
| c/a (-) | 2.431 | 2.443 | 2.496 | 2.444 | 2.39 | 2.402 | 2.492 | 2.38 |
| a (Å) – calc | 3.021 [1] | 2.956 [1] | 2.860 [1] | - | 3.054 [4] | - | 2.858[4] | - |
| c (Å) – calc | 7.367 [1] | 7.235 [1] | 7.134 [1] | - | 7.290 [4] | - | 7.105 [4] | - |
| a (Å) – exp | 3.037 [5] | 2.860 [2] | 2.860 [3] | - | - | - | - | - |
| c (Å) – exp | 7.391 [5] | 7.391 [2] | 7.390 [3] | - | - | - | - | - |
| Magnetism ($\mu_B$ /Å) | NO | NO | NO | NO | YES | YES | YES | YES |
| Fe | - | - | - | - | 2.275 | 2.340; 2.149 | 2.123 | 2.143 |

Model of the Z-phase, black=Nb/V/Mo, white=Cr/Fe, grey = N
Spacegroup P4mm/99 or P4nmm/129





[1] Legut D and Pavlu J 2012 J. Phys.: Condens. Matter 24 195502
[2] Danielsen H K and Hald J 2006 Energy Mater. 1 49
[3] Strang A and Vodarek V 1996 Mater. Sci. Technol. 12 552
[4] Kocer C and Taichi A 2009 Mater. Sci. Engin. 505 (CALPHAD method)
[5] Jack D H and Jack K H 1972 J. Iron Steel Inst. 209 790

# Elastic properties

| | CrNbN | Cr-NbV-N | CrVN | CrMoN | FeNbN | Fe-NbV-N | FeVN | FeMoN |
|---|---|---|---|---|---|---|---|---|
| $C_{11}$ | 539 (537) | 529 (532) | 552 (543) | 510 | 457 | 366 | 438 | 420 |
| $C_{12}$ | 244 (243) | 210 (212) | 204 (190) | 308 | 230 | 271 | 184 | 283 |
| $C_{13}$ | 140 (145) | 141 (139) | 164 (149) | 161 | 142 | 171 | 146 | 195 |
| $C_{33}$ | 485 (528) | 509(497) | 524 (528) | 518 | 404 | 346 | 388 | 358 |
| $C_{44}$ | 112 (120) | 132 (124) | 131 (136) | 71 | 115 | 88 | 118 | 90 |
| $C_{66}$ | 261 (268) | 245 (250) | 237 (237) | 238 | 247 | 194 | 225 | 238 |
| B – ela. | 290 | 283 | 300 | 310 | 260 | 256 | 246 | 283 |
| B – ev. | 287 | 284 | 302 | 309 | 262 | 254 | 247 | 281 |
| C1 | 278 | 394 | 315 | 439 | 210 | 172 | 213 | 182 |
| C2 | 28 | 107 | 33 | -77 | 27 | 83 | 28 | 105 |
| I | 744 | 756 | 748 | 706 | 577 | 370 | 534 | 388 |
| II | 2611 | 2551 | 2692 | 2798 | 2346 | 2304 | 2216 | 2544 |
| III | 230 | 238 | 243 | 201 | 178 | 103 | 175 | 116 |

$$B = 2/9(C_{11} + C_{12} + 2C_{13} + C_{33}/2)$$

$$C_{11} + C_{33} - 2C_{13} > 0, (I)$$

$$2C_{11} + C_{33} + 2C_{12} + 4C_{13} > 0, (II)$$

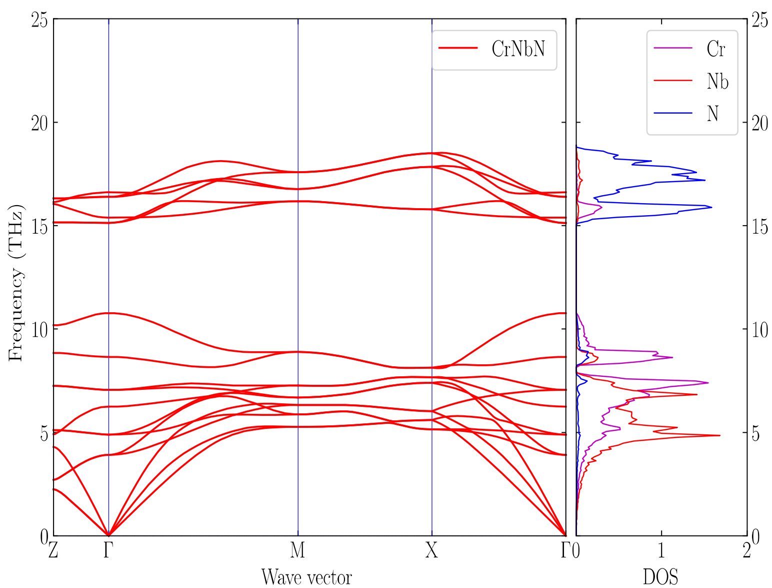
$$1/3(2C_{11} + C_{33}) - B > 0, (III)$$

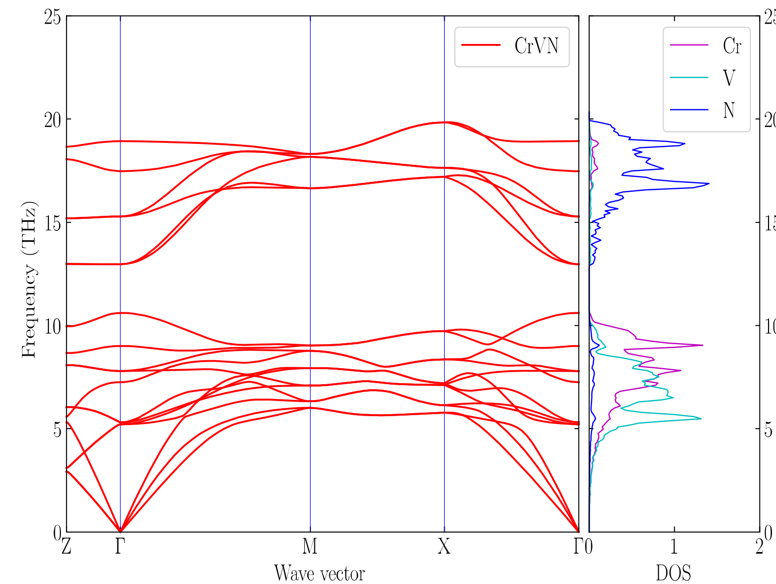
$$C1 = C_{12} - C_{66}$$

$$C2 = C_{13} - C_{44}$$

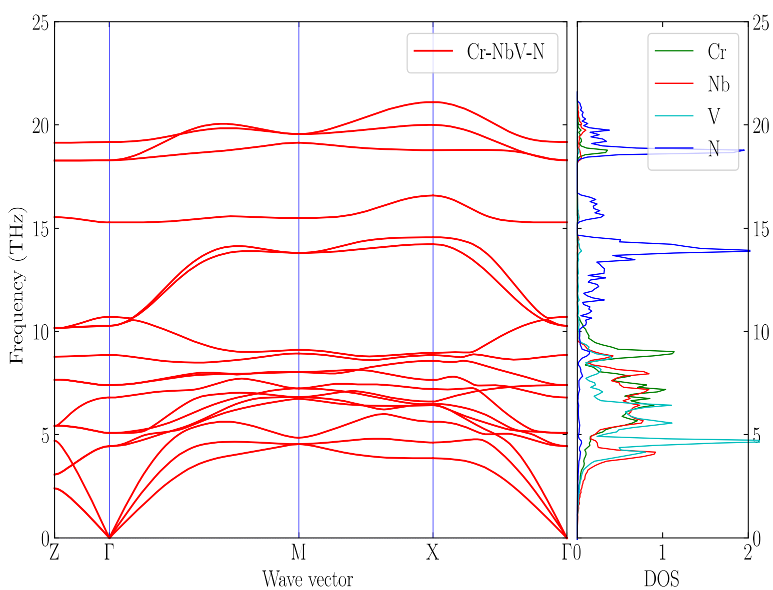
[1] Legut D and Pavlu J 2012 J. Phys.: Condens. Matter 24 195502

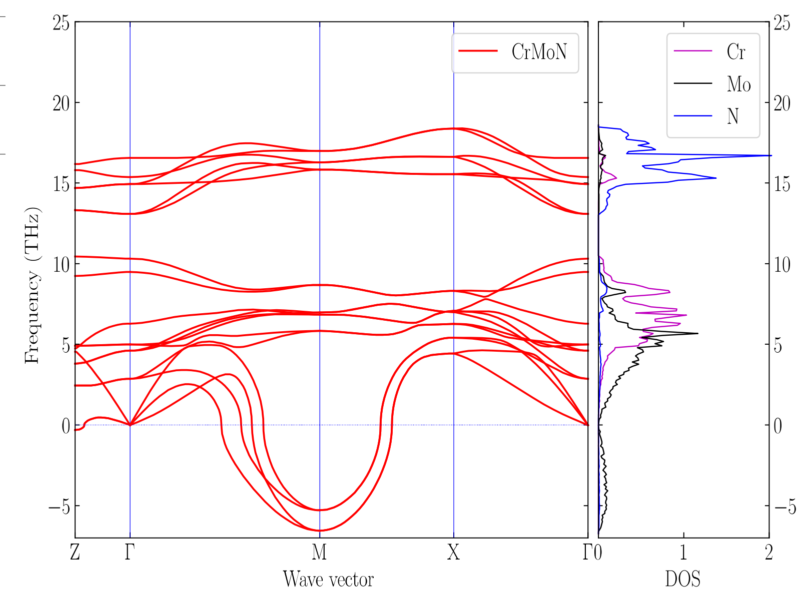
# The lattice dynamics

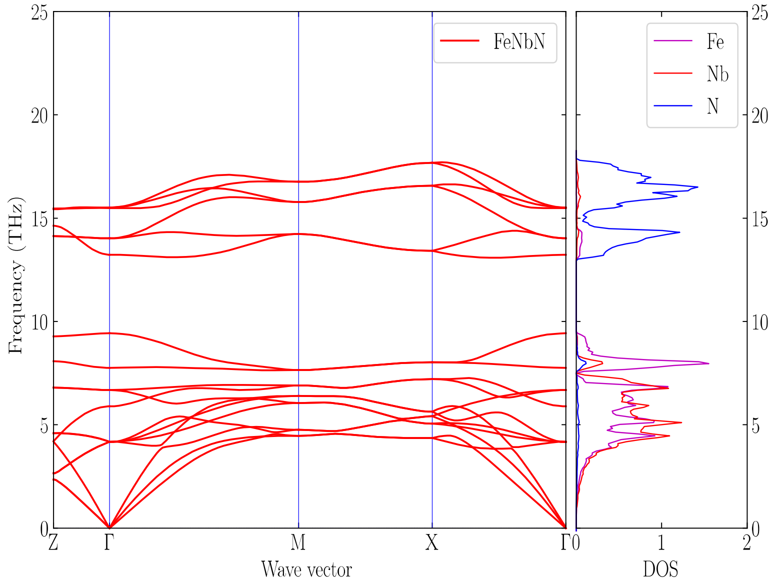


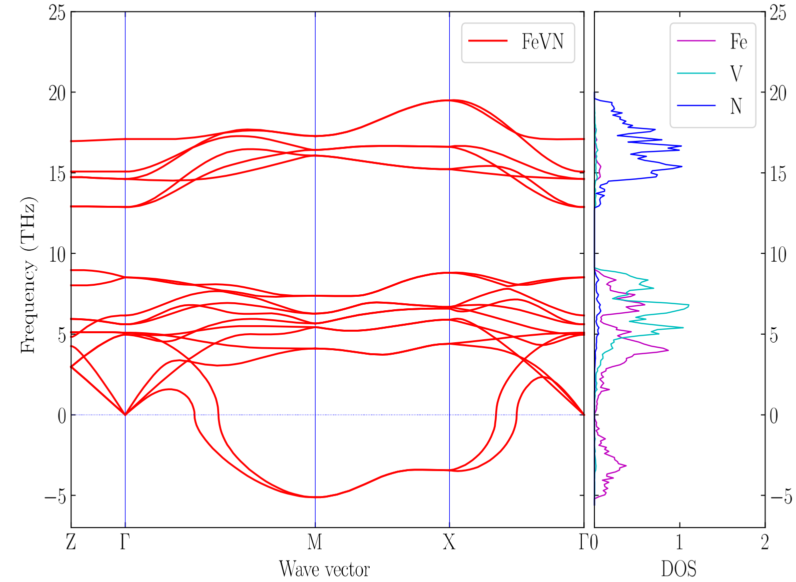




| | Weight (u.m.) |
|---|---|
| Cr | 52 |
| Nb | 93 |
| V | 51 |
| Mo | 96 |
| N | 14 |

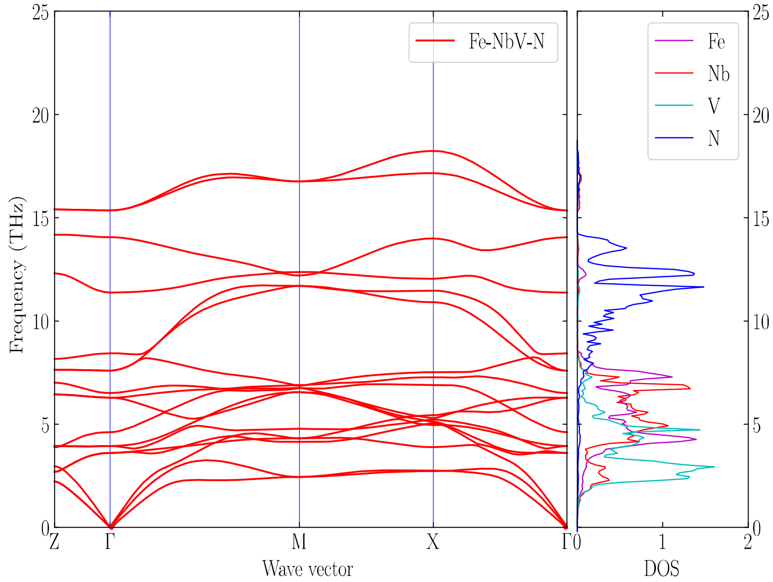


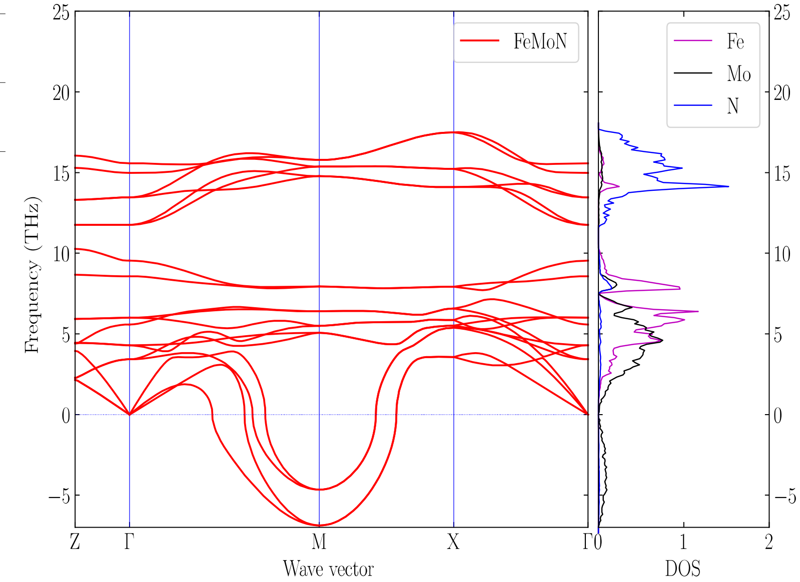





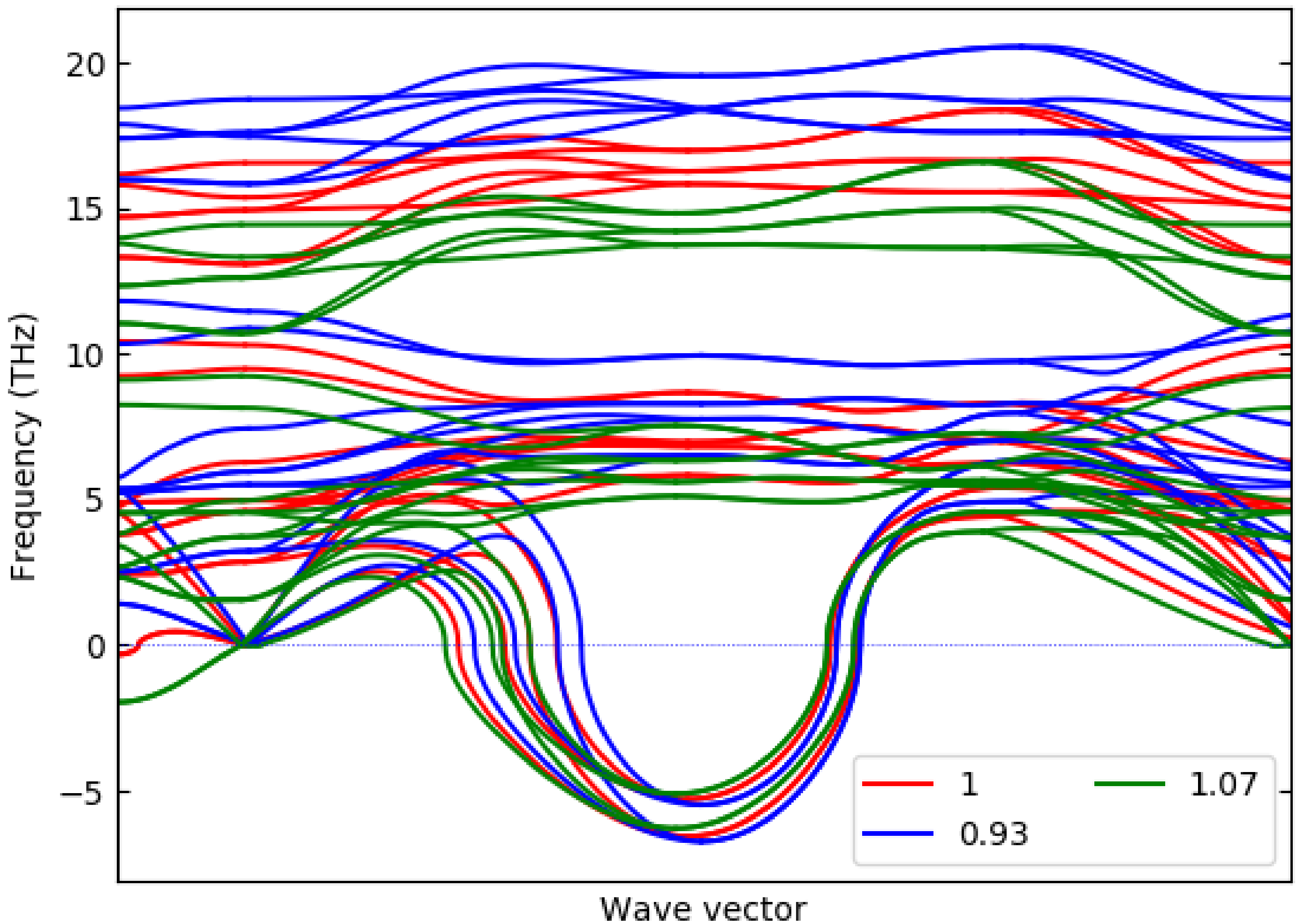



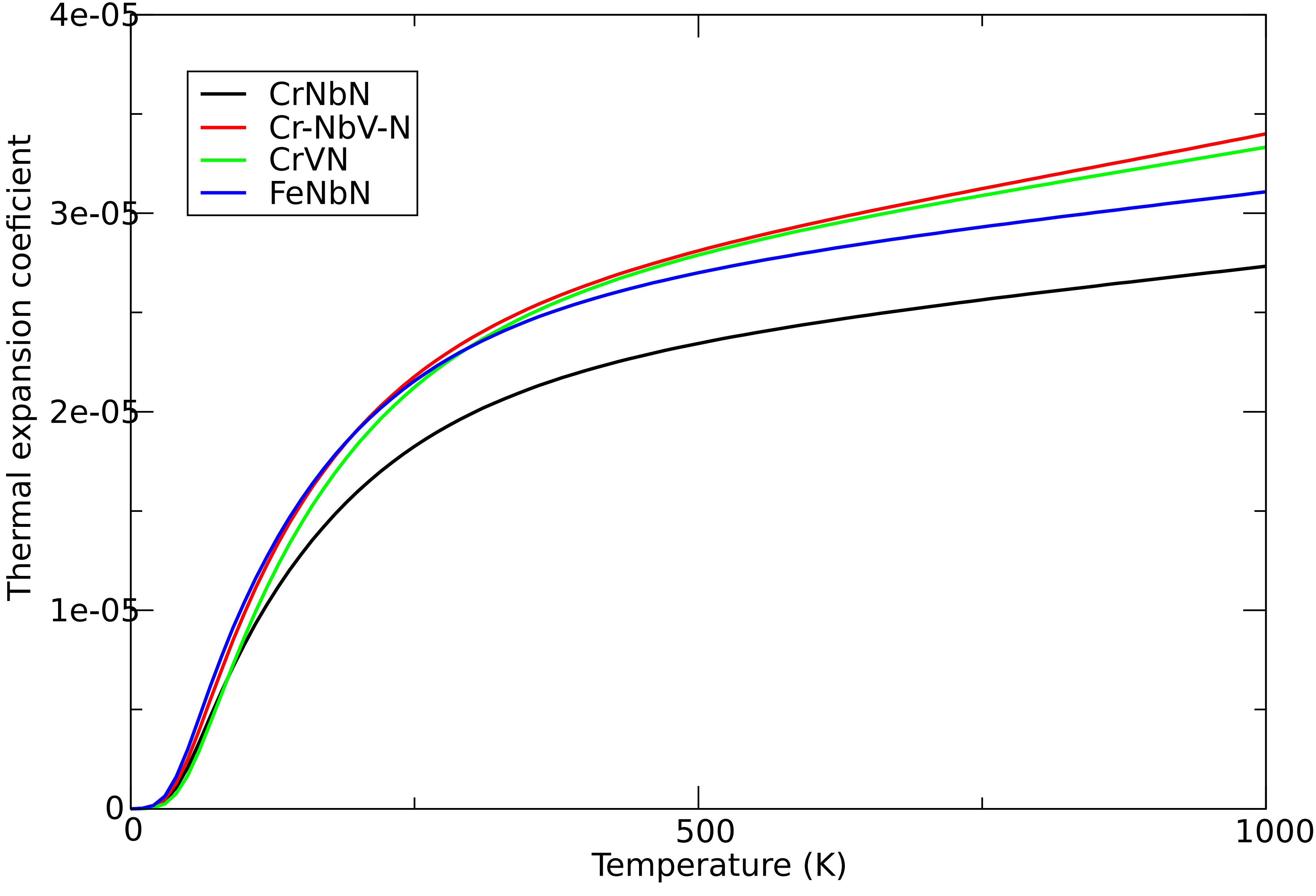

| | Weight (u.m.) |
|---|---|
| Fe | 56 |
| Nb | 93 |
| V | 51 |
| Mo | 96 |
| N | 14 |



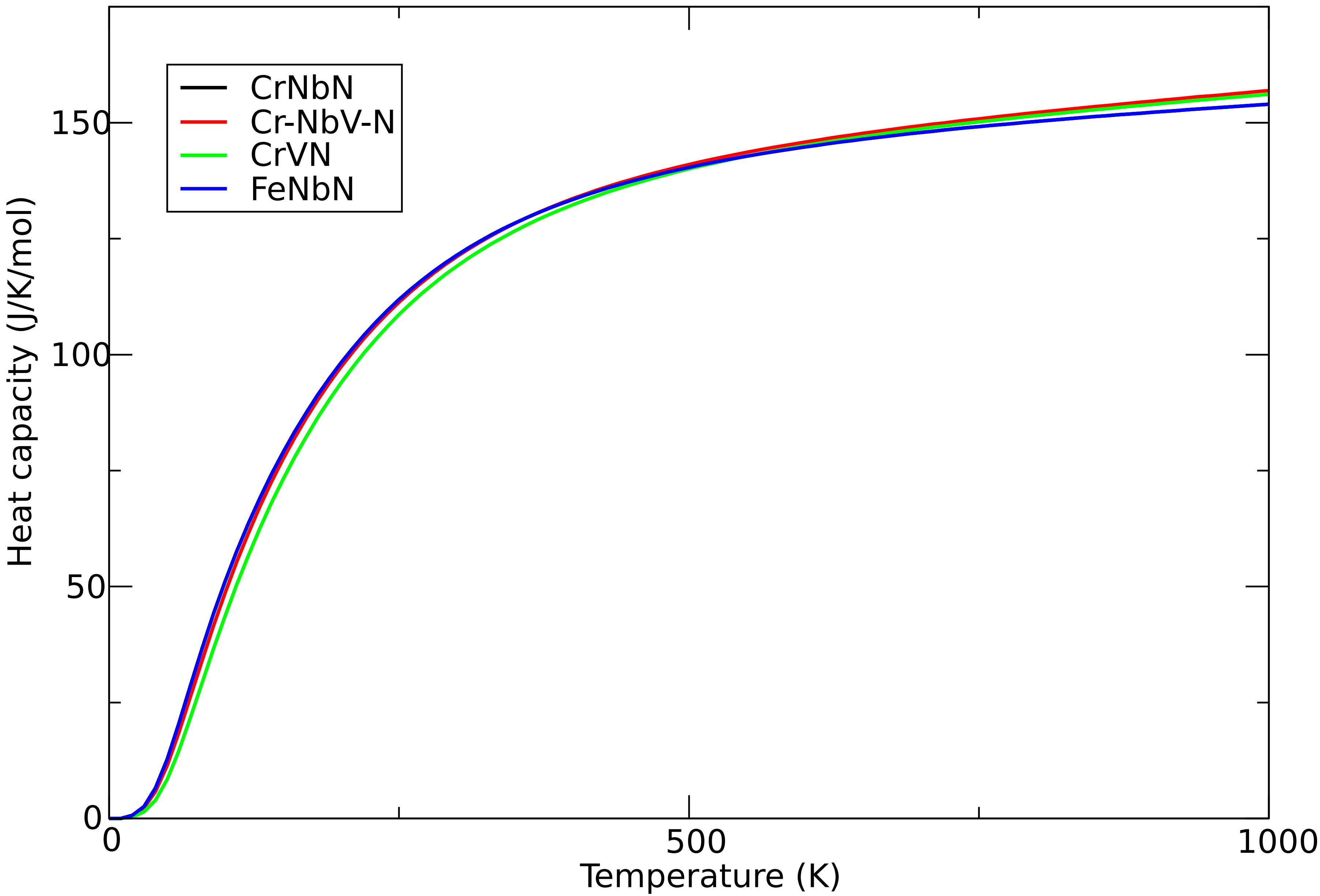



# CrMoN imaginary frequencies





4e-05
3e-05
2e-05
1e-05
0
0
500
1000
Temperature (K)
Thermal expansion coeficient
CrNbN
Cr-NbV-N
CrVN
FeNbN


CrNbN
Cr-NbV-N
CrVN
FeNbN
Heat capacity (J/K/mol)
0
50
100
150
0
500
1000
Temperature (K)

# Thermal expansion of tetragonal structure

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## Electronic Structure and Lattice Dynamics of Elements and Compounds

PETROS SOUVATZIS

[7] P. Souvatzis, ‘Electronic Structure and Lattice Dynamics of Elements and Compounds’, PhD dissertation, Acta Universitatis Upsaliensis, Uppsala, 2007.

$$U(\epsilon_1, \epsilon_3) = \frac{V}{2}[2(C_{11} + C_{12})\epsilon_1^2 + 4C_{13}\epsilon_1\epsilon_3 + C_{33}\epsilon_3^2]$$

$$\epsilon_1 = \frac{1}{3}(\epsilon_v - \epsilon_c) \qquad \epsilon_3 = \frac{1}{3}(\epsilon_v + 2\epsilon_c)$$

$$\epsilon_v = \frac{1}{V} \qquad \epsilon_c = \frac{a}{c}$$

$$F(\epsilon_v, \epsilon_c, T) = U(\epsilon_v, \epsilon_c) + F_{phon}(\epsilon_v, \epsilon_c, T)$$

[7] P. Souvatzis, ‘Electronic Structure and Lattice Dynamics of Elements and Compounds’, PhD dissertation, Acta Universitatis Upsaliensis, Uppsala, 2007.

$$B_{11} = \frac{2}{9}(C_{11} + C_{12} + \frac{1}{2}C_{33} + 2C_{13})$$

$$B_{22} = \frac{2}{9}(C_{11} + C_{12} + 2C_{33} - 4C_{13})$$

$$B_{12} = \frac{1}{9}(C_{33} + C_{13} - C_{11} - C_{12})$$

$$U(\epsilon_v, \epsilon_c) = V[\frac{1}{2}B_{11}\epsilon_v^2 + 2B_{12}\epsilon_v\epsilon_c + \frac{1}{2}B_{22}\epsilon_c^2]$$

[7] P. Souvatzis, ‘Electronic Structure and Lattice Dynamics of Elements and Compounds’, PhD dissertation, Acta Universitatis Upsaliensis, Uppsala, 2007.

$$\alpha_{\perp} = \frac{1}{3V(B_{11}B_{22} - B_{12}^2)}[-(B_{22} + B_{12})\frac{\partial^2 F}{\partial T \partial \epsilon_v} + (B_{12} + B_{11})\frac{\partial^2 F}{\partial T \partial \epsilon_c}]$$

$$\alpha_{\parallel} = \frac{1}{3V(B_{11}B_{22} - B_{12}^2)}[-(B_{22} - 2B_{12})\frac{\partial^2 F}{\partial T \partial \epsilon_v} + (B_{12} - 2B_{11})\frac{\partial^2 F}{\partial T \partial \epsilon_c}]$$

$$\beta = \frac{1}{V(B_{11}B_{22} - B_{12}^2)}[-B_{22}\frac{\partial^2 F}{\partial T \partial \epsilon_v} + B_{11}\frac{\partial^2 F}{\partial T \partial \epsilon_c}]$$

[7] P. Souvatzis, ‘Electronic Structure and Lattice Dynamics of Elements and Compounds’, PhD dissertation, Acta Universitatis Upsaliensis, Uppsala, 2007.

Thanks for attention