Phonon spectra in α and σ phases of FeCr alloy from first principles

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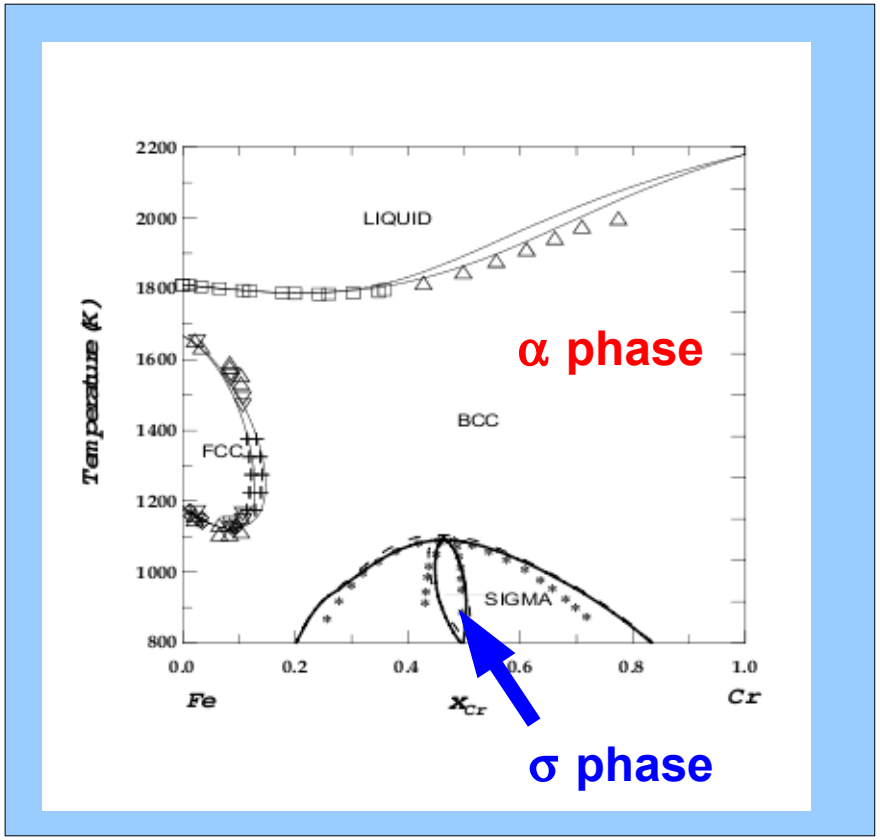
S. M. Dubiel, J. Cieślak, W. Sturhahn, M. Sternik, P. Piekarz, S. Stankov, and K. Parlinski, Vibrational Properties of α- and σ-Phase Fe-Cr Alloy, PRL 104, 155503 (2010)

For many years, FeCr alloy system has been of exceptional scientific and technological interest. Fe-Cr alloys are the basic ingredient of stainless steels that for a century have been one of the most important structural materials.

Phase diagram of FeCr alloy



Structure of alloy constituents:

at low temperature:

pure Fe and Cr have bcc structure

at high temperature: Fe have fcc structure

α phase – bcc solid solutions stable at broad range of compositions and temperatures

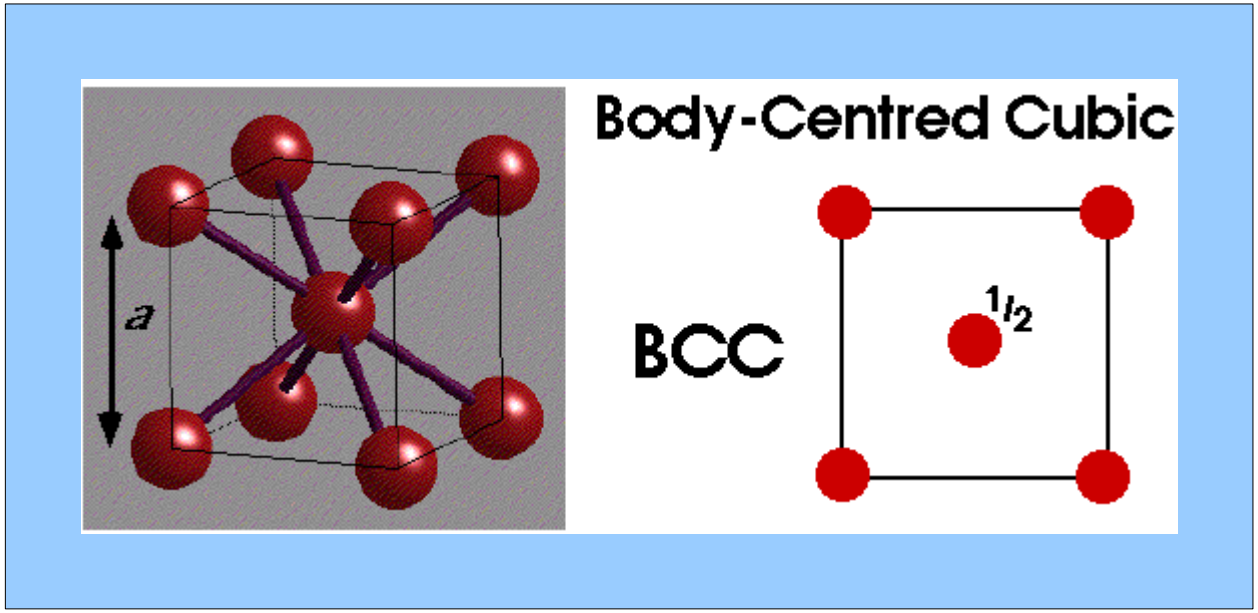
σ phase – around the equiatomic compositions

J. Vrešťál*, J. Houserová* and M. Šob**

Journal of Mining and Metallurgy, 38 (3–4) B (2002) 205 - 211

The FeCr α phase structure

bcc structure
space group Im3m
a = 0.288 nm



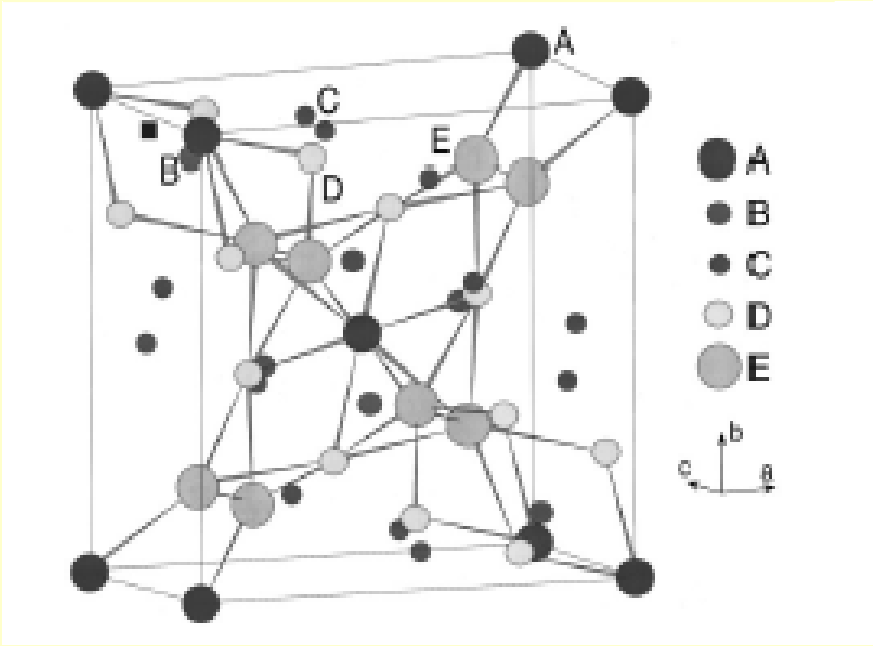
The Fe and Cr atoms are randomly distributed over bcc lattice

The σ phase structure

Tetragonal structure
space group $P4_2/mnm$
a = 0.87968(5) nm
c/a = 0.518

30 atoms distributed over 5 different sites

C. Berne et al., *Phys. Rev. B 64, 144103 (2001)*



The site occupation:

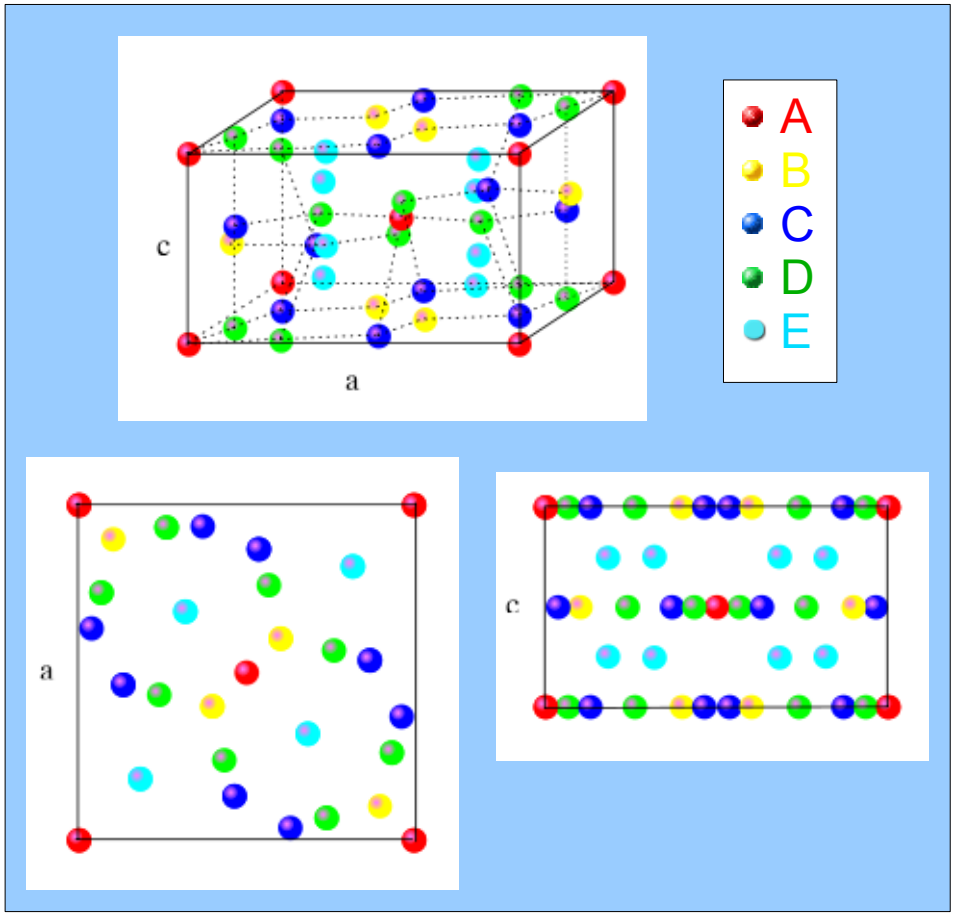
H.L. Yakel, *Acta Cryst. B39, 20 (1983)*

Sublatices	Components	Wyck.	x	y	z
A	0.9 Fe + 0.1 Cr	2a	0	0	0
B	0.7 Cr + 0.3 Fe	4f	0.39875(6)	0.39875(6)	0
C	0.58 Cr + 0.42 Fe	8i	0.46349(6)	0.13123(6)	0
D	0.88 Fe + 0.12 Cr	8i	0.73935(6)	0.06611(6)	0
E	0.72 Cr + 0.28 Fe	8j	0.18267(4)	0.18267(4)	0.25191(1)

A.Gupta et al, Hyp.Int. 54,805 (1990)
from Mossbauer spectroscopy

M.Sluiter et al, PRL 75, 3142 (1995).
from ab-initio calculations

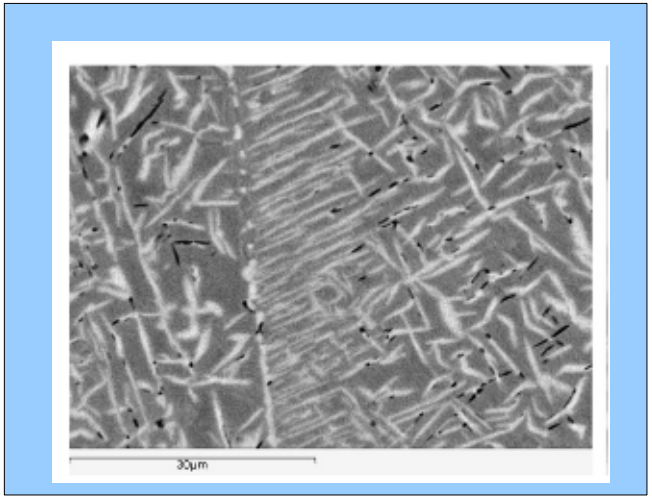
The σ phase structure



A.Błachowski, PhD Thesis, AGH 2000

1923 - a hard nonmagnetic phase in FeCr was found (E.C.Bain, Chem.Met.Eng28(1923))

at present – 110 different intermetallic phases with σ phase structure in more than 40 systems (Co-Cr, Fe-V, Cr-Mn .....) are known



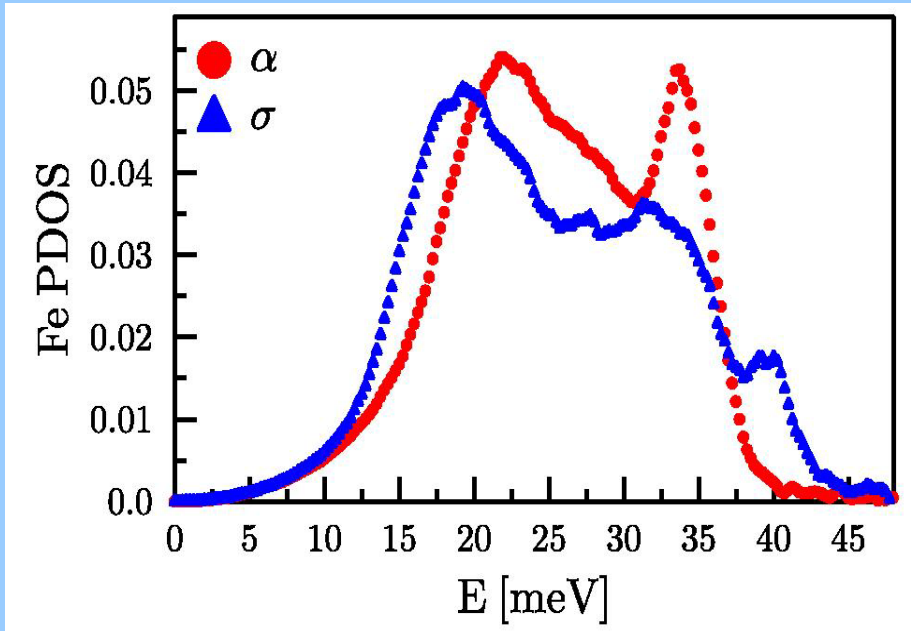
Scanning electron microscope
J.Vrestal, Comp.Mat.Sc.38, 298 (2006)

σ phase has a lamellar morphology which leads to a destructive effect on a mechanical properties of alloys
σ phase is harder than α phase but it is brittle

S.M. Dubiel , J. Cieślak,

W. Sturhahn and S.Stankov

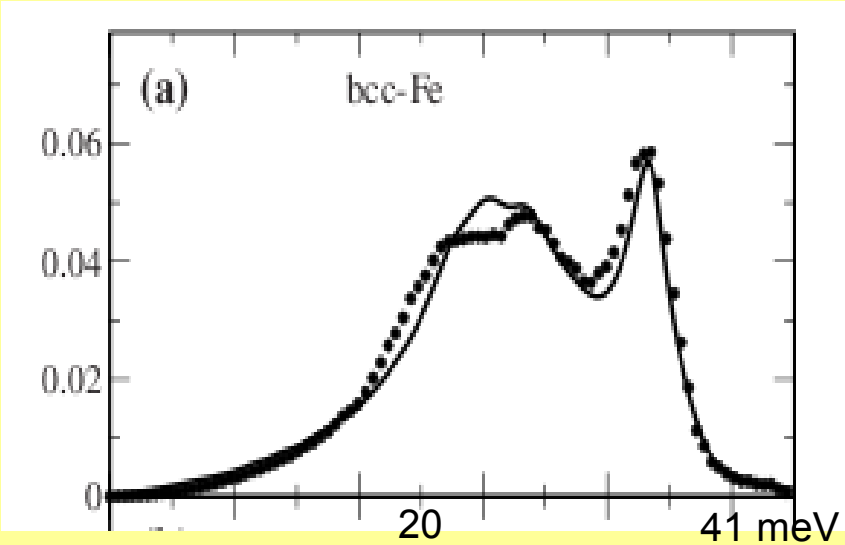
Samples: $Fe_{52.5}Cr_{47.5}$ in α and σ phase



S. Dubiel et al., *PRL 104, 155503 (2010)*

Nuclear resonant inelastic x-ray scattering
Advanced Photon Source, Argonne

bcc-Fe



B.Laenens et al., *PRB 79, 224303 (2009)*

ESRF, Grenoble

Now, the calculations of phonons in ordered systems are performed using the very well known standard method.

How to perform ab-initio calculations for disordered system ?

- To make calculations for all possible configurations and find their contributions to the PDOS. (impractical)
- The coherent potential approximation (CPA) is the most powerfull theoretical tool to study disordered systems (but not phonons)
- The cluster generalization of CPA, so called, itinerant coherent potential approximation (ICPA). (It needs as an input the inter-atomic force constants between various pairs of species)

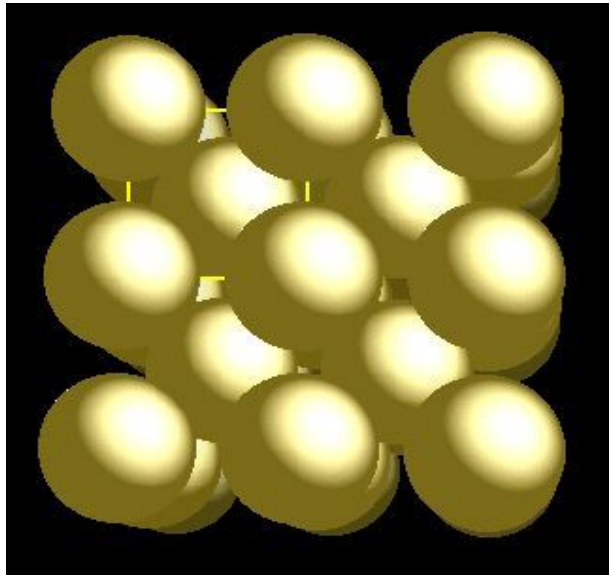
Modelling of α and σ phase

α phase

$Fe_{50}Cr_{50}$ - *the 2x2x2 bcc supercell with 16 atoms (8 Fe and 8 Cr atoms)*

random ditribution – 500 different atomic configurations

we chose just 5 configurations



σ phase

$Fe_{0.48}Cr_{0.52}$ - *the 1×1×1 tetragonal supercell with 30 atoms (14 Fe and 16 Cr atoms)*

Sublatices	*Wyckoff Pos.*	N_{Fe}	*NNN*					
			A	*B*	*C*	*D*	*E*	*Total*
A	*2a*	*2*	---	*4*	---	*4*	*4*	*12*
B	*4f*	*1*	*2*	*1*	*2*	*4*	*6*	*15*
C	*8i*	*3*	---	*1*	*5*	*4*	*4*	*14*
D	*8i*	*7*	*1*	*2*	*4*	*1*	*4*	*12*
E	*8j*	*3*	*1*	*3*	*4*	*4*	*2*	*14*

Calculations

VASP – structure optimization and Hellmann-Feynman forces calculations

- the spin-polarized density functional total energy calculations with GGA
- valence electron configuration: Cr - d^5s^1 ; Fe - d^7s^1
- the full-potential projector augmented-wave (PAW) method.
- K-mesh: α phase - 8×8×8 ; σ phase - 4×4×6

During the optimization, the Hellmann-Feynman (H-F) forces and the stress tensor were calculated

PHONON – phonon dispersions, phonon DOS and thermodynamical functions

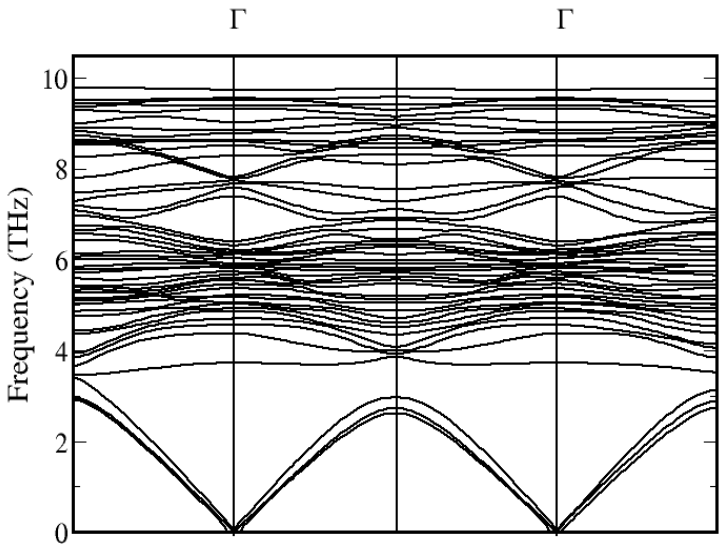
- the H-F forces generated while displacing atoms from their equilibrium positions.
- the number of required displacements is determined by the symmetry of the crystal (*P1*) and by the number of nonequivalent atoms (α phase - 16 ; σ phase - 30)
- a complete set of H-F forces: α phase - 48 ; σ phase - 90
- to minimize systematic errors we applied displacements in positive and negative directions.

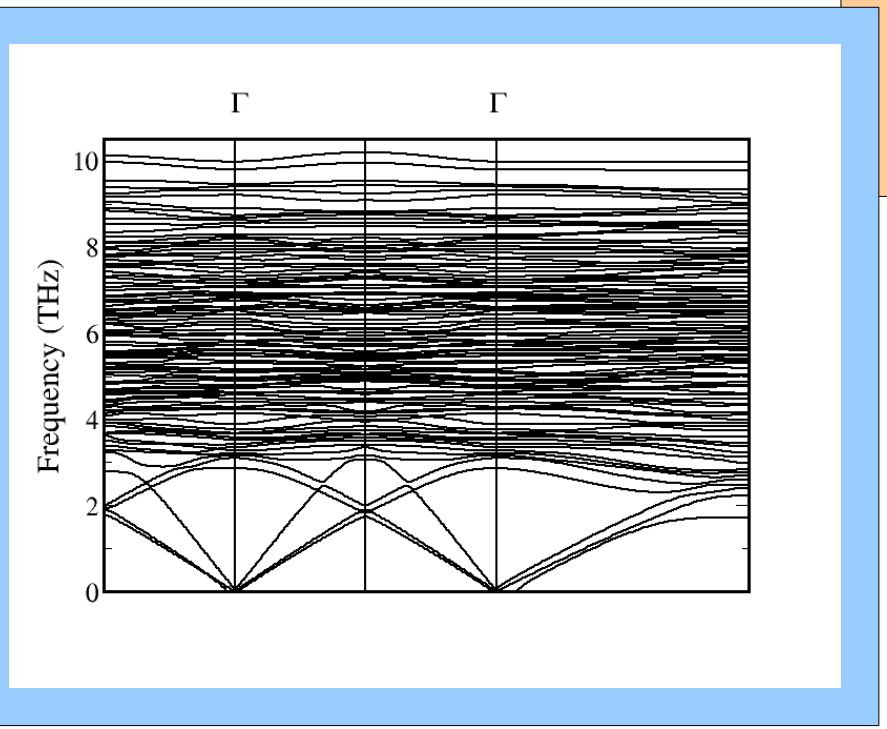
One has to perform 96 (α phase) or 180 (σ phase) single point calculations (VASP) to find the dispersion relations.

The phonon dispersion curves

α phase

48 branches



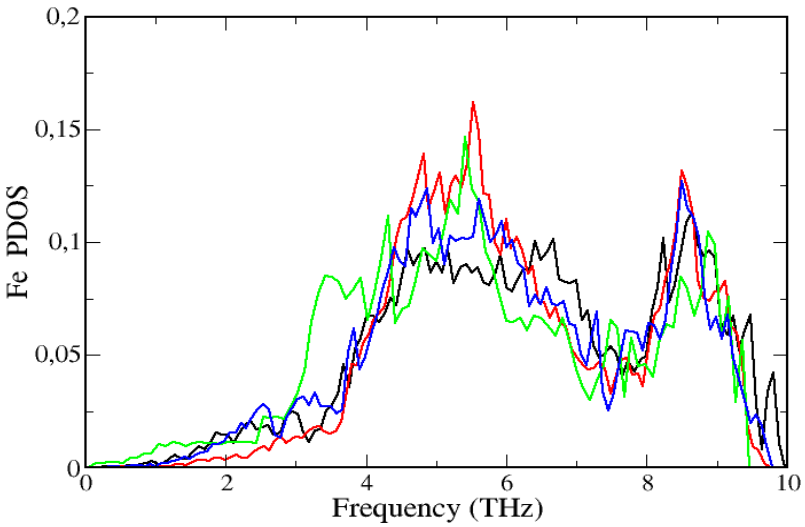


σ phase

90 branches

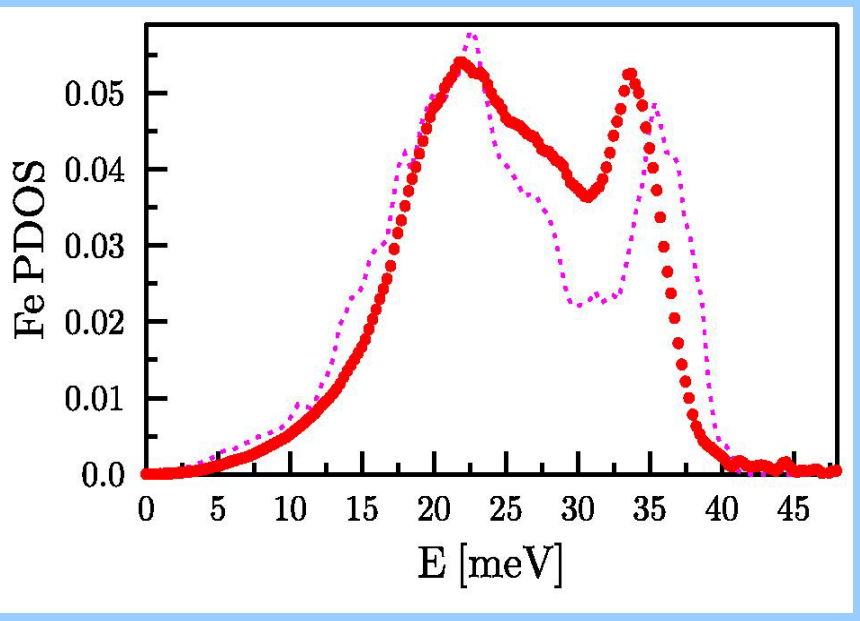
The phonon density of states

α phase



The Fe partial DOS calculated for the chosen configurations.

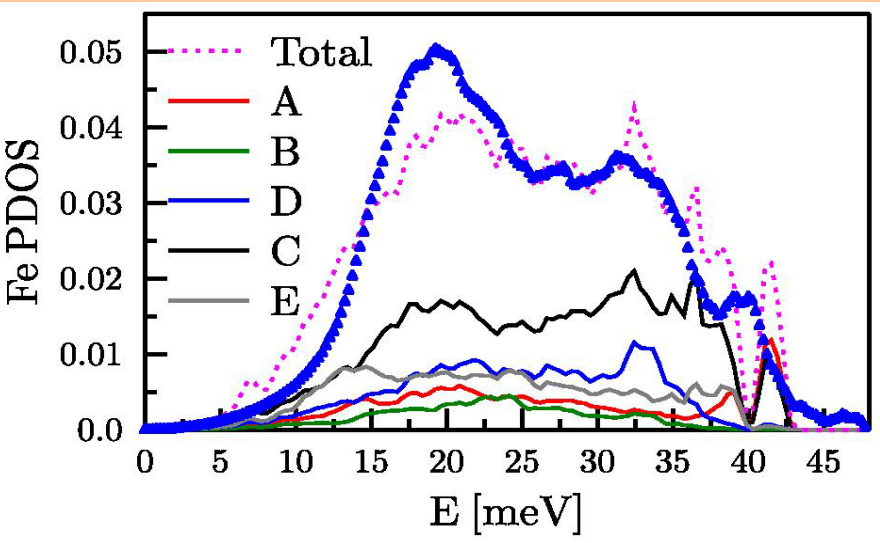
The final DOS calculated using these partial DOS with the same weights.



S. Dubiel et al., *PRL 104, 155503 (2010)*

- experiment
- calculations

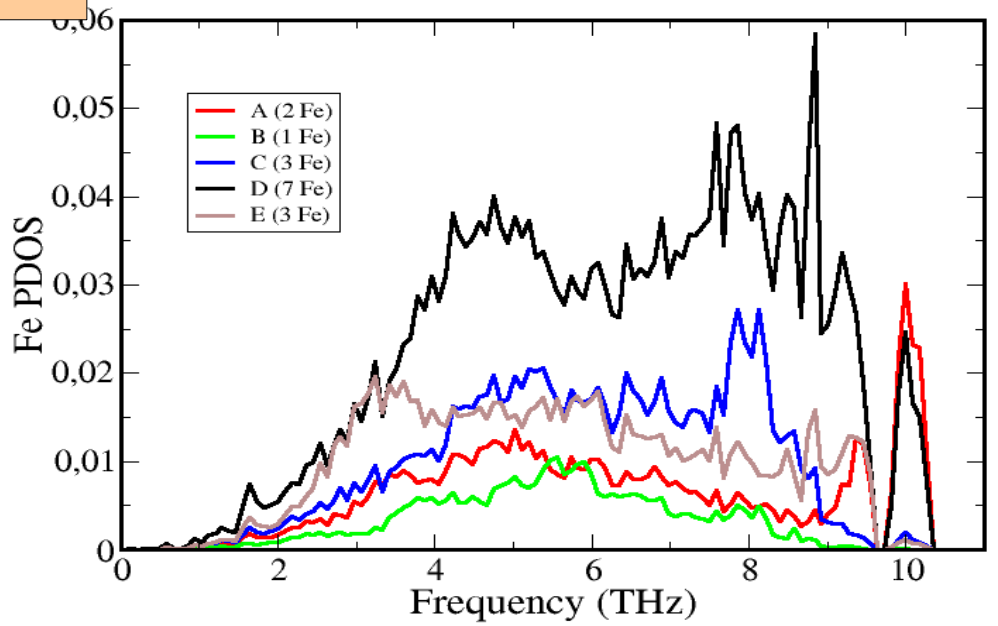
The phonon density of states



S. Dubiel et al., *PRL 104, 155503 (2010)*

σ phase

- experiment
- calculations



the dynamics in particular sublattices are different.

Conclusions

Dynamical properties of such a complex alloy has been studied for the first time within the combined NRIXS and theoretical ab initio approach.

- The phonon DOS of the σ phase was described reasonably well in terms of only one adequately chosen configuration.
- The dynamics in particular sublattices of σ phase are different.
- The phonon DOS of the α phase was sucsessfully calculated using 5 configurations.
- The significant differences in the partial Fe phonon DOS of the α and σ phases of a quasiequiatomic Fe-Cr alloy observed in the INRIXS experiment has been confirmed in the calculations.
- We have also obtained relevant thermodynamic quantities without necessity of using empirical parameters.

Acknowledgments

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Vibrational Properties of α- and σ-Phase Fe-Cr Alloy, *PRL 104, 155503 (2010)*