

Pyrrhotites Revisited in Superspace with Ab-Initio Calculations Insights.

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1 Introduction

- Motivation
- Flexible composition compounds
- Yamamoto and Nakazawa's model
- Occupational probability
- Pyrrhotites (Fe_{1-x}S)

2 Superspace model for Pyrrhotites (Fe_{1-x}S)

- Structural model
- Differences with Yamamoto and Nakazawa's description
- Refinement of $N = 5.5$

3 Ab initio insights

- SIESTA
- What have we done?
- Forces in Superspace

4 Conclusions

Our goals

- Reinvestigation of families of compounds.

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 - Global description through a unique superspace model

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- Reinvestigation of families of compounds.
 - Global description through a unique superspace model
- Check suitability of superspace framework for different families of compounds.

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- Different members have different symmetry and unit cell parameters.
- In some cases, they can be unified in the Superspace framework.
- In most cases there is a relationship between the composition parameter and the modulation parameters.
- Modulations are described with crenel functions.

Yamamoto and Nakazawa's paper

Acta Cryst. (1982). **A38**, 79–86

Modulated Structure of the NC-type ($N = 5.5$) Pyrrhotite, $\text{Fe}_{1-x}\text{S}^*$

BY AKIJI YAMAMOTO AND HIROMOTO NAKAZAWA

National Institute for Research in Inorganic Materials, Sakura-mura, Niihari-gun, Ibaraki 305, Japan

(Received 26 September 1980; accepted 8 July 1981)

Abstract

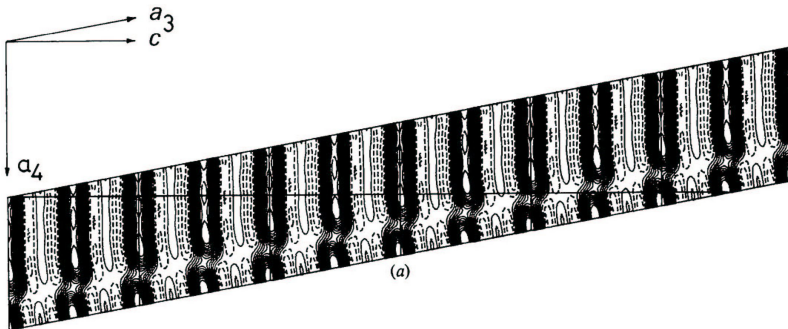
The modulated structure of the NC-type pyrrhotite Fe_{1-x}S with $x = 0.09$ has been determined. The analysis is based on a four-dimensional space group, $W_{qq1}^{pna2_1}$, and an anharmonic modulation model with 53 positional, two thermal, and eight occupational parameters including up to fourth-order harmonics. $a = 11.952$, $b = 6.892$, $c = 5.744$ Å. The final R for 404 observed reflections is 0.097. The modulation wave for occupation probability of Fe shows a strong an-

When k_3 (the \mathbf{c}^* component of \mathbf{k}) is written as $1/N$, the N value continuously changes with temperature and/or composition from 3 to 6 (Nakazawa & Morimoto, 1971).

In the present case, the composition is $\text{Fe}_{10}\text{S}_{11}$ ($x = 0.09$) and N is 5.54. This shows that this is a modulated structure which has a periodic distortion of atomic position and/or wavy distribution of vacancies with wave vector \mathbf{k} . When the period is made approximately commensurate with that of the fundamental cell, the structure is analyzed as a super-

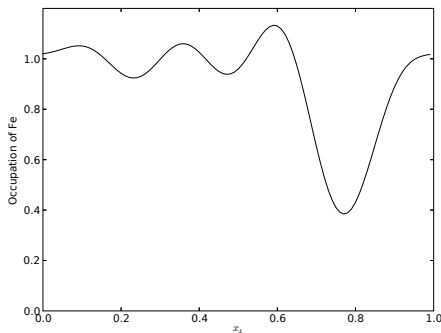
Occupational probability of Fe

- This is what the electronic density looks like.



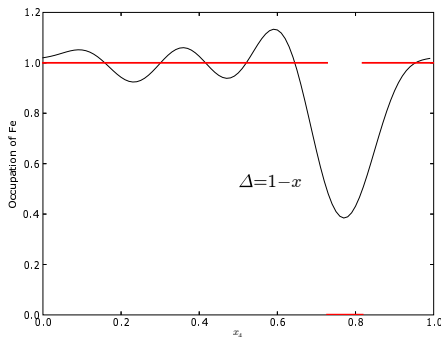
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- Very anharmonic modulation for the occupation of Fe.
- Can it be replaced by a crenel function?



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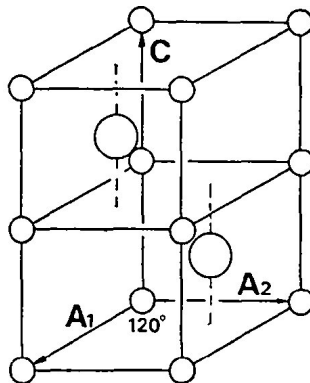
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- Non-stoichiometry is due to Fe vacancies.

Unit cell

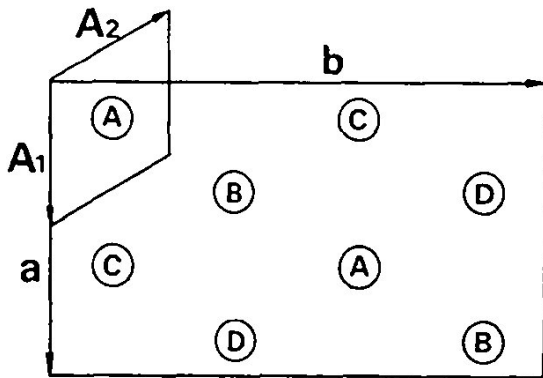
- Fundamental structure (NiAs)



Structural model

Unit cell

- Fundamental structure (NiAs) (small unit cell)
- Used unit cell (big unit cell)



New model

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$$\gamma = 2x = 1/N \quad \text{where } N \text{ is supercell value}$$

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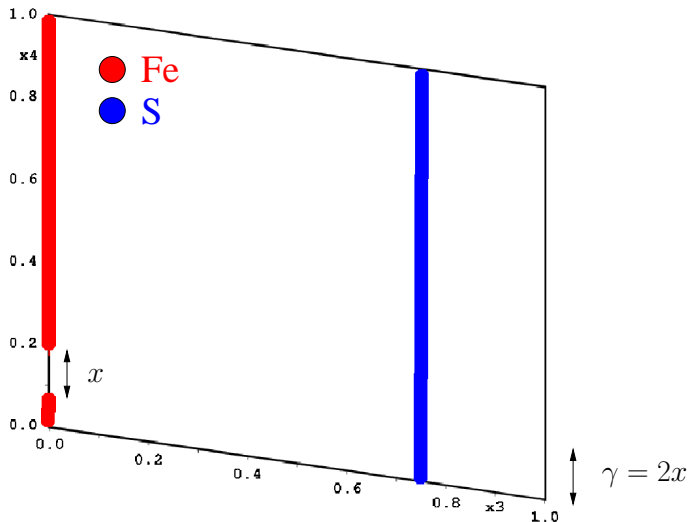
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$$Xddd(00\gamma)qq0$$

$$X = \{ \{E|0000\}, \{E|1/2001/2\} \{E|01/201/2\} \{E|1/21/200\} \}$$

Structural model

Superspace model for $\gamma = 3/17$ $\text{Fe}_{31}\text{S}_{34}$ 

Differences in symmetry

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- New symmetry operation $\{I|0000\}$

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- New extinction rule due to glide plane ($d \perp z$) fulfilled in the dataset.
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- Refinement.

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Refinement of $N = 5.5$

Refinement results

	YN model		New model	
	R_{all}	R_{obs}	R_{all}	R_{obs}
All	10.4	15.9	12.5	17.9
Main	5.8	6.6	6.1	6.7
Satellite 1	12.7	19.8	14.6	17.4
Satellite 2	10.0	16.6	9.6	19.9
Satellite 3	22.0	35.0	31.6	44.4
Satellite 4	35.8	82.4	64.7	112.6
Ref. parameter	63		34	

Table: Refinement parameters

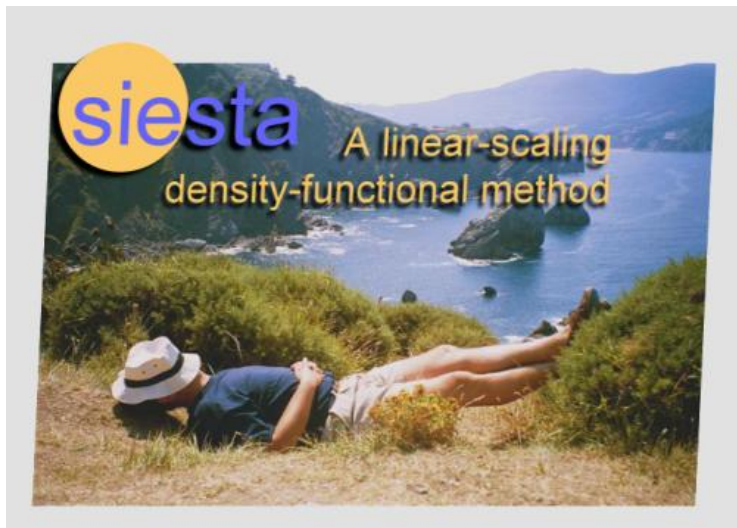
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SIESTA



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What have we done?

Work with *ab-initio* calculation

- From ideal superspace model we get model for $\gamma = 3/17$ ($x = 3/34 \text{ Fe}_{31}\text{S}_{34}$).

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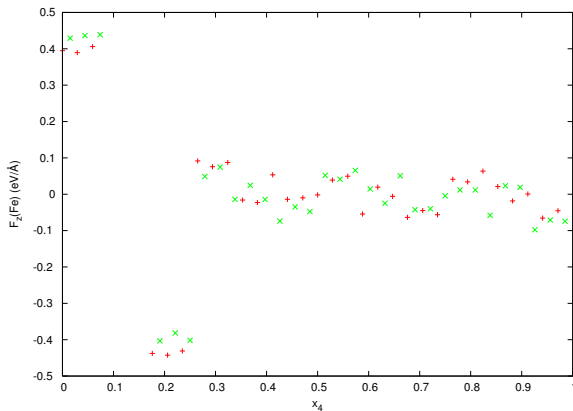
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- We translate the forces to superspace.

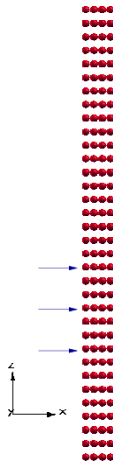
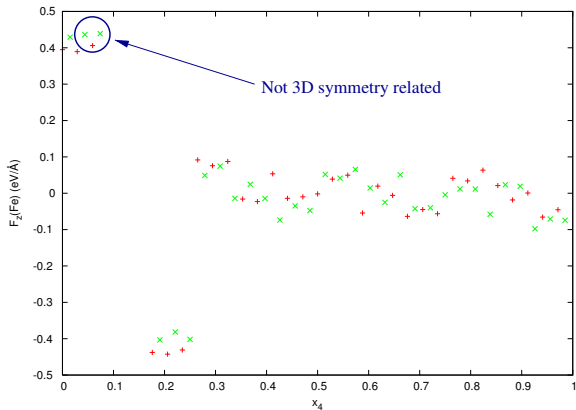
Forces in Superspace

Fe atoms forces



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Conclusions

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- ... be used to study not only displacement modulation, but also other properties (e.g. forces).

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What can be done next?

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- Compare forces of different structures.
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- Measure new members if available.

Acknowledgements

For the help with refinement

- Gotzon Madariaga (Bilbao)
- Andreas Schönleber (Bayreuth)

Thanks!

Only for discussion

Superspace model for flexible compounds

AB_{1-x}

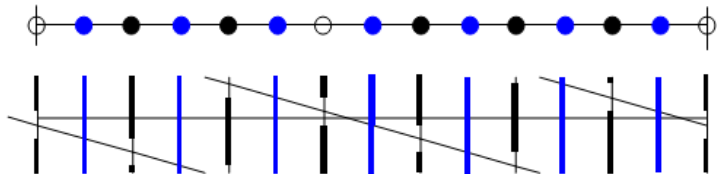
- Flexible compound in 1D



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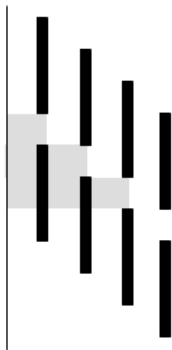
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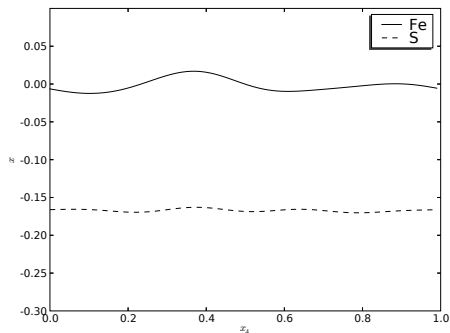
AB_{1-x}

- Flexible compound in 1D $\gamma = 2/7$
- Closeness condition



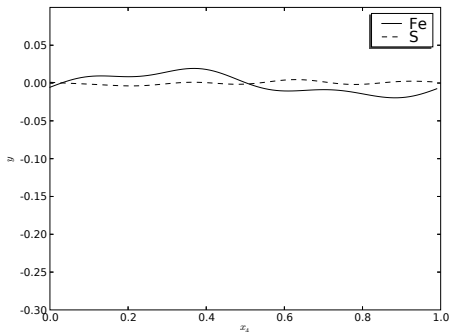
Displacive modulations

- Displacive modulation of x



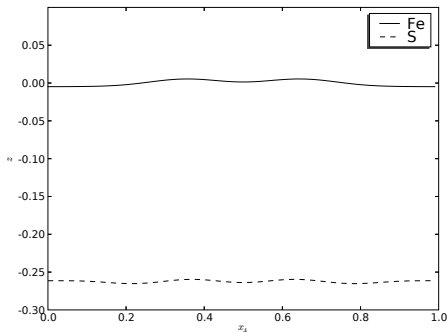
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Yamamoto and Nakazawa's structural model

- Cell parameters.

$$a = 11.952 \text{ \AA} \quad b = 6.802 \text{ \AA} \quad c = 5.744 \text{ \AA}$$
$$\alpha = 90^\circ \quad \beta = 90^\circ \quad \gamma = 90^\circ$$

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Yamamoto and Nakazawa's structural model

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$$Xmm2_1(00\gamma)$$

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Yamamoto and Nakazawa's structural model

- Cell parameters.
- Atomic Domains (Continuous along x_4)
- Symmetry
- Modulation parameters.

	Positional	Occupational	Thermal	Σ
Fe	27/26	8/8	1/1	36/35
S	27/27	0/0	1/1	28/28
Σ	54/53	8/8	2/2	64/63

New structural model

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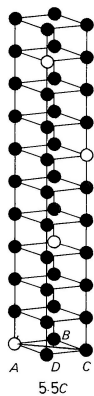
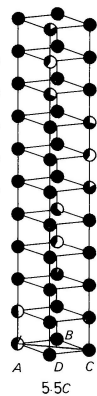
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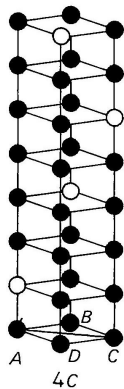
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Table: Parameters

5.5C - $Fe_{10}S_{11}$



$4C - Fe_7S_8$



$6C - Fe_{11}S_{12}$

