Spin Physics and Nanomagnetism

dedicated to the 60th birthday of Professor Chudnovsky March 13-14, 2009New York

Giant Magnetostriction Generated by a Reorientation of Nanomagnetic Particles in Alloys

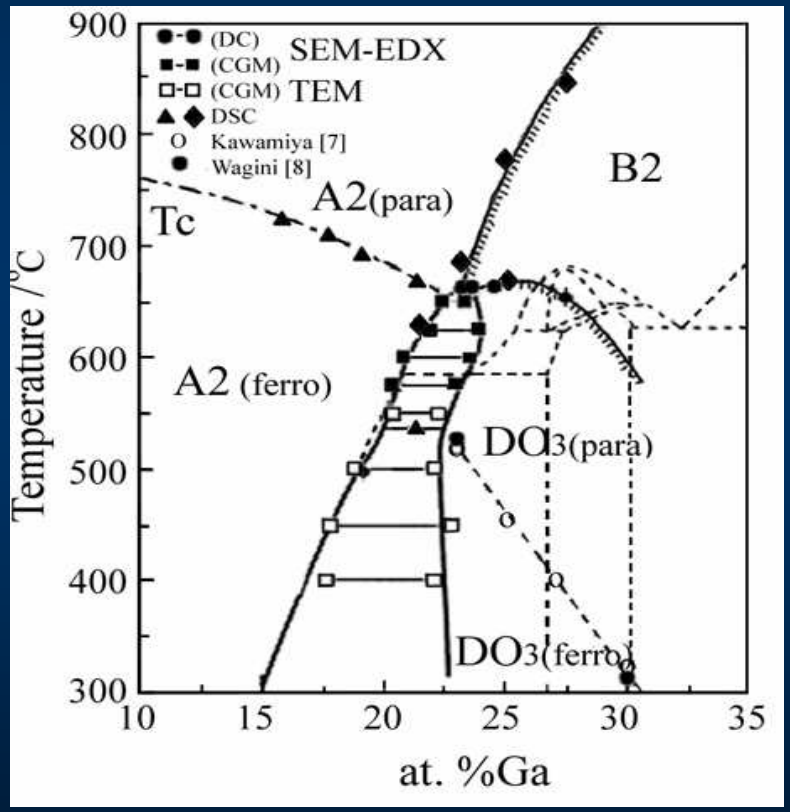
Armen Khachaturyan

Department of Materials Science and Engineering
Rutgers University

Supported by NSF DMR-0704045 and ONR MURI N00014-06-1-0530

Observation of Fe 15-19 at%Ga, BCC alloy with a Giant Magnetostriction up to 400 ppm

(A.E. Clark, J.B. Restorff, M. Wun-Fogle, T. Lograsso, and D.L. Schlagel: *IEEE Trans. On Magnetics*, 2000, vol. 36, pp. 3238-40)

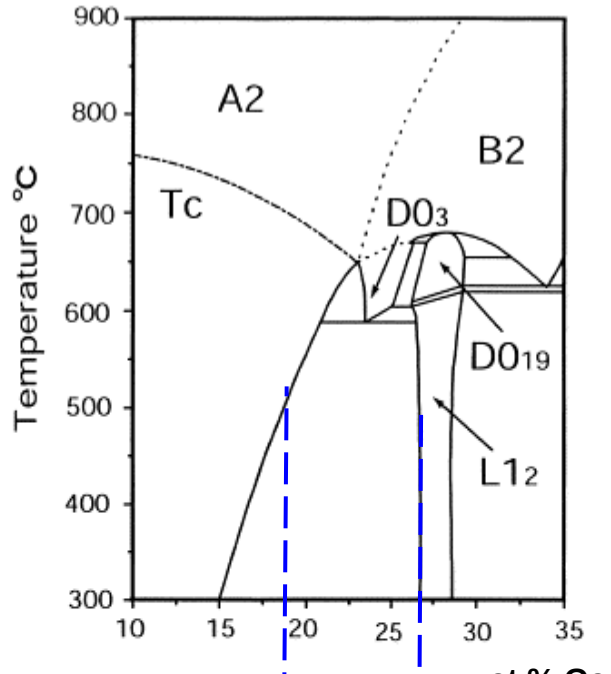


O.Ikeda, et al. : *Journ. of Alloys and Compounds*, 2002, vol.347, pp.198-205

Experimental facts relevant to a question about an origin of Giant Magnetostriction in Fe-Ga

- GM occurs within the BCC field of the Fe-Ga phase diagram
- History dependence of GM: $\lambda_{[100]}$ ~100×10^{-6} to ~400×10^{-6} vs 30-40 $\times10^{-6}$ in the BCC phase
- Concomitant Giant (about 80%) elastic softening of the elastic modulus $C' = (C_{11} - C_{12})/2$ accompanying the GM. The modulus C_{44} is roughly the same as in αFe
- Abnormal anisotropy of GM: $\lambda_{[111]}$ assumes a usual value commensurate with the value for α Fe. It is about two orders of magnitude smaller than $\lambda_{[100]}$
- Absence of the volume magnetostriction
- Strong correlation between the composition of magnetostriction maxima and the equilibrium lines of the phase diagram

Ikeda et al., 2002



Clark, Hathaway, Wun-Fogle, Restoff, Lograsso, Keppens, Petsculescu, Taylor, 2003

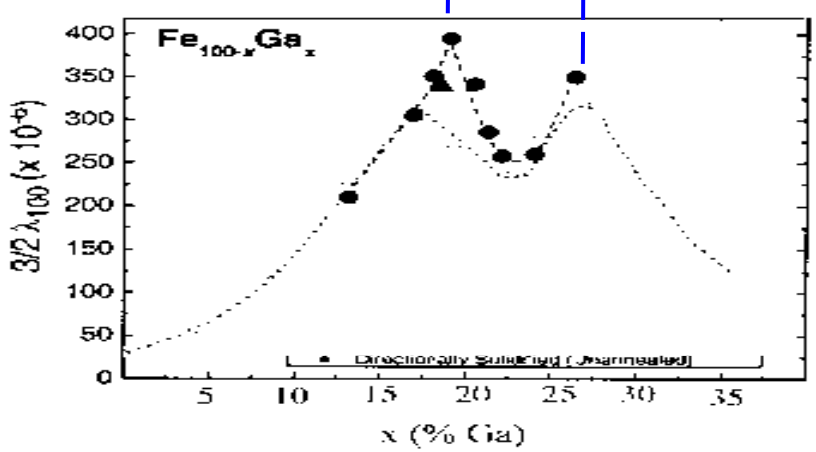


Figure 7: Saturation magnetostriction of $Fe_{1-x}Ga_x$ as a function of Ga

These properties can be explained by a *H* field-induced reorientation of confined tetragonal nano-magnetic precipitates of the precipitate ordered phase

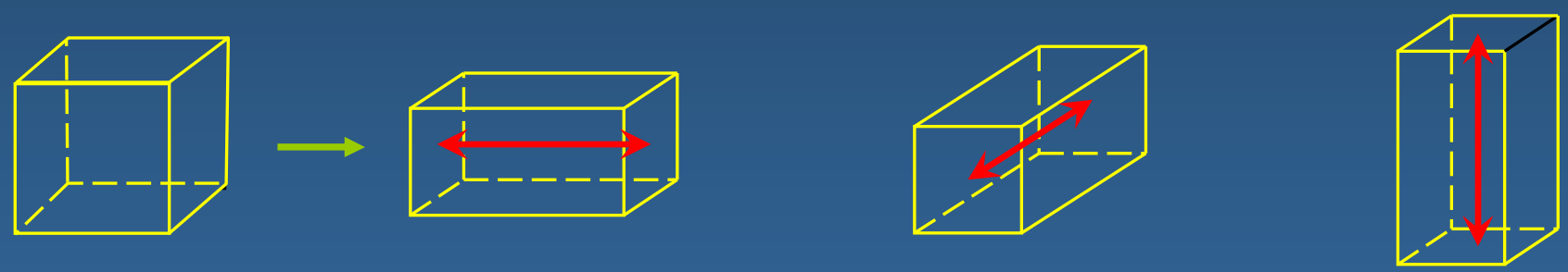
A. Khachaturyan and D. Viehland, Mater. Trans. 38A, 2308-2316; 38A, 2317-2328(2007)

Requirements to a system

- **The system is a decomposing ferromagnetic cubic solid solution**
- **The product phase is also ferromagnetic and has the tetragonal symmetry**
- **Precipitates of the product phase have nano-size**

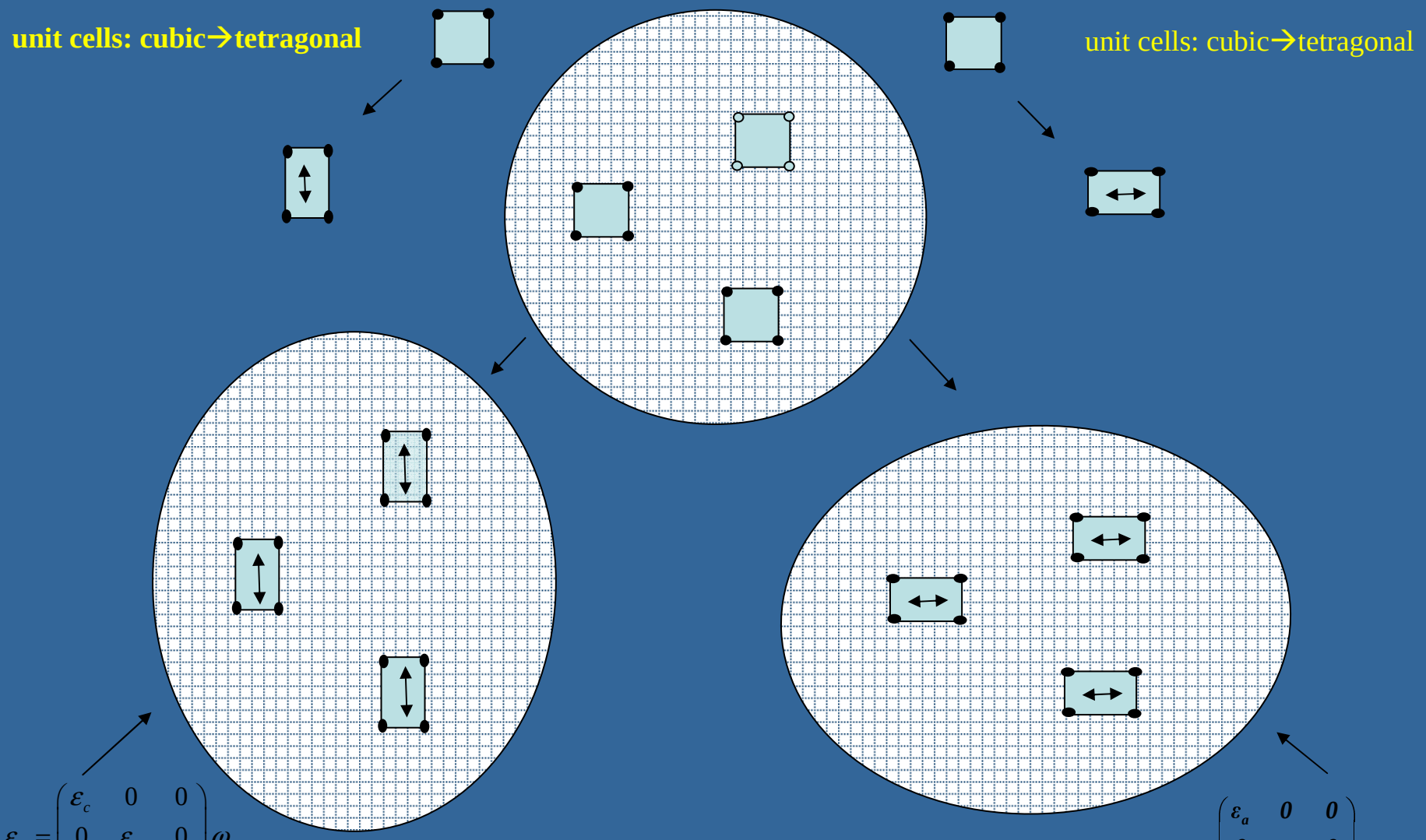
Model of Extrinsic GM:
condined cubic→tetragonal martensitic transformation in nano-precipitates of DO_3 ordered phase

There are three type of structural domains in the cubic → tetragonal crystal lattice rearrangement:



$$\varepsilon_{ij}^{0}(1)=\begin{bmatrix}\alpha_3 & 0 & 0\\ 0 & \alpha_4 & 0\\ 0 & 0 & \alpha_4\end{bmatrix}\qquad \varepsilon_{ij}^{0}(2)=\begin{bmatrix}\alpha_4 & 0 & 0\\ 0 & \alpha_3 & 0\\ 0 & 0 & \alpha_4\end{bmatrix}\qquad \varepsilon_{ij}^{0}(3)=\begin{bmatrix}\alpha_4 & 0 & 0\\ 0 & \alpha_4 & 0\\ 0 & 0 & \alpha_3\end{bmatrix}$$

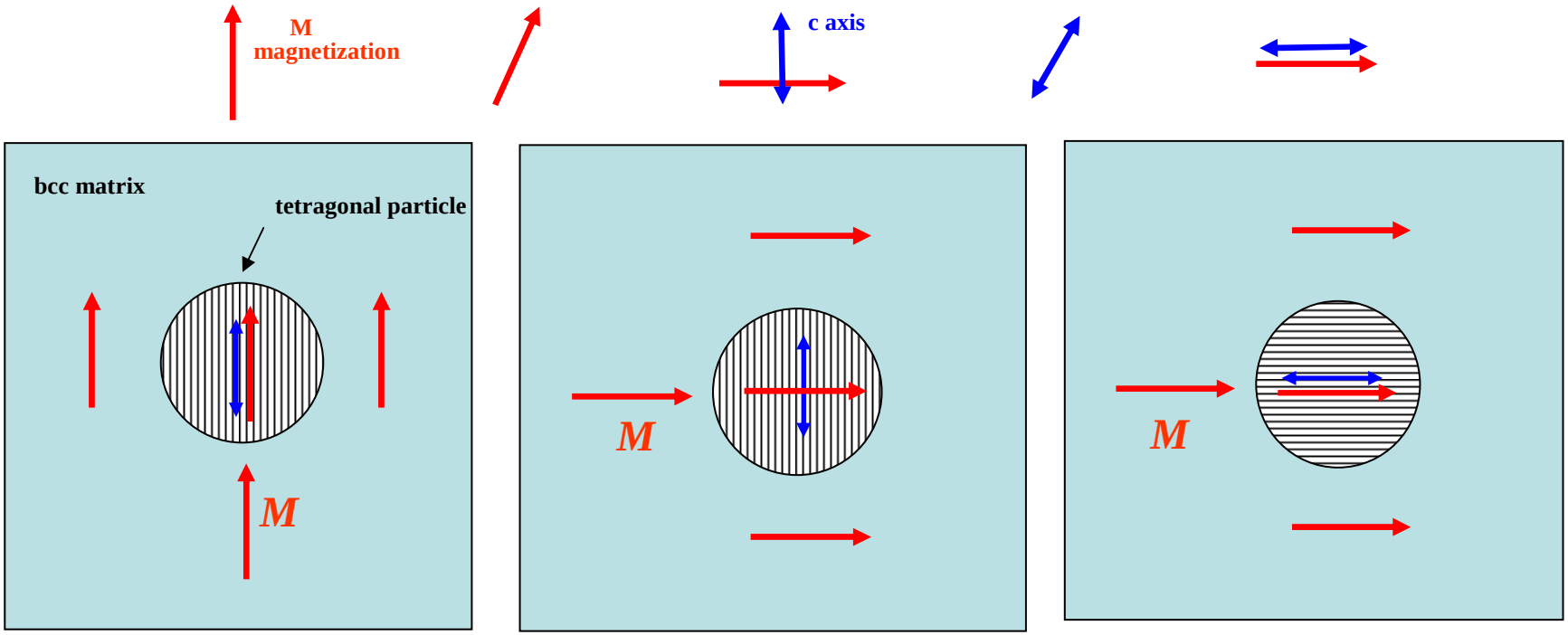
Extrinsic model of the macroscopic strain caused by tetragonal axis reorientation



$$\varepsilon_{ij} = \begin{pmatrix} \varepsilon_c & 0 & 0 \\ 0 & \varepsilon_a & 0 \\ 0 & 0 & \varepsilon_a \end{pmatrix} \omega$$

$$\varepsilon_{ij} = \begin{pmatrix} \varepsilon_a & 0 & 0 \\ 0 & \varepsilon_c & 0 \\ 0 & 0 & \varepsilon_a \end{pmatrix} \omega$$

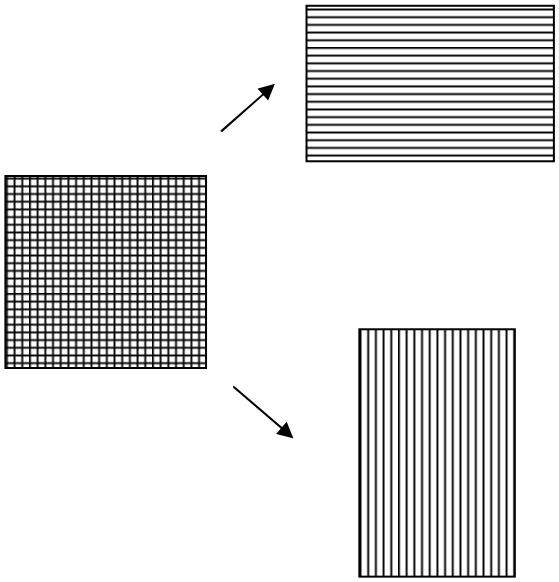
Effect of flip of magnetization in the parent phase on orientation of tetragonal nanomagnetic particle (exchange coupling of tetragonality orientation and magnetization across interface)

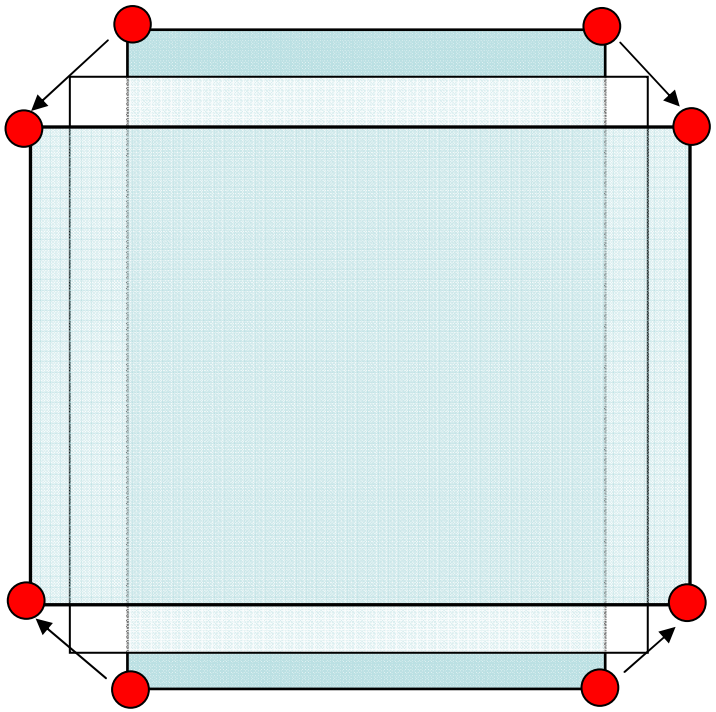


If the magnetic correlation length is greater than the nanoparticle size, the coupling of spins across the interface is an exchange coupling. It aligns magnetizations in parent phase and in the particle (red arrows) in the same direction.

If the magnetic anisotropy of the particle is sufficiently strong, the tetragonality axis of precipitate (blue arrow) should rotate to align the tetragonality axis (easy magnetization direction) along the new magnetization direction.

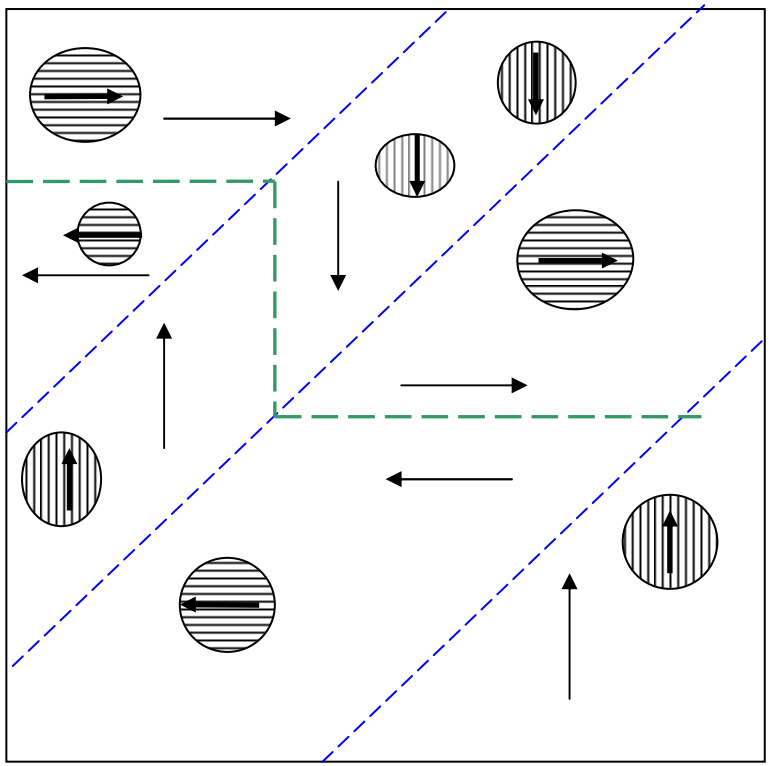
Cubic→tetragonal crystal lattice rearrangement





90° rotation of a structural domain does not require a real “rigid body” lattice rotation.

It is produced by small atomic displacements shown by arrows



Schematic of magnetic domain structure and microstructure of the dispersion of FCT clusters in the K field of Fe-Ga. The clusters are shown by hatching; the direction of hatching indicates the direction of the c-axes; arrows within FCT clusters indicate the direction of magnetic moments; arrows outside the nanoparticles indicate the direction of magnetization of the magnetic domains in the bcc parent phase; and the blue and green lines designate possible 90° and 180° magnetic domain boundaries of the bcc matrix.

Extrinsic model of GM

All these properties can be explained by a *H* field-induced reorientation of confined tetragonal nanomagnetic precipitates of the precipitate ordered phase

Requirements to a system with expected GM:

- **Decomposing ferromagnetic cubic solid solution**
- **The product phase is ferromagnetic and has the tetragonal symmetry**
- **Precipitates of the product phase have nano-size**

Are these predicted requirements met in Fe-Ga system ?

Recent experiments show that they are.

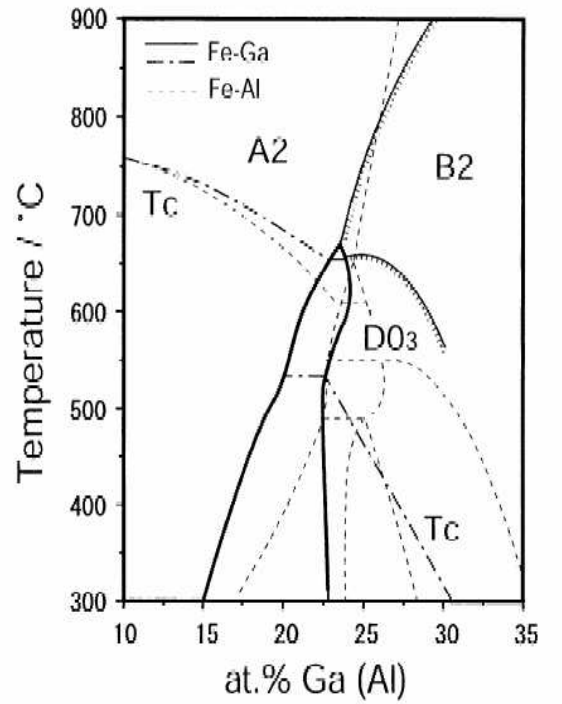
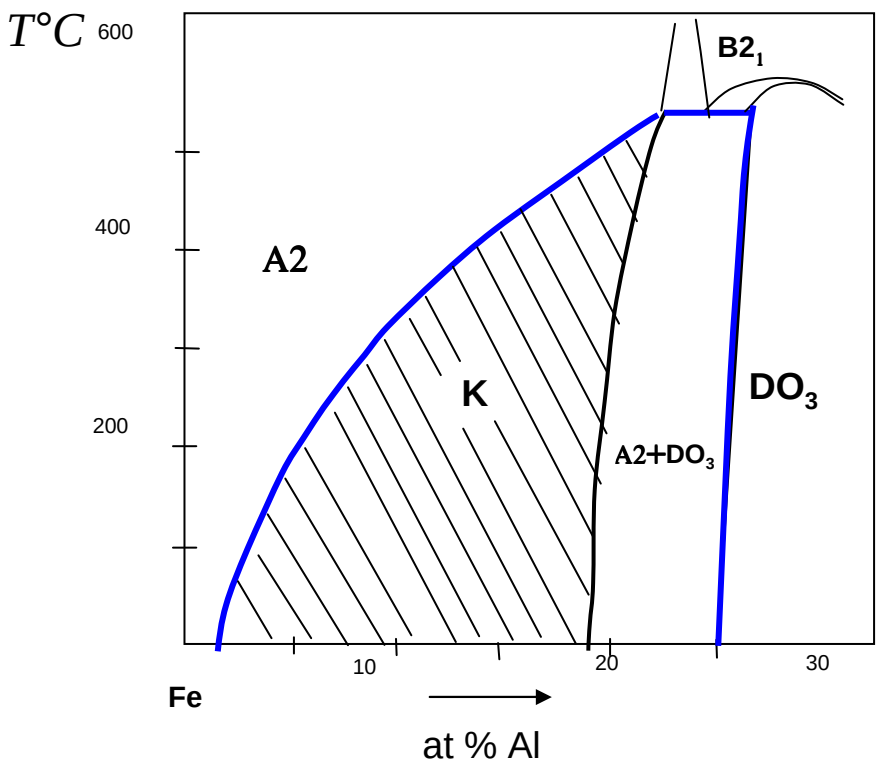


Fig. 10. Phase equilibria concerned with the b.c.c. phases in Fe–Ga system in comparison with those in Fe–Al system.

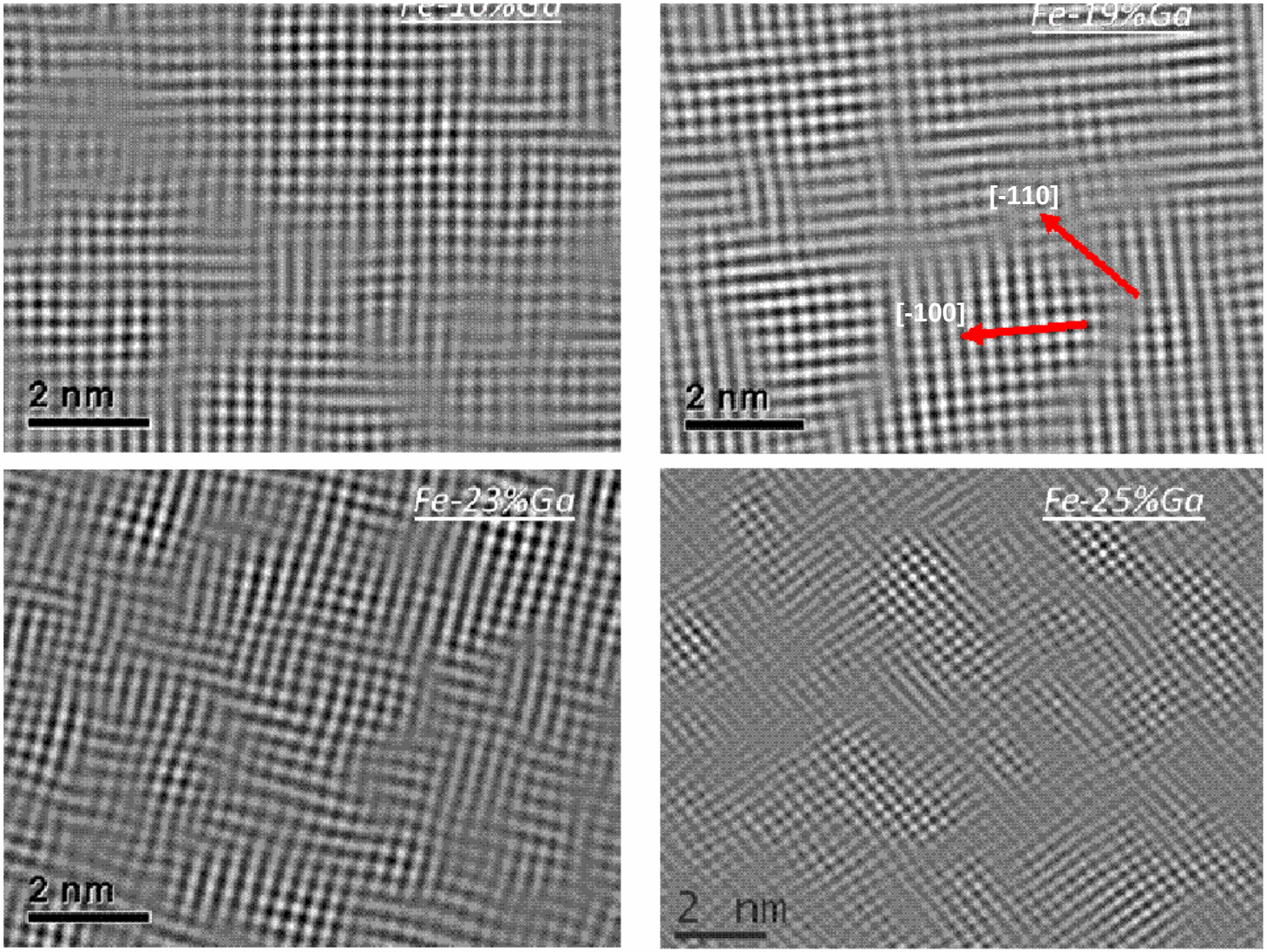
Fe-Ga phase diagram. Dash lines is chemically similar Fe-Al phase diagram

Hint from chemically similar Fe-Al system: TEM observation of coarsening-resistant nano-particles of DO_3 phase



Warlimont H, Thomas G.,
Metal Science J., **4**, 47, (1970)

Dashed K field is a region of the phase diagram with observed nano-particles of the bcc-based ordered DO_3 phase



D. Viehland's et al. 2008

Atomic Density Field Modeling

(Khachaturyan, Problem of Matl Science, 1978)

$$\frac{dn(\boldsymbol{r})_{Ga}}{dt} = \sum_{\boldsymbol{r}'} L(\boldsymbol{r} - \boldsymbol{r}') \frac{\delta F}{\delta n(\boldsymbol{r})_{Ga}}$$

$L(\boldsymbol{r}\text{-}\ \boldsymbol{r}')$ **is the probability of** $\boldsymbol{r} \rightarrow \boldsymbol{r}'$ **diffusion jump,**

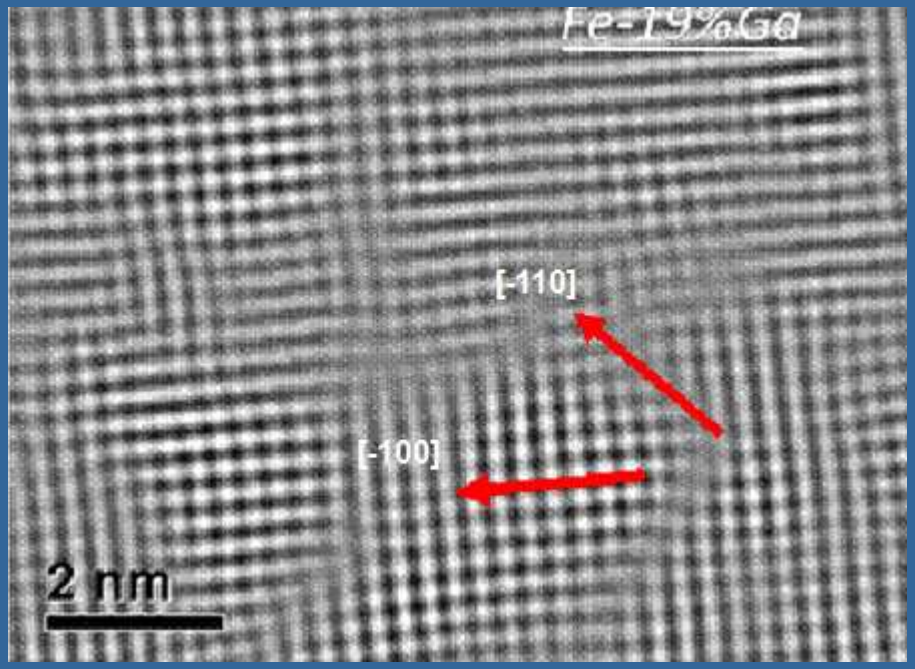
$\boldsymbol{F}$ **is the free energy functional of occupation probabilities** $n(\boldsymbol{r})_{\mathrm{Ga}}$;

$n(\boldsymbol{r})_{\mathrm{Ga}}$ **is an evolving atomic density field defined on the bcc lattice sites.**

Free energy $\boldsymbol{F}$ **includes the strain energy generated by atomic radius misfit**

HTEM observation vs the result of the 3D Atomic Density Function (ADF) modeling of the BCC →DO3 decomposition in Fe-Ga system

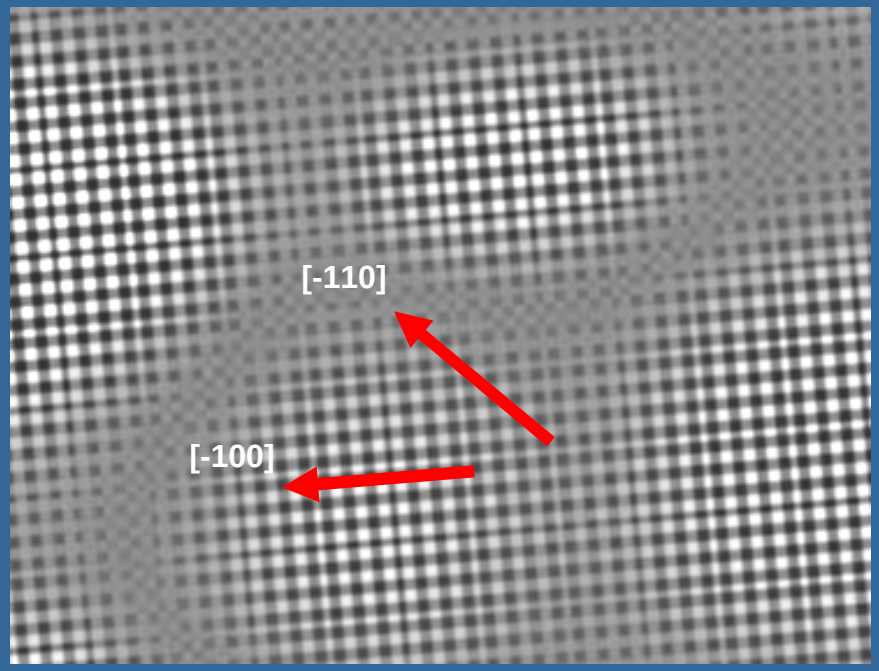
observations



The HTEM image for the Fe-19%Ga alloy in (001) plane

Viehland, et al. Phys. Rev., (2008)

modeling



Visualization of the 3D ADF modeling for Fe-Ga alloy (view normal to the (001) plane of the BCC lattice)

The shades of gray correspond to the average density of Ga averaged over the [001] atomic columns normal to the figure.

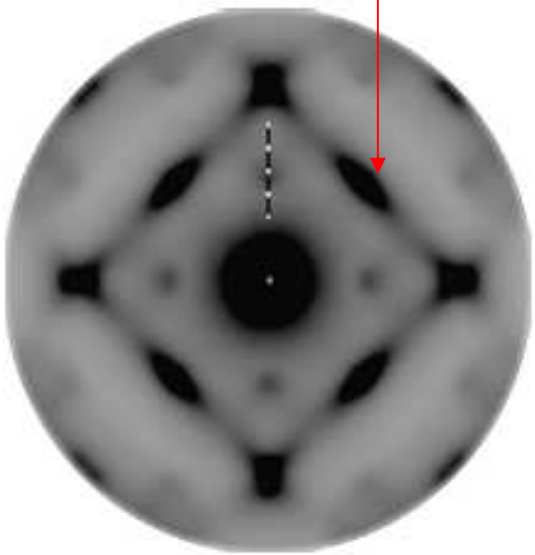
The columns are chosen within a (001) layer whose thickness is 16 atomic planes. The layer cut from the 3D computational volume of the bcc lattice.

J. Boisse, Yong Ni, and A. Khachaturyan (to be publilished)

Fe-18.7at%Ga

(110)

a



Xing, Du, McQueeney, Lagrasso,

Acta Mater. 2008

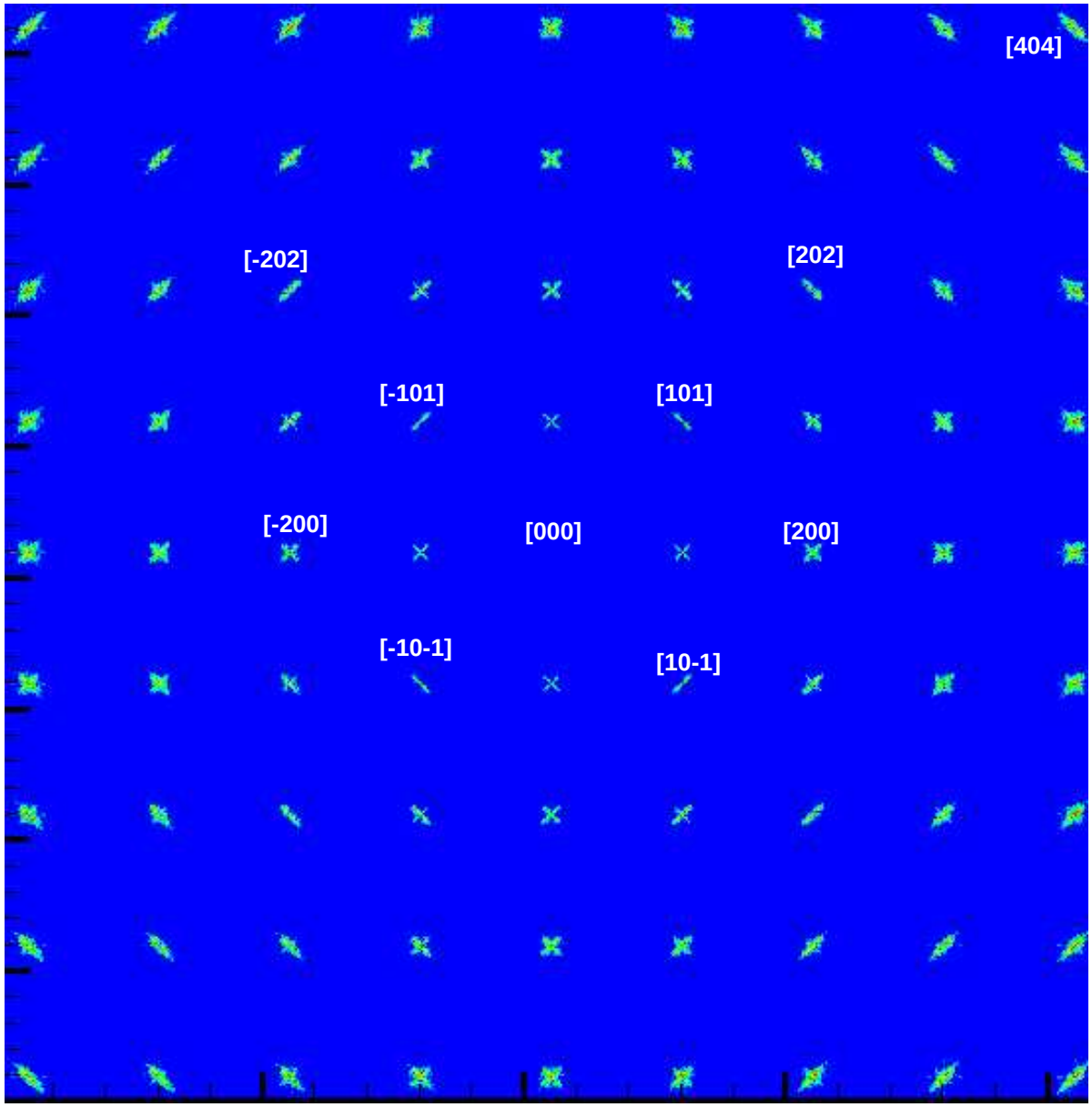
(220)

Рис. 45. Рассчитанная форма узлов обратной решетки для сплава Cu — Be в плоскости (100)* обратного пространства, содержащей ось тетрагональности.

Calculated diffraction pattern in (100)* plane for a dispersion of coherent particles in the fcc cubic matrix formed by tetragonal Bain distortion (for crystal lattice parameters of B2 CuBe precipitates). Cross-like diffuse scattering is caused by elastic displacements generated by tetragonal clusters

A. Khachaturyan, <u>Theory of Phase Transformations in Solids</u>, Publishing House Nauka (Science), in Russian,1974 (pp. 1-382)

Comment: similarity of diffraction patterns is an indication that the pattern from Fe-Ga is generated by tetragonal (DO_{22}) precipitates in the cubic (bcc) matrix.



Map of diffuse intensity generated by tetragonal precipitates in cubic matrix. Crystal lattice is considered primitive

Recent low angle polarized neutron diffraction data do report that:

- **Fe-19 at % Ga solid solution with Giant Magnetostriction 400×10^{-6} is a homogeneous BCC solid solution. It have nanomagnetic precipitates of the tetragonal DO_3 ordered phase of ~ 5 nm radius.**

- **These particles flip their tetroganal axis and magnetization upon application of stress or magnetic field.**

(C. Mudivarthi, M. Laver, J. Cullen, A. Flatau,, M.Wuttig, 2009)

These results together with High Resolution Electron Microscopic data and Synchrotron Single Crystal Diffraction data validate the nanomagnetic model of extrinsic Giant Magnetostriction in Fe-Ga BCC alloys

Giant Magnetostriction in Fe-Ga: observations and prediction of the model

- GM occurs within the BCC field of the Fe-Ga phase diagram
- History dependence of GM: $\lambda_{[100]}$ ~100×10^{-6} to ~400×10^{-6} vs 30-40 $\times10^{-6}$ in the BCC phase
- Concomitant Giant (about 80%) elastic softening of the elastic modulus $C' = (C_{11} - C_{12})/2$ accompanying the GM. The modulus C_{44} is roughly the same as in αFe
- Abnormal anisotropy of GM: $\lambda_{[111]}$ assumes a usual value commensurate with the value for α Fe. It is about two orders of magnitude smaller than $\lambda_{[100]}$
- Absence of the volume magnetostriction
- Strong correlation between the composition of magnetostriction maxima and the equilibrium lines of the phase diagram

Conclusions

- We need nano-size magnetic particles to provide exchange coupling of spins of the particles with those of the matrix. It is 3-4 order of magnitude greater than the Zeeman interaction

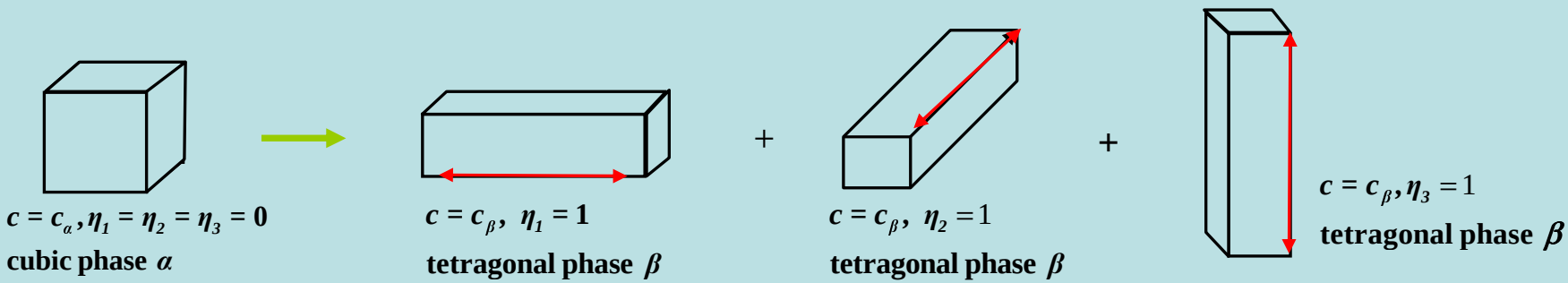
- It is important to have nano-size to avoid magnetic and structural domain formation, which would be detrimental to a crucial property, that is an anhysteretic recoverable strain

- We need a confined displacive transformation inside nanoparticles because this is the displacive transformation strain rather than intrinsic magnetostriction that is a source of extrinsic GM.

- There are strong indications that the Fe-Ga system is not alone. Fe-Ga just a generic example of a possible new class of GM materials, which, in fact, are magnetic relaxors. These magnetic relaxors are conceptually similar to the piezoelectric relaxors that are "champions" of the piezoelectric materials.

The cubic→tetragonal transformation characteristics:

composition, $c(r)$, and three structural parameters describing teragonal domains, $\eta_1(r)$, $\eta_2(r)$, $\eta_3(r)$, with the orientations of c axis along [100], [010] and [001], respectively



$$\frac{\partial c(\mathbf{r},t)}{\partial t} = \nabla\left(M\nabla\frac{\delta F}{\delta c(\mathbf{r},t)}\right) + \zeta^{c}(\mathbf{r},t)$$

$$\frac{\partial \eta_p(\mathbf{r},t)}{\partial t} = -L\frac{\delta F}{\delta \eta_p(\mathbf{r},t)} + \zeta_p^{\eta}(\mathbf{r},t)$$

Phase Field Microelsticity (PFM) modeling

Free energy of an alloy with martensitic transformation that may also undergo decomposition (the strain energy is included)

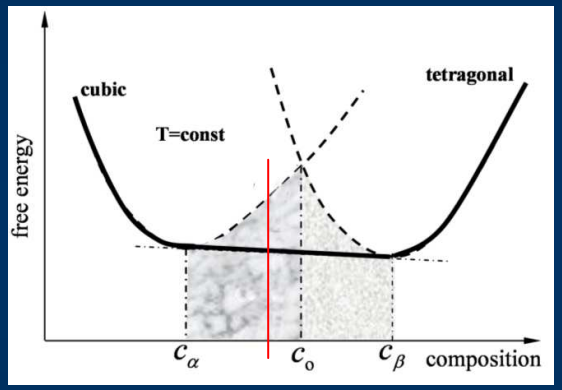
$$F = F(\{c\},\{\eta_1\},\ldots,\{\eta_n\})_L + E^{str}(\{c\},\{\eta_1\},\ldots,\{\eta_n\})$$

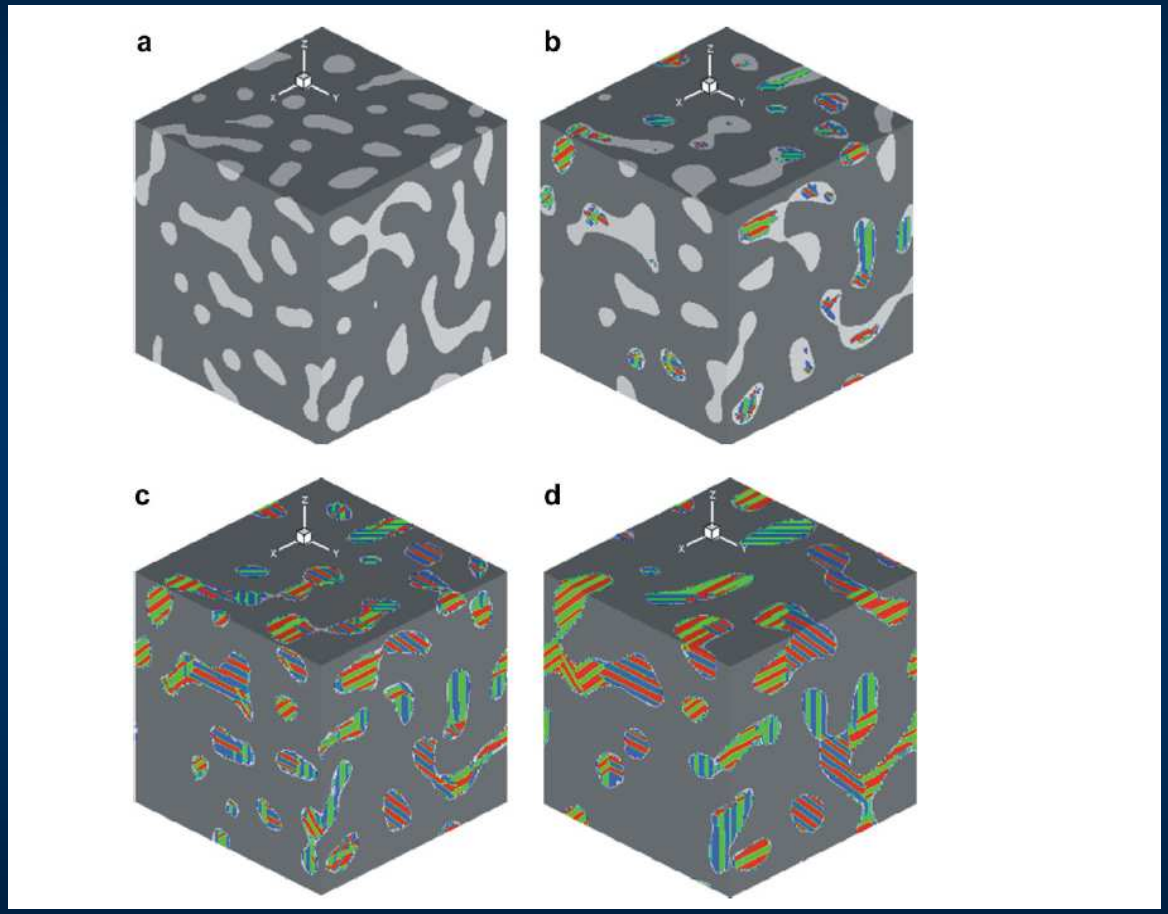
$$F_L = \int_V [\alpha(\nabla c)^2 + \beta((\nabla\eta_1)^2 + \ldots + (\nabla\eta_n)^2) + f\ (c,\eta_1,\ldots\eta_n)]dV$$

$$E^{str} = E^{str}(\{c(r)\},\{\eta(r)_1\},\{\eta(r)_2\},\ldots)$$

$\eta_1, \ldots \eta_n$ are structural parameters related to the Bain strain

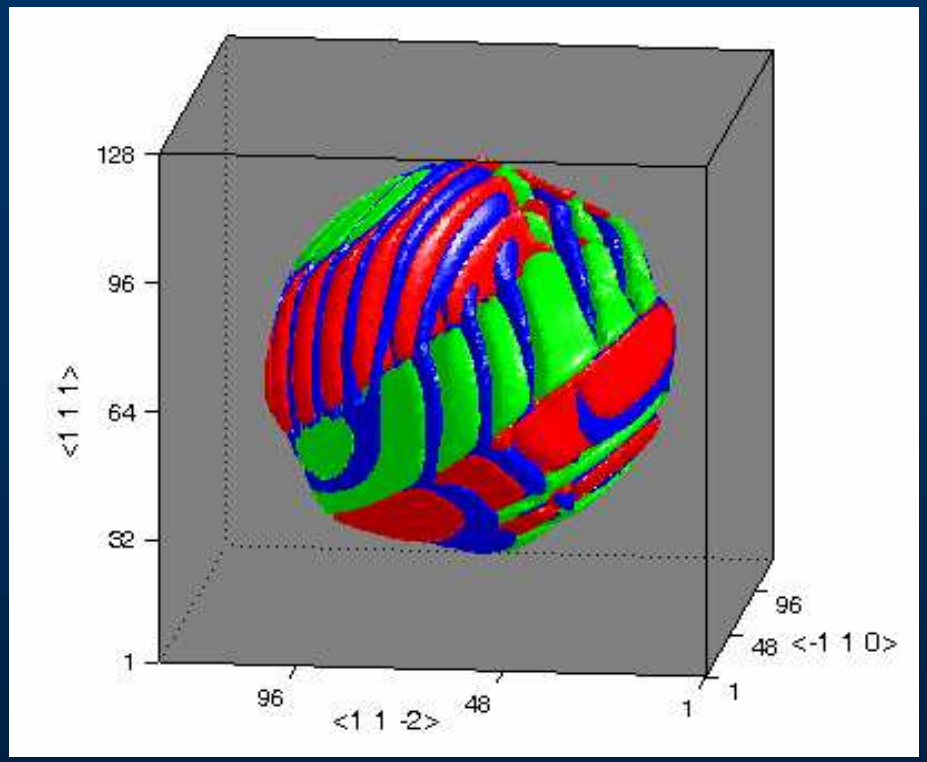
Sequence of transformations in the cubic→tetragonal decomposition





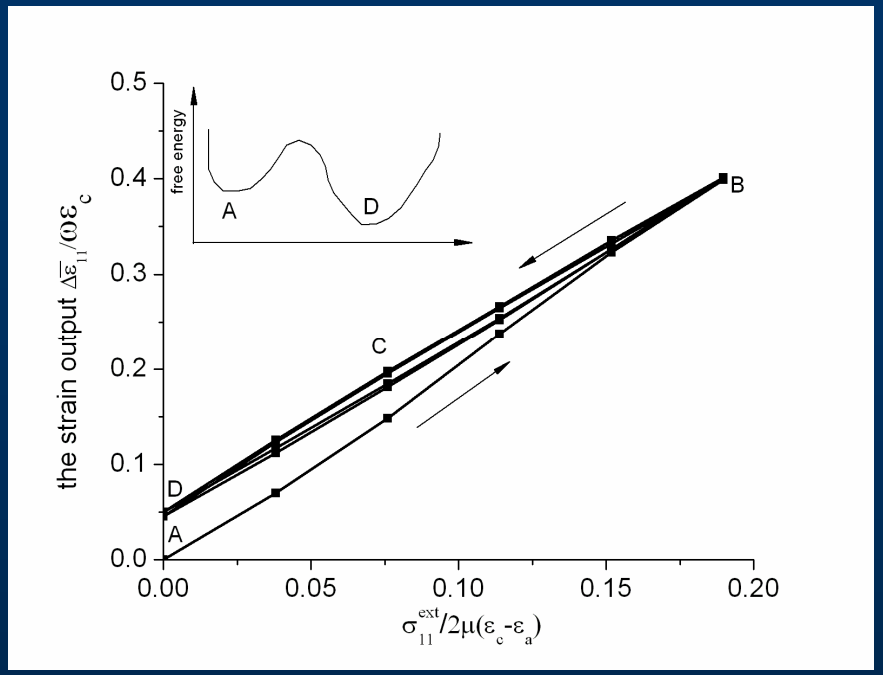
Y. Ni, Y.M. Jin and A.G. Khachaturyan, Acta Mate. 55, 4903(2007)

Appearance of hierarchical structure in the confined martensite (PFM modeling).

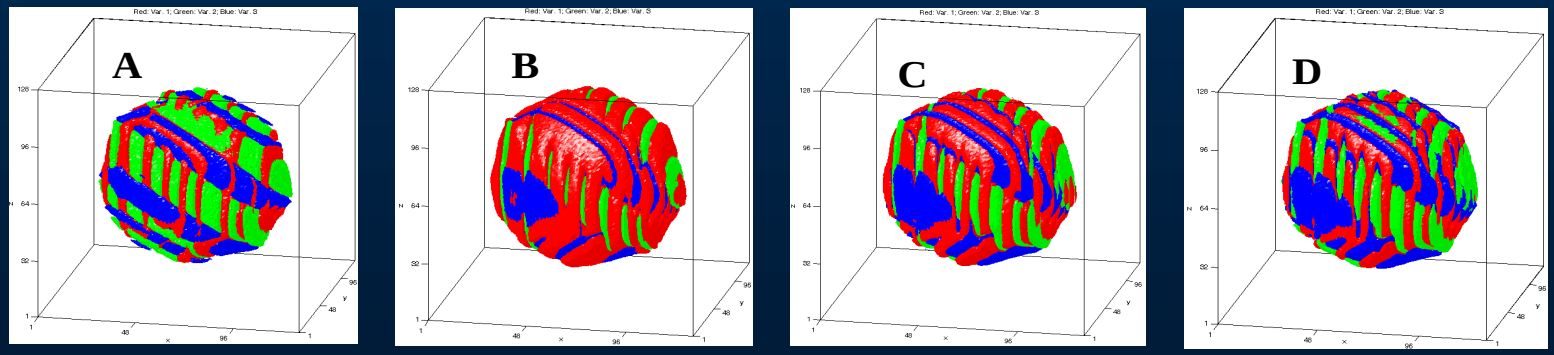


The cubic→tetragonal displacive transformation within the preci[pitate. Three different colors indicate the structural domains with different orientations of the Bain axis. The computational volume is 128 × 128 ×128

Yong Ni and A. Khachaturyan



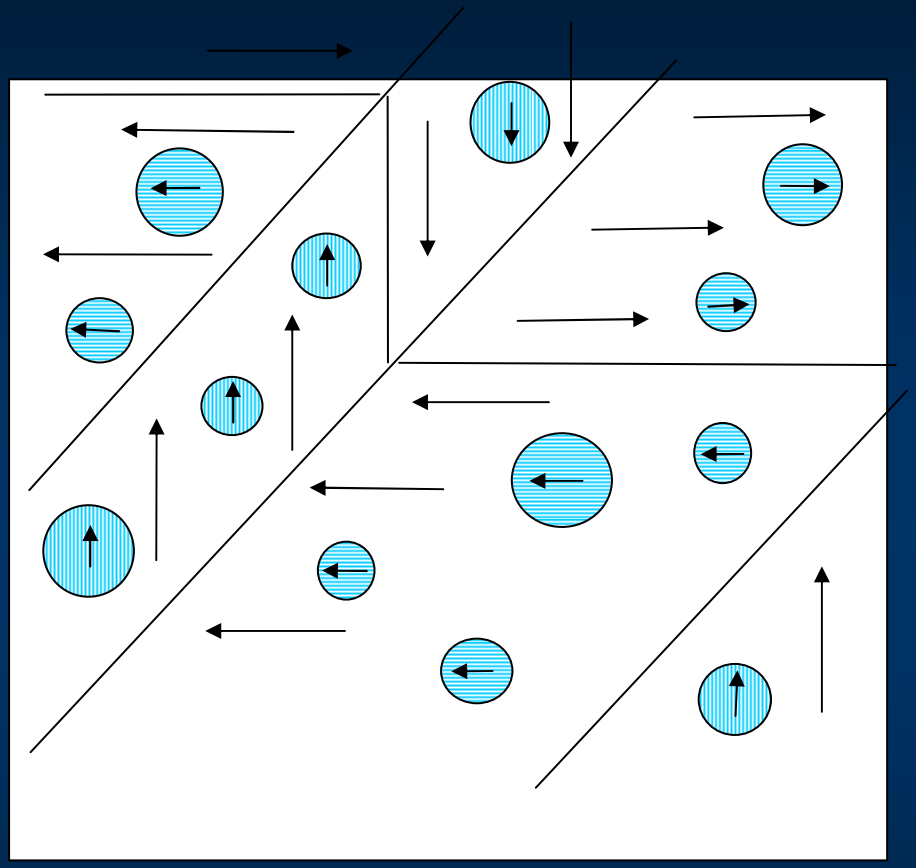
Low hysteresis loop



The hysteresis loop and (b) the corresponding 3D domain microstructures for a cyclic applied stress along (100) axis.

Y. Ni, Y.M. Jin and A.G. Khachaturyan, Acta Mate. 55, 4903(2007)

Spin exchange coupling of magnetizations of tetragonal nano-precipitates and bcc domain matrix



Blue shows DO_{22} (FCT phase) nano-precipitates within the Fe-rich BCC matrix

Large arrows are directions of magnetization of the bcc matrix magnetic domains

Small arrows are directions of magnetization in the FCT nano-precipitates.

Blue hatching indicates a direction of the tetragonal axis of a nanprecipitate. It is always parallel to the magnetization of the surrounding domainin the BCC matrix

Arrows indicate the direction of the magnetization in the BCC matrix and DO_{22} precipitates

Application of *H* moves 90° boundaries of magnetic domains in the BCC matrix. The fractions of the bcc matrix domains, the exchange-induced realignment of magnetization of nano-precipitates within these domains

The *H*-field induced rearrangement of martensitic structure in a confined state and anhysteretic or weakly hysteretic extrinsic giant magnetostriction

- **What we need :**

The formation of (preferably) single variant tetragonal nano-particles in decomposition

Magnetic parent and precipitate phases to be magnetic

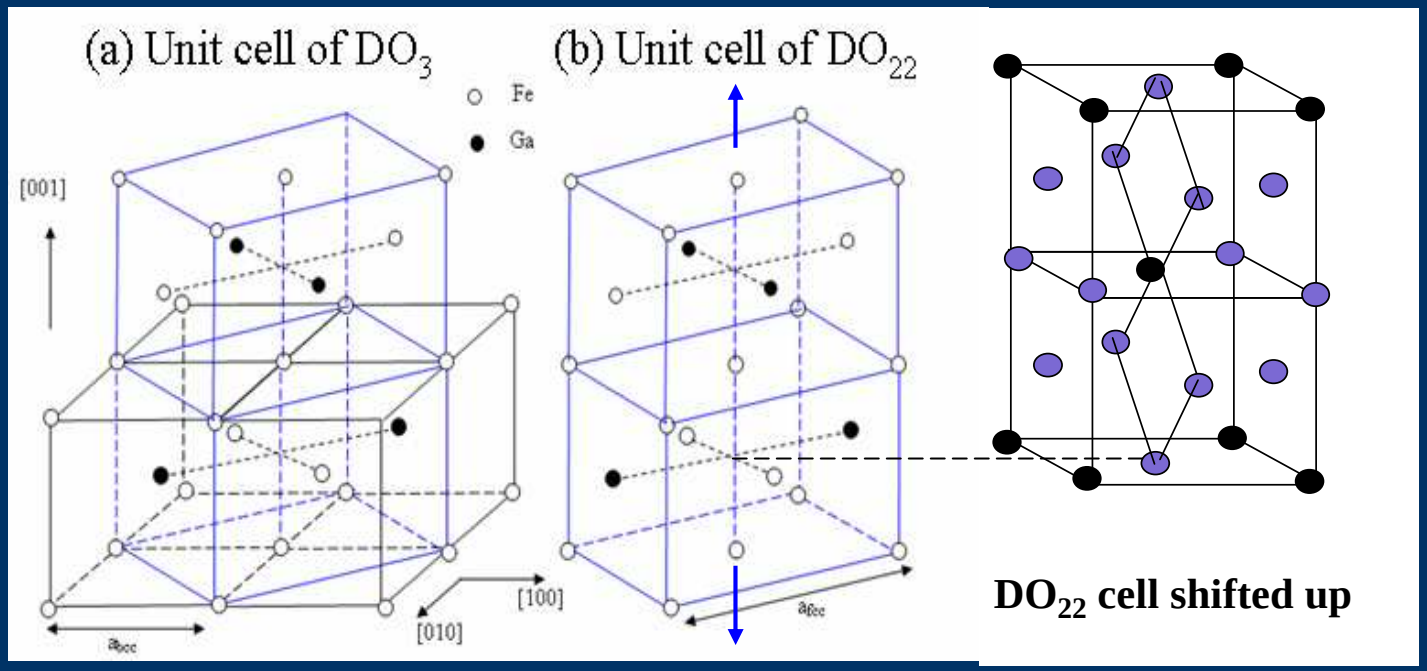
- **What we expect?**

Giant extrinsic magnetostriction.

The theoretical upper limit of the transformation-induced magnetostricrtion is of the same order as the transformation strain at the cubic→tetragonal transformation, this is, $\varepsilon \sim c/a - 1$

This is within the $\varepsilon \sim$ 1000-10,000 ppm range (usual numbers ~10-100ppm). This would make the magnetostrictive material competative with the piezoelectrics with a giant magnetostriction.

$DO_3 \rightarrow FCT(DO_{22})$ Bain displacive transformation



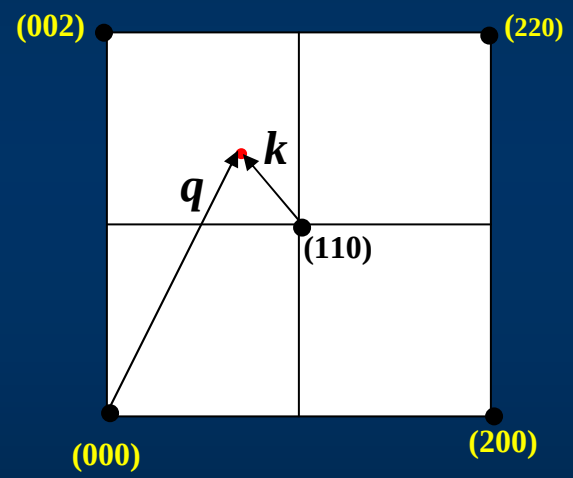
(a) the Bain orientation relations between unit cells of the DO_3 bcc-based cubic ordered phase

(a) the DO_{22} fcc-based tetragonal (FCT) ordered phase obtained by the diffusionless Bain distortion about the [001]bcc axis. The blue lines indicate a unit cell of the product DO_{22} phase within a fragment of a unit cell of the DO_3 phase.

Intensity of diffuse scattering by elastic displacements and difference of atomic factors: (dispersion of the second phase inclusions)

Intensity of diffuse scattering at the point q of the reciprocal lattice by nano particles generating atomic displacements

$$I(\boldsymbol{q},\ \boldsymbol{k}) = \left|\left(c_{Ga} f_{Ga} + c_{Fe} f_{Fe}\right)\left(-i\boldsymbol{q}\cdot\tilde{\boldsymbol{u}}(\boldsymbol{k})\right) + f_{Ga}(q) - f_{Fe}(q)\right|^2 \left|\tilde{\theta}(\boldsymbol{k})\right|^2$$



• **point of measurements**

$\boldsymbol{q} = \boldsymbol{k}_{scat} - \boldsymbol{k}_{incid}$

$\boldsymbol{n} = \boldsymbol{k}/k$

$\tilde{\boldsymbol{u}}(\boldsymbol{k})$ is the Fourier transform of displacement field generated by particles

$\left|\tilde{\theta}(\boldsymbol{k})\right|^2$ is the Laue interference function of precipitates

Diffuse scattering caused by displacements is mostly concentrated near fundamental reciprocal lattice points

Intensity of diffuse scattering by elastic displacements (tetragonal particles)

$$I(\boldsymbol{q},\ \boldsymbol{k}) = \left| \left(c_{Ga} f_{Ga} + c_{Fe} f_{Fe}\right) \frac{\Phi(\boldsymbol{q},\boldsymbol{n})}{k} \ + \ f_{Ga}(q) - f_{Fe}(q) \right|^2 \left|\tilde{\theta}(\boldsymbol{k})\right|^2 \qquad (1)$$

$$\Phi(\boldsymbol{q},\boldsymbol{n}) = \frac{1}{k}\left\{ \left((\boldsymbol{q}\cdot\boldsymbol{n}) - (\boldsymbol{q}\cdot\boldsymbol{e}_3)(\boldsymbol{n}\cdot\boldsymbol{e}_3)\right) \frac{2(\varepsilon_a + \nu\varepsilon_c)}{1-2\nu} + (\boldsymbol{q}\cdot\boldsymbol{n})(\boldsymbol{n}\cdot\boldsymbol{e}_3) \frac{\left(2\nu\varepsilon_a + (1-\nu)\varepsilon_c\right)}{(1-\nu)(1-2\nu)} \right\} \qquad (2)$$

$\boldsymbol{e}_3$ is the unit vector in the direction of the tetragonal axis, ν is Poisson ratio

$\varepsilon_a = \frac{a_t - a_{bcc}}{a_{bcc}}$, $\varepsilon_c = \frac{c_t - a_{bcc}}{a_{bcc}}$ are crystallographic parameters related to the crystal lattice parameters of the bcc phase and tetragonal inclusions

It follows from (2) that the intensity caused by crystal lattice distortion increases as 1/k at k→0 (close to fundamental reciprocal lattice points) and is strongly anisotropic around fundamental reciprocal lattice point (depends on the direction $\boldsymbol{n}=\boldsymbol{k}/k$)

$\left(-i\boldsymbol{q}\cdot\tilde{\boldsymbol{u}}(\boldsymbol{k})\right) = \frac{\Phi(\boldsymbol{q},\boldsymbol{n})}{k}$ **in (1) is found by exact solution of microelsticity equation for a dispersion of multiparticle tetragonal precipitates**

In particular case of cubic precipitate in the cubic matrix and $f_A = f_B$, Eq. (1) is reduced to the Huang equation

The outline of the extrinsic model of GM

- The driving force of a flip of the tetragonality axis in nano-precipitates is the strong exchange rather than weak Zeeman interaction between the magnetization of the matrix and precipitate in a presence of magnetic anisotropy coupling of the direction of magnetization and tetragonality axis.
- This is the case only when precipitates have nano-size and both cubic and tetragonal phases are magnetic.

Outline of the model (continuation)

- Precipitates should be of nano-size to provide a sufficient exchange coupling of magnetic moments of a precipitate and the enveloping magnetic domain of the bcc matrix across cubic/tetragonal phase interfaces

- Such precipitates within bcc single phase field were well documented in the chemically similar Fe-Al system and now in Fe-Ga

Predictions of the Model

1. Existence of tetragonal nano-precipitates

2. Two possible scenarios:

a. single- domain tetragonal DO_{22} precipitates

b. multi-domain tetragonal DO_{22} precipitates

The outline of our extrinsic model:

Giant magnetostriction is a result of the H field -induced *confined* displacive transformation within nano-size precipitates of the bcc-based ordered DO_3 phase within bcc matrix

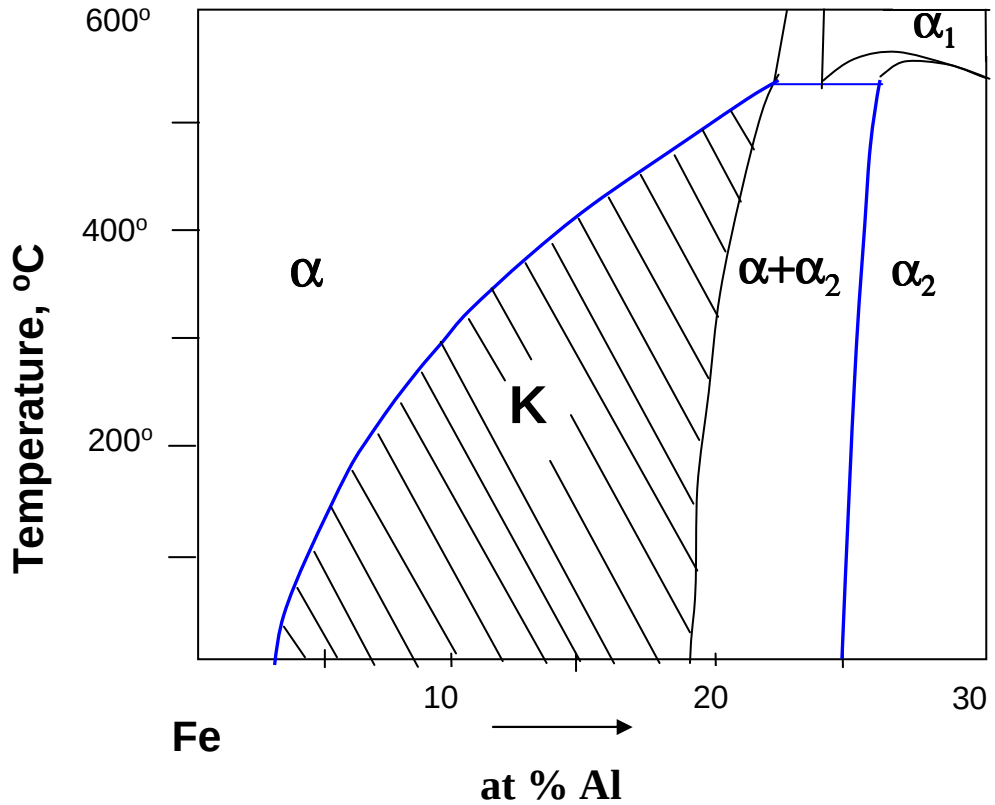
Giant elastic softening is a result of the same (but stress-induced) reorientation within precipitates

Two scenarios

$$\text{BCC} \xrightarrow[\textbf{precipitation}]{} DO_3 \xrightarrow[\textbf{displacive transformation}]{} \text{FCT } (DO_{22})$$

or direct transformation

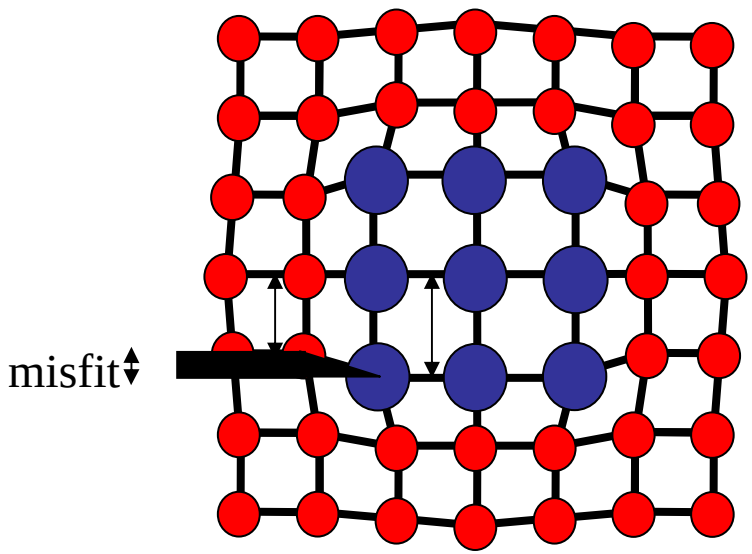
$$\text{BCC} \xrightarrow[\textbf{precipitation of transformed } DO_{22} \textbf{ nanoparticles}]{} \text{FCT } (DO_{22})$$



Phase diagram of Fe-Al system with the K field (H. Warlimont and G. Thomas). The blue lines show the A2 +DO3 two-phase field of the equilibrium phase diagram. The A2 + DO_3 field between the left black and right blue line is the two-phase field of the metastable coherent phase diagram. The K field is shown by hatching.

Mechanism of nano-dispersion formation

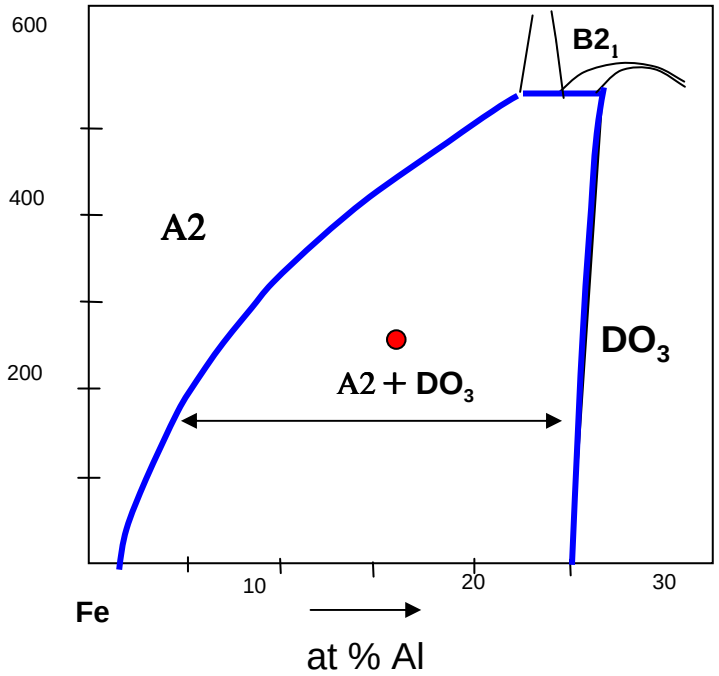
Schematic of a coherent precipitate with a greater crystal lattice parameter



A coherent precipitate with the crystal lattice misfit always generates the elastic strain.

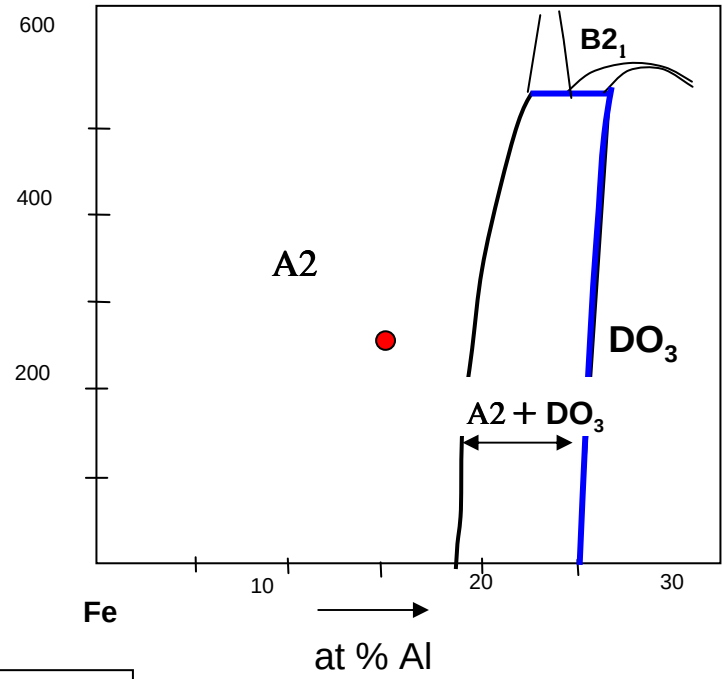
The strain energy increase hinders the formation of the precipitate

equilibrium (stress-free) diagram



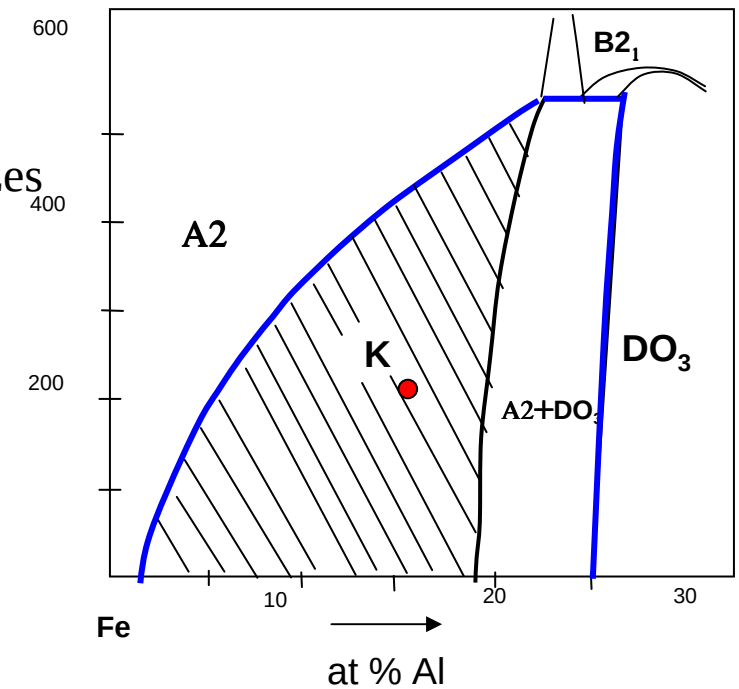
+

coherent phase diagram



=

overlap of both diagrams visualizes K field



K field is single phase field for the coherent diagram and two phase field for equilibrium diagram

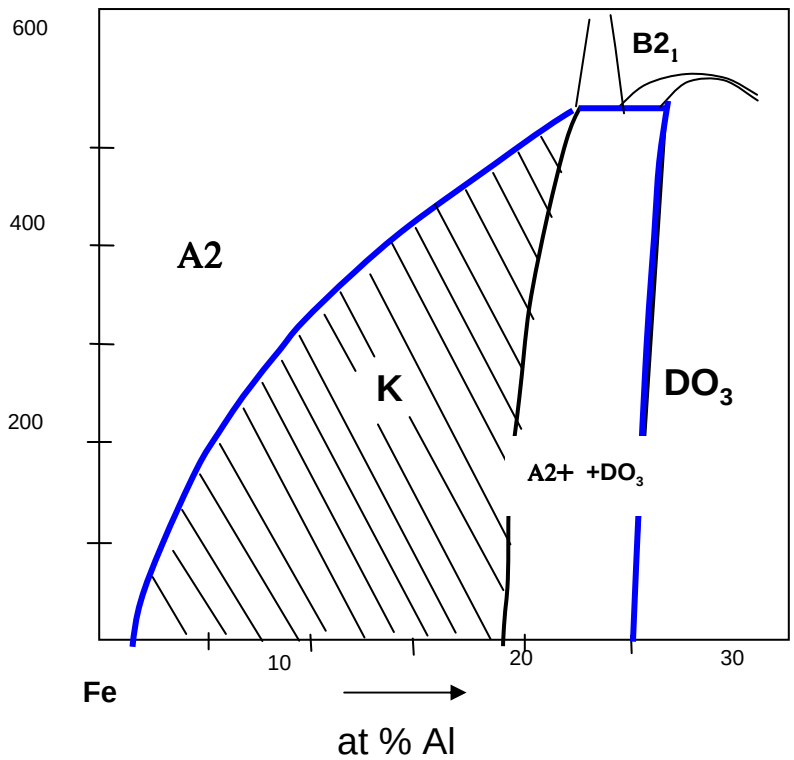
K state theory:
Khachaturyan, Theory of Structural Transfpormations in Solids, Wiley, 1983

Mechanism of nano-dispersion formation (continuation)

K field and a role of excess vacancies

Because of crystal lattice misfit, coherent DO_3 precipitates raise too much strain energy to be formed in the K field.

Only incoherent (stress-free) precipitates can form in K field and only excess vacancies can lift the coherency from the beginning of precipitation



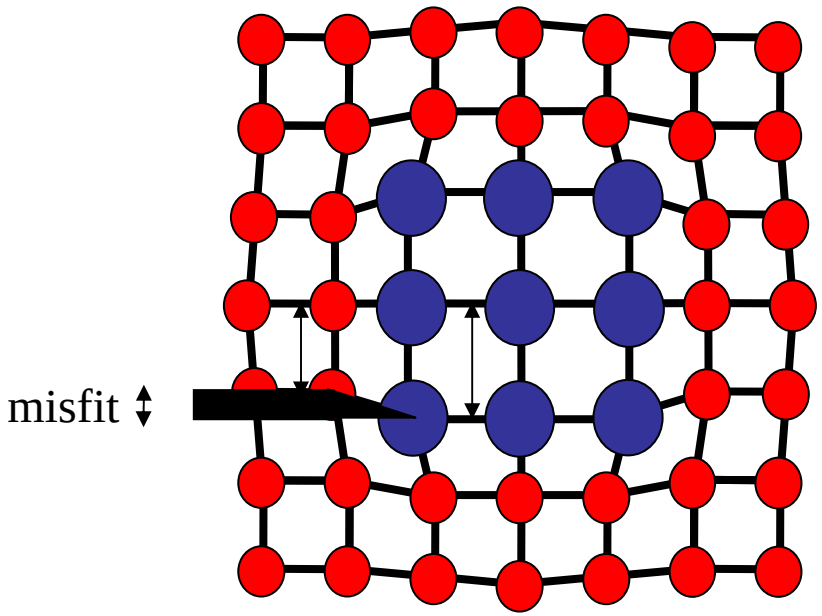
Dashed field is where nanodispersion of the DO3 phase has been observed

Warlimont H, Thomas G.

Metal Science J., **4**, 47, (1970)

and Watanabe et al. found range of formation of nano-precipitates of the DO_3 phase

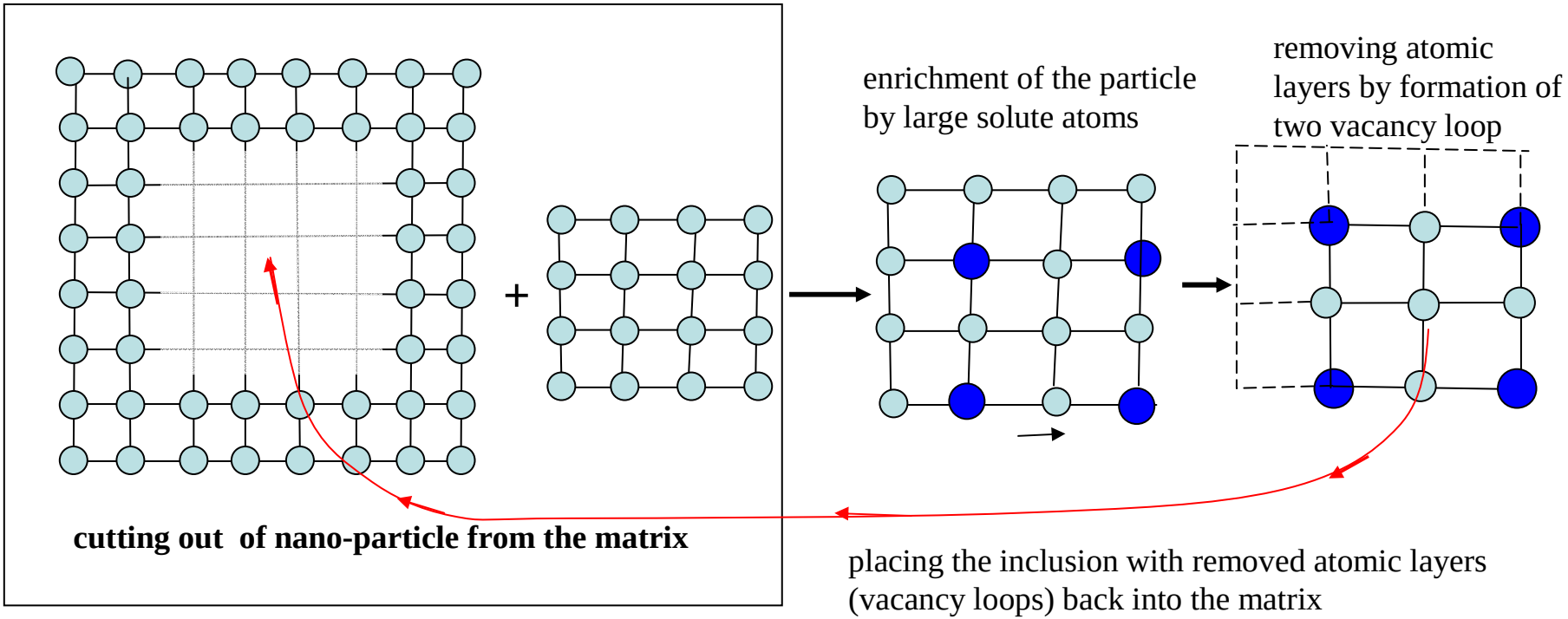
Schematic of a coherent precipitate with a greater crystal lattice parameter

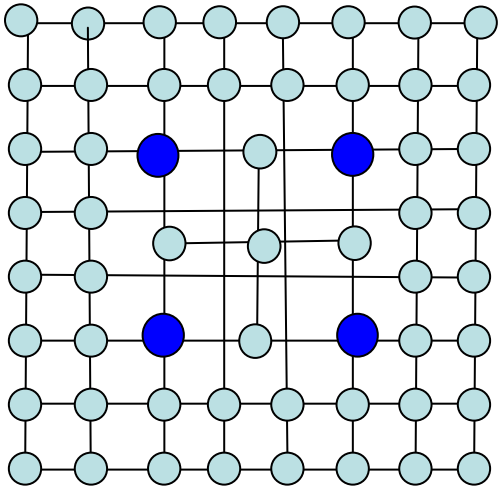


A coherent precipitate with the crystal lattice misfit always generates the elastic strain.

The strain energy increase hinders the formation of the precipitate

Lifting of coherency by vacancy loops





the resultant incoherent stress-free nanoparticle.

There is no elastic strain

K field in the phase diagram and a role of excess vacancies to form nano-precipitrates

(Khachaturyan, Theory of Structural Transformations in Solids, Wiley, 1983)

The most relevant and well known examples are coarsening-resistant nano-precipitates of DO_3 are in Fe-Al and of the B2 ordered phase in fcc Cu-Al.

Thermodynamics of nano-dispersion in K field

- **K field is a *single-phase* field for a coherent precipitation . However, it is also a *two-phase* (BCC+DO_3) field for a stress-free precipitation**
- **In the K field the misfit-induced stress is lifted by excess vacancies**
- **Decomposition in the K field develops as in a ternary alloy.**

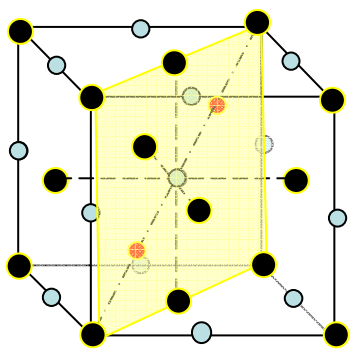
Vacancies in the K field play the role of the third component

Confirmation of tetragonality of DO_3 precipitates

TEM diffraction (SAD) of diffraction splitting in Fe 17at%Ga interpreted as the effect Induced by tetragonally distorted nano-precipitates of DO3 phase

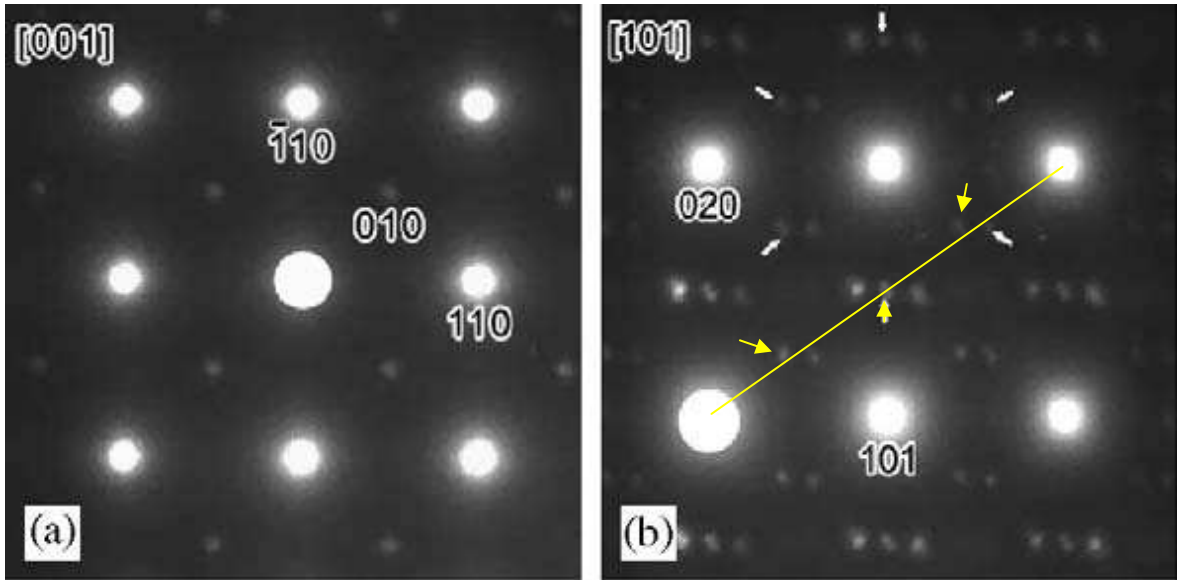
L. Libao et al. / Physica B 365 (2005) 102–108

reciprocal lattice



● $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$ - type superlattice spots of DO_3

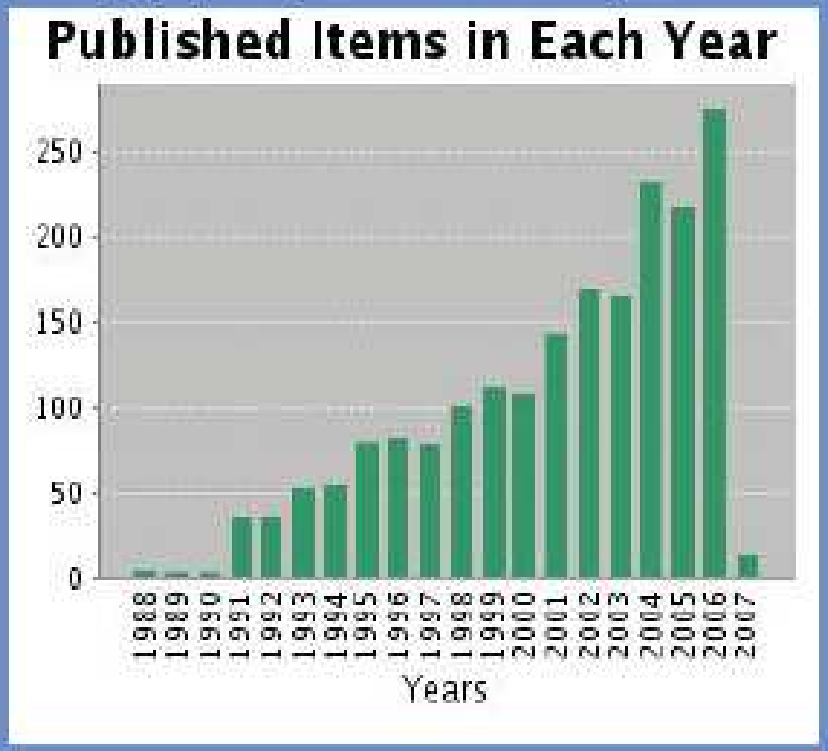
○ (100) – type diffraction spots of both DO3 and B2

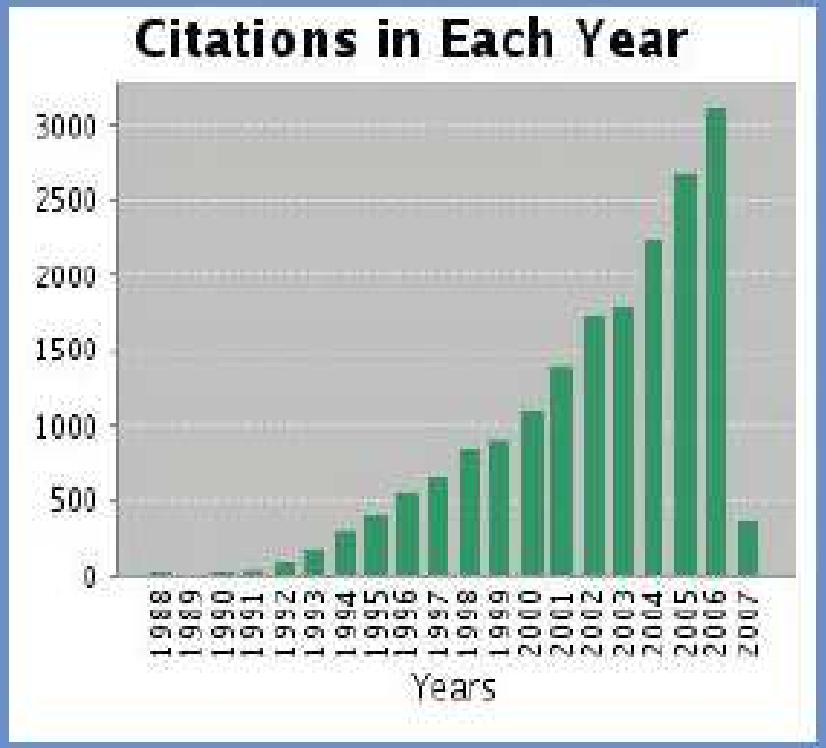


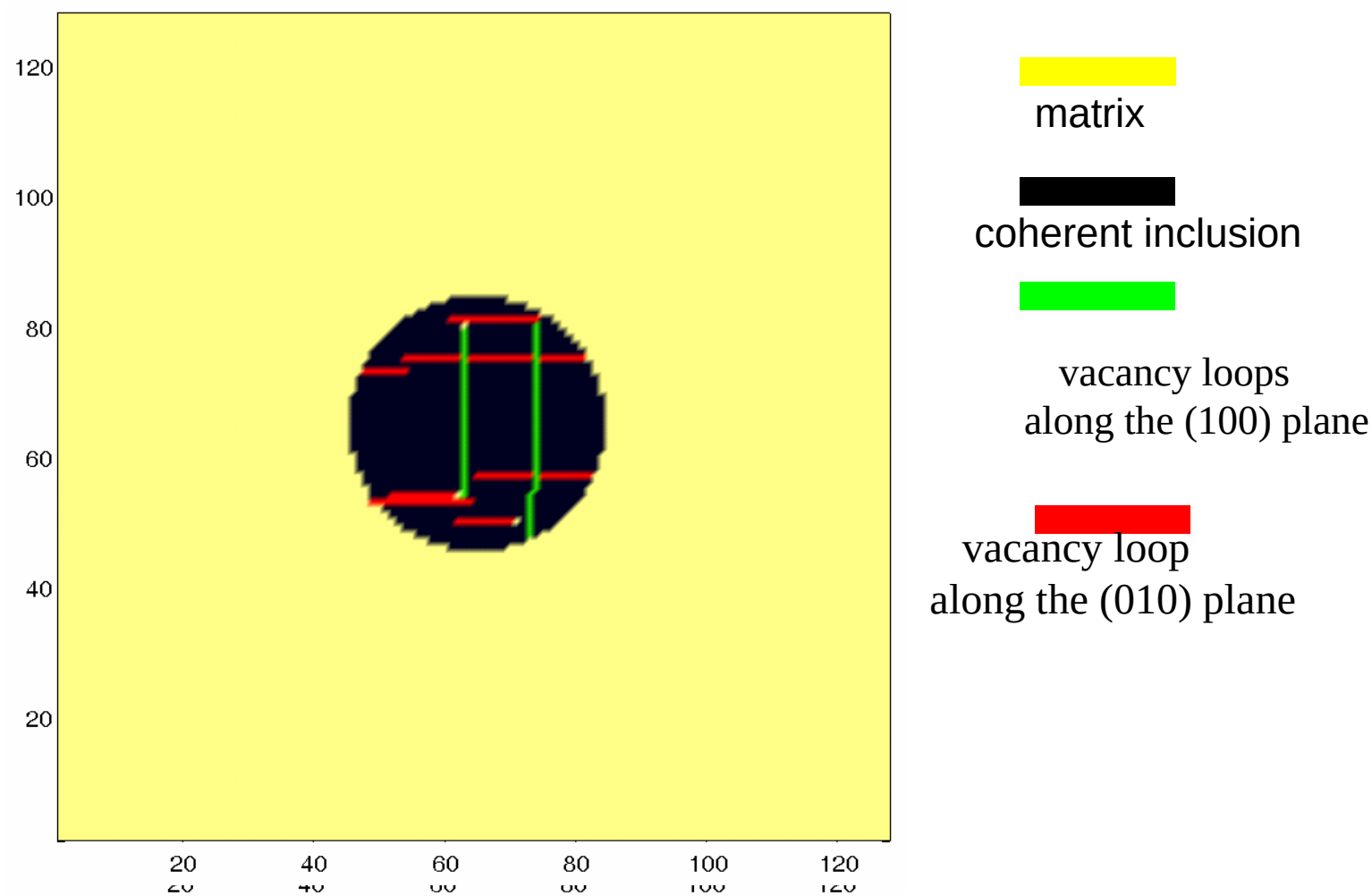
Splitting of the (100) and $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$ DO_3 spots along [101] direction (yellow arrows) is an indication of multidomain structure with (101) boundaries

Modeling is based on our Phase Field Approach

Number of Papers Published and Citations in Phase-Field Method







The preliminary 2D PFM modeling results for vacancy-induced stress-elimination stabilizing nano-precipitates

Condensation of vacancies into a coherent precipitate.
The vacancies spontaneously form stress-relieving [100] and [010] sessile vacancy loops

Confirmed predictions of the extrinsic mechanism of magnetostriction

- **TEM observation of nano-particles within the same composition range**

- **Obsevation of the diffuse scattering typical for the one observed for tetragonal precipitates in the cubic matrix**

- **Vanishing of extrinsic magnetostriction for *H* || $[111]_{bcc}$:**

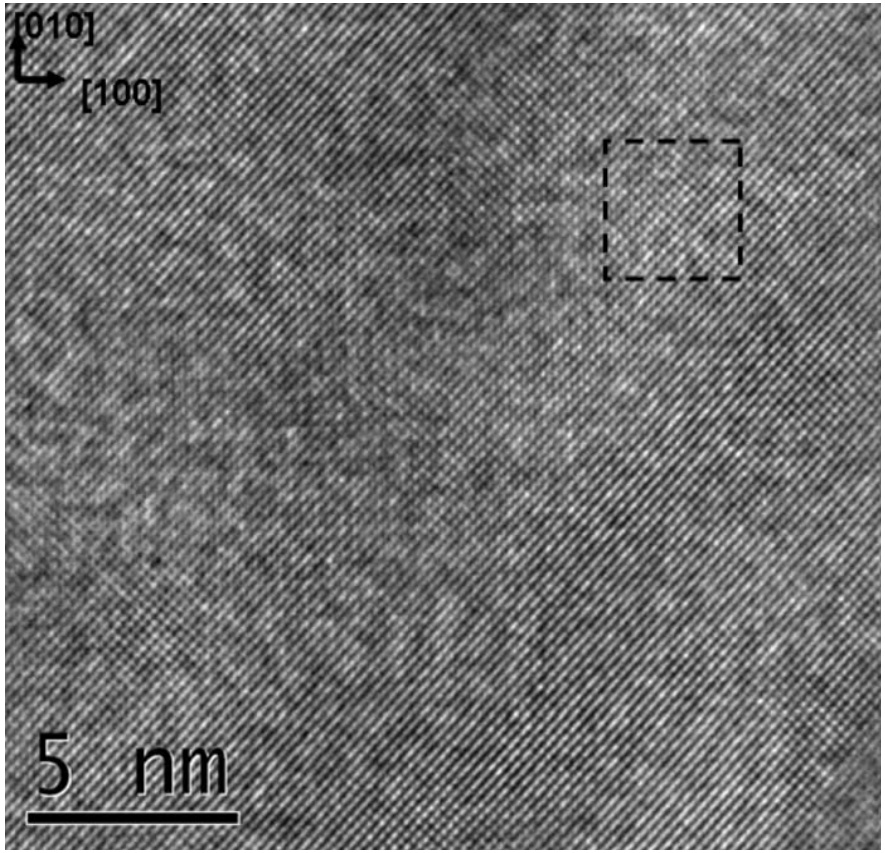
$\lambda^{||}_{[111]}$ is about two orders of magnitude smaller than $\lambda^{||}_{[100]}$ that assumes a usual value commensurate with the value for α Fe.

- **Vanishing of volume magnetostriction: case of reorientation of pre-existing FCT domains**

- **Softening of** C' **elastic modulus (** $C' = (C_{11} - C_{12})/2$ **)** . This occurs **only if the reoriented nano-particles are tetragonal.**

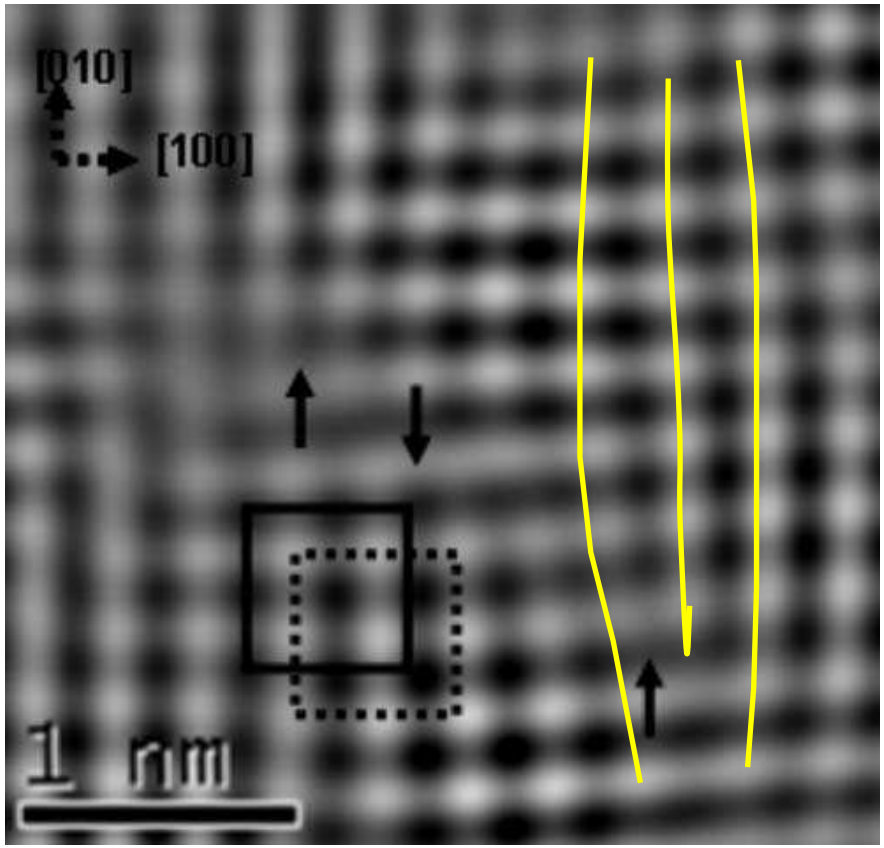
Confirmations of the model predictions:

Observations of nano-precipitates within the bcc stability field of the Fe-Ga phase diagram



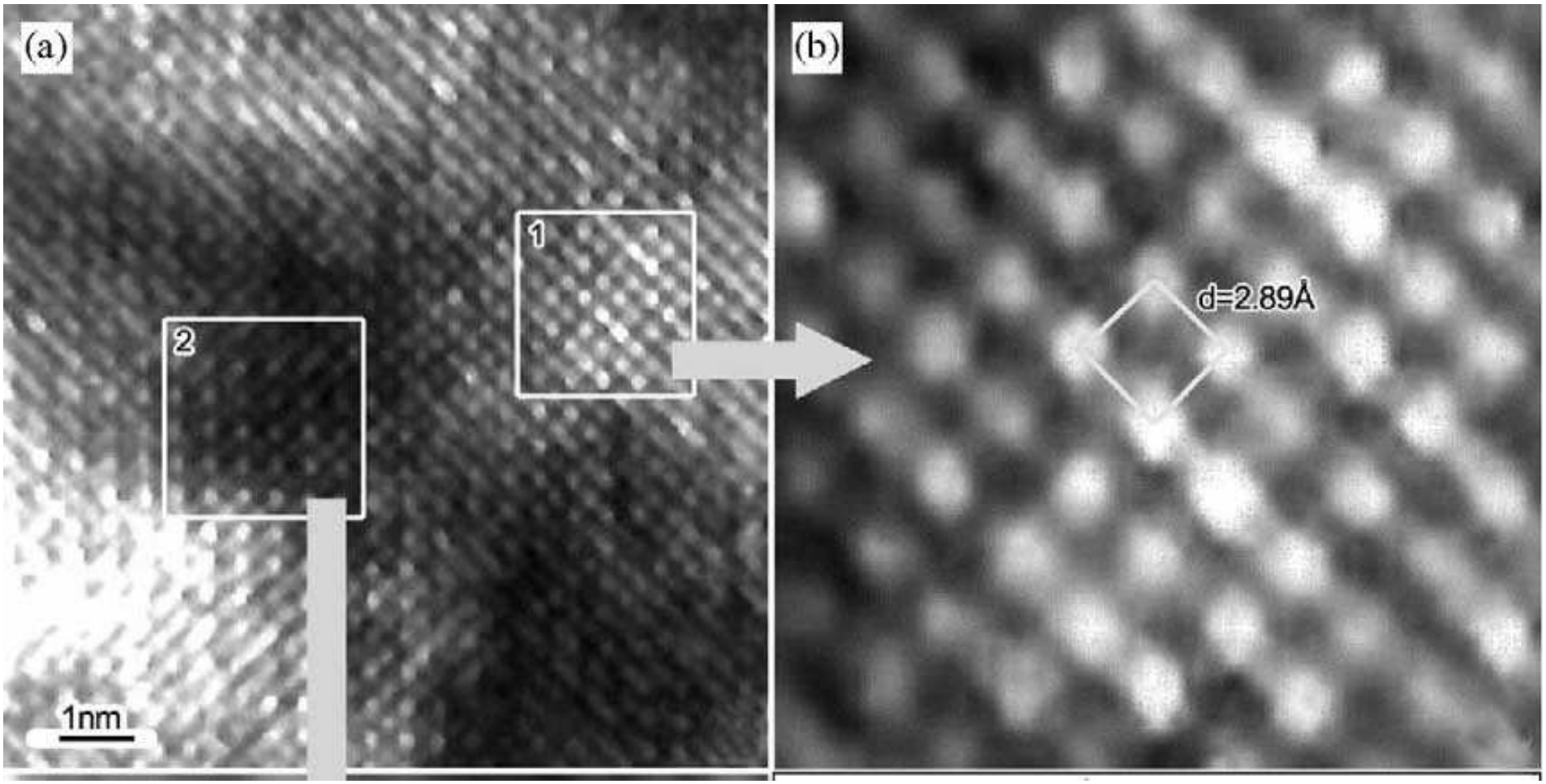
HRTEM micrograph of Fe-19-at %Ga

D. Viehland et al, Phys. Rev. B **77**, 104107 2008



Simulated image obtained by the back Fourier transform of the filtered scattering amplitudes of the (010) reflections from the marked region in lattice image

TEM observation of the FCT nano-precipitates



L. Libao et al. / Physica B 365 (2005) 102–108

OUTLINE

Domain Structure and Giant Response to the Applied Field

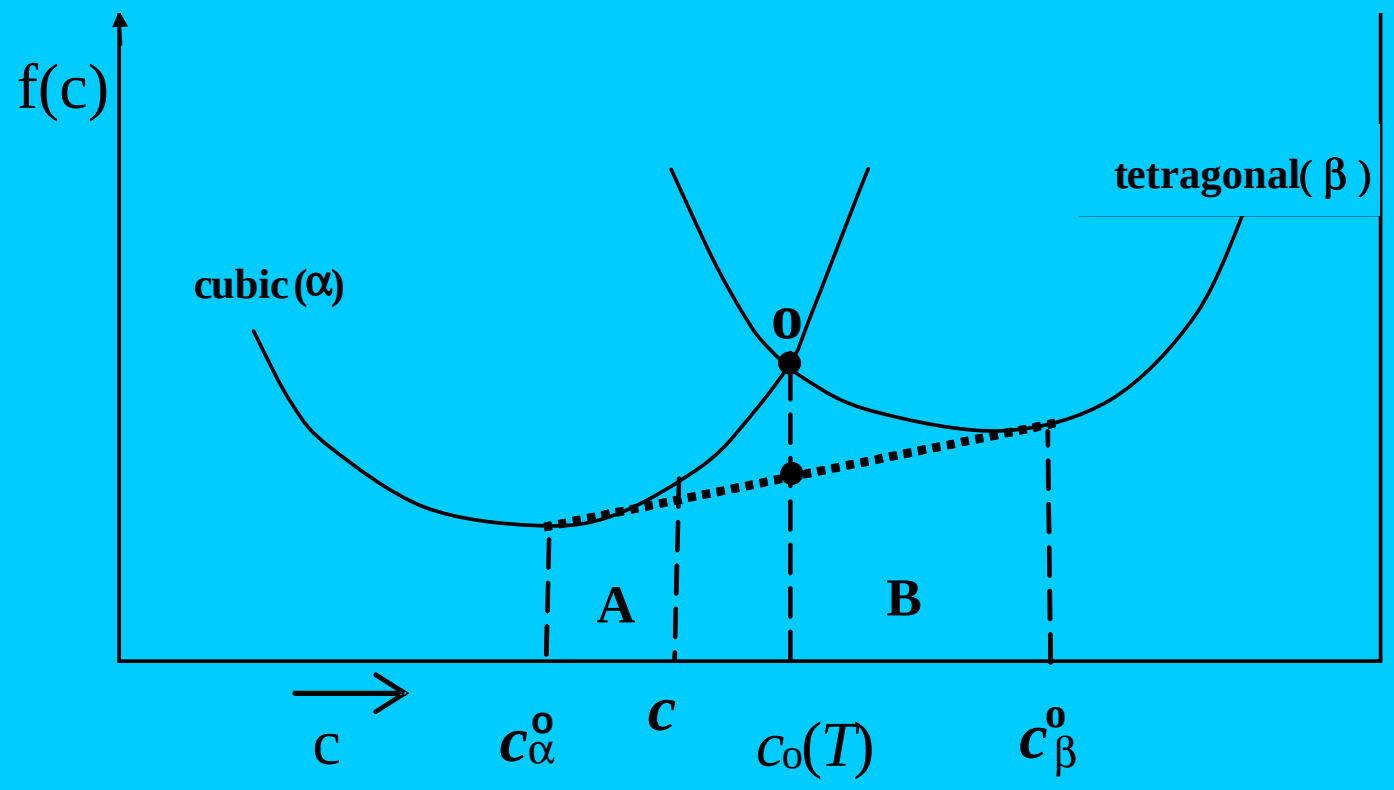
- **Martensitic crystals and strain response to the *applied stress*: hysteretic and anhysteretic response.**

Confined stress-induced rearrangement of structural domains: superelasticity and abnormal softening

- **Martensitic crystals and strain response to the *applied magnetic field* *and MSMA:* hysteretic and anhysteretic response.**

Confined *H* field-induced rearrangement of domains : a giant magnetostriction

Confirmation of tetragonality of nano-precipitates:

- By neutron diffraction data (Viehland et al submiited)
- By SAD (L. Libao et al. / Physica B 365 (2005) 102–108

Schematic free energy vs composition plot for a system with the cubic→tetragonal decomposition