

## Structure and Phase Transitions in Nanocrystals

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### 2.1 Introduction

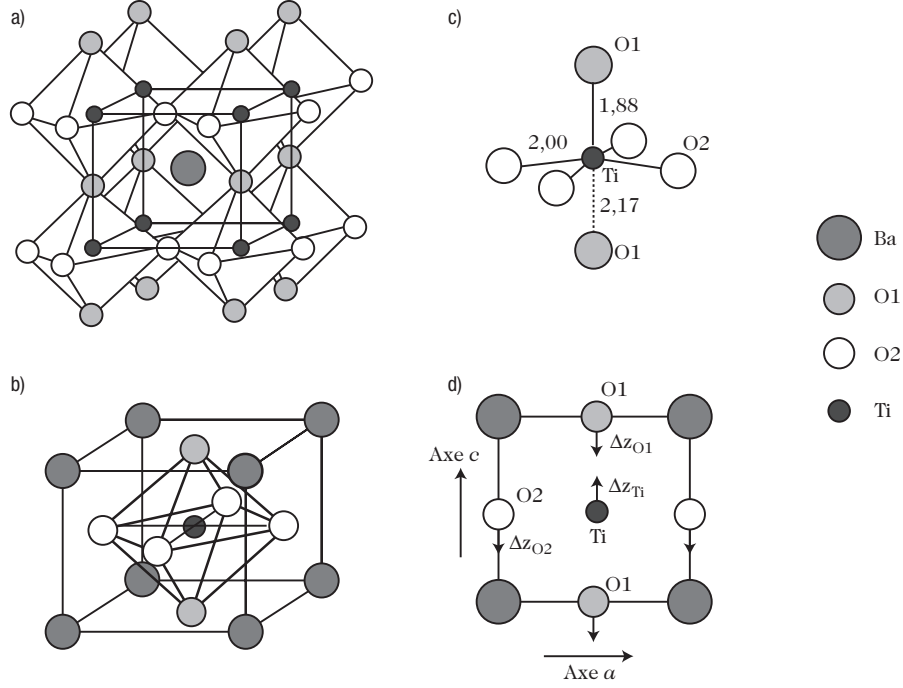
As shown in Chap. 1, the physical properties of conventional materials may change with the size of the grains making them up, even becoming totally different from what is observed in the bulk solid system. One then speaks of grain size dependence. This dependence can be put down to two more or less related effects:

- A size effect, or confinement effect. The nanograin behaves like a kind of box, within which the property may or may not exist [1]. Below a certain critical size, characteristics of the property depend on the grain size. This is the size or confinement effect. The way these characteristics change as a function of size is often non-monotonic and can exhibit extrema.
- A surface or interface effect. In the nanograin, the contribution from layers close to the surface occupies a more and more important place in the overall behaviour of the material as the grain size decreases [1]. The surface energy gradually becomes the dominating contribution to the total energy of the material. Such a property will evolve monotonically with size and can be treated within the framework of thermodynamics.

### Barium Titanate

Barium titanate  $\text{BaTiO}_3$  will be referred to often in the context of experimental results presented in this chapter. Thanks to its crystal structure and dielectric properties, it is a material with a wealth of applications, especially with regard to passive components in electronics and electrotechnics (see Chap. 28). Its crystal structure derives from the crystal structure known as perovskite (see Fig. 2.1). However, depending on the temperature and in normal atmospheric pressure, barium titanate can occur in four different crystal states, all derived from the perovskite structure (see Fig. 2.2).

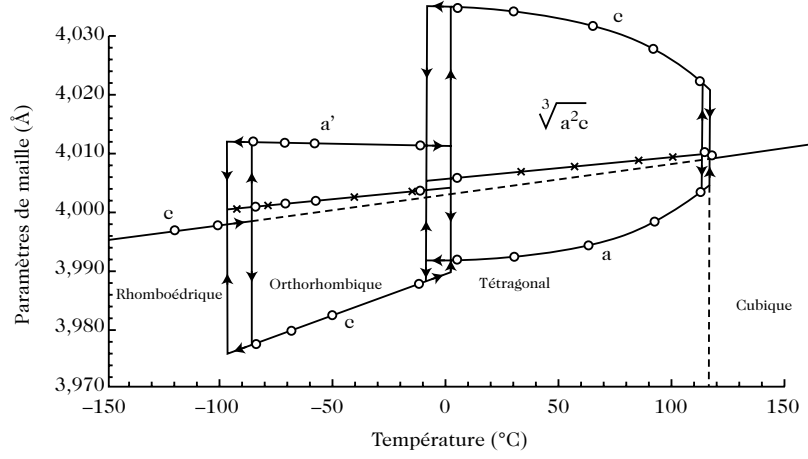
Above about  $120^\circ\text{C}$ ,  $\text{BaTiO}_3$  adopts the ideal perovskite structure (space group  $Pm\bar{3}m$ , centrosymmetric cubic, paraelectric), whereas below this temperature,



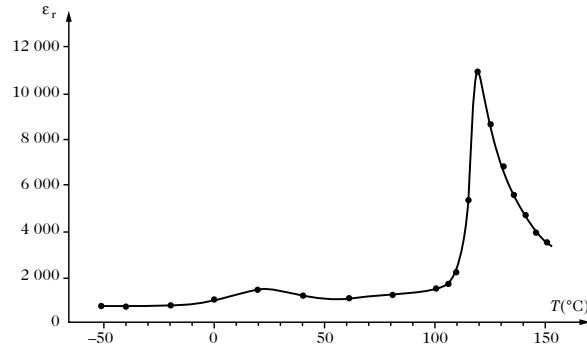
**Fig. 2.1.** Undistorted, i.e., cubic, perovskite crystal structure of  $\text{BaTiO}_3$  above the Curie temperature. (a) Origin at a  $\text{Ba}^{2+}$  ion. (b) Origin at a  $\text{Ti}^{4+}$  ion. (c) and (d) Schematic representation of the tetragonal distortion of the latter below the Curie temperature

called the Curie temperature, the three crystal states of  $\text{BaTiO}_3$  are no longer centrosymmetric. Owing to this feature in particular,  $\text{BaTiO}_3$  then displays the interesting property of being ferroelectric. This fact and the consequences with regard to the dielectric properties of the transition between the ferroelectric and paraelectric states near the Curie temperature are the source of many applications for  $\text{BaTiO}_3$ . In particular, during the transition, the average dielectric constant reaches very high values, whence its use in ceramic capacitors (see Fig. 2.3).

Several properties, like magnetism for example, are grain size dependent. But what about the structure of the nanograins itself? In other words, is the reduction of grain size in the material accompanied by any modification, or even a complete transformation, of this structure? Consider the example of barium titanate  $\text{BaTiO}_3$  in powder form, hence made up of nanograins of various sizes. Figure 2.4 shows the crystal lattice parameters at constant temperature  $T = 25^\circ\text{C}$  and pressure  $P = 1\text{ atm}$  as a function of the dimensions of these nanocrystals [2]. It is clear from the figure that there is a critical diameter  $\Phi_c = 80\text{ nm}$  for the elementary nanocrystals in the powder:

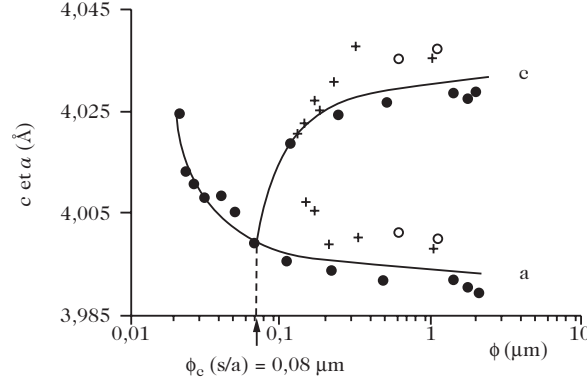


**Fig. 2.2.** Temperature dependence of the lattice parameters of a BaTiO<sub>3</sub> single crystal at standard atmospheric pressure, revealing the three phase transitions between the four most common crystal states of barium titanate



**Fig. 2.3.** Temperature dependence of the average dielectric constant in a pure BaTiO<sub>3</sub> ceramic, revealing the spectacular increase as it transits from the ferroelectric to the paraelectric state

- If  $\Phi > \Phi_c$ , BaTiO<sub>3</sub> crystallises with a tetragonal perovskite lattice, which is the same crystal structure as in the bulk solid. The tetragonal aspect ratio  $c/a$  gets smaller as the size of the nanocrystals decreases. However, it is a remarkable fact that the volume  $v = a^2c$  of the unit cell remains constant [3].
- If  $\Phi < \Phi_c$ , on the other hand, BaTiO<sub>3</sub> crystallises with a cubic perovskite lattice, i.e.,  $c = a$ . Here, in contrast to the tetragonal state,  $a$  increases, and so therefore does the volume  $v = a^3$  of the unit cell, when the size of the nanocrystals gets smaller.



**Fig. 2.4.** Size dependence of the crystallographic lattice parameters  $a$  and  $c$  for  $\text{BaTiO}_3$ , at  $25^\circ\text{C}$  and standard atmospheric pressure in the powdered state [2]

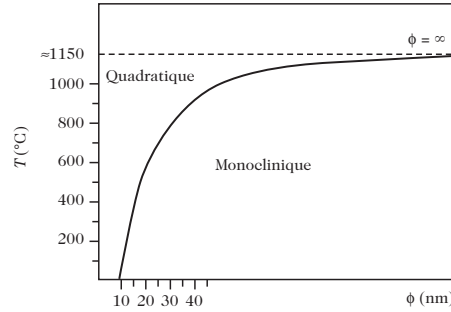
In the light of this example, it is thus clear that the structure of nanomaterials depends on their characteristic dimensions. Phase transitions and variations in lattice parameters can be observed.

The dimensions of nanocrystals thus seem to play an important role in their structure in the broadest possible sense:

- with regard to the nature of the ‘stable’ phase, causing phase transitions at constant temperature and pressure,
- with regard to the geometry and volume of the unit cell, for a given crystal symmetry.

There are two further pieces of data characterising nanocrystals as compared with the bulk solid: the dimensions and also the state of the outer surface or interface. Transitions in nanomaterials are studied by varying these parameters. Hence one can either reduce the size of the nanocrystals whilst keeping the surface in the same state, or one can modify the state of the surface or interface whilst conserving the size of the nanocrystal. The studies described here as examples use one or other of these methods. Note that, in the case of a size reduction, only the chemical composition of the surface or interface can be conserved. Indeed, the energy of the surface or interface will necessarily be modified owing to the reduction in the radius of curvature. We may say that, in this case, size reduction effects and surface effects are closely related.

Grain size dependence is a general property and we shall see below that it is relevant to a wide range of materials such as oxides, ceramics, semiconductors, and also metals. The size reduction of nanograins will also have a significant influence on the difficulty with which phase transitions can be brought about, by modifying the transition energies. Finally, structural states that do not exist in bulk solids, such as liquid–solid equilibria with segregation, have been



**Fig. 2.5.** Temperature of the phase transition in zirconia  $\text{ZrO}_2$  as a function of the average diameter of nanocrystals in powders at standard atmospheric pressure [4, 5]

observed for nanoparticles. In the rest of this chapter, we shall return to these various points and illustrate them with examples.

## 2.2 Crystalline Phase Transitions in Nanocrystals

### 2.2.1 Phase Transitions and Grain Size Dependence

There are many examples of phase transitions occurring whenever the characteristic dimensions of a material go beyond a certain critical value. More interestingly, such transitions are not restricted to any particular type of material. In the following, we shall give some examples, chosen among ceramics, metals, and also semiconductors.

#### Ceramics

The grain size dependence of a phase transition in a ceramic can be illustrated by the monoclinic–tetragonal transition occurring in zirconia. This property has been known and exploited for a long time now [4]. At standard atmospheric pressure and room temperature, zirconia crystallises in a monoclinic (low temperature) form, whereas at high temperature, above 1100–1150°C, its crystal structure is tetragonal. If  $\text{ZrO}_2$  is in the form of ‘crystals’ of the order of 10 nm, it is the tetragonal form that is stable at room temperature. The transition temperature, somewhere between 1100 and 1150°C for micrometric crystals becomes lower as the dimensions of the nanocrystals decrease (see Fig. 2.5) [5]. In fact it has been shown recently that, for temperatures below those illustrated in Fig. 2.5, the tetragonal–monoclinic transition is still present and occurs for grain sizes of the order of 6.9 nm (at 175 K) [6].

Another situation where there is grain size dependence has been established in the case of the Verwey transition, first observed in 1939 by the discontinuous change in conductivity it causes. This transition occurs in magnetite  $\text{Fe}_3\text{O}_4$ , with the so-called spinel crystal structure. Although there is a

wealth of literature on the subject, the mechanisms have not yet been clearly understood. However, a study for nanometric grains has been able to throw some light on the matter [7]. Experiments have also demonstrated a spectacular difference between the temperature predicted for large grains and that observed for nanometric grains (a difference of more than 70 K). It would thus appear that the Verwey transition constitutes another example of grain size dependent phase transition.

## Metals

An example of a grain size dependent phase transition in metals is provided by nickel. In the bulk solid, this metal has fcc structure. However, recent experiments have brought to light a grain size dependent phase transition for very small Ni nanoparticles, chemically synthesised in solution [8]. Indeed for diameters less than 4 nm, the structure is still crystalline, but it becomes hexagonal close packed (hcp) rather than fcc. In the bulk material, an hcp structure is metastable, although it can be obtained in thin films in certain conditions. It should also be noted that the melting temperature of various metals is well known to depend on grain size [9].

## Semiconductors

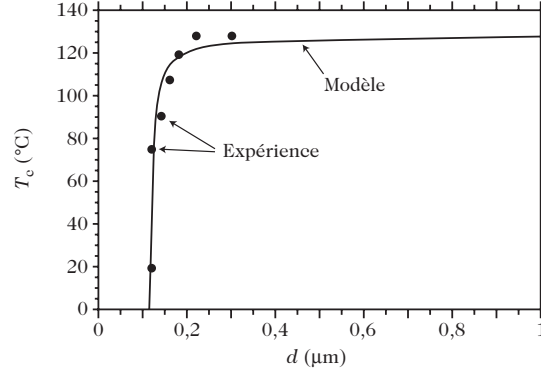
As far as semiconductors are concerned, it is likely that a crystal phase transition depending on nanoparticle size can occur in certain cases. However, the systems investigated as yet have not produced conclusive results. The case of CdS nanoparticles is worth mentioning in this context. These are obtained with a wurtzite-type structure (as in the bulk solid) for diameters greater than 5 nm, whereas for very small sizes (3 nm), a zinc blende structure is observed [10]. However, the latter is apparently metastable and seems to be obtained for purely kinetic reasons during formation.

Grain size dependent crystalline phase transitions exist for a wide range of materials. This is therefore an intrinsic property of nanomaterials.

### 2.2.2 Elementary Thermodynamics of the Grain Size Dependence of Phase Transitions

#### Theory

The various examples described above show that the phase transitions, and more generally the phase diagrams of a material should be considered in a temperature–pressure–grain size space (or rather, reciprocal radius of curvature  $R$  for the latter degree of freedom). However, a general theory has not yet been put together. In this context, it is interesting to see what standard thermodynamics has to say about the matter [11]:



**Fig. 2.6.** Temperature of the tetragonal–cubic phase transition in  $\text{BaTiO}_3$  as a function of the grain size. Calculated result from [11] and experimental result from [12]

- The stable states of the system are no longer governed by the free enthalpy  $G$  at constant  $T$  and  $P$ . This role is fulfilled by a generalised free enthalpy function  $G^*$  given by

$$G^* = G - 2\gamma V/R.$$

- $G^*$  is no longer a state function of the system.  $\gamma$  is the surface energy,  $V$  the molar volume of the material, and  $R$  the radius of the nanocrystal, assumed spherical.
- The equilibrium state of a system made from nanometric grains is no longer obtained by the condition  $dG = 0$ , but rather by  $dG^* = 0$ .
- There is therefore equilibrium between the phase  $\alpha$  and the phase  $\beta$  of the same body if  $G_\alpha^* = G_\beta^*$ .
- For given temperature and pressure, there is a critical radius  $R_c$  at which the phase transition occurs in nanometric grains.
- So the temperature  $T_c$  of the phase transition is, in particular, a function of the radius  $R$  of the nanocrystals:

$$T_c = T(P, R, \gamma_\alpha, \gamma_\beta).$$

This relation has been clearly demonstrated for the tetragonal–cubic transition in  $\text{BaTiO}_3$  (see Fig. 2.6).

### Instability of the Crystal State

It has long been known that, beyond a certain size, the crystal becomes unstable, favouring an amorphous, hence disordered structure. The critical size obviously depends on the material. For example, in the case of silicon, a theoretical study has shown that this crystalline–amorphous transition occurs for sizes of the order of 3 nm [13]. This same study stresses that this phase

transition is discontinuous. It is therefore quite appropriate here to speak of a grain size dependent phase transition.

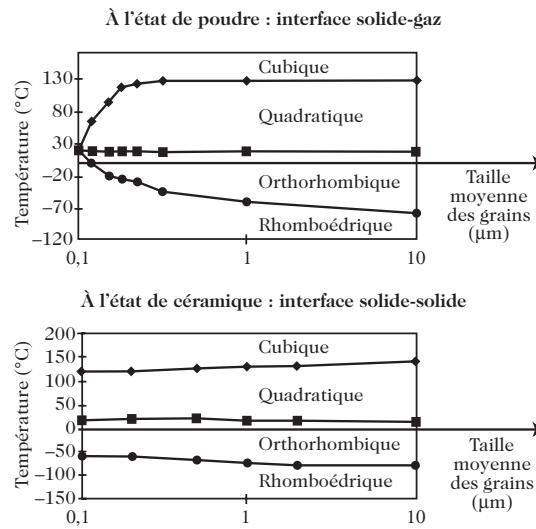
The size of a nanocrystal thus plays the role of a kind of intensive quantity imposing the crystalline or amorphous state in the same way as the temperature or the pressure.

### 2.2.3 Influence of the Surface or Interface on Nanocrystals

Changes can thus be observed in the phase diagram of a material by varying only the size of the constituent grains. In the same way, one may expect to obtain similar effects by altering the surface state of these nanograins whilst keeping their dimensions constant. The modification of this surface or interface energy can be achieved in different ways: either by adsorption of various chemical species or molecules in the case of powdered systems or systems in solution (solid–gas or solid–liquid interface), or by compacting the nanograins, or embedding them within a matrix (solid–solid interface).

#### A Simple Example

Let us return to  $\text{BaTiO}_3$ . Quite recently, the role of the outer interface on transition temperatures in barium titanate has been investigated [14] (Fig. 2.7).



**Fig. 2.7.** Transition temperatures for  $\text{BaTiO}_3$  as a function of grain size [14]. *Upper:* In the powdered state (solid–gas interface). *Lower:* In the ceramic state (solid–solid interface)



In the first case,  $\text{BaTiO}_3$  is in powdered form and hence has an outer surface which is a solid–gas interface. In the second case, the material is in the form of a microstructure composed of agglomerated grains, i.e., a ceramic with varying degrees of density. In this case, there is a solid–solid interface between grains.

The two phase diagrams are clearly different. Thus, for a given grain size and temperature, different phases can be stabilised depending on the state of the interface.

Still in the second case, for a solid–solid interface, a very slight variation is observed in the transition temperatures as a function of grain size. Nanograins in a bulk solid material would therefore appear to behave like large grains. The surface effect would thus seem to disappear if the nanocrystal is bounded by an outer interface with nanocrystals that are identical to it.

### A More Complex Example

Phase transitions on the nanoscale and in ternary systems have rarely been studied, despite the fact that quite spectacular modifications are to be expected in equilibrium diagrams established for large grains. Indeed, since the energy contribution of the interface between the phases increases when the grain size goes down, the phase separations observed in micrometric crystals should disappear at the nanoscale, leading to a single phase. New materials can thus be expected.

An interesting example is provided by nanometric titanium ferrites, which have the formula  $(\text{Fe}_{3-x}\text{Ti}_x)_{1-\delta}\text{O}_4$ , where  $\delta$  (a parameter related to the average valency of cations) represents the deviation from the oxygen stoichiometry of the material [15]. Figure 2.8 shows the phase diagrams of the Fe–Ti–O system obtained for monocrystals that are at least micrometric (Fig. 2.8a), and for nanometric elementary crystals with solid–solid or solid–gas interfaces (Figs. 2.8b and c, respectively). In the latter case, the stability region of the spinel phase extends from  $\delta = 0$  to  $\delta = \delta_{\text{max}}$  for titanium compositions with  $x$  in the range 0.25–0.75. For other compositions, only metastable spinel phases can be synthesised over the whole range of  $\delta$  owing to their much larger grain sizes ( $> 30$  nm), and for which the spinel phase is not stable. Because of the grain size, but also due to the particular interface, a unique face-centered cubic phase is thus stabilised over a wide range of phase diagrams, in contrast to the mixture of phases that occurs for micrometric crystals. Indeed, for the latter, an orthorhombic phase and a rhombohedral phase, or a rhombohedral phase and a face-centered cubic phase coexist over a large part of the diagram, depending on the titanium composition and the deviation from oxygen stoichiometry (see Fig. 2.8a). This phenomenon is explained by the fact that the surface energy that would be created by the fine grains, if these two phases were to coexist, would be too great, so that the system prefers to crystallise in a single phase in the case of nanometric grains.

Reducing the size of a nanocrystal increases the relative importance of the surface or interface between grains. Consequently, the state of the surface or interface also predetermines the properties of the nanomaterial.

#### 2.2.4 Modification of Transition Barriers

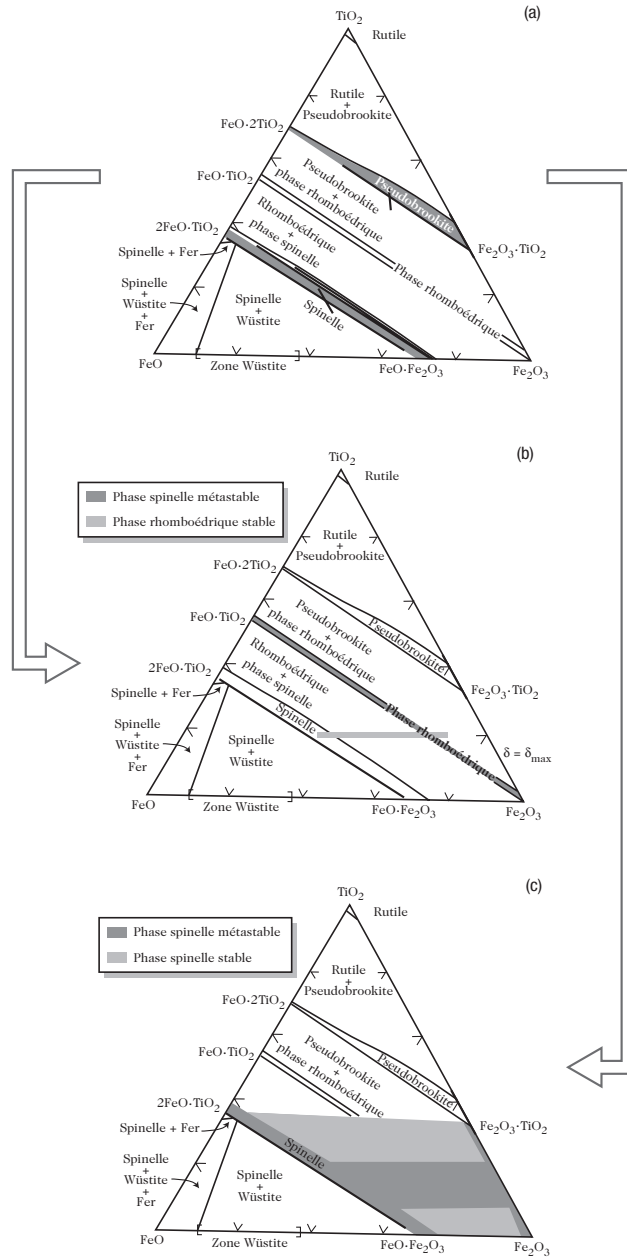
In some cases, exotic crystalline phases have been observed unexpectedly in nanoparticles. For the main part, these phases are not the most stable structures, but are obtained during the formation or synthesis of the nanoparticles, probably for kinetic reasons. It is nevertheless remarkable that it is generally easier to produce these phases in nanocrystals than in the bulk solid. These phases are also generally more stable. For example, Ge nanoparticles formed via a vapour deposition technique possess a certain crystal structure known as ST12 whenever the particle size is less than 4 nm [16], whereas it is the diamond-type cubic structure of the bulk solid that is observed for larger nanoparticles. This ST12 structure also exists for the bulk material, but to obtain it, a considerable pressure must first be applied (around 10 GPa), this causing the formation of a  $\beta$ -Sn type structure, before returning suddenly to atmospheric pressure. This ST12 structure is also metastable in the bulk solid and one only needs to anneal the system in order to recover the cubic diamond structure. What is interesting here is that this annealing stage need only be carried out at 200°C in the bulk solid, whereas one must go to temperatures above 800°C for nanoparticles! We may conclude that the reduction in size of nanocrystals is accompanied by a modification of the transition barriers between the phases.

The effect of size on phase transition barriers can be simply explained using the elementary thermodynamic model discussed above. We assume to begin with that the barrier height is directly proportional to the free energy difference  $\Delta G^*$  between the two phases. Assuming that the molar volume of the two phases is the same, we obtain

$$\Delta G^* = \Delta G - 2\Delta\gamma \frac{V}{R}.$$

The variation of  $\Delta G^*$  as a function of  $R$  thus depends only on the difference of surface energy  $\Delta\gamma$  between the two phases. A reduction in the barrier height, and hence of the transition temperature, may thus occur when the size of the nanocrystals decreases. But it may also increase, as happens for the rhombohedral–orthorhombic transition in BaTiO<sub>3</sub> powders.

It has also been possible to explain modifications in transition barriers using criteria related to crystal defects in nanoparticles. In the bulk solid, phase transitions are helped by the presence of defects in the crystal structure. These facilitate nucleation of the new phase. In contrast, the smaller the nanocrystal, the less likely it is to contain any such defects. It may thus be assumed that size reduction will hinder the transition. However, for low or zero defect



**Fig. 2.8.** (a) High temperature phase diagram for the Fe–Ti–O system in the form of micrometric crystals (pseudobrookite, an orthorhombic phase). (b) and (c) Phase diagrams for the Fe–Ti–O system, corrected in the case of nanomaterials. (b) Spinel and rhombohedral phases formed by mechanosynthesis, where only the titanium composition  $x = 0.5$  has been studied [15], and where the interfaces are mainly of solid–solid type. (c) Stability regions of the spinel phase formed by soft chemistry when the surface energy is of solid–gas type

densities, recent work has shown that an increase in the size of Si or CdSe nanoparticles is accompanied by an increase in the pressure required to bring about the phase transition [17, 18]. There are therefore several mechanisms here and the variation of the transition barrier may be somewhat complex.

Phase transition barriers depend on the size of the nanocrystal, but in a complex way. This variation depends on the state of the surface or interface and the presence or otherwise of crystal defects.

## 2.3 Geometric Evolution of the Lattice in Nanocrystals

### 2.3.1 Grain Size Dependence

Reducing the size of nanocrystals changes the stability of the various crystal phases, so it is reasonable to ask whether this reduction is not also accompanied by some change in the lattice parameters for a given phase. For the moment, this question has received less attention than the phase transitions themselves, largely because experimental determination of lattice parameters is difficult in nanocrystals and requires high accuracy. This means that few data are yet available.

#### Lattice Geometry

##### *Demonstrating Grain Size Dependence*

Let us return to the example of BaTiO<sub>3</sub>, already illustrated in Fig. 2.4 on p. 38. It has been observed that, in the case of the tetragonal perovskite lattice obtained for nanocrystal diameters  $\Phi > 80$  nm, the tetragonal aspect ratio given by  $c/a$  falls off as  $\Phi$  decreases. However, the volume  $V = a^2c$  of the unit cell remains constant [3]. This is therefore a grain size dependence in the geometry of the crystal structure. This phenomenon was first discovered about fifty years ago [19] and then investigated further [3, 20].

##### *Demonstrating the Absence of Grain Size Dependence*

Despite the spectacular and entirely repeatable nature of this observation, it is not universal. Indeed, in the case of zinc oxide, for example, which crystallises according to a hexagonal system, no variation of the ratio  $c/a$  has been observed here when the dimensions of the elementary crystals are reduced from a few microns to a few nanometers [21].

This difference of behaviour is not yet understood. An explanation should probably be sought in the structural differences which induce major differences in physical properties, especially with regard to ferroelectricity. Indeed, the BaTiO<sub>3</sub> lattice is polar, thereby contributing to the ferroelectric nature of

tetragonal BaTiO<sub>3</sub>, whereas the ZnO lattice is not polar. It would seem that, in ferroelectric materials, size effects are relevant even for relatively large sizes and, in these materials, one must take into account changes in the polarisation at the interface between the solid and the surrounding medium. For small crystals of BaTiO<sub>3</sub> and considering only the effects on the crystal state, it is thus observed that the tetragonality of the lattice is already affected for sizes of the order of 1  $\mu\text{m}$ .

### Lattice Parameter

Beyond the critical diameter of 80 nm, BaTiO<sub>3</sub> stabilises in a cubic structure. Figure 2.4 shows an increase in the lattice parameter when the average grain size goes down. It would thus seem that there is a grain size dependence in the volume of the unit cell of the crystal lattice. In fact, as we shall see later, this phenomenon is not, at least not for the main part, related to the reduction in size of the nanocrystals, but is due rather to the action of certain heat treatments used on their surfaces to control their size.

In some cases, a grain size dependence is observed in the parameters specifying the crystal structure. However, the few available examples are insufficient to conclude that this is a general effect, and a fortiori, cannot yet provide a full understanding.

### 2.3.2 Theory

Grain size dependence due to the surface or interface can be described using a thermodynamic approach, by considering the surface or interface as a whole, or using a microscopic approach, describing in detail the relaxation and reconstruction effects. For very small nanocrystals, there are also quantum confinement effects.

#### Thermodynamic Approach

Laplace's law is often used to describe the dependence of the lattice parameter on grain size. This law relates the pressure  $P_{\text{int}}$  inside the grains to the pressure  $P_{\text{ext}}$  outside, the surface energy  $\gamma$ , and the grain size  $\phi$ :

$$P_{\text{int}} = P_{\text{ext}} + 4\gamma/\phi .$$

The term  $4\gamma/\phi$  is positive, since  $\gamma$  is an excess energy at the surface of the solid and hence necessarily positive. Hence, when the grain size  $\phi$  goes down, the term  $4\gamma/\phi$  grows larger, leading to an increased pressure inside the grains. This would mean that the lattice parameter should decrease in every case. This is indeed what is observed for the ferrites of Co and Mn [22]. However,

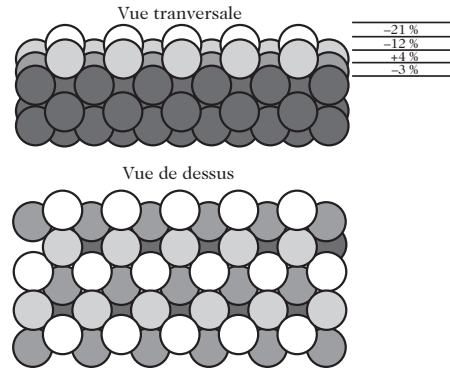
in both  $\text{BaTiO}_3$  [3] and  $\gamma\text{-Fe}_2\text{O}_3$  [23], the lattice parameter actually increases, in direct contradiction with the above law!

A more careful analysis can explain this apparent paradox, showing that it is the surface stress  $\Gamma$  that should appear in the last equation, rather than the surface energy [24]. So there is no longer any contradiction between reducing the grain size and observing an increase in the lattice parameter, since the pressure within the grain can be diminished if the stress  $\Gamma$  is negative. Note that the energy, which depends on the square of the stress, does remain positive. The thermodynamic approach shows that, depending on the state of the surface, one may see either a contraction or an expansion of the atomic bonds within the nanocrystal.

### Microscopic Approach

When a surface is created, the atomic planes near the surface are usually displaced. The direction and magnitude of this relaxation depends on the type of material and also the orientation of the surface. In rare gas crystals or ionic crystals, for example, the bonds between the atoms are relatively long-range. In the bulk, the relative position of the atoms is determined by the competition between the mutual repulsion of the nuclei and long-range forces (Coulombic in the case of ionic crystals). In this case, the atomic planes at the surface expand [25,26]. In the case of face- or body-centered cubic metals, the situation is generally different: for close-packed planes without defects, a very small surface relaxation is generally observed. On the other hand, if a close-packed surface has a certain degree of roughness due to the presence of defects such as steps or islands, or if the surface is not close-packed, the outermost layer will relax considerably towards the core of the material, whilst certain layers further in will move toward the surface. As an example, Fig. 2.9 shows the various motions of the (210) surface planes in platinum [27]. These different relaxations compensate for the fact that the atoms at the surface have fewer near neighbours, whence the electron density is lower there. Relaxation is thus a way of compensating for changes in the electron density in each plane, in such a way as to make it as homogeneous as possible right out to the outermost surface.

Consider now a nanocrystal with approximately spherical shape. Relaxation of the first atomic planes will lead in this case to a pressure exerted by the surface on the core of the nanocrystal, and hence to an increase or a decrease in the lattice parameter. An effect is therefore induced not only by the adsorption state of the surface, but also by the surface itself. This effect is even more marked in semiconductors, where surfaces are generally reconstructed, in order to minimise the number of dangling bonds, which generates large stresses in the first layers. In a nanocrystal, these stresses will also contribute to the surface pressure and to the contraction or expansion of atomic bonds. For example, simulations of Ge nanocrystals with surface composed of



**Fig. 2.9.** Schematic description of surface relaxation effects in the case of a Pt (210) surface. These relaxations are deduced from models based on LEED (low energy electron diffraction) studies [26]

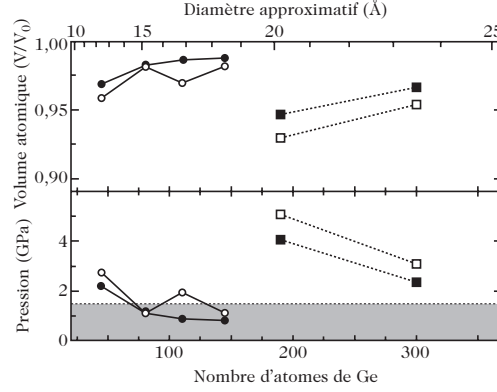
reconstructed layers have indicated a reduction in the structure parameter of up to 6% for 2-nm nanoparticles [28].

We have limited the discussion here to clean surfaces. In the more complicated case where there is adsorption on nanocrystal surfaces, it is not possible a priori to guess whether one will observe a contraction, or rather an expansion of the surface planes, i.e., a reduction or an increase in the lattice parameter. In the present state of our understanding, only a detailed analysis in each particular case can provide an answer to this question.

### Quantum Confinement

A priori, there is no reason to expect any particular variation in the structure parameters due simply to a reduction in the volume of the nanocrystal. However, for very small dimensions, of the order of a few nanometers, a quantum confinement effect occurs, leading among other things to a change in the electronic structure. This change is accompanied by a shortening of the atomic bonds within the nanocrystal. This effect is relatively small and difficult to demonstrate experimentally. However, although this variation is small, it has been obtained in simulations for Ge nanoparticles (see Fig. 2.10) [28, 29]. The surfaces, passivated by hydrogen, have little influence in this case, and the bond contraction observed does indeed arise as a consequence of quantum confinement. The effect nevertheless remains very slight, even for very small nanocrystals with diameters of the order of 2 nm.

The variation of the parameters describing crystal structure can be understood in relation to the nanocrystal surface using either thermodynamic or microscopic approaches.



**Fig. 2.10.** Calculated variation of the atomic volume and the associated pressure as a function of the size of Ge nanocrystals. Two types of structure are considered: diamond cubic (*black symbols*) and ST12 (*white symbols*); and two surface states: hydrogen passivated (*circles*) and with reconstructed layers (*squares*)

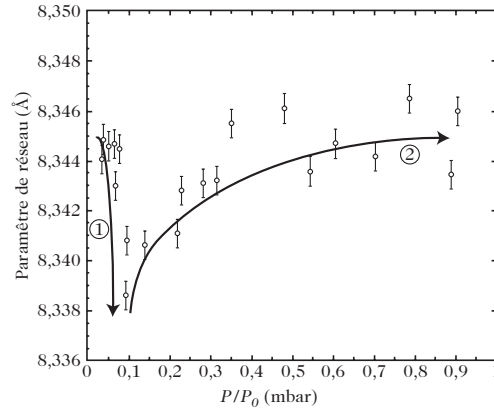
### 2.3.3 Influence of the Nanocrystal Surface or Interface on the Lattice Parameter

Several experiments have shown a relationship between the adsorption state of nanocrystal surfaces and the change in the lattice parameter. Hence, for nanocrystals in ceramic powders like  $\text{BaTiO}_3$  [30] or  $\text{SrTiO}_3$  [31], the presence of water molecules and  $\text{OH}^-$  ions on the surface causes an increase in the lattice parameter. After desorption of the molecules by a suitable heat treatment, the values for the bulk solid are recovered.

Figure 2.11 shows how one may adjust the lattice parameter in  $\gamma\text{-Fe}_2\text{O}_3$  by varying the surface energy of the nanocrystal. There are two clearly distinct regimes: first a contraction of the nanocrystal, and then an expansion. The first regime corresponds to a phase in which  $\text{OH}^-$  and  $\text{H}_2\text{O}$  are chemisorbed on the surface, and an initial water monolayer is formed, with water vapour pressures below a certain critical value. The second regime, on the other hand, corresponds to the formation of water multilayers by physisorption, and the relaxation of the oxide by strengthening of the bonds between the water layers [32]. The existence of two distinct regimes has also been demonstrated for iron nanoparticles coated with a thin layer of  $\gamma\text{-Fe}_2\text{O}_3$  [33], and also when oxygen is adsorbed on carbon nanotubes [34].

The state of the surface or interface of a nanocrystal can affect the crystal structure parameters. However, it is still difficult to predict this effect or estimate its importance.





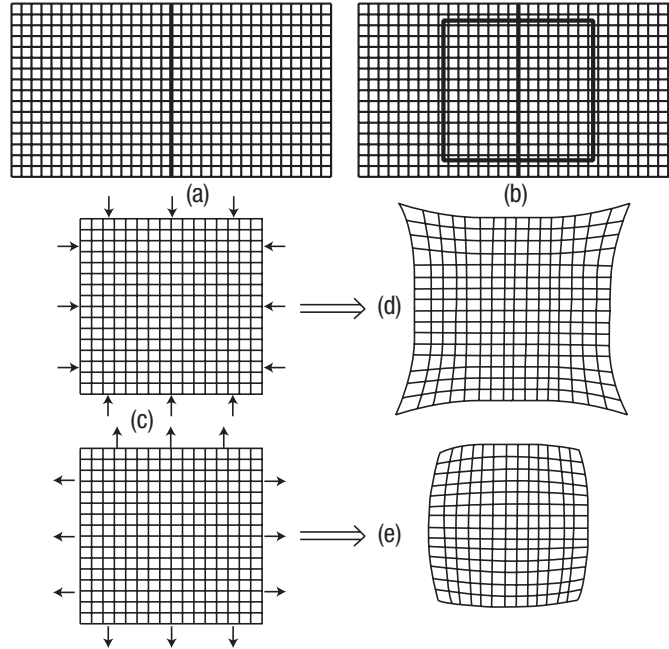
**Fig. 2.11.** Dependence of the lattice parameter for a nanometric  $\gamma\text{-Fe}_2\text{O}_3$  powder on the state of adsorption of water vapour on the powder. For water vapour pressures below a critical value (around  $P/P_0 = 0.1$ ), the formation of a monolayer appears to compress the oxide, whilst for high pressures, the formation of multilayers of water would appear to relax the oxide by strengthening the bonds between water layers [32]. (1) 630 kJ/mol: chemisorption of  $\text{OH}^{2-}$  and physisorption of  $\text{H}_2\text{O}$  (monolayer on  $\gamma\text{-Fe}_2\text{O}_3$ ). (2) 45 kJ/mol: physisorption of  $\text{H}_2\text{O}$  (multilayer on  $\text{H}_2\text{O}$ )

### 2.3.4 Is There a Continuous Variation of the Crystal State Within Nanocrystals?

Experimental results using X-ray diffraction have shown that there is probably, in  $\text{BaTiO}_3$ , a gradient in the crystal organisation as one moves from the surface toward the core of a grain. The average state of the solid is all the more affected by this gradient as the grain size goes down [20]. However, some doubt has been raised concerning this result regarding the evolution of the microstructure in ferroelectric domains, because this too is influenced by grain size and this too shows up in the X-ray diffraction diagram [35, 36].

#### Simple Theoretical Approach

The simplistic idea of obtaining a nanometric grain by ‘cutting’ a nanometric chunk out of an infinite crystal leads one to distinguish the crystalline organisational states in the core of the grain and in those layers influenced by the proximity of the surface (see Fig. 2.12). Following the argument discussed above with regard to surface relaxation, it is easy to imagine that the lattice parameters may vary continuously as one moves away from the surface, inside the crystal.

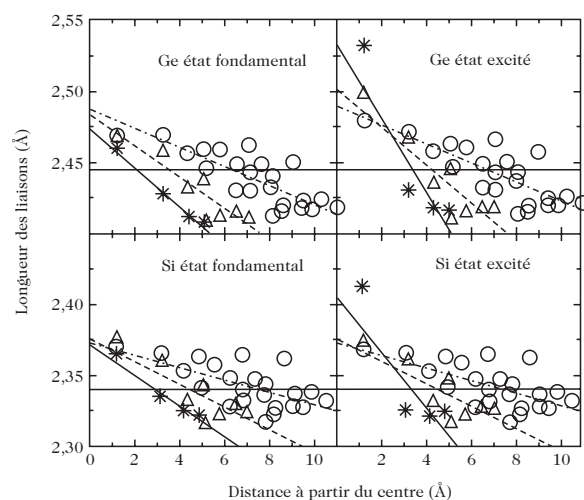


**Fig. 2.12.** Schematic representation of the distortion of the crystal lattices in layers close to the surface of a nanometric grain. **(a)** Infinite undistorted 2D lattice. **(b)** A chunk is cut from the undistorted 2D lattice. **(c)** Isolated chunk, held in the shape of the undistorted lattice by virtue of fictitious stresses equal to those that were exerted by the rest of the lattice on the same chunk before it was cut away. **(d)** Isolated chunk after removal of stresses exerted by the rest of the lattice: the case of an expansion after freeing from stresses. **(e)** Isolated chunk after removal of stresses exerted by the rest of the lattice: the case of a contraction after freeing from stresses

### Simulation

The possibility of bond length variations within nanocrystals as a function of the distance of the bond from the surface has been investigated recently using *ab initio* simulations for Si and Ge [37]. Figure 2.13 shows the way the bond length changes as one moves away from the center of the nanograin. It turns out that, whatever the size of the nanocrystal considered, the crystal structure undergoes a slight dilation at the center which gradually diminishes to become a compression as one approaches the surface. This effect is more important here for Ge than for Si.

In certain cases, simulation predicts an inhomogeneous distribution of the structure parameters within nanocrystals. However, experimental determination remains difficult.



**Fig. 2.13.** Change in bond length as a function of the distance to the center of the nanocrystal for Ge (*top*) and Si (*bottom*) [37]

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