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978-1-107-12313-7 — Imperfections in Crystalline Solids
Wei Cai , William D. Nix
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1 Introduction

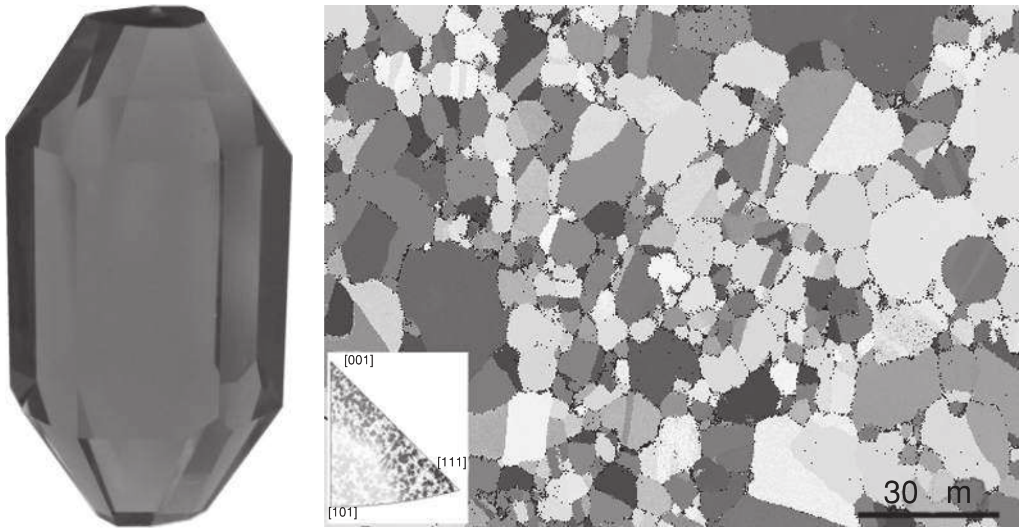
The perfect crystal structure is an idealization of the atomic arrangements in real crystalline materials. After a brief introduction of several common perfect crystal structures, we start our study of imperfections in crystals with some remarks about why so much attention is focused on these defects. The central reason is that perfect crystals, without imperfections, would be relatively uninteresting materials, without most of the useful properties with which we are all familiar. We consider some of the physical properties that crystals would have or not have if they were perfect. Through this thought experiment, we show that most of the useful engineering properties of crystalline materials are defect controlled and thus depend on the properties and behavior of imperfections.

1.1 Perfect crystal structures

1.1.1 Single crystals and polycrystals

The word “crystal” usually brings to mind large mineral (e.g. quartz) blocks on display in museums, or the shiny diamond on a wedding ring. Their faceted surfaces and often distinct geometric shape give rise to a sense of beauty not found in other more “common” materials. As an example, Fig. 1.1a shows a photograph of a ruby crystal. However, crystalline materials are easily found in our everyday life. In fact, most engineering materials are crystalline. Metals, semiconductors, and ceramics are all crystalline materials, even though they may not have faceted surfaces.

The distinction between a large ruby crystal and an engineering metallic alloy is that the former is a single crystal and the latter is usually a polycrystal. A polycrystal is an aggregate of many small single crystals (called grains), each with a different orientation. As an example, Fig. 1.1b shows a micrograph of a nickel-based superalloy (where the word “super” refers to its superior mechanical properties). The size of each single crystal grain in this superalloy is on the order of 10 to 100 micrometers (μm), too small to be seen by the naked eye. That is why the shape of a piece of metal does not seem faceted to the eye; the facets can be observed with the aid of a microscope.



(a) (b)

Figure 1.1. (a) A ruby single crystal (Al_2O_3 doped with Cr^{3+} ions). (b) Electron back-scatter diffraction map of a polycrystalline Ni-based superalloy, with a stereographic triangle showing the orientations of the different grains. Courtesy of Michael D. Uchic, Materials and Manufacturing Directorate, Air Force Research Laboratory, and used with permission. For clarity see color figures on the book website.

If we examine crystalline materials at a length scale smaller than individual grains, then a superalloy and a ruby crystal have something in common. The atoms inside each single crystal grain are arranged in an impressively ordered, periodic array. The distance between each atom and its nearest neighbors are nearly the same everywhere in the crystal. Furthermore, there is long-range order in each crystal grain, meaning that if we know the local orientation of a cluster of atoms at one side of the grain, we can accurately predict the local orientation of another cluster of atoms at the other side of the grain, even if the two clusters may be millions of atomic distances apart. Such long-range order is unique in crystalline solids, and is not present in non-crystalline (i.e. amorphous) solids such as glass or typical polymers (plastics). It is certainly lacking in fluids (except liquid crystals).

The mathematical idealization to describe the long-range order in crystals is the perfect crystal structure. In the following, we describe a few common perfect crystal structures. The description here is meant to be elementary and readers knowledgeable of perfect crystal structures and Miller indices notation may skip on to Section 1.2. However, it should be emphasized that real crystals deviate from this idealization due to the presence of various types of defects, to be introduced later in this chapter. For more discussion of the lattice and crystal structures see [1].

1.1.2 Cubic crystals with simple basis

Simple cubic crystals

The simplest way to construct a perfect crystal structure is to first imagine a simple cubic lattice and then place the same type of atom at every lattice point. The result is a simple cubic crystal structure, as shown in Fig. 1.2.

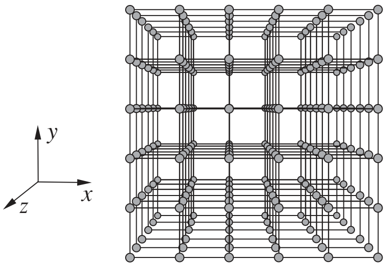


Figure 1.2. A perfect simple cubic crystal structure.

The location of all lattice points can be described by the following expression,

$$\vec{R} = a(u\hat{e}_x + v\hat{e}_y + w\hat{e}_z), \tag{1.1}$$

where a is the *lattice constant*, u, v, w are arbitrary integers, and $\hat{e}_x$, $\hat{e}_y$, $\hat{e}_z$ are unit vectors along the x, y, and z axes. Therefore, any vector or line direction connecting lattice points (i.e. crystallographic directions) can be specified by three integers.[1] In the *Miller indices* notation, the three numbers, u, v, w, are surrounded by square brackets. For example, $[2\,\bar{3}\,4]$ (reads "two three-bar four") represents the vector $(2\hat{e}_x - 3\hat{e}_y + 4\hat{e}_z)$, where it is customary to write the minus sign as a bar on top of the number. Therefore, every point in the simple cubic lattice can be represented by Miller indices as

$$\vec{R} = a[u \quad v \quad w]. \tag{1.2}$$

Angular brackets are used to represent a family of directions that have the same length and are related by symmetry (e.g. reflection). For example, $\langle 2\,3\,4\rangle$ represents the family of directions: $[2\,3\,4]$, $[\bar{2}\,3\,4]$, $[2\,\bar{3}\,4]$, $[2\,3\,\bar{4}]$, $[\bar{2}\,\bar{3}\,4]$, ...

Miller indices can also be used to represent the crystallographic planes. These indices are found by first determining the intercepts that the planes make with the crystallographic axes, dividing each by the lattice constant along that axis, taking the reciprocals and, if necessary, multiplying all of the resulting quantities by the smallest integer to remove any fractions that may have been created. This creates a set of integer Miller indices, h, k, l, for the plane in question, commonly surrounded by parenthesis $(h\,k\,l)$. With this notation any crystallographic plane in a cubic solid can be described by the linear equation $hx + ky + lz = a$. The normal vector extending from the origin to the plane in question is then $a[h\,k\,l]/(h^2 + k^2 + l^2)$; thus the crystallographic direction $[u\,v\,w]$ is perpendicular to the plane $(h\,k\,l)$ if $u = h$, $v = k$, $w = l$. That is, crystallographic directions and planes with the same indices are perpendicular to each other in the cubic crystal system. In addition, it can be shown that the perpendicular distance from the origin to the plane can be expressed as

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}, \tag{1.3}$$

which is the spacing between such crystallographic planes. For crystallographic planes, braces are used to represent a family of planes related by symmetry. For example, $\{2\,3\,4\}$ represents the family of planes: $(2\,3\,4)$, $(\bar{2}\,3\,4)$, $(2\,\bar{3}\,4)$, $(2\,3\,\bar{4})$, $(\bar{2}\,\bar{3}\,4)$, ...

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[1] These numbers may also be fractional numbers for lattices other than the simple cubic lattice.

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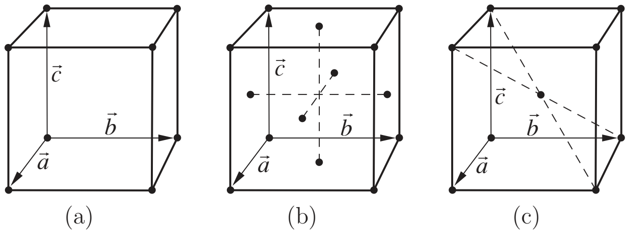

Figure 1.3. (a) The unit cell of a simple cubic lattice. (b) The unit cell of a face-centered cubic (FCC) lattice. (c) The unit cell of a body-centered cubic (BCC) lattice [2].

It is common to define three lattice vectors $\vec{a} = a\hat{e}_x$, $\vec{b} = a\hat{e}_y$, $\vec{c} = a\hat{e}_z$, which are the vectors connecting a lattice point to its neighbors. For the simple cubic lattice, $\vec{a}$, $\vec{b}$, $\vec{c}$ are orthogonal to each other, and all have the same length. These three vectors can be used to construct a cell, which is a cube for the simple cubic lattice, as shown in Fig. 1.3a. In every three-dimensional lattice, we can find such a representative cell that, when repeated, spans all space with no gaps. The smallest possible cell of this type is called the *primitive cell*; each primitive cell contains only one lattice point. However, the lattice is often represented by the *unit cell*, which may have a larger volume than the primitive cell, and hence may contain more than one lattice point. The unit cell is chosen to show the symmetry of the lattice more clearly. For the simple cubic lattice, the unit cell is the same as the primitive cell, which is a cube with lattice points occupying the corners of the cube, as shown in Fig. 1.3a.

It is useful to compute the average volume occupied by each lattice point in the simple cubic lattice, which is the same as the average volume occupied by each atom in the simple cubic crystal structure. Figure 1.3a shows that each unit cell is associated with eight lattice points. However, each lattice point is also shared by eight neighboring unit cells. Therefore, each unit cell contains $8 \times \frac{1}{8} = 1$ lattice point, and the average volume per lattice point is

$$\Omega_{\text{simple cubic}} = \frac{a^3}{8 \times \frac{1}{8}} = a^3. \tag{1.4}$$

Face-centered cubic crystals

While a simple cubic crystal structure is easy to imagine, it is rare to find a crystal in nature with that structure. The most common crystal structures in engineering materials are based on the face-centered cubic (FCC) lattice and the body-centered cubic (BCC) lattice.

The FCC lattice can be visualized by its unit cell, shown in Fig. 1.3b. In addition to placing a point at each of the eight corners of the cube, we also place a point at the center of each of the six faces of the cube. Mathematically, every lattice point in an FCC lattice is given by one of the following expressions in terms of Miller indices:

$$\begin{aligned}
\vec{R} &= a[u \quad v \quad w] \\
\vec{R} &= a[u + 0.5 \quad v + 0.5 \quad w] \\
\vec{R} &= a[u + 0.5 \quad v \quad w + 0.5] \\
\vec{R} &= a[u \quad v + 0.5 \quad w + 0.5].
\end{aligned} \tag{1.5}$$

Gold (Au), silver (Ag), aluminum (Al), and copper (Cu) are all FCC metals.

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Figure 1.3b shows that each FCC unit cell is associated with eight lattice points at the corners and six lattice points at the face centers. However, each corner point is shared by eight neighboring unit cells and each face center point is shared by two neighboring unit cells. Therefore, each unit cell contains $8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4$ lattice points, and the average volume per lattice point is

$$\Omega_{\mathrm{FCC}} = \frac{a^3}{8 \times \frac{1}{8} + 6 \times \frac{1}{2}} = \frac{a^3}{4}. \tag{1.6}$$

This is also the average volume occupied by each atom in the FCC crystal structure. Because the unit cell of the FCC lattice contains more than one lattice point, it is not the primitive cell. The primitive cell of the FCC lattice is a parallelpiped with edges formed by vectors: $\frac{a}{2}[1\,1\,0]$, $\frac{a}{2}[1\,0\,1]$, $\frac{a}{2}[0\,1\,1]$. The cubic symmetry of the FCC lattice is not immediately apparent from its primitive cell.

Body-centered cubic crystals

The unit cell of the BCC lattice is shown in Fig. 1.3c, where a point is placed at the center of the cube, in addition to the eight corners of the cube. Mathematically, the lattice points in a BCC lattice are given by one of the following relations:

$$\begin{aligned} \vec{R} &= a[u \quad v \quad w] \\ \vec{R} &= a[u+0.5 \quad v+0.5 \quad w+0.5]. \end{aligned} \tag{1.7}$$

Tungsten (W), molybdenum (Mo), and tantalum (Ta) are BCC metals. Pure iron (Fe) is also a BCC metal at room temperature.[2]

Figure 1.3(c) shows that each BCC unit cell is associated with eight lattice points at the corners and one lattice point at the body center. While each corner point is shared by eight neighboring unit cells, the point at the body center is not shared with any other unit cells. Therefore, each unit cell contains $8 \times \frac{1}{8} + 1 = 2$ lattice points, and the average volume per lattice point is

$$\Omega_{\mathrm{BCC}} = \frac{a^3}{8 \times \frac{1}{8} + 1} = \frac{a^3}{2}. \tag{1.8}$$

This is also the average volume occupied by each atom in the BCC crystal structure. Because the unit cell of the BCC lattice contains more than one lattice point, it is not the primitive cell. The primitive cell of the BCC lattice is a parallelpiped with edges formed by vectors: $a[1\,1\,\bar{1}]/2$, $a[1\,\bar{1}\,1]/2$, $a[\bar{1}\,1\,1]/2$. The cubic symmetry of the BCC lattice is not immediately apparent from its primitive cell.

The SC, FCC, and BCC lattices, as specified by Eq. (1.2), Eq. (1.5), and Eq. (1.7), respectively, are three types of lattices with different symmetries. The symmetries of infinite, periodic lattices were studied by Auguste Bravais, and these lattices are called *Bravais* lattices. In three dimensions, there are only 14 distinct types of Bravais lattices, which are classified into seven lattice systems [3]. The three lattices (SC, FCC, BCC) introduced here form the cubic lattice system. The hexagonal lattice to be introduced in Section 1.1.4 forms its own (hexagonal) lattice system.

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[2] However, Fe changes to the FCC structure at high temperature, and common stainless steel (an iron–nickel–chromium alloy) also has an FCC structure.

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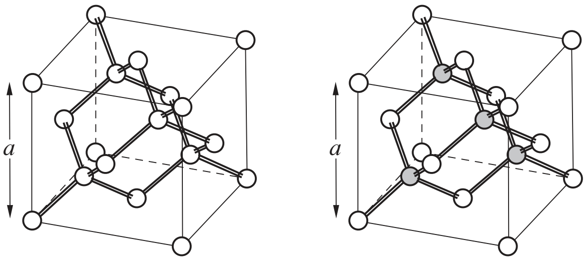

Figure 1.4. (a) The unit cell of the diamond cubic crystal structure. (b) The unit cell of the Zincblende crystal structure. The light and dark spheres represent atoms of two different chemical species. In both (a) and (b), the separation between the two atoms in the basis is $\frac{a}{4}[1\,1\,1]$.

1.1.3 Cubic crystals with complex basis

The crystal structures we have considered so far can be obtained by placing one and the same type of atom at every point of a given lattice. A multi-atom "motif" or "tiling" can be introduced at every lattice point to create more complex crystal structures. Therefore, even though there are only 14 different types of 3D Bravais lattices, the number of possible crystal structures is infinite.

The atomic "motif" placed at each lattice point is called the *basis* of the crystal structure. The basis can be arbitrarily chosen, but exactly the same basis must be placed on every lattice point (no rotation or changing of chemical species is allowed).

For example, a diamond (on a wedding ring) has the diamond cubic (DC) structure, which is created by placing a two-carbon basis at each lattice point of the FCC lattice. Elemental semiconductors such as silicon (Si) and germanium (Ge) have the DC structure. The unit cell of the DC structure is shown in Fig. 1.4a.

Because the DC structure has a two-atom basis, the average volume occupied by each atom in the DC structure is half of that in the FCC structure of the same lattice constant, i.e.

$$\Omega_{\mathrm{DC}} = \frac{\Omega_{\mathrm{FCC}}}{2} = \frac{a^3}{8}. \tag{1.9}$$

Closely related to the DC structure is the Zincblende structure, which is the structure of many Group III–V and II–VI compound semiconductors, such as GaAs, InP, ZnSe, CdTe, etc. The Zincblende structure is formed by placing a basis consisting of two different atoms, such as Ga and As, at every lattice point of the FCC lattice. The unit cell of the Zincblende structure is shown in Fig. 1.4b. Because FCC, DC, and Zincblende crystal structures are all based on the FCC lattice, the types of dislocations (line defects) in these types of crystals are very similar (see Chapter 12).

The sum of the average volume of the two atomic species in the Zincblende structure, e.g. Ga and As, equals the average volume occupied by each lattice point in the FCC lattice, i.e.

$$\Omega_{\mathrm{Ga}} + \Omega_{\mathrm{As}} = \Omega_{\mathrm{FCC}} = \frac{a^3}{4}. \tag{1.10}$$

However, the individual contribution of Ω_{Ga} and Ω_{As} can only be determined by the volume change of the crystal when the mole fraction of Ga and As deviates from the perfect value (50%), i.e. when defects are introduced to the crystal. This will be discussed in Chapter 6.

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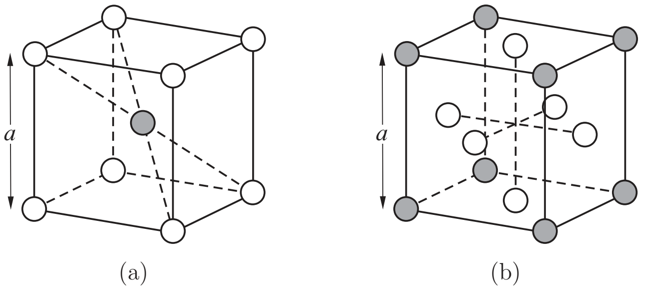


Figure 1.5. (a) The unit cell of the B2 (CsCl) crystal structure. (b) The unit cell of the $L1_2$ (Cu_3Au) crystal structure.

Intermetallic compounds are other types of crystals with multi-atom bases. For example, NiAl has the so-called B2 structure, which is also the structure of CsCl and FeAl. It is obtained by placing a Ni–Al basis at each lattice point of the simple cubic lattice. One atom (say Ni) is placed on the corner of the cube, and the other atom (say Al) is placed at the cube center. The unit cell of the B2 structure is shown in Fig. 1.5a. Note that the B2 structure does not have the BCC lattice, because we are not allowed to place different types of atoms on equivalent lattice points. The average volumes occupied by each Ni atom and Al atom in the NiAl (B2) crystal structure satisfy the relation

$$\Omega_{\mathrm{Ni}} + \Omega_{\mathrm{Al}} = \Omega_{\mathrm{SC}} = a^3. \tag{1.11}$$

Ni_3Al has the so-called $L1_2$ structure, which is also the structure of Cu_3Au and Fe_3Al. It is obtained by placing a four-atom basis (three Ni and one Al) at each lattice point of the simple cubic lattice. The three Ni atoms are placed at the face centers of the cube, and the Al atom is placed at the corner of the cube. The unit cell of the $L1_2$ structure is shown in Fig. 1.5b. The $L1_2$ structure does not have the FCC lattice, for the same reason that the B2 structure does not have the BCC lattice. The average volumes occupied by each Ni atom and Al atom in the Ni_3Al ($L1_2$) crystal structure satisfy the relation

$$3\Omega_{\mathrm{Ni}} + \Omega_{\mathrm{Al}} = \Omega_{\mathrm{SC}} = a^3. \tag{1.12}$$

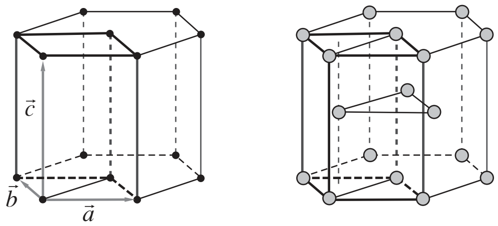
1.1.4 Hexagonal close-packed structure

The hexagonal close-packed (HCP) crystal structure also has a multi-atom basis. Furthermore, it has a *hexagonal lattice*, instead of a cubic lattice. The unit cell of the hexagonal lattice is shown in Fig. 1.6a.

The lattice points of the hexagonal lattice can be described by the relation

$$\vec{R} = i\vec{a} + j\vec{b} + k\vec{c}, \tag{1.13}$$

where i, j, k are arbitrary integers. This is similar to the expression for the simple cubic lattice. The difference here is that the lattice repeat vectors $\vec{a}$ and $\vec{b}$ are at 120° relative to each other, and $\vec{c}$ does not have the same length as $\vec{a}$ and $\vec{b}$. Vectors $\vec{a}$ and $\vec{b}$ still have the same length, and vector $\vec{c}$ is perpendicular to both $\vec{a}$ and $\vec{b}$. The basis of the HCP crystal structure contains two atoms of the same chemical species. The unit cell of the HCP crystal structure is shown in



(a) (b)

Figure 1.6. (a) The hexagonal lattice, whose unit cell is outlined by thick lines. (b) The hexagonal close-packed (HCP) crystal structure, whose unit cell is outlined by thick lines. One of the two atoms in the basis occupies the lattice point. The other atom in the basis lies immediately above the center of the triangle formed by three lattice points below.

Fig. 1.6b. Magnesium (Mg), titanium (Ti), zinc (Zn), and cobalt (Co) are some of the HCP metals.

The average volume occupied by each lattice point in the hexagonal lattice is

$$\Omega_{\text{hex. latt.}} = \frac{\sqrt{3}}{2} a^2 c, \tag{1.14}$$

where $a = |\vec{a}| = |\vec{b}|$, and $c = |\vec{c}|$. The average volume occupied by each atom in the HCP crystal structure is half of that,

$$\Omega_{\text{HCP}} = \frac{\Omega_{\text{hex. latt.}}}{2} = \frac{\sqrt{3}}{4} a^2 c. \tag{1.15}$$

The HCP crystal structure is closely related to the FCC crystal structure. Both FCC and HCP crystal structures are close-packed structures, meaning that they provide the maximum packing density if we imagine packing hard spheres of uniform radius into a pile. When an FCC crystal is viewed along the cubic diagonal direction $\hat{n} = \frac{1}{\sqrt{3}}[1\,1\,1]$, it can be considered as three types of triangular lattices A, B, C, stacked on top of each other in the sequence of $ABCABC\ldots$ (see Section 11.1). If the stacking sequence is changed to $ABABAB\ldots$, we get the HCP crystal structure instead (see Section 11.2.2). Therefore the FCC and HCP crystal structures can be transformed to each other by shear deformation.

1.2 Defect-controlled properties of crystals

While the perfect crystal structure captures the long-range order that exists in crystals, it would be a mistake to think of a real crystal as a collection of atoms located exactly according to the perfect crystal structure. Deviation from the perfect structure, i.e. imperfections, are vital to the physical, chemical, and electronic properties of the crystal. In order to emphasize the imperfection of real crystals, J. Frenkel in the opening chapter of his classic book, *Kinetic Theory of Liquids*, argues that crystalline solids actually have a lot in common with liquids (except for the long-range order, of course). In this section, we imagine how a crystal would behave if all atoms were located at their perfect crystal positions.

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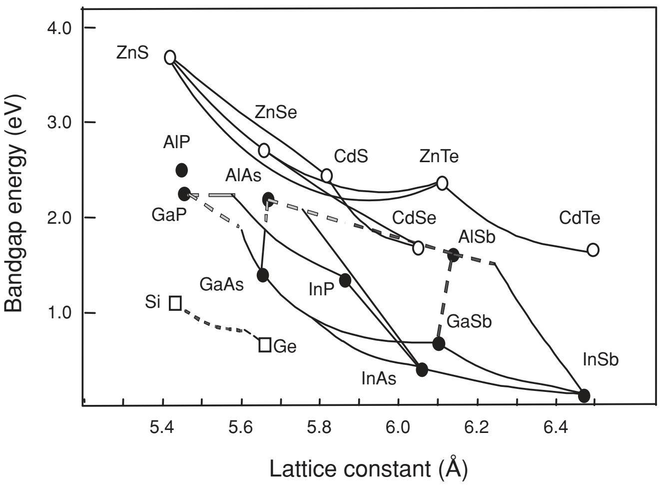

Figure 1.7. Band gap engineering – controlling the electronic band gaps in semiconductors by controlling the composition (point defect concentration). Band gap energy and lattice constant of various III–V semiconductors at room temperature. Figure adapted from one kindly provided by Professor James S. Harris of Stanford University and used with permission.

Consider an absolutely perfect crystal with all of the atoms sitting exactly on their respective lattice points, such as the one shown in Fig. 1.2, and all of the electrons in their lowest energy states. In such a perfect crystal there would be no lattice vibrations or phonons and thus no thermal conductivity. Nor would there be any heat capacity, as the constituent atoms would not be able to store thermal energy in their vibrations.

In addition, for such a perfect crystal, there would be no way to accomplish compositional changes by diffusion because there would be no atomic point defects. This would prevent us from making transistors by diffusion of dopants into silicon or do any other kind of alloying by solid-state diffusion.

Solid solution alloys are also needed for band gap engineering, which leads to semiconductor compounds with different electronic band gaps. As shown in Fig. 1.7, various Group III–V semiconductors (with Zincblende crystal structure, see Section 1.1.3) have different lattice constants as well as different band gaps. The band gap is the energy difference of the electrons between the top of the (filled) valance band and the bottom of the (empty) conduction band. The band gap is directly related to the wavelength of the light that the semiconductor can absorb or emit. By mixing two different semiconductors, e.g. GaAs and InAs, thus creating an imperfect crystal, the lattice constant of the crystal can be tuned between the two limits. The elastic strain on the lattice is coupled to the electronic band structure so that the band gap can also be tuned. The lattice constant and band gap of the impure crystal formed by mixing GaAs and InAs follow the curve connecting GaAs and InAs in Fig. 1.7. Band gap engineering enables, for example, the development of lasers at specific wavelengths for which the absorption in an optical fiber or in air is particularly low. Band gap engineering is made possible only by imperfect crystals.

If we only have perfect crystals to work with, it would not be possible to plastically deform a metal, preventing metal forming, and making it all but impossible to make such things as trains, tractors, airplanes, automobiles, and so on. Such perfect materials would be extremely strong but

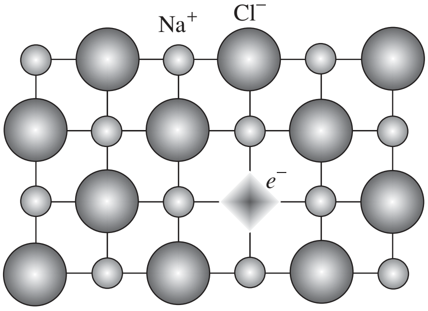

Figure 1.8. F-center in a NaCl crystal.

you could never change their shape by plastic deformation because crystal dislocations would not exist.

You would also not have transformers for changing voltage and current in everyday applications. Transformer cores depend on easy magnetization and demagnetization by the movements of defects in the magnetic structure of the crystals in the cores.

These are but a few examples of the useless properties that crystalline materials would have if they were composed of perfect crystals. Virtually all of the interesting properties that crystalline materials display arise from imperfections.

The control of imperfections in crystalline materials lies at the heart of materials science. Indeed, the very definition of materials science can be stated as: *the synthesis of useful engineering materials and the control of their properties through the control of composition and microstructure*. For crystalline materials the control of microstructure involves the control of crystal imperfections.

It is also worth noting that the most technologically important properties of crystalline materials are defect controlled. While elasticity does not involve defects, strength and plasticity do and so do most of the other engineering properties of interest.

Although one does not usually think of color as a property that can be controlled, for ceramic crystals color is very much defect controlled. Consider corundum or Al_2O_3, which is colorless in its pure state. We call this sapphire. If just 1% of the Al atoms in the crystal lattice are replaced by Cr atoms we have a red crystal called ruby. Alternatively, if 1% of the Al atoms are replaced by Ti or Fe atoms we have a blue crystal called blue sapphire.

Another example involves the color of alkali halide crystals, like KCl and NaCl. When these crystals are pure and relatively perfect they are colorless. By shining X-rays onto these crystals, lattice defects called F-centers,[3] which are anion (Cl^-) vacancies containing a trapped electron, are created (see Fig. 1.8). Such defects cause KCl to turn blue and NaCl to turn yellow. The color is controlled by the energy level of the electron that is trapped in the vacancy. Thus the color of ceramic crystals can be controlled by the control of atomic point defects.

Even though defects control most of the important properties of crystalline materials, typically only a very tiny fraction of all of the atoms in the crystal are involved in defects. Furthermore, defects must be well separated in the crystal lattice in order to have individual properties

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[3] The F stands for Farbe (German for color), so that F-center is also called color center.