Table 1.1. Electron wave lengths (in pm) for selected acceleration voltages V for scanning electron microscopes (left two columns) and transmission electron microscopes (right two columns).

V (Volt)	λ (pm)	V (Volt)	λ (pm)
1 000	38.76	100 000	3.701
5 000	17.30	200 000	2.508
10 000	12.20	300 000	1.969
20 000	8.59	400 000	1.644
		1 000 000	0.872

where $m_n = 1.674\,929 \times 10^{-27}$ kg is the neutron rest mass and v is its velocity. However, neutrons are not charged particles and, therefore, they are not accelerated by a voltage. Neutrons are created in nuclear fission processes inside nuclear reactors, as described in more detail in Chapter 13. Typically, a wide range of neutron velocities emerges from the reactor, and by selecting only neutrons within a certain narrow velocity window, one can select a particular wave length. For instance, to obtain a neutron with a wave length of 0.1 nm, one would have to select a velocity window at $v = 3.96 \times 10^3$ m/s, or approximately 4 km/s. It is also possible to have neutrons reach thermal equilibrium, so that their kinetic energy is:

$$E_{kin} = \frac{1}{2} m_n v^2 = \frac{3}{2} k_B T, \tag{1.7}$$

where $k_B = 1.38 \times 10^{-23}$ J/molecule/K is the Boltzmann constant. The de Broglie relation then becomes:

$$\lambda = \frac{h}{\sqrt{3 m_n k_B T}}. \tag{1.8}$$

1.5 What is a material property?

1.5.1 Definition of a material property

We choose materials to perform well in certain applications. For instance, we use steel beams and cables in bridges, because they provide the strength and load-bearing capacity needed. We use plastics in toys because they can be molded into virtually any shape and they are strong and light weight. When we use a material in a certain application, we know that it will be subjected to particular external conditions, e.g., a constant load, or a high temperature, or perhaps an electrical current running through the material. In all these cases, we must make sure that the material responds in the desired way. For a bridge deck held up by steel cables, we want the cables to retain their strength

all year round, regardless of the weather and temperature, and regardless of the number of cars and trucks crossing the bridge. For a computer chip, we want the semiconductor material to behave predictably for the lifetime of the computer.

In general, we want a material to have a particular response to a given external influence. This basic statement can be cast in more formal, mathematical terms. We will represent the external influence by the symbol $\mathcal{F}$, which stands for *Field*. This could be an electrical or magnetic field, a temperature field, the earth's gravitational field, etc. The material will respond to this field, and the *Response* is described by the symbol $\mathcal{R}$. For instance, the response of a steel beam to an external load (i.e., a weight at the end of the beam) will be a deflection of the beam. The response of a conductor to an electrical field applied between its two ends will be an electrical current running through the conductor. In the most general sense, the relation between field and response is described by:

$$\mathcal{R} = \mathcal{R}(\mathcal{F}), \tag{1.9}$$

i.e., the material response is a function of the externally applied field. It is one of the tasks of a materials scientist to figure out what that function looks like.

Once we recognize that the behavior of a material under certain external conditions can be expressed in mathematical terms, we can employ mathematical tools to further describe and analyze the response of this material. We know from calculus that, for "well-behaved" functions, we can always expand the function into powers of its argument, i.e., construct a Taylor expansion.[4] For equation 1.9 above, the Taylor expansion around $\mathcal{F} = 0$ is given by:

$$\mathcal{R} = \mathcal{R}_0 + \frac{1}{1!}\frac{\partial \mathcal{R}}{\partial \mathcal{F}}\bigg|_{\mathcal{F}=0}\mathcal{F} + \frac{1}{2!}\frac{\partial^2 \mathcal{R}}{\partial \mathcal{F}^2}\bigg|_{\mathcal{F}=0}\mathcal{F}^2 + \frac{1}{3!}\frac{\partial^3 \mathcal{R}}{\partial \mathcal{F}^3}\bigg|_{\mathcal{F}=0}\mathcal{F}^3 + \dots \tag{1.10}$$

where $\mathcal{R}_0$ describes the "state" of the material at zero field. There are two possibilities for $\mathcal{R}_0$:

(i) $\mathcal{R}_0 = 0$: in the absence of an external field ($\mathcal{F} = 0$), there is no permanent (or remanent) material response. For example, if the external field is an applied stress, and the material response is a strain, then at zero stress there is no strain (assuming linear elasticity).

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[4] Recall that a Taylor expansion of a function $f(x)$ around $x = 0$ is given by

$$f(x) = f(0) + \sum_{n=1}^{\infty}\frac{1}{n!}\frac{d^n f}{dx^n}\bigg|_{x=0}x^n$$

where $n! = 1 \times 2 \times 3 \times \dots \times (n-1) \times n$ is the factorial of n. If the function f depends on other variables in addition to x, then the derivatives d^n/dx^n must be replaced by partial derivatives $\partial^n/\partial x^n$.

(ii) $\mathcal{R}_0 \neq 0$: in the absence of an external field ($\mathcal{F} = 0$), there is a permanent material response. For example, in a ferromagnetic material, the net magnetization is nonzero even from zero, even at zero applied field.

If we truncate the series after the second term, i.e., we ignore all derivatives of $\mathcal{R}$ except for the first one), then the expression for $\mathcal{R}$ is simplified dramatically:

$$\mathcal{R} = \mathcal{R}_0 + \frac{\partial \mathcal{R}}{\partial \mathcal{F}}\Big|_{\mathcal{F}=0} \mathcal{F} = \mathcal{R}_0 + \mathbf{P}\mathcal{F} \quad \text{with} \quad \mathbf{P} \equiv \frac{\partial \mathcal{R}}{\partial \mathcal{F}}\Big|_{\mathcal{F}=0} \tag{1.11}$$

This is a *linear* equation between the applied field and the response. The quantity $\mathbf{P}$ is a *material property*. Ignoring the higher order derivatives of $\mathcal{R}$ is generally known as *linear response theory*. This approximation simplifies things considerably and, for many purposes, is a useful and accurate approximation.

Let us consider an example. An electrical conductor, say, a copper wire, is placed between the terminals of a battery. If the wire is 3 meters long, and the battery is capable of producing a 9 V voltage drop, then there is an electric field, E, of 9 volts per 3 meter, or $E = 3\,\text{V/m}$. In response to this field, a current will flow through the wire. The amount of current depends on the cross section of the wire, so it is convenient to work in terms of current density (current per unit area, or A/m^2), j. For most conductors, the relation between current density and electric field is linear, i.e.,

$$j = \sigma E,$$

where σ is known as the *electrical conductivity*, and has units of A/Vm or 1/Ωm, where Ω stands for ohm (1 ohm = 1 V/A). Let us compare this equation with the Taylor expansion in Eq. 1.10. The external field $\mathcal{F}$ is equal to E, and the response $\mathcal{R}$ is equal to j. First of all, when there is no voltage, there will be no current, so that $\mathcal{R}_0 = j_0 = 0$. There is no dependence on powers of E, so there is only one term in the series, namely:

$$j = \frac{\partial j}{\partial E}\Big|_{E=0} E \quad \text{and hence} \quad \sigma \equiv \frac{\partial j}{\partial E}\Big|_{E=0}.$$

We conclude that σ is equal to the first derivative of the current density with respect to the electric field. This proportionality factor does not depend on j or E, therefore we call σ a material property. In more general terms, *a general material property is the proportionality factor between an applied field and the resulting material response.*

1.5.2 Directional dependence of material properties

In the previous section, we saw that the current density, j, in a conductor is proportional to the applied electric field, E. The proportionality factor is the

conductivity σ. All three quantities in the previous relation were scalar quantities. However, we can imagine taking a rectangular block of a conducting material, and applying an electric field between the top and bottom surfaces, or between the front and back surfaces, or between opposite corners. This means that the electric field has both a magnitude and a direction, hence it can be represented by a vector, $\mathbf{E}$.[5] The same thing can be said of the current density, since the current has a magnitude and it runs in a particular direction. Hence, we have a vector $\mathbf{j}$. The relation between electric field and current density then reads:

$$\mathbf{j} = \sigma \mathbf{E}.$$

Since σ is a scalar (i.e., a number), this means that the current density vector is always parallel to the electric field vector. Well, not quite. When we defined the conductivity, we started from the relation:

$$\sigma = \left.\frac{\partial j}{\partial E}\right|_{E=0}.$$

But this relation is only valid for scalar j and E. We must incorporate the fact that both $\mathbf{j}$ and $\mathbf{E}$ are vectors into this equation. Both vectors have components with respect to a standard Cartesian reference frame: $\mathbf{j} = (j_x, j_y, j_z)$ and $\mathbf{E} = (E_x, E_y, E_z)$. So, instead of having only one single value for σ, now we have a total of nine values! Here's how that works. Consider the following expression:

$$\left.\frac{\partial j_x}{\partial E_x}\right|_{E=0}.$$

In other words, this is the derivative of the x-component of the current density with respect to the x-component of the electric field. This derivative will have a particular value (a scalar value) which we will represent by σ_{xx}. Similarly, we can define

$$\sigma_{xy} = \left.\frac{\partial j_x}{\partial E_y}\right|_{E=0},$$

and so on. There are nine such relations, which can be summarized by writing:

$$\sigma_{ij} = \left.\frac{\partial j_i}{\partial E_j}\right|_{E=0},$$

---

[5] In this book, we will always use bold characters to represent vectors.

where the subscripts or indices i and j take on the values x, y, and z. The relation between the current density vector and the electric field vector is then given by:

$$j_x = \sigma_{xx}E_x + \sigma_{xy}E_y + \sigma_{xz}E_z;$$
$$j_y = \sigma_{yx}E_x + \sigma_{yy}E_y + \sigma_{yz}E_z;$$
$$j_z = \sigma_{zx}E_x + \sigma_{zy}E_y + \sigma_{zz}E_z.$$

This relation expresses the fact that the current density, in response to an electric field, need not be parallel to this electric field. Each component of the current density is written as a linear combination of *all* the components of the electric field.

What we learn from the above example is that a material property is not always represented by a simple scalar. If the property connects a vector field to a vector response, then the material property has nine elements, which can be written as a 3×3 matrix. Mathematicians call such a matrix a *tensor*.[6] The question then arises: Do we need nine numbers for the electrical conductivity of every material, or is it possible that some materials need fewer numbers? The answer to this question will become clear in the next section, where we introduce the concept of symmetry. Before we do so, let us first consider the possibility that a material property varies with location in the material.

It is intuitively clear that an external field can depend on location. For instance, the temperature at one end of a material can be different from the temperature at the other end. In mathematical terms, this means that the *gradient* of the temperature does not vanish. It is possible for a material property to show a similar dependence on position within the material. Consider, for instance, a cube of pure silicon. It is clear that the chemical composition of this cube is the same everywhere, since there is only one chemical element present. We say that the composition is *homogeneous*, i.e., the composition does not depend on position. Similarly, the electrical conductivity of pure silicon is the same everywhere, so that the electrical conductivity is homogeneous. Imagine, next, that we implant phosphorus atoms on one side of the cube, to a depth of a few hundred microns. Since the phosphorus concentration is not a constant throughout the cube, we say that the composition is *heterogeneous*, i.e., the concentration depends on the location in the material. Since phosphorus has five electrons in its outer shell, whereas silicon has only four, we see intuitively that the electrical conductivity in the regions that contain P must be different from that of the other regions. In other words, the electrical conductivity of P-doped silicon is heterogeneous if the P is not distributed in a homogeneous way.

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[6] The definition and properties of tensors need not concern us here. It is sufficient that the reader understands that material properties often consist of multiple scalars, arranged in a particular form (in this case, a 3×3 matrix).
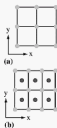
1.5.3 A first encounter with symmetry

Fig. 1.4. Illustration of two simple 2-D crystal structures: (a) is based on a square grid with one type of atoms, while (b) is a rectangular grid with two different kinds of atoms. The electrical conductivities in the x and y directions for (a) are expected to be the same, whereas the most likely different for the second structure.

One might ask what the previous section has to do with crystallography. That's a very good question, and we will attempt to answer it superficially in this section. Consider a 2-D material in which the atoms are arranged as shown schematically in Fig. 1.4(a). All atoms are identical, and they are located on the nodes of a square grid. If we apply an electric field along the x-axis, we will generate a certain current density (assuming that our 2-D material is a conductor). If we apply the same field strength in the y direction, then there is no reason why the current density along y should be any different from that along x. After all, the structure looks exactly the same along the x and y directions. The relation between electric field and current density in this 2-D material can be written as:

$$\begin{pmatrix} j_x \\ j_y \end{pmatrix} = \begin{pmatrix} \sigma_{xx} & \sigma_{xy} \\ \sigma_{yx} & \sigma_{yy} \end{pmatrix} \begin{pmatrix} E_x \\ E_y \end{pmatrix}. \tag{1.12}$$

Since the x and y directions in the crystal are equivalent, we can interchange them. In other words, we interchange the subscripts in the material property matrix:

$$\begin{pmatrix} \sigma_{xx} & \sigma_{xy} \\ \sigma_{yx} & \sigma_{yy} \end{pmatrix} \rightarrow \begin{pmatrix} \sigma_{yy} & \sigma_{yx} \\ \sigma_{xy} & \sigma_{xx} \end{pmatrix}.$$

If we apply the electric field along the same direction as before, we obtain:

$$\begin{pmatrix} j_x \\ j_y \end{pmatrix} = \begin{pmatrix} \sigma_{yy} & \sigma_{yx} \\ \sigma_{xy} & \sigma_{xx} \end{pmatrix} \begin{pmatrix} E_x \\ E_y \end{pmatrix}. \tag{1.13}$$

The response in this case must be equal to the response in (1.12), so that we must have:[7]

$$\begin{pmatrix} \sigma_{xx} & \sigma_{xy} \\ \sigma_{yx} & \sigma_{yy} \end{pmatrix} = \begin{pmatrix} \sigma_{yy} & \sigma_{yx} \\ \sigma_{xy} & \sigma_{xx} \end{pmatrix}, \tag{1.14}$$

which means that

$$\sigma_{xx} = \sigma_{yy} \quad \text{and} \quad \sigma_{xy} = \sigma_{yx}. \tag{1.15}$$

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[7] This procedure is mathematically not entirely rigorous. An exact derivation requires the use of the transformation formula for a second rank tensor, which is beyond the scope of this textbook. The exact derivation for the case illustrated above would result in the following equalities:

$$\sigma_{xx} = \sigma_{yy} \quad \text{and} \quad \sigma_{xy} = -\sigma_{yx}.$$

So, we have established that, for a crystal with the structure shown in Fig. 1.4(a), the components of the conductivity matrix are related to one another by the above relations. The fact that the current densities in the x and y directions must be equal to each other is a reflection of the *symmetry* of the underlying crystal structure.[8] The square character of the grid directly leads to relations 1.15.

This is an example of how the symmetry of a structure imposes constraints on the physical (or material) properties of the structure. This simple observation provides an immediate motivation for a textbook on crystal structures: many material properties are directly determined by the crystal structure of the material, i.e., the precise distribution of the atoms. To understand material properties, and to design materials with new properties, we must, therefore, understand how the atoms are arranged. This consists of two parts: first, we must learn the proper language to describe crystal structures; then, we must learn how to determine where the atoms are located. We will learn both of these aspects in the first half of the book. Then, we will apply what we have learned to a large variety of crystal structures in the second half.

Before we provide a further illustration of what this book is all about, we must conclude the example that we started at the beginning of this section. There is more to material properties than just the underlying crystal structure. Material properties must also satisfy additional laws of physics, in particular, the laws of *thermodynamics*. In the case of electrical conductivity, one can show that the matrix representing the conductivity must always be a symmetric matrix, i.e., $\sigma_{ij} = \sigma_{ji}$. If we apply this to Equations 1.15, taking into account the footnote on page 14, we find that $\sigma_{xy} = -\sigma_{yx}$, and this can only be true if $\sigma_{xy} = 0$. Hence, thermodynamics and symmetry combine to predict that for the crystal structure shown in Fig. 1.4(a), the relation between current density and electric field must be

$$\begin{pmatrix} j_x \\ j_y \end{pmatrix} = \begin{pmatrix} \sigma & 0 \\ 0 & \sigma \end{pmatrix} \begin{pmatrix} E_x \\ E_y \end{pmatrix} = \sigma \begin{pmatrix} E_x \\ E_y \end{pmatrix}.$$

However, if the crystal structure is based on a rectangular grid rather than a square grid, it can be shown (reader exercise) that $\sigma_{xx} \neq \sigma_{yy}$ so that the relation becomes:

$$\begin{pmatrix} j_x \\ j_y \end{pmatrix} = \begin{pmatrix} \sigma_{xx} & 0 \\ 0 & \sigma_{yy} \end{pmatrix} \begin{pmatrix} E_x \\ E_y \end{pmatrix}.$$

For the crystal structure shown in Fig. 1.4(b), it is intuitively clear that the conductivity along the x and y directions must be different, since the sequence of atoms in each direction is different.

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[8] Note that we will define what a crystal structure is in Chapter 3.

When a material property does not depend on the direction of the applied field, then that property is known as an *isotropic* property. Properties that do depend on the direction of the field are *anisotropic* properties. The electrical conductivity in the crystal structure of Fig. 1.4(a) is isotropic, but in Fig. 1.4(b) the conductivity is anisotropic. Note that it is possible to have anisotropic properties that are homogeneous, but heterogeneous across a crystal; if a property is heterogeneous, it means that the value of the material constants (e.g., the value of the electrical conductivity σ) varies with location in the crystal, perhaps due to chemical inhomogeneities.

Note that the above arguments do not say anything at all about the magnitude of the conductivity parameters. Instead, symmetry and thermodynamics only state which parameters must vanish, and how each parameter is related to the others. The magnitude of the parameters must follow from a different branch of physics, known as *solid state physics*, which would use quantum mechanics and other tools to express the conductivity in terms of more fundamental parameters (i.e., the charge distribution in the material). Once again, knowledge of the underlying crystal structure is essential for these kinds of computations.

There are many material properties. The most important ones are linear properties, meaning that there is a direct proportionality between the field and the response. Others are quadratic in the field, or even higher order. Each material property is represented mathematically as a tensor. Tensors of rank zero are scalars, rank one results in a vector, rank two in a 3×3 matrix, and so on. Table 1.2 shows some of the more important material properties that are represented by tensors. The tensors are grouped by rank, and are also labeled (in the last column) by E (equilibrium property) or T (transport property). The number following this letter indicates the maximum number of independent, non-zero elements in the tensor, taking into account symmetries imposed by thermodynamics. The *Field* and *Response* columns contain the following symbols: ΔT = temperature difference, ΔS = entropy change, E_i = electric field components, H_i = magnetic field components, ϵ_{ij} = mechanical strain, D_i = electric displacement, B_i = magnetic induction, σ_{ij} = mechanical stress, $\Delta\beta_{ij}$ = change of the impermeability tensor, j_i = electrical current density, $\nabla_j T$ = temperature gradient, h_i = heat flux, $\nabla_j c$ = concentration gradient, m_i = mass flux, ρ_i^a = antisymmetric part of resistivity tensor, ρ_i^s = symmetric part of resistivity tensor, $\Delta\rho_{ij}$ = change in the component ij of the resistivity tensor, l_i = direction cosines of electromagnetic wave direction in crystal, and G = optical rotation constant.

It is clear from this table that there are quite a few important material properties. While the details of this table go far beyond this textbook, it is instructive to see that the symmetry of the underlying crystal structure of a material has an influence on *all* these properties.

Table 1.2. Materials property and transport tensors (adapted from Nowick (Nowick, 1995)).

Property	Symbol	Field	Response	Type/#
Tensors of Rank 0 (Scalars)				
Specific heat	C	ΔT	$T\Delta S$	E/1
Tensors of Rank 1 (Vectors)				
Electrocaloric	p_i	E_i	ΔS	E/3
Magnetocaloric	q_i	H_i	ΔS	E/3
Pyroelectric	p_i'	ΔT	D_i	E/3
Pyromagnetic	q_i'	ΔT	B_i	E/3
Tensors of Rank 2				
Thermal expansion	α_{ij}	ΔT	ϵ_{ij}	E/6
Piezocaloric effect	α_{ij}'	σ_{ij}	ΔS	E/6
Dielectric permittivity	κ_{ij}	E_j	D_i	E/6
Magnetic permeability	μ_{ij}	H_j	B_i	E/6
Optical activity	g_{ij}	$l_i l_j$	G	E/6
Magnetoelectric polarization	λ_{ij}	H_j	D_i	E/9
Converse magnetoelectric polarization	λ_{ij}'	E_j	B_i	E/9
Electrical conductivity (resistivity)	σ_{ij} (ρ_{ij})	E_j (j_i)	j_i (E_i)	T/6
Thermal conductivity	K_{ij}	$\nabla_j T$	h_i	T/6
Diffusivity	D_{ij}	$\nabla_j c$	m_i	T/6
Thermoelectric power	Σ_{ij}	$\nabla_j T$	E_i	T/9
Hall effect	R_{ij}	B_j	ρ_i^{e}	T/9
Tensors of Rank 3				
Piezoelectricity	d_{ijk}	σ_{jk}	D_i	E/18
Converse piezoelectricity	d_{ijk}'	E_k	ϵ_{ij}	E/18
Piezomagnetism	Q_{ijk}	σ_{jk}	B_i	E/18
Converse piezomagnetism	Q_{ijk}'	H_k	ϵ_{ij}	E/18
Electro-optic effect	r_{ijk}	E_k	$\Delta\beta_{ij}$	E/18
Nernst tensor	Σ_{ijk}	$\nabla_j T B_k$	E_i	T/27
Tensors of Rank 4				
Elasticity	s_{ijkl} (c_{ijkl})	σ_{kl} (ϵ_{kl})	ϵ_{ij} (σ_{ij})	E/21
Electrostriction	γ_{ijkl}	$E_k E_l$	ϵ_{ij}	E/36
Photoelasticity	q_{ijkl}	σ_{kl}	$\Delta\beta_{ij}$	E/36
Kerr effect	p_{ijkl}	$E_k E_l$	$\Delta\beta_{ij}$	E/36
Magnetoresistance	ξ_{ijkl}	$B_k B_l$	ρ_{ij}^{e}	T/36
Piezoresistance	Π_{ijkl}	σ_{kl}	$\Delta\rho_{ij}$	T/36
Magnetothermoelectric power	Σ_{ijkl}	$\nabla_j T B_k B_l$	E_i	T/54
Second order Hall effect	ρ_{ijkl}	$B_j B_k B_l$	ρ_i^{2}	T/30
Tensors of Rank 6				
Third order elasticity	c_{ijklmn}	$\epsilon_{kl}\epsilon_{mn}$	σ_{ij}	E/56