# 15

# Thermal properties

- What is zero-point energy?
- What solids are named high thermal conductivity materials?
- What physical property does thermoelectric refrigeration utilise?

Heat is a form of energy. Thermal properties describe how a solid responds to changes in this thermal energy. In a normal solid, the constituent atoms are in constant vibration, and the vibrations constitute the thermal energy of the material. The physical aspects of thermal properties – temperature, heat capacity, thermal expansion and thermal conductivity – are the external manifestation of these vibrations. Chemical aspects, such as phase changes and rates of reaction, are equally important. Indeed, it will be apparent that chemical aspects of the thermal properties of solids have been considered already throughout this book. For example, the phase equilibria of Chapter 4 are an expression of the thermal properties of solids. The way in which materials respond to changes in thermal energy is defined as the subject of thermodynamics, some aspects of which have been touched on earlier. In this chapter, aspects of the physical properties of solids not covered previously will be outlined and some new concepts introduced.

## 15.1 Temperature effects

### *15.1.1 Heat capacity*

The heat capacity of a solid quantifies the relationship between the temperature of a body and the energy supplied to it. The ideas date from times when heat was thought to be a fluid that could be transferred from one object to another. If a large amount of heat (energy) supplied to a body produced only a small temperature increase, the solid was said to have a large heat capacity. The heat capacity of a material is defined as:

$$C = \frac{dQ}{dT}$$

where $dQ$ is the amount of energy needed to produce a temperature change of $dT$. The units of heat capacity are $\mathrm{J\,K^{-1}}$ per amount of sample, frequently quoted as the molar heat capacity, $\mathrm{J\,K^{-1}\,mol^{-1}}$, or the specific heat capacity, $\mathrm{J\,K^{-1}\,g^{-1}}$. The heat capacity of a solid generally increases with temperature.

The measured value of the heat capacity is found to depend on whether the measurement is made at

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**Table 15.1** The Debye temperature, $\theta_D$, and room temperature heat capacity, $C_p$, of some elements

| Element | $\theta_D$/K | $C_p$/J K$^{-1}$ mol$^{-1}$ |
|---|---|---|
| Li | 345 | 24.9 |
| Na | 158 | 28.2 |
| K | 91 | 29.6 |
| Rb | 56 | 31.1 |
| Cs | 38 | 32.2 |
| C[a] | 2340 | 13.0 |
| Si | 645 | 19.8 |
| Ge | 375 | 23.2 |
| Sn[b] | 230 | 27.1 |
| Pb | 105 | 26.7 |

[a] Diamond.

[b] White tin ($\beta$-tin), tetragonal.

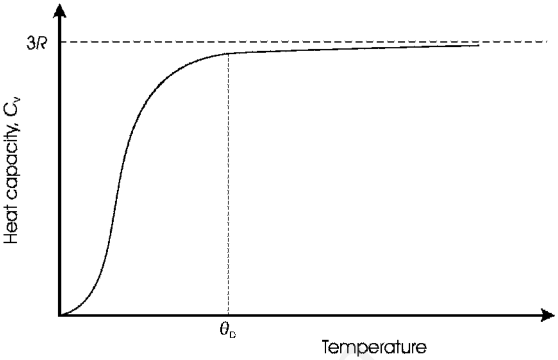


**Figure 15.1** The variation of the heat capacity of a solid with temperature

constant volume, $C_v$, or at constant pressure, $C_p$. The relationship between them is:

$$C_v = \frac{dU}{dT}$$

$$C_p = \frac{dH}{dT}$$

$$C_p = C_v + \text{constant} \times T$$

where $U$ is the internal energy of the material, and $H$ is the enthalpy of the material (see Section S3.2). For solids, the difference between $C_p$ and $C_v$ is very small at room temperature and below. Some room-temperature values of $C_p$ are given in Table 15.1.

### 15.1.2 Theory of heat capacity

Thermal energy is mainly taken up as the vibrations of the atoms in the solid. Classically, the calculation of the heat capacity of a solid was made by assuming that each atom vibrated quite independently of the others. The heat capacity was then the sum of all of the identical atomic contributions, and independent of temperature. The result was

$$C_v(\text{classical}) = 3R = 25\,\text{J K}^{-1}\,\text{mol}^{-1}$$

where $R$ is the gas constant, 8.3145 J K$^{-1}$ mol$^{-1}$. This value is reasonable for high temperatures but is completely incorrect at low temperatures (Figure 15.1). This discrepancy was resolved by realising that the energy of the vibrating atoms, $E$, was quantised in the following way:

$$E = \left(n + \frac{1}{2}\right) h\nu \qquad (15.1)$$

where $n$ is an integer quantum number, $h$ is Planck's constant, and $\nu$ is the vibration frequency. The quantum of vibrational energy is called a phonon. The resulting calculation, by Einstein, which assumed that each atom vibrated independently of the others, was a good overall fit to the data but was not in perfect accord with the experimental values at low temperatures.

Debye improved on the calculation by including the fact that the atomic vibrations throughout the crystal are coupled together, via chemical bonding. The lattice vibrations are then likened to waves throughout the whole of the solid body. The waves must fit into the dimensions of the solid, in a similar way that electron waves must, as illustrated in Figure 2.27. In this model, the lattice vibration waves are equivalent to sound waves of high frequency travelling through the solid. The wavelength, frequency and energy of the vibrations are quantised, and the term phonon is often used for the waves themselves. The heat capacity calculated by Debye is:

$$C_v = 9R\left(\frac{T}{\theta_D}\right)^3 \int_0^{\theta_D/T} \frac{x^4 e^x}{(e^x - 1)} dx$$

$$x = \frac{h\nu}{kT}$$

$$\theta_D = \frac{h\nu_D}{k}$$

where $\theta_D$ is called the Debye temperature, $\nu_D$ is the Debye frequency, $R$ is the gas constant, and $T$ is the temperature (in K). Values of the Debye temperature are given in Table 15.1. Note that the Debye temperature drops systematically on moving down a periodic table group.

For temperatures well above the Debye temperature, the value of $C_v$ is $3R$, where $R$ is the gas constant, $8.3145\ \mathrm{J\,K^{-1}\,mol^{-1}}$. Thus, all solids would be expected to have a high-temperature heat capacity of about $25\ \mathrm{J\,K^{-1}\,mol^{-1}}$, equal to the classical value. As the value of the Debye temperature is below room temperature for many solids, the room-temperature heat capacity can be approximated to $3R$ (Table 15.1).

At temperatures well below the Debye temperature, the value of $C_v$ is given by:

$$C_v = \frac{12\pi^4}{5} R\left(\frac{T}{\theta_D}\right)^3$$

That is,

$$C_v = \text{constant} \times T^3$$

The phonon contribution to the heat capacity is the most important one, but others also occur. As noted in Section 2.3.7, the heat capacity due to free electrons in metals is small but significant heat capacity changes accompany phase changes, such as order–disorder changes of the type noted with respect to ferroelectrics (Sections 11.3.5 and 11.3.6), or when a ferromagnetic solid becomes paramagnetic (Sections 12.1.2 and 12.3.1).

### 15.1.3 Quantum and classical statistics

The energy of the system of vibrating atoms, given by Equation (15.1), shows that the lowest energy possible is not zero, as it is for a classical system, but is equal to $\frac{1}{2}h\nu$. This energy is called zero-point energy. Any quantum mechanical system will possess this amount of energy even when in the lowest energy state.

To calculate the total energy of a system it is necessary to allocate the phonons to the available energy levels (as with electrons, see Section 2.3.7). Phonons are distributed according to Bose–Einstein statistics. This accounting system places no constraints on the number of phonons that can occupy a single energy level (Section S4.12). At low temperatures, all phonons can be in the lowest energy state, giving rise to an appreciable zero-point energy.

Phonons interact with photons, electrons and neutrons, causing scattering. This causes a beam of radiation incident on a crystal to spread out, and a diffracted beam will be broadened by this extra contribution. The extent of the spreading is related to the phonon spectrum in the crystal, and its measurement gives information on the phonon distribution in the solid.

### 15.1.4 Thermal conductivity

When the two ends of a solid are held at different temperatures, heat flows across it from the hot to the cold side (Figure 15.2a). The amount of heat transferred, $Q$, per unit time, depends on the cross-sectional area over which the heat is conducted, $A$, the temperature difference between the hot and cold regions, $T_1 - T_2$, and the separation, $x_1 - x_2$:

$$Q = \frac{\kappa A(T_1 - T_2)}{x_1 - x_2}$$

or

$$\frac{dQ}{dt} = \kappa A \frac{dT}{dx}$$

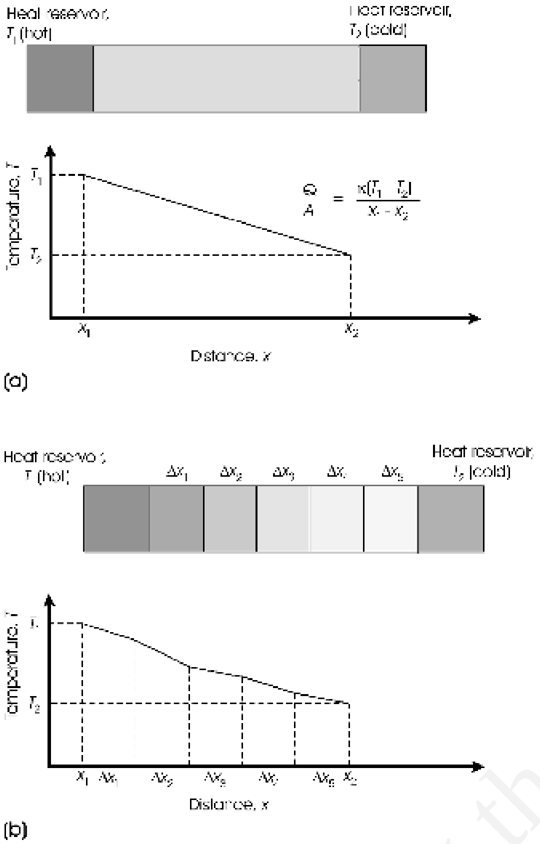


**Figure 15.2** (a) The thermal conductivity of a material is the heat flow from a hot to a cold region. The temperature gradient between the hot and cold ends is a measure of the thermal conductivity of the material. (b) The temperature drop across a series of different materials will vary with the thermal conductivity of each, although the total temperature drop is the same. Note: $Q$, heat transferred; A, cross-sectional area

where d$Q$/d$t$ is the rate of energy transfer, and d$T$/d$x$ is the temperature gradient. The constant of proportionality, $\kappa$, is called the thermal conductivity, with units W m$^{-1}$ K$^{-1}$. When the heat transfer is across a number of materials (Figure 15.2b):

$$\frac{\mathrm{d}Q}{\mathrm{d}t} = A\Delta T\left[\sum_{i=1}^{n}\frac{\Delta x_i}{\kappa_i}\right]^{-1}$$

where $\Delta T$ is the total temperature drop, $T_1 - T_2$, and $\Delta x_i$ is the thickness of a slab of thermal conductivity $\kappa$.

The thermal conductivity of solids varies considerably (Table 15.2). Metals have a high thermal conductivity, with silver having the highest room-temperature thermal conductivity, at 430 W m$^{-1}$ K$^{-1}$. Alloys have lower thermal conductivities than pure metals. Ceramics are even lower, especially porous porcelains or fired clay products (Figure 15.3). The lowest thermal conductivities are shown by plastic foams such as foamed polystyrene. As would be expected, the thermal conductivity of crystals varies with direction. For example, the thermal conductivity of the hexagonal metal cadmium Cd, (A3 structure), is 83 W m$^{-1}$ K$^{-1}$ parallel to the $c$ axis and 104 W m$^{-1}$ K$^{-1}$ parallel to the $a$ axis. At 25 °C, the oxide quartz, which has a hexagonal unit cell, has a thermal conductivity parallel to the $c$ axis of 11 W m$^{-1}$ K$^{-1}$, and 6.5 W m$^{-1}$ K$^{-1}$ parallel to the $a$ axis.

A number of nonmetallic materials are called high thermal conductivity materials. The most notable of these is diamond, with a thermal conductivity of 2000 W m$^{-1}$ K$^{-1}$. All of the others have a diamond-like structure, and include boron nitride, BN, and aluminium nitride, AlN (Table 15.2).

Thermal conductivity is attributed mainly to the mobile electrons present and the vibration waves in the structure, phonons:

$$\kappa = \kappa(\text{electrons}) + \kappa(\text{phonons})$$

Mobile electrons make the greatest contribution, and so metals would be expected to show a much higher thermal conductivity than insulators. At the simplest level the electrons can be imagined as a free-electron gas, moving with a velocity that is higher at the hot end of the solid than at the cold end. (The same model was mentioned in Section 2.3.5, with respect to electrical conductivity.) The kinetic energy is gradually transferred to the cold end by collisions between the electrons themselves and with the atoms in the structure. The thermal conductivity increases as the number of free electrons increases. The model is successful in some ways. For example, it predicts that thermal

**Table 15.2** Coefficients of thermal conductivity, $\kappa$, and thermal expansion

| Material | $\kappa$/W m$^{-1}$ K$^{-1}$ | $\alpha/10^{-6}$ K$^{-1}$ |
|---|---|---|
| Metals: | | |
| Silver | 428 | 18.9 |
| Copper | 403 | 16.5 |
| Gold | 319 | 14.2 |
| Iron | 83.5 | 11.8 |
| Nickel | 94 | 13.4 |
| Titanium | 22 | 8.6[a] |
| Alloys: | | |
| Brass | 106 | 17.5 |
| Bronze | 53 | 17.3 |
| Carbon steel | ~50 | ~10.7 |
| Monel[b] | 21 | ~14 |
| Lead–tin solder | ~50 | ~24 |
| Refractories: | | |
| Alumina | 38 | 5.5 |
| Magnesia | 40 | 9.5 |
| Silica | 1.6 | 0.49 |
| Porcelain | ~2 | ~4.5 |
| Polymers: | | |
| Nylon 6,6 | 0.25 | 80 |
| Polyethylene | ~0.4 | ~200 |
| Polystyrene foam | ~0.04 | – |
| High thermal conductivity materials: | | |
| Diamond | 2000 | 1 |
| Graphite[c] | 2000 | −0.6 |
| Cubic BN | 1300 | – |
| SiC | 490 | 3.3 |
| BeO | 370 | – |
| BP | 360 | – |
| AlN | 320 | – |
| BeS | 300 | – |
| BAs | 210 | – |
| $Si_3N_4$ | 200 | 2.5 |
| GaN | 170 | – |
| Si | 160 | 2.6 |
| AlP | 130 | – |
| GaP | 100 | 4.7 |

– Data could not be located.

[a] Mean value.

[b] 67 wt% Ni, 29 wt% Cu, 4 wt% Fe.

[c] Perpendicular to the *c* axis.

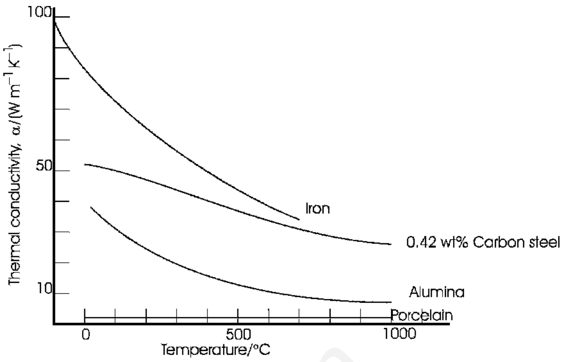


**Figure 15.3** The approximate variation of thermal conductivity with temperature for some common materials

conductivity will be proportional to electrical conductivity. However, it does not explain the differences between one metal and another and, for this, the dynamics of the electrons at the Fermi surface must be employed.

Thermal conductivity in insulators, ceramics and polymers can be explained in terms of a phonon gas. The solid is imagined to contain phonons travelling with a range of kinetic energies, similar to the molecules in a gas or the electron gas just mentioned. At the hot end of a solid the kinetic energy of the phonons is greater than at the cold end. This energy is gradually transferred from hot to cold by phonon–phonon interactions and by interactions between the phonons and the solid structure. The differences between the thermal conductivities of different insulators reflect these interactions.

The thermal conductivity depends on the mean free path of the phonons, which is the distance between collisions of the phonons in the structure. A short mean free path correlates with a low thermal conductivity. Defects in a structure drastically shorten the mean free path and reduce thermal conductivity significantly. An inherent problem with ceramic materials is that they are usually formed by sintering. This process naturally leads to the formation of many internal defects such as grain boundaries, pores and voids. Because of this, the thermal conductivity of sintered bodies is usually much lower than the intrinsic thermal conductivity. Fired-clay ceramics have very high porosity and a very low thermal conductivity. At present, the best sintered ceramic solids have about $\frac{3}{4}$ of the intrinsic thermal conductivity of the parent phase.

Point defects can drastically lower the thermal conductivity of the important carbide and nitride high thermal conductivity ceramics. In this respect, oxygen, which is a common impurity, has been found to be very important. For example, silica ($SiO_2$), an impurity in silicon nitride ($Si_3N_4$), formed by oxidation at high temperatures in air, can react to produce substitutional defects and vacancies in the following way:

$$2SiO_2\,(s) \rightarrow 2Si_{Si} + 4O_N + V_{Si}$$

where $Si_{Si}$ represents silicon atoms on normal silicon sites (not defects), $O_N$ represents oxygen atoms on nitrogen atom sites (substitutional defects) and $V_{Si}$ represents a vacancy on a silicon site (vacancy defects). Thus, two $SiO_2$ units produce five defects in the silicon nitride. Purification therefore forms an important step in the manufacture of high thermal conductivity ceramic materials.

The thermal conductivity of polymers is found to depend on the degree of crystallinity. The crystalline portions of the structure have a higher thermal conductivity than do the disordered regions of the solid. Materials with high porosity, such as plastic foams, have particularly low thermal conductivities. Foamed plastics such as polystyrene are widely used as insulating materials.

### 15.1.5 Heat transfer

When a solid is heated or cooled, heat is transferred through the structure. The equations of heat transfer were initially formulated by Fourier. They predate and are of identical mathematical form to Fick's laws of diffusion (Sections 7.1 and 7.3). In the case of steady-state heat transfer, the one-dimensional heat transfer equation is:

$$J_Q = -K\frac{dT}{dx}$$

where $J_Q$ is the heat flux (units J $m^{-1}\,s^{-1}$), $dT/dx$ is the temperature gradient along the direction of heat flow, taken as $x$, and $K$ is the thermal diffusivity, defined by:

$$K = \frac{\kappa}{\rho C_p}$$

where $\kappa$ is the thermal conductivity, $\rho$ is the density, and $C_p$ is the specific heat capacity (the heat capacity per unit weight) at constant pressure. The units of $K$ are the same as those of the diffusion coefficient ($m^2\,s^{-1}$).

In the case of nonsteady-state heat transfer, the equation is analogous to the diffusion equation:

$$\frac{dT}{dt} = \frac{K d^2T}{dx^2}$$

where $dT/dt$ is the change of temperature with time at a point $x$ in the solid. The solutions to this equation are identical in form to those given in Section 7.2 for the diffusion equation.

### 15.1.6 Thermal expansion

Most materials increase in volume as the temperature is increased, a feature called thermal expansion. There are, though, an increasing number of solids known that contract as the temperature increases.

Thermal expansion is a most important property in practice. It is used in most everyday thermometers. The shattering of ordinary glass on being cooled rapidly is due to the thermal contraction of the outer layers, and is prevented in special glasses such as Pyrex® glass or fused silica, which have low thermal expansion. The thermal expansion of components in electronic devices is important, and the difference in thermal expansion of materials in a construction can lead to grave difficulties. The coincidence of the thermal expansion of steel and concrete at normal temperatures allows the use of steel-reinforced concrete in buildings.

The mean coefficient of linear thermal expansion, $\alpha_{mean}$, of a material is the increase in length per unit length over a temperature interval from $T_\mathrm{i}$ to $T_\mathrm{f}$

$$\alpha_\mathrm{mean} = \frac{l_\mathrm{f} - l_\mathrm{i}}{l_\mathrm{i}}$$

where $T_\mathrm{i}$ is the initial temperature, $T_\mathrm{f}$ is the final temperature, $l_\mathrm{f}$ is the final length, and $l_\mathrm{i}$ is the initial length. The units are $K^{-1}$. In general, for a temperature interval $\Delta T$:

$$\alpha_\mathrm{mean} = \frac{\Delta l}{l_\mathrm{i}}$$

where $\Delta l$ is the length increment. A similar expression can be written for the mean coefficient of volume expansion, also called the cubical expansion coefficient, $\beta_\mathrm{mean}$, over a temperature interval $\Delta T$:

$$\beta_\mathrm{mean} = \frac{\Delta V}{V_\mathrm{i}}$$

where $\Delta V$ is the volume change, and $V_\mathrm{i}$ is the original volume at $T_\mathrm{i}$. The units are $\mathrm{K}^{-1}$.

A reasonable approximation is

$$3\alpha_\mathrm{mean} \approx \beta_\mathrm{mean}$$

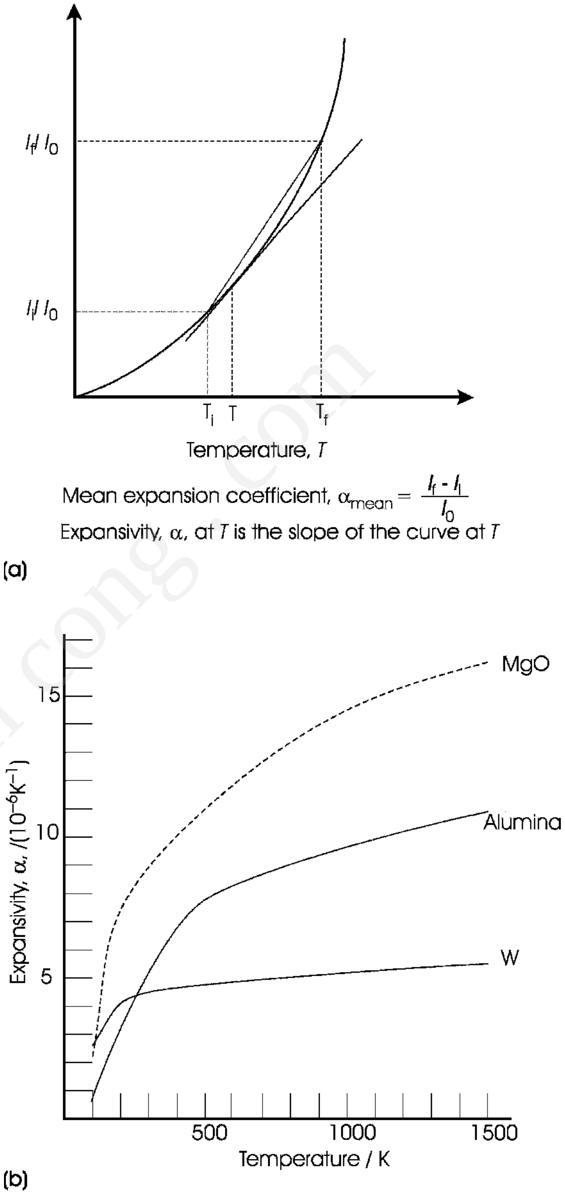
In the case of a solid with different mean thermal expansion coefficients along $x$, $y$ and and $z$ axes ($\alpha_x, \alpha_y$ and $\alpha_z$, respectively):

$$\alpha_x + \alpha_y + \alpha_z \approx \beta_\mathrm{mean}$$

The linear expansivity of a solid, $\alpha$, is defined as the increase in length per unit length at a given temperature:

$$\alpha = \frac{1}{l}\frac{\mathrm{d}l}{\mathrm{d}T}$$

The expansivity is the slope of the $\mathrm{d}l/l$ versus temperature curve at a temperature $T$ (Figure 15.4a) and is often different in value from $\alpha_\mathrm{mean}$. The value of $\alpha_\mathrm{mean}$ tends to the expansivity as $\Delta l$ and $\Delta T$ become small, and both have units of $\mathrm{K}^{-1}$. The expansivity of many solids tends to increase as the temperature increases (Figure 15.4b).



Mean expansion coefficient, $\alpha_\mathrm{mean} = \frac{l_f - l_i}{l_0}$

Expansivity, $\alpha$, at $T$ is the slope of the curve at $T$

**Figure 15.4** (a) The mean coefficient of thermal expansion, $\alpha_\mathrm{mean}$, is not identical to the expansivity, $\alpha$, at all temperatures over the range within which $\alpha_\mathrm{mean}$ is measured. (b) The approximate variation of thermal expansion with temperature for a metal (tungsten, W) and two ceramics (magnesium oxide, MgO, and alumina, $\mathrm{Al_2O_3}$)

The thermal expansion of a multiphase solid depends on the expansivity of the individual components and the ratios present. Thus, the thermal expansion of alloys, glasses and glass ceramics can be tailored by changing the bulk composition of the material. For many applications, a very small coefficient of expansion is desirable, and in cooking ware, for example, glass ceramics with negligible thermal expansion over the temperature ranges encountered in cooking are widely available.

### *15.1.7 Thermal expansion and interatomic potentials*

An idea of the origin of thermal expansion can be obtained from a consideration of the potential energy of a pair of atoms as a function of their spacing (Figure 15.5; see also Section S4.1.7). The extent of the vibrational energy at a low temperature, $T_0$, and energy, $E_0$, leads to a mean separation of the atoms, $r_0$. As the temperature increases, the energy of vibration increases to $E_1$, $E_2$ and so on, and the mean separation to $\mathrm{r}_1$ and $\mathrm{r}_2$, and so on. Because of the asymmetrical nature of the potential energy curve, the midpoint of the vibration has increased. Further temperature increases magnify this off-centre displacement, and the net result is an expansion.

The shape of the interatomic energy curve is related to the chemical bond strength between the atoms. Strong bonds result in a steep potential energy curve that is reasonably symmetrical close to the minimum. Weak bonding results in a flatter curve that is very unsymmetrical (Figure 15.6). This suggests that strongly bonded solids, such as silica and other ceramics, would have low expansivity, whereas polymers, in which the chains are linked by weak chemical bonds, would have high expansivity. This is the case (Table 15.2).

In a real solid, account has to be taken of all the atoms in the unit cell, and the interatomic potentials between each pair of atoms has to be evaluated, so as to obtain the mean change of expansion of the unit cell as a whole. Crystals expand less along directions corresponding to strong bonds and more along directions corresponding to weak bonds. The chain silicates, for example, have a higher coefficient of expansion perpendicular to the chains than parallel to them. In general, crystals of lower than cubic symmetry have different expansivities along the different crystal axes.

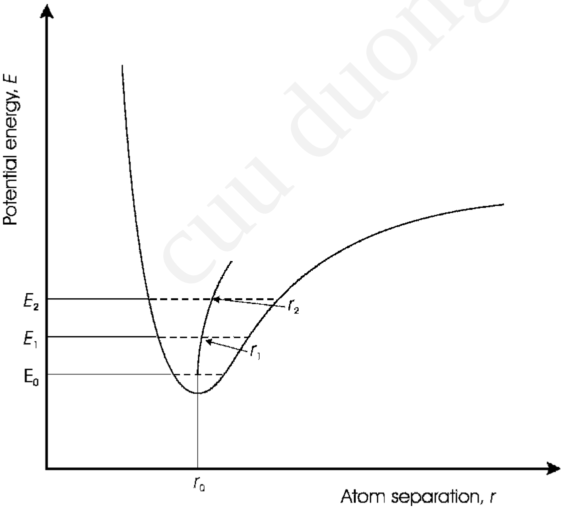


**Figure 15.5** The variation of the potential energy between two atoms linked by a strong chemical bond, as a function of the interatomic spacing

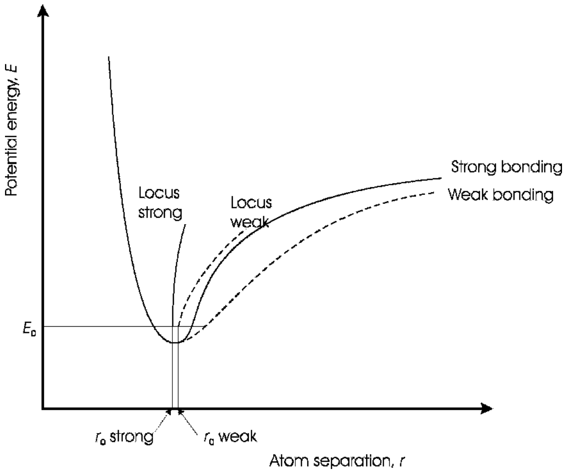


**Figure 15.6** Potential energy curves for a pair of atoms linked by weak and strong bonds. The locus of the centre of the bond between the atoms increases more rapidly in the case of weakly bonded atoms

### *15.1.8 Thermal contraction*

The thermal expansion of a material depends on the overall balance between all of the interatomic and intermolecular forces present. In some cases, this can produce materials that contract as the temperature increases.

The best-known material that behaves in this anomalous fashion is water, between 0 °C and 3.98°C (Figure 15.7). This feature arises from the hydrogen bonding between the molecules and the molecular structure. At lower temperatures, the hydrogen bonds pull the water molecules closer together as the thermal vibrations of the fluid decrease. However, the angular structure prevents them packing closely together and they maintain an open structure that is similar to the structure of ice, which is also open and has a lower density than water. Above a temperature of 3.98°C, the thermal vibrations begin to dominate, molecular rotation in the liquid increases and the molecules are effectively spherical. As the temperature increases, normal expansion is found, as depicted in Figure 15.6. The consequences of this feature of water are important for life on Earth.

Many anisotropic crystals are known that show a contraction along one or two axes as the temperature increases, although other axes may show normal thermal expansion (Figure 15.8). Some of the most important compounds that reveal this behaviour are cordierite ($Mg_2Al_4Si_5O_{12}$), $\beta$-eucryptite ($LiAlSiO_4$), $\beta$-spodumene ($LiAlSi_2O_6$) and $NaZr_2P_3O_{12}$ (NZP). One reason for their importance is that all of these materials exist over a wide composition range. For example, $\beta$-spodumene can take compositions $Li_2Al_2Si_nO_{4+2n}$, in which $n$ can take values from 4 to 9. Similarly, NPZ can form solid solutions in which phosphorus is replaced by silicon, for example, $Na_{1+x}Zr_2P_{3-x}Si_xO_{12}$, and sodium by calcium and strontium, for example, $Ca_{1-x}Sr_xZr_4P_6O_{24}$. This ability allows the thermal expansion and contraction to be carefully tailored, and materials with almost zero thermal expansion produced.

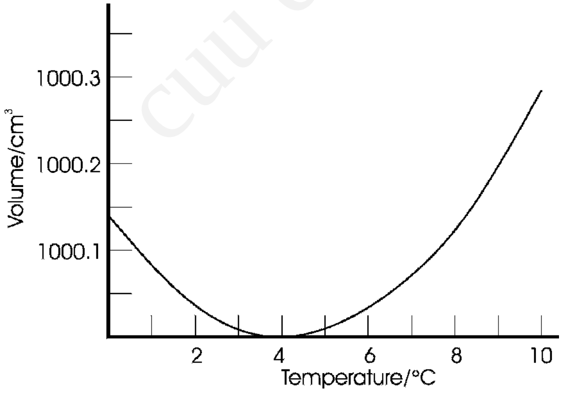


**Figure 15.7** The thermal expansion of water close to 0 °C

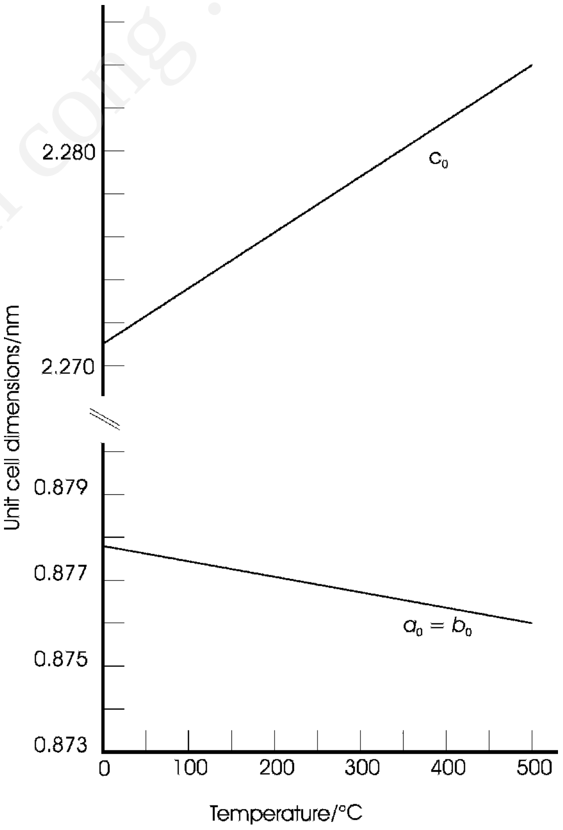


**Figure 15.8** The thermal expansion of the $c$ axis and contraction of the $a$ and $b$ axes for $CaZr_4P_6O_{24}$, redrawn from data in D.K. Agrawal 1994, '[NPZ]: A New Family of Real Materials for Low Thermal Expansion Applications', *Journal of Materials Education* **16** 139–165

There are also materials known in which all axes contract as the temperature rises, including cubic $ZrW_2O_8$ and a silica polymorph with the faujasite structure.

Thermal contraction is not the result of a single mechanism. However, all of the changes can be related to the cation polyhedra that build up the structure. For example, in many ferroelectric perovskite structure compounds, a distortion of the metal–oxygen $MO_6$ octahedra is responsible for the ferroelectric effect (see Section 11.3.7). Frequently, the distortion, which is caused by an off-centring of the cation, causes one of the octahedron diagonals to lengthen, transforming the cubic unit cell into a tetragonal cell. As the temperature increases, the distortion tends to decrease, because of changes in vibrational energy and a decrease in anion–anion repulsion, so that the long diagonal shortens. At the same time, the undistorted diagonals expand normally. In some cases, such as for $PbTiO_3$, the contraction is greater than the expansion, and a polycrystalline sample of $PbTiO_3$ shows overall thermal contraction (Figure 15.9).

In the families of cordierite, $\beta$-eucryptite, $\beta$-cordierite and NZP, a mechanism similar to that giving rise to auxetic (negative Poisson's ratio) materials seems to occur (Section 10.3.2). The structure is built from inflexible layers, similar to those found in clay minerals (see Sub-section 6.2.1.2) linked by Si—O—Si and O—Si—O bonds (Figure 15.10). As the temperature rises the layers expand, mostly laterally. The Si—O bonds linking the layers are strong and do not break to relieve the stress generated. Instead, the bond angles change, and the groups act as hinges that pull the layers closer, giving rise to thermal contraction in a direction normal to the layers.

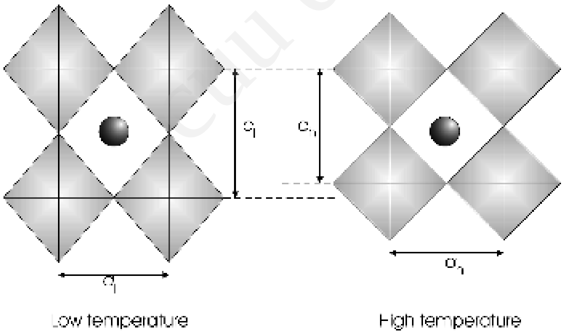


**Figure 15.9** Thermal contraction due to the relief of octahedral distortion in the perovskite structure type. The low-temperature distortions (left) are lost at high temperatures (right) leading to a smaller unit cell

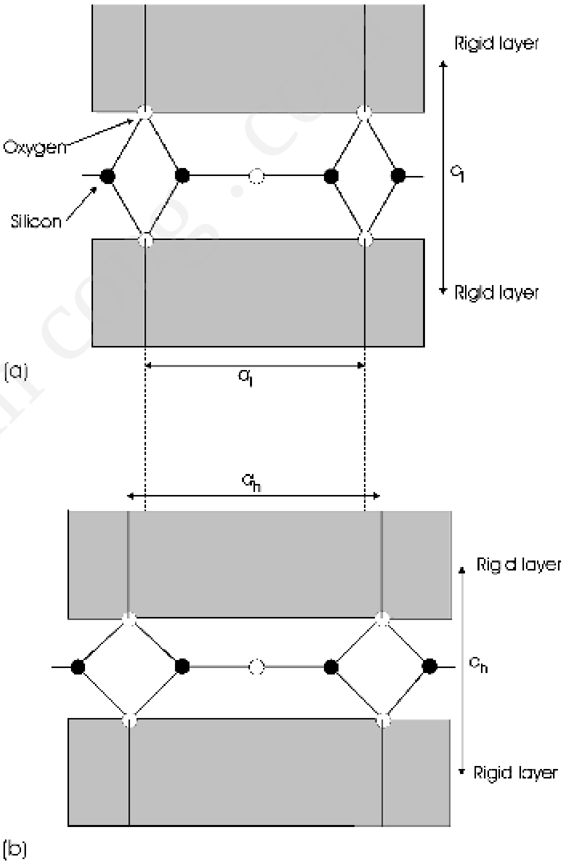


**Figure 15.10** Thermal contraction brought about by silicon–oxygen 'hinges' connecting rigid sheets within a crystal structure: (a) the low-temperature structure and (b) the high-temperature structure. As the rigid sheets expand normally, due to an increase in temperature (from the configuration shown in part a to that shown in part b), the strong silicon–oxygen bonds act as hinges and pull the sheets together (part b). The material shows thermal expansion parallel to the sheets and contraction normal to the sheets

A third group, which includes cubic $Zr_2WO_8$ and $NbOPO_4$, achieves the contraction via rocking of the polyhedra (Figure 15.11). In this group, the polyhedra remain the same shape, but simply tilt in a cooperative fashion as the temperature increases, so that one or more unit cell edges contract while the others expand. In cases where the contraction is sufficient, an overall thermal contraction is observed in polycrystalline samples.

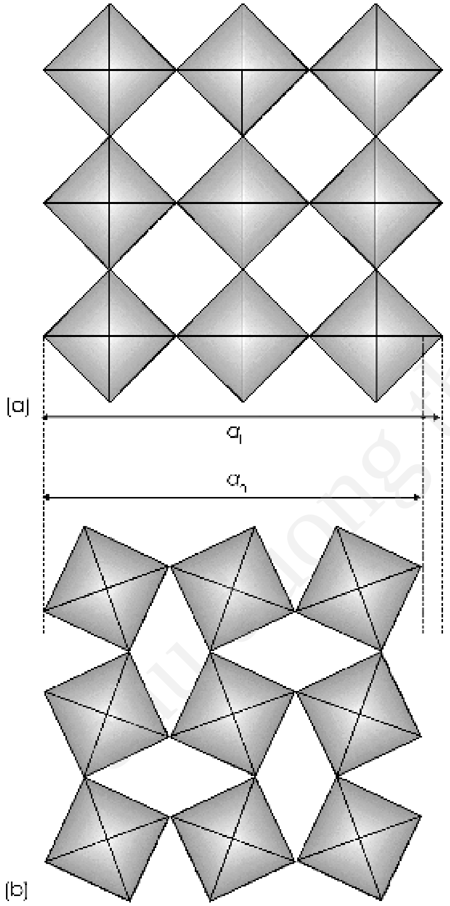


**Figure 15.11** Thermal contraction due to the rotation of polyhedra in the *perovskite* structure type: (a) the low-temperature structure and (b) the high-temperature structure. As the temperature increases, (from part a) to (part b), increased vibration allows the polyhedra to rotate, thus producing a contraction of the unit cell

## 15.2 Thermoelectric effects

### 15.2.1 Thermoelectric coefficients

The first thermoelectric effect to be discovered was the Seebeck effect. In this phenomenon, a current flow is induced in a circuit made of two different conductors A and B when the junctions between the materials are held at different temperatures. The effect is generally observed by breaking the circuit and observing the voltage generated with a potentiometer (Figure 15.12a). This voltage is given by:

$$\Delta V_{AB} = \Sigma_{AB}\Delta T = \Sigma_{AB}(T_H - T_C)$$

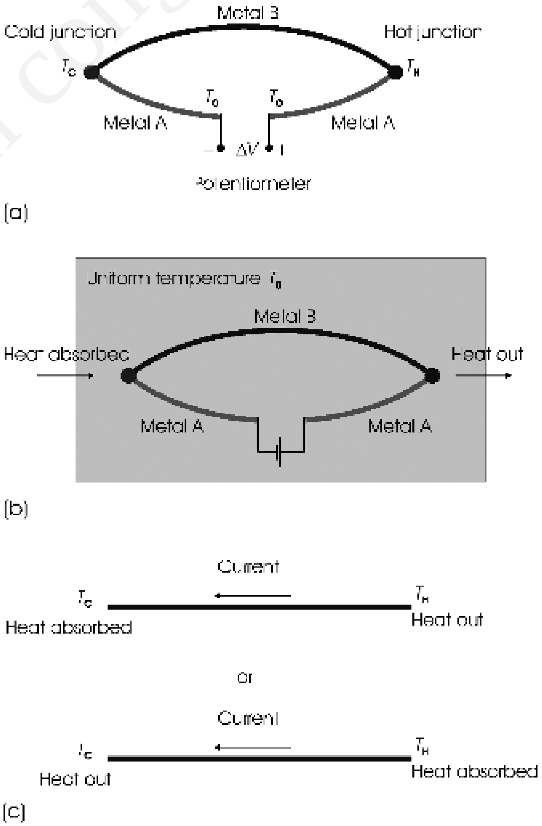


**Figure 15.12** Thermoelectric effects: (a) the Seebeck effect, (b) the Peltier effect and (c) the Thompson effect

where $\Sigma_{AB}$ is called the thermoelectric power or Seebeck coefficient, $\Delta V_{AB}$ is the voltage measured, and $\Delta T$ is the temperature difference between the hot junction (temperature $T_H$) and the cold junction (temperature $T_C$). The Seebeck coefficient, $\Sigma$, has units of $V\,K^{-1}$ and varies significantly with temperature. The voltage depends only on the two materials chosen and the temperature difference between the junctions. The Seebeck coefficient for metals is of the order of $10\,\mu V\,K^{-1}$, and for semiconductors it is about $200\,\mu V\,K^{-1}$.

The complementary effect, in which a current flow induces a temperature difference between the two junctions, is called the Peltier effect (Figure 15.12b). Heat is liberated at one junction and absorbed at the other. If the direction of the current is reversed, the heat output and input occur at the opposite junctions. The amount of heat produced or absorbed, $\Delta Q$, is given by:

$$\Delta Q = \Pi_{AB} It$$

where $\Pi_{AB}$ is the Peltier coefficient, $I$ is the current flowing in the circuit, and $t$ is the time. The units of $\Pi$ are $J\,A^{-1}\,s^{-1}$. Peltier heat production is quite different from Joule heating, which occurs along the length of the conductor instead of at a junction between two materials.

The Seebeck and Peltier effects were shown to be related by Thomson (later Lord Kelvin). The relationship is:

$$\Pi = \Sigma T$$

where the temperature, $T$, is in K. Thomson also predicted the existence of a third thermoelectric effect, now known as the Thomson effect, in which a reversible heating or cooling is observed when a current flows along a (single) conductor that has one end at a different temperature from the other (Figure 15.12c). The amount of heat energy absorbed or given out, $\Delta Q$, is given by:

$$\Delta Q = \tau I t \Delta T$$

where $\tau$ is the Thompson coefficient, $I$ is the current flowing for a time $t$, and $\Delta T$ is the temperature difference between the points of measurement. The units of $\tau$ are $J\,A^{-1}\,s^{-1}\,K^{-1}$.

Although observed at junctions in circuits, the Seebeck and Peltier coefficients are not caused by the junctions themselves. All materials that contain mobile charge carriers show thermoelectric effects when heated. That is, temperature gradients produce electrical effects, and electrical effects produce thermal effects. The appearance of these thermoelectric effects are properties of pure materials, and a material is characterised by an absolute Seebeck coefficient, $\sigma_S$, an absolute Peltier coefficient, $\pi$, and the Thomson coefficient, $\tau$, which only refers to a single material. The Seebeck coefficient, $\Sigma$, and the Peltier coefficient, $\Pi$, apparent in circuits made of two different electronically conducting materials, are relative coefficients, that is, the difference between the absolute coefficients of the two materials. For the arrangement drawn in Figure 15.12a, in which the positive terminal of metal A is connected to the hot junction, the Seebeck coefficient of two the materials $\Sigma_{AB}$, at a temperature $T$, is given by:

$$\Sigma_{AB} = \sigma_S(A) - \sigma_S(B)$$

### 15.2.2 Thermoelectric effects and charge carriers

Thermoelectric effects can be explained by considering the electron, hole and phonon distributions in a material. It is apparent that the charge carriers near to the Fermi surface in the hot region of a single material will have a higher kinetic energy, and hence a higher velocity, than those in the cold region. This means that the net velocity of the charge carriers at the hot end moving towards the cold end will be higher than the net velocity of the charge carriers at the cold end moving towards the hot end. In this situation, more carriers will flow from the hot end towards the cold end than vice versa. This will cause a voltage to build up between the hot and cold ends of the sample. Eventually, equilibrium will be established and a potential will be set up. The same is true for the phonons. As phonons interact strongly with electrons and holes, they will drag these particles along with them, to create an additional potential. The magnitude of the measured thermopower is a complex function of both of these features and varies considerably with temperature. For example, the value of $\sigma_S$ for platinum is approximately $+5\ \mu V\ K^{-1}$ at 100 K and $-2\ \mu V\ K^{-1}$ at 200 K. The thermopower also varies with direction in noncubic crystals.

### *15.2.3 Thermocouples, power generation and refrigeration*

Thermocouples are a widely used application of the Seebeck effect, and they are the main means of temperature monitoring and regulation for measurements of temperatures above about 150 °C (Figure 15.13). This is because the potential generated in the circuit is easily measured, and metal thermocouples capable of operating up to temperatures of almost 2000 °C are available. In practice, one junction is maintained at 0 °C. The voltage generated by a thermocouple is related to the temperature difference between the junctions by a polynomial function, such as

$$T_H = a_0 + a_1 \Delta V + A_2 (\Delta V)^2 + \cdots + a_n (\Delta V)^n$$

where $T_H$ is the temperature of the hot junction, $\Delta V$ is the measured voltage of the thermocouple, and $a_0$, $a_1$ and so on are constants. These coefficients depend on the reference junction temperature and the materials used in the device. The relationship between temperature and voltage is usually found by reference to 'thermocouple tables' supplied by manufacturers or located in handbooks.

A series of thermocouples linked in series form a thermopile (Figure 15.14). This has increased sensitivity compared with a single thermocouple when used to measure temperatures. The same arrangement can be used as a power generator. For this purpose, the low-temperature junctions (temperature $T_C$) are at a fixed temperature by connecting them to a heat sink, and the high-temperature junctions (temperature $T_H$) are in contact with a heat source, such as a radioactive sample. The potentiometer in Figure 15.14 is replaced by whatever needs to be powered by the electricity generated by the Seebeck effect.

Thermoelectric materials are also used for the generation of electricity and for refrigeration

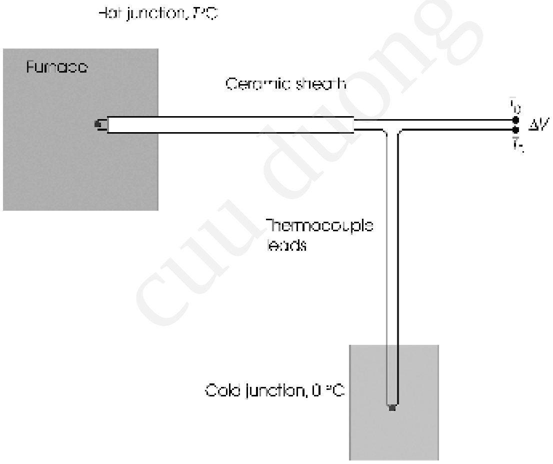


**Figure 15.13** A thermocouple consists of a loop made of two different metals. One junction is kept at 0 °C and the other at the temperature to be measured, for example in a furnace. The voltage developed in the circuit, $\Delta V$, is a measure of the temperature difference between the junctions

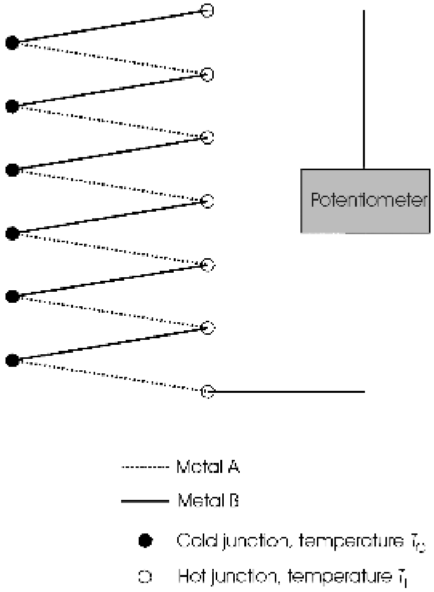


**Figure 15.14** A thermopile, consisting of a number of thermocouples connected in series

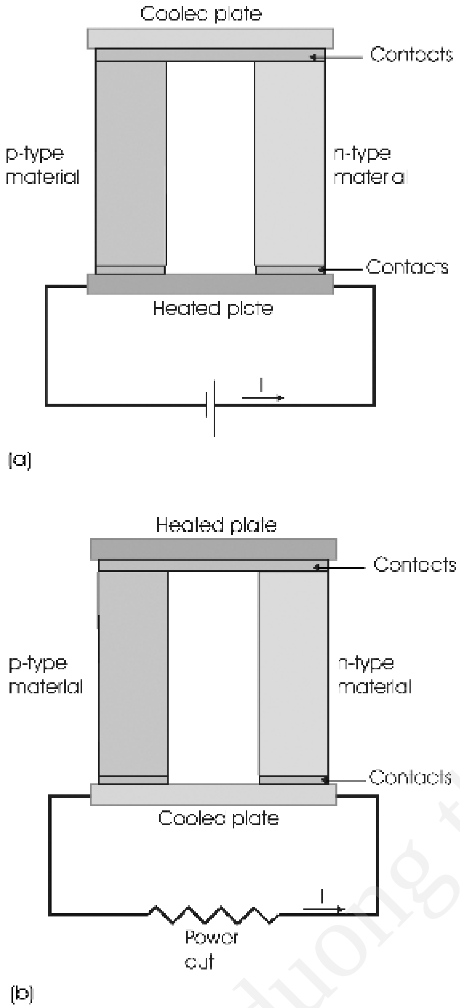


**Figure 15.15** (a) Use of the Peltier effect for thermoelectric heating or cooling. A current, $I$, passed through a circuit containing n-type and p-type thermoelectric materials will cause one plate to become warmer and one to become cooler. Reversal of the current reverses the warm and cool plate. (b) Use of the Peltier effect for thermoelectric power generation. Current, $I$, will flow in a circuit containing a heated plate and a cooled plate connected by an n-type and a p-type thermoelectric material

utilising the Peltier effect. Two thermoelectric materials are coupled by metal plates, which act as the junctions (Figure 15.15a). A current passed through the circuit in one direction will heat one plate and cool the other. If the temperature of the hot junction is constant, maintained by connection to a heat sink, continuous cooling will occur at the cold junction. Alternatively, if the temperature of the cold junction is fixed, continuous heating will occur at the hot junction. A reversal of the current will change the hot plate and cold plate. Such a device is called a heat pump. These are widely used in food and drinks coolers powered by car batteries.

The arrangement can also be used as a power source (Figure 15.15b). If one plate is continuously maintained hotter than the other, a current will flow in the circuit, and power is generated. In this format, these devices are used in space probes that operate too far from the sun for photoelectricity to be used for power supplies. In such cases, heat is generated by the slow decay of radioactive isotopes.

The effectiveness of devices using thermoelectric effects depends on the magnitude of the relative Peltier coefficient, Π, or its equivalent, the relative Seebeck coefficient, Σ. However, these are not the only material parameters of importance. As an example, consider the operation of a heat pump. The amount of heat produced or absorbed is

$$\Pi I = \Sigma T I$$

where $I$ is the current flowing. The requirement for a large Σ acts to rule out metals as components, as metals have very low Seebeck coefficients. However, a low electrical resistivity is needed, to cut down on Joule heating, which points towards metals. Additionally, the thermal conductivity of the thermoelectric elements must be low to reduce the flow of heat from the hot to the cold region. This suggests an insulator, but these have high values of electrical resistivity. All of these conflicting factors are taken into account by using a figure of merit, ZT, for the material, given by:

$$\mathrm{ZT} = \frac{T\Sigma^2}{\kappa\rho}$$

where Σ is the relative Seebeck coefficient of the thermoelectric elements, $\kappa$ is the thermal conductivity, and $\rho$ is the electrical resistivity. The best compromise is given by the material with the highest figure of merit. The figure of merit varies considerably with temperature and, although the best materials have a figure of merit of about 1.0, when combined in a device an overall energy conversion efficiency of only a few percent is realised at present. For small portable coolers, solid solutions of the semiconductors bismuth telluride ($Bi_2Te_3$) and antimony telluride ($Sb_2Te_3$), $Bi_xSb_{1-x}Te_3$, doped p-type and n-type, are used. Space vehicles use silicon–germanium alloys, $Si_xGe_{1-x}$.

## Answers to introductory questions

### What is zero-point energy?

The energy of a system of vibrating atoms, given by Equation (15.1),

$$E = \left(n + \frac{1}{2}\right) h\nu$$

shows that the lowest energy possible, when $n = 0$, is not zero, as it is for a classical system, but is equal to $\frac{1}{2}h\nu$ per atom. There is no restriction on the number of atoms that can occupy this lowest energy level and, at low temperatures, most will occupy this lowest energy state. At the lowest temperature, 0 K, all atoms will be in this lowest energy state and the solid will possess an equivalent amount of energy. This energy is the zero-point energy.

### What solids are named high thermal conductivity materials?

Diamond has long been known to have a very high thermal conductivity. It has been realised that the high thermal conductivity is a reflection of the bonding and structure in diamond. Much effort is currently directed towards reproducing this high thermal conductivity in other materials by synthesis of nonmetallic compounds with the same structure and bonding as in diamond. Recently, a number of such structures have been synthesised. All have high thermal conductivity, and form the high thermal conductivity materials. Notable examples are boron nitride, BN, and aluminium nitride, AlN.

### What physical property does thermoelectric refrigeration utilise?

Thermoelectric materials used for refrigeration utilise the Peltier effect. Two thermoelectric materials are coupled by metal plates, which act as the junctions. A current passed through the circuit in one direction will heat one plate and cool the other. For refrigeration to occur, the temperature of the hot junction is maintained constant by connection to a heat sink, which may simply be a fan. Continuous cooling will occur at the cold junction. These are widely used in food and drinks coolers powered by a car battery.

## Further reading

D.K. Agrawal, 1994, '[NPZ]: A New Family of Real Materials for Low Thermal Expansion Applications', *Journal of Materials Education* **16** 139–165.

R.E. Hummel, 2001, *Electronic Properties of Materials* 3rd edn, Springer, New York.

The *Materials Research Society Bulletin* **26** (June 2001) contains a series of articles on thermal conductivity, including:

G.P. Srivastava, 'Theory of Thermal Conduction in Non-metals', p. 445.

See also:

D.M. Rowe (Ed.), 1995, *CRC Handbook of Thermoelectrics*, CRC Press, Boca Raton, FL.

B.C. Sales, 1998, 'Electron Crystals and Phonon Glasses: A New Path to Improved Thermoelectric Materials'. *Materials Research Society Bulletin* **23** (January) 15–21.

A. W. Sleight, 1998, 'Compounds that Contract on Heating', *Inorganic Chemistry* **37** 2854–2860.

## Problems and exercises

### Quick quiz

1 The heat capacity at constant volume, $C_v$:
   (a) Is greater than the heat capacity at constant pressure, $C_p$

(b) Is less than the heat capacity at constant pressure, $C_p$

(c) Is equal to the heat capacity at constant pressure, $C_p$

2 The low-temperature heat capacity of a solid is proportional to:

(a) $T^3$

(b) $T^{-3}$

(c) $T^{-2}$

3 The high-temperature heat capacity of a solid is approximately:

(a) $2.5\ \mathrm{J\,K^{-1}\,mol^{-1}}$

(b) $25\ \mathrm{J\,K^{-1}\,mol^{-1}}$

(c) $250\ \mathrm{J\,K^{-1}\,mol^{-1}}$

4 The main contribution to the heat capacity of a solid is from:

(a) Phonons (lattice vibrations)

(b) Electrons

(c) Phonons plus electrons

5 The thermal conductivity of a solid is mainly due to:

(a) Phonons (lattice vibrations)

(b) Defects

(c) Free electrons

6 Alloys generally have:

(a) A higher thermal conductivity than the parent metals

(b) A lower thermal conductivity than the parent metals

(c) About the same thermal conductivity as the parent metals

7 Compared with a poorly crystalline polymer, a highly crystalline polymer has:

(a) A lower thermal conductivity

(b) A higher thermal conductivity

(c) About the same thermal conductivity

8 The mean volume expansivity of liquid mercury is $18.2 \times 10^{-5}\ \mathrm{K^{-1}}$. The mean linear expansivity is:

(a) $54.6 \times 10^{-5}\ \mathrm{K^{-1}}$

(b) $6.06 \times 10^{-5}\ \mathrm{K^{-1}}$

(c) $2.63 \times 10^{-5}\ \mathrm{K^{-1}}$

9 Solids linked with strong chemical bonds have:

(a) A lower thermal expansivity than weakly bonded solids

(b) A greater thermal expansivity than weakly bonded solids

(c) About the same thermal expansivity as weakly bonded solids

10 A current flow induced in a circuit made of two different conductors by holding the junctions between the materials at different temperatures is called:

(a) The Peltier effect

(b) The Thomson effect

(c) The Seebeck effect

11 A temperature difference between the two junctions in a circuit made of two different conductors induced by a current flow is called:

(a) The Seebeck effect

(b) The Peltier effect

(c) The Thomson effect

12 A thermocouple makes use of:

(a) The Seebeck effect

(b) The Peltier effect

(c) The Thomson effect

13 Thermoelectric refrigerators utilise:

(a) The Thomson effect

(b) The Seebeck effect

(c) The Peltier effect

### *Calculations and questions*

15.1 How much energy is needed to raise the temperature of 2.5 moles of alumina from 0 °C to 120 °C, taking the specific heat capacity of alumina, $0.907\ \mathrm{J\,K^{-1}\,g^{-1}}$, to be independent of temperature?

15.2 How much energy has to be extracted to lower the temperature of 15 g tungsten metal from 2500 K to 1500 K? The molar heat capacity at 2000 K, 32.26 J $K^{-1}$ $mol^{-1}$, can be considered to apply across the whole of this temperature range.

15.3 The specific heat of silicon at 50 K is 2.162 J $K^{-1}$ $mol^{-1}$. Estimate the value at the boiling point of neon, 27.07 K.

15.4 Calculate the specific heat of silicon at the boiling point of neon by using the fact that the Debye temperature of silicon is 645 K. Compare this with the result in Question 15.3.

15.5 A styrofoam box is used to transport 10 kg meat. The box is 50 cm × 30 cm × 20 cm, and the foam thickness is 5 cm. How long will it take the contents to increase in temperature from the initial 0 °C to 5 °C, assuming that the heat capacity of meat is 4.22 J $K^{-1}$ $g^{-1}$ and the thermal conductivity of styrofoam is 0.035 W $m^{-1}$ $K^{-1}$?

15.6 Show that the equation for the heat transfer across a number of slabs of material with the same surface area, $A$, is

$$\frac{dQ}{dt} = A\Delta T\left[\sum_{i=1}^{n}\frac{\Delta x_i}{\kappa_i}\right]^{-1},$$

where $\Delta T$ is the total temperature drop, $T_1 - T_2$, and $\Delta x_i$ is the thickness of slab $i$, of thermal conductivity $\kappa_i$. [Note: derivation is not given in the answers at the end of this book.]

15.7 A cooking pot of 15 cm diameter and a base of 3 mm copper and 1 mm stainless steel, contains 2 l of water at 20 °C. (a) What is the initial rate of heat transfer if the hot plate is at 150 °C? How does this compare with a pan of the same dimensions with (b) a solid copper bottom 4 mm thick and (c) a solid stainless steel bottom, 4 mm thick. The thermal conductivity of copper is 403 W $m^{-1}$ $K^{-1}$ and that of stainless steel is 18 W $m^{-1}$ $K^{-1}$.

15.8 A window of area 2 m × 1.30 m is glazed with a single sheet of glass 5 mm thick. (a) What is the heat loss per hour from a room at 25 °C when the outside temperature is 4.5 °C? (b) If the area is double glazed with two such sheets, separated by an air gap of 1 cm, what will the heat loss per hour be? The thermal conductivity of the glass is 0.96 W $m^{-1}$ $K^{-1}$ and that of air is $2.41 \times 10^{-2}$ W $m^{-1}$ $K^{-1}$.

15.9 A gap is left between rails in a railway so that the rails can expand without causing track buckling at high temperatures. What gap needs to be left between 10 m rail lengths installed at 10 °C if the ground temperature might reach 50 °C? The expansivity of steel is $10.7 \times 10^{-6}$ $K^{-1}$.

15.10 A volume of mercury of $10^{-6}$ $m^3$ at 20 °C is contained in glass bulb, with expansion taken up by the mercury moving into a capillary 0.5 mm diameter, similar to a mercury thermometer. The aim is to allow the mercury to expand and complete an electrical circuit and activate a cooling device. If the circuit contact is 5 mm above the mercury level at 20 °C, what temperature will activate the device? The mean volume expansivity of liquid mercury is $18.2 \times 10^{-5}$ $K^{-1}$.

15.11 (a) Estimate the mean coefficient of linear expansion for the $a$ and $c$ axes of $CaZr_4P_6O_{24}$, using the data in Figure 15.8. (b) What is the mean coefficient of volume expansion of this material?

15.12 The voltage generated across a Pt–Au thermocouple when the cold junction is at 0 °C and the hot junction is at 100 °C is +780 $\mu$V. The experimental setup is as shown in Figure 15.12a, with Pt as metal B, and Au as metal A. Calculate the average value of $\Sigma_{AuPt}$ over the temperature range. Assuming that the absolute value of the Seebeck coefficient for Pt, $\sigma_S$, is $-6.95\ \mu\text{V K}^{-1}$ over the whole of this temperature range, estimate the average value of the absolute Seebeck coefficient for Au.

15.13 The voltage generated across a Pt–Al thermocouple when the cold junction is at 0 °C and the hot junction is at 100 °C is $+420\ \mu\text{V}$. The experimental setup is as shown in Figure 15.12a, with Pt as metal B, and Al as metal A. Calculate the average value of $\Sigma_{\text{AlPt}}$ over the temperature range. Assuming that the absolute value of the Seebeck coefficient for Pt, $\sigma_S$, is $-6.95\ \mu\text{V K}^{-1}$ over the whole of this temperature range, estimate the average value of the absolute Seebeck coefficient for Al.

15.14 The absolute Seebeck coefficients for lead, $\sigma_{\text{Pb}}$, at 300 K is $-1.047\ \mu\text{K}^{-1}$, and for platinum, $\sigma_{\text{Pt}}$, at 300 K is $-5.05\ \mu\text{V K}^{-1}$. A thermocouple is constructed as in Figure 15.12a, with Pb as metal A, and Pt as metal B. Estimate the voltage generated when the cold junction is at 0 °C and the hot junction at 300 K.