Phase Transitions

What is a phase transition? It means a change of symmetry of the system. Symmetry includes several possibilities:

- The arrangement of atoms or molecules. For example, ice melting or liquid water becoming gaseous water (steam) are examples of changes of arrangement of the $\text{H}_2\text{O}$ molecules;
- A new quantity that reduces the symmetry. I discuss below two examples—ferromagnetism and ferroelectricity;
- The coexistence of spatial regions having qualitatively different properties. For example, a semiconductor can be "doped" so that there are mobile carriers—either electrons or holes—that respond to an electric field and cause an electrical current. Sometimes, however, instead of a single density of carriers $\rho$ (= number of carriers/volume), materials "phase separate" into spatial regions of higher and lower (lower can be zero) carrier densities.

How do I describe a phase transition? The first question is whether the energy of the object—the "system"—changes continuously or discontinuously. Phase transitions in which the energy of the system changes discontinuously are called "first order" phase transitions. Ice melting or liquid water becoming steam are both first order phase transitions.

The other type of phase transition is when the energy changes continuously, but the derivative of the energy with respect to temperature changes discontinuously. Remember, the heat capacity $c_v$ or $c_p$ is the derivative of energy with respect to temperature:

$$C_v = \left(\frac{\partial E}{\partial T}\right) \bigg|_V \quad \text{and} \quad C_p = \left(\frac{\partial E}{\partial T}\right) \bigg|_P$$

So a second order phase transition means that the heat capacity (or, the specific heat $= \text{heat capacity/mole}$) is discontinuous.

When there is a second order phase transition that changes the arrangement of the nuclei, it is easy to see the change— with x-ray diffraction, neutron diffraction, or scanning tunneling microscopy. However, it is important to realize that some changes can accompany second order phase transitions—where the energy itself changes continuously—while others can only be due to first order phase transitions. Figure 1 shows the qualitative idea. Let us start with an isolated atom. Then every direction in space is equivalent to any other direction, so the symmetry is quite high. In fact, the symmetry is as high as it can be in three dimensional space. Suppose that I arrange atoms in an ordered fashion. In three dimensions, the two highest symmetry arrangements are that of a cube and a hexagon. Notice, though, that I can not change in small steps between a hexagon and a cube. Instead, the change between hexagon and cube involves moving atoms around a finite distance—meaning that there is a finite energy cost. Thus, a phase transition between a hexagonal structure and a cubic structure must be a first order phase transition.

Now consider the cube. If I make one axis the least little bit larger— or smaller— than the other two, I change the cube to a solid rectangle. The solid rectangle has a different— and lower— symmetry than the cube. Because the difference in axes can be as little as I wish— and still get a rectangle— the energy needed to make this change in symmetry can approach zero. That is, the energy across the boundary separating a cubic symmetric from a rectangular symmetry is continuous. Thus, a phase transition from cubic to solid rectangular symmetry can be a second order phase transition.

There is another perspective on this idea of symmetry change. Let us remind ourselves that when we say an object has spherical symmetry, we mean that all directions are equivalent. That is, pointing in one or another direction is the same. Thus, in spherical symmetry, two objects with vectors pointing in different directions are equivalent. This means that any direction a vector is pointed in is equivalent to any other, so that the "order" of the vectors is, well, no order at all! Suppose that I follow Fig. 1 and look at both the change from spherical to cubic and from cubic to solid rectangular symmetry. There are several changes I can make to a cube that keeps the cube as it was: i) changing axes from $x$ to $y$ to $z$; ii) rotating about the middle of the cube by $\pm 90^\circ$ or $\pm 180^\circ$; iii) inverting through the middle of the cube. And others as well.
However, not all directions are equivalent, only some- a small number compared to a sphere, certainly. So the system is more ordered as a cube- in the sense that there are fewer equivalent orientations. This is both general and important: lower symmetry and higher order (less randomness) accompany each other. When we compare changing a cube to a solid rectangle, again the symmetry decreases and the order- equivalent orientations- increases.

Now let me talk to you about a different kind of phase transition, one in which the electrons acquire a net magnetization (which is a vector defined as the magnetic moment per volume). The idea of a magnetic moment is in analogy to a little bar magnet that you can buy at a hardware store. The essence of the little bar magnet is having a north magnetic pole and a south magnetic pole, with magnetic field lines pointing from one to the other. That is, there is a magnetic dipole- a physical separation of the magnetic north and south poles. People have defined a unit of little bar magnets, and the magnetization can be thought of as the number of unit little bar magnets per volume of the material. Most any material- even you!- have some non-zero magnetization. However, in the absence of an external applied magnetic field, the little magnets in most materials do not point in any particular direction. Instead, they point randomly. Notice, for the little magnets, there is maximum symmetry- all directions are equivalent- and minimal order (in fact, no order at all).

If I apply an external magnetic field, the little magnets inside a material respond in one of two qualitatively different ways. First, for some materials (called paramagnetic), the energy of the material may become lower if the material is in a magnetic field. These materials can thus lower their energy by moving toward a region of higher magnetic field. I illustrate this in Figure Two, where I sketch a paramagnetic material that physically moves toward the magnet pole with the larger magnetic field. Here a "magnetic field" can be thought of as the number of magnetic field lines per cross-sectional area.

Figure Two also illustrates the other type of material, termed diamagnetic. These materials lower their energy by moving toward regions of lower magnetic field. Virtually any material is either paramagnetic or diamagnetic. The paramagnetic materials move toward regions of greater magnetic field, while diamagnetic materials do the opposite.

What happens with paramagnetic materials and diamagnetic materials is that the external magnetic field induces a magnetization, and a magnetic field, inside the materials. If this magnetic field reinforces the external field, the material is paramagnetic, while if the induced field opposes the external field the material is diamagnetic. Neither material has a net magnetization- or internal magnetic field- when the external field is turned off, because the magnetization of the material is induced solely by the external field.

There are a few materials, however, that have a net magnetization, and internal magnetic field, when there is no external magnetic field. These include the ferromagnetic elements iron, cobalt, nickel and gadolinium. Each of these elements, and all other ferromagnetic materials, have a few things in common:

i) The presence of the little magnets pointing in certain preferred directions, not randomly;

ii) The preferred directions are comparatively few in number but are equivalent. So if pointing in the (x) and (y) directions happen to be two preferred directions, it is as likely to find little magnets pointing in the (x) direction as in the (y) direction;

iii) There is a range of temperature (usually, but not always, the lowest temperatures) for which there is a net magnetization. At a particular temperature, however, having a preferred direction goes away and all directions are equivalent.

So while the atoms (the nuclei) may remain in their symmetry, the magnetization changes symmetry from high symmetry (all directions equivalent, no net magnetization) to lower symmetry (net magnetization). This is in fact what people mean by "ferromagnetism." Iron, cobalt, nickel, gadolinium, and every other ferromagnetic material has such a phase transition temperature. The phase transition temperature for ferromagnets is called the "Curie temperature," after Pierre Curie (Madame Curie's husband), a renowned French scientist in the first part of the 20th century. It is the electrons in materials that lead to magnetization and ferromagnetism, and it is the symmetry of these electrons that determines whether the material is in the ferromagnetic state or the magnetically disordered state.
Ferromagnetism is not the only ordered magnetic state. Figure Three illustrates two types of long-range magnetic order. The circles represent the individual atoms. The arrows represent the little bar magnets (the magnetization). Notice, as Fig. 3(a) illustrates, that all the little bar magnets can be aligned in parallel, yielding ferromagnetism. However, as shown in Fig. 3(b), adjacent magnets can be oppositely aligned. This yields antiferromagnetism, which was discovered by Dr. Néel in France in the 1930’s. Today, as Fig. 3(c) illustrates, combinations of ferromagnetic layers, with adjacent layers aligned antiferromagnetically, is used to make magnetic hard disks with the highest density of information storage.

Another phase transition that lead both to new ideas and new technology is superconductivity. In 1911, at the University of Leiden in the Netherlands, Dr. Onnes discovered superconductivity. He had learned how to liquefy helium, which at one atmosphere pressure remains a gas at all temperatures. This allowed him to reach temperatures as low as approximately 3K, while until then the lowest practical temperature was slightly below 77K, the boiling point of nitrogen. He built a small device in which the helium gas would liquefy, and placed different metals in the liquid helium (at 4.2K) to see what would happen. When he placed a piece of lead in the liquid helium, the electrical resistivity dropped to zero. Recall the idea of electrical resistivity, as shown in Figure Four. Connect a battery- which provides a difference in electrical potential energy (V)- to the two ends of a piece of metal. The electrons in the metal will reduce their potential energy by moving toward the positive side of the battery. They hit something (mostly defects in the material and the nuclei) in the material at locations (x in Fig. 4) and lose their energy, then start again. The result is an electrical current (I). The electrical resistivity \( R = \frac{V}{I} \). Notice that if the electrical resistance is low, this means it takes very little difference in voltage (potential energy) to create an electrical current.

What Dr. Onnes discovered was that the electrical resistance of the piece of lead abruptly decreased to zero (as best he could measure) at a particular temperature of approximately 8.0K. If the lead was below 8.0K, once an electrical current was established, there was an electrical current with no voltage needed. The abruptness of the change from the behavior of a “normal” metal to this new behavior lead scientists to refer to a regular metallic state as the “normal” state, and this new state the “superconducting” state. It took over 15 years for people to begin developing an explanation of this new state of matter, and the microscopic theory was not invented until 1956. In that year, a University of Wisconsin- Madison graduate, John Bardeen (B.S.E.E., M.S.E.E.), his postdoctoral research assistant Dr. Leon Cooper, and his student, Dr. Robert Schrieffer, published their idea. This idea, which came to be called the “BCS” theory, stand as one of the great advances in physics in the 20th century, providing a microscopic explanation of a many-body phenomenon.

Superconductivity is a phase transition- the electrical and magnetic properties of the same material are quite different in the normal and superconducting states. So there should be a difference in symmetry between the two states. But what was the difference in symmetry? It was not the arrangement of nuclei; exhaustive studies of the lattice by x-ray diffraction established that the nuclei kept the same crystal order in both states. Instead, the symmetry difference arose entirely because of the electrons. Let me briefly explain this. I apologize if some parts of my explanation are a tad difficult to follow.

Electricity and magnetism were unified in 1865 by Dr. James Clerk Maxwell, a Scotsman in England. He explained how varying electric fields (E) or magnetic fields (B) could affect the other. These equations are:

\[
\begin{align*}
(1) \quad \nabla \cdot \mathbf{E} &= \frac{\rho_T}{\varepsilon_0} \\
(2) \quad \nabla \cdot \mathbf{B} &= 0 \\
(3) \quad \nabla \times \mathbf{E} + \frac{\partial \mathbf{B}}{\partial t} &= 0 \\
(4) \quad \nabla \times \mathbf{B} - \left(1/c^2\right) \left(\frac{\partial \mathbf{E}}{\partial t}\right) &= \mu_0 \mathbf{J}_m
\end{align*}
\]

where \( \rho_T \) is the total electrical charge density (coulomb/meter\(^2\)), \( c \) is the speed of light, \( \varepsilon_0 \) is the permittivity of free space \( (8.85 \times 10^{-12} \text{ farad/meter}) \), \( \mu_0 \) is the permeability of free space \( (4\pi \times 10^{-7} \text{ henry/meter}) \) and \( \mathbf{J}_m \) is the current density due to the flow of charge in matter (ampere/meter\(^4\)).
Please notice equation (2), above. When the divergence of a vector is zero, the vector can be written as:

$$ B = \nabla \times A $$

where $(A)$ is an arbitrary vector called the vector potential. In fact, not only is $(A)$ arbitrary, it is not unique. Consider another vector $(A_2)$:

$$ A_2 = A + \nabla \phi $$

where $(\phi)$ is any scalar function having first derivatives with respect to $x$, $y$ and $z$. Since the vector identity:

$$ \nabla \times (\nabla \phi) = 0 $$

is always true:

$$ B = \nabla \times A = \nabla \times A_2 $$

is also true. So there is a symmetry here- all vectors $(A)$ and $(A_2)$ are equivalent. This symmetry is called “gauge invariance,” or “gauge symmetry.” What people have learned is that in the normal state, a metal has this gauge invariance, but when the material undergoes the superconducting phase transition, this gauge invariance is broken, and these different vector potentials are no longer equivalent. This is the loss of symmetry for the BCS superconducting phase transition.

In fact, the superconducting phase or state is much more than merely this loss of gauge invariance. In the normal state, it is electrons (or holes) that carry the electrical current in a metal. In the superconducting state, something new happens. I have briefly mentioned the difference between a “fermion” and a “boson.” I noted that electrons are fermions; each electron has an angular momentum $\hbar/2\pi$, where $S = [(1/2)(3/2)]^{1/2}$ and $\hbar = 6.63 \times 10^{-34}$ joule sec. When a metal undergoes a superconducting phase transition, pairs of electrons- called Cooper pairs- are formed. These two electrons pair up, much as two little magnets would pair up. Just as with two magnets, there are two ways to pair up: reinforce their individual angular momenta, or cancel their individual angular momenta. In most superconducting materials- but not all- the two electrons pair up so as to cancel their individual angular momenta. So the Cooper pair of two electrons has zero angular momentum. Because the angular momentum has $S = [(0)(1)]^{1/2} = 0$, the two electrons comprise a single boson. As I mentioned, but have not yet proven, bosons have the property that any number of bosons can occupy the same energy state- in particular, the lowest energy state. The way it works in superconductors discovered before 1986, the electrons that form Cooper pairs all have this same lowest energy. Because they have an electrical charge, of course, they also respond to an electric field and flow, creating an electrical current. However, unlike individual electrons, these Cooper pairs do not break up so easily- in fact, at these low temperatures, the Cooper pairs last an enormously long time. As a result, the electrical current in a superconductor, the so-called “supercurrent,” lasts virtually forever. Because the Cooper pairs do not lose any energy, their electrical resistance is zero, explaining what Dr. Onnes found back in 1911.
Figure One

Hexagon

Cube

Rectangle
Figure Two

Low

High

Magnet Poles

Paramagnetic

Diamagnetic
**Figure Three**

(a)  
\[ \begin{array}{ccc}  
N & S & N \\
S & S & N \\
N & S & S \\
S & N & N \\
S & S & N \\
S & S & S \\
\end{array} \]  

(b)  
\[ \begin{array}{ccc}  
N & S & S \\
S & N & S \\
N & S & N \\
S & N & S \\
S & S & N \\
N & S & N \\
\end{array} \]  

(c)  
\[ \begin{array}{ccc}  
\rightarrow & \rightarrow & \rightarrow \\
\leftarrow & \leftarrow & \leftarrow \\
\rightarrow & \rightarrow & \rightarrow \\
\rightarrow & \rightarrow & \rightarrow \\
\rightarrow & \rightarrow & \rightarrow \\
\end{array} \]  

**Figure Four**

\[ \begin{array}{ccc}  
I \\
\rightarrow & \rightarrow & \rightarrow \\
\rightarrow & \rightarrow & \rightarrow \\
\rightarrow & \rightarrow & \rightarrow \\
I \\
\end{array} \]