1. Types of magnetism.

The purpose of these lectures is to deal with paramagnetism in crystals, but it is useful at the start to review briefly the various types of magnetic behaviour one meets in nature.

*Diamagnetism* is the most frequently observed type, and most simple substances are diamagnetic. Their susceptibility is negative. I.e. a magnetic field induces a magnetic moment in the opposite direction. The absolute value of the susceptibility is very small, and is nearly independent of temperature.

*Paramagnetism.* In paramagnetic substances a magnetic field induces a moment in the same direction, i.e. the susceptibility is positive. The magnitude of the susceptibility is larger than in diamagnetic substances, and generally increases with decreasing temperature.

*Ferromagnetism, antiferromagnetism and ferrimagnetism* are more complicated forms of magnetic behaviour, characterized, among other things, by departures from the proportionality between field and magnetic moment. They will be dealt with in other sets of lectures in the summer school, and it will be sufficient for the present purpose to remark that all real paramagnetic substances probably show this behaviour at sufficiently low temperatures; and conversely, these more complicated types become paramagnetic at elevated temperatures.

2. Fundamentals of paramagnetism.

Many paramagnetic substances obey Curie’s law

\[ \chi = C/T \]

at least approximately. *C* is called the Curie constant.
Most paramagnetic crystals, though not all, are ionic. Their paramagnetism can be traced to certain paramagnetic ions, and to a useful extent one can isolate the idea of ionic susceptibility. Paramagnetic ions invariably contain transition elements, e.g. Fe$^{2+}$, Fe$^{3+}$, Cu$^{2+}$, Fe(CN)$_6^{3-}$, Gd$^{3+}$, UO$_2^{2+}$, etc.

The susceptibility of a crystal is the sum of the ionic susceptibilities of its components. Since there are diamagnetic and paramagnetic ions in a paramagnetic crystal, the total is made up of a paramagnetic part (temperature dependent) and a diamagnetic part (temperature independent). A more complete expression for the susceptibility would then be

\[ \chi = \frac{C}{T} + a, \]

\( a \) being a small negative constant. Sometimes \( a \) is positive, but still small. We then speak of a temperature-independent contribution to the paramagnetism.

In quoting experimental values of ionic susceptibilities it is usual to correct the measurements for the diamagnetism of the various ions making up the crystal.

Curie’s law (2) is a good approximation only for magnetically dilute substances, e.g. those for which the effective field acting on the ion is only the external one. In magnetically dense substances, neighbouring ions influence each other through their magnetic fields and by electron exchange. For magnetically concentrated substances, the Curie-Weiss law often holds:

\[ \chi = \frac{C}{T - \Delta} (+a), \]

where \( \Delta \) is the Weiss constant and is positive for ferromagnetic substances and negative for antiferromagnetic substances. Eq. (3) may hold for magnetically dilute substances too (see (94)).

We shall often in the following, as an approximation, consider atoms and ions as isolated entities. This is not fully correct, for the magnetic properties of a paramagnetic ion in a crystal are strongly influenced by the electric field of the surrounding ions. For instance, in crystals grown from water solution of salts of the first transition group, the magnetic ion is surrounded by six molecules of H$_2$O, or four molecules of H$_2$O and two oxygens associated with some acidic ion, such as SO$_4^{2-}$. In both cases we have six negative charges arranged about the magnetic ion on the vertices of an octahedron. (The H$_2$O even though neutral, is dipolar and points its negative side towards the metal ion.) For instance, the arrangement for CuSO$_4$$\cdot$5H$_2$O is as shown in Fig. 1. A more correct statement is that we shall be considering ionic complexes of