

Chapter 3: Physical properties of ore minerals

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Physical properties of ore minerals are employed in mineral identification and exploration. Here we consider magnetism, electrical conductivity and reflectivity of common sulphides and iron oxides. This chapter also explores the relationship between physical properties on a mineral scale and the behaviour of ore deposits.

Goals:

After reading this chapter you should be able to:

- Describe magnetism of ore minerals
- Relate the magnetic characteristics of minerals to sulphide and oxide ore deposits
- Explain the conductivity of ore minerals
- Assess the likely conductivity of ore deposits based on their mineralogy
- Explain the connection between reflectivity and mineral identification.

3.1 Mineral magnetism

Atomic scale ordering of electrons in iron bearing minerals influences the magnetic behaviour of the minerals and thus is termed magnetic ordering. In turn the size and direction of a magnetic signal is described by the magnetic moment. Magnetic ordering is also affected by temperature to the extent that magnetic moments that are ordered at low temperature can become disordered at high temperature. The temperature at which the magnetic ordering changes to disorder is known as the Curie temperature (T_C) and is 575°C for magnetite and 960°C for hematite or the Néel temperature (T_N) for ilmenite that varies as a function of temperature and Ti content (Fig. 3.01; Banerjee; 1991; Moskowitz, 1991).

Magnetic moment – size and direction of an objects magnetism.

Curie point (T_C): Magnetic disorder in ferromagnets and ferromagnets above the Curie temperature.

Néel point (T_N): Magnetic disorder in antiferromagnets above the Néel temperature.

The Morin transition describes yet another temperature controlled variation in hematite where oblique alignment of magnetic moments occur above the Morin transition at -10°C (Fig. 3.01).

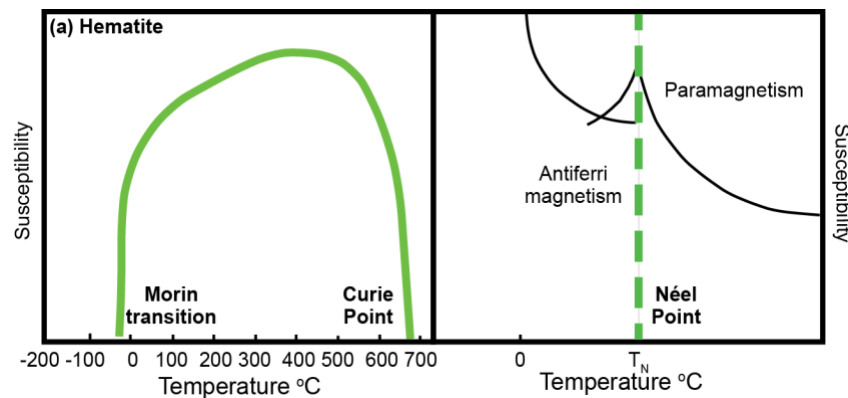


Figure 3.01 Variations in magnetic susceptibility with temperature for (a) hematite and (b) ilmenite. Above the Morin transition hematite displays canted antiferromagnetism, below the Morin transition it is an antiferromagnet. Above the Curie point hematite exhibits magnetic disorder. Likewise, ilmenite is antiferromagnetic below the Néel point and becomes paramagnetic at higher temperature.

Some minerals display intrinsic magnetism whereas others only show magnetic susceptibility, where an applied magnetic field leads to alignment of the magnetic moments in the direction of the magnetic field.

Box 3.1 Atomic scale processes: Crystal field splitting

Cations and anions in a mineral structure will interact due to their charge. Atomic forces lead to the attraction of opposite charges, instead ions of the same charge repel each other. This means that overall the cations and anions will attract each other, whereas the electrons in each species will repel each other. In oxide and sulphide minerals the electron interactions lead to d-shell electron splitting into different energy levels (Fig. 3.02; Pearce et al., 2006). This is referred to as crystal field splitting (Δ_o) and is a function of valency, ion type and interatomic distances. Higher valencies and smaller interatomic distances combined with sulphur or oxygen anions lead to high crystal field splitting.

The spin of an electron contributes a magnetic moment ($1\mu_B$; μ_B = Bohr). If the electrons are spin paired the moments will cancel out producing no net magnetic moment. In many tetrahedrally coordinated transition metals unpaired electrons occur producing no net magnetic moment (Harrison & Feiburg, 2009; Pearce et al., 2006).

Morin transition:
Temperature above which hematite displays canted antiferromagnetism.

Magnetic susceptibility is the increase in magnetisation in an applied magnetic field.

Cation: positively charge ion

Anion: negatively charged ion

Valency: charge of an atom, e.g. Fe^{2+} , Fe^{3+}

Electron shells:

1s

2s, 2p

3s, 3p, 3d

4s, 4p, 4d, 4f

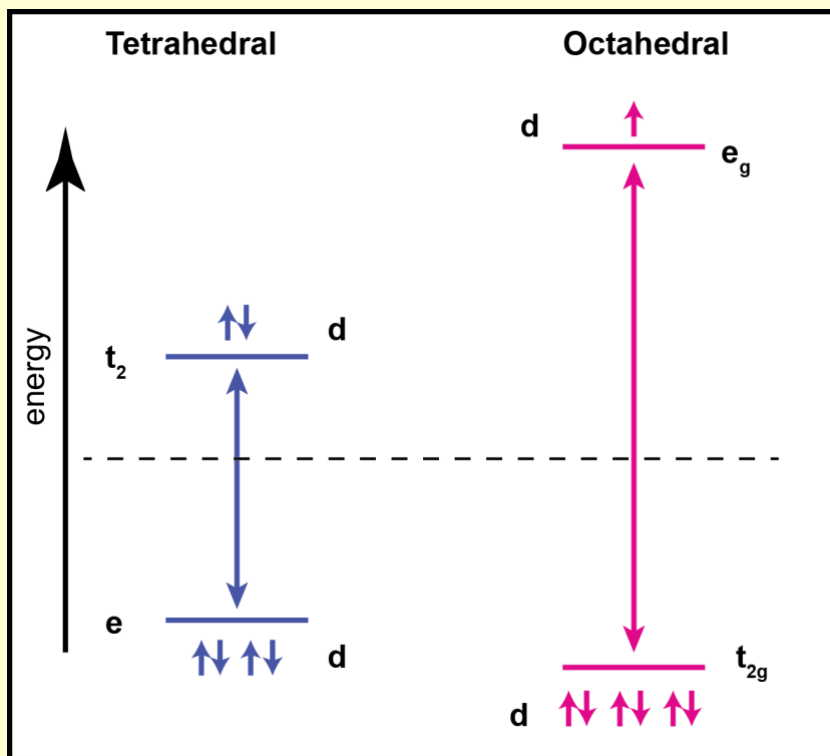


Figure 3.02 Crystal field splitting. Tetrahedral sites accommodate spin paired 3d electrons in t_2 and e energy levels. Octahedral sites arrange the electrons in low or high spin configuration depending on pairing of the 3d electrons in t_{2g} or e_g energy levels, which causes crystal field splitting.

In Ti, Cu and Zn all the d-shell electrons are paired and therefore all 3d orbitals have the same energy. In cations with 4 to 8 electrons in the 3d shell, which are often octahedrally coordinated, electrostatic forces repel the electrons causing crystal field splitting and higher potential energy. The electrons are then arranged in a low energy configuration (t_{2g}) or a high energy configuration (e_g). When there is a large energy difference, the electrons assume the lowest energy state with maximum paired electrons in t_{2g} . This is referred to as low spin. Taking the example of Co^{2+} with 7 d-shell electrons, low spin configuration would be $t_{2g}^6 e_g^1$ and the resulting magnetic susceptibility would be low (Pearce et al., 2006). Where the energy difference is small the electrons spread out into a high spin configuration. For Co^{2+} this would be expressed as $t_{2g}^5 e_g^2$. Ni, Fe, Mn, Co and Cr can assume high or low spins by arranging electrons. Mn and Cr can spread all the d-shell electrons as unpaired electrons between t_{2g} and e_g energy levels, Fe^{3+} has 5 unpaired electrons and Fe^{2+} has 4 unpaired electrons. Given the spin of unpaired electrons leads to net

magnetic moments, high spin leads to high magnetic susceptibility, which is therefore associated with Fe^{2+} , Fe^{3+} , Ni^{3+} , Co^{2+} , Co^{3+} , Cr^{2+} , Mn^{2+} and Mn^{3+} .

3.1.1 Types of magnetic susceptibility

Magnetic susceptibility occurs when diamagnetic or paramagnetic minerals are exposed to a magnetic field. Diamagnetic minerals are characterised by filled electron shells, which are commonly observed in minerals that are poor in iron and other transition metals. Therefore no interactions between electrons occur and there is no net magnetic moment. In the presence of an applied magnetic field such minerals display negative magnetism, which is constant despite variations in temperature conditions (Fig. 3.03a,b; Moskowitz 1991). Silicate and carbonate minerals that contain little iron or titanium are diamagnetic.

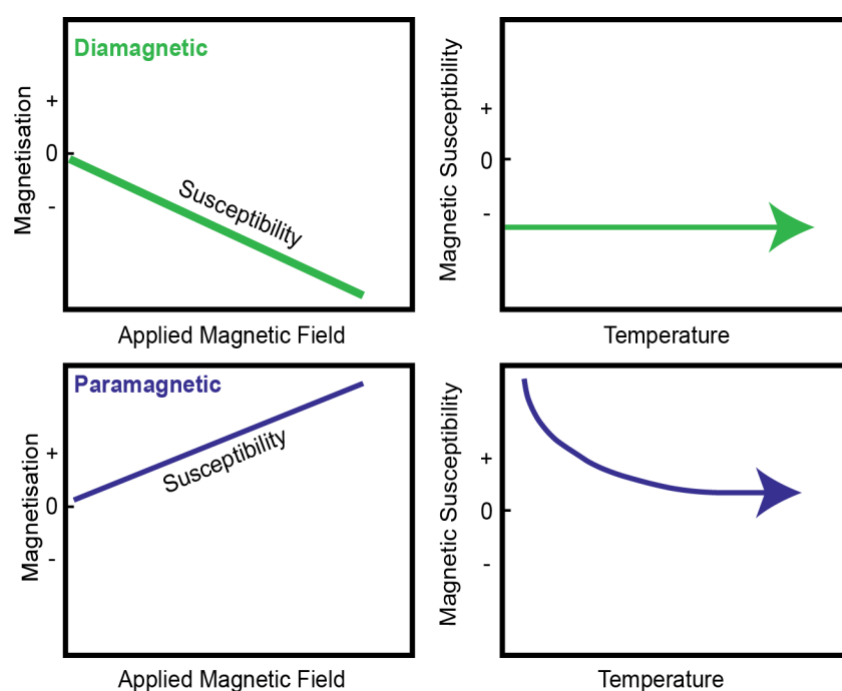


Figure 3.03 Magnetism and magnetic susceptibility of diamagnetic and paramagnetic minerals in an applied magnetic field. Diamagnetic minerals show negative susceptibility which is constant with increasing temperature. Whereas paramagnetic minerals display positive susceptibility which decreases exponentially with increasing temperature.

In paramagnetic minerals there is naturally very little interaction between the individual moments of the atoms, due to most of the electrons being evenly paired (Harrison & Feiburg, 2009). Therefore

under normal conditions there is no magnetic ordering with the magnetic moments showing random orientations and no resulting magnetism. When a magnetic field is applied, such as the Earth's magnetic field, a partial alignment of magnetic moments occurs. This generates a weak positive magnetism (Moskowitz, 1991). The resulting magnetism is temperature dependent, where, as temperature increases the partial alignment of magnetic moments is weakened and the magnetic susceptibility decreases (Fig. 3.03c,d). Above the Curie temperature magnetic disorder remains. Paramagnetic susceptibility is typically proportional to the iron content of the material, for instance iron-rich minerals such as biotite, pyrite, clay minerals and siderite show paramagnetic behaviour.

Box 3.2 Atomic scale electron interactions

The interactions between cations are moderated by the anions and can be described by a few exchange mechanisms. Superexchange is covalent sharing of electrons between the anion and the 3-d shell of the cation (Fig. 3.04). Indirect exchange is achieved by moving an electron in the anion close to the cation electron orbit. Double exchange occurs when there are mixed valencies in the structure and the anion and cations both swap electrons.

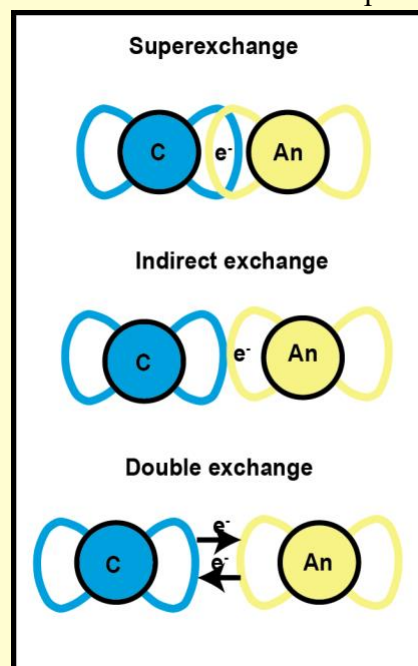


Figure 3.04 Electron interactions between cations and anions. Superexchange represents covalent sharing of electrons. Indirect exchange occurs when electrons in an anion are situated near to a cation and in the case of double exchange the cation and anion swap electrons.

Pyrite exhibits spin paired electrons, with 6 electrons in the 3-d shell organised in three t_{2g} orbitals, in low spin configuration. Due to the

distortion of the pyrite crystal lattice the electrons become partially aligned producing a paramagnetic moment in an applied magnetic field (Pearce et al., 1991). Although pentlandites contain Fe and Ni, the electrons are spin paired in a low spin configuration producing paramagnetism.

3.1.2 Magnetic minerals

Intrinsic magnetism forms three groups; ferromagnetism, antiferromagnetism and ferrimagnetism. In ferromagnetism the magnetic moments are oriented in one direction and parallel to each other such that the magnetic moments accumulate, giving a large magnetic moments (Fig, 3.05; Banerjee 1991; Moskowitz, 1991; Pearce et al., 2006; Harrison & Feiburg, 2009). Ferromagnetism is associated with high spin arrangements of electrons maximising the net magnetic moment and is typically associated with Fe, Ni and Co. Ferromagnetism is found in few natural minerals of which the sulphides CoS_2 and CuCr_2S_4 are noteworthy (Pearce et al., 2006).

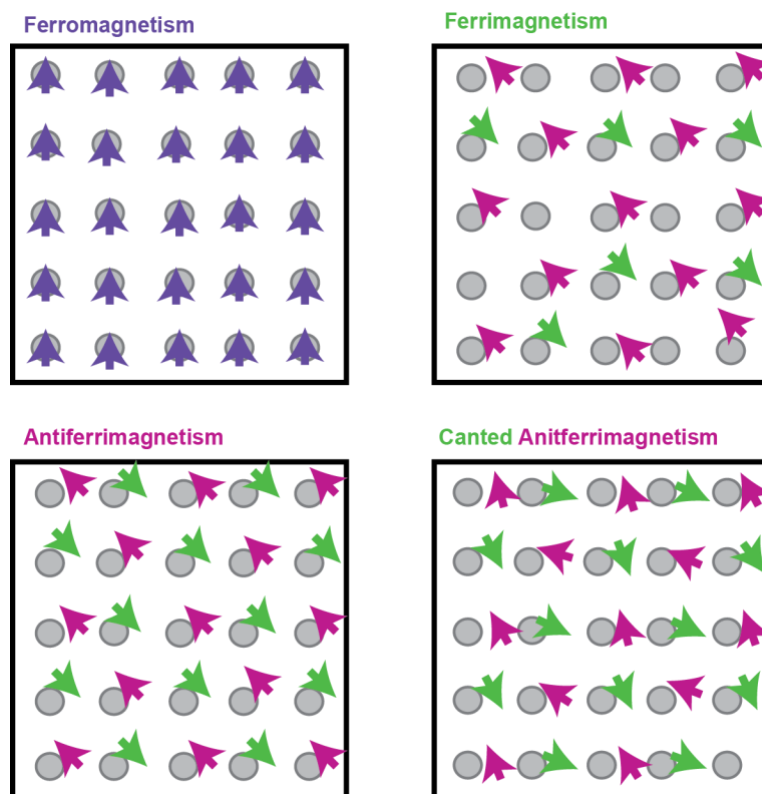


Figure 3.05 Types of magnetism. In ferromagnetism the electron spins are all aligned in the same direction. In ferrimagnetism the electron spins are layered in opposite directions but one direction is dominant producing a net magnetism. In antiferromagnetism the opposing electron spins are equal and cancel each other out, therefore there is no net magnetic moments. In canted antiferromagnetism the electron spins are oblique to each other resulting in a weak net magnetic moments.

Antiferromagnetism is where the magnetic moments are equal and opposite, such that they cancel out producing no net magnetism (Fig. 3.05). Above the Néel temperature (T_N), the moments become disordered and paramagnetism occurs (Fig. 3.01; Moskowitz 1991). Antiferromagnetic minerals are relatively common among the ore minerals. The pyrrhotite group with cation deficient non-stoichiometric ($\text{Fe,Co,Ni}_{1-x}\text{S}$) structures are typically antiferromagnetic as is vaesite (NiS_2) (Pearce et al., 2006).

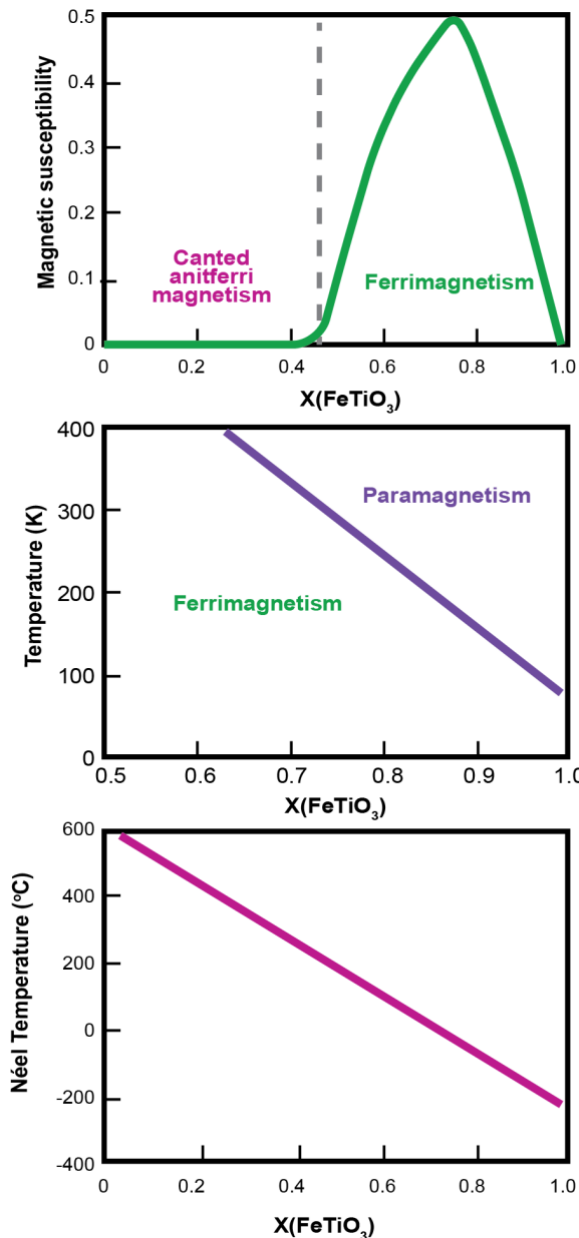


Figure 3.06
Magnetic susceptibility of the hematite-ilmenite series as a function of Ti-content. The transition from ferrimagnetic to paramagnetic occurs at higher Ti-contents with decreasing temperature, also reflected in the variation of the Néel point.

In hematite the magnetic moments are parallel within layers and oriented in opposite directions between planes producing antiferromagnetism (Fig. 3.05b). However between the Morin transition (-10°C) and the Curie point (960°C ; Fig. 3.01), the spin moments become slightly oblique to each other. The obliquity

produces canted antiferromagnetism, where the magnetic moments are misaligned leading to a weak net magnetic moment.

Ilmenite is a perfect antiferromagnet, exhibiting a change to paramagnetism above the Néel point (Banerjee 1991; Moskowitz 1991). The Néel temperature decreases with increasing Ti substitution (Fig. 3.06). The magnetic ordering changes from the canted antiferromagnetism of hematite to the perfect antiferromagnetism of ilmenite at $\text{Fe}_{1.5}\text{Ti}_{0.5}\text{O}_3$ (Fig. 3.06). Antiferromagnetism in the hematite-ilmenite series involves superexchange and indirect exchange interactions (Fig. 3.04).

Ferrimagnetism is a more complex ordering system, where sublattices of cations are interlayered with anions (Fig. 3.05; Banerjee 1991; Moskowitz 1991). This interlayering promotes superexchange or indirect exchange interactions. The magnetic moments of different layers in the mineral structure are typically aligned in opposite directions. However the magnitude of magnetic moments is commonly not equal and therefore a net magnetism results. Many oxides, especially those with a spinel structure, with tetrahedrally and octahedrally co-ordinated cation layers are ferrimagnets.

Magnetite exhibits ferrimagnetic ordering of non-equal spin moments where Fe^{3+} is found in the tetrahedral (-5 mB) and octahedral (+5 mB) sites and cancels out, but the Fe^{2+} in the octahedral site (+4.2 mB) leads to the net magnetism. Substitution of Ti^{4+} with paired electrons and no magnetic moment balanced with Fe^{2+} for Fe^{3+} , decreases the net magnetic moment towards titanomagnetite. Magnetic ordering in ferrimagnets is also controlled by temperature. The thermal energy leads to disorder above the Curie temperature (Banerjee 1991; Moskowitz 1991).

Sulphides that display ferrimagnetism are monoclinic pyrrhotite and chromium sulphide with a spinel structure (Pearce et al., 2006).

3.1.3 Magnetism of ore deposits

In summary magnetite is a ferrimagnet, hematite-ilmenite, vaesite and pyrrhotite are antiferromagnets. Pentlandite, pyrite and siderite are paramagnetic. Therefore massive iron ore deposits hosting dominantly magnetite such as iron-apatite ore deposits e.g. Kiruna would exhibit strong net magnetism and thus would easily be explored by aeromagnetic surveys. Iron skarn deposits are also often

magnetite bearing and although less massive would likely be evident in a ground based magnetic survey. Banded Iron formations host hematite, which shows canted antiferromagnetism and would likely be revealed by a local ground magnetic survey. Exsolution of canted antiferromagnetic hematite and antiferromagnetic to paramagnetic ilmenite shows increased magnetism (McEnroe et al., 2009), and are thus of potential for exploration with magnetic surveys.

The stratabound layers of a Ni-Cu-PGE deposit hosting pentlandite of paramagnetic character, may be detectable by ground based magnetic surveys. Disseminated ores containing paramagnetic pyrite would be much more difficult to detect with magnetic methods.

3.2 Mineral conductivity

Conductivity can be considered as the ease with which energy in the form of heat or electrical current moves through a material. In pure metals the bonding is metallic and the electrons are delocalised allowing them to flow through the material and carry an electric current. Most ore minerals display ionic bonding with occasional covalent bonding occurring. Therefore the electrons are confined to electron shells and have less potential to flow with a current. However as we will see they can exhibit semi-conductive behaviour in some cases.

Box 3.3 Atomic scale processes: Band theory

In the atomic structure electrons are allocated to electron shells or orbitals around the nucleus. The electrons in the outer shells can exhibit partially delocalised behaviour especially when 3d, 4s and 4p orbitals of the cations overlap with 3s and 3p orbitals of the anion such as sulphur. A band represents a closely spaced energy level and the valence band is filled by low energy 3s and 3p electron shells (Fig. 3.07; Pearce et al., 2006). The 3d electrons are hosted at higher energy levels, with high spin configurations in eg reaching even higher energy levels than the paired low spin electron configurations. The highest paired 3d sites can be considered as an extension of the valence band. A conduction band or antibonding orbital will be at even higher energy levels above 4p and 4s orbitals of transition metals. Cation-anion interactions increase the size of the 3d orbitals into broad d-bands. This allows the 3d electrons to become delocalised.

Bonding:

Metallic – delocalised electrons

Ionic – exchange of electrons forms cations and anions

Covalent – sharing electrons

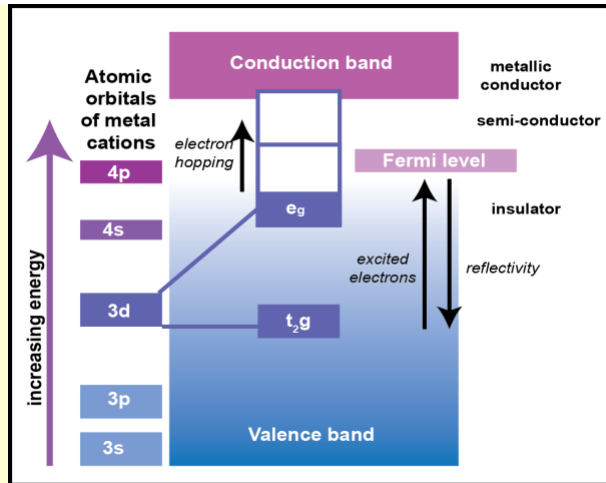


Figure 3.07 Conductivity and reflectivity theory. Electrons in 3d shells are located in t_{2g} and e_g energy levels. Those in the e_g energy level can hop to higher energy allowing the broad d-band to overlap with the conduction band and create semi-conductive behaviour. When light is shined on ore minerals the 3d electrons can be excited to the Fermi level, when they return to their ground state they emit light causing reflectivity.

3.2.1 Conductivity

Metallic conductivity occurs when the highest 3d orbitals or valence band overlap with the conduction band (Fig. 3.08). In contrast a large gap characterises an insulator, and a small gap, where the broad d-band approaches the conduction band produces a semi-conductor. Under high temperature conditions the thermal energy in semiconductors leads to hopping of electrons into the conduction band. Therefore in the presence of an applied electric field, semi-conductors would transmit an electrical current.

Metallic conduction or low resistivity can be classified into several types. Firstly, n-type conductors occur where there is an overlap between the 3d orbital and the conduction band (Pearce et al., 2006). Secondly, p-type is associated with electron vacancies in the valence band facilitating the movement of electrons. The final type is the broad d-bands caused by interaction between electrons in the 3d shell. This last category is temperature dependent, referred to as Pauli conductivity and frequently occurs in paramagnetic minerals.

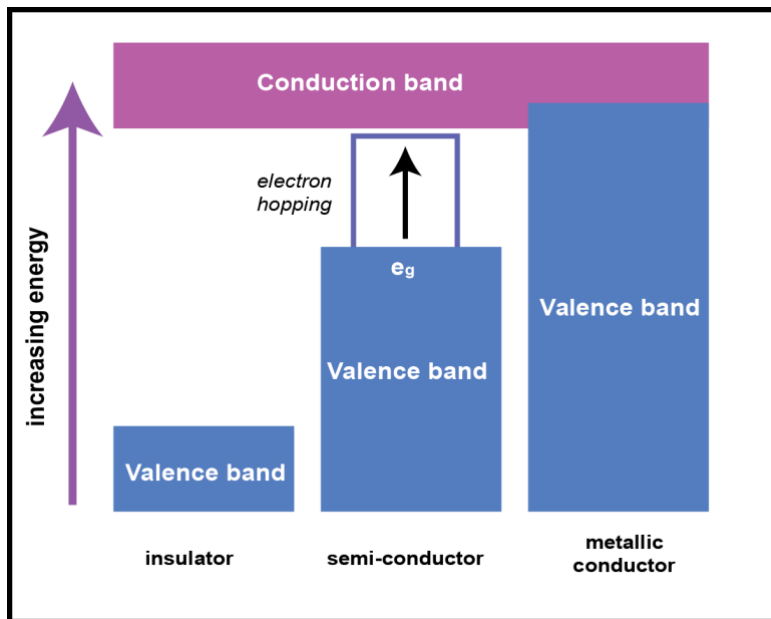


Figure 3.08 Types of conductivity. A large gap between the valence band and the conduction band produces insulators. An overlap between the valence band and the conduction band causes the material to be a metallic conductor. A small gap with 3d electrons in the eg configuration allows electron hopping and results in semi-conductors.

3.2.2 Ore mineral conductivity

Key to conductivity are Fe, Ni, Cu and Co. N-type conductivity is exhibited by pentlandite (NiS) with the niccolite structure, as well as CoS and Co_{1-x}S . P-type conductivity is typically associated with Cu^{2+} and Cu^{1+} . Semi-conductivity to metallic conductivity due to broad d-bands is common in many ore minerals.

Pyrite has six 3d electrons, which are usually spin paired, accompanied by covalent mixing in the eg site of Fe^{2+} , such that a narrow antibonding band is formed. The result is that pyrite displays Pauli paramagnetic conduction. The pyrite group minerals exhibit less covalent mixing and more unpaired electrons in high spin arrangement as Co, Ni and Cu are substituted for Fe. In response Fe rich pyrite is a semi-conductor that shows successively more metallic conduction as Co, Ni and Cu are incorporated.

The pentlandites display mixing between electron orbitals of the octahedral cations and the sulphide anions producing a narrow eg band. The 3d band is broader due to unpaired electrons in the tetrahedral t2g band, which interact with others in a so called cluster. The cations in the tetrahedral and octahedral sites are involved in cation-anion interactions with the sulphide anions leading to

Conductivity – potential to carry an electrical current.

Resistivity – resistance to an electrical current.

coalescence of the 3d band into a single, broad partly filled band. This results in significant semi-conductivity for the pendlandite group minerals (Pearce et al., 2006).

Pauli-paramagnetic metallic conduction is also exhibited by derivatives of pendlandite and pyrrhotite (Co_3S_4 , NiS, Co_9S_8 , Ni_3S_2 and Fe_{1-x}S). Semi-conductors to conductive minerals produced by large 3d-bands are also found in galena, magnetite, ilmenite, molybdenite and the Cu sulphides chalcopyrite, bornite, chalcocite and covellite (Banerjee 1991; Moskowitz 1991; Pearce et al., 2006). In contrast hematite displays a large gap between the valence and conduction bands forming an insulator with high resistivity (Banerjee 1991; Moskowitz 1991).

3.2.3 Conductivity and resistivity of ore deposits

Many ore minerals are semi-conductors to conductors in their own right. However as loose or disseminated grains in an ore deposit they are often unconnected, therefore the flow of a current is interrupted. Massive ore deposits are much more suitable for geophysical surveys employing conductivity or resistivity techniques.

Crustal lithologies such as igneous and metamorphic rocks have resistivity of 1000 to 100,000 Ωm , as they weather or alter the resistivity decreases (Fig. 3.09). Disseminated sulphides, such as in porphyry deposits, hosted in altered supracrustal lithologies are expected to have similar resistivity to their host rocks. Sedimentary rocks and hematite-rich Banded Iron Formation (BIF) are expected to have resistivity of 5 to 100,000 Ωm .

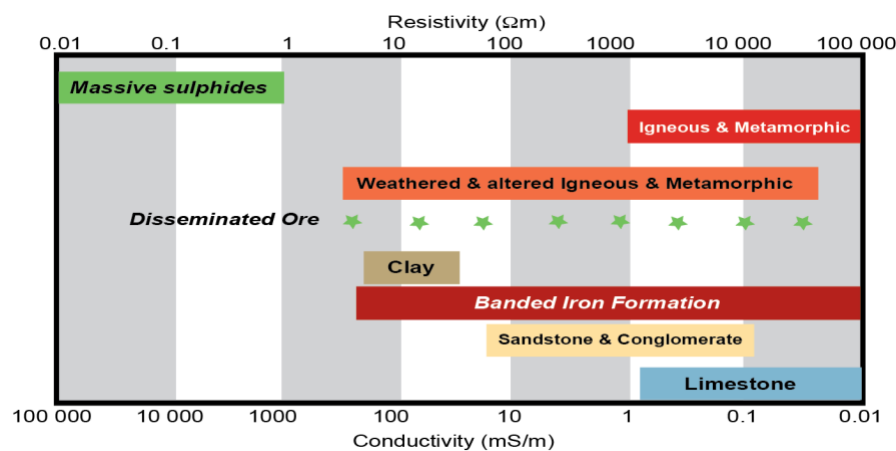


Figure 3.09 Conductivity and resistivity in rocks and ore deposits. Massive sulphide ores are the most conductive, whereas disseminated ore and Banded Iron Formations have conductivities similar to their host

rocks.

Massive sulphides associated with VMS, SEDEX or MVT deposits hosting pyrite, chalcopyrite and galena, which are highly conductive minerals would be good targets for exploration by resistivity. Likewise pyrrhotite and pentlandites hosted by magmatic Ni-Cu-PGE deposits could be expected to show relatively low resistivity compared to the host igneous rocks.

3.3 Mineral reflectivity

Reflectivity, also known as reflectance, is an important optical property used in reflected light microscopy and outcrop scale images to identify ore minerals.

$$\text{Reflectivity (R)} = \text{Reflected light (I)} / \text{Incident light (I}_0\text{)}$$

In other words the fraction of light reflected compared to the incoming light. If $R = 1$, then all of the light is being reflected (100%). Reflectivity is a function of the refractive index and the adsorption co-efficient of the mineral. The refractive index is a measure of the free electrons per molecule and thus we once again turn to band theory. When a sample absorbs light, unpaired electrons can be excited to higher energy levels. The potential energy of the excited electron is described by the Fermi level. When the excited electron returns to the ground state, the light is emitted, causing reflectivity seen in a microscope or lustre in hand specimen.

The Fermi level is an electronic transition found in between 3d orbitals and the conduction band (Fig. 3.07). Electrons in the 3d-bands therefore contribute to reflectivity. An applied light source has more potential to excite t_{2g} electrons to higher energy levels than e_g electrons, which are already at relatively high energy levels. For this reason pyrite displays higher reflectivity (52%), than vaesite (27%). In other words the more Ni, Cu or Co that substitutes into the system the smaller the difference between the excited energy level and the 3d-band and therefore the lower the reflectivity.

Silver and gold have the highest reflectivity (80-90%; Criddle & Stanely, 2012). In turn pyrite, galena, chalcopyrite and hematite have intermediate reflectivity (30-60%) and ilmenite, sphalerite and cassiterite have low reflectivity (10-25%; Fig. 3.10).

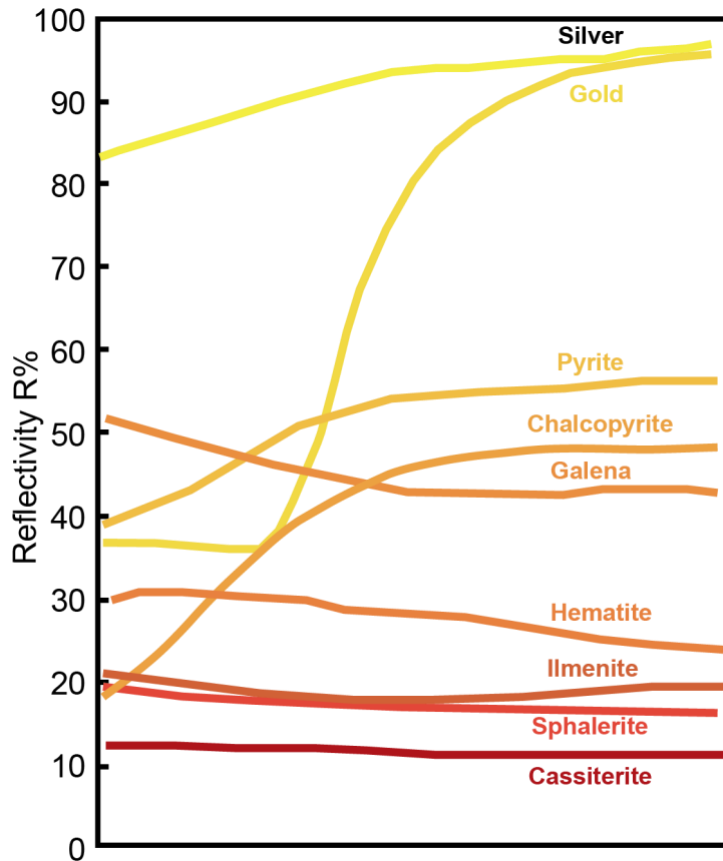


Figure 3.10 Reflectivity of ore minerals.

Study Questions

- 1) Determine the possible electron spin configurations for Ni^{3+} with 8 d-electrons or Fe^{2+} with 6 d-electrons. How does the spin configuration connect with the magnetic susceptibility?
- 2) What type of magnetism is exhibited by pyrite, pyrrhotite, pentlandite, hematite, ilmenite and magnetite? How does the magnetic ordering vary with temperature or composition of the minerals?
- 3) Explain the relationship between band width and mineral conductivity for the following minerals; magnetite, hematite, pyrite, chalcopyrite, pyrrhotite and galena.
- 4) Discuss giving reasons, whether VMS or porphyry deposits would be more conductive.
- 5) Explain giving examples the link between band theory and mineral reflectivity.

Sources and Further reading

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