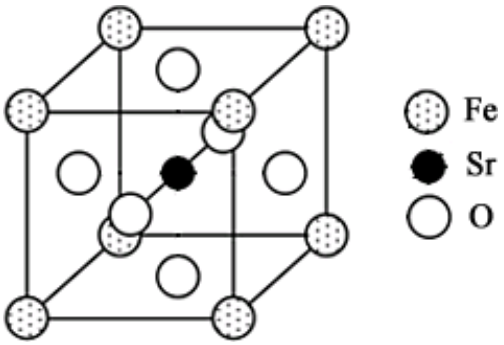
Marks 9

- $SrFeO_3$ crystallises with the perovskite structure, shown below. The structure is cubic with iron atoms on each corner, oxygen atoms at the centre of each face and a strontium atom at the centre of the cube. Mixed metal oxides such as this are of current research interest because of their magnetic and possible superconducting properties.



Show the structure is consistent with the formula $SrFeO_3$ and give the coordination numbers of the Sr, Fe and O atoms.

There is a Fe atom on each of the 8 corners, each of which is shared between 8 cells so contribute 1/8 to each: number of Fe atoms = 8 × 1/8 = 1.

There is a O atom on each of the 6 faces, each of which is shared between 2 cells so contribute 1/2 to each: number of O atoms = 6 × 1/2 = 3.

There is a single Sr atom which is at the centre and is unshared: number of Sr atoms = 1.

The formula is thus $FeSrO_3$.

Each Fe atom is surrounded by 12 O atoms: it has a coordination number of 12.

Each Sr atom is surrounded by 6 O atoms: it has a coordination number of 6.

Each O atom is surrounded by 2 Sr atoms, at a distance of 0.5*a*, and 4 Fe atoms, at a distance of 0.707*a*. As coordination number is defined as the number of nearest neighbours, it is 2.

Using the box notation to represent atomic orbitals, work out how many unpaired electrons are present on the iron cation in this compound.

As Sr^{2+} and $3O^{2-}$ are present, iron must have an oxidation number of +4. As iron has 8 valence electrons, Fe^{4+} has (8 – 4) = 4 valence electrons and a d^4 configuration. These are arranged in the five *d* orbitals to minimise repulsion by maximising the number of unpaired spins:

↑	↑	↑	↑	

There are 4 unpaired electrons

ANSWER CONTINUES ON THE NEXT PAGE

It is possible to substitute the Sr^{2+} ions at the centre of the unit cell by La^{3+} ions to make a series of compounds with the formula $La_{1-x}Sr_xFeO_3$ with $0 \leq x \leq 1$. Suggest why this substitution is achieved without significant change to the unit cell dimensions and describe how charge balance is achieved in these compounds.

La^{3+} has a similar size to Sr^{2+} as they are diagonally related on the Periodic Table. La^{3+} has an extra shell but has a higher charge. As a result, La^{3+} is able to occupy the same position in the unit cell as Sr^{2+} without the unit cell being strained.

Each time a La^{3+} replaces a Sr^{2+}, a Fe^{4+} is reduced to Fe^{3+} to ensure charge balance is maintained.