4. Representative Conducting Oxides

In this chapter, various representative oxides will be discussed in detail to present useful ideas on their electronic transport phenomena. They are representative by virtue of the following characteristic features:

ReO₃ (Sect. 4.1): The structure is simple cubic and it shows the highest conductivity in the normal oxides. The conduction band is a simple $de - O_{2p}$ type.

SnO₂ and TiO₂ (Sect. 4.2): SnO₂ is sometimes called a transparent metal and it is a broad s – p band semiconductor. TiO₂ has the same lattice structure but its electron-phonon interaction is large and it is often disputed whether the electrons form large polarons or localized small polarons.

LiTi₂O₄ and LiV₂O₄ (Sect. 4.3): LiTi₂O₄ may be considered as a heavily doped TiO₂. When the polarons condense in such a substance with a strong electron-phonon interaction, superconductivity appears, and until the discovery of Cu-oxides, its critical temperature of 13.7 K was the highest among the oxides. In metallic LiV₂O₄, a localized moment appears, in contrast to LiTi₂O₄.

WO₃ and $M_x$WO₃ (Sect. 4.4): The carriers may be large polarons in WO₃. They are heavily doped in $M_x$WO₃ where the $M$ ions distribute randomly and there a metal-insulator transition occurs at certain carrier concentrations. Percolation theory will be useful here.

$M_x$V₂O₅ and $M_x$MoO₃ (Sect. 4.5): These are low dimensional substances. The former is quasi-one dimensional and the carriers may be small polarons. A bipolaron state has been reported. Mo-bronzes form various low dimensional lattices and charge density waves, CDWs, have been observed.

NiO (Sect. 4.6): NiO is an insulator while the simple Hartree–Fock mean field theory predicts that it should be metallic. In this material, the localized nature of the electrons is strong due to the strong electron correlation and many investigations have been carried out to elucidate a “hopping” conduction. However, the nature of the electrons is not yet clear.

V₂O₃ (Sect. 4.7): This shows two metal-insulator transitions. The higher temperature one may be the Mott transition with the metallic phase at the lower temperature side. Below the lower transition temperature, the crystal becomes antiferromagnetic and insulating, accompanied by lattice distortion.

Fe₃O₄ (Sect. 4.8): This is ferrimagnetic below 860 K and shows a transition at 123 K with a jump in the electrical conductivity, which was ascribed to the order-disorder transition of Fe²⁺ and Fe³⁺. Many results have been accumulated on the nature of correlated polarons in this fluctuating-valence-material.
EuO (Sect. 4.9): This is a ferromagnetic NaCl type oxide. The reduced material shows the metallic conductivity below the Curie temperature and the conductivity jump there is of order $10^{13}$. The MIT is due to the magnetic interaction between the localized $4f$ magnetic moments and the propagating electrons.

High $T_c$ Cu-Oxides (Sect. 4.10): These are $d\gamma$ conductors whereas most of the metallic oxides are $de$ conductors. CuO$_2$ planes constitute a multilayer structure and the superconducting transition temperature increases with the layer number at least up to four and is higher than 120 K.

4.1 ReO$_3$: The Most Conductive $de$ Conductor

ReO$_3$ has the simplest structure among $d$ electron conductors and its conductivity is comparable with that of metallic Ag. The color is purple red and it is an ionic crystal. Electrons are scattered by both acoustic and optic phonons. The Fermi level lies in the $de$ band which can be approximately represented analytically and is two dimensional though the lattice is three dimensional. The electron-phonon interaction is weak and ReO$_3$ is not superconducting down to 20 mK.

4.1.1 Crystal Structure

In Fig. 4.1, the crystal structure of ReO$_3$ is shown. The lattice parameter is 0.374 nm at 300 K. As seen from the figure, the unit of ReO$_3$ is periodically arranged in a simple cubic lattice. If the vacant cube corner is occupied by a cation, it becomes the perovskite structure, and it is possible to dope Na and K into this site. Re is in the cubic symmetry position but O is in an axial symmetry position and the environment of O perpendicular to the axis is vacant.