Chapter 3

DC Conductivity of Nanostructured Nickel Oxide
3.1 Introduction

Nanostructured materials are known to exhibit profoundly varied electrical properties in comparison with those of single crystals, polycrystals, glasses and thin films with the same average chemical composition. These variations in the electrical properties are a result of the band structure modification, quantum confinement of charge carriers and dominant contributions from the largely defective and strained grain boundaries in nanostructured materials.¹⁻¹⁵

Experimentally, it has been observed that nanostructured samples of metals like Cu, Pd and Fe, and alloys like (Fe₉₉Cu₁)Si₉B₁₃ and Ni-P have a reduced value of electrical conductivity than those of their single crystalline and coarse-grained polycrystalline counterparts.⁶⁻⁹ In the case of undoped semiconductor nanoparticles, a decrease in the value of conductivity is expected due to the narrowing of valence and conduction bands resulting in an increase of the forbidden energy gap.⁵,¹¹ However, in semiconductor nanostructures, lattice defects may form acceptor-like or donor-like levels in the forbidden energy gap which can act as trapping centers and may affect the electrical response of the sample.⁵,¹¹ Enhancement of conductivity by orders of magnitude one and three over those of corresponding single crystals was reported respectively for nanostructured ZnS and CdS samples.¹¹

Nickel oxide (NiO) is an interesting material due to its complex band structure¹⁶⁻²² and less well understood conductivity mechanism.²²,⁴⁷ Nickel oxide
having a very low electrical conductivity of less than $\sim 10^{-13}$ ohm$^{-1}$cm$^{-1}$ at room temperature is classified as a 'Mott-Hubbard insulator'.\textsuperscript{17,22-26} Though NiO is perhaps the most extensively and carefully studied narrow band transition metal oxide, in the form of single crystals, coarse-grained polycrystals and thin films, a complete theory of the conductivity mechanisms involved has not yet evolved.\textsuperscript{22-47} Different possible conductivity mechanisms have been suggested to be operative in NiO at different temperature ranges. All proposed mechanisms highlight the importance of the 'localized' (very narrow) 3d band of Ni$^{2+}$ and the comparatively wide 2p band of O$^{2-}$ lying just below the Fermi level.\textsuperscript{22-26}

Earlier works have shown that doping with monovalent impurities like Li$^+$ can increase the conductivity of NiO\textsuperscript{22-26,28,32-34} For pure NiO, increase in the number of Ni$^{2+}$ vacancies in the sample can enhance the conductivity.\textsuperscript{22-26,30,33,35,44-47} Nanomaterials, in general, have very high surface area to volume ratio and hence in nanostructured nickel oxide samples consolidated in the form of a cylindrical pellet, a large portion of the material resides in the interfacial region constituted by the grain boundaries and the triple junctions.\textsuperscript{7} It may be interesting to study the role of the largely defective interfacial region on the electrical response of nanostructured nickel oxide. In this chapter, the study of dc electrical conductivity of nanostructured nickel oxide samples having different average grain sizes ranging from 2-3 nm to 16-17 nm in the temperature range 313 – 423 K is presented.

3.2 Experimental

Details of the procedure for the synthesis of nanostructured nickel oxide samples having different average grain sizes have been presented in Chapter 2. DC conductivity studies of nanostructured nickel oxide samples were carried out for five different average grain sizes ranging from 2-3 nm to 16-17 nm. For reference, sample codes are assigned to the samples, which are listed in Table 3.1, together with the average grain sizes.
Table 3.1. Sample codes assigned to nanostructured nickel oxide samples used for the dc conductivity study

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Average grain size (μm)</th>
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</thead>
<tbody>
<tr>
<td>N1</td>
<td>2-3</td>
</tr>
<tr>
<td>N2</td>
<td>4-5</td>
</tr>
<tr>
<td>N3</td>
<td>5-7</td>
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<tr>
<td>N4</td>
<td>12-13</td>
</tr>
<tr>
<td>N5</td>
<td>16-17</td>
</tr>
</tbody>
</table>

Nanostructured nickel oxide samples were consolidated in the form of cylindrical pellets having a diameter of 13mm and thickness about 1mm by applying a uniaxial force of 4 tons for two minutes using a hydraulic press. Extreme care was taken to see that the pelletisation of all the samples were done under identical conditions. Conducting silver epoxy was carefully applied on both the faces of the pellets to serve as electrodes. The pellets were first air dried for 30 minutes and then heat treated at 90°C for 15 minutes in a hot air oven for electrode curing.

Electrical measurements were carried out in an evacuated dielectric cell. Before taking the actual measurements, each pellet was subjected to a heat and cool run between 313 and 423 K in vacuum in order to remove any residual strain due to pelletisation. DC electrical resistance, R, of the sample pellets was measured using a KEITHLEY 614 Electrometer, operating in the constant current mode. DC conductivity of the samples were calculated using the equation, \( \sigma_{\text{DC}} = \frac{d}{RA} \), where d and A are respectively the thickness and the area of cross-section of the cylindrical pellet. The electrical measurements were performed between 313 and 423 K with a 10 K interval. The electrical measurements were intentionally limited to a maximum temperature of 423 K to avoid any aggregation of the particles during measurements and to ensure that for each sample the observed variation of dc conductivity with temperature is not due to any change in the average grain size during measurement.
Sufficient stabilization time was ensured at each particular temperature, which was kept constant with an accuracy of ±1 K. No hysteresis was observed in the temperature variation of conductivity. The repeatability of the results was found to be good.

3.3 Results

The variation of dc conductivity, $\sigma_{DC}$, of the samples over the temperature range 313 – 423 K is shown in Figure 3.1.

![Figure 3.1](image_url)

Figure 3.1. Temperature dependent variation of $\sigma_{DC}$ of nanostructured nickel oxide samples having different average grain sizes.

For the sample N1 having the smallest average grain size, the value of $\sigma_{DC}$ is found to increase from $(5.60 \pm 0.23) \times 10^{-6}$ ohm$^{-1}$cm$^{-1}$ at 313 K to $(9.54 \pm 0.39) \times 10^{-5}$ ohm$^{-1}$cm$^{-1}$ at 423 K. N2 is the sample that shows the maximum value of conductivity at all temperatures, its values being $(1.79 \pm 0.08) \times 10^{-5}$ ohm$^{-1}$cm$^{-1}$, and $(2.80 \pm 0.12) \times 10^{-4}$ ohm$^{-1}$cm$^{-1}$ at 313 K and 423 K respectively. The numerical values
of $\sigma_{DC}$ for the sample N3 are found to lie between those for N1 and N2 at all temperatures. The variation of $\sigma_{DC}$ with temperature is Arrhenius type for samples N1, N2, N3 and it was noted that the activation energy is approximately 0.30 eV for all the three samples over the entire temperature range of observation. For the samples N4 and N5 having larger average particle sizes, the conductivity values are found to be about one order of magnitude less than that of N1 over the entire range of temperature. Further, $\sigma_{DC}$ of N4 and N5 is only a weak function of temperature. The numerical values of $\sigma_{DC}$ of N4 and N5 are respectively $(7.63 \pm 0.31) \times 10^{-7}$ ohm$^{-1}$cm$^{-1}$ and N5 $(7.11 \pm 0.28) \times 10^{-7}$ ohm$^{-1}$cm$^{-1}$ at 313 K, and $(3.29 \pm 0.13) \times 10^{-5}$ ohm$^{-1}$cm$^{-1}$ and $(4.6 \pm 0.18) \times 10^{-5}$ ohm$^{-1}$cm$^{-1}$ at 423K. Also, the activation energies for the samples N4 and N5 are noted to be 0.38 and 0.40 eV respectively.

![Figure 3.2. Variation of $\sigma_{DC}$ with the average grain size for nanostructured nickel oxide samples at different temperatures](image)

It is important to note that the dc conductivity of all the five samples is much higher than that of NiO single crystals; the conductivity at the lowest temperature of observation for N2, the most conducting sample, is nearly eight orders of magnitude
higher than the room temperature conductivity of NiO single crystals which is much less than $10^{-13}$ ohm$^{-1}$ cm$^{-1}$.\textsuperscript{22-27} It may also be noted that, $\sigma_{\text{DC}}$ is conspicuously size dependent; it increases as the grain size increases, tends to saturate, and then falls off and attains a somewhat steady value. Figure 3.2 shows the variation of $\sigma_{\text{DC}}$ with the average grain size for three different temperatures. The variation has the same general form at other temperatures as well. The dependence of $\sigma_{\text{DC}}$ on the average grain size is more explicit for samples having smaller average grain sizes, as expected.

3.4 Discussion

Wittenauer and Van Zandt, had systematically studied the electrical conduction in pure stoichiometric NiO single crystals using two probe and three probe measurements.\textsuperscript{30} They concluded that in NiO samples which have an apparent room temperature resistivity of $10^{11} - 10^{13}$ ohm cm, there exists a low resistivity surface layer which masks the bulk resistivity in two probe and four probe measurements.\textsuperscript{25} Further, it was pointed out that this surface layer of thickness about 50 atomic layers was less stoichiometric than the bulk, which suggests a defect dependent conductivity mechanism for the surface conduction. The activation energy for conduction was reported to be $\sim 1.85$ eV for the bulk while it varied between 0.6 - 1 eV for the surface layer.\textsuperscript{25} The latter values are very close to the activation energy for conduction in nanostructured nickel oxide samples of the present study.

Since nanostructured materials in general have very large surface area to volume ratios, in light of Wittenauer's results, one has to expect $\sigma_{\text{DC}}$ of nanostructured nickel oxide to be conspicuously larger than that of bulk NiO. In the present study, the conductivity of nanostructured nickel oxide samples are found to be larger by six to eight orders of magnitude over that of NiO single crystals. To account for the observed results in nanostructured NiO, a detailed analysis correlating factors such as the numerical value of conductivity, possible conductivity mechanisms, corresponding activation energies, the role of largely defective interfacial region and the possible modification of the band structure is present in this section.
Nickel oxide has a complex band structure due to the presence of multiple valence (3d band of Ni\(^{2+}\) and 2p band of O\(^{2-}\)) and conduction (4s band of Ni\(^{2+}\) and 3s band of O\(^{2-}\)) bands.\(^{16-26}\) Further, the 3d band of Ni\(^{2+}\) is very narrow (< 0.01 eV) and can not be considered as an electron band in the ordinary sense; it is more appropriate to treat the 3d band of Ni\(^{2+}\) as somewhat spread out levels referred to as 'localized band'.\(^{22,23,26}\) The response of charge carriers in such localized bands is quite different from those in conventional one-electron energy bands.\(^{26}\) In undoped NiO, due to a wide forbidden energy gap of approximately 3.8 eV, conduction at temperatures below 1000 K is predominantly extrinsic and is associated with the Ni\(^{2+}\) vacancies.\(^{22-47}\) Presence of each Ni\(^{2+}\) vacancy in the lattice leads to the transformation of two adjacent Ni\(^{2+}\) ions into Ni\(^{3+}\) ions to acquire charge neutrality and induces a lattice distortion.\(^{26}\) Each Ni\(^{2+}\) vacancy along with the two Ni\(^{3+}\) ions on opposite nearest neighbor positions constitutes a bound quadrupole, which is the lowest energy state possible. Either one or both the holes associated with such a quadrupole complex may become free by two possible mechanisms. If a 3d electron from an adjacent Ni\(^{2+}\) ion is transferred to one Ni\(^{3+}\) ion in the quadrupole, a hole is created in the 3d band. This hole along with the associated lattice distortion constitutes a small polaron in the localized 3d band of Ni\(^{2+}\). Alternately, if a 2p electron from a nearby O\(^{2-}\) ion is transferred to one Ni\(^{3+}\) ion in the quadrupole complex, a hole is induced in the 2p band of O\(^{2-}\). This hole along with the associated lattice distortion constitutes a large polaron in the 2p band of O\(^{2-}\). In pure NiO, at temperatures below 1000 K two competing mechanisms, one due to small polarons in the 3d band of Ni\(^{2+}\) and the other due to large polarons in the 2p band of O\(^{2-}\), contribute to conductivity.\(^{26}\) At temperatures above 100 K, small polarons conduct only by means of thermally activated hopping with activation energy of 0.01 eV.\(^{25-27}\) However, this hopping conduction is reported to be completely unobservable in dc measurements due to low mobility.\(^{26}\) Hence the predominant conductivity mechanism in undoped bulk crystals of NiO in the temperature range 200-1000 K is the band like conduction due to the large polarons in the 2p band of O\(^{2-}\) with activation energy of approximately 0.6 eV.\(^{26}\)

The effect of Ni\(^{2+}\) vacancies on the band structure of NiO is similar to that of an acceptor impurity like Li\(^{+}\).\(^{22,26,36}\) The Ni\(^{2+}\) vacancies correspond to an acceptor-like
level in the forbidden energy gap close to the Fermi level just above the localized 3d band of Ni\(^{2+}\) and comparatively wide 2p band of O\(^2-\). It is possible that more than one acceptor-like level is formed by Ni\(^{2+}\) vacancies due to the different possible geometrical configuration of the two holes around the vacancy. These localized levels act as traps for any electron excited from the 3d band of Ni\(^{2+}\) and 2p band of O\(^2-\). As the number of Ni\(^{2+}\) vacancies in the sample increases, the number of small polarons in the localized 3d band of Ni\(^{2+}\) and the large polarons in the 2p band of O\(^2-\) increase enhancing the conductivity.

In the present study, all the nanostructured nickel oxide samples show Arrhenius type (band like) conduction with activation energies comparable to the activation energy for large polaron conduction in NiO single crystals (~ 0.6 eV). Since the observed activation energies are very large compared to the activation energy associated with the thermally activated hopping of small polarons (~ 0.01 eV), it may be argued that the predominant conductivity mechanism in nanostructured nickel oxide over the temperature range of observation is the band like conduction due to large polarons in the 2p band of O\(^2-\). The 'large polaron radius' in NiO is about two lattice spacing, (2a ≈ 8 Å), and this is the lower limit of applicability of the theory of large polaron conduction. Since in the present study, even the sample having smallest average particle size of about 2-3 nm (N1) has a spatial extension more than 30 times the 'large polaron radius', the theory of large polaron conduction should be applicable to nanostructured nickel oxide as well. Hence the large conductivity in undoped nanostructured nickel oxide samples compared to that of the bulk points to the presence of a large number of Ni\(^{2+}\) vacancies in the samples.

From the numerical value of conductivity, \(\sigma_{DC}\), an estimation of the density of 'uncompensated' Ni\(^{2+}\) vacancies in the nanostructured nickel oxide samples can be carried out using the relation

\[
\sigma_{DC} = 2 N_{Ni}^{2+} e \mu \exp \left( -E_g / kT \right) \quad \text{-------- (3.1)}
\]
where \( N_{Ni}^{2+} \) is the density of \( Ni^{2+} \) vacancies in the sample, \( e \) the electronic charge, \( \mu \) the mobility of the large polaron at temperature \( T \) K, \( E_g \) the activation energy in joules obtained from the Arrhenius plots, \( k \) the Boltzmann's constant and \( T \) the temperature of the sample in Kelvin. The factor \( \gamma \) is included in the equation for the reason that each \( Ni^{2+} \) vacancy can contribute two polarons. Calculations using Equation (3.1) revealed that in all the nanostructured nickel oxide samples the density of \( Ni^{2+} \) vacancies varied between \( 10^{12} \) - \( 10^{16} \) cm\(^{-3} \). For the above calculation the mobility of the large polaron, \( \mu \) was taken to be the same as that for \( NiO \) single crystals, viz. \( 5 \text{cm}^2/\text{V-sec} \) at 300K and \( \mu \) at different temperatures was calculated using the equation \( \mu = \mu_0 \exp (-E_a / kT) \) with \( E_a = -0.075 \text{ eV} \). The estimation of density of \( Ni^{2+} \) vacancies from conductivity data alone is not a rigorous one, since the presence of one \( O^{2-} \) vacancy can nullify the effect of one \( Ni^{2+} \) by self-compensation. However, all the nanostructured nickel oxide samples in the present study were air annealed and hence the possibility of high density of oxygen vacancy in the samples can be considered to be negligible. Hence it may be argued that the density of uncompensated \( Ni^{2+} \) vacancies obtained from Equation (3.1) is nearly equal to the actual density of \( Ni^{2+} \) vacancies in the samples. The density of \( Ni^{2+} \) ions in a single crystal of \( NiO \), devoid of any defects is \( 5.6 \times 10^{22} \) cm\(^{-3} \). It is evident from the calculations that at least one \( Ni^{2+} \) vacancy is present for every \( 10^6 \) - \( 10^8 \) \( Ni^{2+} \) ions in nanostructured nickel oxide in the present study. The high density of \( Ni^{2+} \) vacancies (of the order of \( 10^{14} \) to \( 10^{16} \) cm\(^{-3} \)), which is justifiable in view of the large volume fraction of the interfacial region of the nanostructured materials, explains the large enhancement in conductivity of the order of six to eight in magnitude for the present samples in comparison with that of \( NiO \) single crystals.

Activation energies for all the nanostructured nickel oxide samples in the present study are found to be slightly less than that for \( NiO \) single crystals. This lowering of activation energy can be explained by two different approaches, both highlighting the enormously defective nature of nanoparticles. As evident from the above calculations, nanostructured nickel oxide samples contain a large number of \( Ni^{2+} \) vacancies and hence a large number of quadrupole complexes, which can contribute to
polarization, are present. This will cause an increase in the effective dielectric constant of the samples. The coupling constant, $\alpha$, for the large polarons is given by

$$\alpha = \left( \frac{e^2}{2\hbar} \right) \left( \frac{1}{\varepsilon_0} - \frac{1}{\varepsilon_\infty} \right) \left( \frac{2m^*}{\hbar \omega_0} \right)$$

where $e$ is the electronic charge, $\hbar$ the Plank's constant, $\varepsilon_0$ the static dielectric constant, $\varepsilon_\infty$ the high frequency dielectric constant, $m^*$ the effective mass of the hole in the 2p band of $O^{2-}$ and $\omega_0$ the longitudinal optical phonon frequency.\textsuperscript{26} Hence an increase in the effective dielectric constant will cause a decrease in the numerical value of coupling constant $\alpha$. This in turn causes a decrease in the large polaron binding energy, $E_b = (\alpha \hbar \omega_0)^{1/2}$, in nanostructured nickel oxide samples.\textsuperscript{26} This 'screening' due to the large density of quadrupole complexes associated with the Ni$^{2+}$ vacancies qualitatively accounts for the slight decrease in activation energy for nanophase nickel oxide. A quantitative analysis would be possible once the exact values of the involved parameters are experimentally determined. The second approach is to consider the possible modification of the band structure for nickel oxide in the nanosize regime. Generally, for semiconductor nanostructures, narrowing of valence and conduction bands in comparison with those of the corresponding single crystals is expected.\textsuperscript{5} In the case of nickel oxide, as the 3d band of Ni$^{2+}$ is already localized even in bulk samples, it may not be affected significantly by the finite size of the nanostructured samples in the present study. However, the 2p band of $O^{2-}$ may be narrowed down in nanostructured nickel oxide samples. Further, due to the high density of Ni$^{2+}$ vacancies, the acceptor like levels, acting as trapping centers, will be more close to the valence bands thereby increasing the probability of formation of polarons. When the number of polarons in the 2p band is much more than the number of $O^{2-}$ vacancies, the Fermi level drops below the normal level resulting in a decrease in the activation energy. Such a decrease in the activation energy by about 0.2 eV has been reported in the case of Li$^+$ doped NiO crystals when the number of polarons in the 2p band exceeded twice the number of oxygen vacancies.\textsuperscript{26} The magnitude of decrease in activation energy for nanostructured nickel oxide samples in the present study is 0.2 to 0.3 eV. This suggests that the modification of the band structure due to the finite size
of the nanostructured samples and the large number of polarons due to the large density of Ni$^{2+}$ vacancies are the factors operative in decreasing the activation energy.

It may be noted from Figure 3.2 that the dc conductivity, $\sigma_{\text{DC}}$, of nanostructured nickel oxide samples is conspicuously size dependent; it increases as the grain size increases, tends to saturate, and then falls off and attains a somewhat steady value. Also, the dependence of $\sigma_{\text{DC}}$ on the grain size is more explicit for samples having smaller average grain sizes. In nanostructured samples, a large portion of the material resides in the interfacial region and the structure and the volume fraction of the interfacial region have an important role in determining the transport properties.$^{7,48,49}$ The interfacial region of nanostructured materials is composed of grain boundaries and triple junctions.$^{7,49}$ Triple junctions which are intersection lines of three or more adjoining grains form a very important component of the interface along with grain boundaries in determining the transport properties as the grain size becomes smaller than about 10nm.$^{7,49}$ This is in sharp contrast with the case of coarse-grained samples where the effect of the triple junctions is negligible or altogether absent.$^{49}$

According to Bollman, triple junctions in nanostructured materials should be viewed as line defects, which are analogous to dislocations.$^{50,51}$ Hence the interfacial region of nanostructured materials can be pictured as constituting a potential barrier for the charge carriers with triple junctions corresponding to the maxima of the barrier.$^{49-52}$ Earlier works on coarse-grained NiO samples, where the interfacial region is almost completely constituted by grain boundaries, have shown that the high density of Ni$^{2+}$ vacancies associated with the grain boundaries enhances conductivity.$^{23-26}$ However, the triple junctions in nanostructured nickel oxide samples may justifiably have a reverse effect on conductivity. The physical basis for this assumption lies in the fact that the triple junction represents a maxima of a potential barrier and cause scattering of the charge carriers, resulting in a decreased rate of charge transport.$^{7,49-52}$ Thus, since the grain boundaries and triple junctions of nanostructured nickel oxide has contrasting effects on conductivity, the value of $\sigma_{\text{DC}}$ for the nanoparticle samples having very small average grain size ($< 10$nm) will be determined by the relative volume fractions of the grain boundaries and triple junctions constituting the interfacial region. In the
following semi-quantitative analysis, an explanation for the observed variation pattern of $\sigma_{DC}$ with average grain size is presented on the basis of the variation of the volume fractions of the grain boundary ($V_{gb}$) and triple junctions ($V_{tj}$) with the average grain size.

For nanocrystalline samples shapes such as regular a 14 sided tetrakaidecahedron for the grains is more realistic than spheres, cylinders, cubes etc., and many earlier workers have employed this shape for calculating the interfacial volume fractions and the results from such calculations have been successfully complemented by experimental techniques such as small angle neutron scattering and positron annihilation spectroscopy.\textsuperscript{7,49,50} Further, crystallographic studies have concluded that the growth of NiO crystallites occurs in the regular tetrakaidecahedron shape.\textsuperscript{53} An estimation of the volume fractions of the total interfacial region ($V_{if}$), grain boundary ($V_{gb}$) and triple junctions ($V_{tj}$) are carried out for the present samples assuming the grains to have a regular 14 sided tetrakaidecahedron shape with hexagonal faces representing grain boundaries and edges corresponding to triple junctions. The volume fractions are given by

$$V_{if} = 1 - [(d-D)/d]^3 \quad \text{(3.3)}$$

$$V_{gb} = [3D (d-D)^2]/d^3 \quad \text{(3.4)}$$

$$V_{tj} = [V_{if} - V_{gb}] \quad \text{(3.5)}$$

where $d$ is the average grain size which is assumed to be the maximum diameter of an inscribed sphere and $D/2$ is the thickness of the interfacial region (outer skin of the tetrakaidecahedron).\textsuperscript{7,49} For all the calculations $D/2$ is assumed to be equal to 0.5 nm which is realistic in the size range of the samples in the present study.\textsuperscript{49,54}

Figure 3.3 shows the variation of $V_{if}$, $V_{gb}$, $V_{tj}$ and $V_{gb} - V_{tj}$ with average grain size size. The total interfacial region is maximum for the sample N1 with smallest average grain size (2-3 nm) and decreases gradually as the particle size increases to
16-17 nm for the sample N5. It may be clearly noted from Figure 3.3 that although both $V_{\text{gb}}$ and $V_{\text{tj}}$ decrease as the grain size increases they do not exhibit the same pattern, whereas $V_{\text{gb}}$ falls smoothly as the grain size is increased, $V_{\text{tj}}$ falls sharply as the grain size increases from 2-3 nm for the sample N1 to 4-5 nm for the sample N2 and thereafter falls smoothly. For samples having larger average grain size $V_{\text{if}}$, $V_{\text{gb}}$ and $V_{\text{tj}}$ are almost independent of the average grain size and the volume fraction of the triple junctions constitutes only a very small portion of the total interfacial volume fraction ($V_{\text{if}}$). As already explained, the grain boundaries and triple junctions in nanostructured nickel oxide have opposing effects on the conductivity and hence $\sigma_{\text{DC}}$ should be proportional to the difference of the volume fractions, $V_{\text{gb}} - V_{\text{tj}}$. The variation of $V_{\text{gb}} - V_{\text{tj}}$ with average grain size is also shown in Figure 3.3. This pattern is identical

Figure 3.3. Variation of the calculated volume fractions of the total interfacial region ($V_{\text{if}}$), grain boundaries ($V_{\text{gb}}$), triple junctions ($V_{\text{tj}}$) and ($V_{\text{gb}} - V_{\text{tj}}$) with the average grain size.
to the pattern in Figure 3.2 and explains the observed variation of $\sigma_{\text{DC}}$ with average grain size. Thus it is emphasized that for nanostructured materials having very small average grain sizes ($<10$ nm), in addition to the grain boundaries, triple junctions become a very important constituent of the interfacial region in determining the transport properties. The dominant effect of the triple junctions is one of the important and interesting distinctions of nanostructured samples from coarse-grained polycrystalline samples having the same average chemical composition.

The above discussion shows that the observed enhancement in $\sigma_{\text{DC}}$ of nanostructured nickel oxide samples can be attributed to the high density of Ni$^{2+}$ vacancies associated with the surface region. Analysis of the results reveal that the band like conduction due to large polarons in the 2p band of O$^{2-}$ is the predominant conductivity mechanism in nanostructured nickel oxide over the temperature range studied. While the Ni$^{2+}$ vacancies associated with the interfacial region tends to increase the conductivity, the grain boundaries and triple junctions present a potential barrier to the transport of charge carriers. The effect of triple junctions, which correspond to the maxima of the barrier, is to decrease $\sigma_{\text{DC}}$ by causing scattering of the charge carriers. It is shown that the variation of the volume fractions of the grain boundaries and the triple junctions relative to the total volume of the interfacial region decide the variation pattern of $\sigma_{\text{DC}}$ with the average grain size.

3.5 Conclusion

The dc conductivity of nanostructured nickel oxide samples having different average grain sizes ranging from 2-3 nm to 16-17 nm were measured in the temperature range 313 – 423 K. For all the samples, the dc conductivity, $\sigma_{\text{DC}}$, were found to be enhanced by six to eight orders of magnitude over that of single crystals. This enhancement in of $\sigma_{\text{DC}}$ is explained as due to the high density of Ni$^{2+}$ vacancies in the nanostructured samples. The dc conductivity in nanostructured nickel oxide in the temperature range 313- 423 K is predominantly due to large polarons in 2p band of O$^{2-}$. The observed lowering of activation energy for the nanostructured samples in
comparison with that of NiO single crystal is explained on the basis of the low spatial extension and high defect density of nanostructured samples. The observed variation of $\sigma_{DC}$ with average grain size is explained by considering the combined effects of the grain boundaries and the triple junctions on the electrical transport in nanostructured nickel oxide.

3.6 References