Pergamon

Materials Research Bulletin 36 (2001) 21–33

Materials
Research
Bulletin

DC conductivity of consolidated nanoparticles of NiO

V. Biju, M. Abdul Khadar*

Department of Physics, University of Kerala, Kariavattom Campus, Thiruvananthapuram, Kerala,
PIN- 695 581, India

(Refereed)
Received 25 January 2000; accepted 26 June 2000

Abstract

DC conductivity of consolidated nanoparticles of NiO, having different average particle sizes (2.5nm-17nm) was measured in the temperature range 313 K to 423 K. The conductivity of NiO nanoparticles are found to be enhanced by six to eight orders of magnitude over that of NiO single crystals. This large enhancement in conductivity is attributed to the high density of Ni^{2+} vacancy in the nanoparticles. Calculation of activation energy, leads to the conclusion that the most prominent conductivity mechanism over the temperature range of observation is the large polaron conduction associated with holes in the 2p band of O^{2-}. The decrease in activation energy for the samples in comparison with that of the bulk material is explained on the basis of the enormously defective nature of nanoparticles. In the last part of the discussion, the effect of interfacial region on the electrical conductivity of the samples is analyzed, by taking into account the contributions due to grain boundaries and triple junctions. A semi-quantitative explanation for the observed variation of conductivity with particle size is presented on the basis of the assumption that the role of the triple junctions is to reduce the conductivity. The importance of triple junctions in determining the transport properties of nanoparticles is emphasized. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: A. Nanostructures; A. Oxides; D. Electrical properties

1. Introduction

Electrical properties of consolidated nanoparticles, of both metals and semiconductors, show large deviation from those of their single crystal and polycrystalline counterparts

---

* Corresponding author. Fax: +91-471-307-158.
E-mail address: makhadar@mail.com (M.A. Khadar).

PII: S0025-5408(01)00488-3

[1–11]. The drastic variation of electrical properties of materials in the nanosize regime is mainly attributed to the quantum confinement of charge carriers and associated modification of the band structure [1–5]. In addition to the possible device applications, a detailed analysis of electrical properties of nanostructured materials will lead to a better understanding of the evolution of band structure of solids as they are formed from individual atoms or ions.

Experimentally, it has been observed that consolidated nanoparticles of metals like Cu, Pd and Fe, and of alloys like $(Fe_{99}Cu_1)$ Si_9B_{13} and Ni-P have a reduced value of conductivity than those of the single crystal or coarse-grained materials [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 forbidden energy gap [5,10,11]. However, in semiconductor nanostructures, lattice defects may form acceptor-like or donor-like levels in the forbidden energy gap. Such levels can act as trapping centers and may affect the electrical response of the sample [5]. Enhancement of conductivity by orders of magnitude one and three over that of single crystals was reported respectively for undoped ZnS and CdS nanoparticles [10] The enhancement was qualitatively explained as due to the accumulation of charge carriers (electrons) in the shallow random potential wells associated with the defects on the surface of nanoparticles followed by thermally activated detrapping of such carriers [10].

NiO is a very interesting material due to its complex band structure [12–17] and less well understood conductivity mechanism [17–25]. Pure NiO is classified as a 'Mott-Hubbard insulator' with room temperature conductivity less than 10^{-13} ohm^{-1} cm^{-1} in which electrical conduction at room temperature is due to holes of intermediate mass [13,17–21]. Different possible conductivity mechanisms have been reported to be operative in NiO at different temperature ranges [17–21]. 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. Earlier works have shown that doping with monovalent impurities like Li^+ can increase the conductivity of NiO [17–21,23]. For pure NiO, increase in the number of Ni^{2+} vacancies (defects) in the sample can enhance the conductivity [17–21]. Nanoparticles, in general, have very high surface to volume ratio and hence in consolidated nanoparticles of NiO, a large portion of the material resides in the interfacial region constituted by grain boundaries and triple junctions. It may be interesting to study the role of the largely defective interfacial region on the electrical response of NiO nanoparticles. In the present article we report the dc electrical studies of consolidated nanoparticles of NiO having different average particle sizes (2.5 nm to 17 nm) in the temperature range 313–423 K. The electrical measurements were intentionally limited to a maximum temperature of 423 K to avoid aggregation of particles and to ensure that the average particle size remained the same during the electrical measurements.

2. Sample preparation and experimental procedure

Nickel carbonate nanoparticles were prepared by arrested chemical precipitation using Ethylenedinitrilotetraacetic acid disodium salt, EDTA, as stabilizer. Nickel nitrate and Ammonium carbonate were used as the starting materials. All the chemicals used were of

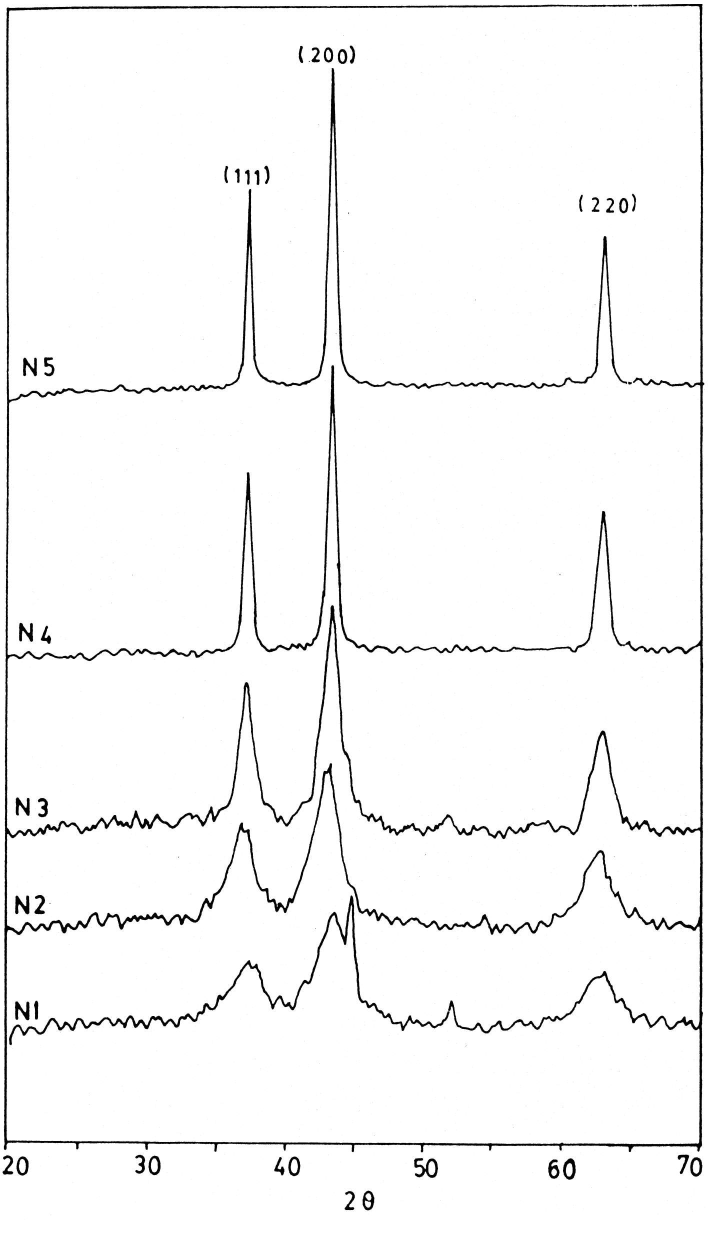

Fig. 1. X-ray diffraction patterns of NiO nanoparticle samples.

analytical grade. NiO nanoparticles were obtained by the decomposition of the carbonate precursor at 523 K. The decomposition temperature was chosen after carrying out TGA analysis of the carbonate precursor. NiO nanoparticles of different average particle sizes were obtained by air annealing the samples at higher temperatures.

The X-ray diffraction patterns of the samples are given in Fig. 1. The average size of the nanoparticles were calculated from the line broadening of the X-ray diffraction peaks (all the

Table 1
Details of NiO nanoparticle samples

Sample code	Annealing temperature (K)	Duration (Hrs)	Average particle size (nm)
N1	523	1	2–3
N2	573	1	4–5
N3	623	1	5–7
N4	723	1	12–13
N5	773	1	16–17

three peaks), corrected for instrumental broadening, using Scherrer's Eq. (26). For convenience, sample codes were assigned to the samples, which are listed in Table 1, along with the annealing temperature and duration, and average particle size.

The nanoparticle 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 paint was carefully painted 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 a dielectric cell evacuated to a vacuum of the order of 10^{-3} torr. Before taking actual measurements, each pellet was subjected to a heat and cool run between 313 K and 423 K in vacuum in order to remove any residual strain due to pelletisation. DC electrical resistance of the sample pellets was measured using KEITHLEY 614 Electrometer, operating in the constant current mode. The electrical measurements were performed between 313 K 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 average particle size. Sufficient stabilization time was ensured at each particular temperature, which was kept constant with an accuracy of ±1 K. No hysterisis was observed in the temperature variation of conductivity. The repeatability of the results was found to be good.

3. Results

The variation of dc conductivity, $\boldsymbol{\sigma}_{\mathbf{dc}}$, of the samples over the temperature range 313–423 K is shown in Fig. 2. $\boldsymbol{\sigma}_{\mathbf{dc}}$ of the sample N1 having the smallest average particle size is found to increase from a value of $(5.60 \pm 0.23) \times 10^{-6}$ ohm^{-1} cm^{-1} at 313 K to the value of $(9.54 \pm 0.39) \times 10^{-5}$ 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 $\boldsymbol{\sigma}_{\mathbf{dc}}$ of the sample N3 are found to lie between those for N1 and N2 at all temperatures. The

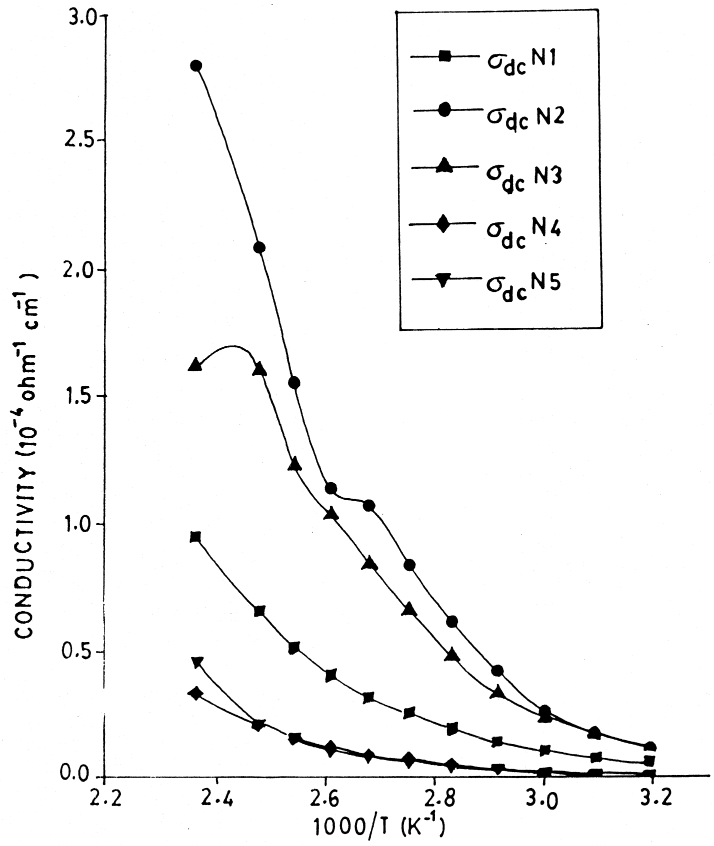

Fig. 2. Temperature variation of dc conductivity of consolidated nanoparticles of NiO having different average particle sizes.

variation of σ_{dc} with temperature is Arrhenius type for samples N1, N2, N3 and it may be noted that the activation energy is approximately 0.3 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, σ_{dc} of N4 and N5 is only a weak function of temperature. The numerical values of σ_{dc} of N4 and N5 are respectively $(7.63 \pm 0.31) \times 10^{-7}$ ohm^{-1} cm^{-1} and $(7.11 \pm 0.28) \times 10^{-7}$ 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. The activation energies for conduction of N4 and N5 are nearly equal ($\approx$0.4 eV) up to the temperature 363K, while it is respectively 0.3 eV and 0.5 eV over the rest of the temperature range.

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} [18]. It may also be noted that, σ_{dc} is conspicuously size dependent; it increases as the

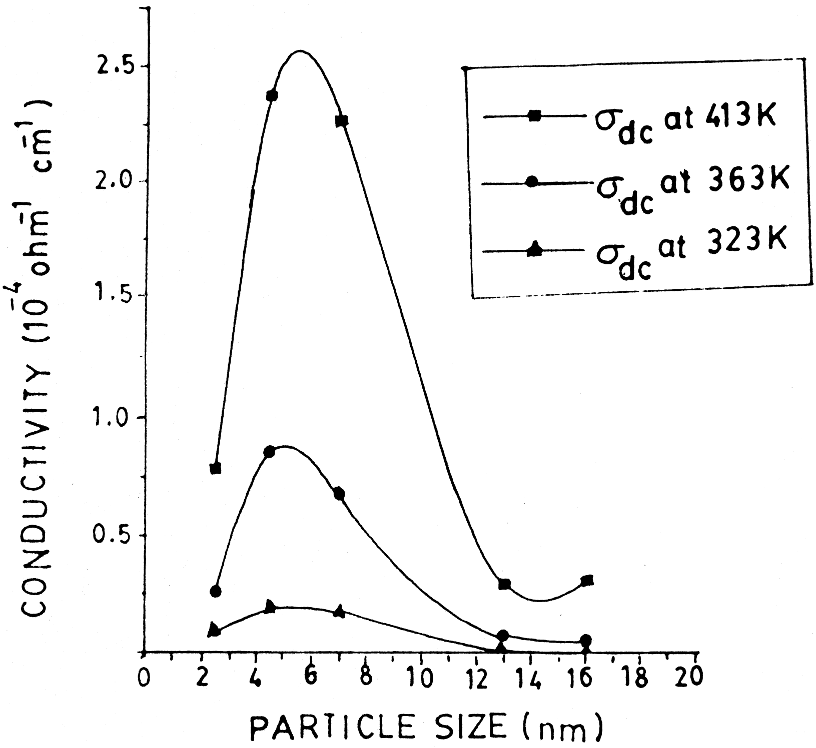

Fig. 3. Variation of dc conductivity of consolidated nanoparticles of NiO with average particle size.

particle size increases, tends to saturate, and then falls off and attains a somewhat steady value. Fig. 3 shows the variation of σ_{dc} with particle size for three temperatures. The variation has the same general form at other temperatures as well. The dependence of σ_{dc} on particle size is more explicit for samples having smaller average particle size, as expected.

4. Discussion

Wittenauer et al had systematically studied the electrical conduction in pure stoichiometric NiO single crystals using two probe and three probe measurements [25]. 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 [25]. Further, it was concluded 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 [25]. The activation energy for conduction was reported to be ~1.85 eV for the bulk while it varied between 0.6–1 eV for the surface layer [25]. The latter values are very close to activation energy for conduction in consolidated NiO nanoparticle samples of the present study. If the description of nanoparticles as being constituted mostly by surface atoms is physically correct, then in light of

Wittenauer's results, one has to expect $\boldsymbol{\sigma}_{\mathbf{dc}}$ of consolidated nanoparticles of NiO to be conspicuously larger than that of bulk NiO. In the present study, the conductivity of nanoparticles of NiO is 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, we present in the following section 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.

NiO 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 [17–21]. 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' [17,18,21]. The response of charge carriers in such localized bands is quite different from those in conventional one-electron energy bands [21]. 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 [17,18,21]. 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 [21]. 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 [21]. 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+} [21]. 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-} [21]. 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 [21]. At temperatures above 100 K, small polarons conduct only by means of thermally activated hopping with activation energy of 0.01 eV [20–22]. However, this hopping conduction is reported to be completely unobservable in dc measurements due to low mobility [21]. 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 [21].

The effect of Ni^{2+} vacancies on the band structure of NiO is similar to that of an acceptor impurity like Li^{+} [17,21]. 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 [21]. 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 NiO nanoparticle 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 NiO nanoparticles 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 [21]. Since in the present study even the sample having smallest average particle size of approximately 2.5 nm (N1) has a spatial extension more than 30 times the 'large polaron radius', the theory of large polaron conduction should be applicable to the NiO nanoparticles as well. Hence the large conductivity in undoped NiO nanoparticle 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, $\boldsymbol{\sigma_{dc}}$, an estimation of the density of 'uncompensated' Ni^{2+} vacancies in the NiO nanoparticle samples can be carried out using the relation

$$\sigma_{dc} = 2\ N_{Ni}{}^{2+}\ e\ \mu\ \exp(-E_g/kT) \tag{1}$$

where $N_{Ni}{}^{2+}$ is the density of Ni^{2+} vacancies in the sample, e the electronic charge, μ the mobility of the large polaron at temperature T K, E_g the activation energy in joules obtained from Arrhenius plots, k the Boltzmann's constant and T the temperature of the sample in Kelvin [21]. The factor 2 is included in the equation for the reason that each Ni^{2+} vacancy can contribute two polarons. Calculations using Eq. (1) revealed that in all the NiO nanoparticle samples the density of Ni^{2+} vacancies varied between $\sim 10^{12}$-10^{16} cm^{-3}. For the above calculation the mobility of the large polaron, μ was taken to be the same as that for NiO single crystals, viz. 5cm^2/V-sec at 300K and μ at different temperatures was calculated using the equation $\mu = \mu_0 \exp(-E_a/kT)$ with $E_a = -0.075$ eV [21]. 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 [21]. However, all the NiO nanoparticle 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 Eq. (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 5.6×10^{22} cm^{-3} [19]. 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 NiO nanoparticles 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 nanoparticles, 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 NiO nanoparticle samples 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, NiO nanoparticles 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, α, for the large polarons is given by

$$\alpha = (e^2/2h)\ (1/\varepsilon_0 - 1/\varepsilon_\infty)\ (2m{*}/\ hT_0) \tag{2}$$

where e is the electronic charge, h the Plank's constant, ϵ_0 the static dielectric constant, ϵ_∞ the high frequency dielectric constant, m* the effective mass of the hole in the 2p band of O^{2-} where ω_0 is the longitudinal optical phonon frequency [21]. Hence an increase in the effective dielectric constant will cause a decrease in the numerical value of coupling constant α. This in turn causes a decrease in the large polaron binding energy, $E_b \cong (\alpha h\omega_0)^{1/2}$, in NiO nanoparticles [21]. 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 NiO nanoparticles. 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 NiO in the nanosize regime. Generally, for semiconductor nanostructures, narrowing of valence and conduction bands is expected due to quantum size effect. In the case of NiO, 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 nanoparticles in the present study. However, the 2p band of O^{2-} may be narrowed down in NiO nanoparticle 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 [21]. The magnitude of decrease in activation energy for NiO nanoparticles in the present study is 0.2 to 0.3 eV. This suggests that the modification of the band structure due to the quantum size effect and the associated increase in the number of polarons are the factors operative in decreasing the activation energy.

In the last part of the discussion, we analyze the effect of the interfacial region on the electrical response of consolidated NiO nanoparticles. In consolidated nanoparticle samples, a large portion of the material resides in the interfacial region, which is composed of the grain boundaries and triple junctions [6,27,28]. Triple junctions are intersection lines of three or more adjoining grains [6,27,28]. The volume fraction associated with the triple junctions display a greater grain size dependence than that of the grain boundaries and the most significant contribution of the triple junctions to bulk properties of materials is expected to occur with materials having grain sizes less than 10 nm [27]. It had been reported that the electrochemical and mechanical properties of triple junctions are distinctly different from those of grain boundaries [27]. According to Bollman, triple junctions should be viewed as line defects, which are analogous to dislocations [28]. It is reported that the interfacial region of nanograins act as a potential barrier for the transport of charge carriers; dislocations form the maxima of the barrier which effectively scatters the charge carriers [29]. At very small sizes ($<$10nm), the triple junctions become an important component of the microstructure and the effect of the interfacial region on electrical properties is not that due to the grain boundaries alone [6,27]. It had been reported that the influence of the triple junctions on the nanocrystal properties is ultimately dependent on the relative volume fraction of the triple junction in the total interfacial volume fraction of the nanoparticles [27]. 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 all the samples in the present study. For the calculation, grains were assumed to have regular 14 sided tetrakaidecahedron shapes with hexagonal faces representing grain boundaries and edges corresponding to triple junctions. Such a shape for the grains is more realistic than spherical or cubical shape [6,27]. The volume fractions are given by,

$$V_{if} = 1 - [(d - \Delta)/d]^3 \tag{3}$$

$$V_{gb} = [3\Delta(d - \Delta)^2]/d^3 \tag{4}$$

$$V_{tj} = [V_{if} - V_{gb}] \tag{5}$$

where d is the average particle size and is assumed to be the maximum diameter of an inscribed sphere and $\Delta/2$ is the thickness of the interfacial region (outer skin of the tetrakaidecahedron) [6,27]. For all the calculations $\Delta/2$ is assumed to be equal to 0.5 nm which is realistic in the size range of the particles in the present study [27].

The variation of V_{if}, V_{gb}, V_{tj} and V_{gb}-V_{tj} are shown in Fig. 4. As evident from Fig. 4, total volume fraction of the interfacial region is maximum for sample N1 (with an average particle size 2.5 nm) and it decreases gradually as the particle size increases to ~17 nm for sample N5. Also, from Fig. 4 it is clear that although both V_{gb} and V_{tj} decrease as the particle size increases, they do not exhibit the same pattern. V_{gb} falls smoothly as the particle size increases. In contrast V_{tj} falls sharply as the particle size increases from 2.5 nm to 4.5 nm and thereafter falls smoothly. It may be noted that at larger particle sizes V_{if}, V_{gb} and V_{tj} are not strong functions of particle size and that the volume fraction of the triple junctions (V_{tj}) constitutes only a very small portion of the total interfacial volume fraction (V_{if}). The difference in the variation pattern of V_{gb} and V_{tj} and their relative values perhaps hold the key for explaining the variation of $\boldsymbol{\sigma}_{\mathbf{dc}}$ with particle size (Fig. 3). For nanoparticles with small average particle size, the effect of the interfacial region in conductivity should be viewed as the sum of the contributions due to grain boundaries and triple junctions, unlike for coarse grained samples where the triple junctions are negligible or altogether absent. It has been reported that in polycrystalline NiO samples, the grain boundary enhances conductivity since it contains a large number of Ni^{2+} vacancies [18,19,21]. There is no reason for the grain boundaries in NiO nanoparticles to behave differently and the large enhancement in conductivity for NiO nanoparticles is attributable to the very high value of volume fraction of the grain boundary. However, if we assume that the triple junctions have a reverse effect on conductivity, we can account for the variation pattern of $\boldsymbol{\sigma}_{\mathbf{dc}}$ with particle size (Fig. 3). The physical basis for this assumption lies in the fact that triple junctions, like disloca-

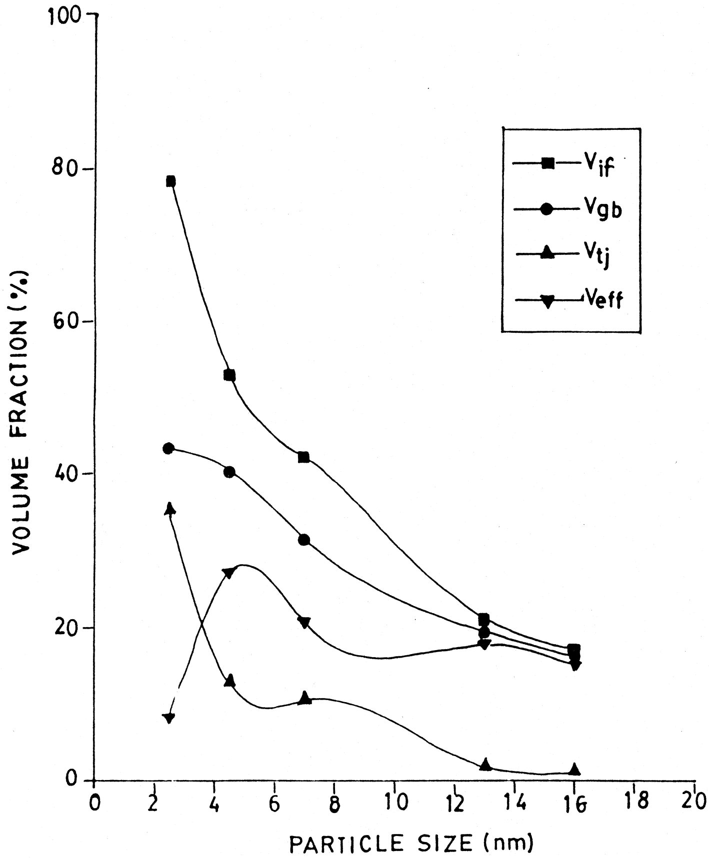

Fig. 4. Variation of volume fractions of total interfacial region (Vif), grain boundaries (Vgb), triple junctions (Vtj) and V_{eff} = Vgb-V_{tj} as a function of average particle size.

tions, should correspond to maxima of a potential barrier, causing scattering of charge carriers and there by decreasing the electrical conductivity [28,29]. With the assumption that the effect of grain boundary and triple junctions on conductivity are linear, the numerical value of conductivity, $\boldsymbol{\sigma}_{dc}$ should vary according to the difference of volume fractions $V_{eff} = V_{gb} - V_{tj}$. It may be noted here that the above discussion is based on the assumption that the charge carrier mobility is the same for grain boundaries and triple junctions. The variation of V_{eff} with particle size is shown in Fig. 4. This pattern is identical to the pattern in Fig. 3 and explains the observed variation of $\boldsymbol{\sigma}_{dc}$ with particle size. It should be noted that for samples N4 and N5, with larger average particle sizes, triple junctions are no more important and the interfacial contribution is that due to the grain boundaries alone. It may be concluded that triple junctions should be viewed as an important factor determining the transport properties of materials in the nanosize regime.

The above discussion shows that the observed enhancement in $\boldsymbol{\sigma}_{dc}$ of consolidated nanoparticles of NiO can be attributed to the high density of Ni^{2+} vacancies associated with the surface of nanoparticles. 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 NiO nanoparticles 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 triple junctions which correspond to the maxima of the barrier cause a decrease in $\boldsymbol{\sigma}_{\mathbf{dc}}$ by scattering of the charge carriers. It is shown that the variation of the volume fractions of the grain boundaries and triple junctions relative to the total volume of the interfacial region decide the variation pattern of $\boldsymbol{\sigma}_{\mathbf{dc}}$ with particle size.

5. Conclusion

NiO nanoparticles having different average particle sizes were prepared. The dc conductivity of all the samples were found to be enhanced by six to eight orders of magnitude over that of single crystals. This enhancement in of $\boldsymbol{\sigma}_{\mathbf{dc}}$ is explained as due to the high density of Ni^{2+} vacancies in nanoparticle samples. The conductivity in NiO nanoparticles 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 of the samples from that of NiO single crystals is explained on the basis of the low spatial extension and high defect density of nanoparticles. The variation pattern of $\boldsymbol{\sigma}_{\mathbf{dc}}$ with particle size is explained by considering the combined effects of grain boundaries and triple junctions on the electrical transport in nanostructured NiO.

Acknowledgments

One of the authors, V. Biju, acknowledges Council of Scientific and Industrial Research (CSIR), Government of India, for financial support as Junior Research Fellowship.

References

[1] P. Marquardt, G. Nimtz, B. Muhlschlegel, On the quasi-static conductivity of sub-micrometer crystals, Solid State Commun. 65 (6) (1988) 539–542.

[2] P. Marquardt, Quantum-size affected conductivity of mesoscopic metal particles, Phys. Lett. A (Netherlands) 123 (7) (1987) 65–68.

[3] K. Frahm, B. Muhlschlegel, R. Nemeth, Size dependent ac conductivity of small metal particles, Z. Phys. B Condens. Mater. 78 (1990) 91–97.

[4] P.J. Yetman, J.C. Gill, Size dependent threshold fields for Frohlich conduction in niobium triselenide: possible evidence for pinning by the crystal surface, Solid State Commun. 62 (3) (1987) 201–206.

[5] L. Brus, Electronic wavefunctions in semiconductor clusters: experiment and theory, J. Phys. Chem. 90 (1986) 2555–2560.

[6] C. Suryanarayana, Structure and properties of nanocrystalline materials, Bull. Mater. Sci. 17 (4) (1994) 307–346.

[7] Y.M. Chiang, E.B. Lavik, D.A. Blom, Defect thermodynamics and electrical properties of nanocrystalline oxides: pure and doped CeO_2, Nanostruct. Mater. 9 (1997) 633–642.

[8] L.W. Molencamp, H. van Houten, A.A.M. Staring, C.W.J. Beenakker, Quantum effects in thermal and thermoelectric transport in semiconductor nanostructures, Physica Scripta T49 (1993) 441–445.
[9] K. Lu, J.T. Wang, W.D. Wei, Comparison of nanocrystalline and amorphous Ni-P alloys, J. Phys. D Appl. Phys. 25 (1992) 808–812.
[10] M. Abdul Khadar, B. Thomas, DC conductivity of nanoparticles of CdS and ZnS, Nanostruct. Mater. 10 (4) (1998) 593–600.
[11] M. Abdul Khadar, B. Thomas, Investigation of electrical properties of certain II-VI materials in the nanosize regime, in: K.P. Jain (Ed.), Physics of Semiconductor Nanostructures, Narosa Publishing House, New Delhi, 1997.
[12] G.K. Werthein, S. Huffner, X-ray photoemission bands structure of some transition-metal oxides, Phys. Rev. Lett. 28 (16) (1972) 1028–1031.
[13] J. Zaanen, G.A. Sawatzky, J.W. Allen, Band gaps and electronic structure of transition-metal compounds, Phys. Rev. Lett. 55 (4) (1985) 418–421.
[14] L.F. Mattheiss, Electronic structure of the 3d transition metal monoxides: I Energy band results, Phys. Rev. B 5 (2) (1972) 290–315.
[15] T. Takahashi, Electronic excitations in NiO, Ann. Phys. 5 (3) (1996) 247–257.
[16] F. Aryasetiwan, K. Karlsson, GW spectral functions of Gd and NiO, Phys. Rev. B 54 (8) (1996) 5353–5357.
[17] Walter J. Moore, Seven Solid States, W.A. Benjamin, Inc, New York, 1967.
[18] F.J. Morin, Electrical properties of NiO, Phys. Rev. B 93 (6) (1954) 1199–1204.
[19] G. Paravano, Thermoelectric behaviour of nickel oxide, J. Chem. Phys. 23 (1) (1955) 5–10.
[20] D.P. Snowden, H. Saltzburg, Hopping conduction in NiO, Phys. Rev. Lett. 14 (13) (1965) 497–499.
[21] David Adler, Julius Feinleib, Electrical and optical properties of narrow-band materials, Phys. Rev. B 2 (8) (1970) 3112–3134.
[22] P. Lunkenheimer, A. Loidl, Correlated barrier hopping in NiO films, Phys. Rev. Lett. 44 (11) (1991) 5927–5930.
[23] P. Puspharajah, S. Radhakrishna, Transparent conducting Li-doped nickel oxide thin films by spray pyrolysis technique, J. Mater. Sci. 32 (1997) 3001–3006.
[24] Yoshnobu Nakumara, Hiroshi Ogara, Tetsnya Nakashima, Akura Kishimoto, Hiroaki Yanagida, Strain-dependent electrical conductivity in the system NiO-CaO, J. Am. Ceram. Soc. 80 (6) (1997) 1609–1611.
[25] Michael A. Wittenauer, L.L. Van Zandt, Surface conduction versus bulk conduction in pure stoichiometric NiO crystals, Philos. Mag. B 46 (6) (1982) 659–667.
[26] G. Palumbo, S.J. Thorpe, K.T. Aust, On the contribution of triple junction to the structure and properties of nanocrystalline materials, Scr. Metall. Mater. 24 (1990) 1347–1350.
[27] W. Bollmann, Triple lines in polycrystalline aggregates as disclinations, Philos. Mag. A 49 (1) 73–79.
[28] E.Z. Meilikhov, R.M. Farzetdinova, Branching of electron current and quantum effects in two-dimensional dislocation barrier of n-type semiconductor, Physica. E 3 (1998) 190–197.