Influence of surfactants on the electrical resistivity and thermopower of Ni nanoparticles

Netram Kaurav\textsuperscript{1}, Gunadhor S Okram\textsuperscript{2} and V Ganesan\textsuperscript{2}

\textsuperscript{1} Department of Physics, Government Holkar Science College, A.B. Road, Indore 452001, MP, India
\textsuperscript{2} UGC-DAE Consortium for Scientific Research, Khandwa Road, Indore 452001, MP, India
E-mail: okram@csr.res.in and okramgs@gmail.com

Received 7 July 2014, revised 2 September 2014
Accepted for publication 24 September 2014
Published 22 October 2014

Abstract

Compacted pellets of nanocrystalline nickel (NC-Ni) with an average particle size ranging from 18 to 33 nm were prepared using a variety of surfactants. They were characterized well and were studied with regard to the influence of the surfactants on the electrical resistivity and thermopower in the temperature range from 5 to 300 K. It was found that the type of surfactant used is more important than the average particle size in their electrical transport and detail transport behaviors. Moreover, the observed thermopower and resistivity features were different than those normally seen in well-known materials. This is interpreted to be indicative of the attractive features of these surfactants can bring to the design of nanostructured thermoelectric materials with enhanced thermoelectric figures of merit.

Keywords: surfactant, resistivity, thermopower, compacted nanoparticles, anomalous electrical transport

1. Introduction

Nanocrystalline (NC) metallic nanoparticles such as the ferromagnetic metals Fe, Co, and Ni have been widely studied because of their use in many applications, including magnetic fluids [1], magnetic recording media [2], biomedical applications [3, 4], and catalysis [5]. In particular, nanostructured Ni particles have important applications ranging from magnetic sensors [6] and memory devices to biomolecular separations [1, 3]. Synthetic protocols are believed to be important in order to take maximum advantage of the novel properties that are often affected by particle size, shape, and crystalline phase. So far, numerous physical and chemical methods have been used to produce metal nanoparticles, including metal evaporation-condensation [7], laser ablation techniques [8], electrochemical methods [9], sonochemical
synthesis [10], metal salt reduction [11], and neutral organometallic precursor decomposition [12]. Generally, chemical synthesis methods have the advantages of simplicity and low cost compared to physical approaches. Moreover, chemical synthesis methods allow the production of large quantities of nanoparticles of defined forms with a fairly narrow particle size distribution.

An important feature in the production of the nanoparticles is the ability to keep them physically isolated one from another to prevent reversible aggregation. The stability of the nanoparticles is commonly achieved using different protective molecules, which bind on the surface of nanoparticles, helping them avoid aggregation [13, 14]. Consequently, their physical and chemical properties depend on the size, shape, crystalline phase control, well-controlled mean size with a narrow size distribution [15–17], and nanolattice formation [18]. Interestingly, the polyol process uses a polyalcohol (ethylene glycol, for example) as both a solvent and a reducing agent to produce nanoparticles from a metallic cationic precursor [19–21]. In this process, the polyol itself can act as a protective agent to avoid particle agglomeration and growth.

Furthermore, one of the important factors of the nanoscale regime is the presence of a large percentage of surface atoms and/or a large amount of grain boundaries (GBs), which give rise to the unusual properties of NC materials compared to conventional polycrystals or single crystals with the same chemical composition [22]. It has been established that the electrical resistivity (ρ) is not determined by the material alone, but by its size as well [23–28]. In this regard, fascinating aspects of nanostructures include the spatial confinement of carriers and the corresponding change in the carrier density of states [22, 29, 30]. With nanoparticles as quantum wells, phonon dispersion and group velocities change due to the spatial confinement induced by GBs [29]. Phonon confinement affects all phonon relaxation rates and should affect thermoelectric transport as it does electrical transport, where GB disorder prevails [22, 30, 31]. The scattering due to small size and more GBs manifests as the residual resistivity at $T \leq 20 \text{K}$ in nearly all metallic solids. If the NC material is comparatively more disordered [32] or has a proximity effect due to its substrate or matrix [33], the resistivity can show localization instead of causing a constant residual value. The nearly comparable situation of matrix dependence could be applicable to the solution method of preparation of samples, and in-depth investigations are essential when one uses different surfactants for generating nanoparticles in their compacted forms. In this situation, when a surfactant molecule or its head sticks to the nascent metal surface in restricted small size, the energy levels or Fermi energy of the electrons in the equilibrated state could be modified. This equilibrated Fermi energy will be decided by the final state of electronic distribution in contact with a particular surfactant, since they should have distinct interactions [22, 28].

In order to investigate some of these aspects, we have chosen ethylene glycol (EG), CH$_2$OHCH$_2$OH, diethylene glycol (DEG), OHCH$_2$CH$_2$OH, polyethylene glycol (PEG), H-(O-CH$_2$-CH$_2$)$_n$-OH, oleic acid (OA), CH$_3$(CH$_2$)$_7$CH=CH(CH$_2$)$_7$COOH, urea (UR), CO(CH$_2$)$_2$ and tetrapropylammonium hydroxide (TPAH), (C$_4$H$_9$)$_4$NOH as surfactants or stabilizers for preparing NC-Ni. From the chemical point of view, EG with both polar and nonpolar ends is miscible with both water and organic compounds. DEG has similar properties to EG, but it has an oxygen double bond. PEG may have chains emanating from a central core group. OA is a long-chain organic compound with a double bond, which is mostly centered for reaction with other compounds. UR with a carbonyl group is soluble in water but is neither acidic nor alkaline. TPAH is soluble in organic solvents. How will they influence the metastably small but
metallic nanoparticles, and how will they create barriers among the latter and hence influence the electronic transport in this composite-like nanostructures? These questions are a matter of utmost interest for use in future interconnections and material properties.

This work aims to explore the influence of these surfactants on the magnetoresistive and thermopower behaviors of nickel nanoparticles at low temperatures by implementing a synthetic protocol that uses EG and DEG as both solvents and reducing agents, wherein nickel acetylacetonate is thermally decomposed to generate the nanoparticles. Preliminary results were reported earlier [34]. In this paper, we present detailed results and analysis. Employing EG and/or DEG not only simplifies the preparation processes but also provides interesting routes for preparing high-quality nanoparticles of controlled structure, size, and morphology. Our findings suggest the significant influence of surfactants on the contrasting behaviors of resistivity and thermopower, thereby providing a promising approach to the realization and/or design of thermoelectric materials that enhance the thermoelectric figure of merit.

2. Experiment

2.1. Sample preparations

Nanocrystalline Ni (NC-Ni) samples were prepared by refluxing the solution of nickel acetate, NiAc, Ni(Ac)₂4H₂O in EG (CH₂OH-CH₂OH)/DEG (C₄H₁₀O₃). A series of NC-Ni samples were prepared in different capping agents. Typically, 0.1 M (1.2424 g) of NiAc was dispersed in 50 ml of EG/DEG and refluxed for about one h at ~190 °C. As the reflux was in progress, after about 30 min, the solution, which was initially a light green color, first turned milky green and then slowly turned dark brown, demonstrating the dispersion of black Ni particles. The surfactant(s) was/were added after two hours of stirring the polyol mixed with NiAc. After this, two h of additional stirring was done. Then, the resulting solution was refluxed for two hours.

A few milligrams of OA as a surfactant were used for the Ni-1 sample. A few milligrams of UR and PEG were added as surfactants for the Ni-2 sample. Similarly, OA and TPAH were used as surfactants for the Ni-3 sample. The Ni-4, Ni-5, and Ni-6 samples were prepared with DEG only (Ni-5), instead of EG using TPAH alone (Ni-4) or OA alone (Ni-6) as surfactants. It was noted that if we added more oleic acid, it resulted in the formation of oleic acetates or corresponding acetates.

2.2. Characterization and other physical measurements

The characterization of the particle size, structure, and crystallographic nature of the nanoparticles forms an essential part of the data analysis. The NC-Ni samples used in this investigation are polycrystalline in nature. Both this polycrystalline nature and the determination of the average particle sizes have been established from x-ray diffraction (XRD) data. The nanostructure was also investigated using atomic force microscopy (AFM). Magnetoresistivity measurements were performed with a standard four-probe technique using a commercial cryostat (OXFORD Instruments, Inc., UK) in the temperature range of 5 to 300 K, and up to 8 Tesla magnetic fields. Thermopower measurements down to liquid helium temperature (5–300 K) were carried out using our homemade setups [35]. Correction for the reference copper in the thermopower measurements was done, which was crucial for the accurate determination of the measured thermopower.
3. Characterization

3.1. X-ray diffraction

Figure 1 shows the XRD patterns of the samples with different surfactants. The diffraction pattern exhibited four distinctive peaks near 44.58°, 51.74°, 76.4°, and 93°, which can be indexed as (111), (200), (220), and (311) reflections, respectively, of fcc nickel (JCPDS#). It is clear that all the peaks correspond to the fcc structure of the Ni metal, and there is no sign of the formation of hcp Ni. Upon exposure to air, the NC-Ni synthesized via thermal decomposition can potentially oxidize to NiO [36, 37]. No nickel oxide peaks were observed in the nickel nanoparticles synthesized in this work because of the surrounding capping layer on the surface of the nanoparticles. The extra peak seen in some samples, indicated by stars (*) in figure 1, is assigned to the presence of hydroxide (OH), which was removed by keeping the sample in an oven at a temperature between 60 °C to 80 °C for two days before taking the electrical transport measurements. The crystallite size \(D\), which was calculated using the Scherrer equation in the XRD patterns, is found to be \(\sim 18\) to 33 nm, showing the influence of surfactants on size. Here, \(D\) was calculated from full width at half maximum of the most intense diffraction peak (111).

3.2. Atomic force microscopy

To understand the particle size and microstructure better, we have taken the AFM images of samples Ni-2, Ni-5, and Ni-6 of different surfactants. Their representative AFM images are presented in the left panels of figures 2(a)–(c). The size \(D\), estimated from the images of 50–100 nanoparticles by noting the frequency of particles, is found to be \(34 \pm 1\), \(42 \pm 1\), and \(44 \pm 2\) nm for Ni-2, Ni-5, and Ni-6, respectively. As illustration, a bar chart was plotted and a Gaussian fitting was performed, as seen in the right panels of figures 2(a)–(c). One can see that the grain sizes obtained from AFM are different than those estimated by XRD for the same sample (table 1), which is related to the sensitivity of each technique. XRD provides average coherence length related to local periodicity inside the grains, even though the area involved for observation is global. Therefore, the average coherence length is usually smaller than the actual

![Figure 1. The XRD patterns of the samples with different surfactants. The extra peak (indicated by *) seen in some samples is the presence of OH.](image-url)
physical size seen through AFM. This gives a real space distribution of grains in a small region. However, in this research we used XRD-estimated particle size to interpret our results. Regarding the presence of surfactants on the surface of the particles, experimental confirmation using methods such as Fourier transform infrared spectroscopy has not been completed. The surfactants are presumed to be present since earlier reports strongly suggest that they are present [18, 38], and hence affect properties of these nanoparticles.

Figure 2. AFM images (left panels) and particle size distribution (right panels) of (a) Ni-2 [PEG + UR], (b) Ni-5 [DEG], and (c) Ni-6 [DEG + OA] samples.
4. Results and discussion

4.1. Electrical resistivity

Figure 3 shows the temperature dependence of the electrical resistivity, $\rho_n(T)$, of the compacted NC-Ni samples with $D \sim 18$–32 nm in the temperature range from 5 to 300 K. The prepared powder was compacted into pellets by applying a pressure of about 2 GPa. This gives an average sample density of about 85% of the bulk density, which agrees well with previously reported data [28]. The electrical resistivity (figure 3) exhibits the strong influence of the different surfactants. The $\rho$ values at 300 K and 5 K are seen to have systematic change, as shown in the inset of figure 3. Interestingly, the samples prepared with EG as the base solvent-cum-surfactant show much higher values of resistivity than those prepared with DEG, indicating that the electron localization due to EG at the GBs (and EG itself) causes significant reduction in the conductivity compared to both its bulk counterpart and DEG. This would be correlated to the presence of DEG with an oxygen double bond, which probably creates a situation where the electrons are more delocalized compared to those in the presence of EG. For the samples with OA in EG (Ni-1, 31 nm), or PEG and UR together in EG (Ni-2, 18 nm), $\rho$ is high and nearly the same. This indicates that the influence of OA with a double bond and a long carbon chain provides the least delocalization among all the samples, irrespective of its larger particle size compared to others, especially the Ni-2 sample. Comparatively, UR with a carbonyl group and PEG with a long chain, in addition Ni-2’s smaller particle size (18 nm)
compared to Ni-1 (31 nm), do not lead to much higher resistivity, as one can see in [31]. This would indicate that the electron localization with OA is much stronger than that of the combined effect of UR and PEG. In contrast, TPAH enhances the electron delocalization, which in turn nullifies the role of OA in a 32 nm (Ni-3) sample. This leads to a reduction in $\rho$ by an order.

However, the situation changes completely when DEG is used as the solvent-cum-surfactant, wherein $\rho$ is drastically smaller than that of the other samples, defying the relatively much smaller size of Ni-4 (23 nm), Ni-5 (21 nm), and Ni-6 (20 nm), which is in disagreement with the concept of enhanced $\rho$ with size reduction [31]. This is in addition to the modified and enhanced roles of either OA or TPAH in the delocalization of the electrons in the presence of DEG, in contrast to the role of EG. Clearly, the GB region with DEG is relatively very favorable, with better electron delocalization compared to the GB in EG, as the resistivity features and values suggest. By further comparing the surfactants OA and TPAH, we observed that OA degrades the delocalization (i.e., $\rho_{\text{Ni5}} > \rho_{\text{Ni4}}$ at least at 300 K), but TPAH enhances the electron delocalization due to DEG. This leads the Ni-6 sample to be the one with the smallest resistivity despite the fact that it is the sample with the smallest particle size, which is in complete contradistinction to the EG (Ni-1, Ni-2, Ni-3) samples, wherein the converse is true. Even with these significant changes in $\rho$, the slopes remain positive throughout the temperature range, in spite of their high values. The large $\rho$ nature of the compacted NC-Ni pellets is attributed to both the disorder in GB regions that effectively represents a series-resistor network [28, 31] and to its interactions with the surfactants [16, 17, 38].

The positive slopes, however, rule out any drastic disorder in the system that can give rise to effects such as electron localization [33, 39]. The relatively more resistive nature of the compacted NC-Ni pellets with EG, compared to the compacted pellets with DEG, is attributed to the disorder in the GB regions combined with the better, more localizing nature of the former. This consequently leads to enhanced scattering even at the higher particle size, $D$. This trend clearly indicates the significant role of GBs and surfactants in affecting the smooth flow of charge carriers. The other possibility comes from the confinement of phonons, which is also enhanced due to the GBs present in the system [22, 31]. It has previously been shown that the phonon confinement affects all phonon relaxation rates, and should affect thermal transport, wherein GB disorder prevails [22]. With these features, it is also important to note that the resistivity of the Ni-1 and Ni-2 samples crosses near 220 K, while the resistivity of the Ni-4 and Ni-5 samples crosses near 20 K, indicating that the slopes are also affected by UR and TPAH as surfactants. The present NC-Ni samples thus provide an opportunity to understand these processes based on phonon confinement, which might be one of the important factors responsible for the observed anomalous nature of thermopower presented later in this paper.

### 4.2. Magnetoresistance

The magnetoresistance (MR) properties of the synthesized NC-Ni samples were also investigated. The magnitude of MR is defined as: $\Delta R/R(0) = (R(H) - R(0))/R(0)$, where $R(H)$ and $R(0)$ are the resistances at a given temperature in the presence and absence of a magnetic field, $H$, respectively. Figure 4 shows the temperature variation of $\%MR$ in NC-Ni samples in the presence of an applied magnetic field of 8 T. It has been found that the $\%MR$ for samples with EG (Ni-1, Ni-2, and Ni-3) as one of the surfactants exhibit quite a dramatic response to temperature. The MR of the Ni-1 and Ni-3 samples decreases with increasing temperature, and
becomes negative at higher temperatures of 150 K and 240 K, respectively. The Ni-1 sample especially shows the largest range of MR values for the temperature range studied. When TPAH is introduced as a surfactant in Ni-3, the MR evolves into higher values at lower temperatures, turning negative marginally above 240 K. However, with the use of UR and PEG with EG (Ni-2), an overall smaller %MR was found, with negative values throughout the temperature range we studied. Thus, all the samples made with EG show a negative value that is significantly large near room temperature. Conversely, samples made with DEG only, or with TPAH and OA separately, exhibit very marginally increasing trends with positive MR values, in accordance with earlier observations [40]. This overall scenario corroborating the significantly anomalous electrical transport behavior seen in resistivity clearly reflects the usually observed negative and positive MR in the interfaces [41], nanocomposite fibers [42], organic semiconductor devices [43], and multiwalled carbon nanotube nanocomposites [44].

The larger particle size of the EG samples, wherein the presence of a sufficient concentration of ferromagnetic (FM) clusters of Ni is expected, seems to suffice for the observation of MR in these samples. Due to the randomly distributed moments of FM clusters as well as the large grain contact resistance, magnetic disorder may play a key role in electron localization. Under an applied magnetic field, the orientation of random FM clusters is forced to align uniformly to reduce the magnetic disorder, which favors electron delocalization and results in a significant drop in resistivity. On the contrary, negligible MR has been observed for the NC-Ni prepared with DEG (Ni-4 to Ni-6) as the solvent-cum-surfactant. The insensitivity of these samples to the magnetic field is also consistent in the picture as augmented above. These samples, with a smaller particle size than that of the EG samples, have probably reduced the ferromagnetic clusters of Ni without effective magnetism, which is in line with earlier reports [17].

4.3. Thermopower

Figure 5 displays the temperature dependence of the thermopower, $S_n(T)$, of the NC-Ni samples in the temperature range from 5 to 300 K. The $S(T)$ data of Ni bulk (99.99%) is also included for comparison, which shows a negative sign, a broad phonon drag peak around 50 K, and values that lie within $-20 \mu\text{VK}^{-1}$. These features have also been exhibited by the NC-Ni
samples, but the thermopower is found to be positive at low temperatures and the magnitude of $S$ changes with the type of surfactant. As the temperature increases, all samples except for the Ni-2 sample display a positive sign up to $\sim 35$ K, turning negative above this temperature. On close observation, one can see that these features evolve into a very dominant role for the surfactants, in defiance of the size-dependent $S$ observed earlier [22]. The EG (Ni-2) sample prepared in PEG with UR exhibits the smallest $S$ and a broader positive $S$ region at low temperatures, but it also showed a second maximal resistivity at 300 K (Figure 2) in spite of the fact that its particle size (18 nm) is the smallest, compared to the particle sizes of Ni-1 (31 nm) and Ni-3 (32 nm) among the samples prepared in EG, and is also smaller than the three samples prepared in DEG: Ni-4 (23 nm), Ni-5 (21 nm), and Ni-6 (20 nm). The $S$ of the latter three samples should have been smaller than that of Ni-2, because of their lower resistivity values. This, however, runs contrary to a common perception: the higher the resistivity, the bigger the thermopower [45]. Overall, the general trend of these nanoparticle samples seen in resistivity is not followed in thermopower. Regarding the hump, it turns out to be prominent and sharp for Ni-3 (32 nm), but quite flattened for Ni-2 (18 nm). These contrasting features exhibited in thermopower and resistivity, which is contradictory to what is normally seen in metals and alloys [45] and even in semiconductors [46], might indicate some attractive features related to designing thermoelectric materials with an enhanced thermoelectric figure of merit [47]. They therefore suggest the critical roles of EG, DEG, PEG, OA, UR, and TPAH, both as surfactants and with regard to their interactions with nanoscale metallic surfaces.

These features might indicate a substantial change in the band structure or the conduction mechanism at the nanoscale. The flipping of sign of the thermopower in these NC-Ni samples indicates, in principle, the involvement of both the electrons and holes in the electrical transport. From $\sim 150$ to 300 K, the magnitude of $S$ ($|S|$) generally increases systematically as the temperature rises, indicating that the diffusion thermoelectric transport prevails in the high-temperature regime, with electrons as majority charge carriers. Our results clearly indicate the distinct behavior of the NC-Ni samples at low temperatures, which is associated with the sharp onset of a negative phonon drag peak. This is intriguing, as it is distinct from that of the bulk (electron-like throughout the temperature range), since the thermopower in general is dependent
on the topology of the Fermi surface, and consequently is closely related with the energy (E) and phonon wave vector (\(k\)) dependence of the relaxation time, \(\tau(E, k)\).

In the low temperature limit, the carrier relaxation time is limited by impurity scattering. From the extrapolation of the electrical resistivity of Ni-nanoparticles (figure 3) to zero temperature, it turns out that the present samples correspond to a distinct value of resistivity at zero temperature. This means that there is an essential presence of equivalent impurity scattering in the present samples. Thus, for low temperatures, where phonons have not yet started to play a significant role, the electrical resistivity is proportional to the inverse of the relaxation time. For a three-dimensional system, the electron diffusion contribution to the thermopower is distinguished by its simple linear temperature dependence. The low- and high-temperature phonon drag and diffusion mechanisms have been adequately discussed for metals [45, 48]. In the low-temperature regime, the thermopower follows the relation

\[ S = AT + BT^3. \]  

Here, the first term in the isotropic relaxation time approximation represents the contribution from the diffusion component \(S^d\), and is linear in \(T\). The second term corresponds to the phonon drag contribution \(S^{ph}\) at low temperature, which is analogous to the specific heat that follows the Debye \(T^3\) law. On the other hand, at higher temperatures, the conventional diffusion and phonon drag component to \(S\) is written as

\[ S = aT + b/T. \]  

Here, \(A\) (or \(a\)) and \(B\) (or \(b\)) are the diffusion coefficient and phonon drag coefficient at low (high) temperatures, respectively. In order to elucidate these mechanisms and to extract the diffusion coefficient \((a\) or \(A\)) and phonon drag coefficient \((b\) or \(B\)) from the observed thermopower of NC-Ni samples, we have plotted \(S/T\) versus \(T^2\) and \(S/T\) versus \(T^{-2}\) for the low and high temperature regions in figures 6 and 7, respectively. We have plotted in turn the resultant \(A\) and \(B\) (figure 6, inset) and \(a\) and \(b\) (figure 7, inset) coefficients versus surfactants. One can see that the magnitude of coefficient \(A\) in the low-temperature regime is higher when compared to the bulk Ni sample. Conversely, \(|B|\) is found to be lower when compared to the bulk Ni sample. Thus, the diffusion and phonon drag contribution coefficients operate opposite
to each other, as expected. For the high-temperature regime, the value of coefficient $a$ is found to be higher in the Ni-2 sample ($D = 18$ nm) than in the other samples. In other words, the phonon contributions or confinement is prominent in this sample compared to other larger nanoparticle samples.

To further elucidate the speculation on the phonon confinement effect in the present NC-Ni samples, we recall that the effect of electron-phonon confinement would manifest itself as a broad hump in $S$ at low temperatures for highly disordered GB scattering [22, 49]. In the present case, the low temperature limited resistivity for all measured NC-Ni samples is less than $2 \text{m} \Omega \text{cm}$ (figure 3), suggesting that the phonon confinement effect in thermopower is expected to be noticeable in these compacted nanoparticles. Significantly disordered GBs in nanocrystalline metals introduce numerous interfaces, leading to extra scattering centers due to the size effect for electrons and phonons [22, 49]. To get the extra contributions of phonon drag and diffusion thermopower due to disorder at the GBs and particle size, the difference in $S$, $\Delta S = S_n - S_{\text{bulk}}$, is plotted in figure 8. One can see that the absolute value of $\Delta S$ is significantly larger for all the samples compared to $S$ (i.e., there is significant enhancement in $S$ in the NC-Ni samples, with a systematic variation of $\Delta S$ as a function of temperature). The higher $\Delta S$ value is found in the Ni-2 sample ($D = 18$ nm), as expected. We attribute this to the random nature of the GBs and surface atoms. As the GBs and surface atoms increase with a decrease in particle size, $|\Delta S|$ systematically increases, and consequently the diffusion and phonon-drag contributions become relatively more prominent than those in bulk [5]. Notably, $\Delta S$ exhibits broader peaks with a marginal shift in position to lower $T$ as $\text{size}$ decreases. These results clearly indicate the dominant role of GB disorder with additional factors due to the different surfactants, which influence the scattering of phonons and electrons in a significant way.

5. Conclusions

In conclusion, several compacted Ni nanoparticles with average particle sizes ($D$) ranging from $\sim 18$ to $33$ nm have been prepared using EG, DEG, PEG, OA, UR, and TPAH as surfactants. They were characterized using XRD, AFM, electrical resistivity, magnetoresistance, and

![Figure 7. Diffusion and phonon drag contributions of various NC-Ni samples. $S/T$ is found to be linear with $1/T^2$ above 150 K. The inset shows the coefficients $a$ and $b$ in equation (2) plots against surfactants.](image-url)
thermopower to elucidate the critical role of the surfactants. The observed electrical resistivity \( r_n(T) \) data for all samples are typical of a good metal and have a fairly linear temperature dependence of resistivity down to about 50 K. It is found that the samples prepared with EG as the base solvent-cum-surfactant show much higher values of resistivity compared to those prepared with DEG, indicating that the grain contacts are relatively much more conductive in the EG samples than in the DEG samples, eventually producing negative and significant values of MR. In contrast, the trends in thermopower are different from those seen in resistivity, which is contradictory to what is normally seen in most known materials. This might suggest attractive features that may enhance the thermoelectric figure of merit, and hence the important roles of surfactants, when designing thermoelectric materials.

Acknowledgments

The authors gratefully acknowledge the assistance rendered by Joffy of Barkatullah University, Bhopal, MP in the sample preparation, M Gupta and R Rawat, UGC-DAE CSR, Indore for XRD, resistivity, and magnetoresistance data collection, respectively.

References

[1] Pileni M-P 2001 Adv. Funct. Mater. 11 323–36
[2] Sun S, Murray C B, Weller D, Folks L and Moser A 2000 Science 287 1989–92
[3] Lee K-B, Park S and Mirkin C A 2004 Angew. Chem. Int. Edn 43 3048–50
[4] Pankhurst Q A, Connolly J, Jones S K and Dobson J 2003 J. Phys. D: Appl. Phys. 36 R167–81
[5] Park J et al 2005 Adv. Mater. 17 429–34
[6] Wang Z K, Kuok M H, Ng S C, Lockwood D J, Cottam M G, Nielsch K, Wehrpohn R B and Gosele U 2002 Phys. Rev. Lett. 89 027201
[7] Förster H, Wolfrum C and Peukert W 2012 J Nanopart. Res. 14 926
[8] Zhang J and Lan C Q 2008 Mater. Lett. 62 1521–4
[9] Yu P, Qian Q, Wang X, Cheng H, Ohsaka T and Mao L 2010 J. Mater. Chem. 20 5820–2
[10] Okitsu K 2011 Sonochemical synthesis of metal nanoparticles Theoretical and Experimental Sonochemistry Involving Inorganic Systems ed A Muthupandian (Berlin: Springer) pp 131–50

Figure 8. Difference thermopower, \( \Delta S \), of compacted NC-Ni samples.
[11] Bönnemann H and Richards R M 2001 *Eur. J. Inorg. Chem.* **2001** 2455–80
[12] Chen Y, Peng D-L, Lin D and Luo X 2007 Nanotechnology **18** 505703
[13] Brust M, Walker M, Bethell D, Schiffrin D J and Whyman R 1994 *J. Chem. Soc. Chem. Commun.* **7** 801–2
[14] Oliveira M M, Ugarte D, Zanchet D and Zarin A J G 2005 *J. Colloid Interface Sci.* **292** 429–35
[15] He Q, Yuan T, Yan X, Luo Z, Haldolaarachchige N, Young D P, Wei S and Guo Z 2014 *Chem. Commun.* **50** 201–3
[16] He Q, Yuan T, Luo Z, Haldolaarachchige N, Young D P, Wei S and Guo Z 2013 *Chem. Commun.* **49** 2679–81
[17] Singh J, Kaurav N, Lalla N P and Okram G S 2014 *J. Mater. Chem. C* **2** 8918–24
[18] Okram G S and Kaurav N 2011 *Adv. Sci. Lett.* **4** 132–5
[19] Oliveira M M, Ugarte D, Zanchet D and Zarbin A J G 2005 *J. Chem. Soc. Chem. Commun.* **7** 801–2
[20] Oxford M M, Ugarte D, Zanchet D and Zarbin A J G 2005 *J. Colloid Interface Sci.* **292** 429–35
[21] He Q, Yuan T, Wei S, Haldolaarachchige N, Luo Z, Young D P, Khasanov A and Guo Z 2012 *Angew. Chem. Int. Ed.* **51** 8842–5
[22] Brust M, Walker M, Bethell D, Schiffrin D J and Whyman R 1994 *J. Chem. Soc. Chem. Commun.* **7** 801–2
[23] Oliveira M M, Ugarte D, Zanchet D and Zarbin A J G 2005 *J. Colloid Interface Sci.* **292** 429–35
[24] He Q, Yuan T, Wei S, Haldolaarachchige N, Luo Z, Young D P, Khasanov A and Guo Z 2012 *Angew. Chem. Int. Ed.* **51** 8842–5
[25] Okram G S and Kaurav N 2011 *Adv. Sci. Lett.* **4** 132–5
[26] Okram G S and Kaurav N 2011 *J. Mater. Chem. C* **2** 8918–24
[27] Okram G S and Kaurav N 2011 *J. Nanosci. Nanotechnol.* **8** 4127–31
[28] Okram G S, Soni A and Rawat R 2008 *Nanotechnology* **19** 185711
[29] Okram G S, Soni A and Rawat R 2008 *Nanotechnology* **19** 185711
[30] Bönnemann H and Richards R M 2001 *Eur. J. Inorg. Chem.* **2001** 2455–80
[31] Chen Y, Peng D-L, Lin D and Luo X 2007 Nanotechnology **18** 505703
[32] Brust M, Walker M, Bethell D, Schiffrin D J and Whyman R 1994 *J. Chem. Soc. Chem. Commun.* **7** 801–2
[33] Oliveira M M, Ugarte D, Zanchet D and Zarin A J G 2005 *J. Colloid Interface Sci.* **292** 429–35
[34] He Q, Yuan T, Yan X, Luo Z, Haldolaarachchige N, Young D P, Wei S and Guo Z 2014 *Chem. Commun.* **50** 201–3
[35] He Q, Yuan T, Luo Z, Haldolaarachchige N, Young D P, Wei S and Guo Z 2013 *Chem. Commun.* **49** 2679–81
[36] Singh J, Kaurav N, Lalla N P and Okram G S 2014 *J. Mater. Chem. C* **2** 8918–24
[37] Okram G S and Kaurav N 2011 *Adv. Sci. Lett.* **4** 132–5
[38] Oliveira M M, Ugarte D, Zanchet D and Zarbin A J G 2005 *J. Colloid Interface Sci.* **292** 429–35
[39] He Q, Yuan T, Wei S, Haldolaarachchige N, Luo Z, Young D P, Khasanov A and Guo Z 2012 *Angew. Chem. Int. Ed.* **51** 8842–5
[40] Okram G S, Devi K N, Sanatombi H, Soni A, Ganesan V and Phase D M 2008 *J. Nanosci. Nanotechnol.* **8** 4127–31
[41] Couto G G, Klein J J, Schreiner W H, de Oliveira A J A and Zarbin A J G 2007 *J. Colloid Interface Sci.* **311** 461–8
[42] Soni A and Okram G S 2009 *Appl. Phys. Lett.* **95** 013101
[43] Durkan C and Welland M E 2000 *Phys. Rev.* **B** **61** 14215–8
[44] Steinhögl W, Schindler G, Steinlesberger G and Engelhardt M 2002 *Phys. Rev.* **B** **66** 075414
[45] Wu W, Brongersma S H, Hove M V and Maex K 2004 *Appl. Phys. Lett.* **84** 2838–40
[46] Josell D, Burkhard C, Li Y, Cheng Y-W, Keller R R, Witt C A, Kelley D R, Bonevich J E, Baker B C and Moffat T P 2004 *J. Appl. Phys.* **96** 759–68
[47] Bid A, Bora A and Raychaudhuri A K 2006 *Phys. Rev.* **B** **74** 035426
[48] Okram G S and Kaurav N 2011 *J. Appl. Phys.* **110** 023713
[49] Bönnemann H and Richards R M 2001 *Eur. J. Inorg. Chem.* **2001** 2455–80
[50] Chen Y, Peng D-L, Lin D and Luo X 2007 Nanotechnology **18** 505703
[51] Brust M, Walker M, Bethell D, Schiffrin D J and Whyman R 1994 *J. Chem. Soc. Chem. Commun.* **7** 801–2