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# Modification in electrical transport with a change in geometry from a nanowire to a nanotube of copper: effect of the extra surface

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**Abstract.** We have studied the temperature-dependent (3–300 K) electrical resistance of metal nanowires and nanotubes of the same diameter with the specific aim to understand the changes in electrical transport brought about by a change in the geometry of a nanowire to a nanotube. Single crystalline nanowires and nanotubes of copper were synthesized by electrodeposition in nanoporous alumina templates. The temperature-dependent resistivity data have been analysed using the Bloch-Grüneisen function for the lattice contribution to resistivity, and the characteristic Debye temperature  $\theta_{\rm R}$  was determined along with the residual resistivity  $\rho_0$ . Substantial size effects were observed in both the parameters  $\rho_0$  and  $\theta_R$ , where the former is enhanced and the latter is suppressed from bulk to nanowires and further to nanotubes. It has been observed that the transport parameters in the nanotubes with wall thickness t are similar to those of a nanowire with diameter d, where  $d \approx 2t$  in the specific size range used in this work. It is suggested that appreciable size effects in the electrical transport parameters occur due to the extra surface in the nanotube. In both nanotubes and nanowires, the single parameter that determines the size effect is the surface area to volume ratio.

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Metal nanotubes represent a class of one-dimensional nanostructures that are of immense scientific and technological significance. There has been a considerable number of reports in the literature on the growth and structural characterization of metal nanotubes [1-9]. However, there are no published investigations on the electrical resistance of metal nanotubes and in particular temperature-dependent resistivity. The study of electrical properties has become important in light of their potential application in nanoelectronic devices. Electrical resistivity  $(\rho(T))$ , in particular the residual resistivity  $\rho_0 (= \rho(4.2 \text{ K}))$ , and the temperature-dependent part of the resistivity  $\rho_{\rm L}(T) = \rho(T) - \rho_0$  (the lattice contribution) provide important information on the basic mechanism that determines the resistivity of solids. In particular, it allows us to determine the Debye temperature, which is an important physical quantity related to the thermal and thermodynamic properties. Temperature-dependent resistivities (covering the temperature range 3–300 K) have previously been investigated in detail in high-quality crystalline nanowires of Ag, Cu [10] and Ni [11–13]. These studies clearly established that the Bloch–Grüneisen (BG) theory of electron-phonon interaction, with a size-dependent Debye temperature ( $\theta_R$ ), is applicable to metal nanowires with diameter down to 15 nm, and also illustrated the role of diffused surface in determining the residual resistivity  $\rho_0$ . These observations are important in the overall context of the uses of metal nanowires/nanotubes. In contrast to nanowires, there is no published investigation of electrical measurements of metal nanotubes. There are reports of temperature-dependent electrical resistivity studies done in semiconducting Bi nanotubes [14, 15] that show a negative temperature coefficient of resistivity. In this paper, we investigate the applicability of BG theory and surface scattering (as in the case of nanowires) to the temperature-dependent resistivity of nanotubes (which show metallic resistivity with a positive temperature coefficient of resistivity) with the aim to understand the differences observed in the parameters describing the electrical transport in a thin nanotube and nanowire of equal outer diameter and similar crystallinity. A nanotube with two surfaces can behave as a nanowire (with an additional surface) or it can behave as a metal film of thickness t which has been rolled into a tube. The paper addresses some of the issues that will be revealed by the experimental data and the accompanying analysis.

Here we have carried out a detailed investigation of the temperature-dependent electrical resistivity ( $\rho(T)$ ) of Cu nanotubes (diameter  $\approx 230$  nm and wall thickness  $\approx 18$  nm) as well as Cu nanowires (230 nm and lower diameter) over the temperature range 3 K < T < 300 K with the aim to compare the electrical transport of a nanotube to a nanowire with a similar diameter and to understand how the size effects place a nanotube in the size effect trend observed in nanowires. The investigation reported here allows us to measure the residual resistivity  $\rho_0$ as well as the Debye temperature ( $\theta_{\rm R}$ ) in the metal nanotubes and the nanowires and study their dependence on the physical dimensions and geometry. Our results show substantial size effects that show up as a suppression of the Debye temperature  $\theta_{R}$  (which has been determined from electrical resistivity data) and also as an enhancement of the residual resistivity  $\rho_0$  from bulk to nanowires and further to nanotubes. While size effects on electrical resistivity in nanowires [10–13] and in thin films [16, 18] of metals have been investigated before, the investigation of size effects in metal nanotubes and the correlation with nanowires has not been performed earlier.

#### 1. Experiment

#### 1.1. Growth of metal nanowires and nanotubes

The nanowire and nanotube arrays used in this experiment were prepared by electrodeposition of Cu inside nanoporous anodic alumina templates. Whereas deposition of the nanowire was done by conventional electrodeposition using an electric field along the axial direction of the pore in the template, for the deposition of nanotubes we used a rotating electric field applied transversally to the growth direction along with the axial field. The deposition was carried out in a bath containing the electrolyte CuSO<sub>4</sub>.5H<sub>2</sub>O with the working electrode (a 200 nm silver layer evaporated on one side of the template) at a potential of -0.3 V with respect to the reference electrode (saturated calomel). A detailed study of the mechanism of the formation has been elucidated in our paper [9] dedicated to the synthesis using this method.

#### 1.2. Structural characterization

The nanowires and nanotubes formed inside the cylindrical pores of the templates were well characterized by x-ray diffraction (XRD), scanning electron microscopy (SEM) including quantitative energy dispersive x-ray analysis (EDX) and transmission electron microscopy (TEM). The nanowires as well as nanotubes thus grown were found to be single crystalline with FCC structure with preferential growth along the (220) direction as shown in figures 1(c)and (d).

Representative SEM images of the nanowire and nanotube arrays are shown in figures 1(a) and (b), respectively. The data are similar to those obtained in our previous publication [9]. The reproducibility of the data (including electrical measurements) has been tested over at least ten growth runs. The diameters of pores inside the alumina templates have a very narrow size distribution (rms value of diameter distribution  $\pm 5\%$ ). The diameter and thickness of the nanowires were measured after growth by taking samples from different parts of the templates. The physical dimensions of nanowires and nanotubes used in the investigation are given in table 1. Due to the single crystalline nature of the nanotube and nanowires, the residual

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**Figure 1.** SEM images (scale bar:  $1 \mu m$ ): (a) Cu nanowire arrays and (b) Cu nanotube arrays. XRD patterns: (c) Cu nanowire arrays and (d) Cu nanotube arrays.

**Table 1.** Comparison of parameters obtained by fitting equation (1) for different copper samples with diameter (d)/thickness (t).

Sample	$\Theta_{\mathbf{R}}(\mathbf{K})$	$\rho_0 \left( \Omega  \mathrm{m} \right)$
Tube ( $d \approx 230 \text{ nm}, t \approx 18 \text{ nm}$ )	221	$1.09  imes 10^{-8}$
Wire ( $d \approx 230 \text{ nm}$ )	265	$4.76  imes 10^{-9}$
Wire $(d \approx 50 \mathrm{nm})$	231	$1.02  imes 10^{-8}$
Wire $(d \approx 15 \text{ nm})$	180	$2.20  imes 10^{-8}$
Bulk wire	320	$1.20  imes 10^{-11}$

resistivity is primarily limited by the surface scattering. This is an important condition that allows us to study the scattering of electrons from the surfaces of the nanowires and nanotubes.

Nanotubes that are thinner than the dimension used here are very fragile and do not survive the temperature cycling needed to establish the reproducibility of the resistance data. Tubes with larger thickness or lower diameter (with thickness comparable to the radius) have thickness distribution problems along their length related to the intrinsic growth mechanism due to the continuously increasing ionic concentration and the correspondingly changing growth front with time [9]. This often leads to measurement limitations and data that do not suit the relevant analysis, as thicker nanotubes have slightly (with the variations comparable to thickness at the thinner end) varying inner diameter depending on the time of growth. It is observed that such tubes, although they can be grown successfully [9], do not meet the requirements of the analysis schemes we use in this paper or for that matter the quantitative estimation of size effects. Thus,



**Figure 2.** Resistivity as a function of temperature for the nanotube, the nanowire and the bulk reference wire. The lines through the data are a fit to BG function. The inset error (%) plot shows the deviation of the fit from the data for the nanotube. The inset cartoon shows the scheme of the pseudo four-probe measurement on arrays of nanowires/nanotubes.

we choose a diameter of 230 nm for the nanowires and nanotubes (with optimum thickness  $\approx \frac{1}{10}$  diameter) because of the uniform thickness, robustness and reproducibility of measurements for comparison. To understand how the nanotube parameters compare with the trend observed in nanowires of copper, we also present the measurement results on nanowires of lower diameter in table 1.

#### 1.3. Electrical measurements

The electrical resistance measurements were carried out by retaining the wires as well as the nanotubes within the alumina templates. The resistances of the nanowire and nanotube arrays were measured by a pseudo four-probe method, in which two electrical leads were attached to each of the two sides of the template containing nanowires/nanotubes using silver epoxy as shown in figure 2. In such measurements, the contact resistance can be an issue. In order to estimate the magnitude of the contact resistance in this kind of pseudo four-probe measurement, we made similar measurements with a superconducting solder and contacts. We did not observe any significant change in either the temperature-dependent resistance or the value of evaluated resistivity of the sample as we went down to the superconducting transition temperature of the contacts. Our observations revealed that the contact resistance is much less (<2%) when compared with the actual resistance of the nanowire or nanotube arrays, which thus rules out a predominant contribution of the contacts. Thus the resistance that we measure by the pseudo four-probe method on metal nanowire or nanotube arrays mainly corresponds to the

actual sample resistance. Furthermore, in our previous work [13, 19], we have validated that the value of electrical resistivity obtained by the pseudo four-probe method matches well with the resistivity measured by the four-probe method on a single Ni nanowire. The method and some issues related to contact resistance and contact noise have been discussed in detail in previous publications by our group [10, 11, 17]. To avoid electromigration damage we used a low-frequency ac signal with a low current amplitude with peak current density  $\approx 5 \times 10^8$  A m<sup>-2</sup> or less. It has been established [20] that these nanowires when retained inside a template can withstand current density in excess of  $10^{10}$  A m<sup>-2</sup>. The resistance was measured using a phasesensitive detection scheme with a resolution of  $\pm 5$  ppm. The as-grown nanotubes are brittle in character (break under the ultrasonication needed to disperse them) mainly due to their small wall thickness. As a result, it was not possible to separate them from the templates and make single-nanotube electrical measurements as has been done for the nanowires, as stated before.

#### 2. Results

Figure 2 shows the electrical resistivity of the Cu nanotubes measured from 3 to 300 K as compared with that of a Cu nanowire of the same diameter (230 nm) and that of a high-purity copper wire (diameter = 50  $\mu$ m) that is taken as the 'bulk' reference. The method of obtaining the absolute value of resistivity from the resistance data taken in the array has been discussed in detail in [10, 11, 13]. We follow the same method to obtain the absolute value of the  $\rho$  data here. (We briefly state the method later on.) The resistivity of the nanotube at 300 K is  $\approx 1.5$ times that of the nanowire of the same diameter and  $\approx 2.2$  times that of the bulk. The residual resistivity ratios (RRR) of the nanowires (RRR = 5.5) and the nanotubes (RRR = 3.5) are much less than that of the bulk wire (RRR = 1350). The enhancements of the  $\rho$  of the nanotube as well as that of the nanowire arise from the enhancement of  $\rho_0$  as well as the suppression of the Debye temperature  $\theta_R$ , both arising from size effects. We will discuss these later on.

In general, the electrical resistivity  $(\rho(T))$  of a simple non-magnetic metal consists of the residual resistivity  $(\rho_0)$  (originating mainly from impurities, internal boundaries and scattering from external surfaces) and the temperature-dependent resistivity  $(\rho_L(T))$  arising due to electron–phonon (lattice) interactions. We may write

$$\rho(T) = \rho_0 + \rho_{\rm L}(T). \tag{1}$$

In simple metals such as Cu (bulk), the temperature-dependent part  $\rho_L(T)$  is well described by the following BG function [21]:

$$\rho_{\rm L}(T) = \alpha_{\rm el-ph} \left(\frac{T}{\theta_{\rm R}}\right)^5 \int_0^{\frac{\theta_{\rm R}}{T}} \frac{x^5 {\rm d}x}{({\rm e}^x - 1)(1 - {\rm e}^{-x})},\tag{2}$$

where  $\alpha_{el-ph}$  is the electron-phonon coupling constant and  $\theta_R$  is the characteristic Debye temperature. We note that in general, in bulk metals, the Debye temperature  $\theta_R$  obtained from the resistance data using the BG equation is close to but somewhat lower ( $\approx 10\%$ ) than the Debye temperature  $\theta_D$  obtained from the heat capacity data. For instance, in Cu, the bulk  $\theta_R$  for pure Cu (bulk) is  $\approx 320$  K and  $\theta_D$  is 340 K. The applicability of the BG equation in nanowires of FCC metals down to a diameter of 13 nm has been shown before [10, 11]. The dependences of the Debye temperature and residual resistivity on size in metal nanowires of both non-magnetic [10] and ferromagnetic [11–13] metals have been carefully addressed through the measurement of  $\rho(T)$  over an extensive range. In this paper, we first check the applicability of BG equation (2) to the nanotubes and also make a comparison of the characteristic transport parameters ( $\rho_0$  and  $\theta_R$ ) to those of nanowires of similar dimensions. We have fitted the resistivity data of the nanotube to equations (1) and (2). As can be seen in figure 2, the fits to equations (1) and (2) are excellent. It is noted that the  $\theta_R$  can be obtained from equations (1) and (2) even if the fits are done to the resistance data. Thus any uncertainty in the determination of the absolute value of  $\rho$  does not affect the determination of  $\theta_R$ . The inset of figure 2 shows the quality of the fit. The typical fit error is less than  $\pm 0.3\%$  throughout the entire temperature range.

The parameters obtained from the fit to equations (1) and (2) are shown in table 1. Measurement of the Debye temperature of a metal nanotube has not been done before and thus is a new observation. It is seen that the Debye temperature ( $\theta_R = 221$  K) estimated from the resistance data in the case of the nanotube is very much suppressed compared to that of a nanowire of nearly the same diameter ( $\theta_R = 265$  K) and the suppression is more substantial when compared to that of bulk Cu ( $\theta_R = 320$  K). In addition to the aim to compare the modification in electrical transport from a nanowire to a thin nanotube of diameter 230 nm, as presented in table 1, measurements were carried out on copper nanowires of diameter 50 and 15 nm with an aim to understand how the nanotube parameter compares to the trend followed by nanowires similar to the wall thickness of the tube. We note that to check such effects using nanotubes of thinner diameter or larger thickness has not been feasible because of practical limitations described in section 1, which are the reasons for choosing the optimum thickness and diameter for comparison.

The resistivity  $\rho$  of these nanostructures can be determined from the resistance data taken in an array. This procedure has been developed in [10]. Briefly, the relationship between the Debye temperature and the resistivity  $\rho(T)$  at a temperature T can be given as

$$\rho_{\rm n}(T) = \frac{\beta_{\rm b}}{\beta_{\rm n}} \frac{\theta_{\rm R}^{\rm b}}{\theta_{\rm R}^{\rm n}} \rho_{\rm b}(T), \tag{3}$$

where the suffixes n and b correspond to the nano and bulk, respectively, and  $\beta = \frac{1}{R} \frac{dR}{dT}$  is the measured temperature coefficient of resistivity at temperature *T* in the temperature range close to or above  $\theta_R$ . All the quantities in equation (3) on the right-hand side are determined from the experiment and hence  $\rho_n(T)$  can be determined. As stated before,  $\theta_R$  can be determined from the resistance data and knowledge of  $\rho$  is not needed. Generally, for a given array  $\rho_n$  is determined close to the room temperature. Once  $\rho_n$  for a given array is known, the number of wires (which are connected in parallel) in that array can be found from the measured resistance. The resistivities shown in figure 2 have been obtained by the above method.

#### 3. Discussion

The enhancement of resistivity in nanotubes arises from two definite contributions. One is the enhancement of the residual resistivity  $\rho_0$  and the other is the suppression of Debye temperature  $\theta_R$  that enhances the temperature-dependent part  $\rho_L(T)$ . Both these effects have a distinct dependence on the size as discussed below. The systematic dependence of the two parameters,  $\rho_0$  and  $\theta_R$ , on the surface can be seen in figure 3, where we plot these two quantities for both the nanowires and the nanotube as a function of the surface area (*S*) to volume (*V*) ratio ( $\frac{S}{V}$ ). For the nanowire of diameter *d* and length  $l \gg d$  (high aspect ratio),  $\frac{S}{V} \approx \frac{4}{d}$ . For the nanotube with outer radius *r* and length  $l \gg R$ ,  $\frac{S}{V} \approx \frac{2\pi(R+r)l}{\pi(R^2-r^2)l} = \frac{2}{t}$ , where (R-r) = t is the wall thickness of the nanotube. Figure 3 shows the data taken on both nanotubes and nanowires; it



**Figure 3.** Dependence of the Debye temperature  $\theta_{\rm R}$  and the residual resistivity  $\rho_0$  on the surface area to volume ratio.

shows that there is a monotonic decrease of the  $\theta_R$  and an enhancement of the  $\rho_0$  as the physical dimension of the nanowires/nanotubes decreases and  $\frac{S}{V}$  increases. This systematic dependence of the two parameters on  $\frac{S}{V}$  shows the dominant role of the surface. From the dependence of  $\rho_0$  as well as  $\theta_R$  on the ratio  $\frac{S}{V}$ , it appears that the nanotube seems to have an effective diameter  $d_{\text{eff}}$  that is equal to 2t. Also, when the inner radius  $r \to 0$ , the tube approaches the wire limit with diameter 2t. Below, we discuss in detail the information that can be obtained from the size dependence of these parameters, and also rationalize the observed dependence on  $\frac{S}{V}$ .

#### 3.1. Size dependence of $\theta_{\rm R}$

Suppression of Debye temperatures ( $\theta_R$  or  $\theta_D$ ) has been seen in nanomaterials with different physical forms such as nanoparticles [22, 23] and, as stated before, in nanowires and very thin films. Depression of the Debye temperature, as we show below, has an inverse power-law dependence on the size (physical dimension). The suppression of  $\theta_R$  has a thermodynamic basis. The Debye temperature  $\theta_D$  is known to be linked to the melting temperature  $T_M$  through the Lindemann relation [23]

$$\theta_{\rm D} = C \sqrt{\frac{T_{\rm M}}{M V^{2/3}}},\tag{4}$$

where *C* is a constant, *M* is the molecular weight and *V* is the molecular volume of the solid. It is thus expected that suppression of the Debye temperatures ( $\theta_D$  as well as  $\theta_R$ ) may be linked to the suppression of the melting temperature  $\Delta T_M$ . It has been experimentally observed and theoretically justified [24] that  $\Delta T_M$  follows an inverse power-law dependence on the physical dimension ( $\omega$ ) of the nanomaterial,  $\Delta T_M \propto \omega^\eta$ , where  $\eta$  is negative. For a nanowire with length  $\gg$  diameter and spherical nanoparticles,  $\omega = d$ . From the analysis of the available data it has been shown [24] that the exponent  $\eta$  has a dependence on the physical form.  $\eta \approx (-1.2 \text{ to } -1.4)$  for nanoparticles,  $\approx -1$  for films and  $\approx -0.5$  to -0.6 for nanowires. The





**Figure 4.** Dependence of the suppression of  $\theta_R$  on the diameter of nanowires and on the wall thickness of the nanotube. The nanowire equivalent diameter *d* for a nanotube is 2t.

origin of the power-law dependence of the melting point depression has been discussed using the concept of non-extensive thermodynamics [24] and the dependence of the power-law exponent  $(\eta)$  on the physical form was shown to arise from the power-law dependences of the volume as well as the extensivity parameter on the dimension  $\omega$ . Using equation (4), we can relate the change in  $\theta_{\rm R}$  to  $\Delta T_{\rm M}$  so that  $\Delta \theta_{\rm R}^2$  should follow the same power-law dependence on  $\omega$  as  $\Delta T_{\rm M}$ and  $\Delta \theta_R^2 \propto \omega^{\eta}$ . We check this dependence for the nanowires as well as the nanotube. The data are shown in figure 4 where we plot  $\ln \Delta \theta_{\rm R}^2$  against  $\ln(d)$  for nanowires ranging in diameter from 230 to 15 nm. We find that the data for the nanotube also fit into the same trend in the graph when the effective diameter is taken as  $\approx 2t$ . From the slope of the graph in figure 4, we get the exponent  $\eta \approx -0.65 \pm 0.03$ . This is very close to the value of  $\eta$  found from the dependence of  $\Delta T_{\rm M}$  on  $\omega$ , which for nanowires is  $\approx (-0.5 \text{ to } -0.6)$ . This analysis places the suppression for  $\theta_{\rm R}$  on the same thermodynamic basis as that for  $T_{\rm M}$ , a viewpoint that was not explored earlier and that places the nanotube in the same class as nanowires and not in the same class as the thin film that was found to have an  $\eta \approx -1$ . The approach to the size dependence of the Debye temperatures of nanowires and tubes that has been proposed here is new physics and has so far not been explored in this context. It will be fruitful to also explore this correlation of suppression of the Debye temperatures and suppression of melting temperatures in other nanomaterials that have different physical forms.

#### *3.2.* Enhancement of $\rho_0$

The absolute value of the residual resistivity ( $\rho_0$ ) allows us to investigate the role of surface scattering. This is a topic under considerable active research due its technological importance in determining the resistivity of interconnects for nanoelectronics [25]. There are a number of factors that contribute to  $\rho_0$ , including chemical impurities, physical defects, internal boundaries





**Figure 5.** Dependence of  $\rho(d)_0$  on  $d^{-1}$ . The line shows the fit (equation (5)) considering *L* to be the Debye mean free path for the bulk sample. The nanowire equivalent diameter for the nanotube is 2t.

and the surface scattering. The wires and nanotubes grown in this investigation are chemically pure with chemical impurities less than 0.5 at.% as determined by quantitative EDX analysis. Taking the approximate change in the resistivity due to impurities as  $10^{-8} \Omega m (at.\%)^{-1}$  [26], we find that the contribution to the residual resistivity from the impurities will be  $\leq 5 \times 10^{-9} \Omega m$ , which is much less than the observed value of the residual resistivities for both the nanotubes and nanowires with smaller diameter. Thus the chemical impurity can be ruled out as a major cause of the residual resistivity although it will have some contribution.

From the TEM images as well as local area electron diffraction patterns (not shown), we establish that the nanowires as well as the nanotubes used here do not have a large number of internal boundaries. In that case, the predominant cause of the residual resistivity can be the surface scattering. As can be seen in figure 5, the  $\rho_0$  show a clean dependence on the  $\frac{S}{V}$  ratio. This is a manifestation of the predominant dependence of the residual resistivity on surface scattering.

The evaluation of the resistivity due to partial diffused scattering of electrons from the surface (as is generally the case) can be involved. In general, the surface scattering can be characterized by the specularity factor p, where p is the fraction of electrons getting elastically scattered from the wire boundary. p = 1 for complete specular reflection and 0 for completely diffused scattering. An estimation of the specularity of the surface (p) can be made from the simple relation [27] for wires of diameter  $d \ll L$  (electron mean free path in bulk):

$$\rho(d)_0 = \rho_i + \frac{1-p}{1+p} \left(\frac{L}{d}\right) \left(\rho(\text{bulk})_0\right),\tag{5}$$

where  $\rho(d)_0$  is the residual resistivity of the nanowire of diameter d.  $\rho(\text{bulk})_0$  is the residual resistivity of the bulk metal at 4.2 K, which in this case is  $\approx 1.2 \times 10^{-11} \Omega \text{ m}$ . L is the

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electron mean free path in the bulk and has a value  $\approx 58 \,\mu\text{m}$ . (The product  $\rho$ (bulk)<sub>0</sub> L =  $6.9 \times 10^{-16} \,\Omega \,\mathrm{m^2}$  is close to the theoretical value  $\approx 6.6 \times 10^{-16} \,\Omega \,\mathrm{m^2}$  [28].) The constant term (independent of diameter)  $\rho_i$  is added to account for any small but finite contributions from chemical impurities and other residual scattering mechanisms that can arise from internal surfaces. For simplicity this is taken as the same for all the wires, since they are grown from the same bath using similar conditions for growth. As stated before, we expect  $\rho_i \leq 5 \times 10^{-9} \,\Omega$  m, which is estimated from the chemical impurities. The dependence of  $\rho(d)_0$  on  $d^{-1}$  can be seen in figure 5 where we also show the datum corresponding to the nanotube with equivalent nanowire diameter 2t. From the fit to equation (5) (shown in figure 5) we obtained  $p = 0.43 \pm 0.03$  for the nanowires and  $\rho_i = 3.8 \pm 0.4 \times 10^{-9} \,\Omega$  m. The value of  $\rho_i$  is in good agreement with the upper bound that we estimated from the impurity analysis. Using this value of p and the value of  $\rho_i$  and  $d_{\text{eff}} = 2t$ , we obtain an estimate of  $\rho(d)_0$  for the nanotube  $\approx 1.05 \times 10^{-9} \Omega$  m, which is close to the measured value of  $1.1 \times 10^{-9} \Omega$  m. It thus appears that the simple theory of surface scattering as given in equation (5) can explain the size dependence of  $\rho(d)_0$ . The value of the specularity factor p = 0.43 is, interestingly, very close to that found in Cu interconnects grown by damascene technique trenches in a  $SiO_2$  matrix lined with Ta [29]. We note that the error in estimation of the values of p and  $\eta$  in our analysis lies between 4.5 and 7% and goes to a maximum of  $\approx 10\%$  in the case of  $\rho_i$ . These values are in a reasonably acceptable limit taking into account the limited number of sampling points that we have.

For a partially specular surface (p = 0.43), it is expected that the mean free path at T = 4.2 K will be larger than the lateral dimension. We can evaluate the mean free path  $l_d$  for electrons in nanowires of narrow diameter d at 4.2 K using the relation [30] that is valid for  $d \ll$  length (high aspect ratio):

$$l_d \approx \frac{1+p}{1-p}d.$$
(6)

For the nanowires the ratio of the mean free path to diameter is  $\approx 2.5$ , and for the nanotube the ratio of the mean free path to thickness is  $\approx 5$ . The nanowires as well as the nanotubes used in this work are crystalline so that scattering from internal surfaces is not significant. The chemical purity is high enough to make the residual resistivity due to such impurities low. These reasons, as stated before, allow the electrons to reach the surfaces and get scattered by them.

The size dependences seen in both the nanowires and the nanotube show up in the two transport parameters, namely the residual resistivity  $\rho_0$  and the Debye temperature  $\theta_R$  which together can determine the absolute value of the resistivity at any temperature T. It is seen that both the parameters  $\theta_R$  and the residual resistivity  $\rho(d)_0$  show a distinct dependence on single dimension. For the nanowire the dimension is the diameter d, while for the nanotube (with wall thickness t) the lateral dimension appears to be an 'effective diameter' which is  $\approx 2t$ . The surface area to volume ratio  $(\frac{S}{V})$  for a long wire is  $\frac{4}{d}$ , whereas for a nanotube,  $\frac{S}{V} \approx \frac{2}{t}$ . Since, for a nanotube, the effective diameter  $d_{\text{eff}}$  appears to be 2t, the ratio  $\frac{S}{V} \approx \frac{4}{d_{\text{eff}}}$ . The observed monotonic dependences of both  $\rho_0$  and  $\theta_R$  on  $\frac{S}{V}$  (see figure 3) can thus be rationalized. We find that the nanotube is distinct from a thin film rolled into a tube.

The observation that the transport parameters in the nanotubes with wall thickness t are similar to those of a nanowire with diameter d, where  $d \approx 2t$ , is made in the specific context of the size range used in this experiment performed to understand the modification in the electrical transport from a nanowire to a thin nanotube of the same diameter. We are not in a position to generalize this observation in the absence of robust measurements made on nanotubes with

different wall thicknesses and diameters, which we did not include owing to technical difficulties and analysis anomalies as described in section 1.2.

#### 4. Conclusions

In summary, we have studied the electrical transport in Cu nanotubes and nanowires, which have been synthesized by electrodeposition inside porous anodic alumina templates, in order to probe the modifications in electrical transport as the geometry and size are modified. The nanotubes have been synthesized using a rotating electric field. We find that the temperature-dependent resistivity in the nanotube (wall thickness  $\approx 18$  nm) can be explained by the BG theory with a single parameter, the Debye temperature  $\theta_{\rm R}$ . The electrical resistivity of the nanotube characterized by the two parameters  $\theta_{\rm R}$  and the residual resistivity  $\rho_0$  shows appreciable size effects, which show up as a suppression of  $\theta_{\rm R}$  and an enhancement of  $\rho_0$ . A comparison has been made to the same physical parameters measured in a Cu nanowire grown by the same method. Both the parameters for the nanotubular arrays fit into the trend followed by nanowire arrays showing a clean dependence on  $\frac{S}{V}$ . It was found that the suppression of the Debye temperature has a similar thermodynamic basis that leads to the suppression of  $T_{\rm M}$  in these materials which follow a power-law dependence on the dimension. The residual resistivity ( $\rho_0$ ) of the nanotubes, similar to the nanowires, depends predominantly on the scattering of electrons from boundary surfaces. The electrons have semi-diffused scattering from surfaces with a specularity factor  $p \approx 0.43$  and the mean free path at T = 4.2 K was estimated to be  $\approx 5$  times that of the wall thickness t. We find that the transport parameters ( $\rho_0$  and  $\theta_R$ ) of the nanotube (wall thickness t) with two extra surfaces are similar to that of a nanowire of diameter  $\approx 2t$  in the specific size range studied in this investigation.

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