Temperature dependence of the resistance of metallic nanowires of diameter ⩾15 nm: Applicability of Bloch-Grüneisen theorem

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We have measured the resistances (and resistivities) of Ag and Cu nanowires of diameters ranging from 15 to 200 nm in the temperature range 4.2–300 K with the specific aim of assessing the applicability of the Bloch-Grüneisen formula for electron-phonon resistivity in these nanowires. The wires were grown within polymeric templates by electrodeposition. We find that in all the samples the resistance reaches a residual value at $T=4.2$ K and the temperature dependence of resistance can be fitted to the Bloch-Grüneisen formula in the entire temperature range with a well-defined transport Debye temperature (Θ_R). The values of the Debye temperature obtained from the fits lie within 8% of the bulk value for Ag wires of diameter 15 nm while for Cu nanowires of the same diameter the Debye temperature is significantly less than the bulk value. The electron-phonon coupling constants (measured by $\alpha_{el\text{-}ph}$ or α_R) in the nanowires were found to have the same value as in the bulk. The resistivities of the wires were seen to increase as the wire diameter was decreased. This increase in the resistivity of the wires may be attributed to surface scattering of conduction electrons. The specularity p was estimated to be about 0.5. The observed results allow us to obtain the resistivities exactly from the resistance and give us a method of obtaining the exact numbers of wires within the measured array (grown within the template).

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I. INTRODUCTION

The resistivity (ρ) of a metallic nanowire is a topic of considerable current interest. For nanowires with diameters approaching molecular dimensions the transport is likely to be quantum in nature.[1] However, there is a considerable size range (diameter greater than a few nanometers) where the issues of quantum transport (like quantized conductance) are not important. Yet the study of the resistivity of such nanowires is of interest because this is likely to be the dimension of metallic interconnects in electronic devices in the near future. In this size regime the concept of Boltzmann transport is at its limits of applicability. A proper understanding of the resistivity in this regime is needed because it allows one to get a quantitative estimate of the resistance of the wire from its dimension without actually measuring it. In the regime where the width of the wire is a few tens of nanometers or less, it has been established adequately that ρ is not determined by the material alone but by its size as well.[2–6] For wires of these dimensions, the mean free path is comparable to or even larger than the wire width (particularly for clean wires) and one would expect the size effect to be operative. In this range, ρ typically increases as the width of the wire is decreased. This is a serious issue in interconnects as an increase in the resistance of the wire increases the propagation delay time constant of the system and hence slows down the speed of the device. Recent investigations have focused on understanding the size effect in wires of width below 100 nm so that a predictive relation can be obtained.[2–6] The problem gets complicated due to the added contribution of grain boundary scattering. The size effect (arising mainly from the surface scattering) and the internal grain boundary scattering (along with scattering from impurities or point defects) constitute the temperature-independent part of the resistivity and this shows up as the residual resistivity at $T\leqslant 20$ K in most metallic solids. (If the wire is disordered the resistivity instead of showing a constant residual value at low temperature can show an upturn often associated with effects such as localization.[7]) Understanding these effects for a nanowire will thus give us a control on the residual resistivity of the nanowire. However, understanding the residual resistivity alone is not enough to get a complete understanding of the ρ in nanowires because at room temperatures, for a good metallic nanowire, a substantial part of the resistivity should arise from the temperature-dependent part which in a nonmagnetic metal arises from the electron-phonon interaction.[8] A good estimate and a quantitative way of predicting the resistivity contribution from the electron-phonon interaction is thus needed. In this paper the principal focus is on the specific issue of the contribution of electron-phonon scattering to the resistivity of metallic nanowires and we establish by experiments to what extent such established theory as the Bloch-Grüneisen theory[8] is applicable as the wire diameter goes down to as small as 15 nm.

The temperature dependence of the resistivity of nanowires has been studied both theoretically and experimentally.[9–14] Previous experimental studies on nanowires of elemental metals and alloys have established that in wires with diameter (or width) ⩾15 nm, the temperature dependence of resistance is metallic, reaching a residual resistivity at low temperature (if the wires are not disordered[9]) with $\rho \propto T$ for $T\geqslant 100$ K. For wires with smaller diameter and width (typically ⩽10 nm) the resistivity can have a negative temperature coefficient. This has been seen in wires of Au,[9] AuPd alloy,[10] Zn,[11] Cu,[12] and Sn (Ref. 13) (before it becomes superconducting at $T_c\approx 3.7$ K). However, there has not been any experimental study that specifically addresses this issue in well-characterized nanowires over an extensive

range of temperatures and wire diameters and analyzes the data quantitatively. With these objectives we have studied the resistance of metallic nanowires (silver and copper) as a function of the wire diameter (15–200 nm) in the temperature range 4.2–300 K. The systematic investigation allows us to separate out the temperature-independent part $R(0)$ from the temperature-dependent part $\delta R(T)$ [we write $R(T) = R(0) + \delta R(T)$]. We analyzed the data in the framework of the Bloch-Grüneisen theory. This allowed us to estimate the effective Debye temperature from the temperature dependence of the resistance. In addition, a clear evaluation of the residual resistivity allowed us to establish the dependence of the resistivity on the diameter of the wire. To our knowledge this is the first experimental study of the resistance of metallic nanowires over such an extensive range of temperature and size where the applicability of the Bloch-Grüneisen formula has been tested quantitatively.

II. ELECTRON-PHONON INTERACTION AND THE BLOCH-GRÜNEISEN FORMULA

The electron-phonon interaction and the Bloch-Grüneisen formula have been adequately discussed in standard textbooks.[8] However, for the purpose of quick reference as well as for completeness we give the important relations briefly in this section. In a nonmagnetic metallic crystalline solid the temperature dependence of the electrical resistivity arises mainly from the electron-phonon interaction[8] and can be explained in the framework of the Boltzmann transport theory using the Bloch-Grüneisen formula

$$\rho(T) = \rho(0) + \rho_{el\text{-}ph}(T),$$

$$\rho_{el\text{-}ph}(T) = \alpha_{el\text{-}ph}\left(\frac{T}{\Theta_R}\right)^n \int_0^{\Theta_R/T} \frac{x^n}{(e^x - 1)(1 - e^{-x})} dx, \quad (1)$$

where $\rho(0)$ is the residual resistivity due to defect scattering and is essentially temperature independent. The temperature-dependent part of the resistivity $\rho_{el\text{-}ph}(T)$ arises from electron-phonon interaction. The constant n generally takes the values 2, 3, and 5 depending on the nature of interaction and for a nonmagnetic elemental metal like Cu, Ag, or Au with reasonable mean free path $n=5$. $\alpha_{el\text{-}ph}$ is a constant that is proportional to $\lambda_{tr}\omega_D/\omega_p^2$ where λ_{tr} is the electron-phonon coupling constant, ω_D is the Debye frequency, and ω_p is the plasma frequency.[17] Θ_R is the Debye temperature as obtained from resistivity measurements and matches very closely with the values of Debye temperature obtained from specific heat measurements. In the cases of bulk silver and copper with $n=5$, $\Theta_R \sim 200$ and ~ 320 K, respectively.[18]

In the Bloch-Grüneisen formula, the phonons that contribute to the electron-phonon interaction are the acoustic phonons and one can get a simple one-parameter scaling of the temperature dependence of the resistivity (ρ) where the only relevant parameter is the Debye temperature Θ_R. For the specific case of $n=5$,

$$\frac{\rho_{el\text{-}ph}(T)}{\rho_{\Theta_R}} = \alpha_R\left(\frac{T}{\Theta_R}\right)^5 \int_0^{\Theta_R/T} \frac{x^5}{(e^x - 1)(1 - e^{-x})} dx, \quad (2)$$

where ρ_{Θ_R} is the resistivity at the temperature $T=\Theta_R$. Thus the temperature dependence of the electrical resistance of a metal provides a useful method to estimate its effective Debye temperature. For acoustic phonons the value of α_R is 4.225.[19] Even when there is an uncertainty in the physical dimensions (which introduces uncertainty in the determination of ρ from R) the above relation can be utilized because one can write

$$\frac{R(T) - R_{4.2K}}{R_{\Theta R}} = \frac{\delta R(T)}{R_{\Theta R}} = \frac{\rho_{el\text{-}ph}(T)}{\rho_{\Theta_R}}. \quad (3)$$

The measurements carried out in this paper also allow us to investigate how the electron-phonon interaction gets modified in nanowires due to size reduction and manifests itself in the temperature dependence of the resistance. The lower limit of the integral in Eq. (1) being zero is the result of a tacit assumption that we are dealing with bulk material and hence the system size does not impose a boundary condition on the maximum allowed phonon wavelength. This assumption may no longer be valid for wires of very small diameters. Thus the lower limit in the integral will now have a finite nonzero value. We wanted to investigate at what diameters of the wire the size really begins to affect the phonon spectrum (and hence the electrical resistivity) of the wire.

III. EXPERIMENT

The nanowires of Ag and Cu with average diameters in the range of 15–200 nm and length 6 μm were electrochemically deposited from $AgNO_3$ and $CuSO_4$, respectively using polycarbonate membranes as templates.[20,21] The schematic arrangement of the growth setup is given in Fig. 1(a). During the growth, one of the electrodes was attached to one side of the membrane while the other electrode was a microtip of radius of curvature $\simeq 100$ μm fitted to a micropositioner. This electrode can be placed at a specific area on the membrane and the growth can thus be localized. The wires grow by filling the pores from end to end and as soon as one or more wires completes the path from one electrode to the other the growth stops. The wires after growth can be removed from the membrane by dissolving the polymer in dichloromethane. This is needed for the microscopic characterization of the wires as described below. The wires after growth were annealed at 375 K for 24 h in vacuum under a dc current of 1 mA. The postdeposition annealing is needed to stabilize the resistance of the wires. For all successive measurements the current through the sample was kept lower than 100 μA.

The structural and crystallographic nature of the wires form an important part in the analysis of the data. The wires used in this investigation are single crystalline in nature. This has been established by such techniques as x-ray diffraction (XRD), field-emission gun scanning electron microscopy (SEM), and high-resolution transmission electron micros-

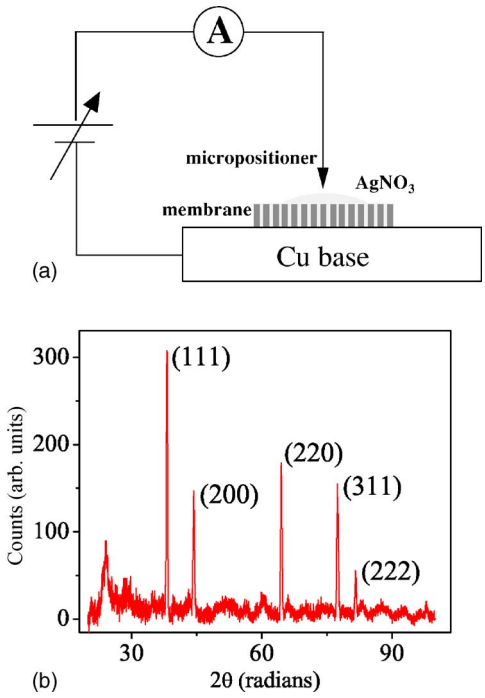

FIG. 1. (Color online) (a) A schematic of the setup used for making the nanowires. (b) XRD of 100 nm Ag wires. The peaks have been indexed to fcc Ag.

copy (HRTEM). The TEM was done in a Tecnai G^2 30 machine operated at 300 KV with a nominal magnification of 1×10^6.

IV. BASIC RESULTS

The XRD data are shown in Fig. 1(b). The XRD data were indexed as a fcc lattice. The data as shown in Fig. 1(b) do not show any impurity peak. Similar data were also obtained for Cu and are not shown to avoid duplication. Figure 2(a) shows the SEM image of a collection of Ag nanowires of diameter 100 nm taken after partially removing the membrane while Fig. 2(b) shows the SEM image of a single Ag wire of diameter 200 nm. The average diameters of the wires match with the nominal diameters of the pores of the templates in which they were grown.

In Fig. 3 we show typical TEM data taken on a 15 nm Ag wire. The diffraction data are also shown and can be indexed into (220) planes. The TEM data show that the wires are single crystalline with the presence of twins in them. They also show that there are no other substantial structural defects like grain boundaries or dislocations present in the sample. The growth direction as seen from the TEM data is [100].

The resistance of the wires was measured in a bath-type helium cryostat in the temperature range 4.2–300 K using ac phase-sensitive detection with a lock-in amplifier. The measurements were carried out by retaining the wires within the polymeric membrane. On each of the two sides of the membrane two electrical leads were attached using silver epoxy. Though the measurements were made with the wires retained within the membrane, the system is an array of parallel nanowires where the individual wires are well separated by the insulating membrane. A typical sample may contain 2–50 wires. A very important issue in this measurement is the contribution of the contacts to the measurement. We have paid attention to this aspect and measured the resistance by making the contact in different ways. In addition to silver epoxy contacts, we used evaporated silver films to make con-

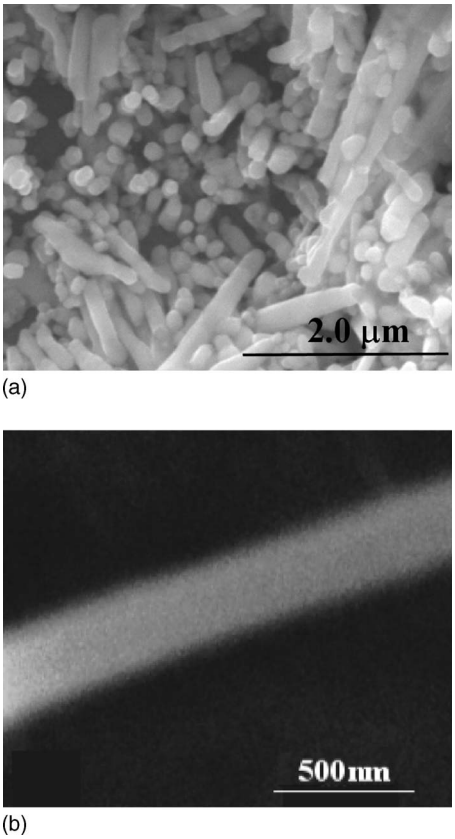

FIG. 2. SEM image of (a) 100 nm Ag wires taken after dissolving off the template in dichloromethane and (b) a single 200 nm Ag wire.

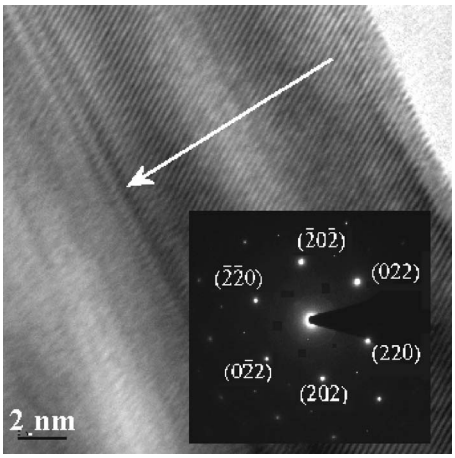

FIG. 3. HRTEM image of a 15 nm Ag wire. The arrow points out the twin boundary present in the sample. The inset shows the selective area diffraction pattern. The growth direction of the wires as seen from TEM is [100].

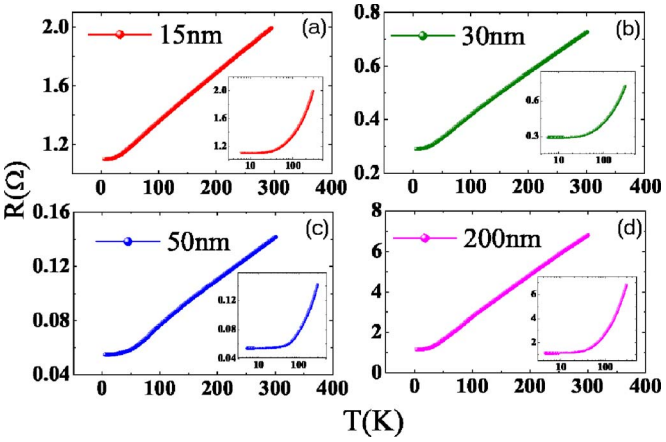

FIG. 4. (Color online) Resistance of arrays of Ag wires of diameter (a) 15, (b) 30, (c) 50, and (d) 200 nm. The inset shows the resistance with the temperature axis in a logarithmic scale in order to show more clearly the low-temperature behavior of the resistance.

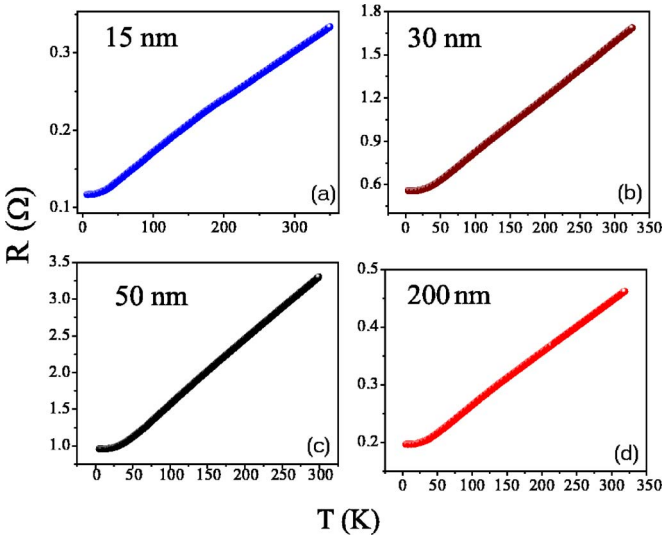

FIG. 5. (Color online) Resistance of arrays of Cu wires of diameter (a) 15, (b) 30, (c) 50, and (d) 200 nm.

tact, which we find gave similar results. We also made contacts using wires tinned with Pb-Sn solder where we find that the change in the resistance of the sample as we go below the superconducting transition temperature (~7 K) of the solder is negligibly small (≤2–3%). All these tests rule out any predominant contribution from the contacts. In the context of this paper we note that the small contact resistance, even if it is present, will make a small additive contribution to the temperature-independent part of the resistance only. The particular issues of contact resistance as well as contact noise have been discussed in some details in previous publications by the group.[20,22]

Figure 4 shows the collection of resistance data on arrays of Ag wires with diameters ranging from 15 to 200 nm. The insets show the same resistance plotted with a logarithmic scale for the temperature axis to show more clearly the low-temperature behavior of the resistance. The data for the Cu nanowires are shown in Fig. 5. The resistance data are typical of a good metal. Both the Ag and Cu nanowire arrays have a fairly linear temperature dependence of resistance down to about 100 K and reach a residual resistance below 40–50 K with a residual resistivity ratio $\rho_{300\ \mathrm{K}}/\rho_{4.2\ \mathrm{K}} \sim 3$. The resistance does not show any upturn at low temperature, thus ruling out any significant disorder in the system that can give rise to effects such as localization.[23] The value of the temperature coefficient of the resistivity $\beta = 1/R(dR/dT)$ for the wires lies within $\sim 4 \times 10^{-3}$ and $\sim 2.5 \times 10^{-3}$ K^{-1}, respectively at 300 K. This matches well with the values for high-purity Ag and Cu (approximately 3.8×10^{-3} and 3.9×10^{-3} K^{-1} respectively[24]). This also emphasizes the essentially defect-free nature of the wires (as also established by the TEM images) as the presence of defects can reduce the value β significantly. When the mean free path l_{mfp} is so small that one reaches the Ioffe-Regel criterion $k_F l_{mfp} \approx 1$,[25] β becomes very small ($\ll 10^{-4}$).[26]

V. DISCUSSION

A. Applicability of Bloch-Grüneisen theorem

We fitted the observed resistance data to the Bloch-Grüneisen function [Eq. (1)] and made the important observation that the resistance data for wires of all diameters (in the range 15–200 nm) could be fitted to the above mentioned function over the entire temperature range (4.2–300 K) of investigation for integral values of n using the Debye temperature (Θ_R) and $\alpha_{el\text{-}ph}$ as the only two adjustable fit parameters. The fit parameters were optimized to give a relative fit error [defined as $(R_{measured} - R_{fit})/R_{measured} \times 100\%$] of less than ±0.5% or better over the whole temperature range. A typical fit is shown in Fig. 6 for Ag wires of diameter 15 nm. In the inset we show the fit error, which is less than ±0.2%. It was seen that $n=5$ gave the best fit for

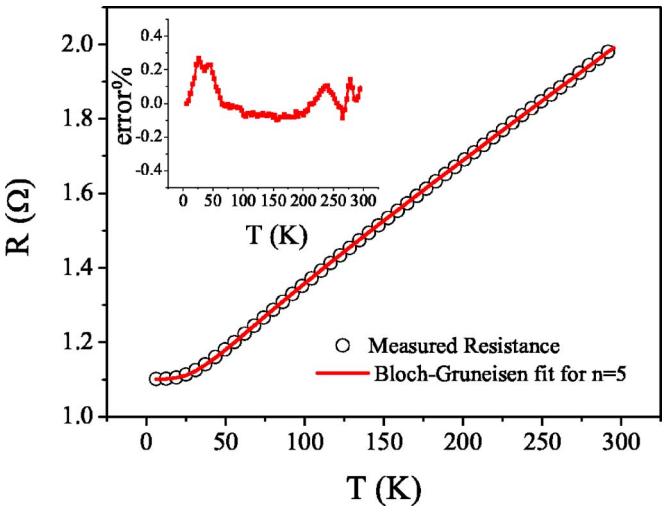

FIG. 6. (Color online) Fit to Bloch-Grüneisen formula [Eq. (1)] to the measured resistivity data for a 15 nm Ag wire. The inset shows the fit error (for definition see text) for $n=5$.

TABLE I. The values of Θ_R and α_R [see Eq. (3)] obtained from resistance data for Ag and Cu wires of different diameters. Θ_R for bulk Ag and Cu are 200 and 320 K, respectively.

Sample	Diameter (nm)	Θ_R (K)	% reduction	α_R
Ag	15	184	8	4.226
Ag	30	170	15	4.227
Ag	100	174	13	4.225
Ag	200	187	6.5	4.226
Cu	15	180	43	4.271
Cu	30	235	26	4.224
Cu	50	231	28	4.225
Cu	200	200	37	4.235

the wires. The values of Θ_R, as obtained from the fits (with $n=5$), are tabulated in Table I. Note that for the fit to the Bloch-Grüneisen function we have used the resistance data directly because, as explained later, there is a substantial uncertainty in the determination of the number of wires in an array. The use of the resistance data for the fit does not change Θ_R. (Note that we use $\alpha'_{el\text{-}ph}$ as a fit parameter in this case. This is related to $\alpha_{el\text{-}ph}$ by the relation $\alpha'_{el\text{-}ph}=\frac{l}{NA}\alpha_{el\text{-}ph}$, where l and A are the length and area of cross section, respectively, and are known from experiment.) Using the method discussed later in this paper (and in the Appendix) we can calculate the value of N more accurately and hence the value of $\alpha_{el\text{-}ph}$ from the fit parameter $\alpha'_{el\text{-}ph}$. The value of $\alpha_{el\text{-}ph}$ thus estimated is $\approx 4.6\times 10^{-8}\ \Omega$ m for the Ag and $\approx 4\times 10^{-8}\ \Omega$ m for Cu wires. This implies that the coupling constant is essentially unchanged on size reduction.

The values of Θ_R for all the samples measured were found to be close to but significantly smaller than the bulk value as measured in a reference sample. (For a reference sample we used a thermally evaporated high-quality Ag thin film of thickness 150 nm. The film was evaporated in an UHV chamber with a base pressure 10^{-8} mbar from an effusion cell. It has a room-temperature resistivity of $1.63\times 10^{-8}\ \Omega$ m and a residual resistivity ratio of about 10. Θ_R for this sample matches that of the bulk.) Analysis of the data as summarized in Table I indicates that Θ_R has a reduction of $\approx 8-15$ % for Ag and $\approx 25-40$ % for Cu. The analysis thus gives us a direct way to estimate the Debye temperature in the nanowires. The observation of a softening of Θ_R is significant as is also the fact that it is material dependent, being strong in Cu and not so significant in Ag.

The applicability of the Bloch-Grüneisen theorem can be better appreciated when we analyze the data using the scaling equation (2). We checked the scaling equation by plotting (see Fig. 7) $(R_T-R_{4.2\ \mathrm{K}})/R_D$ as a function of T/Θ_R. Here R_D is the value of the measured resistance at $T=\theta_R$. It can be seen that all the resistance data collapse into one curve signifying that the one-parameter scaling law holds. From Table I it can be seen that the value of the constant α_R is roughly the same for all the nanowires and is the value (4.225) predicted by the simple acoustic phonon-electron coupling theory.[19] The observation that the Bloch-Grünesien theorem is quantitatively applicable in the nanowires of at least two

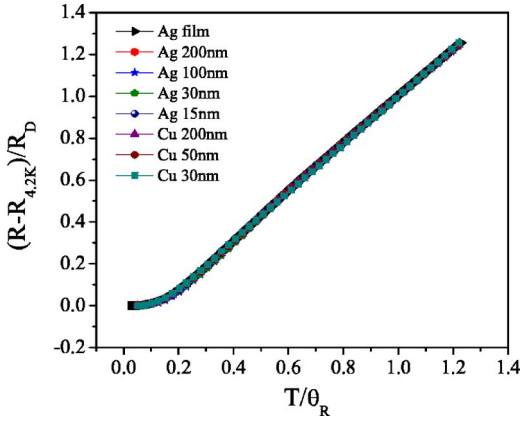

FIG. 7. (Color online) Plot of $(R_T-R_{4.2\ \mathrm{K}})/R_D$ as a function of T/Θ_R [see Eq. (3)]. Here R_D is the value of the measured resistance at $T=\theta_R$.

materials studied down to 15 nm diameter is extremely important. It establishes that the temperature-dependent part of the resistivity (as arising from the electron–acoustic-phonon interaction) is unchanged on size reduction down to 15 nm. The implication of the observation is that one now has a tool with which one can obtain the electron-phonon contribution to the resistivity with good quantitative accuracy. We will show below that this basic observation can be utilized to calculate or estimate the resistivity of metallic nanowires even if the exact number of wires in an array is not known.

The number of wires in such a sample array vary from about 2 to 50 as was estimated using the bulk value of the resistivity. This is a very rough estimate as the resistivity in this range depends on the diameter or width of the wire. Hence we do not use this in our calculations. It is to be noted that the exact value of the resistivity is not needed to check the applicability of the Bloch-Grüneisen theorem as the analysis for the determination of Θ_R was carried out using the resistance instead of the resistivity. Neither is the exact value of ρ needed to check Eq. (2). As a result the exact number of wires in the array was not needed for any of the evaluation so far. Below we describe a method of estimating the resistivity of the samples which also gave us a better estimate of the number of wires in each sample.

B. Dependence of phonon contribution to resistance on the size of the wire

The applicability of the Bloch-Grüneisen theorem would imply that the basic electron–acoustic-phonon interaction as well as the simple Debye phonon spectrum (phonon density of states proportional to ω^2 where ω is the phonon frequency) remains unchanged on size reduction. This would raise the question—to what size can one reduce the wire diameter before the deviation from the simple Bloch-Grüneisen theorem begins to show up? To estimate the effect of size reduction, if any, on the phonon contribution to the resistance of a wire, we study the variation of the integrand of Eq. (1) as a function of x, where $x=\Theta/T=hc/\lambda k_B T$. (Here c is the sound velocity averaged over all the acoustic modes and λ is the phonon wavelength.) At a given temperature T

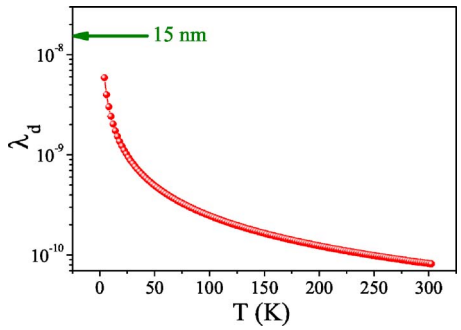

FIG. 8. (Color online) Plot of the dominant phonon wavelength λ_d as a function of temperature for $n=5$. The arrow points to 15 nm, the diameter of the narrowest wire measured by us.

the dominant contribution to the integral in Eq. (1) comes from the value of x for which the integrand has a maximum. We define this value of x as x_d, the dominant value of x at a given temperature. x_d depends on the value of n (for $n=5$, $x_d=5$). Thus at a temperature T the phonons having a wavelength $\approx\lambda_d=hc/x_dk_BT=hc/5k_BT$ are the dominant phonons that contribute most to the temperature-dependent part of the resistance of a metal. The values of λ_d (for $n=5$) as a function of temperature T are plotted in Fig. 8. We can see from the plot that even at 4.2 K, the value of λ_d is much smaller than 10 nm. Thus for a wire of diameter 15 nm, the phonons that make the maximum contribution to the temperature-dependent part of the resistance (down to the lowest temperature measured) are not affected by the wire dimensions. At higher temperatures λ_d becomes smaller (being proportional to $1/T$). So in all the samples studied by us down to the lowest diameter phonon confinement is not an issue and hence contribution to the temperature-dependent part of the resistivity is expected to follow the same Bloch-Grüneisen function valid for a three-dimensional bulk metal albeit with a reduced Θ_R. To test the effect of phonon confinement and to evaluate the effect of finite size of the wire on the electron-phonon part of the resistivity, we have fitted the resistance data to the Bloch-Grüneisen function with the lower limit of the integral changed to $x_{min}=\theta_{min}/T$ where $\theta_{min}=hc/dk_B$ (d being the diameter of the wire). We do not find any significant change in the quality of the fit or in the value of the fit parameters. This is because even for wires of diameter 15 nm, $x_{min}\sim 0.5$ at 30 K and the values of x in this range hardly make any contribution to the Bloch-Grüneisen integral in Eq. (1). Presumably at even lower temperatures $T<0.5$ K one would expect that for wires of this size the finite-size effect should show up in the Bloch-Grüneisen estimate of the temperature-dependent part of the resistivity ρ. However, in this temperature range in a real wire the residual resistivity will mask any effect of the temperature-dependent part.

C. Estimation of resistivity from the resistance data and its dependence on wire diameter

We noted before that the evaluation of the resistivity from the directly observed resistance data is prone to error due to the uncertainty in the actual number of wires that make up the array. The observation that the phonon contribution to the electrical resistance of the nanowires is unchanged from that of the bulk allows us to estimate the value of the resistivity of the wires from the measured resistance without having to know the number of wires present in the sample. We elaborate this in the Appendix. Let the resistance of one wire be $R_1=\rho l/A$, where ρ is the resistivity of the material, l is the length, and A is the cross-sectional area of the wire. Therefore the resistance of N identical wires in parallel is

$$R_N=\rho l/AN. \tag{4}$$

The facts that the temperature dependence of the resistivity arises from the electron-phonon interaction and that the same relation (with the same $\alpha_{el\text{-}ph}$ and α_R) governs the electron-phonon interaction in the nanowire as in the bulk crystalline material can be utilized to get (see the Appendix)

$$\rho=\rho_0\frac{\beta_0}{\beta}\frac{\Theta_{R0}}{\Theta_R}, \tag{5}$$

where β $[=(1/R_N)dR_N/dT]$ is the measured temperature coefficient of resistivity of the wire array, β_0 is the temperature coefficient of resistivity of the bulk material, ρ_0 is the bulk resistivity at that temperature, and Θ_{R0} is the Debye temperature of the bulk material. (This equation is valid strictly in the high-temperature limit where the temperature-dependent part of the electrical resistivity of a metal is due only to phonon scattering. In the nanowires used by us the temperature-dependent part solely arises from the electron-phonon interaction, as established by analysis of the data in the previous section.)

We calculate β from the measured resistance near room temperature. Using the resistivity at 295 K thus estimated and from the measured resistance of the wire arrays we can find the number of wires in a given array (N) using Eq. (4). From this we can evaluate the resistivity as a function of temperature for all the wires. This is shown in Fig. 9 for Ag wires as well as the Cu wires. One can see a systematic variation of ρ as a function of temperature for wires of different diameters. The value of the resistivity at 295 K, the residual resistivity, as well as the mean free path (l_{mfp}) of the electrons calculated from the resistivity at $T=295$ K are shown in Table II. For this calculation we assumed bulk electron density. In Fig. 10(a) we also plot the residual resistivity $\rho_{4.2\text{ K}}$ as well as $\rho_{295\text{ K}}$ as a function of d for the Ag wires. [The bulk value of the resistivity of high-purity Ag (1.6

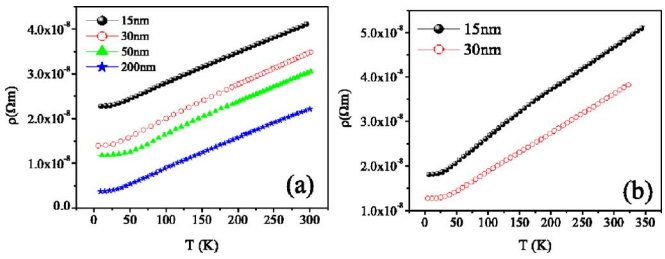

FIG. 9. (Color online) Plot of the resistivity of Ag and Cu nanowires as a function of temperature. The resistivity was obtained using the method described in the text.

TABLE II. The values of ρ at 295 K, the residual resistivity at 4.2 K, and l_{mfp} at 295 K for wires of different diameters.

Sample	Diameter (nm)	$\rho_{295\ K}$ ($\mu\Omega$ cm)	$\rho_{4.2\ K}$ ($\mu\Omega$ cm)	l_{mfp} (nm)
Ag	15	4.11	2.27	20
Ag	30	3.49	1.39	24
Ag	50	2.92	1.17	29
Ag	100	2.78	1.15	30
Ag	200	2.33	0.37	36
Cu	15	5.67	2.2	12
Cu	30	3.58	1.27	18
Cu	50	3.09	1.02	21

$\times 10^{-8}$ Ω m) at 295 K is shown as an arrow.] We have plotted the ratio l_{mfp}/d at 295 K as a function of d in Fig. 10(b). It clearly shows that in wires of small diameters the l_{mfp} can be substantially larger than d and that the ratio l_{mfp}/d increases as d is reduced. For wires of diameter 15 nm l_{mfp}/d approaches a value 1.5. We also note that the value of $k_F l$ is significantly larger than 1, thus justifying the applicability of the Bloch-Grüneisen theorem in these samples.

From Table II as well as from Figs. 9 and 10 we can see that there is a significant increase in the residual resistivity as the diameter of the wires is decreased. The increase is systematic. All wires have the same chemical purity and hence the enhancement of $\rho_{4.2\ K}$ on reduction of d is not due to impurity contribution. For wires in the diameter range that we are studying, the resistivity is expected to increase with a decrease in the wire diameter for two probable reasons.

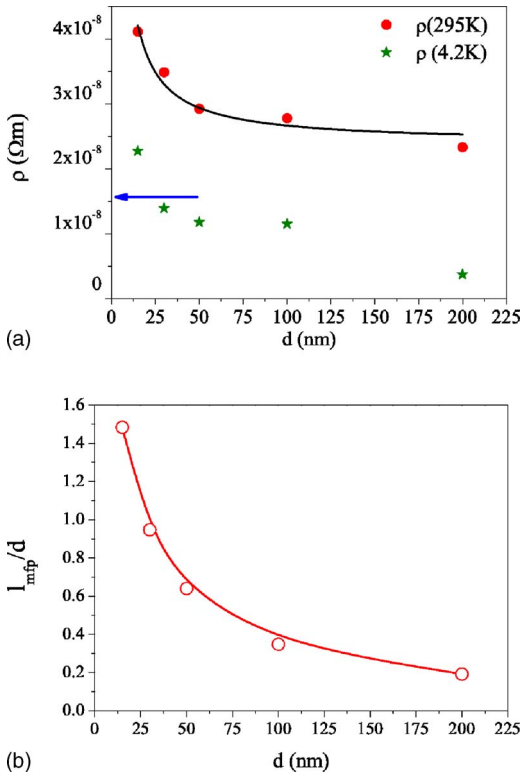

FIG. 10. (Color online) (a) Plot of the resistivity of Ag nanowires at 295 K and the residual resistivity as a function of the wire diameter. The line is the fit to the data using Eq. (6). The arrow is the bulk value of the resistivity of Ag, 1.629×10^{-8} Ω m. (b) Plot of l_{mfp}/d as a function of d for Ag nanowires. The solid line is a guide to the eye.

(1) As the mean free path of the electrons is now of the order of (and in some cases larger than) the diameter of the wire, the bulk assumption is no longer valid and the electron starts seeing the external surface of the sample. The scattering of the electrons from the boundaries of the sample increases the resistivity. This effect is generally quantified by the specularity parameter p that represents the fraction of conduction electrons reflecting specularly from the surface.[15]

(2) As the mean grain size in narrow polycrystalline wires and thin films is generally of the same order as the diameter or thickness, a reduction in the sample size increases the number of grain boundaries. This excess grain boundary scattering leads to an increase in the resistivity of the material over the bulk value.[16]

The TEM images show that there is no significant presence of grain boundaries in the wires studied by us. The twin boundaries seen are generally weak scatterers and do not contribute significantly to the resistivity. We analyze the resistivity data in the light of the surface scattering model of Dingle[27] and Chambers.[28] According to these authors, for cylindrical wires of an isotropic metal, the dependence of the resistivity on the wire diameter varies as

$$\rho_d = \rho_0 + \rho_0(1-p)l_0/d, \tag{6}$$

where ρ_d is the resistivity of the wire of diameter d, ρ_0 is the "bulk" or the so called intrinsic resistivity for the material of the wire, p is the specularity which denotes the fraction of conduction electrons undergoing specular reflection at the wire surface, and l_0 is the bulk mean free path. The quantity $\rho_0 l_0$ is the property of the wire and is temperature independent. To check the validity of the model we have evaluated the value of $\rho_0 l_0$ at several different temperatures and got similar values to within ±3%. For Ag wires $\rho_0 l_0 \approx 5.5 \times 10^{-16}$ Ω m^2. (Note: In this analysis we use only the data of Ag wires as they are of higher chemical purity and contain less density of defects.) In Fig. 10(a) we show calculated value of ρ_d for $p \approx 0.5$. The calculated values closely match the observed data. The value of specularity factor $p \approx 0.5$ obtained from our data is very close to the values (0.3–0.5) reported previously for metallic films of similar dimensions.[2,4]

To summarize, we have measured the resistances (and resistivities) of Ag and Cu nanowires of diameters ranging from 15 to 200 nm in the temperature range 4.2–300 K. We find that the temperature dependence of resistance can be fitted to a Bloch-Grüneisen formula in the entire temperature range. This ensures that the Debye temperature is a viable parameter and this allows us to obtain a value for the Debye temperatures. The values of Debye temperature obtained from the fits lie within 8% of the bulk value for Ag wires of diameter 15 nm. However, there is significant softening of the Debye temperature for Cu nanowires with the same diameter. The electron-phonon coupling constants (measured by $\alpha_{el\text{-}ph}$ or α_R) in the nanowires were found to have the

same value as in the bulk. The resistivities of the wires were seen to increase as the wire diameter was decreased. This increase in the resistivity of the wires may be attributed to surface scattering of conduction electrons. The specularity p was estimated to be about 0.5.

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APPENDIX

The resistivity ρ can be written as $\rho(T)=\rho(0)+\rho_{el\text{-}ph}(T)$ where $\rho_{el\text{-}ph}(T)$ is the temperature dependent part of the resistivity due to the phonons and $\rho(0)$ is the residual resistivity due to defect and surface scattering. The fact that the grain boundary scattering and surface scattering contributions to the resistivity are independent of temperature (at least at high temperatures) has recently been shown experimentally.[3] So we can have

$$\frac{d\rho}{dT}=\frac{d\rho_{el\text{-}ph}}{dT}. \tag{A1}$$

At high temperatures, $d\rho/dT \propto 1/\Theta_R$ and since the coupling constant $\alpha_{el\text{-}ph}$ is nearly the same for all the nanowires with the same chemical elements (established by this experiment) we can write

$$\frac{d\rho_{el\text{-}ph}}{dT}=\frac{d\rho_{(el\text{-}ph)0}}{dT}\frac{\Theta_{R0}}{\Theta_R}=\frac{d\rho_0}{dT}\left(\frac{\Theta_{R0}}{\Theta_R}\right), \tag{A2}$$

where ρ_0 refers to the bulk resistivity of the material and Θ_{R0} is the bulk Debye temperature. From Eq. (4) we get

$$\frac{dR_N}{dT}=\frac{l}{NA}\frac{d\rho}{dT}=\frac{l}{NA}\frac{d\rho_0}{dT}\frac{\Theta_{R0}}{\Theta_R}=\frac{l\rho_0}{NA}\frac{\Theta_{R0}}{\Theta_R}\beta_0=\frac{R_N\rho_0}{\rho}\frac{\Theta_{R0}}{\Theta_R}\beta_0, \tag{A3}$$

where β_0 is the temperature coefficient of resistivity of the bulk material. Equation (A3) immediately yields

$$\rho=\rho_0\frac{\beta_0}{\beta}\frac{\Theta_{R0}}{\Theta_R}, \tag{A4}$$

where $\beta\ [=1/R_N(dR_N/dT)]$ is the measured temperature coefficient of resistivity of the wire array.

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