Determination of the hopping contribution to the thermopower in bismuth infiltrated colloidal crystals

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(Received 26 July 2007; accepted 17 October 2007; published online 11 December 2007)

Conductivity and thermopower measurements of artificial three dimensional bismuth crystals are presented. Due to the size dependent band gap of bismuth, electron transport in the bismuth crystals is a combination of both metallic and hopping conduction. The conductivity and thermopower due to the hopping pathways alone can be extracted through a comparison of the properties of the artificial bismuth crystal before and after it is compressed into bulk bismuth. In this way, evidence for the influence of electron-electron interactions on the hopping conductivity is obtained. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2822463]

INTRODUCTION

In a variety of disordered systems[1–9] electrical transport occurs by hopping between localized states. As first described by Mott,[10] conductivity via variable range hopping in a three dimensional sample is predicted to decrease with decreasing temperature, according to

$$\sigma(T) = \sigma_0 \exp[-(T_0/T)^{1/4}].$$

Later, Efros and Shlovoskii[11] and Efros[12] showed that if electron-electron interactions are included, a Coulomb gap forms, leading to a somewhat different temperature dependence of the conductivity for thermal energy kT below the Coulomb gap energy,

$$\sigma(T) = \sigma_0 \exp[-(T_0'/T)^{1/2}],$$

independent of sample dimension. Experimental evidence for a transition from a $\exp[T^{-1/4}]$ to a $\exp[T^{-1/2}]$ dependence in the conductance with decreasing temperature has been reported by a number of groups;[13–17] however, it is inherently difficult to discern the small difference between the two dependencies. An alternative method to distinguish between interacting and noninteracting hopping processes was put forward by Burns and Chaikin,[18] and relies on the thermoelectric power. They showed that the thermopower for a noninteracting three dimensional Mott system goes to zero with a $\sqrt{T}$ dependence, while for a hopping system with electron-electron interactions, the thermopower goes to a constant nonzero value at zero temperature. While in principle this provides an easier method to distinguish between interacting and noninteracting hopping processes, the experimental evidence for this effect is still very limited. One problem is that the conductivity of disordered samples at low temperature is extremely low, making it difficult to measure the thermopower.

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In this paper, we describe electronic and thermoelectronic measurements of an artificial three dimensional crystal, in which evidence for Efros-type variable range hopping conductivity including electron-electron interactions is observed. The sample is formed by heat injecting bismuth into a silica colloidal crystal, and then etching away the silica template. Hopping conductivity occurs across constricted bismuth interstitial regions which are insulating at room temperature. Because bismuth is malleable and a low melting point metal, it is possible to transform the artificial crystalline structure into bulk bismuth simply by compressing the sample. This allows for direct comparison between hopping conductivity and metallic transport within the same sample. In this way it is possible to extract the hopping contribution to the thermopower from a sample in which both metallic and hopping conductivity pathways exist.

SAMPLE FABRICATION

Our samples are formed by melt injection of bismuth into silica colloidal crystals. The colloidal crystals (obtained from Dr. A. A. Zakhidov, University of Texas at Dallas) are grown using slow sedimentation of monodispersed aqueous silica colloids in a glass cylinder, followed by sintering at 700–750 °C for several hours.[19] The resulting crystal consists of closely packed, interconnected silicon dioxide spheres arranged in a fcc lattice (Fig. 1) with interconnected octahedral and tetrahedral voids between the spheres. The silica colloids used in this investigation have average sphere diameters of 300 nm and octahedral [A in Fig. 1(c)] and tetrahedral voids [B in Fig. 1(c)] of approximately 120 and 60 nm in diameter, respectively. The voids are interconnected by narrow regions [C in Fig. 1(c)] that are 10–20 nm in diameter.

The voids are filled with bismuth using the melt-injection method. A silica colloidal crystal approximately $5 \times 5 \times 4$ mm^3 in size is combined with 99.999% pure 100 mesh bismuth powder in a stainless steel capsule. The infiltration is done by applying a load of 13 000–15 000 lbs

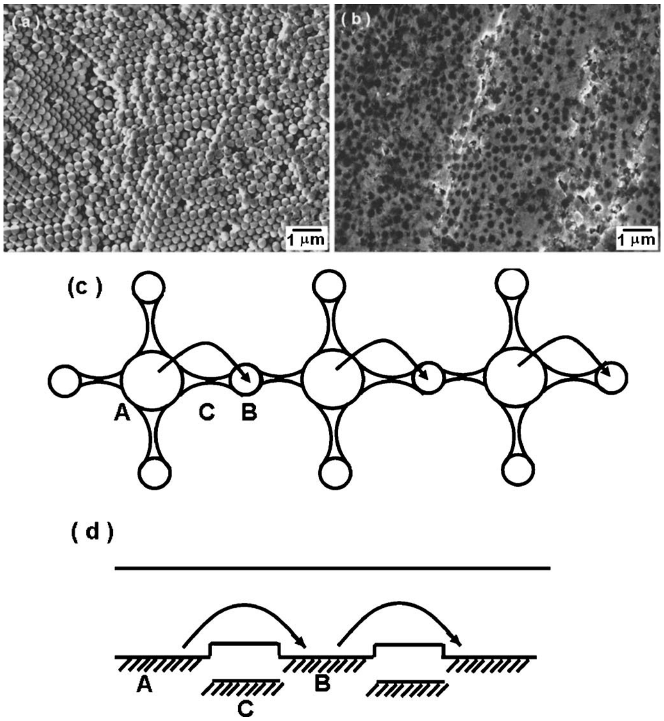

FIG. 1. Silica colloidal crystal (a) before and (b) after infiltration with bismuth. In (b), the dark regions are the silica spheres and the bright regions are the bismuth infiltrated voids. (c) A sketch showing the bismuth crystal formed by filling the voids between the silica colloids. (A) are the octahedral voids, (B) are the tetrahedral voids, and (C) are the interconnects between the voids. (d) Schematic representation of the band diagram across the interconnects between the voids and the hopping conduction pathway (denoted by the arrows).

(8–10 kbars) on the capsule at a temperature of approximately 350 °C for 1–2 h. The bismuth infiltrated colloidal sample is then removed from the capsule by cutting off the stainless steel cap using a diamond saw. Next, the bismuth/silica mixture is mechanically polished to remove the excess uninfiltrated bismuth. Finally, a bismuth inverse replica of the colloidal crystal (approximately $2\times2\times1$ mm^3 in size) is obtained by etching out the silica spheres using a 2% HF acid solution. Figure 1 shows the silica colloidal crystals (a) before and (b) after filling with the bismuth. The long range order of the samples can be clearly seen.

It is known that the electrical properties of nanometer scale bismuth samples are strongly dependent on sample size.[20] Bulk bismuth is a semimetal with overlapping valence and conduction bands and shows metallic conductivity. However, the energy separation between valence and conduction bands increases with decreasing sample size, until eventually a band gap opens up for bismuth nanowires with diameters less than 50 nm.[21] In our samples, the size dependent band gap makes it so there will be a different band gap in different regions of the crystal, even though the crystal is made from only one material. The bismuth regions filling the 120 and 60 nm diameter voids are large enough that the conduction and valence bands will still overlap. The bismuth in the interconnecting regions is much more confined, however, and should show a relatively large separation between valence and conduction bands. Using the results of Lin *et al.*[22] we approximate that the band gap in the 10–20 nm diameter

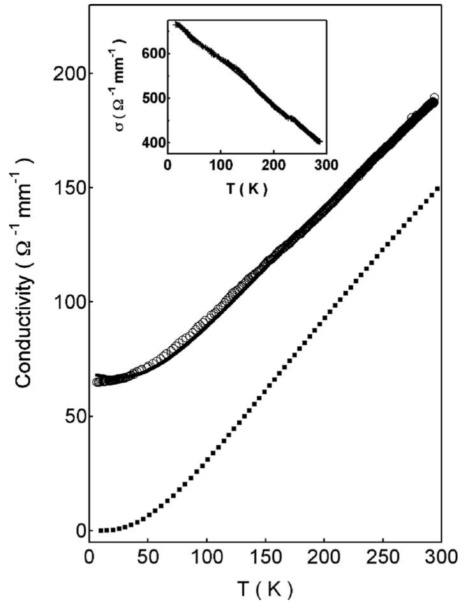

FIG. 2. Conductivity of a bismuth artificial crystal (sample B) as a function of temperature. The circles show the measured conductivity, and the solid line is a fit to the equation $\sigma=\varphi\sigma_m+(1-\varphi)\sigma_h$. The dashed line is the conductivity extracted for the hopping pathways alone. Inset: the conductivity vs temperature for sample B after compression into bulk bismuth. The solid line shows a linear fit to the data.

interconnecting regions should be 80–90 meV, corresponding to a thermal energy of 900–1000 K. At room temperature then, transport must occur by hopping from bismuth island to bismuth island, across the barriers formed in the narrow interconnecting regions. This hopping process is shown schematically in Fig. 1(d).

For conductivity and thermopower measurements, the bismuth sample is thermally anchored to an integrated circuit (IC) chip package consisting of two copper plates separated by an air gap. A platinum heater is mounted on one of the copper plates. The gap between the copper plates ensures that the heat pulse travels through the sample and not the chip package. Four wires are attached to the sample using silver paste: two gold-chromel wires on opposite edges of the sample act as thermocouples/current contacts and two copper wires on one face of the sample act as voltage contacts. The chip package containing the sample is inserted into an IC receptacle mounted on the cold finger of a closed cycle refrigerator (Janis Inc.) operating from 300 K down to 8 K.

RESULTS AND DISCUSSIONS

Conductivity

The electrical conductivity is measured by applying an excitation current through the thermocouple wires and measuring the voltage across the copper wires. Figure 2 shows the conductivity of a representative bismuth colloidal replica sample (similar results were observed in the measurements of two additional samples). The samples are robust to thermal cycling and show similar results for ascending and descending temperatures. The conductivity decreases with decreasing temperature, as would be expected if hopping conductivity is the dominant transport mechanism. However, the conductivity does not approach zero at low temperature, but instead levels off at a finite value. We believe this is because there are imperfections present in the colloidal crystal which when transferred to the bismuth replica create metallic conducting pathways that short out some percentage of the hopping pathways. At low temperature, the contribution from the hopping conduction paths becomes negligible and the metallic pathways dominate conduction through the sample. Since bismuth is malleable, and is a low melting point metal, there is a straightforward way to extract the hopping conductivity from the data. The crystalline structure including the narrow interconnecting regions can be removed by heating the sample just below the melting point of bismuth (220–250 °C) while applying a small amount of pressure. This produces a bulk bismuth sample that has approximately the same material properties as the original bismuth inverse replica, but without the confined high band gap regions (because of the high heat and pressure used to produce the inverse replica, its material properties are expected to be somewhat different than of a generic bismuth sample).

The conductivity of the bismuth inverse replica sample after compression is shown in the inset to Fig. 2. Rather than decreasing with decreasing temperature, the conductivity now increases with decreasing temperature, as is typical for metallic conduction.[23] A linear fit $\sigma_m = a + bT$ to the metallic temperature dependence gives $a = 685\ \Omega\,\mathrm{mm}^{-1}$ and $b = 0.99\ \mathrm{K}^{-1}$. This information can now be used to extract the hopping conductivity in the crystalline bismuth sample. Prior to compression, the conductivity of the bismuth replica is a combination of the hopping conductivity σ_h and the metallic conductivity σ_m. For the hopping conductivity, we assume the presence of electron-electron interactions giving $\sigma_h = \sigma_0 \exp(-\sqrt{T_0'/T})$ (σ_0 and T_0 are treated as fitting parameters), while for metallic conductivity we use σ_m determined from the compressed sample. The total conductivity is then

$$\sigma = \varphi \sigma_m + (1 - \varphi)\sigma_h, \tag{1}$$

where φ is the percentage of the sample volume occupied by metallic conducting pathways. As shown in Fig. 2, a fit of the conductivity of the bismuth artificial crystal to Eq. (1) is quite good and gives a value for φ of 10%. By subtracting off the metallic conductivity, we can now extract the hopping conductivity σ_h from the data. This is shown as a dashed line in Fig. 2; the hopping conductivity goes to zero with decreasing temperature as expected.

While the formula for the hopping conductivity including electron-electron interactions fits the data well, it is not possible to distinguish definitively between a $\exp[T^{-1/4}]$ and a $\exp[T^{-1/2}]$ dependence. We thus turn to the thermopower to help identify the specific hopping mechanism.

Thermopower

Thermopower is measured using the analog subtraction method.[24] This consists of heating the sample using a voltage pulse (of varying amplitude of 0–10 V) and measuring the temperature gradient across the two thermocouples. The thermopower is then calculated using a simple analog subtraction circuit containing three instrumentation amplifiers. Figure 3 shows the thermopower measured as a function of temperature for two different bismuth artificial crystals. Sample A is measured from 300 to 50 K, and sample B is measured from 300 to 8 K. (Sample B is the same sample whose conductivity was described above.) In both cases, the thermopower is negative at room temperature and decreases in magnitude as the temperature decreases. There is also a clear flattening out of the thermopower in the temperature range of 100–50 K. Below 50 K, the thermopower of sample B tends toward zero.

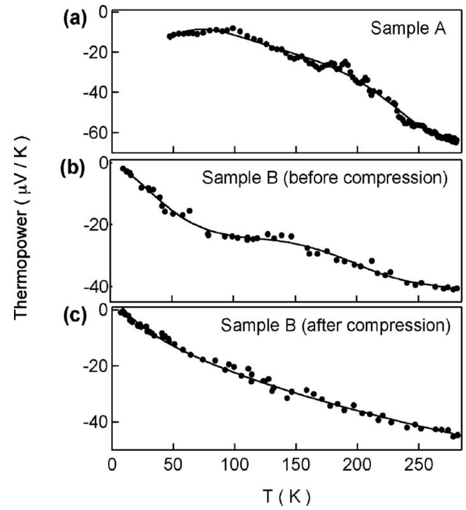

FIG. 3. Thermopower of (a) sample A (b) sample B before compression, and (c) sample B after compression as a function of temperature.

This flattening of the thermopower with decreasing temperature is not observed in any published thermopower measurements of bismuth: the thermopower of bismuth nanowires decreases approximately linearly in magnitude with decreasing temperature (even in nanowires narrow enough to show a semiconducting conductivity),[21,25,26] while the thermopower of bulk bismuth decreases linearly with decreasing temperature at low temperatures and tends toward a constant value at high temperatures.[27,28] In neither case is a flat, temperature independent regime observed in the thermopower as the temperature decreases. This suggests that the flattening of the thermopower with decreasing temperature is due to the hopping component of the conductivity in the artificial crystals. Further evidence is provided by measurements of the thermopower of sample B, performed after the sample is compressed to reform a bulk bismuth sample. This is shown in Fig. 3(c). After compression, the temperature independent regime is no longer observed, and instead the thermopower tends quasilinearly to zero as temperature decreases, similar to what is observed in bulk bismuth and bismuth nanowires.

The thermopower of the bismuth artificial crystal α is a combination of the thermopower from both the hopping α_h and metallic α_m transport paths,

$$\alpha = \frac{\alpha_m \sigma_m + \alpha_h \sigma_h}{\sigma_m + \sigma_h}. \tag{2}$$

As the temperature goes to zero, the hopping conductivity also goes to zero, and the total thermopower is simply that of the metallic pathways. In our samples then, we do not expect

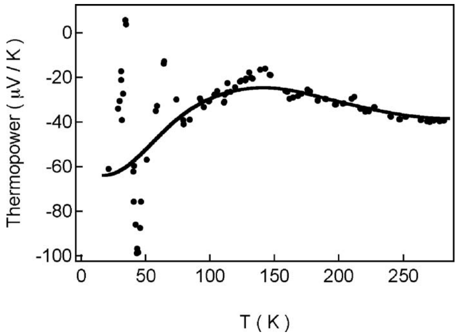

FIG. 4. Thermopower of the extracted hopping mechanism as a function of temperature. The solid line is obtained by taking the local average of the extracted thermopower.

to see the thermopower tend toward a constant, nonzero value at zero temperature, even if the Efros-type variable range hopping model applies. (A similar situation occurs in any disordered sample, unless hopping conductivity is the only transport mechanism present.)

Using our combined measurements, however, we can extract from Eq. (2) the thermopower due to the hopping conductivity. The hopping and metallic conductivities, σ_m and σ_h, are taken from our analysis above, while α and α_m are taken from the thermopower measurements of the bismuth colloidal crystal—before and after compression, respectively. The resulting thermopower due to hopping conductivity extracted in this way is shown in Fig. 4. The small difference between the thermopower in the compressed and noncompressed samples (α and α_m) introduces increasingly large noise based fluctuations in the data as the temperature decreases. As a guide to the eye then, the solid line shows the approximate local average value of the thermopower. Plotted in this way, it is clear that α_h does not go to zero with decreasing temperature, but instead increases in magnitude, and then levels off below a temperature of about 150 K. This is in qualitative agreement with the theory of Burns and Chaikin for a hopping system in the presence of electron-electron interactions. We note, however, that the limited minimum temperature of our measurement setup makes it difficult to say with certainty that the thermopower will continue to remain at a nonzero value as the temperature drops below 8 K. Further, more precise measurements of this type at lower temperatures are needed.

CONCLUSIONS

In conclusion, by comparing the properties of a bismuth artificial crystal with bulk bismuth, we have demonstrated a method to extract the conductivity and the thermopower due to hopping conduction. The hopping contribution to the thermopower shows a clear flattening out with decreasing temperature and tends toward a finite value at zero temperature, indicating the onset of Efros-type hopping conductivity at a temperature of 100 K. Further measurements are needed to determine whether this effect survives down to temperatures below 10 K.

ACKNOWLEDGMENTS

Funding provided by the National Science Foundation, Grant No. 0508211.

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