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Anomalous Efros–Shklovskii variable range hopping conduction in composites of polymer and iron carbide nanoparticles embedded in carbon

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Abstract

Efros–Shklovskii variable range hopping (ES-VRH) conduction mechanism [$\rho = \rho_0 \exp(T_{\mathrm{ES}}/T)^{1/2}$] is observed in composites of polymer and iron carbide nanoparticles embedded in carbon relatively at high temperatures. A crossover from one ES-VRH type to another ES-VRH type is observed with different ES temperature (T_{ES}) and prefactor (ρ_0) as temperature decreases.

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1. Introduction

Mott to Efros–Shklovskii variable range hopping (ES-VRH) crossover has been observed in many localized systems as temperature decreases [1–3]. This kind of crossover was predicted by Efros and Shklovskii prior to the experimental observations [4,5]. In principle variable range hopping conduction is possible at sufficiently low temperatures where activated type of conduction is not possible. Coulomb interaction in hopping regime which produces a gap (coulomb) in density of states is responsible for ES-VRH type of conduction mechanism. Mott to ES, VRH crossover is observed as temperatures recedes from high to low because at higher temperature hopping becomes much larger than the coulomb gap and its effect is suppressed [5]. In few of the system it has been found that the ES to Mott VRH crossover is due to filling of Coulomb gap in higher temperature range [8]. The cause of this crossover is due to change in electronic density of states (DOS). At higher temperatures where Mott law is obeyed DOS, $g(E)$ is a constant whereas at lower temperatures where Efros–Shklovskii VRH is obeyed density of states near Fermi energy (E_F) varies as $g(E) = g_0|E - E_F|^{D-1}$ and takes parabolic form in three dimensions. In intermediately and highly compensated semiconductor DOS is not constant and it decays in entire energy range (to its peak value at $E = 0$). In those cases in entire VRH temperature region conduction mechanism is governed by ES-VRH and crossover from Mott to Efros VRH is absent.

In this Letter we are reporting the crossover from one ES-VRH dependence to another ES-VRH dependence of resistivity in two different temperature regions in polymer composites system. This is in contrast with existing experimental evidences. The resistivity behaves as $\ln(\rho/\rho_0) = (T_{\mathrm{ES}}/T)^{1/2}$ from 300 K to 55 K and there is a transition below this temperature. Again in the temperature range 30 K–6 K ES-VRH is followed by the composites with different ρ_0 and T_{ES}.

2. Experimental

Iron-carbide nanoparticles embedded in carbon matrix (soot) are prepared by pyrolysis of maleic anhydride and ferrocene (2 : 1 molecular weight ratio) at 980 °C for $5\frac{1}{2}$ hours [18]. The final product is black color soot which is used as filler. The nanoparticles are less than 100 nm in size and there are few layers of graphene on it. Composites are prepared by the dispersion

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of filler in poly(vinyl chloride) (PVC) in different proportions. PVC is first dissolved in Tetrahydrofuran (THF) and filler is ultrasonically dispersed in solution to obtain a good dispersion. The details of sample preparation and characterization is discussed elsewhere [17]. The conventional four probe method is used to measure the low temperature transport inside a commercial Janis liquid Helium cryostat with superconducting magnet attachment. The contacts were made by silver paint. Below 15 K the temperature was controlled within the limit of 0.005 K where as near to room temperature the fluctuation was less than 0.2 K. To eliminate the error due to temperature fluctuation 20 reading were taken in each positive as well as negative current directions and averaged.

3. Results and discussions

Polymer composites are macroscopically disordered systems and conduction mechanism is well described by hopping conduction. In many of the cases in those materials temperature dependence of resistivity follows

$$\rho = BT^{-p}\exp(T_0/T)^n \tag{1}$$

in a large temperature range (300 K–4.2 K) [9,10] and the pre-exponential factor ($BT^{-p} = \rho_0$) has weak temperature dependence. The value of n varies widely between 1/4 and 1 depending on the different physical situations. In fact the exponent can take any value (< 1) depending on the form of DOS. If DOS varies as $g(E) = g_0|E - E_F|^m$ then n is given by $(m + 1)/(m + 4)$ [11]. Superlocalized model of variable range hopping also predicts different values of exponent [12,13]. Lien et al. [14] have reported the 2D Mott VRH dependence ($\ln R\alpha T^{-1/3}$) from 300 K to 60 K in amorphous indium oxide and nickel-silicon films and a crossover to harder soft gap ($\ln R\alpha T^{-n}$) with exponent (n) 0.77. A transition in resistivity from soft gap (ES-VRH) to hard gap (activated type) is also reported as temperature goes down [15,16]. In fact many types of crossovers have been observed namely, Mott-VRH to ES-VRH, ES-VRH to activated type, Mott-VRH to some arbitrary VRH and a comprehensive theoretical model is missing. The mathematical model suggested by Aharony et al. [3] and theoretical model by Lien et al. [14] are quite a useful in describing the different type of crossovers.

Fig. 1 shows the plot of $\ln\rho$ vs $T^{-1/2}$ in temperature range 300 K–1.3 K and change in slope is found nearly at 45 K. For clarity $\ln\rho$ vs. $T^{-1/2}$ is plotted in temperature range 300 K–10 K (Fig. 2) and a crossover is observed (hump in between 55 K–35 K). ES-VRH is followed in between 300 K–55 K and 30 K–6 K on either side of hump. Mott and other VRH expressions have been tried but ES-VRH was found to be best least square fit. The magnetotransport properties have been studied from 300 K to 8 K and the response of the samples too, confirms crossover. The magnetoresistance [$\mathrm{MR} = \frac{\rho(H)-\rho(0)}{\rho(0)}$] is negative at 300 K in entire range of magnetic field (0–11 T). Its value gradually decreases (magnetoconductance MC increases) up to 55 K and below this temperature it starts increasing (MC decreasing) and finally it becomes positive at somewhere near to 15 K. Below this temperature MR monotonically increases. At low temperatures and low fields $\ln[\rho(B)/\rho(0)]$ is proportional to B^2. In simplest picture the positive MR at low temperatures is observed in strongly localized system is due to shrinkage of impurity orbitals wave function which lead to sharp decrease in overlap of wave-functions resulting in positive MR [5,19]. The quadratic dependence is consistent with the theory developed for field dependence on transport properties of localized system [5]. This kind of dependence is observed when hopping length (R_{hop}) is quite large compare to localization length ξ. This relation ($R_{\mathrm{hop}} \ll \xi$) holds good at low temperature as $R_{\mathrm{hop}} \approx T^{-1/2}$ [6]. At higher temperatures where $R_{\mathrm{hop}} \sim \xi$ the backscattering becomes important and weak localization effect dominates which does not come in picture at low temperatures due to larger hopping length [7]. It is weak localization which is responsible for positive MC at higher temperatures.

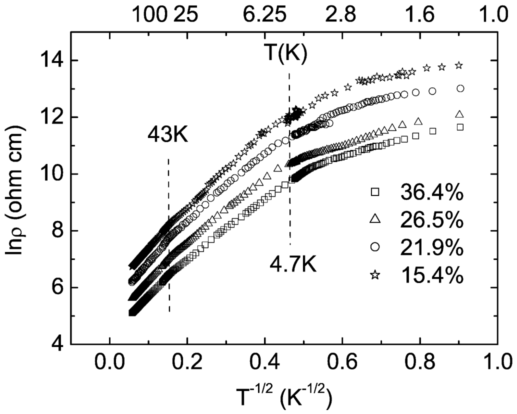

Fig. 1. $\ln\rho$ vs $T^{-1/2}$ plots from 300 K–1.3 K for composites having different proportion of filler. Percentage of filler in samples are marked near the symbols inside the figure. The dotted vertical lines show the eye estimated temperatures where crossovers occur.

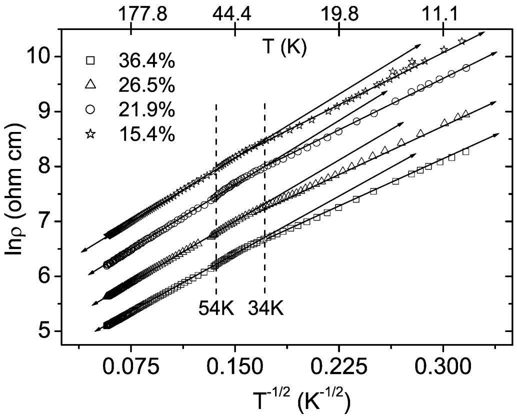

Fig. 2. $\ln\rho$ vs $T^{-1/2}$ plots from 300 K–10 K. The temperature range between the vertical dotted line is crossover range. The arrowed line is freely hand drawn straight line between the extreme points. There is a noticeable change in the slope after the crossover. The crossover region is independent of the samples.

To calculate the different parameters of the ES-VRH, straight lines have been fitted in $\ln\rho$ vs. $T^{-1/2}$ plots of two different ES-VRH regions (300 K–55 K and 30 K–6 K) as shown in the Fig. 3. The value of T_{ES} and ρ_0 are calculated from the slope and intercept respectively of the straight line fit. The localiza-