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Quantum interference of electrons in multiwall carbon nanotubes

Akihiko Fujiwara,* Kozue Tomiyama,† and Hiroyoshi Suematsu
Department of Physics, School of Science, University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan

Motoo Yumura and Kunio Uchida
Department of Chemical Systems, National Institute of Materials and Chemical Research, 1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan

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In magnetoresistance measurements of a single multiwall carbon nanotube we have observed the periodic oscillation which increases in amplitude below 30 K. The period has the angular dependence of $1/\cos\theta$, θ being the angle between the nanotube axis and magnetic field, and it corresponds to the field that the magnetic flux penetrating a nanotube equals one-third of a flux quanta, $h/3e$. The observation is explained in terms of the Aharonov-Bohm effect for three coexisting nanotubes with different chiralities. [S0163-1829(99)12643-2]

I. INTRODUCTION

Since its discovery,[1] the carbon nanotube (CNT) has attracted great attention as a very interesting electronic material because of the one-dimensional structure and the tubular honeycomb network in the nanometer scale.[2–4] Theoretical studies of the CNT (Refs. 5–8) predict some novel electronic properties such as the band-structure characteristic of the periodic honeycomb network and the magnetic quantum effect. The band structure of the CNT is either semiconductive or metallic depending on the chirality and the diameter of the tube; the energy gap (E_g) of semiconductor phase is inversely proportional to the diameter, and a typical E_g is 36 meV for a CNT of 200 Å in diameter. Some experimental works confirm these electronic structures.[9,10] Another interesting feature is the magnetic interference effect predicted by Ajiki and Ando.[8] When a magnetic field is applied to a metallic CNT, the energy gap opens and increases linearly with field, and after reaching the maximum value of $3E_g/2$ at $\phi = h/2e$, it decreases again to zero at $\phi=\phi_0\equiv h/e$, where ϕ is the magnetic flux penetrating the cross section of a CNT. Namely, the band structure changes from metallic to semiconductive and revolves in the period of ϕ_0. This phenomenon is analogous to the Aharonov-Bohm (AB) effect.[11] A similar interference effect was observed in a normal-metal cylinder made of single-crystal bismuth.[12] Very recently, Bachtold *et al.*[13] have reported periodic oscillations of magnetoresistance (MR) in multiwall (MW) CNT, and ascribed it to Altshuler-Aronov-Spivak (AAS) effect[14] because the period corresponds to $\phi=\phi_0/2$. They consider that CNT's are always metallic independent of the strength of magnetic field.

In this paper we present the quantum interference effect of electrons in the MR measurement of a MWCNT. MR shows an oscillatory dependence on magnetic field, and the observed period corresponds to $\phi_0/3$ and has the angle dependence of $1/\cos\theta$, θ being the angle between field and the CNT axis. The observed oscillation is ascribed to the AB effect mentioned above, and the period of $\phi_0/3$ can be understood by the coexistence of the three types of CNT's with different chirality.

II. EXPERIMENT

MWCNT's were obtained from carbon soot (Type I, Vacuum Metallurgical Co. Ltd., Japan) by repetition of physical purification processes, that is, the centrifugation at 5000 rpm for 20 min. and filtration; we did not use any chemical process such as oxidation treatment, because these processes may lead serious damages on the surface of MWCNT's which act as electronic scattering centers.

In this work, we measured the resistance of a single MWCNT by using directly attached electric contacts, as shown in a scanning electron microscope (SEM) image (Fig. 1). The contacts were made by the electron-beam-lithography technique in the following processes. MWCNT's, which were ultrasonically dispersed in methyl alcohol, were placed onto a substrate of oxidized Si wafer. After spin-coated with a positive photoresist, the lead pattern of contacts with 1.25 μm pitch and 10 μm in length was drawn by an electron beam. The exposed pattern was removed by a solvent, on which gold was deposited. In this method, we could not control the position of an MWCNT relative to contacts, so that after patterning of gold contacts we have to choose a good sample in which only a single CNT intersects four contact leads; the sample in Fig. 1 is a successful one. The dc MR measurements were carried out by using Quantum Design model PPMS physical property measurement system with a rotating sample mount. The measurements were performed in the Ohmic region, usually in the region from 5 to 30 nA. We will present the experimental results for two samples, nos. 1 and 2, with 190 and 390 Å in diameter d and 1.0 and 0.6 μm in voltage contact distance, respectively. The inner diameter is estimated as about 30 Å for both samples from the transmission electron microscope (TEM) observation of samples in the same lot. In the present case we have not found any mechanical stress coming from bending, defects, or flexure reported previously,[4,15] although MR occasionally jumps irreversibly in the region of very high fields, which might arise from adisplacement of sample due to a strong galvanomagnetic force.

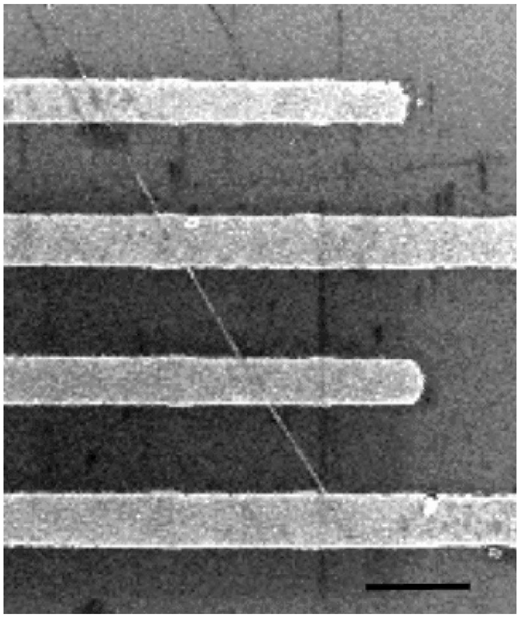

FIG. 1. SEM image of a CNT and gold contacts for transport measurements. The scale bar is 1 μm. The stripe-shaped gray areas are gold leads and the fine line presents a MWCNT.

III. RESULTS AND DISCUSSION

Figure 2 shows the magnetoresistance of samples 1 and 2 for the magnetic field parallel to the CNT axis at some temperatures. For both samples, we observe a periodic oscillation, whose amplitude increases significantly at low temperatures. The period of the major oscillation is determined as 4.3 T for sample 1 and 1.1 T for sample 2 by fitting to a triangular wave. These observed periods are about one third of those estimated from the outside diameter by assuming the AB effect, that is, 14.6 and 3.5 T for samples 1 and 2, respectively. The difference of the period will be discussed later.

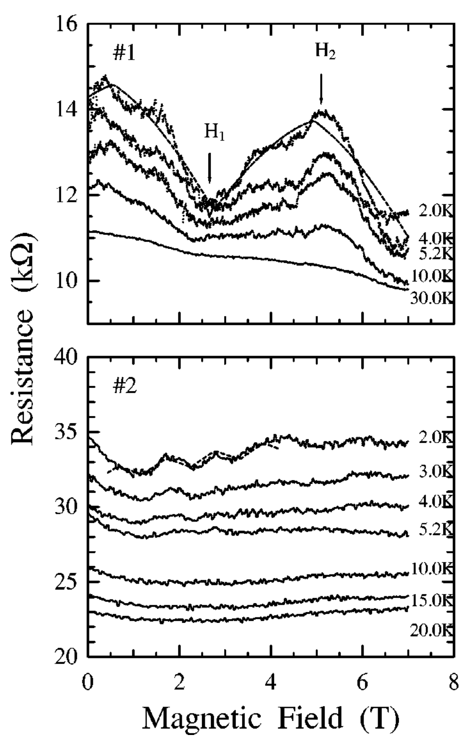

FIG. 2. Magnetoresistance of samples 1 and 2 for various temperatures with a magnetic field parallel to the CNT axis. The dashed lines are fitting results for data at $T=2$ K by Eq. (3.4).

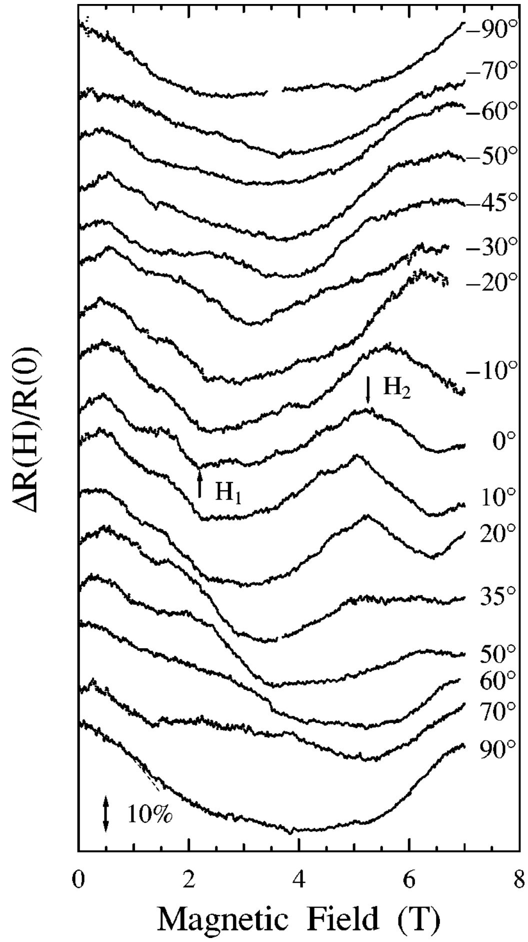

FIG. 3. Magnetoresistance of sample 1 at $T=2$ K for various angles θ. The dashed line is a fitting result for transverse magnetoresistance in order to obtain the phase coherence length l_ϕ.

Figure 3 shows the angle (θ) dependence of magnetoresistance of sample 1 at $T=2.0$ K, where θ stands for the angle between the magnetic field and the CNT axis. The peak field (and bottom field) strongly depends on θ, and, as shown in Fig. 4, the θ dependence of the peak field H_n can be presented by the relation

$$H_n(\theta)=\frac{H_{n,0}}{\cos\theta}, \tag{3.1}$$

where n is the index of the peak and $H_{n,0}$ is the peak field at $\theta=0°$. The solid lines in Fig. 4 show the best fit to this relation, where we assumed a small-angle deviation δ of the CNT axis from $\theta=0°$ due to a possible experimental misalignment. Fitting results are listed in Table I. The observed angle dependence of $H_n(\theta)$ tells us that the MR peak field is

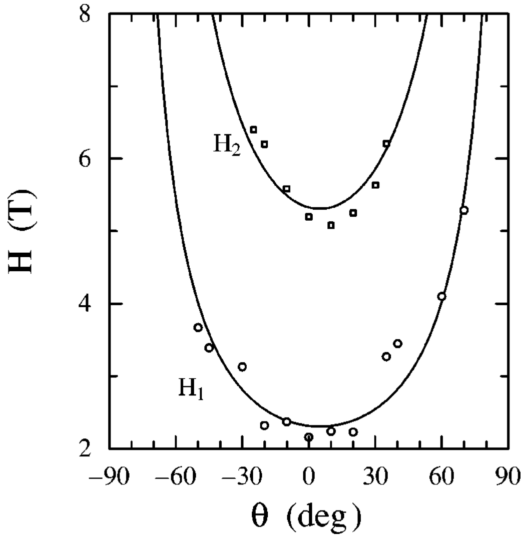

FIG. 4. θ dependence of peak positions for H_1 and H_2 in Fig. 3. The solid lines are fitting results by Eq. (3.1).

determined by the parallel component of magnetic field to the CNT axis, namely, the magnetic flux penetrating the cross section of the CNT.

We discuss the origin of the present oscillation. As electron interference effects in a ring or tube, we consider two cases, the AB effect predicted by Ajiki and Ando[8] and the AAS effect.[14] The difference between them are the oscillation period and the temperature dependence of the oscillation amplitude. The periods of the AB effect is expected to be h/e while that of the AAS effect is $h/2e$. The magnetic field corresponding to a flux quantum, ($H_0 \equiv 4\phi_0/\pi d^2$), is 14.6 and 3.5 T for samples 1 and 2, respectively. The observed periods are very close to one-third of these calculated values for both samples; that is, the period of the observed oscillation is $h/3e$. It is well known that the CNT has three types of electronic structure depending on the chirality and the diameter, which is indexed by a chiral vector (n,m) (n,m: positive integer).[5] The electronic structure of a (n,m) CNT can be determined by a parameter $\nu(=0,\pm 1)$,[5,8] when we define

$$n-m=3N+\nu \tag{3.2}$$

with integer N. The CNT with $\nu=0$ and ± 1 are metallic and semiconductive, respectively. In a magnetic field, we can expect the AB effect mentioned in Sec. I. When we consider a metallic CNT ($\nu=0$), E_g, which is zero at $\phi=0$, increases linearly with field, and through a maximum value at $\phi=h/2e$ it decreases again to zero at $\phi=h/e$. For semiconductor phases ($\nu=\pm 1$), the field dependence of E_g has the same period as the metallic phase, but with the different phase shift; namely, the zero gap field is shifted by $h/3e$ and $2h/3e$ for $\nu=-1$ and 1, respectively. Therefore E_g of a CNT is described as

$$E_g^{\nu}(H) \equiv \frac{3}{2} E_g \times F_{tw}\left(\frac{H}{H_0}+\frac{\nu}{3}\right), \tag{3.3}$$

where $F_{tw}(x)$ is a triangle wave function (cf. Fig. 2 in Ref. 8). In the MWCNT we expect the coexistence of all the types of CNT's, and the metallic resistivity appears at $H = nh/3e (n=0,1,2,\ldots)$, because they make a parallel circuit. Therefore the period becomes $h/3e$, which is in agreement with the observed one. The resistance of a MWCNT for the parallel circuit of three CNT's can be described by

$$R(H)=\left[\sum_{\nu=-1}^{1} \frac{1}{R_\nu} \exp\left(\frac{-E_g^{\nu}(H)}{k_B T}\right)\right]^{-1} + R'H, \tag{3.4}$$

where R_ν is the resistance at $E_g=0$, k_B is Boltzmann constant and R' is the coefficient of the nonoscillation term of magnetoresistance. Here, we assume that all ν CNT's have the same R_ν and the same diameter for simplicity. The fitting results are plotted in Fig. 2 with dashed lines, and the fitting parameters are listed in Table II. For the best fitting we needed a small amount of offset shift of field, δH; the reason for δH is not clear at present.

The obtained period H_0 (13.11 T for sample 1 and 3.17 T for sample 2) is in good agreement with that estimated from diameter, $4\phi_0/\pi d^2$ (14.6 and 3.5 T, respectively), when taking account of the ambiguity in diameter estimation. However, the obtained E_g, 1.7×10^{-4} eV (sample 1) and 2.7×10^{-5} eV (sample 2), are two or three orders of magnitude smaller than theoretically expected values (that is, 3.7×10^{-2} eV for sample 1 and 1.8×10^{-2} eV for sample 2). For such a large reduction of E_g we can consider some possibilities as follows. The major effect may be the short coherence length of electrons due to imperfections on tubular networks. In order to observe the AB effect, the phase coherent length of electron, l_ϕ, should be much larger than πd, but actually there are many imperfections on a CNT. We estimate experimentally l_ϕ from the low-field coefficient of the H^2 dependence in transverse MR (Refs. 16 and 17) on assumption that the present sample is in the weak localization regime.[18,19] The obtained l_ϕ for sample 1 at $T=2$ K is

TABLE I. Results of the fitting for θ dependence of the peak positions by Eq. (3.1). Fitting parameters are $H_{1,0}$, $H_{2,0}$, and δ.

n	$H_{n,0}$ (T)	δ (deg)
$1(H_1)$	2.4	5.0
$2(H_2)$	7.1	

TABLE II. Results of the fitting for magnetoresistance at $T=2$ K by Eq. (3.4). Fitting regions are $H=0$–7.0 T and $H=0.5$–4.0 T for samples 1 and 2, respectively.

	R_ν (kΩ)	E_g (10^{-5} eV)	H_0 (T)	δH (T)	R' (kΩ/T)
Sample 1	21.3 ± 0.1	16.9 ± 0.1	13.11 ± 0.05	-1.62 ± 0.02	-0.194 ± 0.004
Sample 2	85.6 ± 0.4	2.7 ± 0.1	3.17 ± 0.02	0.14 ± 0.01	0.48 ± 0.01

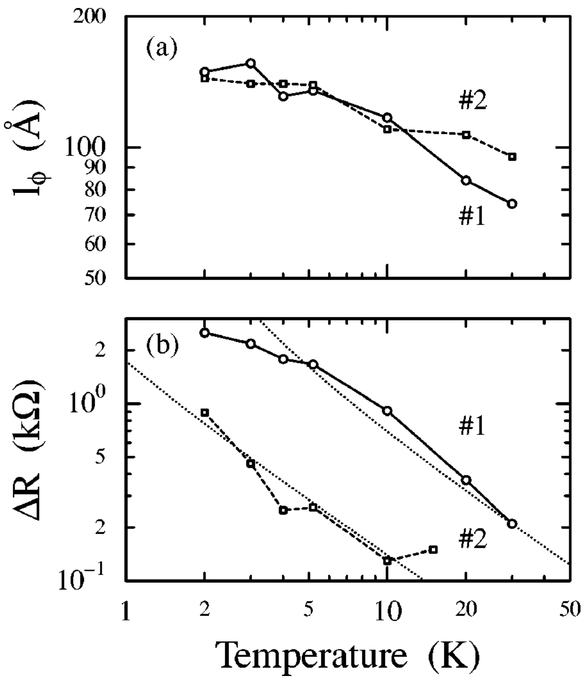

FIG. 5. Temperature dependence of (a) the phase coherence length and (b) the amplitude of the oscillation for samples 1 and 2. The dotted lines are fitting results by Eq. (3.5).

150 Å; a fitting curve is plotted by a dashed line in Fig. 3. The temperature dependences of l_ϕ for samples 1 and 2 are shown in Fig. 5(a). Thus l_ϕ in our case is a little smaller than πd; our sample is considered as an electronic two-dimensional system. This small l_ϕ brings a broadening of band edge and reduces E_g effectively. The second is the effect of inner CNT's. We so far assume that a few most outer walls contribute the conduction. However, if electrons penetrate into inner walls, the oscillation should be smeared out by superposition of different period ones due to different diameter. The third is the effect of the interwall interaction. In theoretical calculation of E_g the interaction between neighboring walls is not taken into account, which exists in MWCNT's. The tight-binding calculation for a double wall CNT (Ref. 20) gives a smaller E_g than the SWCNT, although the effect might be very small.

Now we will discuss the temperature dependence of the amplitude of the oscillation, which is shown in Fig. 5(b). The amplitude for the AB effect in a metal ring can be expressed as $\Delta G(T) \propto T^{-1/2}\exp(-d/2l_\phi(T))$.[21] However, in the case of CNT's the AB effect appears as the change of E_g. Therefore it can be written by Eq. (3.4),

$$\Delta R(T)=R_\nu\left\{\left[\exp\left(-\frac{3E_g}{2k_BT}\right)+2\exp\left(-\frac{E_g}{2k_BT}\right)\right]^{-1} -\left[1+2\exp\left(-\frac{E_g}{k_BT}\right)\right]^{-1}\right\}. \tag{3.5}$$

We assume a constant R_ν, because R_ν has a T dependence much weaker than the exponential term in Eq. (3.5). As shown in Fig. 5(b), Eq. (3.5) explains well the experimental data as a whole. An interesting feature of Figs. 5(a) and (b) is that l_ϕ and the amplitude of oscillation show a quite similar T dependence. These facts indicate that the amplitude is possibly dependent on l_ϕ and the oscillation arises from the interference effect of electron.

IV. SUMMARY AND CONCLUSIONS

In transport measurements of single multiwall-carbon nanotubes (MWCNT's) with 190 and 390 Å in diameter, we have observed periodic oscillations in magnetoresistance whose amplitude increases significantly below 30 K. The oscillation periods for two samples correspond to the field that the magnetic flux penetrating a CNT equals one-third of the flux quanta, $h/3e$, which is realized for all the angle of field relative to the CNT axis. We can understand that this oscillation is ascribed to the Aharonov-Bohm (AB) effect predicted theoretically by Ajiki and Ando, and the factor 1/3 comes from the coexistence of CNT's with three different chiralities, which is inherent in MWCNT's. This is the first observation of the AB effect in CNT's.

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*Author to whom correspondence should be addressed. Electronic address: fujiwara@phys.s.u-tokyo.ac.jp
†Present address: Technical Research Institute, Toppan Printing Co. Ltd., Sugito-machi, Kitakatsushika-gun, Saitama 345-8508, Japan.
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