

Effects of magnetic field and disorder on the electronic properties of carbon nanotubes

Stephan Roche

Department of Applied Physics, University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8654, Japan

Riichiro Saito

Department of Electronic Engineering, University of Electro-communications, 1-5-1 Chofugaoka Chofu, Tokyo 182-8585, Japan

(Received 20 August 1998)

The electronic properties of carbon nanotubes are investigated in the presence of a magnetic field perpendicular to the nanotube axis and disorder introduced through site-energy randomness. The magnetic field is shown to induce a metal-insulator transition for the metallic (9,0),(12,0) . . . nanotubes in the absence of disorder. It is also shown that semiconducting nanotubes can become metallic with increasing magnetic strength. The low disorder limit preserved the electronic structure whereas the metal-insulator transition remains even in the strong disorder limit. These results may find experimental confirmation with tunneling spectroscopy measurements. [S0163-1829(99)03907-7]

I. INTRODUCTION

The discovery of carbon nanotubes (CN's) by Iijima¹ has sparked a tremendous amount of activity and interest from basic research to applied technology.² These carbon-based structures have spectacular electronic properties but the range of their applications is much broader than electronics, and, in particular, due to potential marked mechanical properties, they could become serious competitors to composite materials. CN's consists of coaxially rolled graphite sheets determined by only two integers, and depending on the choice of m and n , a metallic, semiconducting or insulating behavior is exhibited. Given their extremely small diameter (1 to 20 nm), CN's turn out to be serious candidates for the next generation of microelectronic elementary devices often referred to the unprecedented "Nanotechnology Era."³

The understanding of the pure CN's is now very mature,² and researches are now focusing on the effects of topological (such as pentagon-heptagon pair defects^{4,5}) and chemical disorder on "ideal properties" in order to make CN's, operational devices for microelectronics. Yet a transistor device has been designed from CN's, and shown to operate at room temperature.⁶ Other mesoscopic effects, such as universal conductance fluctuations (UCF's) appearing at low temperature have also been revealed in CN's.⁷ From nanotubes, one-dimensional (quantum wires⁸) or zero-dimensional (quantum dots⁵) molecular systems have been conceived.

To strengthen the usefulness of CN's, the understanding of the influence of defects in nanostructures deserves particular attention since at such very small scale, any disruptions of local order may affect dramatically the physical response of the nanodevice. For the implementation to efficient technological devices, one needs to seriously understand, control, and possibly confine the magnitude of these inherent quantum fluctuations, induced by disorder or magnetic field.

Usually, classical theory enables an elegant description of electronic properties for crystalline materials through the use of quantum mechanics and symmetry principles. However, real materials always enclosed impurities, dislocations, or more general form of disorder which generally imply to go

beyond usual paradigms that have been used successfully for pure systems. To investigate tunneling spectroscopy experiments or electronic conductivity measurements, one may alternatively tackle the problems of aperiodicity by using real-space methods.⁹

Conductivity measurements have been performed on bundles of single-walled carbon nanotubes by means of a scanning tunneling microscope (STM).¹⁰ By moving the tip along the length of the nanotubes, sharp deviations in the I - V characteristics could be observed and related to electronic properties predicted theoretically. Notwithstanding, the scanning tunneling experiment is a local measurement of current from the tip to the nanotube surface and gives basically local informations such as local density of states (LDoS).¹¹ Further measurements of the electronic conductivity involve the study of CN-based junctions. Finally, nanotubes have been recently shown to be nanometer-sized probes for imaging in chemistry and biology, improving substantially the actual resolution of scanning probes.¹²

Investigation of electronic properties are generally confined to a description of the so-called electronic spectrum of a given material. From the spectrum, one can typically distinguish a semiconductor from a metallic sample by identification of a gap at Fermi energy. Within this framework, we will show that interesting effects are driven by the strength of the magnetic field, or energy fluctuations in the site energies. In particular metal-insulator transition will be studied, by considering the density of states when site randomness and magnetic field act simultaneously.

II. MAGNETIC-FIELD-INDUCED METAL-INSULATOR TRANSITION

To evaluate the density of states (DoS) of the carbon nanotubes, we use the recursion method¹³ which enables a study of structural imperfections and disorder, as discussed by Charlier, Ebbesen, and Lambin.⁴ The Green's function from which one estimates the DoS are calculated as a continuous fraction expansion, which requires to be properly terminated. Besides, finite imaginary part of the Green's

function is necessary to achieve numerical convergence of the expansion if the system presents gaps in the electronic structure. The DoS on a given initial state $|\psi_0\rangle$ is evaluated from $\langle\psi_0|G(z=E+i\eta)|\psi_0\rangle$ by tridiagonalization of the corresponding tight-binding Hamiltonian. A proper terminator has to be computed with respect to the asymptotic behavior of recursion coefficients a_n, b_n associated to the recursion procedure. For a metallic CN, the series a_n, b_n exhibit well-defined limits a_∞ and b_∞ enabling a simple termination of the Green's function. For the semiconducting (10,0) CN, the series of b_n coefficients encompass small fluctuations confined around 4.25 and 4.75 (in γ units, with γ the coupling constant between neighboring carbon atoms). This unveils the presence of a gap in the structure which may be completely resolved by appropriate terminator.¹⁴ Furthermore, when dealing with magnetic field that may lead to Landau-level structure, suitable termination can be implemented.¹⁵

However, one notes that η may also have some physical significance. Indeed, real materials usually enclose inherent disorder that leads to a finite mean free path, or scattering rates. Then, the first approximation to account for such elastic/inelastic relaxation times, is to introduced a finite imaginary part of the Green's function (Fermi's Golden rule). Finally, contrary to diagonalization methods for finite-length systems, a discussion about scaling properties is beyond the scope of the recursion method. Finite-size effects due to boundary conditions will strongly affect physical properties. For instance, close to a metal-insulator transition, characteristic properties like localization length will be driven by scaling exponents. Here, large systems are used to achieve the convergence of continuous fraction expansion before finite-size effects occur. It is equivalent to consider an infinite homogeneous structure. Actually, local properties such as LDoS are weakly affected by boundary effects when the nanotube is sufficiently long. In the following, we will keep a finite imaginary part for the Green's function keeping in mind the previous discussion.

We consider a tight-binding description of the graphite π bands, with only first-neighbor C-C interactions $\gamma=V_{pp}\pi$ which is taken as -2.75 eV. The magnetic field is considered to be perpendicular to the nanotube axis so that the potential vector is given by $A=[0,(LB/2\pi)\sin(2\pi/L)\mathcal{X}]$,¹⁶ with $a_{cc}=1.42$ Å, $L=|C_h|=\sqrt{3}a_{cc}\sqrt{n^2+m^2+nm}$, and the modulus of the chiral vector defined by $C_h=n\mathbf{a}_1+m\mathbf{a}_2$.² The effects of the magnetic field are driven by the phase factors $\exp[(ie/\hbar c)\gamma_{ij}]$ introduced in the hopping integrals between two sites $\mathbf{R}_i=\{\mathcal{X}_i,\mathcal{Y}_i\}$ and \mathbf{R}_j . They are generally defined by the potential vectors through the Peierls substitution:

$$\gamma_{ij}=\frac{2\pi}{\varphi_0}\int_{R_i}^{R_j}\mathbf{A}\cdot d\mathbf{r},$$

where $\varphi_0=hc/e$ is the quantum flux. After simple algebra, assuming $\Delta\mathcal{X}=\mathcal{X}_i-\mathcal{X}_j$ and $\Delta\mathcal{Y}=\mathcal{Y}_i-\mathcal{Y}_j$ one finds that the proper phase factors in our case are given by²

$$\begin{aligned}\gamma_{ij}(\Delta\mathcal{X}\neq 0)&=\left(\frac{L}{2\pi}\right)^2 B\frac{\Delta\mathcal{Y}}{\Delta\mathcal{X}} \\ &\times\left[-\cos\frac{2\pi}{L}(\mathcal{X}+\Delta\mathcal{X})+\cos\left(\frac{2\pi\mathcal{X}}{L}\right)\right],\end{aligned}$$

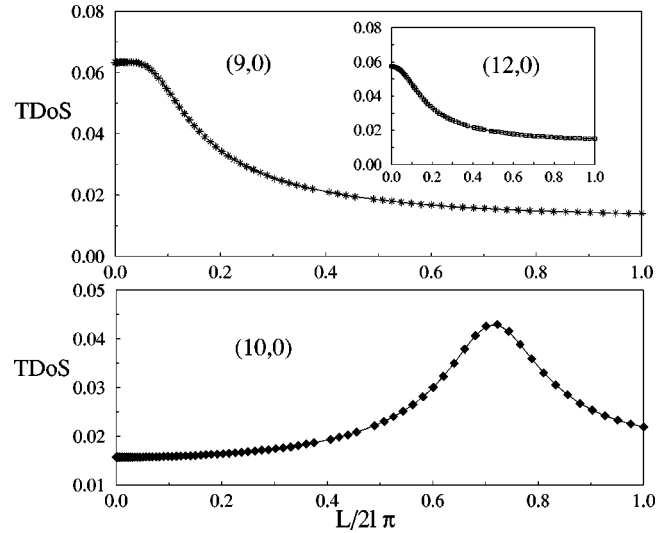


FIG. 1. Evolution of the TDoS for (9,0) and (10,0) CN's as a function of magnetic field.

$$\gamma_{ij}(\Delta\mathcal{X}=0)=\left(\frac{L}{2\pi}\right)\Delta\mathcal{Y}B\sin\frac{2\pi\mathcal{X}}{L}. \quad (1)$$

In Fig. 1, we show the total density of states (TDoS) at Fermi level as a function of the effective magnetic field defined by $\nu=L/2\pi\ell$, where $\ell=\sqrt{\hbar c/eB}$ is the magnetic length. For the two metallic nanotubes (9,0) and (12,0), the TDoS at Fermi level decreases as the magnetic strength is increasing. For higher values of magnetic field, our results are in agreement which has been found by exact diagonalizations.² As $\nu\rightarrow 1$, the TDoS, at Fermi energy, approaches the same value (≈ 0.014) as the semiconducting (10,0) CN for zero magnetic field.

On Fig. 2, the bold curve is the metallic CN (9,0), whereas the dashed-bullet line stands for the semiconducting CN (10,0) both in the absence of magnetic field B . The normal curve corresponds to a metallic CN with magnetic field

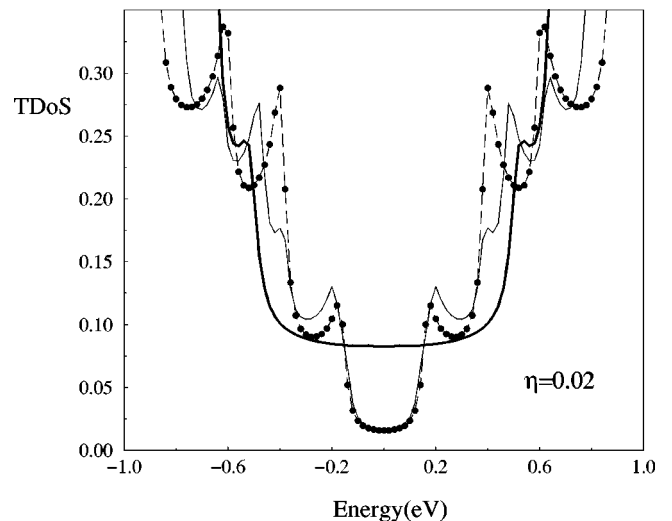


FIG. 2. Comparison of TDoS for a metallic (9,0) CN (bold line), a metallic (9,0) CN under the influence of magnetic field. $\nu=0.8$ (bullet line) and a semiconducting (10,0) CN (solid line) for the same value of η .

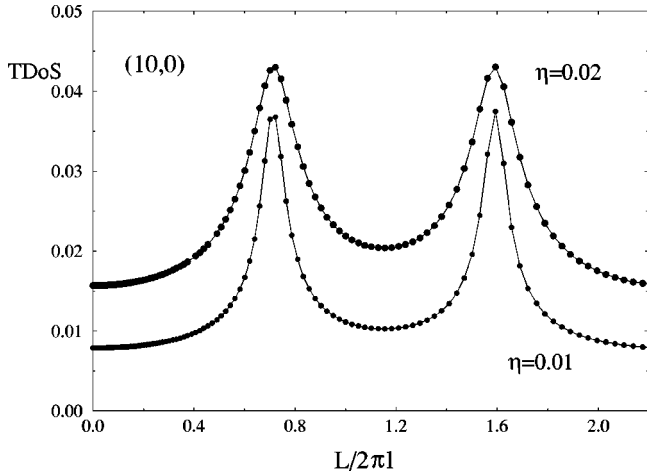


FIG. 3. Effect of the finite imaginary part of Green's function (η) on TDoS for a semiconducting (10,0) CN.

$\nu=0.8$. It can be seen that for $\nu=0.8$, the TDoS in the vicinity of the Fermi level, presents a pseudogap (due to finite η) very similar to the one of the (10,0) semiconducting nanotube for the same value of $\eta=0.02$. Furthermore, we estimate the width $\Delta_g \approx 1.1$ eV, which is in good agreement with typical values found in experiments.¹¹ This surprising result shows that the magnetic field induces a metal-insulator transition. From $\nu=0$ to $\nu=0.8$, a continuous metal-insulator transition can be drawn.

The semiconducting case in Fig. 1 is also interesting since a transition from semiconducting to metallic is seen to occur for $\nu \sim 0.7$. In Fig. 3, the effect of η on the semiconducting case is illustrated. As η is reduced, the TDoS at Fermi level (given in states/eV/graphite unit cell units) follows such that $\text{TDoS}(E_F, \eta_1)/\text{TDoS}(E_F, \eta_2) = \eta_1/\eta_2$. Accordingly, a continuous transition, as η tends to zero, from insulator to metal (for ν of about 0.7) turns out to be an inherent feature of the semiconducting CN. Besides, Fig. 3 also shows the oscillation pattern that is driven by the magnetic field.

For the metallic CN, the normalized TDoS at Fermi

level is given by $8/\sqrt{3}\pi a \gamma$ in the unit of states/ γ /(length along the nanotube),² with $a=2.46$ Å, so that the expected real TDoS(E_F) for (9,0) nanotube is given by 0.08168 states/ γ /(graphite unit cell). From our results, we find that $\text{TDoS}(E_F, \eta=0.02)=0.08238$ and $\text{TDoS}(E_F, \eta=0.01)=0.0812$ which are qualitatively in good agreement with the theoretical result. We have checked that the integral density of states (IDoS) is normalized.

For the (9,0) CN, Ajiki and Ando¹⁶ predicted that the DoS, for magnetic field parallel to the nanotube axis and in the framework of $\mathbf{k} \cdot \mathbf{p}$ approximation, should exhibit φ_0 -periodic oscillations ($\varphi_0=ch/e$ the quantum flux). In our case, for $\nu=0$ to $\nu=0.8$, the finite density of states in the vicinity of Fermi level (Fig. 4) is deepened and finally reaches the same value as the semiconducting CN for the same value of η . Afterwards, TDoS undergoes as a function of ν nonperiodic oscillations, as it can be seen when ν increases from 1 to 1.4.

To conclude this first part, from our results it seems that magnetic field leads to a oscillatory behavior of the TDoS at Fermi level between metallic and semiconducting electronic states. This effect has been illustrated symmetrically on semiconducting and metallic nanotubes for a broad range of magnetic field strengths. Although we did not present calculations for armchair and chiral nanotubes in this paper, we think that the results will also be similar for this other class of carbon nanotubes.

III. COMBINATION OF RANDOMNESS AND MAGNETIC-FIELD EFFECTS

As mentioned previously, it is of great necessity to analyze the stability of physical patterns that emerge from perfect nanotubes when introducing disorder. So far much consideration has been given to the so-called heptagon-pentagon pair defects since their presence is to be expected in any junction devices.⁴ Hereafter, we will focus rather on the effect of Anderson-type disorder on spectral properties, investigating to which extent randomness is able to modify the

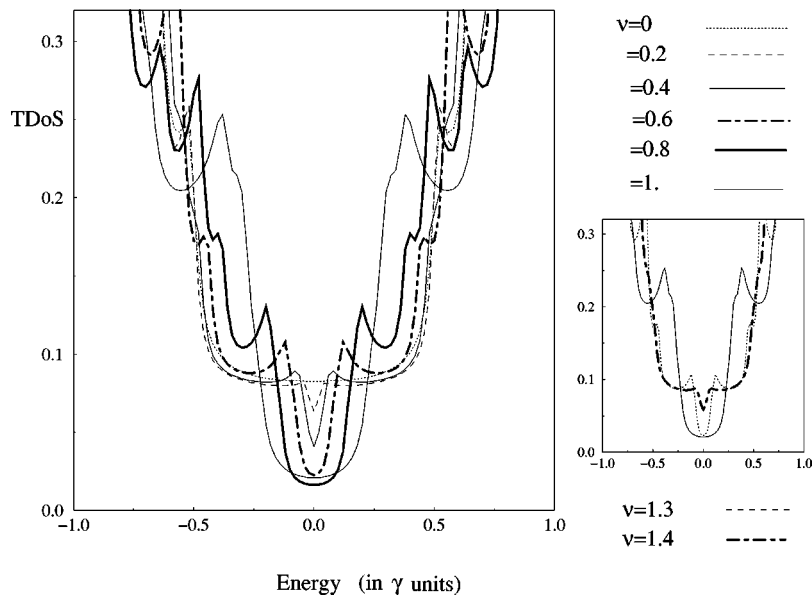


FIG. 4. TDoS for metallic (9,0) CN for different values of ν .

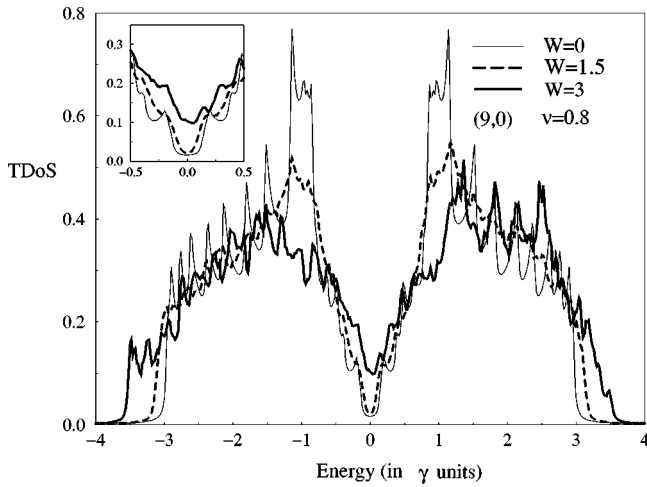


FIG. 5. TDoS of (9,0) CN as a function of energy for different values of disorder and a magnetic field corresponding to $\nu=0.8$.

previously unveiled pattern. We concentrate our study in the metallic CN case, restricting our discussion to (9,0) CN, given that similar patterns were observed in others metallic ones.

The effect of randomness is now considered on the site energies of the tight-binding Hamiltonian with $\sum_{n_x, n_y} \varepsilon_n |n_x, n_y\rangle \langle n_x, n_y|$. The site energies are randomly chosen in the interval $[-W/2, W/2]$, with uniform probability distribution. Accordingly, the strength of disorder is measured by W . To evaluate the TDoS, we use an average on typically 100 different configurations.

The TDoS as a function of Fermi energy for $\nu=0.8$ with different values of randomness, in the vicinity of the Fermi energy ($E_F=0$ eV) has been studied. Values of randomness strength $W=0, 0.5, 1, 2,$ and 3 have been considered and are given in γ units. The electronic structure at Fermi level is affected in several ways. First, it is interesting to point out that disorder up to $W=1.0$ does not break localization properties of nanotubes. Unlike the usual 1D system where the slightest disorder induces Anderson localization mechanism,

CN may be considered as marginal one-dimensional (1D) quantum nanostructures where quantum confinement takes place but existing phenomena in 1D structures undergo specific alterations, the effect of disorder being one of them. One has to reach higher values of disorder strengths ($W \sim 1.5$) to break such localization.

If we consider the enlargement of the DoS over the entire bandwidth (Fig. 5), one clearly sees that from $W=1.5$, all the one-dimensional van Hove singularities have disappeared. This is a signature that quantum confinement has been disrupted by disorder. Besides, for $W=3$ bandwidth is enlarged by $1/4$ of the total bandwidth, which is a rather small increase of the bandwidth. Probably the localization length is then smaller than the circumference of the CN.

We then consider the evolution of local and total densities of states as a function of ν for $W=0, 0.5, 1.5$. In Fig. 6, the case $W=0$ is given and compared with low-disorder limit $W=0.5$ (inset). For each value of ν , we plot a different LDoS on a given site. The effect of low disorder is shown not to affect significantly the general metal-insulator pattern discussed earlier. This is also the case for stronger disorder. However, for a disorder width as large as 1.5 (lower part of Fig. 6), the LDoS in the low-magnetic-field regime is strongly affected by the appearance of strong fluctuations between different LDoS's, the periods of which further increases with magnetic strength. As ν approaches 1, one recovers the basic pattern that magnetic field will induce a metal-insulator transition. Averaging over some 10 LDoS's reduces the amplitude of such fluctuations, but the TDoS at Fermi energy for the low disorder limit seems to be increased (bold curve in lower part of Fig. 6).

We believe that this effect of fluctuations may have significant consequences on the electronic properties of CN, for instance, affecting the ideal properties of nanoscale metal-semiconductor contact devices⁸ made from CN. This should also be considered carefully in relation to UCF. Indeed, it is generally assumed that UCF reflects the microscopic random potential where electrons are propagating. The pattern of the fluctuations of conductance as a function of Fermi energy or magnetic field, being quite random but reproducible and

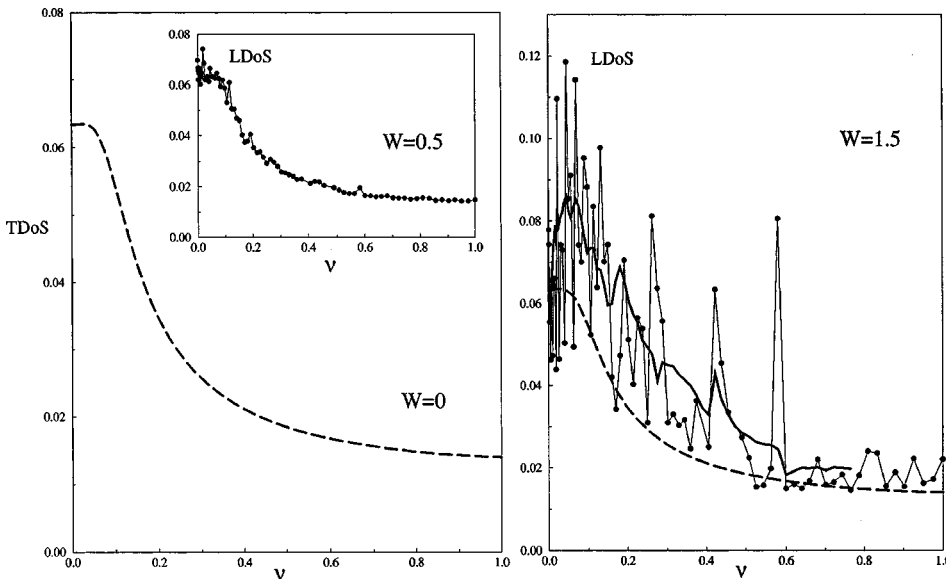


FIG. 6. On the left-hand side picture, TDoS and LDoS (inset) of carbon nanotube (9,0), as a function of magnetic field are presented for disorder strengths $W=0, 0.5$. On the right-hand side picture, TDoS (dashed line) for $W=0$ is plotted together with different LDoS (bullet line) and average LDoS on 10 sites (bold line) for disorder $W=1.5$.

fluctuating from sample to sample. The only common feature is that the fluctuations are of order of e^2/h independently of sample quality, size, and so forth.

To some extent, the LDoS from one site to another is also related to the local potential around a given carbon atom, and if general UCF may be seen as a consequence of fluctuations in the potential distribution, universal fingerprints may also emerge in local spectral properties. Besides, as the LDoS can be directly related to tunneling current from tips to the surface, such fluctuations may be indirectly related to STM experiments. Calculation of Kubo conductivity by means of the real-space recursion method⁹ may also lead to valuable information about transport properties.¹⁷

IV. CONCLUSION

We have shown several patterns occurring in the electronic spectra of metallic or semiconducting carbon nanotubes and induced by magnetic field and disorder. Magnetic

field was shown to lead to a continuous metal-insulator transition in both kinds of CN, whereas disorder was shown not to be modified qualitatively the above-mentioned pattern. Strong fluctuations of the LDoS as a function of site environment and magnetic field were found and may be of importance when designing junction devices.

ACKNOWLEDGMENTS

S.R. is indebted to the European Commission and the Japanese Society for Promotion of Science (JSPS) for joint financial support (Contract No. ERIC17CT960010), and to Professor T. Fujiwara from the Department of Applied Physics of Tokyo University for his kind hospitality. Part of the work by R.S. was supported by a Grant-in Aid for Scientific Research (No. 10137216) from the Ministry of Education and Science of Japan. The work of S. R. has been conducted within the GERMA project (Groupe d'Etude et de Recherches sur les matériaux avancés).

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