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Dielectric relaxation of a reentrant nematic-liquid-crystal mixture by time-domain reflectometry

R. Nozaki, T. K. Bose, and S. Yagihara*

Groupe de Recherche sur les Diélectriques, Département de Physique, Université du Québec à Trois-Rivières,
Code Postale 500 Trois-Rivières, Québec, Canada G9A 5H7

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Complex-permittivity measurements of a reentrant nematic-liquid-crystal mixture, 4-*n*-hexyloxy-4′-cyanobiphenyl and 4-*n*-octyloxy-4′-cyanobiphenyl, for both the parallel and perpendicular components, have been performed by time-domain reflectometry in the frequency range between 300 kHz and 10 GHz and at temperatures from 58 °C (above the nematic and smectic-*A* phase-transition temperatures) down to 25 °C (below the smectic-*A* and the reentrant nematic phase-transition temperatures). It is shown that the molecular rotation around the short axis in the reentrant nematic phase is much hindered compared to that in the nematic phase, but the motion around the long axis is the same for both phases. It is also shown that, for the parallel component, the activation energy for the smectic-*A* phase is larger than that for the nematic phase but similar to that of the reentrant nematic phase. Finally, the transition between the reentrant nematic and the solid phases is discussed.

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I. INTRODUCTION

We have already shown that the time-domain reflectometry (TDR) is one of the most appropriate techniques to study the dielectric properties of liquid crystals over a wide frequency range [1–4]. Dielectric-relaxation phenomena of liquid crystals observed in the radio and microwave frequency range are easily studied by the TDR method.

In the case of liquid crystals, two kinds of dielectric relaxation are well known. One is due to the rotational motion of molecule around the short axis and the other is around the long axis. Normally, the frequency range for the former relaxation is between 100 kHz and 10 MHz [1,2,6,7]. On the other hand, a broad relaxation in the frequency range between 100 MHz and 10 GHz is usually observed for the rotation around the long axis [1,2,7].

In this paper, we present experimental results of the dielectric-relaxation study for the mixture of 4-*n*-hexyloxy-4′-cyanobiphenyl (6OCB) and 4-*n*-octyloxy-4′-cyanobiphenyl (8OCB). This 6OCB-8OCB mixture possesses a reentrant nematic phase [5]. For the parallel component of the complex permittivity, where the electric field is parallel to the molecular long axis, the relaxation frequency is due to molecular rotation around the short axis [6,7], and is about a few megahertz [8].

For the perpendicular component of the complex permittivity, where the electric field is perpendicular to the molecular long axis, the relaxation frequency is due to the molecular rotation around the long axis [6,7]. Only static permittivity results exist in the literature for the perpendicular component [8,9]. No one has ever reported the dynamical study for the perpendicular component.

We present here a dielectric study of the mixture, 27.3 wt. % of 6OCB in 8OCB, both for the parallel as well as the perpendicular components. The complex-permittivity measurements have been performed by means of the TDR method in the frequency range between 300 kHz and 10 GHz at temperatures from 58 °C down to 25 °C.

It is found that the molecular motion around the short axis in the reentrant nematic phase is much hindered compared to that of the high-temperature nematic phase. This result agrees with that obtained by Ratna, Shashidhar, and Rao [8]. However, we observed that for the parallel component, the activation energy in the smectic phase is larger than that in the nematic phase, contrary to the result given by Ratna, Shashidhar, and Rao [8]. Further, it is also found that a reentrant nematic and the solid phase transitions show anomalous behavior of dielectric parameters.

II. EXPERIMENT

The liquid-crystal mixture (6OCB 27.3 wt. % in 8OCB) was prepared from pure substances given by Raman Institute of Science, Bangalore, India. The transition temperature T_{SN} (between the smectic-*A* and the nematic phases) and T_{RS} (between the reentrant nematic and the smectic-*A* phases) are 40.3 °C and 35.7 °C, respectively.

The complex-permittivity measurements of the mixture in the frequency range from 300 kHz to 10 GHz were performed by means of the time-domain-reflectometry method using a Hewlett-Packard system (Model HP54120T). The experimental setup and the detailed procedure to obtain the complex permittivity by use of the TDR system have already been reported [2,4].

Two static magnets with the pole-face diameter of 70 mm were used to produce a uniform magnetic field. The distance between the poles is 15 mm and the magnetic-flux density is 14 000 G. The experimental dielectric cell connected with a coaxial line is positioned between the poles. The coaxial line used is a flexible 50-Ω line (Model DGM024, frequency range dc–18.5 GHz, Junkohsha, Japan).

In order to make an anisotropic measurement, two different cell configurations have been used. A parallel-plate capacitor with a plate diameter of 4 mm and the distance between the two plates 0.5 mm is placed at the end of a 3.5-mm 50-Ω coaxial line using a SMA (subminiature series A) female-female connector. In this case, the plates are perpendicular to the magnetic field so that the measurement gives the perpendicular component of the complex permittivity $\epsilon^*_\perp$. The effective electrical length of the cell is 6.7 mm.

The other cell has the normal coaxial configuration so that the half-parallel and half-perpendicular component of the complex permittivity $\epsilon_{\rm hp}$ is obtained. This cell is also attached to the SMA connector located at the end of 50-Ω coaxial line. The mechanical and the effective electrical cell lengths are, respectively, 10 mm and 29.5 mm.

The cell temperature is stabilized by using a water-flow jacket controlled by a refrigerated bath circulator (NESLAB; Model RTE-210). In order to change the temperature, the setting point for the bath is controlled by a 16-bit DOS-based computer using a 12-bit digital-to-analog converter. In this work, all the complex-permittivity measurements have been taken using the cooling path with two different cooling rates, 4.05 °C/h (fast) and 1.76 °C/h (slow).

III. RESULTS AND ANALYSIS

Frequency dependence of the half-parallel and the half-perpendicular component of the complex permittivity $\epsilon^*_{\rm hp}$ for the liquid-crystal mixture at 58 °C (in the nematic phase) is shown in Fig. 1. It is very clear that a large relaxation exists around 2 MHz. At the higher-frequency side of the relaxation, another somewhat broad relaxation seems to exist around 100 MHz.

In Fig. 2, a similar plot for the perpendicular component of the complex permittivity $\epsilon^*_\perp$ is shown. It is clear from the figure that a broad relaxation exists around 100 MHz.

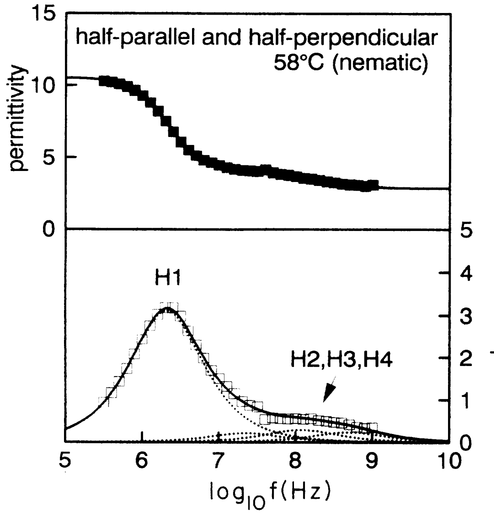

FIG. 1. Frequency dependences of permittivity and loss for half-parallel and half-perpendicular component at 58 °C. Solid curves are obtained from Eq. (3). Dotted curves show result of decomposition.

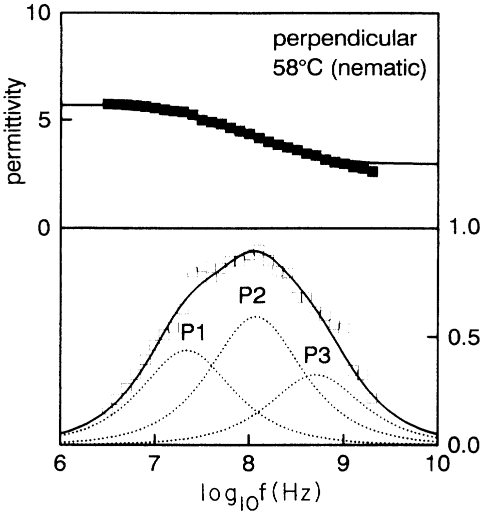

FIG. 2. Frequency dependences of permittivity and loss for perpendicular component at 58 °C. Solid curves are obtained from Eq. (2). Dotted curves show result of decomposition.

We performed a spectral decomposition procedure based on multiple Debye processes [3,10]. The following equation is used to describe the experimental data:

$$\epsilon^*_{\rm expt} = \sum_k^m \frac{\Delta_\epsilon k}{(1+j\omega\tau_k)} + \epsilon_\infty , \qquad (1)$$

where $\epsilon^*_{\rm expt}$ is the measured complex permittivity, ω is the angular frequency, and ϵ_∞ is the high-frequency limiting permittivity. $\Delta\epsilon_k$ and τ_k are the dielectric-relaxation strength and time, respectively, for the kth process. The number of processes m involved in the measured data is estimated using a least-squares-fitting procedure.

It is found that the experimental results for the perpendicular component of the complex permittivity $\epsilon^*_\perp$ are well explained by using three Debye processes (processes P1, P2, and P3), as shown below:

$$\epsilon^*_\perp = \sum_{k={\rm P1,P2,P3}} \frac{\Delta\epsilon_k}{(1+j\omega\tau_k)} + \epsilon_{\infty\perp} , \qquad (2)$$

where $\epsilon_{\infty\perp}$ is the high-frequency limiting permittivity of the perpendicular component.

On the other hand, for the half-parallel and half-perpendicular component, it is found that the large relaxation in the frequency region near 2 MHz can be explained exactly only by one Debye process (process H1). The broad relaxation at the higher-frequency side can be well described by use of three Debye processes (processes H2, H3, and H4). In this case, the half-parallel and half-perpendicular component of the complex permittivity $\epsilon^*_{\rm hp}$ is given by

$$\epsilon^*_{\rm hp} = \frac{\Delta\epsilon_{\rm H1}}{(1+j\omega\tau_{\rm H1})} + \sum_{k={\rm H2,H3,H4}} \frac{\Delta\epsilon_k}{(1+j\omega\tau_k)} + \epsilon_{\infty{\rm hp}} , \qquad (3)$$

where $\epsilon_{\infty{\rm hp}}$ is the high-frequency limiting permittivity of the half-parallel and half-perpendicular component. The first term in Eq. (3) describes the dominant relaxation and the remaining terms give the higher-frequency relation. Examples of the decomposition are also shown in Figs. 1 and 2.

According to these figures, each relaxation frequency (which gives maximum loss at this frequency) of the three processes at higher-frequency side of the half-parallel and half-perpendicular component of the complex permittivity (H2, H3, and H4) correspond well to the three processes in the perpendicular component (P1, P2, and P3). It is also found that the value of each dielectric-relaxation strength of the three processes (H2, H3, and H4) is approximately half of that of the corresponding process (P1, P2, and P3).

Based on these facts, it can be concluded that somewhat broad relaxation at the higher-frequency side in the half-parallel and the half-perpendicular component of the complex permittivity is essentially due to the relaxation of the perpendicular component. We have observed similar results for 4-*n*-heptyl-4′-cyanobiphenyl (7CB) and 4-*n*-octyl-4′-cyanobiphenyl (8CB) [2].

Finally, we can obtain the dielectric parameters for relaxations in the parallel and perpendicular components from the relation

$$\epsilon^*_{\mathrm{hp}}=\tfrac{1}{2}(\epsilon^*_{\parallel}+\epsilon^*_{\perp}) , \tag{4}$$

where $\epsilon^*_{\parallel}$ is the parallel component of the complex permittivity.

First, for the perpendicular component, the relaxation strength $\Delta\epsilon_{\perp}$ and the static permittivity $\epsilon_{S\perp}$ are calculated from each of the three processes shown below:

$$\Delta\epsilon_{\perp}=\Delta\epsilon_{\mathrm{P1}}+\Delta\epsilon_{\mathrm{P2}}+\Delta\epsilon_{\mathrm{P3}} , \tag{5}$$

$$\epsilon_{S\perp}=\Delta\epsilon_{\perp}+\epsilon_{\infty\perp} . \tag{6}$$

The dielectric-relaxation time τ_{P2} can be used as a dominant one for the perpendicular component $\tau_{\perp}$; then

$$\tau_{\perp}=\tau_{\mathrm{P2}} . \tag{7}$$

On the other hand, for the parallel component, the dielectric strength $\Delta\epsilon_{\parallel}$, the static permittivity $\epsilon_{s_{\parallel}}$, and the relaxation time $\tau_{\parallel}$ are given by

$$\Delta\epsilon_{\parallel}=2\Delta\epsilon_{\mathrm{H1}} , \tag{8}$$

$$\epsilon_{S\parallel}=\Delta\epsilon_{\parallel}+2\epsilon_{\infty\mathrm{hp}}-\epsilon_{\infty\perp} , \tag{9}$$

$$\tau_{\parallel}=\tau_{\mathrm{H1}} . \tag{10}$$

Temperature dependence of the static permittivity for both the parallel and the perpendicular components are shown in Fig. 3. In this case, two kinds of experimental results with different cooling rates, as we have already mentioned, are shown. The value of the static permittivity agrees well with the literature values [8,9] in the nematic phase and the smectic-*A* phase, and also with the higher-temperature region in the reentrant nematic phase. In the lower-temperature region in the reentrant nematic phase, however, we have quite different results from those in the literature. It is found that at certain temperatures below T_{RS}, the value of the static permittivity sometimes decreases quickly with decreasing temperature for both the components.

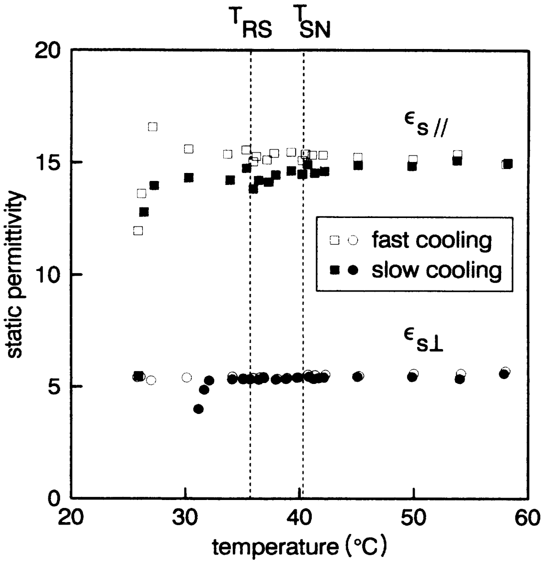

FIG. 3. Temperature dependence of static permittivity.

The logarithm of frequency giving the maximum loss for the relaxation in the parallel component $\log_{10}f_{m\parallel}$ [$=\log_{10}(2\pi\tau_{\parallel})^{-1}$], is plotted against the reciprocal of the absolute temperature $1/T$ in Fig. 4. In the same figure, the dielectric strength of the relaxation $\Delta\epsilon_{\parallel}$ is also plotted.

Figure 4 shows that $\log_{10}f_{m\parallel}$ is proportional to $1/T$ and exhibits discontinuities at the transition temperatures. Ratna, Shashidhar, and Rao [8] have reported that

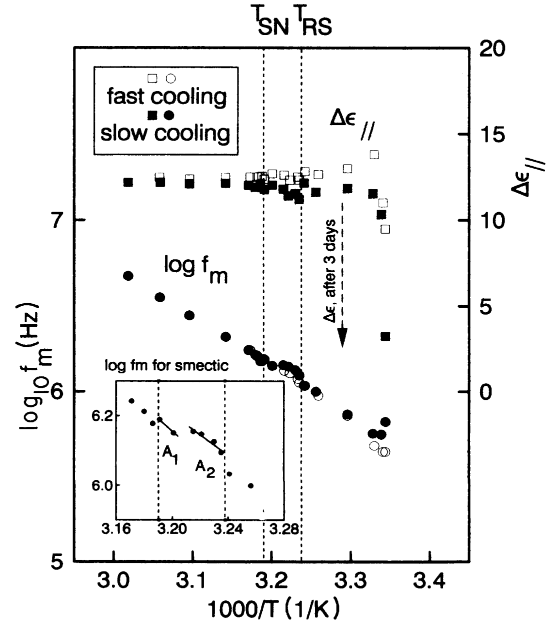

FIG. 4. $\mathrm{Log}_{10}f_{m\parallel}$ and $\Delta\epsilon_{\parallel}$ vs $1/T$.

TABLE I. ΔH in eV for 6OCB-8OCB mixture at various phases.

Parallel component			
nematic	smectic-A_1	smectic-A_2	reentrant nematic
0.56	0.75	0.68	0.71

Perpendicular component		
nematic	smectic-A	reentrant nematic
0.20	0.33	0.23

in the smectic-A phase, there are two temperature regions that give different apparent activation energies. We also observe similar phenomenon as can be seen in Fig. 4. We identify these two regions as smectic-A_1 and smectic-A_2.

The value of $\Delta\epsilon_\parallel$ is almost constant over wide temperature range, although the data below T_{SN} are somewhat distorted. However, it decreases quickly at a certain temperature below T_{RS}. From the comparison with the result for the static permittivity (Fig. 3), it may be concluded that the decrease of $\epsilon_{s\parallel}$ is due to the decrease of $\Delta\epsilon_\parallel$.

Values of apparent activation energy ΔH for nematic, smectic-A_1, smectic-A_2, and reentrant nematic phases are given in Table I. For the calculation of ΔH in the reentrant nematic phase, the data points at which $\Delta\epsilon_\parallel$ decreases are not used.

For the perpendicular component, $\log_{10} f_{m\perp}$ $[=\log_{10}(2\pi\tau_\perp)^{-1}]$ and $\Delta\epsilon_\perp$ are shown in Fig. 5. We also observe linear relation between $\log_{10} f_{m\perp}$ and $1/T$. Discontinuities in $\log f_{m\perp}$ at the transition temperatures are also found but no additional discontinuity can be seen in the smectic-A phase. The value of $\Delta\epsilon_\perp$ seems to have positive temperature dependence but the change in the temperature range used here is very small. It is also clear that $\Delta\epsilon_\perp$ decreases quickly with fast cooling rate at certain temperatures below T_{RS} but does not show this phenomenon for the slow cooling rate. Anyway, from the comparison between Figs. 3 and 5, it may be concluded that the decrease of $\Delta\epsilon_{s\perp}$ is essentially due to the decrease of $\Delta\epsilon_\perp$.

The values of ΔH for each phase are listed in Table I. For the calculation, we follow the same procedure as is done for the parallel component; the data with decreased $\Delta\epsilon_\perp$ are not used.

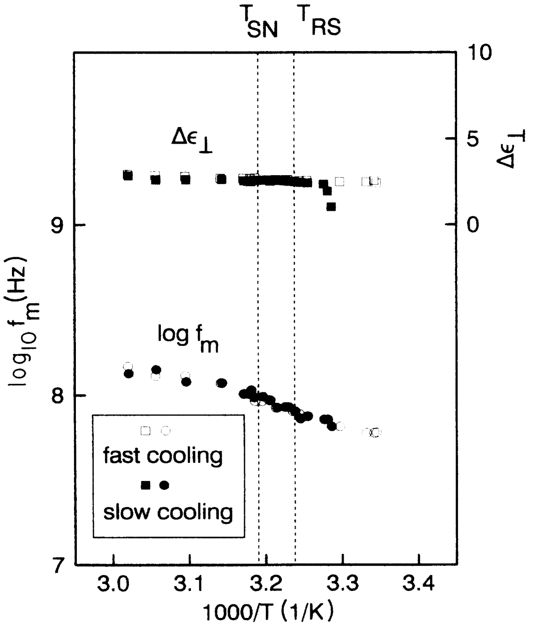

FIG. 5. $\mathrm{Log}_{10} f_{m\perp}$ and $\Delta\epsilon_\perp$ vs $1/T$.

IV. DISCUSSION

The values of ΔH for the parallel component have been reported by Ratna, Shashidhar, and Rao [8]. In the case of the smectic-A phase, our values of the activation energy 0.75 and 0.68 eV, respectively, for the smectic-A_1 and smectic-A_2, are in good agreement with the values 0.73 and 0.71 eV obtained by Ratna, Shashidhar, and Rao [8].

Our value of ΔH for the nematic phase 0.56 eV is smaller than 0.82 eV found by Ratna, Shashidhar, and Rao. Although the composition of our mixture is different from their composition, the difference in the ΔH value seems to be significantly large. The discrepancy may be due to the fact that our temperature range used for nematic measurements is almost 18 °C, which is much larger compared to their range of 3 °C. Finally, the lower ΔH value for the nematic phase is more plausible because the nematic phase is expected to have lower viscosity than the smectic phase.

According to our results for the parallel component, the value of ΔH in the reentrant nematic phase 0.71 eV is greater than 0.56 eV in the nematic phase. This tendency has also been observed by Ratna, Shashidhar, and Rao [8], who suggested that the rotational motion around the short axis is much hindered in the reentrant nematic phase.

Contrary to the parallel component, the value of ΔH for the perpendicular component in the nematic phase 0.20 eV is very similar to that in the reentrant nematic phase 0.23 eV. This suggests that the molecular motion around the long axis is very similar between the two phases.

The value that we determined for the parallel component in the reentrant nematic phase 0.71 eV is small compared to the value of 1.71 eV given by Ratna, Shashidhar, and Rao [8]. It should be noted that in our calculation of ΔH for the reentrant nematic phase, we only include the data before the sharp decrease of $\Delta\epsilon$ (Fig. 4). Actually, the value of ΔH given by using the data with fast cooling rate below the temperature at which $\Delta\epsilon_\parallel$ begins to decrease with decreasing temperature is 0.88 eV, which is larger than 0.71 eV. This may perhaps explain the discrepancy between our two values.

As we have already mentioned earlier in this paper, the values of $\Delta\epsilon_\parallel$ decrease drastically at a certain temperature below T_{RS} as shown in Fig. 4. Since the temperature dependence of $\Delta\epsilon_\parallel$ clearly follows step change, the observed anomalous phenomenon is probably due to order-disorder transition (first-order transition) [11].

It is well known that the reentrant nematic phase passes into the "solid" phase at a lower temperature [8]. Although precise transition temperature between the reentrant nematic and the solid phases T_{RX}, has not been discussed, it seems possible that all these anomalous phenomena are due to this transition.

According to the x-ray study of the mixture [14], it has been suggested that the molecules tend to make antiparallel pairs in the reentrant nematic phase with decreasing temperature. Since the dipole moment attached to the molecule is parallel to its long axis, such antiparallel pairs make the macroscopic polarization small. However, there is substantial pair formation even in the normal nematic phase for this kind of biphenyl liquid crystals. Hence any additional contribution from the antiparallel pairs in the reentrant nematic phase resulting in the decrease of $\Delta\epsilon_{\parallel}$ near T_{RX} would be rather small.

According to Zeller [12], the parallel components of the complex permittivity in some nematic liquid crystals show glass transition phenomena. In this case, temperature dependence of the dielectric-relaxation time follows the Vogel-Fulcher law. This suggests that the free volume is essential for the rotational molecular motion around the short axis [13]. Near T_{RX}, the rotational motion would be hindered because of decreasing free volume. The larger value of ΔH (0.88 eV) obtained for the lower-temperature region below T_{RX} may be due to this effect.

However, the relaxation frequency for the perpendicular component is not affected by the transition at all. According to [12], the rotational diffusion is essential for the motion around the long axis rather than free volume. On the other hand, because of the decrease of $\Delta\epsilon_{\perp}$, it would be natural to consider that the degree of freedom for the motion is restricted below T_{RX} even though the rate of the motion remains unchanged.

The value of T_{RX} obtained here by the parallel component measurement with constant cooling rate is about 25 °C (Fig. 3). This agrees with the value reported by Ratna, Shashidhar, and Rao [8] even for the mixture with different composition. However, the perpendicular component measurement with fast cooling rate shows that this transition occurs even at 32°C as indicated in Fig. 3. Therefore, we performed another measurement for the parallel component in the same manner as we used with a constant cooling rate. But, in this case, we decreased temperature only down to 30 °C and kept it constant. Finally, after 3 days, the value of $\Delta\epsilon_{\parallel}$ decreased as shown in Fig. 4.

This behavior observed in $\Delta\epsilon$ both for the parallel and the perpendicular component measurement is very similar to well-known supercooled liquids. It seems that the reentrant nematic phase is easy to be supercooled with decreasing temperature. Thus determination of T_{RX} should be done carefully by using very slow cooling rate. Further work in this domain may give us more useful information to understand the reentrant nematic phase.

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*Present address: Department of Communication Engineering, Tokai University Junior College, 2-3-23 Takanawa, Minato-ku, Tokyo 194, Japan.

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