

# Carbon nanothermometer containing gallium

Gallium's macroscopic properties are retained on a miniature scale in this nanodevice.

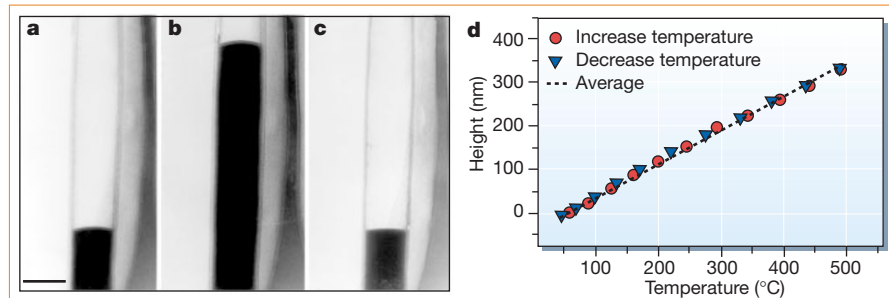
Many applications have been found for carbon nanotubes<sup>1–8</sup>, and we can now add a role as a 'nanothermometer' to this list. We describe how the height of a continuous, unidimensional column of liquid gallium inside a carbon nanotube (up to about 10 micrometres long and about 75 nanometres in diameter) varies linearly and reproducibly in the temperature range 50–500 °C, with an expansion coefficient that is the same as for gallium in the macroscopic state. We chose gallium as our thermal indicator because it has one of the greatest liquid ranges of any metal (29.78–2,403 °C) and a low vapour pressure even at high temperatures<sup>9</sup>. This nanothermometer should be suitable for use in a wide variety of microenvironments.

We investigated the behaviour of gallium inside carbon nanotubes (diameter, 40–150 nm) using a microscope equipped with a Gatan holder and twin heating system. Figure 1a–c shows a gallium column of diameter 75 nm and a continuous length of up to 7,560 nm. When the column temperature is increased or decreased in the range 50–500 °C, the gallium level rises or falls consistently.

The variation with temperature of the height of the gallium meniscus in its carbon nanotube is plotted in Fig. 1d, using the level at 58 °C as a reference. Changes in the length and diameter of the carbon nanotube itself can be disregarded because of the minute linear expansion coefficient<sup>10</sup> of graphite (about  $-1 \times 10^{-6}$  per °C at 20–500 °C), so the height of the gallium column is determined by its volume at that temperature.

The volumetric change of liquid gallium in the macroscopic state upon heating is described by  $v_t = v_0(1 + \alpha\Delta t)$ , where  $v_t$  and  $v_0$  are the volumes at temperatures  $t$  and  $t_0$  respectively,  $\Delta t = t - t_0$ , and  $\alpha$  is the volumetric-expansion coefficient ( $0.1015 \times 10^{-3}$  per °C at 30–977 °C, derived from measurements of density against temperature<sup>9</sup>). Our results indicate that this description also applies to nanoquantities of one-dimensional liquid gallium: calculations on the basis of its change in volume with temperature give a value for  $\alpha$  of  $0.095 \pm 0.006 \times 10^{-3}$  per °C, which is comparable to that for macroscopic liquid gallium. In this respect, the expansion coefficient differs from another basic thermal property, the melting point, which is greatly influenced by the surface effect<sup>11</sup>.

Because the gallium meniscus level in a carbon nanotube moves linearly and reproducibly with temperature in the range 50–500 °C, it meets the requirements of a filled-system thermometer in this range. For such a nanothermometer, the temperature



**Figure 1** Expansion of gallium inside a carbon nanotube with increasing temperature. **a–c**, Changing level of the gallium meniscus at 58 °C (**a**), 490 °C (**b**) and 45 °C (**c**); scale bar, 75 nm. **d**, Height of the gallium meniscus plotted against temperature, measured in steps of 30–50 °C; results are averaged (green curve) from closely similar measurements obtained during heating (red) and cooling (blue). The nanothermometer was synthesized in a vertical radiofrequency furnace (which differs from a one-step arc-discharge method). A homogeneous mixture of Ga<sub>2</sub>O<sub>3</sub> and pure, amorphous, active carbon (weight ratio, 7.8:1) was reacted in an open carbon crucible under a flow of pure N<sub>2</sub> gas: at 1,360 °C, the reaction Ga<sub>2</sub>O<sub>3</sub>(solid) + 2C(solid) → Ga<sub>2</sub>O(vapour) + 2CO(vapour) occurs. However, on the inner surface of a pure graphite outlet pipe at the top of the furnace, the temperature is lower (around 800 °C), causing the reaction Ga<sub>2</sub>O(vapour) + 3CO(vapour) → 2Ga(liquid) + C(solid) + 2CO<sub>2</sub>(vapour) to occur, during which the 'nanothermometers' are created.

can be measured as  $t = 58 + \Delta h/0.753$ , where  $\Delta h$  (in nm) is the difference in the height of the gallium column at  $t$  °C and 58 °C.

It should be feasible to read the temperature recorded by the nanothermometer *in situ* with the help of a scanning electron microscope, given that the walls of the carbon nanotube and the space inside, as well as the gallium level, can be clearly seen even using an instrument operated at 10 keV. Because it has a measuring range of 50–500 °C, our nanothermometer will extend temperature measurement beyond the 4–80 K range attainable by resistance micrometre-sized cryogenic thermometers<sup>12</sup>. It is easy to use, as the gallium meniscus is almost perpendicular to the inner surface of the carbon nanotube and the liquid column is continuous and long (up to 10 μm). The potential application proposed here follows on from several studies based on the discovery that carbon nanotubes can be filled with metal<sup>13</sup>.

## Psychobiology

### Speech sounds learned by sleeping newborns

It is not yet clear whether humans are able to learn while they are sleeping<sup>1,2</sup>. Here we show that full-term human newborns can be taught to discriminate between similar vowel sounds when they are fast asleep. It is possible that such sleep training soon after birth could find application in clinical or educational situations<sup>3,4</sup>.

We used mismatch negativity (MMN) to determine the ability of human newborns to detect a change in speech sounds.

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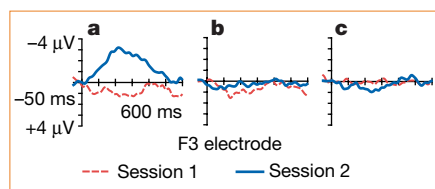
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MMN is an attention-independent electrophysiological brain response which is elicited by infrequent discriminable changes in auditory stimuli<sup>5</sup>. MMN can be observed in young infants throughout all sleep stages as well as when they are awake<sup>6–8</sup>.

We used MMN recordings to analyse the responses of three groups of full-term newborns (experimental group,  $n = 15$ , age 1–7 days; two control groups,  $n = 15$  in both, age 2–7 days) to the vowel sounds /y/ ('standard',  $p = 0.8$ ), /i/, and /y/i/ ('deviants',  $p = 0.1$  for each) while they were asleep (for details of stimuli, see ref. 6). All groups underwent identical MMN recording sessions in the evening (session



**Figure 1** Mismatch negativity (MMN) results from two recording sessions, one in the evening and one the next morning, of responses to deviant speech sounds (/y/) in three groups (one experimental and two control groups) of human newborns. **a**, Experimental group, which underwent nocturnal training. The significant difference between results from the pre- and post-training sessions in this group suggests that sleeping newborns are better able to discriminate the speech sounds /y/ and /y/i/ after training. **b, c**, Control group 1 (**b**), which was not exposed to any training, and control group 2 (**c**), which was trained to discriminate between other vowel sounds, show no difference between the two sessions. The electro-encephalographic output was averaged and digitally filtered (1–30 Hz) at two frontal and two central scalp sites as well as two eye electrodes (for exclusion criteria and other details, see ref. 6). Mean MMN amplitude was calculated relative to a 60-ms period centred on the largest peak between 150 and 400 ms from stimulus onset in all except the eye electrodes. The presence of MMN was tested by using two-tailed *t*-tests for dependent samples.

1) and the next morning (session 2); the experimental group also had a session the following evening (session 3). Control group 1 received no training during the night, but the experimental group and control group 2 were exposed to nocturnal auditory training during sleep between sessions 1 and 2. Each MMN recording session lasted for just under 1 hour; in the experimental group, the training session was carried out over 2.5–5.0 hours. The experimental group and control group 2 were treated identically in sessions 1 and 2, except that during training the second control group was presented with /a/ and /e/ sounds instead of /y/ and /i/.

Throughout all sessions in all groups, a randomized sequence consisting of standards and deviants was presented online. In addition to pre-training stimuli with the experimental group, during session 2 we presented stimuli of different pitches that were otherwise identical: this was to determine whether the infants were simply learning acoustical discrimination or whether their increased discrimination ability was related to speech sounds.

The results from both pre- and post-training sessions showed that MMN responses to the acoustically ‘easier’ /i/ deviant stimulus (*t*(14) varying between 2.5–5.8) were statistically significant in all groups. In session 1, the MMN amplitude was significantly smaller for the deviant /y/i/ than for /i/ in all groups, but no differences were found between the groups (*F*(1,84), 8.62, *P*<0.004) in a three-way ANOVA analysis (group *X*, stimulus *X*, electrode (F3, F4, C3, C4)). The difference between sessions 1 and 2 in all groups and

for both deviants was separately tested by using a two-way ANOVA (session *X*, electrode). In both control groups, no statistical difference in MMN amplitude was found between sessions 1 and 2.

Our main finding was that experimental subjects learned to discriminate both deviants from the standard after training (Fig. 1). In this group, the MMN elicited by /y/i/ was not significant in session 1 (mean, -0.28; s.d. 2.19) but it was in session 2 (mean, -3.76; s.d. 2.04). The difference between sessions 1 and 2 was *F*(1,28), 16.58, *P*<0.0003. Moreover, the MMN response for the /i/ deviant increased strikingly in amplitude after training (*F*(1,28), 27.57, *P*<0.00001). There was no significant reduction in MMN amplitude between sessions 2 and 3 for either deviant in the experimental group.

The experimental group learned not only to discriminate between the stimuli to which they were exposed during training, but also between stimuli (not presented to them during training) that had different F0 values (pitch) but were otherwise identical. The differences obtained in session 2 in response to the trained and non-trained stimuli were tested by using two-way ANOVAs (deviant (trained and untrained), *X* electrode): no significant deviant effect was found for either deviant. Moreover, the experimental group exhibited a significant MMN response to both deviants in session 3, indicating that the training effect lasted for some time. In separate two-way ANOVAs (session *X*, electrode), no significant session effect was found for either deviant.

We have shown that newborns can assimilate auditory information while they are sleeping, suggesting that this route to learning may be more efficient in neonates than it is generally thought to be in adults.

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Microstructures

## Spin-engineering magnetic media

The explosion in demand for increased data-storage density is driving the exploration of new magnetic media.

Here we describe a new type of magnetic medium in which the spin configurations are engineered in chemically homogeneous magnetic films: regularly arranged in-plane and out-of-plane spin configurations are defined by altering the magnetic anisotropy. These spin-engineered media not only maintain the surface planarity but also the homogeneity of the magnetic materials, and our method is likely to find immediate application on account of its simplicity and ease of integration.

Two approaches are being used in the search for ultrahigh-density magnetic recording media. One is based on a conventional, continuous film medium, in which the storage density is increased by stabilizing the nanoscale magnetic domains in order to resist the thermal self-erasure effect<sup>1</sup>. The other depends on the patterning of magnetic films into magnetically isolated dots<sup>2</sup>, with each dot containing two discrete magnetized states with equal but opposite magnetic moments. Each dot is thus able to store one bit of information.

We used a modulated single/polycrystalline substrate surface to modify locally the magnetic anisotropy in subsequently deposited magnetic films, which induces the desired artificial magnetic structure. Selective epitaxial growth introduces an alternation between single-crystal and polycrystalline structures in the film, according to the substrate patterning (Fig. 1a). Epitaxial Ni/Cu(001) films of appropriate thickness show perpendicular magnetization, which is due to the magneto-elastic interaction induced by the Ni/Cu(001) interface<sup>3,4</sup>. In contrast, the magnetization of polycrystalline nickel lies in the film plane because of the dominant demagnetizing field. The substrates used are GaAs(001) and two types of pattern were chosen: wire and dot array.

The arrays were obtained by lithography