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Disorder effects in low concentration dispersions of small quartz spheres in cyanobiphenyl liquid crystals

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A photopyroelectric study of the specific heat and the thermal conductivity of small quartz sphere (aerosil) dispersions in heptylcyanobiphenyl (7CB) and octylcyanobiphenyl (8CB) liquid crystals with a concentration $\rho_s = 0.005\ \mathrm{g\,cm^{-3}}$ is reported. The thermal conductivity data show that, even at this low concentration, the elastic strain introduced in the liquid crystal by the aerosil particle is not completely annealed at the nematic-isotropic (NI) phase transition. In 8CB, annealing has been found at the smectic-nematic phase transition, while in the case of 7CB it occurs in the nematic phase also. Moreover, the depression of the NI transition temperature has been found to be much smaller than the one predicted by a random field model in which quenched disorder simply affects the average order of the sample and no effects of the elastic strain are considered. [S1063-651X(99)50911-2]

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It has been recently suggested [1] that hydrophilic small quartz sphere (aerosil) particles with a diameter of approximately 7 nm [2] dispersed in a liquid crystal (LC) form a gel if their density is larger than $\rho_s = 0.01\ \mathrm{g\,cm^{-3}}$. These particles are small quartz spheres that, due to the hydroxyl groups covering their surface, can hydrogen bond in a network and allow the introduction of disorder in LCs. This is essentially due to the hydrophilic coating of the spheres that provides a strong homeotropic anchoring of the LC molecules at the particle surface and therefore produces a local distortion of the director resulting in an elastic strain (ES) which increases with decreasing pore size and therefore with increasing ρ_s. If $\rho_s < 0.1\ \mathrm{g\,cm^{-3}}$, the gel is "soft," this meaning that the bonds among the spheres can easily break, allowing a rearrangement of the particle to form a network in which the elastic energy and therefore the ES in the LC are minimized. If $\rho_s > 0.1\ \mathrm{g\,cm^{-3}}$, the gel is "rigid" and the ES is quenched.

The mechanisms described above have been used to interpret the experimental results up till now available in the literature [1,3–6]. A substantial decrease of the transition temperature and a broadening of the specific heat (c) peaks have been found in dispersions with $\rho_s > 0.1\ \mathrm{g\,cm^{-3}}$. These results have been shown to be quite similar to the ones obtained in aerogel [7] and randomly interconnected porous media [8], and this is not surprising if one considers the rigid nature of the gel formed at these concentrations. In both cases the experimental results have been explained in terms of the quenched ES present in the sample [1]. For concentrations $\rho_s < 0.1\ \mathrm{g\,cm^{-3}}$ the observed behavior of aerosil dispersions [1] differ substantially from the aerogel one: the decrease of transition temperatures show a complicated behavior as a function of ρ_s, while the peaks in c remain sharp. Moreover, the specific heat critical exponent α at the smectic-A–nematic (AN) transition tends to the one predicted by the three-dimensional (3D) XY model as ρ_s is increased up to $0.1\ \mathrm{g\,cm^{-3}}$. It has been suggested [1] that in this so called "annealed strain" regime the ES is mostly annealed at the nematic-isotropic (NI) phase transition through a rearrangement of the particles and that these dispersions can be approximately described by a random field (RF) model, where the random dilution (RD) of quenched disorder simply affects the average order in the sample. No elastic strain effects are considered in this model and the description should become more and more accurate with decreasing ρ_s.

No unambiguous experimental evidence has been reported on this point, however, and the role of the ES at very low ρ_s has not been completely clarified. This is particularly important if one considers that, at least in a region close to the aerosil particle and because of the strong anchoring of the LC molecules at its surface, some elastic distortion of the local orientation, and therefore some ES, is always present. Moreover, the dynamics of the annealing of the disorder introduced by the aerosil is also not completely understood. Let us consider the case of octylcyanobiphenyl (8CB) liquid crystals in the annealed strain regime ($\rho_s < 0.1\ \mathrm{g\,cm^{-3}}$): if the sample is cooled from the isotropic phase to the nematic one, then the appearance of the orientational order induces a particle rearrangement that reduces the disorder in the sample. It is not clear, however, if all the disorder that can be annealed is already removed at the NI transition or if a part of it is still present in the nematic phase. The presence of quenched disorder in the ordered phases, as recently shown in Ref. [9], and its possible annealing at the AN transition could have some important consequences on the interpretation of the experimental results.

In this Rapid Communication we report on simultaneous photopyroelectric measurements [10,11] of specific heat and thermal conductivity (k) of 8CB and heptylcyanobiphenyl (7CB) small quartz sphere (aerosil) dispersions with $\rho_s = 0.005\ \mathrm{g\,cm^{-3}}$, in which, being below the gelation threshold of $\rho_s = 0.01\ \mathrm{g\,cm^{-3}}$, no gel is formed. We have been able to study dispersions with very low ρ_s thanks to the sensitivity of k, that is a transport property and it is therefore much more affected by the disorder introduced in the LC than static quantities. The disorder introduced by aerosil, which is responsible, in a homeotropically aligned sample, of

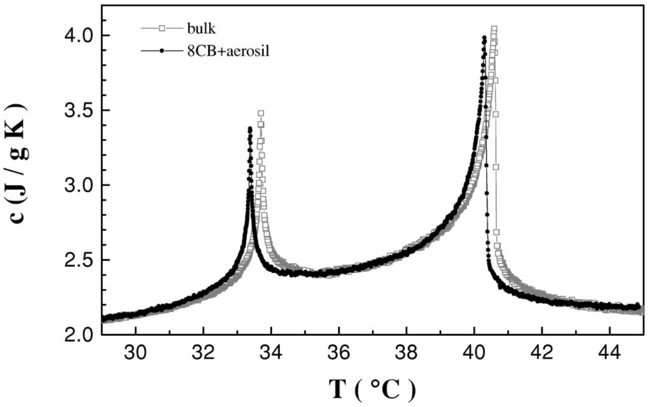

FIG. 1. Specific heat as a function of temperature for bulk 8CB and 8CB+aerosil dispersion.

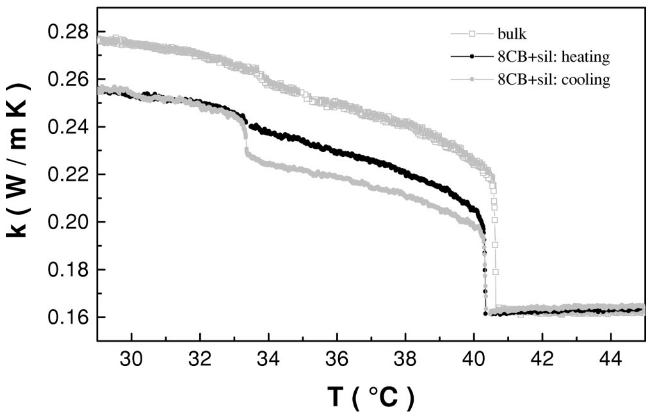

FIG. 2. Thermal conductivity as a function of temperature for bulk homeotropic 8CB and 8CB+aerosil dispersion. Gray and black dots correspond to data sets taken on cooling and on heating, respectively.

the significantly smaller k values we have found in the LC ordered phases with respect to the bulk ones, is shown to be (partially) annealed not only at the NI transition but also at the AN one. Some quenched disorder is therefore present in the nematic phase and this, together with possible elastic effects associated with it, could be the reason for the strong disagreement we have found between the depression of T_{NI} in our samples and the one predicted by the RF (RD) model [12]. It will be shown, in the case of 7CB, which has a much wider nematic range with respect to 8CB, that annealing does not take place at the phase transitions only but also in the nematic phase, the driving force for such a process being the increase of orientational order. It will also be shown that the annealing which take place below T_{NI} is also responsible for the thermal hysteresis found in the thermal conductivity behavior.

Figure 1 shows the specific heat versus temperature data for a homeotropic 8CB+aerosil dispersion, obtained on cooling from the isotropic phase and on heating from the smectic A phase and prepared following the procedure reported in Ref. [6]. Also reported in the figure are the data obtained in the same temperature range for bulk homeotropic 8CB. A downshift of both T_{NI} and T_{AN} transition temperatures is evident in the dispersion with respect to the bulk: for the NI transition we found $(\Delta T_{NI})_{\text{exp}}=270$ mK while for the AN one $(\Delta T_{AN})_{\text{exp}}=310$ mK. It is interesting to note that even with a very low ρ_s, such as the one we have used, with no gel formed, the observed ΔT_{NI} is approximately one half of the one observed in a sample with $\rho_s=0.02\ \text{g cm}^{-3}$ [1]. This reduction in ΔT_{NI}, which is obviously associated with a reduction of the quenched disorder in the sample due to the lower particle concentration, does not scale linearly with ρ_s. This result, which is in contradiction with the prediction of the RF (RD) model, where ΔT_{NI} is expected to be linearly dependent on ρ_s, could be, however, due to the fact that $0.02\ \text{g cm}^{-3}$ is not a sufficiently small concentration to make the ES present in the sample negligible. If we assume, however, that $T(p)_{NI}=T(0)_{NI}(1-p)$ [12], where p is the amount of quenched disorder, which in our case is approximately $p\simeq 0.6\rho_s$ [1], we have $(\Delta T)_{RFI}\simeq 0.94$ K, which is about three times larger than the experimental value we have measured. Also in a dispersion with $\rho_s=0.02\ \text{g cm}^{-3}$ the theoretical value $(\Delta T)_{RFI}\simeq 4$ K was much larger than the experimental value $(\Delta T_{NI})_{\text{exp}}=790$ mK. Some doubts then arise on the applicability of the RF (RD) model at low ρ_s. In our opinion, as will be discussed in more detail later on, the discrepancy we have found between the experimental and theoretical values of ΔT_{NI} is due to some non-negligible ES present in our sample, though, as already said, there is no gel formed and therefore the ability of the isolated strands of aerosil particles in reducing the strain is increased. In other words the description in terms of RF models should include elastic effects associated with the presence of ES. The effect of internal elastic stress in random field models has been recently studied theoretically [13] at the polydomain-monodomain transition in nematic elastomers under an external strain field, but no prediction is at present available at the NI transition. The considerations reported above are also valid for the shift in T_{AN}.

We have performed a power law fitting of the high resolution specific heat data close to the AN transition. The critical exponent we have found $\alpha=(0.28\pm 0.04)$ is slightly smaller the one we have found in the bulk [$\alpha=(0.32\pm 0.04)$ [11]], the difference being, however, within the statistical uncertainty. No significant variation has been found in the A^-/A^+ ratio. The results are consistent with the ones reported in Ref. [1] and they show that the critical behavior of the specific heat is not particularly sensitive to the small amount of disorder present in our sample, because of the very small ρ_s.

Figure 2 shows the thermal conductivity versus T of the dispersion and the one of the bulk, taken from Ref. [11], both being homeotropically aligned. As already discussed in Ref. [14], the thermal conductivity of the bulk is approximately constant in the isotropic phase and has a discontinuity at T_{NI} due to the first order character of the transition. It is, moreover, strongly dependent on the orientational order and this accounts for its increase, in homeotropic bulk samples, with decreasing temperature. A more rapid increase with decreasing temperature is found close to T_{AN} on the smectic side and this is due to the smectic layering contribution to the orientational order.

The data sets obtained on cooling and heating overlap in the smectic and isotropic phases but a significant difference between the two has been found in the nematic phase. In particular, k values obtained on cooling from the isotropic phase are systematically smaller than the ones found in the nematic phase on heating from the smectic one. Since, as said before, a decrease of the thermal conductivity in a homeotropic sample at a given temperature is due to a decrease of the orientational order, the results shown in Fig. 2 suggest that there is less orientational order in the nematic phase on cooling than the one obtained on heating.

This can be explained as follows: when the sample is cooled from the isotropic phase, the appearance of the nematic order and the presence of the surface induced homeotropic alignment, produces a rearrangement of the aerosil particles that anneals part of the ES present in the sample. The residual ES produce a decrease of the orientational order with respect to the bulk and, therefore, a smaller value of k in the nematic phase. The amount of the strain is small enough not to affect the critical behavior of c but it could account for the discrepancy between the ΔT_{NI} value we have found and the one predicted by the RF (RD) model. When decreasing the temperature the sample goes across the AN transition and a further reduction of the ES takes place because of the rearrangement of the LC and aerosil particles due to the aligning field and the appearance of smectic layering. This process produces the increase of k in the smectic phase, which is much larger than the one found in the bulk, where, as said before, the smectic layering also produces an increase of the orientational order. If the sample is then heated from the smectic phase, the observed decrease of k is simply due to the decrease of orientational order with temperature as in the case of bulk samples. To check this point we have renormalized the k value obtained on heating to bulk ones and we have found the same temperature dependence.

The scenario that comes out from the analysis of the experimental results reported above seems to be more complicated than the one described in Ref. [1] for LC+aerosil dispersions with $\rho_s < 0.1\ \mathrm{g\,cm^{-3}}$. The hysteresis in k clearly indicates that even with very low concentrations, there is some ES present in the nematic phase and that the description of the dispersion in the in terms of a RF (RD) model could not be appropriate. Moreover, annealing of this strain occurs at the AN transition due to the appearance of the translational order. Though we have found only minor variations in the critical behavior of the specific heat of the dispersion with respect to the bulk one, the presence of strain and its partial annealing at T_{AN} raises some doubts on the applicability of the usual cross-over from 3D XY to mean field tricritical description for the AN transition [15], even with a very low ρ_s value. It has been recently suggested [9] that the presence of an arbitrary small amount of quenched disorder in a LC can give rise to smectic and nematic Bragg glasses, which have different properties with respect to the usual nematic and smectic phases and, possibly, different phase transitions. We think that the theoretical models mentioned above (RF with the inclusion of elastic effects, Bragg glasses) could give a more appropriate description of the system we have investigated, but more theoretical effort is needed on these issues.

A question may arise at this point on the influence of the aligning field due to surface treatment on the conclusions reported above, and, therefore, on the mechanisms responsible for the annealing of the disorder. Figure 3 shows specific heat versus temperature data for not aligned 7CB + aerosil dispersion with $\rho_s = 0.005\ \mathrm{g\,cm^{-3}}$. The two data sets have been obtained on both cooling and on heating and while they almost overlap in the isotropic and nematic phases, a significantly different behavior has been found in the phase transition region. It must be pointed out that the model we have used to calculate the c value from the photopyroelectric signal amplitude and phase, as in the case of others ac calorimetric technique, is valid for homogeneous samples only. Since the NI transition is of the first order, a two phase coexistence region is present close to T_{NI} and therefore the sample is not homogeneous. This means that the c values in the two phase region are affected by some artifacts, but we believe that qualitatively the difference in the c temperature dependence observed in this region on cooling and on heating is real.

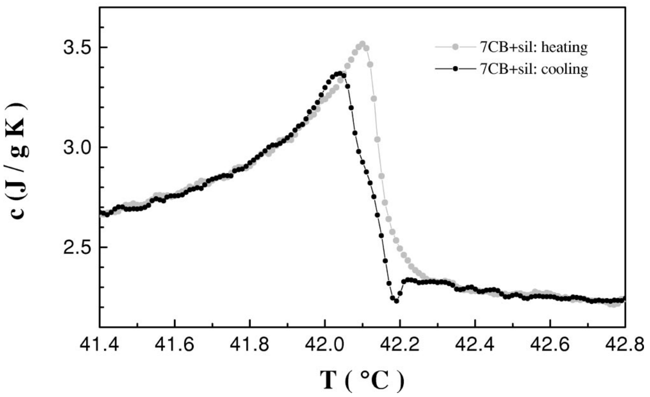

FIG. 3. Specific heat as a function of temperature for 7CB +aerosil dispersion. Black and gray dots correspond to data sets taken on cooling from the isotropic phase and on heating from the smectic phase, respectively.

A similar behavior for the specific heat has been already reported for unaligned 8CB + aerosil dispersions close to T_{NI} [1]. In particular a double peak structure has been found in c for $\rho < 0.183\ \mathrm{g\,cm^{-3}}$ and it has been attributed to annealed elastic strain (peak at higher temperature) and to elastic strain coarsening with increasing ρ_s (rounded peak at lower temperature). It has been shown, moreover, that when increasing the concentration, the latter becomes more and more important and remains the only peak present for $\rho_s > 0.183\ \mathrm{g\,cm^{-3}}$. The double peak structure was reproducible on heating and cooling.

If we assume that the above-mentioned interpretation is also applicable to our sample and therefore that the shoulder and the peak in c shown in Fig. 3 are due to annealed and quenched strain respectively, then we have to explain why we have different behavior on heating and on cooling. We think that, a weak homeotropic alignment is present in the sample, as confirmed by the k values found in the nematic phase that are larger than the ones in the isotropic phase. This effect is probably due to a weak homeotropic anchoring that is always present at the cell surfaces [10] and that, due to the small thickness of our cell, propagates throughout the LC volume. Since this field is much smaller than the one present in the case of treated cell walls, its contribution to the annealing at T_{NI} is obviously smaller, with an amount of ES that remains quenched larger than the one found in aligned samples. This can account for the peak and the shoulder in c obtained on cooling from the isotropic phase. If the tempera-

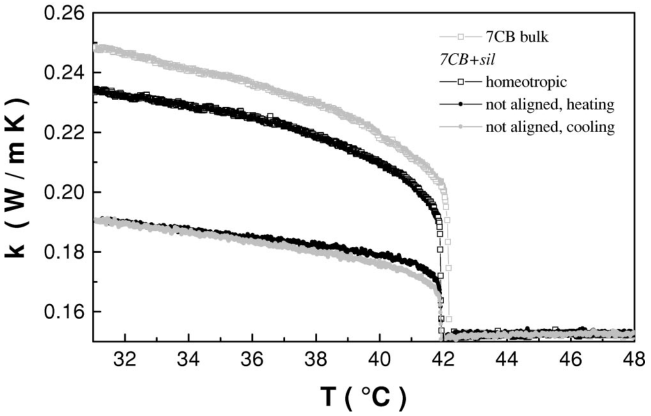

FIG. 4. Thermal conductivity as a function of temperature for bulk 7CB and 7CB+aerosil dispersion (see text).

ture is decreased below T_{NI}, the combined action of the weak aligning field due to the surfaces and the increase of the orientational order further anneals the ES present in the sample, being, as in the case of 8CB, this annealing irreversible, unless the sample is heated into the isotropic phase. This is confirmed by the results we have obtained heating the sample from the nematic phase: the k values are systematically larger below T_{NI} than the ones obtained on cooling (Fig. 4) and a single peak structure has been found in c (Fig. 3). Similar irreversible effects due to the presence of an aligning field have been observed in light scattering experiments on 8CB+aerosil dispersion under an electric field [16].

To further check this point, we have performed measurements on homeotropically surface aligned 7CB + aerosil samples. No significant differences in c (not shown) on heating and cooling at T_{NI} were found in these samples. This suggests that the strong field that is now present is sufficient to drastically reduce the strain at the NI transition. This is confirmed also by the k data reported in Fig. 4, where a systematically larger value, and therefore a larger orientational order, is found in the nematic phase with respect to the one obtained in not aligned samples.

We have also performed measurements on unaligned 8CB + aerosil dispersions (not shown), and we found a single peak structure close to T_{NI}. This means that the strength of the weak aligning field due to the cell walls, is larger for this compound. This is also confirmed by the thermal conductivity data in the nematic phase (not shown), that are more closer to bulk value in this case than in 7CB.

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