

Eclogitic Diamond Formation at Jwaneng: No Room for a Recycled Component

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Eclogitic diamonds have a large range of $\delta^{13}\text{C}$ values, whereas peridotitic diamonds do not. Paired $\delta^{15}\text{N}$ - $\delta^{13}\text{C}$ -N variations in 40 eclogitic diamonds from the Jwaneng kimberlite in Botswana show that neither the influence of recycled biogenic carbon nor the global and primordial heterogeneity of mantle carbon are likely for the origin of the large $\delta^{13}\text{C}$ range; the data instead support a fractionation process. It is proposed that carbonatitic mantle melts from which diamonds crystallize undergo different evolutions before diamond precipitation, when percolating through either a peridotite or an eclogite. These different evolutions, reflecting the presence or absence of olivine, can account for their respective $\delta^{13}\text{C}$ distributions.

Diamonds are among the best sources of information about the mineralogy and chemistry and the volatiles of the Earth's mantle (1, 2). Two main diamond types are identified on the basis of silicate and oxide (1, 2) or sulphide (3) inclusions. These major groups have inclusions that are similar (but chemically distinct) to either olivine-bearing peridotites or eclogites and are commonly referred to as peridotitic (P-type) or eclogitic (E-type) diamonds. Regarding the origin of P-type diamonds, there is general agreement that because they have carbon isotopic compositions within the mantle range [$\delta^{13}\text{C}$ from -10 to 0 per mil, mostly at $\delta^{13}\text{C} \approx -5$ per mil (4–8)], they formed in the lithospheric mantle from species derived from within the upper mantle [reviewed in (5)].

The origin of the E-type diamonds, however, is more controversial. They have more variable $\delta^{13}\text{C}$ values, which range between -34.5 and 2.7 per mil (6–8). The principal debate is whether the variable $\delta^{13}\text{C}$ values displayed by eclogitic diamonds are a consequence of biospheric input through subduction (5, 9), primordial mantle heterogeneity (8), or high-temperature fractionation of carbon in the mantle (7, 10).

To evaluate the origin of E-type diamonds, we studied the $\delta^{15}\text{N}$ characteristics (4, 11) of eclogitic diamonds originating from the Jwaneng kimberlite in Botswana, a mine known to provide diamonds having a large $\delta^{13}\text{C}$ range. On the basis of the measured $\delta^{13}\text{C}$ values (12), we selected 31 silicate-bearing and 9 sulfide-bearing diamonds belonging to the eclogitic paragenesis (13). As shown in Table 1, our mea-

sured $\delta^{13}\text{C}$ values range from -21.1 to -2.7 per mil (Fig. 1) and cover not only the main diamond $\delta^{13}\text{C}$ range (6, 7), but also the entire $\delta^{13}\text{C}$ range defined by diamonds from South African kimberlites (8). The $\delta^{13}\text{C}$ values are consistent with earlier measurements (12). The $\delta^{15}\text{N}$ values range from -10.1 to -1.1 per mil with a mean value of -5.5 per mil (Fig. 2). From the present study, the overall $\delta^{13}\text{C}$ and nitrogen content characteristics at Jwaneng are similar to other worldwide populations of eclogitic diamonds. For example, nitrogen concentrations are statistically higher in eclogitic diamonds (Fig. 3) (8); diamonds associated with the lowest $\delta^{13}\text{C}$ values are generally characterized by lower nitrogen contents and, within the scale of the sample set, $\delta^{13}\text{C}$ is roughly correlated with nitrogen content but shows no correlation with $\delta^{15}\text{N}$ (Fig. 4).

The two sedimentary, carbon-bearing endmembers are carbonates, with $\delta^{13}\text{C} \approx 0$ per mil, and organic matter, with $\delta^{13}\text{C} \approx -25$ per mil (14). These values cover the full diamond $\delta^{13}\text{C}$ range. Nitrogen is the main diamond impurity (average ≈ 300 ppm), strongly bonded within carbon atoms, and is present, initially, as a simple 1:1 substitution. Nitrogen is a useful tracer for sediments because it is initially associated only with organic matter as a result of biological fixation. Since the Archean, organic

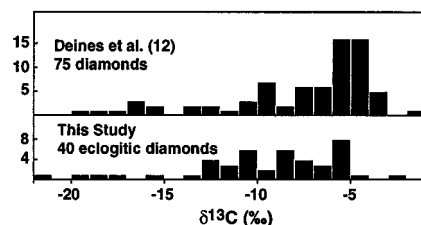


Fig. 1. Carbon isotopic composition of diamonds from Jwaneng (Botswana). Diamonds from this location cover the main diamond $\delta^{13}\text{C}$ range (5–8) and the whole range defined by South African kimberlites (8).

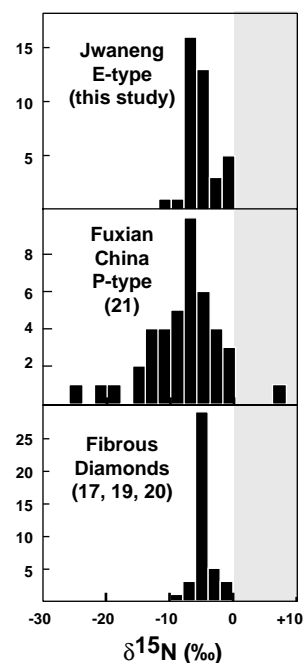


Fig. 2. $\delta^{15}\text{N}$ histogram of eclogitic diamonds from Jwaneng and for other mantle derived samples. The gray field defines the main range displayed by organic nitrogen.

matter has positive $\delta^{15}\text{N}$ values (15). With increasing metamorphism, nitrogen will be stable as ammonium ions substituting for potassium ions in K-bearing minerals, and its isotopic composition evolves toward even higher $\delta^{15}\text{N}$ values (16). In contrast, most mantle $\delta^{15}\text{N}$ values found in diamonds (17–22), peridotitic diamonds in particular (21), and mid-ocean ridge basalt (MORB) vesicles (23) are negative. That fibrous (rapid growth) and octahedral (relatively slow growth) diamonds have the same $\delta^{15}\text{N}$ mode showed that fractionation of N isotopes during diamond growth is also unlikely (21). The comparison of $\delta^{15}\text{N}$ values in eclogitic diamonds with those of metasedimentary nitrogen is tempting because eclogitic diamonds are relatively young

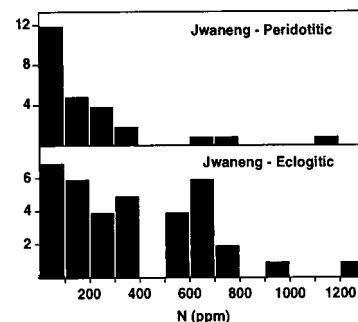


Fig. 3. Comparison of N contents in peridotitic and eclogitic diamonds. Eclogitic diamonds contain statistically higher N contents than the peridotitic (12).

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[mostly middle Proterozoic (24)], allowing primary mantle-derived diamonds to be distinguished from those made of subduction-related material.

Consequently, if eclogitic diamonds

form from recycled biogenic carbon, they should contain positive to highly positive $\delta^{15}\text{N}$ values, particularly when displaying low $\delta^{13}\text{C}$ values, matching those of the original organic matter. However, the $\delta^{15}\text{N}$

values of eclogitic diamonds from Jwaneng are all negative. The mean $\delta^{15}\text{N}$ value of Jwaneng eclogitic diamonds is nearly identical to the $\delta^{15}\text{N}$ value of well-mixed mantle (≈ -5 to -6 per mil) inferred from fibrous (17, 19, 20), peridotitic diamonds (21, 22) and MORB values (23) (Fig. 2). In addition, as shown by Fig. 5, more complicated models involving mixing between mantle and a subduction-derived component are unlikely (no linear relation). These would have to combine a nitrogen-rich mantle (represented by peridotitic diamonds) with a nitrogen-poor eclogitic subducting slab (made up of recycled oceanic crust and sediments, both deprived of nitrogen through metamorphism). As a consequence we would expect a higher nitrogen content in P-type diamonds relative to that of E-type. On the contrary, worldwide observations show that E-type diamonds, typified by Jwaneng samples (Fig. 3), are significantly richer in nitrogen than P-type ones (8, 12). Eclogitic diamonds from Jwaneng are thus unlikely to crystallize from recycled carbon, as suggested by Deines and his group from carbon isotope characteristics and detailed chemical considerations of diamond inclusions (8, 12). The same can be concluded from $\delta^{15}\text{N}$ values of eclogitic diamonds from Kimberley Pool (22) except that these diamonds do not display the full "eclogitic" $\delta^{13}\text{C}$ range (22).

In meteorites, whole-rock $\delta^{15}\text{N}$ values have a range of more than 100 per mil. Because nitrogen is less abundant than carbon, nitrogen isotopes should be more sensitive to a primordial mantle heterogeneity than carbon isotopes. In other words, if eclogitic diamonds originated from several distinct locations of a primordial isotopically heterogeneous mantle, we must expect several distinct nitrogen isotopic signatures. Because Jwaneng eclogitic diamonds show little variability in $\delta^{15}\text{N}$ compared with their $\delta^{13}\text{C}$ range, it is unlikely that these diamonds could be formed in several distinct environments, as was suggested in (12) on the basis of $\delta^{13}\text{C}$ values together with a detailed chemical analysis of the inclusions. We conclude that the large range of $\delta^{13}\text{C}$ values results from a high-temperature fractionation process.

Batch equilibrium crystallization cannot account for the large $\delta^{13}\text{C}$ range; instead, extensive evolution by Rayleigh distillation (continuous extraction of melts or fluids) is needed (7, 10, 25) which has been shown to be possible, on theoretical and experimental grounds, in the C-O-H system (26). We consider diamond crystallization to occur from asthenosphere-derived carbonate melts introduced into a more reduced continental lithosphere (27). In such a model, diamond precipitation occurs from a carbonate-carbon reservoir entering redox

Table 1. $\delta^{13}\text{C}$ - $\delta^{15}\text{N}$ -N content and aggregation state obtained on eclogitic diamonds from Jwaneng. %B, the percentage of diamond N present in the B form (13). The multiple values are from a single diamond chip.

Sample	Weight (mg)	$\delta^{13}\text{C}$	$\delta^{15}\text{N}$	N	%B
JW 1	1.7179	-21.13	-1.6	84	97-91
JW 2	2.3735	-15.20	-1.9	70	41-41
JW 3	1.3155	-5.19	-5.8	839	4
JW 4	3.2039	-12.06	-6.3	490	21
JW 5	2.0521	-7.08	-2.9	640	80-70
JW 6	2.6896	-7.56		12	
JW 7	3.9194	-7.96	-3.1	605	85-81
JW 8	2.6812	-5.18	-4.8	1011	65-5
JW 9	1.0004	-5.65	-6.7	834	19-1
JW 10	2.6558	-5.68	-8.5	764	16
JW 13	3.4796	-12.24	-5.8	513	19-12
JW 14	0.7152	-11.95	-5.4	319	59-55-54
JW 15	0.6045	-10.83	-5.4	377	98-55-39
JW 16	1.9884	-8.67	-6.7	645	10-2
JW 18	1.2692	-5.76	-4.3	649	43-34
JW 19	1.2932	-14.72	-5.1	312	10
	1.1412	-11.26	-6.2	466	36
	2.2194	-10.42	-6.8	528	9
JW 20	2.2385	-11.22	-3.7	508	17-11
JW 21	3.6613	-19.81		27	
JW 22	2.8350	-5.04	-10.1	715	16-2
JW 24	2.6458	-10.06	-1.8	156	95-93
JW 25	1.4403	-5.22	-7.3	1528	48-44
JW 26	1.5046	-10.92	-4.8	214	77
JW 27	1.8253	-8.67	-7.2	698	27-27
JW 28	1.9619	-10.35	-7.1	424	9
JW 33	2.3837	-5.25	-6.5	921	94
JW 35	0.9933	-10.14	-7.2	410	10
JW 36	2.8755	-12.10	-6.3	536	51
JW 37	2.2116	-12.81	-6.4	321	88-53
JW 42	2.8605	-18.30	-2.0	103	90
JW 46	1.4350	-13.02	-1.1	166	94
JW 48	2.4694	-17.39	-5.3	284	57-30
JW 49	1.5870	-6.67	-5.5	514	30-14
JW 50	1.8405	-6.58	-7.6	773	32-30
JW 51	1.3348	-9.38	-6.7	265	0-0
JW 53	2.4164	-4.96	-5.2	655	76-69
JW 54	4.0829	-6.41	-4.2	1015	43-41
JW 57	2.2865	-8.61	-8.0	438	8-0
JW 58	1.3529	-7.79	-7.4	449	
JW 59	0.9991	-2.71		11	
JW 60	2.4877	-10.92	-5.5	508	44-28

Fig. 4. $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values of Jwaneng eclogitic diamonds. For convenience, Kimberley Pool eclogitic diamonds (22) are shown, as are the fields defined by worldwide peridotitic (21, 22), fibrous (17, 19), and low $\delta^{13}\text{C}$ (18) diamonds.

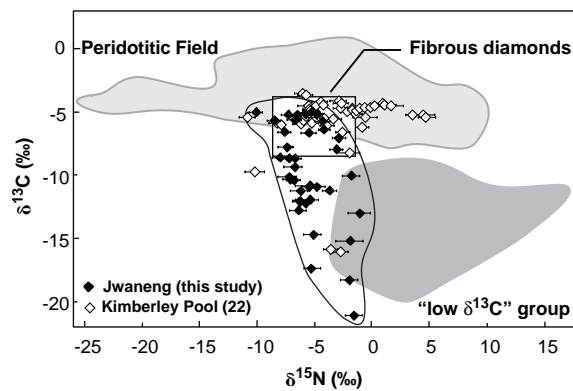
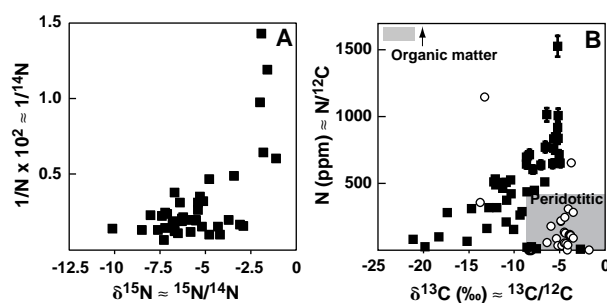


Fig. 5. (A) $\delta^{15}\text{N}$ -1/N and **(B)** $\delta^{13}\text{C}$ -N/C diagrams. These figures show that a mixing relation is unlikely for Jwaneng eclogitic diamonds. Because organic matter (gray field) shows high N/C ratios ($\sim 50,000$ ppm), we would expect to observe increasing N contents with decreasing $\delta^{13}\text{C}$ values. On the contrary, Jwaneng eclogitic diamonds rather show decreasing N contents with decreasing $\delta^{13}\text{C}$ values.



conditions mostly between WM and IW buffers (27, 28). The $\delta^{13}\text{C}$ evolution of the carbon reservoir results from the escape of CO_2 and not from diamond precipitation, which can represent only a minor part of the reservoir with high CO_2 -carbonate fractionation factors (26). Respective stabilities of diamond-bearing eclogites and peridotites and diamond precipitation reactions from carbonate-bearing fluids in eclogites and peridotites (29) have been determined (28).

The way in which carbonatitic melts react and evolve in a peridotitic or in an eclogitic environment is known to be different (28). In a peridotite, olivine is present and will react with any CO_2 produced from carbonates to recreate carbonates again (28, 30, 31). Oxidized carbon thus remains stable only as carbonate, and throughout, no isotope reservoir effect can be produced before its precipitation as diamond. In contrast, in an eclogite assemblage olivine is absent and carbonate and CO_2 -bearing fluids can coexist (28). In this case, the evolution of carbonatitic melts by a loss of CO_2 leaves a residue depleted in ^{13}C , accounting for the lower $\delta^{13}\text{C}$ of eclogitic diamonds. Luth (28) suggested why diamond-bearing eclogite xenoliths are more abundant than diamond-bearing peridotite xenoliths in kimberlites. We suggest that Luth's results [through reaction 4 in (28)] also support the respective diamond $\delta^{13}\text{C}$ ranges.

As for carbon, diamond is unlikely to be responsible for the slight $\delta^{15}\text{N}$ variations (Fig. 4), and diamonds probably record $\delta^{15}\text{N}$ variations produced before diamond crystallization. Such a conclusion can be easily reached from a mass-balance equation. Because initial mantle concentrations are estimated to be ~ 300 ppm for carbon (32) and 1 ppm (33) to 36 (34) ppm for nitrogen, diamond nitrogen concentrations of 120,000 ppm [that is, $(1/300) \times 10^{-6}$] and 3500 ppm [$(36/300) \times 10^{-6}$] are expected if all carbon and nitrogen were contained within the diamond (35), whereas the average N content of eclogitic diamonds from Jwaneng is only about 380 ppm (12). Within the continental lithosphere and over the

main depth interval of eclogitic diamond formation, carbonates (28, 32) and a yet to be found nitrogen bearer [possibly osbornite (TiN) (34) or sinoite ($\text{Si}_2\text{N}_2\text{O}$)] may be, respectively, the most significant carbon and nitrogen mantle host phases. Hence, diamonds record essentially $\delta^{13}\text{C}$ variations produced by the carbonate- CO_2 system, whereas $\delta^{15}\text{N}$ variations are likely to be produced by a nitride- $\text{N}_{2\text{-fluid}}$ system.

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$$\delta^{13}\text{C} = \left[\frac{^{13}\text{C}_{\text{unk}}/^{12}\text{C}_{\text{unk}}}{^{13}\text{C}_{\text{std}}/^{12}\text{C}_{\text{std}}} - 1 \right] \times 1000$$
 and the nitrogen isotopic composition is given by
$$\delta^{15}\text{N} = \left[\frac{^{15}\text{N}_{\text{unk}}/^{14}\text{N}_{\text{unk}}}{^{15}\text{N}_{\text{std}}/^{14}\text{N}_{\text{std}}} - 1 \right] \times 1000$$
 where unk refers to the sample and std to the standard (Pee Dee Belemnite in the case of $\delta^{13}\text{C}$ and atmosphere in the case of $\delta^{15}\text{N}$).
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deconvoluted into their different components with a precision of $\pm 5\%$ by using coefficients of 16.5 atoms ppm cm^{-1} for A [S. R. Boyd, I. Kiflawi, G. S. Woods, *Philos. Mag. B* **69**, 1149 (1994)] and of 79.4 atoms ppm cm^{-1} for B [_____, *ibid.* **72**, 351 (1995)].

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- Also D. P. Matthey [*Terra Cognita* **7**, 31 (1987)], preferring a model of heterogeneity introduced through subduction, pointed out the possibility of Rayleigh distillation.
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- Nonmetasomatized diamondiferous peridotite and eclogite xenoliths derived from the continental lithosphere actually show redox states between the iron-wüstite (IW) and wüstite magnetite (WM) buffers [S. E. Haggerty, *Nature* **320**, 34 (1986); S. E. Haggerty, in *Continental Mantle*, M. A. Menzies, Ed. (Oxford Univ. Press, Oxford, 1990), pp. 87–109; C. Ballhaus, *Contrib. Mineral. Petrol.* **114**, 331 (1993); A. Kadik, *Phys. Earth Planet. Inter.* **100**, 157 (1997) and references therein]. In contrast, metasomatized mantle xenoliths show higher oxygen fugacity (f_{O_2}) values [G. S. Mattioli, M. B. Baker, M. J. Ritter, E. M. Stolper, *J. Geol.* **97**, 521 (1989)]. Crystallization of diamonds over a range of f_{O_2} values is supported by their syngenetic inclusion content. Moissanite (SiC) has been identified [I. Leung, *Am. Mineral.* **75**, 1110 (1991), and references therein]. At the opposite end, carbonates and CO_2 are reported in fibrous diamonds [(20); O. Navon, I. D. Hutcheon, G. R. Rossman, G. J. Wasserburg, *Nature* **355**, 784 (1988); O. Navon, *ibid.* **353**, 746 (1991)] and as syngenetic inclusions in octahedrally shaped diamonds [(36); A. Wand, J. D. Pasteris, H. O. A. Meyer, M. L. Dele-Duboi, *Earth Planet. Sci. Lett.* **141**, 293 (1996); P. McDade, J. W. Harris, V. M. Goldschmidt, *Conf. Abstr.* **1**, 391 (1996)]. CO_2 has also been identified in some of our Jwaneng

E-type samples (JW 1, 14, 15, 26, 28, 37, and 48) (36). Finally, precipitation of diamonds from volatile-rich fluids is also substantiated by diamonds themselves and their impurities. For example, in addition to carbon, diamonds contain nitrogen, hydrogen, boron, and sulfur, all behaving as volatiles. In our model, the resulting oxidation state of mantle rocks and the stability of the diamond and carbonate are imposed by the amount of the oxidized infiltrating fluids or melts relative to that of reduced host rocks.

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$2CaCO_3 \rightarrow 2Mg_2SiO_4 + 2CaMgSi_2O_6 + 2C + 2O_2$ in lherzolites for peridotites; and $CaMg(CO_3)_2 + 2SiO_2 \rightarrow CaMgSi_2O_6 + 2C + 2O_2$ and $C + O_2 \rightarrow CO_2$ in eclogite.

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Multiple-Step Melting in Two-Dimensional Hexatic Liquid-Crystal Films

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An unexpected three-stage melting transition has been observed in two-dimensional (2D) free-standing liquid-crystal films by in situ electron-diffraction and optical-reflectivity measurements. These data suggest the existence of two phases between the 2D solid and liquid: a hexatic phase and, at a higher temperature, an intermediate liquid phase with hexatic-like positional correlations (~40 angstroms) but no long-range orientational order. Previous high-resolution heat-capacity measurements have revealed a divergent-like anomaly at the hexatic-liquid transition that sharply contradicts the predictions of 2D melting theories. The observation of an intermediate isotropic phase may alter our understanding of 2D melting and lead to reconciliation between current experiments and theories.

What processes are involved when 2D systems melt? Theories of 2D melting (1–3) suggest a mechanism in which a 2D solid could melt through the dissociation of topological defect pairs (4). In particular, Halperin and Nelson (2) proposed a two-stage melting process involving an intermediate hexatic phase between the 2D crystalline phase and the isotropic liquid. The hexatic phase exhibits short-range positional but quasi long-range bond-orientational order characterized by sixfold symmetry (5). The 3D analog of the hexatic phase was first identified in a liquid-crystal (LC) compound (6). Subsequently, hexatic order has been reported in free-standing LC films (7, 8) and various 2D systems such as colloidal crystals (9), high-temperature superconductors (10), magnetic-bubble lattices (11), charge-density waves (12), and Langmuir-

Blodgett films (13). Among those 2D systems, thin free-standing LC films, without the complication of any substrate, have offered unique opportunities to test the melting theories. To date, apparent discrepancies have persisted between experimental observations and theoretical predictions, including an inexplicably strong thermal anomaly at the hexatic-liquid transition instead of the expected continuous Kosterlitz-Thouless (KT)-type behavior (14). To investigate these phenomena, we report in situ electron diffraction (ED), high-resolution heat capacity (C_p) (signal to noise ratio $\sim 3 \times 10^4$), and optical reflectivity (signal/noise $\sim 2 \times 10^4$) measurements on 2D LC films of *n*-pentyl-4'-*n*-pentanoyloxy-biphenyl-4-carboxylate (54COOBC).

Our experimental techniques for making ED (15), C_p (16), and optical reflectivity (17) measurements have been described elsewhere. The free-standing LC films are soaplike films suspended across an aperture (18), with a diameter of 1 mm for ED measurements and 1 cm for C_p and optical-reflectivity measurements. The 54COOBC molecules are rodlike with a size of 25 Å by 5 Å (diameter). This compound exhibits orthogonal layered mesophases, namely, the smectic-A (Sm-A), hexatic-B (Hex-B), and crystal-B (Cry-B) phases, where Sm-A is

composed of liquid layers, Hex-B is a stacked hexatic phase, and Cry-B is a hexagonal crystalline phase (19). The phase sequence for bulk 54COOBC is:

Sm-A (55°C) Hex-B (53°C) Cry-B.

We studied two-layer films of thickness ~ 50 Å, which display 2D scaling behavior in the hexatic regime and hence are effectively 2D systems (20). The ED patterns obtained from two-layer films (Fig. 1) suggest the following phase sequence:

Sm-A (66.3°C) Sm-A' (63.0°C)

Hex-B (60.1°C) Cry-B.

Above 66.3°C, the film was in the Sm-A phase. Its ED pattern was typified by a diffuse ring of constant intensity that one expects from a 2D liquid (Fig. 1A). At about 66.3°C, the diffuse ring of the Sm-A phase sharpened in the radial direction, but the intensity remained uniform around the ring (Fig. 1B). This unexpected ED pattern, which we characterize as smectic-A' (Sm-A'), suggests a higher degree of in-plane positional correlations than that in an ordinary liquid and similar to that found in a hexatic phase. However, the lack of sixfold modulation of the diffraction intensity around the ring indicates the absence of long-range bond-orientational order within our probing electron beam of diameter 50 μm. At around 63.0°C, a single-domain Hex-B phase with long-range bond-orientational order appeared, which features six symmetric arcs (Fig. 1C). The azimuthal width of the arcs diminished gradually with decreasing temperature, suggesting an increase in bond-orientational order. The film made another transition at about 60.1°C to the hexagonal Cry-B phase, with an ED pattern consisting of six sharp Bragg spots indicative of long-range positional order (Fig. 1D).

To yield additional information about both the bond-orientational order and the positional order in the two-layer 54COOBC film, we analyzed the ED data by fitting the circular intensity of the hexatic arcs (χ -scan) as a function of the azimuthal angle (7) to obtain the sixfold

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