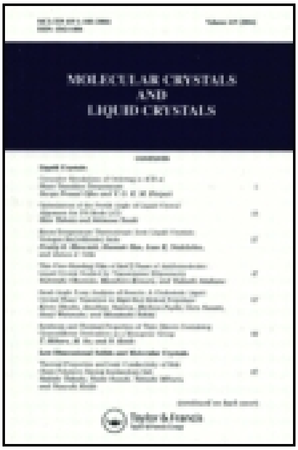

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl18

A Model for the Formation of BPIII and Experimental Evidence

R. L. Rakes Jr. [a] & P. H. Keyes [a]
[a] Department of Physics & Astronomy, Wayne State University, Detroit, MI, 48202, USA

Version of record first published: 24 Sep 2006.

To cite this article: R. L. Rakes Jr. & P. H. Keyes (1991): A Model for the Formation of BPIII and Experimental Evidence, Molecular Crystals and Liquid Crystals, 198:1, 79-89

To link to this article: http://dx.doi.org/10.1080/00268949108033385

Mol. Cryst. Liq. Cryst., 1991, Vol. 198, pp. 79–89
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

A Model for the Formation of BPIII and Experimental Evidence

R. L. RAKES, Jr. and P. H. KEYES

Department of Physics & Astronomy, Wayne State University, Detroit, MI 48202, USA

(Received July 25, 1990)

Calculations of the effects of fluctuations on the cubic blue phases (BPI and BPII) have shown that these lattices are always unstable in the limit of sufficiently high chirality. The point of instability, as estimated by the Lindemann melting criterion, is the same as the temperature at which BPIII appears.

To test this theory measurements have been made of the Debye-Waller factors as a function of temperature for large single crystals of BPII in various orientations as the transition to BPIII is approached from below. We observe large temperature effects consistent with the "melting" mechanism outlined above. There are other evidences of strong temperature dependent dynamical processes, possibly related to thermal diffuse scattering, which are also discussed.

Three possible models for the structure of BPIII which could result from this scenario are considered. One is that of an optically isotropic fluid whose orientational order parameter is *octupolar* rather than quadrupolar, as is usual. The other two models involve two different ways of realizing the state of orientational disorder.

Keywords: blue phases, liquid crystals, Debye-Waller factor

INTRODUCTION

It is now well established that the highest temperature blue phase, BPIII, appears at large chiralities and that the stronger the chirality, the greater the temperature range of this phase.[1] A simple model for this behavior has previously been suggested: the cubic lattices which constitute the lower temperature blue phases, BPI and BPII, have an inherent instability with respect to lattice fluctuations which becomes more severe the smaller the lattice parameter.[2]

First we review the lattice instability argument. Then we present new experimental evidence which argues in its favor. Finally we discuss various possibilities for "melted lattice" models of BPIII and their implications for future experiments.

THE INSTABILITY OF HIGH CHIRALITY LATTICES

The demonstration of the instability follows some arguments which are quite standard[3] but new insofar as their application to the blue phase problem is concerned. Let

$\mathbf{u}(\mathbf{r})$ be a vector field which represents the displacement of equivalent lattice sites from their lowest energy positions. The increase in free energy per unit volume associated with fluctuations of the lattice will be quadratic in the gradients of $\mathbf{u}$ and, in terms of the Fourier amplitudes $\mathbf{u}_\mathbf{k}$ will be given by:

$$\Delta F = \frac{1}{2} C \sum_{\mathbf{k}} |\mathrm{u}_\mathrm{k}|^2 k^2, \tag{1}$$

where C is an elastic constant.[3] Here we are assuming for simplicity that the fluctuations are isotropic; in the more general case where they are not, the constant C is replaced by a tensor as is discussed in Reference 2.

From the equipartition theorem the average square of the fluctuations is found to be:

$$\langle \mathbf{u}^2 \rangle = \frac{k_B T}{(2\pi)^3} \int_0^{2\pi/a} \frac{d\mathbf{k}}{Ck^2} = \frac{k_B T}{\pi C a}, \tag{2}$$

where a is the lattice parameter. As Landau[4] and Peierls[5] first pointed out, the integral in Equation 2 would diverge in one or two dimensions, proving that lattices with long range order cannot exist in these dimensions. But even in three dimensions a crystal eventually becomes unstable when it is heated to its melting point and Lindemann[6] argued that this happens when the root-mean-squared fluctuations become too large, which usually means that they are of the order of 10 to 20% of the lattice parameter a.

Does this Lindemann criterion, which seems to work so well for a very wide variety of atomic crystals, apply to the blue phase lattices as well? The answer seems to be yes; the measured values of the C (and to a lesser extent a) are found to decrease with increasing temperature and when they are used to estimate u_{RMS} by means of Equation 2, it is found that the lattice fluctuations are indeed of the order of 10 to 20% of a at the highest temperature at which a cubic blue phase is found.[2] Moreover, in all three cases in which the elastic constants have been measured[7-9] and for which this argument seems to hold, there are strong indications, if not direct proof, that the phase to which the blue phase lattice transforms as it reaches this Lindemann threshold is the amorphous BPIII.

Thus it would seem that the mechanism responsible for the formation of BPIII is the "melting" of the cubic blue phase lattice when the fluctuations become too large. But why does this scenario tend to prevail at high chiralities? To answer this question we must first deduce the relationship between the elastic constant C appearing in the above equations and the Frank elastic constants appropriate to liquid crystal phases. From simple dimensional analysis we expect

$$C \sim K/a^2, \tag{3}$$

where K is an average Frank constant. The relation in Equation 3 is also found in the specific calculations performed by Dmitrienko.[10] Then, in a form suitable for the direct application of the Lindemann criterion, we find

$$\frac{u_{\mathrm{RMS}}}{a} \sim \sqrt{\frac{k_B T}{\pi K a}}. \tag{4}$$

From this equation it is easy to see why it is expected that the blue phase lattices will become unstable in the high chirality limit ($a \rightarrow 0$).

An even more direct and crucial test of the above concepts than is given by the experiments determining the elastic constant can be made through the measurement of the Debye-Waller factors, as will now be discussed.

THE DEBYE-WALLER FACTOR

As is well known,[11] the principal effect of the thermal vibrations of the lattice on the Bragg reflections is to reduce their intensities by a factor

$$e^{-2W} = e^{-\frac{1}{3}\langle u^2\rangle q^2}, \tag{5}$$

where $2W$ is the Debye-Waller factor, q is the scattering wave vector, and the equality follows for isotropic fluctuations, which we have been assuming.

A particularly sensitive test of the instability concept discussed above would be to observe this temperature reduction of the selective reflections for different values of q as BPII is heated up toward the transition to BPIII. These measurements would provide probably the most direct determination that is possible of the temperature dependence of $\langle u^2\rangle$ and each value of q for which this experiment is performed would constitute essentially an independent determination of this important quantity. The change of q could be accomplished by varying the scattering angle or, as we have actually done and as is more convenient for the polarizing microscope, one could look at the selective reflections in back scattering for different Bragg planes. In this latter case the value of q is given by:

$$q = \frac{2\pi}{a}\sqrt{h^2 + k^2 + l^2}, \tag{6}$$

where h,k,l are the Miller indices. The physical reason for the q^2 dependence of the Debye-Waller factor in this case is simply that the Bragg planes which are closer together will be more greatly affected by the lattice vibrations.

For our experimental studies we have chosen the compound (+)-2-methylbutyl-*p*-[(*p*-methoxybenzylidene)amino]cinnamate (MBMBAC), which has a BPIII phase clearly identifiable in the polarizing microscope and a BPII phase lying below it which exhibits four Bragg reflections in the visible or near-visible spectrum, thus enabling us to measure the Debye-Waller factor for four different values of q. (It should perhaps be noted that the BPII of MBMBAC was initially reported to have an additional Bragg reflection in the far infrared,[12] on the basis of which it was deduced that the structure of this phase was face-centered-cubic.[13] A subsequent study[14] has shown that the earlier experiment and this interpretation were in error and that the BPII of MBMBAC is simple-cubic as are all other known BPIII's.)

The reflected light from the polarizing microscope was passed through a fiber bundle to the entrance slit of a monochrometer. The exit slit of the monochrometer was removed and replaced by a 1020 pixel linear diode array, effectively constituting 1020 separate exit slits, across which the dispersed spectrum of light shone. The diode array was interfaced to a computer which could update the reflected spectrum in a matter of a second or less. This rapid scanning capability became important because there was a gradual downward shift of the transition temperatures with time, which, considering the narrow range of the blue phases, could have become a considerable source of error.

Figure 1 shows the refection spectrum for a large BPII platelet oriented in the (100) direction. Such a platelet is most easily grown by slowly shearing the sample, placed between two glass cover slips, while it is in the BPII phase. This action produces a platelet which appears deep violet to the eye owing to the (200) reflection; the (100) is just outside of the visible spectrum but shows up quite clearly in the recorded spectrum simultaneously with the (200) reflection.

Spectra were recorded at 0.01°C intervals as the sample was heated from the temperature where BPI disappeared to where BPIII first began to enter the field of view. The change in the (100) reflection was barely discernible over this tem-

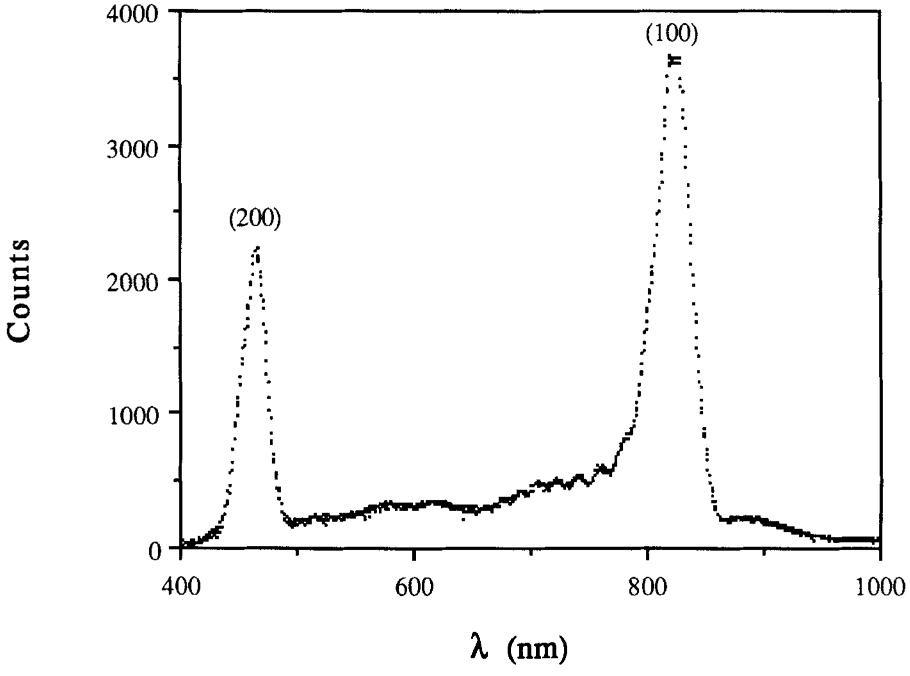

FIGURE 1 The reflection spectrum for a platelet oriented in the (100) direction.

perature range, whereas the decrease of the (200) peak was dramatic, as is shown in Figure 2. Results intermediate between these two extremes were found for the (110) and (111) reflections, as shown in Figures 3 and 4. The (110) platelet was produced by first shearing the cholesteric phase and then heating it up through the BPI phase on into BPII, where it appeared as a uniform yellow platelet. Platelets with the (111) orientation were formed by cooling the isotropic phase through the BPIII range on into the BPII region; many small blue platelets usually result from this operation and given time they meld into one larger platelet.

In Figure 5 are displayed the heights of these various peaks as a function of temperature and also shown are linear fits to the data. (The data for the different peaks have been scaled by arbitrary amounts to avoid having the lines cross.) The behavior is just as expected; the temperature effect is greater for the larger scattering wavevectors. This dependence can be analyzed more quantitatively. By doing linear fits to the temperature variation of the logarithms of the intensities (the scaling factors then of course become irrelevant) we have, according to Equation 5, a quantity which ought to scale like q^2, which Figure 6 makes clear is indeed the case. From the slope of the line in Figure 6 we can determine the temperature derivative of $\langle u^2 \rangle$ and then, multiplying by 0.06°C, the range of BPII, we find that the quantity u_{RMS}/a has increased by 14% over this temperature interval. We thereby establish a lower limit on the amount of lattice fluctuations which from the Lindemann criterion provides a sufficient reason for the destruction of the BPII lattice at the transition to the BPIII phase.

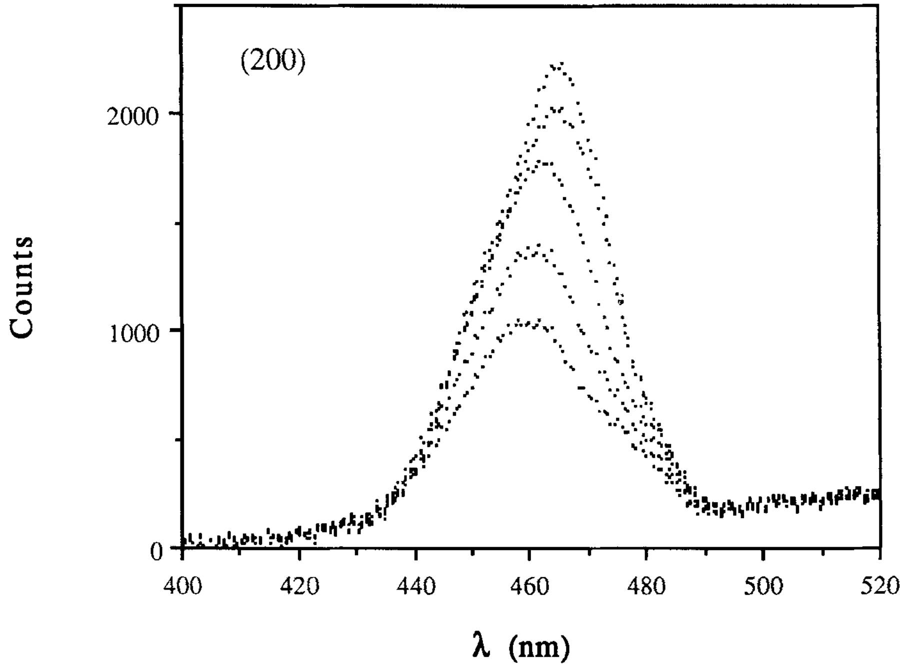

FIGURE 2 Detail of the (200) peak as a function of temperature for 0.01°C intervals. Peak height *decreases* with increasing temperature.

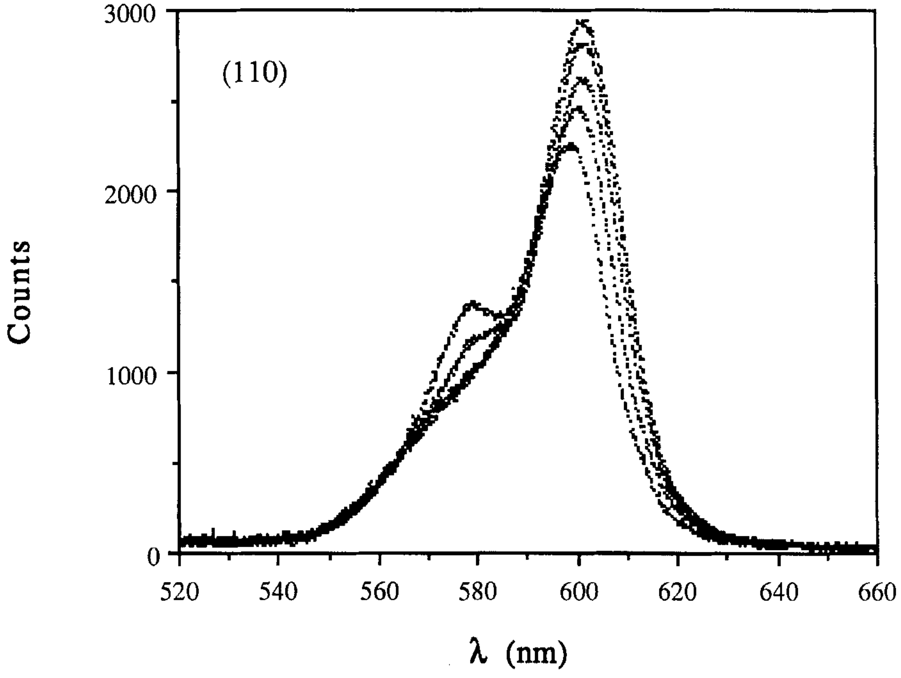

FIGURE 3 The same as Figure 2 for the (110) reflection. Note, however, that in this case as the main peak diminishes a shorter wavelength peak *grows* in intensity.

Although the experimental data on the whole lend very encouraging additional support to the proposed mechanism for the formation of BPIII, there remains one puzzling feature which we have not yet succeeded in understanding. As may be seen in Figure 3, a new satellite peak appearing at shorter wavelengths emerges as the fluctuations increase and the main peak becomes smaller. We suspect that this may be a result of the thermal diffuse scattering—some normally weak multiple-scattering process which somehow becomes enhanced by the lattice fluctuations. Another possibility is that this emerging peak is associated with some new incipient blue phase which is interceded by BPIII, or perhaps is even associated with it.

POSSIBLE MODELS FOR BPIII

If BPIII is a "melted blue phase," a new type of isotropic liquid(!), one must wonder what type of structure or long range order if any it has to distinguish it from the ordinary isotropic phase. We will consider three possibilities here: one model in which the molecules still possess long range orientational order, although not the usual quadrupolar order, and two others in which there is only short range orientational order but perhaps a vestige of global "topological order" which differentiates BPIII from the isotropic phase and still permits a phase transition between these two phases. In these models the BPII (or BPI) to BPIII and BPIII

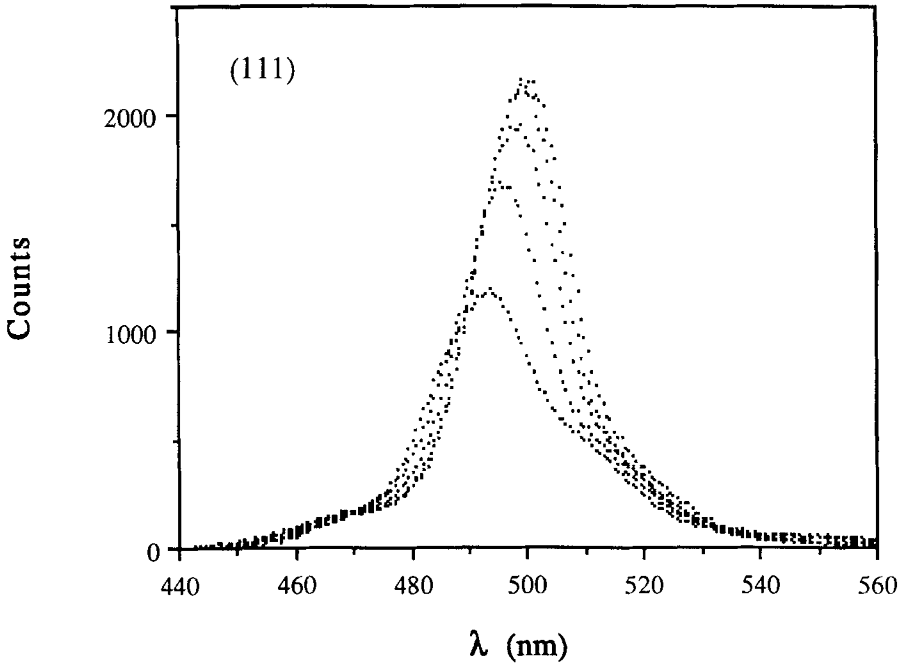

FIGURE 4 The same as Figure 2 for the (111) reflection.

to isotropic phase transitions may either or perhaps both be similar to a Kosterlitz-Thouless type of transition (although probably not second order). In fact our thinking has been greatly motivated by analogy to some of the exotic *K-T* processes which apply to vector order parameters and to atomic lattices, particularly in two dimensions. We of course have no way of knowing at this time whether or not similar things could take place in three dimensional systems having tensor order parameters. We offer these speculations in order to generate new thinking about BPIII, new experiments, and new theories, all of which are badly needed at present.

Model I

The process of defect-mediated melting in two dimensions, leading to a new type of mesophase—the hexatic phase—with its characteristic bond-orientational-order (BOO), is by now well known.[15] Because the statistical mechanics is much more difficult to do in three dimensions, it is not at all clear whether or not this type of defect-mediated melting is possible in this case, but Nelson and Toner[16] have shown that if it does take place it too would lead to a new mesophase—an isotropic liquid with BOO. There are as yet no known examples of transitions to such a mesophase in atomic crystals, but we here introduce and explore the notion that this may be the nature of the melting transition to BPIII.

Consider, for example, the screw dislocation depicted in Figure 7b. As discussed by Nelson and Toner,[16] a defect such as this destroys the long range periodicity of the lattice but preserves the BOO. In the case of this lattice of interlaced tubes it

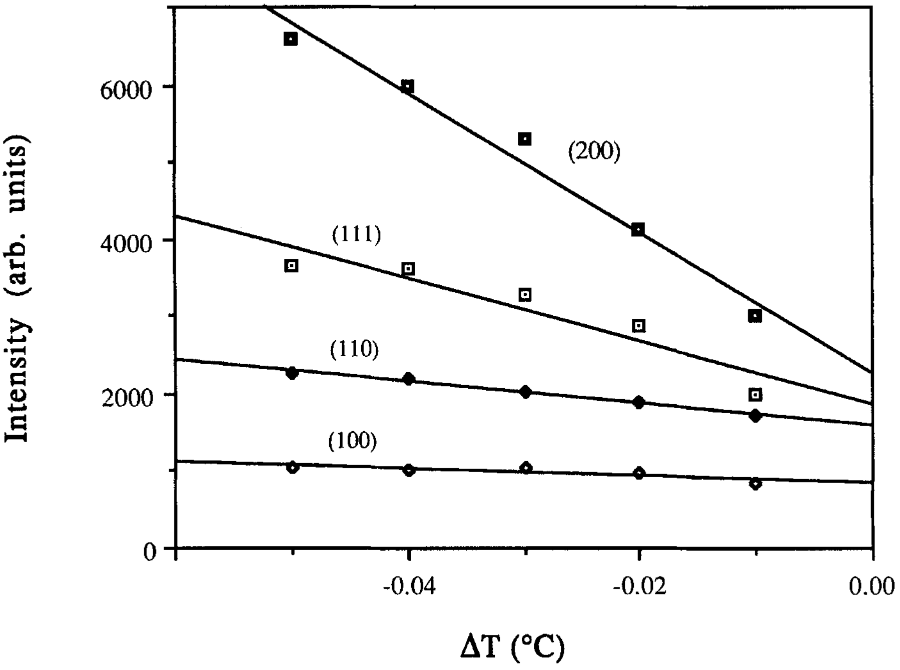

FIGURE 5 The peak intensities versus temperature in the BPII region on the approach to the BPIII transition.

is probably preferable to replace the concept of bond orientation by "tube orientation." It is easy to convince oneself, by analogy to the atomic lattice case, that defects such as that in Figure 7b will reduce but not obliterate the average tendency for the tubes' axes to point toward the faces of a cube. This disposition in turn implies that there still exists a net orientational ordering of the molecules of the *octupolar* type[17] (as well as higher multipole moments).

It should perhaps be recalled that the *quadrupolar* order parameters of the blue phase lattices are all associated with the periodicity of the lattice. That is, they all multiply sinusoidal functions having wavevectors corresponding to those of the lattice.[18] There is, however, no quadrupolar order parameter associated with zero wavevector; in other words the average of Y_{20} is always zero, which is why these phases lack a birefringence. When the lattice melts there will be no long range quadrupolar ordering of any type, periodic or not. If, however, the melting is by a dislocation mechanism as discussed above, there will still be non-zero averages for at least the octupole moments Y_{40}, Y_{44} and $Y_{4,-4}$.[16]

There are several observable consequences of having this long range octupolar ordering. First of all, there will of course still be a transition to a truly isotropic phase at some higher temperature. Mean field theory predicts that this will be a first order transition, but there are other indications that it could be second order.[16] Secondly, even though the octupolar phase is optically isotropic, it should be anisotropic with respect to its elastic properties, its non-linear dielectric behavior, and its electro-optic coefficients,[19] all of which involve tensors which are fourth

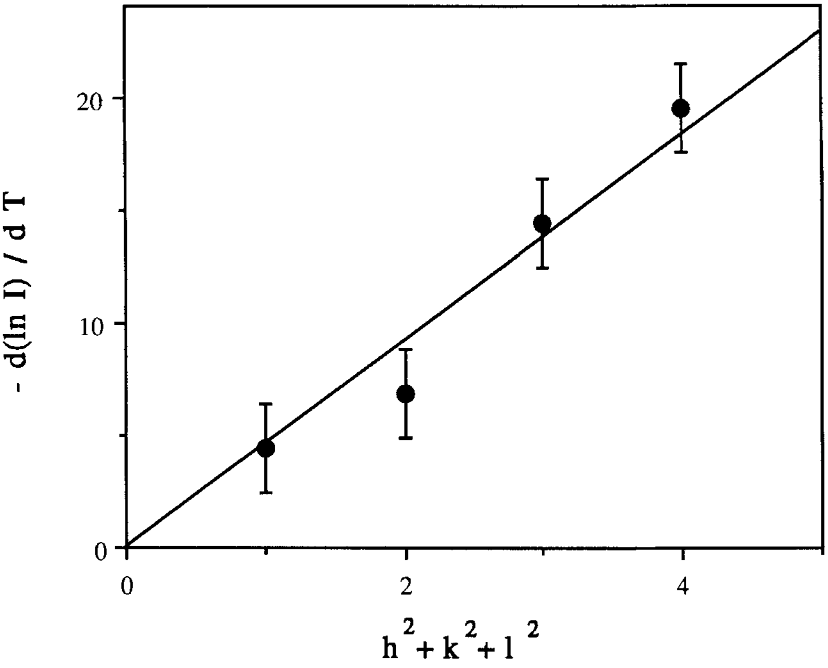

FIGURE 6 The negative of the logarithmic temperature derivative of the reflection intensities versus the sum of the squares of the Miller indicies, demonstrating the q^2 dependence of the Debye-Waller factor.

rank, as is the octupolar tensor. Finally, since the defect structures arising from BPI and from BPII should be distinguishable from each other, one would imagine that there would be, corresponding to the two types of blue phase lattices, two distinct BPIII's and a transition between them in some region. This last consequence should probably have been observed already, although it is conceivable that it could have been overlooked owing to the difficulty in viewing the BPIII region.

Model II

Here we imagine that the fluctuations which melt the lattice are so strong that they also destroy the long range orientational order to all orders of multipoles, but there is still a qualitatve difference in the type of short range order compared to what is found in the higher temperature isotropic phase. The situation is somewhat analogous to the two-dimensional *x-y* model which shows no net magnetism at any finite temperature because of spin wave fluctuations, but nonetheless exhibits a sharp phase change—the Kosterlitz-Thouless transition[20]—where the correlations change from algebraic to exponential decay. A sudden change in the *q* dependence of the structure factor, as would be revealed by a scattering experiment, would indicate that such a transition had taken place, although the chiral liquid crystal is more complicated than the magnetic case, because in the former the correlations are modulated due to the twisting of the local director.

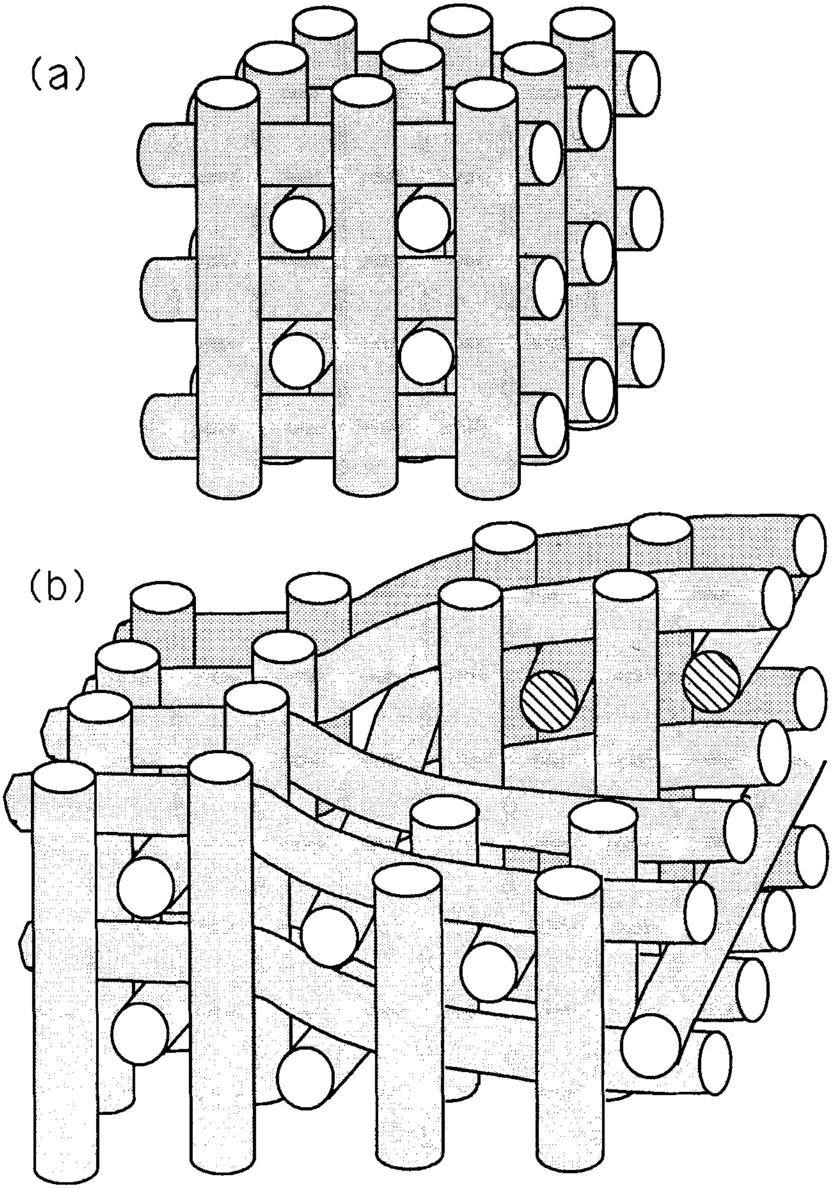

FIGURE 7 (a) The O^2 interlaced tube model of BPII. (b) A screw dislocation.

Model III

This is similar to the above model except that now there is no qualitative difference in the nature of the short range order in BPIII and the isotropic phase; both would exhibit modulated exponential decay but would differ quantitatively in the degree of order. The transition between the two phases would have to be first order, because they have exactly the same symmetry, but could disappear at a critical point as, say the chirality is increased.

CONCLUSION

We have shown theoretically why the blue phase lattices must undergo a type of melting transition in the limit of high chirality, which we take to be the transition to BPIII, and have presented measurements of the Debye-Waller factors which support this theory. The implications for the structure of BPIII and the nature of its phase transitions have also been discussed with three possible models for BPIII having been suggested. Although there are points to be made both in favor and against each of these models, and our own inclination would be to support model II at present, we believe that more data are needed before a firm conclusion can be reached. It is conceivable that more than one of these possibilities is realized depending upon chirality and/or temperature. It is also entirely possible, of course, that Nature has chosen a totally different approach from what we have imagined. Some clever experimenting is needed; many of the differences between these various possibilities are subtle and will not easily be revealed.

Acknowledgment

The support of the National Science Foundation through grant DMR-8909815 is gratefully acknowledged. We also would like to thank D.R. Nelson for a helpful comment.

References

1. J. D. Miller, P. R. Battle, P. J. Collings, D. K. Yang, and P. P. Crooker, *Phys. Rev. A*, **35**, 3959 (1987).
2. P. H. Keyes, *Phys. Rev. Lett*, **65**, 436 (1990).
3. L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Pergamon Press, Oxford, 1980), Sec. 137.
4. L. D. Landau, *Phys. Z. SowjUn.*, **2**, 26 (1937).
5. R. E. Peierls, *Annls. Inst. Henri Poincaré*, **5**, 177 (1935).
6. F. Lindemann, *Phys. Z.*, **11**, 609 (1910).
7. P. E. Cladis, P. Pieranski and M. Joanicot, *Phys. Rev. Lett.*, **52**, 542 (1984).
8. N. A. Clark, S. T. Vohra, and M. A. Handschy, *Phys. Rev. Lett.*, **52**, 57 (1984).
9. R. N. Kleiman, D. J. Bishop, R. Pindak, and P. Taborek, *Phys. Rev. Lett.*, **53**, 2137 (1984).
10. V. E. Dmitrienko, *Pisma Zh. éksp. teor. Fiz.*, **43**, 324 (1986) [*JETP Lett.*, **43**, 420 (1986)].
11. See, e.g., C. Kittel, *Introduction to Solid State Physics*, 6th ed. (John Wiley & Sons, New York, 1986).
12. W. Kuczyn'ski, *Mol. Cryst. Liq. Cryst.*, **130**, 1 (1985); *Phys. Lett.*, **110A**, 405 (1985).
13. P. H. Keyes, *Phys. Rev. Lett.*, **59**, 83 (1987).
14. B. Jérôme, P. Pieranski, V. Godec, G. Haran, and C. Germain, *J. Phys. France*, **49**, 837 (1988).
15. For reviews see: D. R. Nelson in *Phase Transitions and Critical Phenomena 7*, C. Comb and J. L. Lebowitz, eds. (Academic Press, New York, 1983); and K. J. Strandburg, *Rev. Mod. Phys.*, **60**, 161 (1988).
16. D. R. Nelson and J. Toner, *Phys. Rev. B.*, **24**, 363 (1981).
17. Octupolar liquid crystals of a different sort have previously been discussed by E. I. Kats, *Usp. Fiz. Nauk*, **142**, 99 (1984) [*Sov. Phys. Usp.*, **27**, 42 (1984)].
18. See, e.g., R. M. Hornreich and S. Shtrikman, *Mol. Cryst. Liq. Cryst.*, **165**, 183 (1989); V. A. Belyakov and V. E. Dmitrienko, *Usp. Fiz. Nauk.*, **146**, 369 (1985) [*Sov. Phys. Usp.*, **28**, 535 (1985)]; D. C. Wright and N. D. Mermin, *Rev. Mod. Phys.*, **61**, 385 (1989).
19. V. E. Dmitrienko, *Liq. Cryst.*, **5**, 847 (1989).
20. J. M. Kosterlitz and D. J. Thouless, *J. Phys. C.*, **6**, 1181 (1973); J. M. Kosterlitz, *J. Phys. C.*, **7**, 1046 (1974).