Precise Determination of the Orientation of the Dzialoshinskii-Moriya Vector in κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl

Dylan F. Smith* and Charles P. Slichter
Department of Physics, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801, USA

John A. Schlueter, Aravinda M. Kini, and Roxanne G. Daugherty
Materials Science Division, Argonne National Laboratory, Argonne, Illinois 60439, USA
(Received 10 June 2004; published 14 October 2004)

A novel electron spin-reorientation transition is discovered by ^{13}C NMR in the quasi-two-dimensional organic antiferromagnet κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl. The spin reorientation occurs as an external field is swept through the orientation of the characteristic vector of the Dzialoshinskii-Moriya (DM) interaction, thus providing a precise determination of the orientation of the DM vector. Such a spin reorientation could help to characterize the DM interaction in other antiferromagnetic systems.

DOI: 10.1103/PhysRevLett.93.167002 PACS numbers: 74.70.Kn, 75.25.+z, 75.50.Ee, 76.60.Jx

In recent years numerous studies have shown the strong influence that the Dzialoshinskii-Moriya (DM) exchange interaction can have on magnetic ordering in antiferromagnetic materials. In a previous study using ^{13}C NMR, we showed the importance of the DM interaction for the magnetic ordering in κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl [1], an organic compound that is an antiferromagnet at ambient pressure ($T_N = 27$ K) [2] and a superconductor at 300 atm ($T_c = 13$ K) [3] [BEDT-TTF, hereafter abbreviated as ET, is bis(ethylenedithio)tetrathiafulvalene]. In this Letter, we present an experimental method for determining the precise orientation of the DM interaction when simple symmetry arguments are not sufficient, as in the case of κ-(ET)$_2$Cu[N(CN)$_2$]Cl. This technique is linked to the observation of a novel spin reorientation (SR) driven by the DM interaction. While to our knowledge this SR has not been previously observed, it should be present in many of the systems with the DM interaction.

The conventional SR transition is known as a spin-flop transition and results from competition between the Zeeman and the symmetric anisotropic exchange (or single-site anisotropy) interaction in the presence of a much larger isotropic exchange interaction. The anisotropy leads to an easy axis along which the spins lie in zero field. When a field is increased from zero along the direction of the easy axis, the spins lie along the easy axis until the spin-flop field is reached, at which point they flop into a configuration perpendicular to the field.

Spin reorientations have also been found to be caused by the field-dependent competition between symmetric anisotropic or interlayer exchange interactions and the antisymmetric DM interaction. An example is seen in the complicated field dependence of the magnetic structure of La_2CuO_4, a parent compound of the cuprate superconductors [4–6]. The DM interaction has recently been shown to contribute to SR transitions in other systems such as $K_2V_3O_8$ [7] and $BaCu_2Si_2O_7$ [8], and its influence has been seen in systems such as Cu benzoate [9], NaV_2O_5 [10], and V_{15} [11], among others.

The SR presented in this Letter differs from these previous findings in that it results not from the competition between the DM interaction and any other anisotropy, but follows from the form of the DM interaction itself in the presence of the larger isotropic exchange and Zeeman interactions. We describe the phenomenon using a mean-field picture in which neighboring electron spins $\boldsymbol{S}_1$ and $\boldsymbol{S}_2$ are located on distinct magnetic sublattices with moments $\boldsymbol{M}_1$ and $\boldsymbol{M}_2$. It is helpful to make a change of basis from the sublattice moments $\boldsymbol{M}_1$ and $\boldsymbol{M}_2$ to the staggered moment $\boldsymbol{M}^\dagger = \frac{1}{2}(\boldsymbol{M}_1 - \boldsymbol{M}_2)$, which characterizes the antiferromagnetic order, and the ferromagnetic moment $\boldsymbol{M}^F = \frac{1}{2}(\boldsymbol{M}_1 - \boldsymbol{M}_2)$, which characterizes the canting of the spins away from antiparallel alignment, as shown in Fig. 1. It is important to note that $\boldsymbol{M}^\dagger \perp \boldsymbol{M}^F$. In the presence of a large isotropic (Heisenberg) exchange interaction $E_{\mathrm{iso}} = A\boldsymbol{M}_1 \cdot \boldsymbol{M}_2 = A(|\boldsymbol{M}^F|^2 - |\boldsymbol{M}^\dagger|^2)$, the spins minimize the energy by aligning in an antiparallel orientation so that $|\boldsymbol{M}^F| = 0$ and $|\boldsymbol{M}^\dagger| = M$, where M is the magnitude of the electron spin moment of both sublattices. Since the SR discussed here also occurs in the presence of an isoptropic exchange interaction that is larger than any other interaction, we assume $|\boldsymbol{M}^\dagger| \gg |\boldsymbol{M}^F|$.

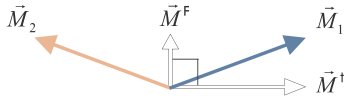

FIG. 1 (color online). Change of basis from sublattice moments $\boldsymbol{M}_1$ and $\boldsymbol{M}_2$ to staggered $\boldsymbol{M}^\dagger$ and ferromagnetic $\boldsymbol{M}^F$ moments.

The energy of the antisymmetric DM interaction between the moments is

$$E_{\mathrm{DM}} = \boldsymbol{D} \cdot (\boldsymbol{M}_1 \times \boldsymbol{M}_2) = 2\boldsymbol{D} \cdot (\boldsymbol{M}^{\dagger} \times \boldsymbol{M}^{F}), \quad (1)$$

where $\boldsymbol{D}$ is the DM vector. The effect of a weak antisymmetric DM interaction [12] in the presence of a large isotropic exchange interaction is to cant the spins away from their antiparallel alignment, generating a weak M^F at the expense of $M^{\dagger}$, and causing both $\boldsymbol{M}^F$ and $\boldsymbol{M}^{\dagger}$ to lie in plane perpendicular to $\boldsymbol{D}$. In the absence of an external field or anisotropy there is no preferred direction for $\boldsymbol{M}^F$ and $\boldsymbol{M}^{\dagger}$ in this plane. Application of a magnetic field $\boldsymbol{H}$ introduces the Zeeman interaction, $E_{\mathrm{Zeeman}} = -\boldsymbol{H} \cdot (\boldsymbol{M}_1 + \boldsymbol{M}_2) = -\boldsymbol{H} \cdot \boldsymbol{M}^F$, and causes $\boldsymbol{M}^F$ to lie along $\boldsymbol{H}$, breaking the degeneracy of the DM interaction. Figure 2 shows an example of this for $\boldsymbol{D}$ along z. In the absence of a field, $\boldsymbol{M}^{\dagger}$ and $\boldsymbol{M}^F$ lie in the x-y plane, and the two states of Fig. 2 are degenerate. Note that the configuration of these two states differs by a reversal of the electron spin orientation at every site. If a weak field is applied along $+x$ $(-x)$, the degeneracy of the states of Fig. 2 is broken and the ground states have $\boldsymbol{M}^F$ along $+x$ $(-x)$.

The SR transition we report occurs when the orientation of $\boldsymbol{H}$ is swept through $\boldsymbol{D}$. Using the example of Fig. 2, if the orientation of a weak $\boldsymbol{H}$ is swept through z in the x-z plane, $\boldsymbol{M}^F$ will change sign to follow the x component of $\boldsymbol{H}$ due to the Zeeman interaction, causing $\boldsymbol{M}^{\dagger}$ to change sign also in order to keep the DM energy minimized. This swapping of the orientations of the magnetic sublattices (changing of sign of $\boldsymbol{M}^{\dagger}$) as $\boldsymbol{H}$ is swept through $\boldsymbol{D}$ is the essence of the transition. As the transition occurs at $\boldsymbol{H} \parallel \boldsymbol{D}$, it provides a direct measurement of the orientation of $\boldsymbol{D}$—valuable information in systems such as κ-$(ET)_2Cu[N(CN)_2]Cl$ where the orientation of $\boldsymbol{D}$ is not fully specified by symmetry arguments.

Experimental evidence of such an SR transition in κ-$(ET)_2Cu[N(CN)_2]Cl$ is shown in Fig. 3. The figure shows ^{13}C NMR frequencies as a function of the direction of the applied field in the a-b plane of the crystal. The two sets of shift data came from the two inequivalent layers of κ-$(ET)_2Cu[N(CN)_2]Cl$, denoted A and B. From our previous symmetry analysis we know that each layer has a distinct $\boldsymbol{D}$ and that both $\boldsymbol{D}$'s lie in the a-b plane, but that the direction within the plane is not determined by the crystal symmetry [1]. As discussed later, the discontinuities seen in the shift data occur at the SR transitions when the orientation of $\boldsymbol{H}$ passes through the orientation of the $\boldsymbol{D}$'s, thus revealing the orientation of the $\boldsymbol{D}$'s. Note that at an orientation where a discontinuity occurs in the data of one layer, the data in the other layer are continuous, supporting our prior claims [1] that the interlayer interactions can be neglected for the purposes the magnetic ordering and that the DM vectors of the two planes have different orientations.

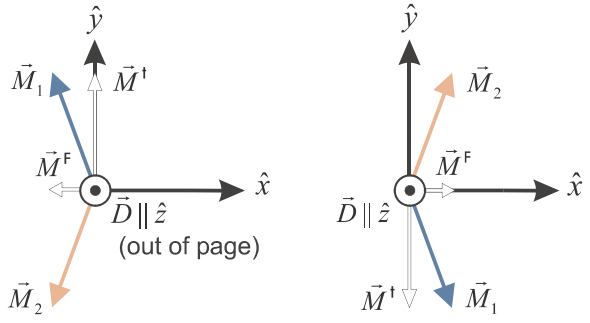

FIG. 2 (color online). Two spin configurations with the same DM interaction energy are shown for the case of $\boldsymbol{D} \parallel z$. The configuration on the left is the ground state for $\boldsymbol{H}$ along $-x$, the configuration on the right the ground state for $\boldsymbol{H}$ along $+x$.

The data were taken in a field of 8.3 T and at a temperature of 10 K, a temperature significantly below the Néel temperature, $T_N = 27$ K. These resonances originate from the "inner" site of the two "central" ^{13}C of the ET molecules in an isotopically labeled sample of κ-$(^{13}C_2$-$ET)_2Cu[N(CN)_2]Cl$ [15]. The inner label refers to the two ^{13}C closest to the center of a dimer, and the "outer" label refers to the remaining two ^{13}C. The data for the outer sites show similar but smaller discontinuities in the frequency at the same angles for which the discontinuities occur in the inner site data of Fig. 3. All of the data were obtained from a "point-by-point" sampling of the absorption resonance line using a spin-echo pulse sequence [16], and are presented in terms of a shift from the room temperature ^{13}C resonance frequency of a reference sample (TMS).

We observed no hysteresis in the orientation of the discontinuities while sweeping the field orientation forward and backward, but we cannot rule out some small amount of hysteresis of order $\pm 1°$. Also, the discontinuities could be observed while keeping the sample at 10 K and in a fixed field strength, varying only the field orientation. These results suggest that the discontinuities

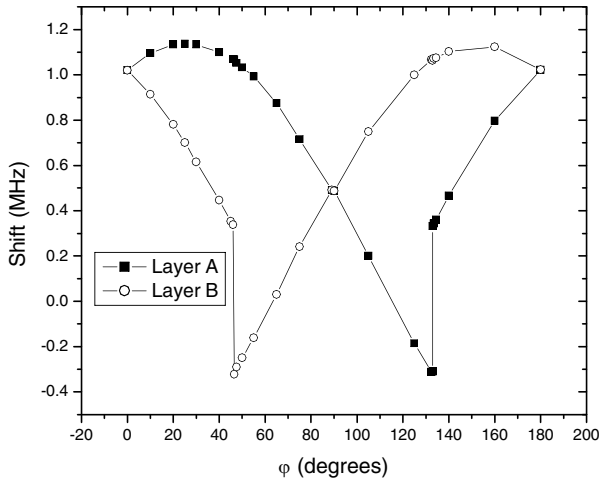

FIG. 3. Shift in ^{13}C inner site resonance frequencies as a function of orientation of the applied field in the a-b plane. Lines are provided as a guide to the eye.

occur at an orientation that is independent of the temperature-field history of the sample.

The full set of data for the a-b and b-c planes for both inner and outer sites is shown in Fig. 4. We have used the convention that θ is the polar angle from c, and ϕ is the azimuthal angle from a to b.

There are several notable features of our data. First, that the discontinuities are seen at all suggests that the SR driven by the DM interaction does indeed occur. Although this SR is essentially a swapping of the two magnetic sublattices and so is unlikely to be resolved by magnetometry, we explain here how it should manifest as a sudden frequency shift in NMR. In the field regime used, the nuclear spin Hamiltonian at a given site i should be dominated by the Zeeman interaction and the nuclear-electron spin interaction. The resonance frequency of a nucleus at site i is then determined by the effective field generated from these two interactions, which can be written as

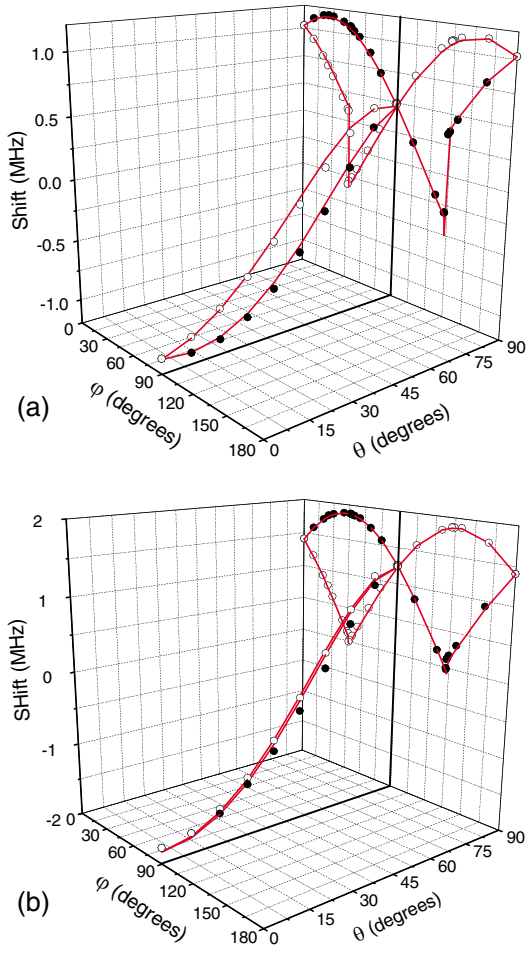

FIG. 4 (color online). Shift in ^{13}C resonance frequencies as a function of orientation of the applied field in the a-b plane ($\theta = 90°$) and the b-c plane ($\phi = 90°$) for both layer A (closed circles) and layer B (open circles): (a) inner site; (b) outer site. Lines are from fits to the data using Eqs. (2) and (3).

$$\boldsymbol{H}_{\mathrm{eff},i}(T) = \boldsymbol{H} + \frac{\mathbf{A}_i(T)}{\gamma_n \gamma_e \hbar^2} \cdot \boldsymbol{M}_i(T), \tag{2}$$

where $\mathbf{A}_i$ is the hyperfine tensor at site i, γ_n and γ_e are the gyromagnetic ratios of the nuclear and electron spins, and $\boldsymbol{M}_i$ is the electron spin moment at site i. For an anisotropic $\mathbf{A}_i$, as found in κ-$(ET)_2Cu[N(CN)_2]Cl$, a flop of the electron spin at a given site, i.e., a change of sign of $\boldsymbol{M}_i$, changes the effective field and manifests itself as a sudden change in the resonance frequency. Our data are the first observations of such an SR of which we are aware.

Another feature of the data is the absence of discontinuities in the b-c plane. This result is consistent with the symmetry analysis given in our previous work, where we showed that symmetry arguments constrain $\boldsymbol{D}_A$ and $\boldsymbol{D}_B$ to lie in the a-b plane. The symmetry analysis also indicated that $\boldsymbol{D}_A$ and $\boldsymbol{D}_B$ are related by a reflection in the b-c plane, so that if $\phi_{ab}^A = 90° + x$ is the orientation of $\boldsymbol{D}_A$ in the a-b plane, then $\phi_{ab}^B = 90° - x$ is the orientation of $\boldsymbol{D}_B$ in the a-b plane. We found a discontinuity in layer B at $\phi_{ab}^B = 46 \pm 0.5°$ and in layer A at $\phi_{ab}^A = 133 \pm 1°$, consistent with the symmetry constraint for $x = 44 \pm 1°$. Magnetometry results of our previous study had given $x = 26 \pm 13°$. Thus our previous method of determining the DM vector through a macroscopic magnetometry study, while providing a rough estimate of the DM orientation and strength, is far less precise than the microscopic method of determining the orientation of $\boldsymbol{D}$ presented here.

In addition to providing a determination of the orientation of the DM vectors, these data enabled a determination of the hyperfine tensors in the antiferromagnetic state. The hyperfine tensors were found by fitting the shift data using Eq. (2) with the $\mathbf{A}_i$'s as fit parameters. To do this it is necessary to have an expression for $\boldsymbol{M}_i$ as a function of the field orientation, now provided. We begin by noting that although the magnetic interactions in κ-$(ET)_2Cu[N(CN)_2]Cl$ include exchange anisotropy (hence the spin-flop transition of Ref. [2]), the applied field in which our data are taken is high enough that the Zeeman and DM interactions win out over this anisotropy. This is because both the Zeeman and DM interaction energies increase with increasing $\boldsymbol{M}^F$ and the anisotropic exchange does not (for $\boldsymbol{M}^F \ll \boldsymbol{M}^\dagger$). In this "high-field" regime, $\boldsymbol{M}^F$ is roughly along $\boldsymbol{H}$ and the orientation of $\boldsymbol{M}^\dagger$ in the plane perpendicular to $\boldsymbol{H}$ is determined by Eq. (1), so that $\boldsymbol{M}^\dagger$ tends to lie perpendicular to $\boldsymbol{D}$ also. Neglecting canting, the resulting ordering is described by

$$\boldsymbol{m}^\dagger = \boldsymbol{d} \times \boldsymbol{h}, \tag{3}$$

where lowercase letters are used to denote unit vectors. This expression makes it clear that $\boldsymbol{M}^\dagger$ changes sign as the orientation of the applied field is swept in a plane through the orientation of $\boldsymbol{D}$ or $-\boldsymbol{D}$.

In fitting the data, we assumed that Eq. (3) accurately describes the electron spin ordering. Note that in using

this expression we ignored several factors, including the weak anisotropy of the g-shift tensor [17], the canting of the electron spins, and any interaction between the inner and outer nuclei. We also assumed that the principle axes of the hyperfine tensor at a given site are near the principle axes of the ET molecule at that site. However, we allowed for a rotation (α) of the principle axes of the hyperfine tensor away from those of the ET molecule along one axis to provide for the effect of dimerization between adjacent ET molecules [15]. The orientation of $\phi_{ab} = 46.5°$ was included as a fit parameter, constrained to a range consistent with the observed discontinuity, 46° to 46.5°. For the magnitude of the electron spin magnetization in Eq. (2), M_i, we used $0.5\mu_B$ per dimer, a value consistent with results of our prior work [1].

The shifts resulting from the best fit to the tensors are represented by the lines in Fig. 4. The shift data, including the discontinuities, are well represented by the fit curve. The results of the fits at 10 K, assuming $0.5\mu_B$ per dimer, are given in the following table:

	A_{xx} (MHz)	A_{yy} (MHz)	A_{zz} (MHz)	α
Inner	-0.9 ± 1.3	0.2 ± 0.6	9.3 ± 0.7	$7.6° \pm 0.8°$
Outer	0.8 ± 0.1	3.5 ± 0.6	18.2 ± 0.6	$-3.9° \pm 0.2°$

For both the inner and outer sites, the best fit was found with an orientation of $\phi_{ab} = 46.5°$ for the DM vector of layer B.

The room temperature values of the hyperfine tensors are provided here for comparison:

	A_{xx} (MHz)	A_{yy} (MHz)	A_{zz} (MHz)	α
Inner	-1.6 ± 0.5	-3.4 ± 0.5	10.0 ± 0.5	$7.9° \pm 0.8°$
Outer	1.2 ± 0.2	-0.4 ± 0.2	16.8 ± 0.2	$-0.9° \pm 0.1°$

Significant changes are seen between room temperature and 10 K in A_{yy} of the inner site, and in A_{yy}, A_{zz}, and α of the outer site. A temperature-dependent hyperfine interaction was suggested in our previous work on κ-$(ET)_2Cu[N(CN)_2]Cl$, and has also been suggested for κ-$(ET)_2Cu[N(CN)_2]Br$ [18], so the changes are not surprising. In fact, the tensors at 10 K and room temperatures are remarkably similar, given that the room temperature parameters are based on a measured susceptibility and the 10 K parameters are based on the assumption of $0.5\mu_B$ per dimer. The similarity between the two sets of parameters supports our assumption of $0.5\mu_B$ per dimer.

In conclusion, we have predicted and observed what to our knowledge is a novel feature of magnetic systems with the Dzialoshinskii-Moriya interaction—a spin reorientation occurring when an external field is swept through the orientation of the DM vector. Though so far observed only in κ-$(ET)_2Cu[N(CN)_2]Cl$, we expect that such a reorientation should be observable at high fields in many different antiferromagnetic systems with the DM interaction. The advantage of using this SR to study the DM interaction is that the SR occurs in a high-field regime where complications introduced by anisotropic interactions are negligible. NMR proves to be an ideal probe of this spin reorientation and provides a precise determination of the orientation of the DM vector, which could be useful in systems where the orientation of the DM vector is not fixed by symmetry constraints.

We thank Arnaud Comment for helpful discussions and Stewart DeSoto for use of the goniometer probe. This work was supported by the U.S. Department of Energy, Division of Materials Sciences, through the Frederick Seitz Materials Research Laboratory at the University of Illinois at Urbana-Champaign under Grant No. DEFG02-91ER45439, and through Argonne National Laboratory under Contract No. W-31-109-ENG-38.

*Electronic address: dfsmith@uiuc.edu

[1] D. F. Smith, S. M. DeSoto, C. P. Slichter, J. A. Schlueter, A. M. Kini, and R. G. Daugherty, Phys. Rev. B **68**, 024512 (2003).
[2] K. Miyagawa, A. Kawamoto, Y. Nakazawa, and K. Kanoda, Phys. Rev. Lett. **75**, 1174 (1995).
[3] J. M. Williams *et al.*, Inorg. Chem. **29**, 3272 (1990).
[4] T. Thio, T. R. Thurston, N. W. Preyer, P. J. Picone, M. A. Kastner, H. P. Jenssen, D. R. Gabbe, C. Y. Chen, R. J. Birgeneau, and A. Aharony, Phys. Rev. B **38**, 905 (1988).
[5] T. Thio, C. Y. Chen, B. S. Freer, D. R. Gabbe, H. P. Jenssen, M. A. Kastner, P. J. Picone, N. W. Preyer, and R. J. Birgeneau, Phys. Rev. B **41**, 231 (1990).
[6] D. Coffey, K. S. Bedell, and S. A. Trugman, Phys. Rev. B **42**, 6509 (1990).
[7] M. D. Lumsden, B. C. Sales, D. Mandrus, S. E. Nagler, and J. R. Thompson, Phys. Rev. Lett. **86**, 159 (2001).
[8] I. Tsukada, J. Takeya, T. Masuda, and K. Uchinokura, Phys. Rev. Lett. **87**, 127203 (2001).
[9] M. Oshikawa and I. Affleck, Phys. Rev. Lett. **79**, 2883 (1997).
[10] M. Lohmann, H.-A. Krug von Nidda, M. V. Eremin, A. Loidl, G. Obermeier, and S. Horn, Phys. Rev. Lett. **85**, 1742 (2000).
[11] N. P. Konstantinidis and D. Coffey, Phys. Rev. B **66**, 174426 (2002).
[12] Here we neglect the accompanying symmetric Kaplan–Shekhtman–Entin-Wohlman–Aharony term [13,14] since the antisymmetric term will dominate in a strong enough field.
[13] T. A. Kaplan, Z. Phys. B **49**, 313 (1983).
[14] L. Shekhtman, O. Entin-Wohlman, and A. Aharony, Phys. Rev. Lett. **69**, 836 (1992).
[15] S. M. De Soto, C. P. Slichter, A. M. Kini, H. H. Wang, U. Geiser, and J. M. Williams, Phys. Rev. B **52**, 10 364 (1995).
[16] C. P. Slichter, *Principles of Magnetic Resonance* (Springer-Verlag, Berlin, 1990).
[17] M. Kubota, G. Saito, H. Ito, T. Ishiguro, and N. Kojima, Mol. Cryst. Liq. Cryst. **284**, 367 (1996).
[18] S. M. De Soto, Ph.D. thesis, University of Illinois at Urbana-Champaign, 1995.