

Orientational Coupling Amplification in Ferroelectric Nematic Colloids

Fenghua Li,¹ Oleksandr Buchnev,² Chae Il Cheon,³ Anatoliy Glushchenko,⁴ Victor Reshetnyak,⁵ Yuri Reznikov,² Timothy J. Sluckin,⁶ and John L. West¹

¹Liquid Crystal Institute, Kent State University, Kent, Ohio 44242, USA

²Institute of Physics, Ukrainian Academy of Science, Kyiv, Ukraine

³Hoseo University, Baebang, Asan, Chungnam 336-795, Korea

⁴University of Colorado at Colorado Springs, Colorado Springs, Colorado 80933, USA

⁵Kyiv Taras Shevchenko University, Kyiv, Ukraine

⁶School of Mathematics, University of Southampton, Southampton SO17 1BJ, United Kingdom

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We investigated the physical properties of low concentration ferroelectric nematic colloids, using calorimetry, optical methods, infrared spectroscopy, and capacitance studies. The resulting homogeneous colloids possess a significantly amplified nematic orientational coupling. We find that the nematic orientation coupling increases by $\sim 10\%$ for particle concentrations of 0.2%. A manifestation of the increased orientational order is that the clearing temperature of a nematic colloid increases by up to 40 °C compared to the pure liquid crystal host. A theoretical model is proposed in which the ferroelectric particles induce local dipoles whose effective interaction is proportional to the square of the orientational order parameter.

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Colloids with LC matrices exhibit a rich set of behaviors [1–6]. LC-microcolloidal particle ($\geq 1 \mu\text{m}$) anchoring can produce long-range orientational distortions around the particles, causing strong interactions which can give rise to well-ordered particle structures in the liquid crystal matrix (e.g., lattices or chains) [2,3]. However, these phenomena usually occur in concentrated dispersions, with particle volume fraction $c_{\text{part}} \geq 30\%$. The particle-induced director distortions extend over macroscopic scales, causing the suspensions to scatter light strongly [5,7]. In addition, the impurities normally decrease the nematic clearing temperature T_{NI} [8]. These colloids cannot replace conventional nematic materials in optical applications.

Ferroelectric nanocolloidal liquid crystals (FNCLCs), consisting of a very low concentration ($c_{\text{part}} \leq 1\%$) of submicron ferroelectric particles suspended in a LC host, behave very differently from classic LC colloids. We present results here which show massive increases in T_{NI} , of the order of 40 °C, for mass impurity concentrations of the order of 0.2%. But here the low concentration causes the suspension-matrix interaction to be insufficient to disturb the LC orientation. Thus FNCLCs can act like a conventional nematic material in optical applications.

Previous work has shown hints of anomalous dielectric anisotropy and other physical properties in FNCLCs for display applications [9–12], in the context of application-led studies. The new elements in this work are the following: (a) these anomalies are general features of this class of materials; (b) the sheer size of the effect, an increase of 40 °C in T_{NI} at a mass concentration of 2 parts in 1000, is unprecedented; and (c) we introduce a theoretical paradigm which accounts for all the anomalies semi-quantitatively.

The theoretical picture involves augmenting the standard Grandjean-Maier-Saupe (GMS) molecular field the-

ory [13] of the nematic phase. The GMS theory posits the existence of an effective nematic interaction energy parameter $\mathcal{U} \approx 4.54k_B T_{\text{NI}}$ and an orientational contribution to the energy per LC particle $-(1/2)\mathcal{U}S^2$, where S is the (scalar) nematic order parameter. Increasing \mathcal{U} increases T_{NI} . In our picture the colloidal nanoparticles produce locally large electric fields, which polarize the nematic molecules. The mean induced dipole moment is proportional to the average polarizability and hence to S . The integrated dipolar interaction between the induced dipoles is thus proportional to S^2 , providing an additional component $\Delta\mathcal{U}$ to the effective nematic interaction. This raises T_{NI} and also increases local order at given T . Estimates of $\Delta\mathcal{U}$ from different experiments are consistent, verifying the hypothesis.

Most of our experiments utilized the nematic LC MLC-6609 from Merck ($T_{\text{NI}} = 91.5^\circ\text{C}$), doped with BaTiO_3 nanoparticles from Aldrich. The nanoparticle dimension was 50–100 nm, which is determined in the transmission electron microscopy (TEM) picture shown in the inset of Fig. 1.

The FNCLC colloid is extremely stable. The powder from Aldrich contained macroscopic aggregates of BaTiO_3 . To destroy the aggregates, the particles were milled in a solvent in the presence of an oleic acid surfactant. Occasionally, some aggregation occurred several weeks after cell preparation. Usually, however, phase separation did not occur over a cell life of over 1 yr. We give details of the preparation process elsewhere [9].

The clearing temperature T_{NI} was determined using differential scanning calorimetry (DSC) at a rate of 5 K min⁻¹. The resulting DSC scans for the pure MLC-6609 and for the colloid ($c_{\text{part}} \approx 0.2\%$) are shown in Fig. 1. When the BaTiO_3 nanoparticles are introduced, the clearing temperature increases by 38.7 °C. A lower mass frac-

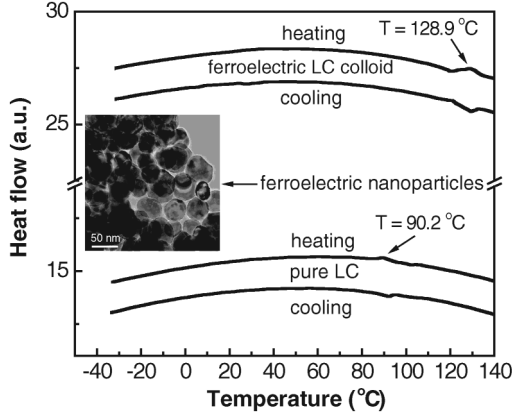


FIG. 1. DSC graphs for heating and cooling of the samples with pure LC MLC-6609 (bottom pair of the curves) and colloids of BaTiO₃ in MLC-6609 (top pair of the curves), $c_{\text{part}} \approx 0.2\%$. Inset: TEM picture of ferroelectric nanoparticles.

tion ($c_{\text{part}} \approx 0.05\%$) produced a reduced shift $\Delta T_{\text{NI}} = 23.1^\circ\text{C}$. The changes in T_{NI} were confirmed using polarized optical microscope.

We also measured other LC properties in the colloidal suspension, in order to check the hypothesis that the increase in T_{NI} is a consequence solely of an increased effective nematic interaction. First, we measured order parameters, using Fourier-transform infrared spectroscopy and observing the dichroism of the characteristic functional groups of the nematic matrix components. We used the stretch vibration of $C=C$ groups of benzene rings ($\nu = 1513\text{ cm}^{-1}$) because this group is oriented along the long axis of the LC molecules. The $C=C$ band dichroism was measured using a Magna 550 FTIR (Nicolet) spectrometer in NaCl cells of $16\ \mu\text{m}$ thickness. The spectrometer was equipped with a hot stage and wire-grid polarizers. The LC and the colloid were homogeneously aligned using a thin ($<0.1\ \mu\text{m}$) rubbed polyimide alignment layer. The order parameter was evaluated using the formula $S = (D - 1)/(D + 2)$, where $D = A_{\parallel}/A_{\perp}$ is the dichroism of absorbance parallel (A_{\parallel}) and perpendicular (A_{\perp}) to the IR beam polarization. Figure 2 shows the temperature dependence of the resulting order parameters, in both the pure MLC-6609 and the ferroelectric colloid ($c_{\text{part}} \approx 0.2\%$). The clearing temperature increase is mirrored by an order parameter increase; at 30°C the order parameter gain, $S_{\text{COL}}/S_{\text{LC}} = 1.2$.

A further measurement compares the optical birefringence of the colloid to that of the pure nematic. We assume the ferroelectric nanoparticles act as effective molecular dopants. The birefringence of the colloid can then be written as [14]

$$n_a^{\text{COL}} = \frac{4\pi FN_{\text{LC}}\gamma_a^{\text{COL}}}{n_e^{\text{COL}} + n_o^{\text{COL}}} S_{\text{COL}}, \quad (1)$$

where F is the local field factor, $\gamma_a^{\text{COL}} = (1 - c_{\text{part}})\gamma_a^{\text{LC}} +$

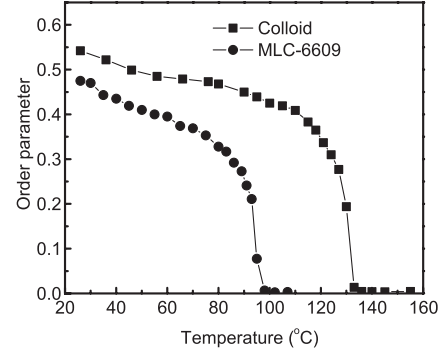


FIG. 2. Temperature dependences of the order parameter of MLC-6609 and the ferroelectric colloid ($c_{\text{part}} \approx 0.2\%$).

$c_{\text{part}}(\gamma_a^{\text{part}})$ with γ_a^{LC} is the LC molecular polarizability anisotropy and γ_a^{part} is the polarizability anisotropy of the ferroelectric particles. The birefringence gain with respect to the pure LC is then given by

$$\frac{n_a^{\text{COL}}}{n_a^{\text{LC}}} = \frac{(n_e^{\text{LC}} + n_o^{\text{LC}})}{(n_e^{\text{COL}} + n_o^{\text{COL}})} \frac{\gamma_a^{\text{COL}}}{\gamma_a^{\text{LC}}} \frac{S_{\text{COL}}}{S_{\text{LC}}}. \quad (2)$$

The birefringence gain in the colloid involves three separate components. The first is the statistical mechanics-induced order parameter increase. The second depends also on the effective anisotropy of both the ferroelectric particles and LC molecules, the values of which are not known. Finally, the gain depends on the ratio of the refractive indices of the LC and the colloid. We measured these refractive indices and find that the ratio is essentially unity.

Experimentally we obtained $n_a(T)$ using an Abbé refractometer. An independent set of experiments used a retardation technique measuring the phase shift between e and o waves $\varphi = \pi dn_a/\lambda$ in planar cells ($d = 12\ \mu\text{m}$). The results of the two sets of measurements were in agreement. In Fig. 3 we show the temperature dependence of the birefringence in the pure LC and in one colloidal sample ($c_{\text{part}} \approx 0.05\%$). At 32°C the predicted

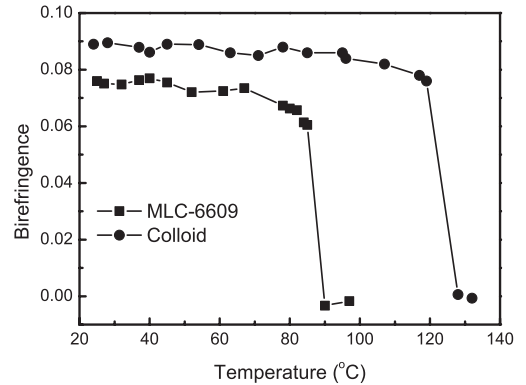


FIG. 3. Temperature dependence of the birefringence of MLC-6609 and the ferroelectric colloid ($c_{\text{part}} \approx 0.05\%$).

$n_a^{\text{COL}}/n_a^{\text{LC}} = 1.2$ agrees with the experimental value $S_{\text{COL}}/S_{\text{LC}} = 1.2$. The birefringence increases in n and S in the FNCLC are consistent. We find that at 32°C , $\varepsilon_a^{\text{COL}}/\varepsilon_a^{\text{LC}} = 1.54$. This result is close, but not identical, to $(n_a^{\text{COL}})^2/(n_a^{\text{LC}})^2 \approx S_{\text{COL}}^2/S_{\text{LC}}^2 = 1.44$. We speculate that this discrepancy may be due to an extra contribution at low frequencies from the ferroelectric colloidal particles to the effective dielectric function of the colloid [15].

Our hypothesis is that the birefringence gain is a consequence only of the increase in S . If this is the case, then the ratio of the low frequency (i.e., $\nu \approx 1$ kHz) colloidal dielectric constant to that in the pure LC should be the same as that at optical frequencies: $\varepsilon_a^{\text{COL}}/\varepsilon_a^{\text{LC}} = (n_a^{\text{COL}})^2/(n_a^{\text{LC}})^2 \approx S_{\text{COL}}^2/S_{\text{LC}}^2$. We used a Hewlett-Packard 4194A impedance analyzer to measure the LC cell capacitance. The cells were $15 \mu\text{m}$ thick, and the dielectric anisotropy was determined by comparing results with planar and homeotropic orientation. In Fig. 4, we present results for the temperature dependence of the dielectric anisotropy $\varepsilon_a(T)$.

Smaller increase in the clearing point have been observed for other LC host systems (for example, ZLI-2248, ZLI-4801, and 5CB), doped with both $\text{Sn}_2\text{P}_2\text{S}_6$ and BaTiO_3 nanoparticles. The increases are always accompanied by increases in the dielectric anisotropy and birefringence.

All our experiments are explicable by supposing the effective orientational interaction; \mathcal{U} increases in the FNCLC. In our principal sample we find $\mathcal{U}_{\text{COL}}/\mathcal{U}_{\text{LC}} = T_{\text{NI}}^{\text{COL}}/T_{\text{NI}}^{\text{LC}} \approx 1.1$. We now consider the orientational effect of additional terms in the FNCLC free energy. We assume for simplicity that the ferroelectric particles are spherical in shape. The spontaneous polarization of the monodomain particles is assumed the same as that of a BaTiO_3 monocrystal, 0.26 C m^{-2} [16]. The permanent polarization \mathbf{P} of a ferroelectric particle creates a locally large electric field $\sim 7 \times 10^9 \text{ V m}^{-1}$ [17]:

$$\mathbf{E}_P = \frac{R^3}{3\varepsilon_0} \left(3 \frac{(\mathbf{P} \cdot \mathbf{r})\mathbf{r}}{r^5} - \frac{\mathbf{P}}{r^3} \right), \quad (3)$$

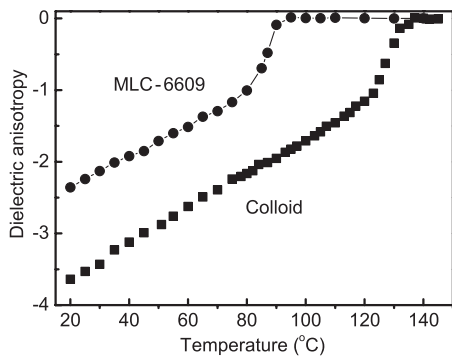


FIG. 4. Temperature dependences of the dielectric anisotropy of MLC-6609 and the ferroelectric colloid ($c_{\text{part}} \approx 0.2\%$).

where R is the particle radius. This field induces a dipole moment \mathbf{G}_i in a host LC molecule i with long axis \mathbf{l} , where $\mathbf{G}_i = \varepsilon_0 \boldsymbol{\beta} \cdot \mathbf{E}_P \sim 1/r^3$. The low frequency molecular polarizability tensor $\boldsymbol{\beta} = \beta_0 \mathbf{I} + \beta_a [\mathbf{l} \otimes \mathbf{l} - (1/3)\mathbf{I}]$, with β_a the anisotropic component. The mean of this quantity is $\langle \beta_{\alpha\beta} \rangle = \beta_0 \delta_{\alpha\beta} + (2/3)\beta_a Q_{\alpha\beta}$, with the nematic order parameter tensor $Q_{\alpha\beta} = (1/2)S(3n_\alpha n_\beta - \delta_{\alpha\beta})$, and with S the scalar order parameter.

The interaction between the electric field \mathbf{E}_P and the induced LC molecular dipole \mathbf{G}_i is given by $U_{\text{LC-P}} \sim \sum \varepsilon_0 \boldsymbol{\beta}_i \cdot \mathbf{E}_P(\mathbf{r}_i) \mathbf{E}_P(\mathbf{r}_i)$. The magnitude of the interaction between the induced dipoles is

$$U_{\text{COL}}^{\text{add}} \sim \sum_{\text{particles}, i \neq j} \frac{\mathbf{G}_i}{4\pi\varepsilon_0} \left[\frac{\mathbf{G}_j}{|\Delta\mathbf{r}_{i,j}|^3} - 3 \frac{(\mathbf{G}_j \cdot \Delta\mathbf{r}_{i,j})\Delta\mathbf{r}_{i,j}}{|\Delta\mathbf{r}_{i,j}|^5} \right], \quad (4)$$

where $\mathbf{r}_i - \mathbf{r}_j = \Delta\mathbf{r}_{i,j}$.

We now suppose the most important contributions come from the z nearest neighbor molecules, separated by distance L . We average Eq. (4) over all LC molecule orientations. There is a contribution depending on β_0 , which is independent of the degree of orientation in the system. We select the contribution of order β_a^2 . After averaging, this provides a contribution of order S^2 [18] and is

$$U_a \sim \frac{1}{2} z \frac{(\varepsilon_0 \beta_a S)^2}{4\pi\varepsilon_0 L^3} \sum_{\text{particles}, i} (\mathbf{E}_P(\mathbf{r}_i))^2, \quad (5)$$

where the factor of $1/2$ avoids double counting. The quantity $\sum_{\text{particles}, i} (\mathbf{E}_P(\mathbf{r}_i))^2$ can be determined by integrating \mathbf{E}_P calculated from Eq. (3). The integration occurs outside the ferroelectric particles, which are assumed to be spherical and of radius R ; the cross terms in the square cancel. There is now a power-counting argument, leading to the following result:

$$\sum_{\text{particles}, i} (\mathbf{E}_P(\mathbf{r}_i))^2 = N_{\text{LC}} \frac{4\pi P^2 R^3}{27\varepsilon_0^2}, \quad (6)$$

with N_{LC} the LC molecular concentration. Hence we find $U_a \sim -(1/2)eS^2$, with

$$e \approx \frac{1}{27} z N_{\text{LC}} N_{\text{part}} \frac{\beta_a^2 P^2}{\varepsilon_0} \left(\frac{R}{L} \right)^3 = \frac{z\eta N_{\text{LC}} \beta_a^2 P^2}{36\pi\varepsilon_0 L^3}, \quad (7)$$

with N_{part} and η the colloidal particle volume concentration and fraction, respectively. The key parameter e is the proportionality coefficient characterizing the response of the intermolecular interaction to the field due to the ferroelectric particle. The shift in the Maier-Saupe parameter \mathcal{U} is given by $e = N_{\text{LC}} \Delta\mathcal{U}$, which directly yields the shift in the clearing point $\Delta\mathcal{U} = 4.54 k_B \Delta T_{\text{NI}}$. At fixed η , in this approximation, the effect is *independent* of particle size.

To make quantitative estimates, we take $P = 0.26 \text{ C m}^{-2}$, $N_{\text{part}} = 7 \times 10^{19} \text{ m}^{-3}$, $N_{\text{LC}} = 2 \times 10^{27} \text{ m}^{-3}$, $N = 6$, $R = 50 \text{ nm}$, and $L = 0.5 \text{ nm}$. Using $\beta_a N_{\text{LC}} \approx \varepsilon_a$

[14] and $\varepsilon_a \approx 1$, we find $e \approx 0.9 \times 10^7 \text{ J m}^{-3}$. The resulting shift $\Delta T_{\text{NI}} \approx 70 \text{ }^\circ\text{C}$ is in qualitative agreement with our experimental observations.

Our model does not take into account other possible contributions to the intermolecular interaction. There may be image forces or quadrupole interactions that remain important even above the Curie temperature. These may be significant as a result of the high nanoparticle dielectric constant, causing ΔT_{NI} to be underestimated.

The observed effect requires e as large as possible at fixed η . In the calculation of e the key step lies between Eqs. (4) and (5). This step replaces a scalar product of fields at neighboring points by the square of a local field. Mathematically this requires a perturbation in a small parameter (L/R), which is zero in the large colloidal limit. In the molecular impurity limit, by contrast, this quantity is of the order of unity. Thus the supramolecular size of the impurity particles causes the huge effect. In principle, this conclusion is testable by varying the particle size.

The effect is proportional to the nanoparticle volume, but should not grow without limit. Large particles generate orientational defects in their neighborhood, which destroy the colloidal homogeneity and lower orientational order. We estimate the critical particle size $R_{\text{max}} \sim \zeta = K/W$, the so-called surface extrapolation length [2], where K is a Frank constant. For typical values $K \sim 10^{-11} \text{ N}$ and $W \sim 10^{-4} \text{ J m}^{-2}$, R_{max} should be of the order of 100 nm.

In sufficiently large colloidal particles, the ferroelectric material is expected to form a polydomain structure. In small systems, the ferroelectric mean field will be insufficient to maintain a ferroelectric ground state. Despite ongoing debates, ferroelectricity is thought to vanish for particles of dimensions smaller than $\sim 10 \text{ nm}$ [19]. We therefore speculate the optimal size of the ferroelectric particles in homogeneous LC colloids to be in the range 10–100 nm. In addition, for small colloidal particles the orientational entropy of the colloidal particles plays a further role which reduces the effective polarization.

In conclusion, our results clearly show the unique properties of ferroelectric nanoparticles/LC colloids. Since the size of the particles is much larger than the LC molecular dimension, the strong electric field from the particles influences a large number of neighboring LC molecules ($\sim 10^3$). The huge ferroelectric dipole moment of the nanoparticles produces a powerful field inducing dipolar intermolecular interactions that compete with the spontaneous intermolecular interaction. The additional interaction then leads to a dramatic increase in the LC mean field interaction and then to a giant increase in the clearing temperature. This statement remains true even for very low colloidal particle concentrations.

The dramatic effects seem to occur when the colloidal particle sizes are large enough to directly influence a large number of molecules, but small enough that they do not disturb the director field. The optimal range for the particle

size is 10–100 nm. The presence of larger particles would destroy the LC colloid homogeneity, whereas smaller particles are not ferroelectric. The increased nematic mean field interaction causes the homogeneous ferroelectric LC colloid to have a higher birefringence, dielectric anisotropy, and order parameter than the pure LC material. These results are not only true in the model systems which we have investigated in detail, but are also a general feature of colloidal suspensions made from ferroelectric colloidal particles dispersed in thermotropic liquid crystal matrices. As a result ferroelectric nanoparticles/LC colloids offer an innovative simple and effective means to control precisely the physical properties of liquid crystalline materials.

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- [1] F. Brochard and P.G. de Gennes, *J. Phys. (Paris)* **31**, 691 (1970).
 - [2] H. Stark, *Phys. Rep.* **351**, 387 (2001).
 - [3] P. Poulin *et al.*, *Science* **275**, 1770 (1997).
 - [4] S.P. Meeker *et al.*, *Phys. Rev. E* **61**, R6083 (2000).
 - [5] A. Glushchenko *et al.*, *Liq. Cryst.* **23**, 241 (1997).
 - [6] T. Jin and D. Finotello, *Phys. Rev. E* **69**, 041704 (2004).
 - [7] B.J. Liang and S.H. Chen, *Phys. Rev. A* **39**, 1441 (1989).
 - [8] D.E. Martire *et al.*, *J. Chem. Phys.* **64**, 1456 (1976).
 - [9] Y. Reznikov *et al.*, *Appl. Phys. Lett.* **82**, 1917 (2003).
 - [10] E. Ouskova *et al.*, *Liq. Cryst.* **30**, 1235 (2003).
 - [11] Y. Reznikov *et al.*, *Proc. SPIE-Int. Soc. Opt. Eng.* **5741**, 171 (2005).
 - [12] C.I. Cheon *et al.*, *SID 2005 Digest* **45.2**, 1 (2005).
 - [13] F. Grandjean, *C.R. Acad. Sci., Ser. I, Math.* **164**, 280 (1917); W. Maier and A. Saupe, *Z. Naturforsch.* **13a**, 564 (1958).
 - [14] L.M. Blinov, *Electro-Optical and Magneto-Optical Properties of Liquid Crystals* (Wiley, New York, 1993).
 - [15] V.Yu. Reshetnyak, *Mol. Cryst. Liq. Cryst.* **421**, 219 (2004).
 - [16] B. Jaffe, W.R. Cook, Jr., and H. Jaffe, *Piezoelectric Ceramics* (Academic Press, New York, 1971).
 - [17] L.D. Landau, E.M. Lifshitz, and L.P. Pitaevskii, *Electrodynamics of Continuous Media* (Pergamon Press, New York, 1984), Chap. II.
 - [18] There may also be a term linear in S ; see, e.g., I. Lelidis and G. Durand, *Phys. Rev. Lett.* **73**, 672 (1994).
 - [19] M. Tanaka and Y. Makino, *Ferroelectr., Lett. Sect.* **24**, 13 (1998); S. Tsunekawa *et al.*, *Phys. Rev. B* **62**, 3065 (2000).