

## Field dependence of glassy freezing in a relaxor ferroelectric

Matthew Delgado, Eugene V. Colla, Philip Griffin, and Michael B. Weissman

*Department of Physics, University of Illinois at Urbana-Champaign, 1110 West Green Street, Urbana, Illinois 61801-3080, USA*

Dwight Viehland

*Department of Materials Science and Engineering, Virginia Tech, 201 Holden Hall (0237), Blacksburg, Virginia 24061, USA*

(Received 17 December 2008; revised manuscript received 5 February 2009; published 23 April 2009)

Multifrequency susceptibility measurements on the perovskite relaxor ferroelectric  $(\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3)_{0.88}(\text{PbTiO}_3)_{0.12}$  were performed at various strengths of dc electric field applied along the [111] direction. The temperature-frequency dependences fit the Vogel-Fulcher form, allowing the extraction of a frequency-independent glassy freezing temperature. These Vogel-Fulcher temperatures showed significant reductions in applied fields, following an empirical Gabay-Toulouse form, similar to vector spin glasses. The magnitude of the sensitivity indicates that the glassy state is formed by interactions among the same entities which account for the susceptibility, i.e., the polar nanoregions. That interpretation is supported by other data showing a loss of Vogel-Fulcher behavior in a powder sample of  $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ , with grains too small to support large-scale internanoregion cooperativity.

DOI: [10.1103/PhysRevB.79.140102](https://doi.org/10.1103/PhysRevB.79.140102)

PACS number(s): 77.84.Dy, 75.10.Nr, 64.70.P-, 77.22.Gm

### I. INTRODUCTION

The large susceptibility of perovskite relaxor ferroelectrics, such as  $(\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3)_{1-x}(\text{PbTiO}_3)_x$  (PMN-PT), comes from ferroelectriclike polar nanoregions (PNRs), typically about 10 nm in size.<sup>1,2</sup> Upon lowering the temperature ( $T$ ) the PNRs grow slightly<sup>3</sup> but do not form long-range ferroelectric order. Instead, the ac dielectric susceptibility shows a frequency-dependent peak vs  $T$  as the PNR orientations undergo some sort of glassy kinetic freezing. Explanations for that kinetic freezing include simple growth of barriers as PNR grow in fixed random fields,<sup>4</sup> growth of kinetic barriers as PNR interact with a glass of interacting unit-cell displacements orthogonal to the PNR polarization,<sup>5</sup> and various forms of glass formed as a result of inter-PNR interactions.<sup>6,7</sup> We have presented considerable evidence that in perovskite relaxors (with an average cubic symmetry), unlike uniaxial relaxors,<sup>8</sup> a low-temperature spin glass is present even when the PNRs are too highly polarized to support any spin-glass order.<sup>9</sup> However, it has not been clear whether that result could be extrapolated to conclude that the kinetic effects causing the loss of susceptibility were due to those same unit-cell-scale degrees of freedom involved in the aging. Here we show, using the field dependence of the glassy freezing temperature, that the main freezing effect is due to inter-PNR interactions rather than to the more local, less polar degrees of freedom which become important at lower  $T$ . We point out also that previously observed<sup>10</sup> dependence on grain size in powder samples of the temperature dependence of the kinetics supports a picture of glassiness forming from interacting units of about the size of PNR.

The temperature of the peak in the  $\chi'(f)$ ,  $T_p(f)$  is a decreasing function of applied electric field  $E$  for small  $E$  in the perovskite relaxors. (e.g., Refs. 11 and 12) Since for spin-glass models and materials the freezing temperature is a decreasing function of the applied magnetic field, it is possible that there is a useful analogy between the two effects. In order to make a good comparison, particularly to determine the exponent connecting the reduction in the freezing tem-

perature to the applied field, it is important to first extract an accurate frequency-independent freezing temperature from the frequency-dependent  $T_p(f)$  rather than to simply use the previously reported  $T_p(f)$ . This extraction requires an accurate set of  $T_p(f)$  taken over a wide range of  $f$ , as discussed below.

The slow kinetics observed in the susceptibility  $\chi'(T, f)$  show a distinctly non-Arrhenius dependence on  $T$  and frequency ( $f$ ),<sup>13,14</sup> roughly similar to spin glasses<sup>15</sup> and other cooperative glasses.<sup>16</sup> The dependence  $T_p(f)$  on  $f$  can be fit with the Vogel-Fulcher form,

$$f = f_0 e^{-T_A/(T_p - T_{VF})}, \quad (1)$$

where  $f_0$  is an attempt rate and  $T_A$  as well as the Vogel-Fulcher temperature,  $T_{VF}$ , are fitting parameters.<sup>17</sup>  $T_{VF}$  is taken to be the empirical glass transition temperature.

In spin glasses, the freezing temperature  $T_f$  (whether taken to be a sharp kinetic crossover or a true phase transition) decreases in an applied field,  $H$ .<sup>15</sup> The qualitative explanation is simple: as the spins are aligned, there are fewer of them free to form a glass (in the Ising case<sup>18</sup>) or weaker thermally free interacting moments (in the vector spin case). The functional dependences of the freezing temperature on field are different for these two cases. Theoretical arguments indicate that  $T_f(H)$  vector spin glasses should follow a Gabay-Toulouse (GT) line as follows:<sup>19</sup>

$$\tau \equiv \frac{T_f(H)}{T_f(0)} = 1 - \left( \frac{\mu H}{k_B T_f(0)} \right)^2, \quad (2)$$

where  $\mu$  is (approximately, in practice) the single-spin moment and  $k_B$  is Boltzmann's constant. This sort of behavior has been observed experimentally.<sup>20</sup>

In this Rapid Communication we focus on the dependence of  $T_{VF}$  of the common perovskite relaxor PMN-12%PT on applied electric field,  $E_{dc}$ . The significant reduction in  $T_{VF}$  as a function of  $E_{dc}$ , will be found to fit a dielectric GT line surprisingly well if one assumes that interactions among the

PNR are the basis of the glassy freezing. The same interpretation also is supported by finite-size effects on the form of the  $T$ - $f$  dependence of  $\chi(T, f)$  in powder samples with small grains.<sup>17</sup>

## II. EXPERIMENT AND RESULTS

Multifrequency measurements of the in-phase susceptibility  $\chi'(T, f)$  were performed on single-crystal PMN-PT ( $x = 0.12$ ), grown by a modified Bridgeman technique by TRS Technologies of State College, PA. The sample was about  $\sim 0.52$  mm thick and  $\sim 5$  mm on each side, oriented with the [111] direction parallel to the applied field. The electrodes were made by sputtering a 100 nm Au layer onto a 10 nm Cr underlayer on each side of the sample. One side was fully covered while the other had a 1.91-mm-diameter circular electrode.

The temperature  $T$  was controlled via a Linear Research model 130 feedback system in a standard nitrogen transfer line cryostat, with the sample space maintained under vacuum by a mechanical pump. Prior to each temperature sweep, the sample was annealed at  $T=450$  K for several hours to erase the history of the polarization. The sample was cooled from  $T=450$  K to  $T=350$  K at  $dT/dt=4$  K/min, with the fast rate used to save time. From  $T=350$  K to a  $T$  just above the empirical FE freezing temperature we used  $|dT/dt|=0.1$  K/min upon cooling and warming to ensure that an accurate measurement of the temperature was obtained at each measurement frequency.

All the ac susceptibility measurements used an ac measuring field of approximately 2 V/cm which is significantly smaller than the dc field applied during the measurements. During the temperature scan measurements were made with a lock-in amplifier at frequencies  $f=5, 10, 50, 100, 500, 1$  k, 5 k, 10 k, and 50 k Hz. The output time constant was  $10/f$  for low  $f$ , and the time spent at each  $f$  before switching to the next was  $1$  s +  $100/f$ .  $\chi(T, f)$  was measured at the following fixed fields:  $E_{dc}=0, 0.4, 0.8, 1.1,$  and  $1.41$  kV/cm. The external field was applied at the onset of cooling and remained on during heating.

In Fig. 1 we show the typical  $\chi'(T, f)$  curves, taken at different  $f$ , measured in zero field (ZF). The peak in  $\chi'(T, f)$ ,  $T_p(f)$ , was determined by fitting a third-order polynomial in a temperature window of about 6 K around the  $\chi'(T, f)$  peak. (The width of the window varied with frequency measured as low frequencies have broader peaks in  $\chi'$ .) The resulting fit was then differentiated to find the maximum. The  $T_p(f)$  were fit to Eq. (1), giving  $T_{VF}$ . We checked that  $T_p$  was insensitive to our choice of window, within the range used, to within 20 mK.

Figure 2 shows the VF fit at  $E_{dc}=0$  and at 1.13 kV/cm, giving  $T_{VF}=309.17 \pm 0.6$  K and  $300.5 \pm 1.5$  K, respectively. The  $T_{VF}$ 's obtained from data taken while warming were identical within error bars to those found upon cooling, showing (among other things) that the sweep rate is sufficiently slow.

Figure 3 shows the empirical  $E_{dc}$ - $T$  quasiphase diagram including  $T_{VF}(E_{dc})$  as well as the approximate empirical freezing line and the (near-equilibrium<sup>21</sup>) melting line, each

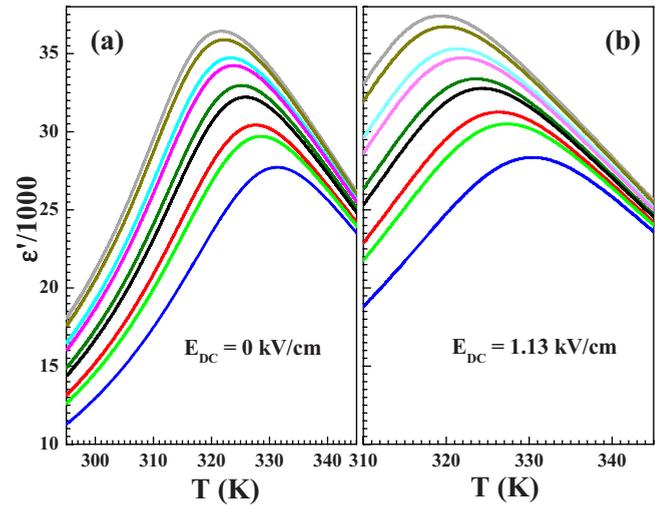


FIG. 1. (Color online) The real susceptibilities at 5, 10, 50, 100, 500, 1 k, 5 k, 10 k, and 50 k Hz are shown upon cooling in zero field and 1.13 kV/cm. The highest frequency is furthest to the right.

determined from peaks in pyroelectric current upon heating or cooling. (For our current purposes, the interesting behavior at high  $E$  of the FE melting and freezing, which is believed to involve a critical point terminating the equilibrium transition line,<sup>22</sup> is largely irrelevant.) The  $T_{VF}$  points to the left of the freezing line are based entirely on fits to data taken to the right of the freezing line.  $T_{VF}$  drops with increasing  $|E_{dc}|$ , opposite to the behavior of the equilibrium (melting) FE transition line, and reminiscent of spin-glass behavior.

## III. DISCUSSION

In order to semiquantitatively compare the reduction in  $\tau$ , i.e.,  $T_{VF}(E_{dc})/T_{VF}(0)$ , vs  $|E_{dc}|$  with spin-glass behavior, we

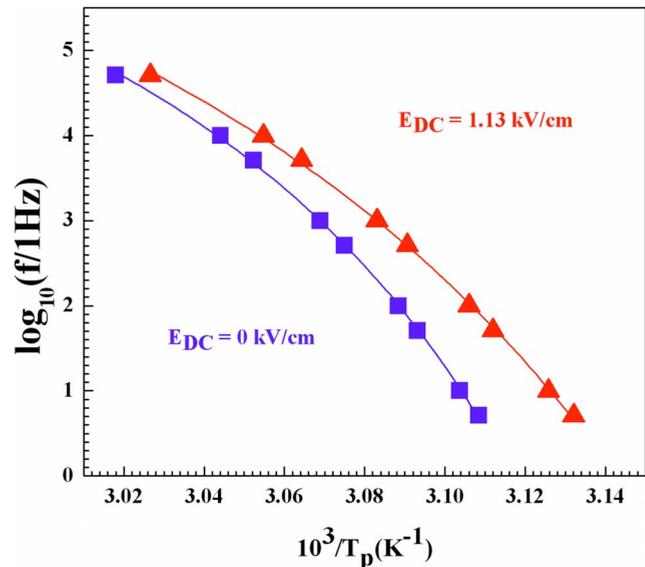


FIG. 2. (Color online) The  $\log(f/1 \text{ Hz})$  vs  $T^{-1}$  is plotted for two different external fields with  $T_{\max}$  measured from the susceptibility upon cooling. Squares:  $E_{dc}=0$  kV/cm, fit with  $T_{VF}=309.17$  K. Triangles:  $E_{dc}=1.13$  kV/cm, fit with  $T_{VF}=300.49$  K.

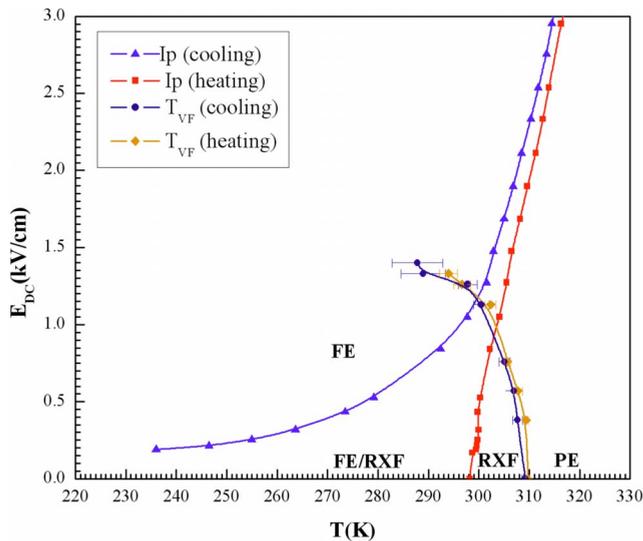


FIG. 3. (Color online) The phase diagram for PMN-12%PT is plotted with the freezing line (triangles), melting line (squares),  $T_{VF}$  (cooling) line (circles), and  $T_{VF}$  (heating) line (diamonds) versus  $E_{dc}$ . The phases are ferroelectric (FE), nonergodic relaxor (RXF), ergodic relaxor, or paraelectric (PE), with one region (FE/RXF) showing history-dependent phase. The freezing line is the measured temperature where the peak pyroelectric current ( $I_p$ ) occurs upon cooling in field. The melting line was determined from the peak in  $I_p$  upon heating.  $T_{VF}$  (cooling) and  $T_{VF}$  (heating) are calculated from the peaks in susceptibility upon cooling and heating, respectively.

convert  $E_{dc}$  to dimensionless form. For the field, the conversion for a spin glass involves multiplying  $E_{dc}$  by the dipole moment of the individual spins and dividing by the thermal energy scale. In this case, the dipole moments of the PNR are only roughly known, and the response to fields is limited not only by the thermal energy but also by random fields. Therefore we believe that the appropriate dimensionless form of  $E_{dc}$  for a glass composed of PNR should correspond approximately to the polarization divided by the saturation polarization,  $P_S$ . Thus we fit  $\tau(E_{dc})$  with the following form:

$$C \frac{\chi' E_{dc}}{P_S} = (1 - \tau)^p, \quad (3)$$

where  $C$  is a dimensionless constant. For the GT form,  $p = 0.5$  and  $C$  is of order unity. Fitting our data while fixing  $T_{VF}(0)$  at 309.17 K and allowing  $p$  and  $C$  to float gives  $p = 0.55 \pm 0.03$  and  $C = 1.52 \pm 0.16$  (Fig. 4). The closeness of  $p$  to the simple GT value of 0.5 suggests fitting with  $p = 0.5$ , while allowing  $T_{VF}(0)$  to float within the error bars. This procedure also produces a good fit, with  $T_{VF}(0) = 308.74 \pm 0.08$  K (well within the direct experimental error bars for that quantity) and  $C = 1.77 \pm 0.03$ . The data points at large  $E_{dc}$  that do not fit the curve are based on data taken near the transition to the FE phase, in which a peculiar double-peaked  $\chi'(T)$  is found, possibly influenced by the proximity of a critical point.<sup>22</sup>

If the glassy regime of this relaxor was simply driven by interactions among PNR with choices of eight easy axes, it

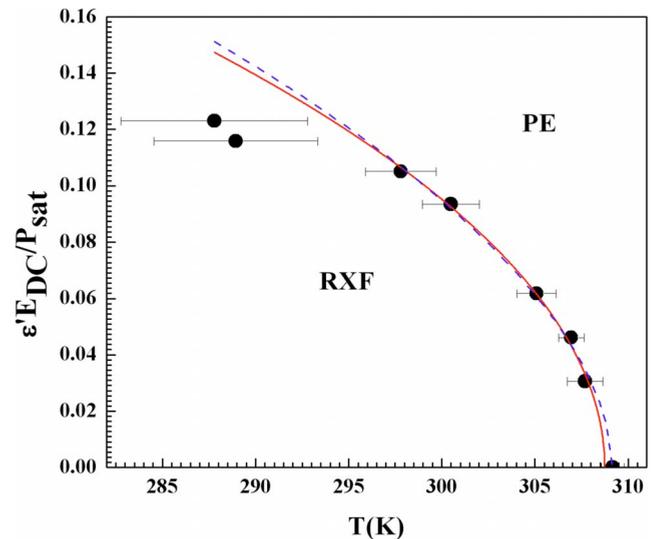


FIG. 4. (Color online) The dividing line  $T_{VF}(E_{dc})$  between the RXF and the paraelectric phase is shown. The solid line is a GT-type fit with  $p = 0.5$ , giving  $T_{VF}(0) = 308.74 \pm 0.08$  K and  $C = 1.77 \pm 0.03$ . The dashed line fixes  $T_{VF} = 309.17$  K, giving  $p = 0.55 \pm 0.03$  and  $C = 1.52 \pm 0.16$ .

would be somewhat surprising for the  $E_{dc}$ - $T_{VF}$  curve to fit GT-type Eq. (3) since that applies to systems without local anisotropy. It is known, however, that the spatial-average anisotropy is fairly weak.<sup>23</sup> Even more surprising, Eq. (3) works even though the relaxor has very prominent random fields helping to lower its susceptibility, unlike standard spin glasses, for which time-reversal symmetry forbids random fields. Furthermore, according to neutron-scattering data, the ferroelectric correlations of which the PNR consists continue to grow somewhat in length near the vicinity of the kinetic freezing,<sup>3</sup> which again would be expected to alter the  $E$ - $T$  freezing line. Thus we do not claim that this fit confirms some prior prediction. Nevertheless, the strong GT-type sensitivity of  $T_{VF}$  to polarization would be hard to understand unless, as in the spin-glass case, the polarizing entities are the same things whose interactions drive the formation of the glassy state. For example, the entities (probably unit-cell displacements orthogonal to PNR polarizations)<sup>5,8</sup> which contribute low- $T$  spin-glass-like aging in polarized states well above the GT line<sup>9</sup> would be very unlikely candidates to show simple GT behavior with  $C$  of order unity.

There are several independent pieces of evidence to support this conclusion. If the relaxor glassy state is formed by interactions among PNR, one would expect that the formation of the glass would be disrupted by finite-size effects in grains which contain only a few PNR. Just such loss of V-F behavior has been found in powder samples, only when the grain size is small.<sup>10</sup> (We have replicated those results in detail for one such sample.) However, the attempt rates determined from approximate Arrhenius fits for these small-grain powder samples are unphysically large,<sup>17</sup> indicating that the freezing still involves growth of thermodynamic correlations but not with the longer-range correlations needed to support a distinct transition temperature.

One would also expect that relaxor materials which are driven by very different physics, for example, uniaxial ma-

materials, approximately describable by a random-field Ising model should not show GT-type behavior. In fact, for one such material  $T_p$  shows no clear systematic decrease with polarization, i.e.,  $C < 0.03$ .<sup>8</sup> In contrast we now have preliminary results on a plain PMN crystal which approximately fit the GT form with  $C$  about one.

Finally, we comment on two possible issues connected with this interpretation. First, in the best-developed model treating the PNR orientations as nearly isotropic, the spherical random-field random bond mean-field model, it has been shown that there is no GT line.<sup>2</sup> However, that argument

concerns a true phase transition line, not the sort of sharp kinetic crossovers which occur in many glass transitions, and which are identified by Vogel-Fulcher behavior.<sup>16</sup> Second, we emphasize again that the spin-glass-like aging found above the GT line and well below  $T_{VF}$  in PMN-12%PT must originate in a different glassy order parameter than the one involved in the freezing at  $T_{VF}$ .<sup>9</sup> For those aging effects, the most plausible origin remains a glass of constrained unit-cell displacements orthogonal to the [111] PNR polarization directions.<sup>5,8,24</sup> Thus two distinct glassy order parameters exist in parallel.

<sup>1</sup>L. E. Cross, *Ferroelectrics* **151**, 305 (1994).

<sup>2</sup>L. E. Cross, *Ferroelectrics* **76**, 241 (1987).

<sup>3</sup>G. Xu, G. Shirane, J. R. D. Copley, and P. M. Gehring, *Phys. Rev. B* **69**, 064112 (2004).

<sup>4</sup>V. Westphal, W. Kleemann, and M. D. Glinchuk, *Phys. Rev. Lett.* **68**, 847 (1992).

<sup>5</sup>E. V. Colla, M. B. Weissman, P. M. Gehring, G. Xu, H. Luo, P. Gemeiner, and B. Dkhil, *Phys. Rev. B* **75**, 024103 (2007).

<sup>6</sup>D. Viehland, J. F. Li, S. J. Jang, L. E. Cross, and M. Wuttig, *Phys. Rev. B* **46**, 8013 (1992).

<sup>7</sup>S. Vakhrushev, A. Nabereznov, S. K. Sinha, Y. P. Feng, and T. Egami, *J. Phys. Chem. Solids* **57**, 1517 (1996).

<sup>8</sup>L. K. Chao, E. V. Colla, M. B. Weissman, and D. D. Viehland, *Phys. Rev. B* **72**, 134105 (2005).

<sup>9</sup>Eugene V. Colla, P. Griffin, M. Delgado, M. B. Weissman, X. Long, and Z.-G. Ye, *Phys. Rev. B* **78**, 054103 (2008).

<sup>10</sup>J. Carreaud, C. Bogicevic, B. Dkhil, and J. M. Kiat, *Appl. Phys. Lett.* **92**, 242902 (2008).

<sup>11</sup>E. V. Colla, E. Y. Koroleva, N. M. Okuneva, and S. B. Vakhrushev, *Ferroelectrics* **184**, 209 (1996).

<sup>12</sup>S. I. Raevskaya, A. S. Emelyanov, F. I. Savenko, M. S. Panchevlyuga, I. P. Raevski, S. A. Prosdandeev, E. V. Colla, H. Chen, S.

G. Lu, R. Blinc, Z. Kutnjak, P. Gemeiner, B. Dkhil, and L. S. Kamzina, *Phys. Rev. B* **76**, 060101(R) (2007).

<sup>13</sup>E. V. Colla, E. L. Furman, S. M. Gupta, N. K. Yushin, and D. Viehland, *J. Appl. Phys.* **85**, 1693 (1999).

<sup>14</sup>A. A. Bokov and Z. G. Ye, *Phys. Rev. B* **65**, 144112 (2002).

<sup>15</sup>K. Binder and A. P. Young, *Rev. Mod. Phys.* **58**, 801 (1986).

<sup>16</sup>C. A. Angell, *J. Non-Cryst. Solids* **131-133**, 13 (1991).

<sup>17</sup>D. Viehland, S. J. Jang, L. E. Cross, and M. Wuttig, *J. Appl. Phys.* **68**, 2916 (1990).

<sup>18</sup>J. R. L. d. Almeida and D. J. Thouless, *J. Phys. A* **11**, 983 (1978).

<sup>19</sup>M. Gabay and G. Toulouse, *Phys. Rev. Lett.* **47**, 201 (1981).

<sup>20</sup>G. G. Kenning, D. Chu, and R. Orbach, *Phys. Rev. Lett.* **66**, 2923 (1991).

<sup>21</sup>E. V. Colla, D. Vigil, J. Timmerwilke, M. B. Weissman, D. D. Viehland, and B. Dkhil, *Phys. Rev. B* **75**, 214201 (2007).

<sup>22</sup>Z. Kutnjak, J. Petzelt, and R. Blinc, *Nature (London)* **441**, 956 (2006).

<sup>23</sup>H. Cao, J. Li, D. Viehland, and G. Xu, *Phys. Rev. B* **73**, 184110 (2006).

<sup>24</sup>L. K. Chao, E. V. Colla, and M. B. Weissman, *Phys. Rev. B* **74**, 014105 (2006).