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Griffiths phase manifestation in disordered dielectrics

V.A. Stephanovich[a]

Institute of Mathematics, University of Opole, Oleska 48, 45-052, Opole, Poland
and
Institute of Semiconductor Physics NAS of Ukraine, Prospect Nauki 45, 252650 Kiev, Ukraine

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Abstract. We predict the existence of a Griffiths phase in dielectrics with a concentrational crossover between dipole glass (electric analog of spin glass) and ferroelectricity. Particular representatives of the above substances are $KTaO_3$:Li, Nb, Na, or relaxor ferroelectrics like $Pb_{1-x}La_xZr_{0.65}Ti_{0.35}O_3$. Since this phase exists above the ferroelectric phase-transition temperature (but below that temperature for ordered substances), we call it a "para-glass phase". We assert that the difference between paraelectric and para-glass phases in the above substances is the existence of clusters (inherent to the "ordinary" Griffiths phase of Ising magnets) of correlated dipoles. We show that randomness plays a decisive role in the Griffiths (para-glass) phase formation: this phase does not exist in a mean field approximation. To investigate the Griffiths phase properties, we calculate the density of Yang-Lee (YL) zeros in the partition function and find that it has "tails" inherent to the Griffiths phase in the above temperature interval. We perform calculations on the basis of our self-consistent equation for the long-range order parameter in an external electric field. This equation has been derived in the framework of the random field theory. The latter automatically incorporates both short-range (due to indirect interaction *via* transverse optical phonons of the host lattice) and long-range (ordinary dipole-dipole) interactions between impurity dipoles, so that the problem of long-range interaction considerations does not appear in it.

PACS. 64.70.Pf Glass transitions – 77.80.Bh Phase transitions and Curie point

It was shown by Griffiths [1] that the free energy of a dilute Ising ferromagnet is a nonanalytic function of the external magnetic field for all temperatures between the critical value $T_c(x)$ (x is the concentration of lattice sites without Ising spins) and $T_c(1)$ of the corresponding nondilute system. The manifestation of nonanalyticity in the original article of Griffiths was the distribution of the zeros in the partition function Z (the Yang-Lee (YL) zeros) in the plane of complex magnetic fields $H = i\theta$. Namely, below $T_c(1)$ YL-zeros appear arbitrarily close to the point $H = 0$, implying a zero radius of convergence for expansions of thermodynamic quantities in powers of H. The "visible sign" of such nonanalyticity is the appearance of a "tail" in the density of YL zeros $\rho(\theta)$ at $T_c(x) < T < T_c(1)$.

Dielectric systems are, in many respects, different from magnetic ones. The main difference is that the main interaction in dielectrics is the long-range dipole-dipole interaction, whereas in magnets the latter is a small relativistic correction to the short-range exchange interaction. It was shown in [2] that the dipole-dipole interaction in disordered dielectrics does not prevent the occurrence of the aforementioned "tails" in $\rho(\theta)$ and thus to the realization of a Griffiths phase analog.

In the present paper we investigate the manifestation of a Griffiths phase in dielectrics, where both long-range ferroelectric order and dipole glass (say, "dielectric spin glass") phase can occur depending on the impurity-dipole concentration. Particular representatives of such substances are $KTaO_3$:Li, Nb, Na, where Li, Nb or Na, being off-center ions, constitute the impurity dipoles with a discrete number of permissible orientations in the host $KTaO_3$ matrix (see [3] for details). Other particular representatives of the aforementioned class of substances are relaxor ferroelectrics like $Pb_{1-x}La_xZr_{0.65}Ti_{0.35}O_3$ (PLZT), which can be considered as some reference phase (in the case of PLZT it is $PbZr_{0.65}Ti_{0.35}O_3$ having long-range ferroelectric order) "spoiled" by intrinsic defects of a different kind, playing the role of impurity dipoles (see [4] for details).

Although the description of these disordered dielectrics is still not complete at present, we suggested a so-called random local field method (see *e.g.* [5] and references therein) for their description. This method captures remarkably well the peculiarities of the physical properties of these substances, namely a concentrational crossover between ferroelectric and dipole glass phases, the existence of a mixed ferro-glass phase, and the nonexponential long-time relaxation in glass and ferro-glass phases [5].

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[a] e-mail: `stefcan@netscape.net`

In this method, we derive the equation for the long-range order parameter L. This equation was obtained self-consistently through the distribution function of random fields acting between impurity dipoles (see [5] for details). The specific form of this equation depends on the particular number of orientations of the impurity dipoles in the host crystal matrix. For the simplest case of impurity dipoles with only two permissible orientations this equation has the form

$$\begin{aligned} L &= \frac{1}{\beta}\int_{-\infty}^{\infty}\tanh(\beta E)\, f(E,L)\mathrm{d}E, \\ f(E,L) &= \frac{1}{2\pi}\int_{-\infty}^{\infty}\exp(\mathrm{i}E\rho)\exp\left[F_1(\rho)+\mathrm{i}F_2(\rho)\right]\mathrm{d}\rho, \\ F_1(\rho) &= n\int_V\left[\cos(\mathcal{K}_{zz}\rho)-1\right]\mathrm{d}^3r, \\ F_2(\rho) &= nL\int_V \sin(\mathcal{K}_{zz}\rho)\mathrm{d}^3r \\ &\equiv nE_0(\rho)L, \\ \beta &= \frac{1}{k_{\mathrm{B}}T}, \end{aligned} \tag{1}$$

where n is the concentration of impurities, $f(E,L)$ is a distribution function of random fields (see *e.g.* [5]), $F_1(\rho)$ is "responsible" for the dispersion of random fields, $F_2(\rho)$ for the mean value of the random field, $\mathcal{K}_{zz}$ is a component of the tensor of interaction $\mathcal{K}_{\alpha\beta}(\mathbf{r})$ ($\alpha, \beta = x, y, z$, $\mathbf{r}$ is the interimpurity separation) between impurity dipoles in the highly polarizable dielectric host. The general form of $\mathcal{K}_{\alpha\beta}$ reads (see *e.g.* [6] and references therein)

$$\begin{aligned} \mathcal{K}_{\alpha\beta}(\mathbf{r}) &= \frac{d^{*2}}{\varepsilon_0 r^3}\Big\{ f_1(r/r_{\mathrm{c}})\delta_{\alpha\beta} \\ &\quad +(3m_\alpha m_\beta-\delta_{\alpha\beta})\big(1+f_2(r/r_{\mathrm{c}})\big)\Big\}, \\ \mathbf{m} &= \frac{\mathbf{r}}{r} \end{aligned} \tag{2}$$

where ε_0 is the host lattice's static dielectric permittivity, d^* is the effective dipole moment of the impurity (see *e.g.* [3]), r_{c} is the host lattice's correlation radius (two impurities at a distance less than or equal to r_{c} "feel" each other). The physical reason for the appearance of r_{c} and the functions $f_1(x), f_2(x) \propto x^2\exp(-x)$ is the indirect interaction of impurity dipoles *via* the host lattice's soft phonon mode (see *e.g.* [6] and references therein). If the latter interaction is absent, we have $r_{\mathrm{c}} \to 0$, $f_1(r/r_{\mathrm{c}}), f_2(r/r_{\mathrm{c}}) \to 0$ so that (2) gives the ordinary dipole-dipole interaction. It is seen that interaction (2) incorporates both a long-range part (term $(3m_\alpha m_\beta-\delta_{\alpha\beta})/r^3$) and a short-range part (terms containing $f_1(x)$ and $f_2(x)$). The explicit form of the functions f_1 and f_2 can be found in [4,6].

It can be shown (see *e.g.* [5]) that at high impurity concentrations the distribution function of random fields has a Gaussian form. This form can be obtained from (1) by the expansion of the integrands in $F_{1,2}(\rho)$ up to first leading order. This gives

$$\begin{aligned} &F_1(\rho)=c\rho^2,\ \ F_2(\rho)=nE_0L, \\ &c=\frac{16\pi}{15}\frac{\left(nd^{*2}\right)^2}{(\varepsilon_0)^2 nr_{\mathrm{c}}^3},\ \ E_0=4\pi\frac{nd^{*2}}{\varepsilon_0}\cdot \end{aligned} \tag{3}$$

Since the case of a Gaussian distribution function implies the strongest (both long-range and short-range) interaction between impurity dipoles (and consequently their clusters) this case can be regarded as the most difficult for a Griffiths phase to occur. We shall demonstrate the manifestation of a Griffiths phase for this case with the understanding that for lower impurity dipole concentration the realization of a Griffiths phase is easier.

The equation for the order parameter for a Gaussian distribution function takes the form

$$\begin{aligned} L=\frac{2}{\pi}\int_0^\infty\int_0^\infty &\tanh\left(\frac{E}{kT}\right)\exp(-c\rho^2) \\ &\times\sin(\rho E)\sin\rho(\mathcal{E}+E_0L)\,\mathrm{d}\rho\mathrm{d}E, \end{aligned} \tag{4}$$

where $\mathcal{E}$ is an external electric field. We introduce the following dimensionless variables

$$\begin{aligned} &\frac{\mathcal{E}}{E_0}=h,\quad \rho E_0=y,\quad \frac{E}{E_0}=x, \\ &\frac{kT}{E_0}=\tau,\ \ \frac{c}{E_0^2}=\frac{1}{15\pi z},\ \ z=nr_{\mathrm{c}}^3. \end{aligned} \tag{5}$$

With these variables, the equation for L takes the form

$$\begin{aligned} L=\frac{2}{\pi}\int_0^\infty\int_0^\infty &\tanh\left(\frac{x}{\tau}\right)\exp\left(-\frac{y^2}{15\pi z}\right) \\ &\times\sin(xy)\sin y\,(h+L)\,\mathrm{d}x\mathrm{d}y. \end{aligned} \tag{6}$$

Integration over x in (6) gives

$$\tau\int_0^\infty\exp\left(-\frac{y^2}{15\pi z}\right)\frac{\sin y(h+L)}{\sinh\left(\frac{\pi y\tau}{2}\right)}\mathrm{d}y=L. \tag{7}$$

We shall investigate the Griffiths phase properties on the basis of equation (7).

The equation for the phase transition temperature τ_{c} can be obtained from (7) at $L\to 0$ (of course, at $h=0$)

$$\tau_{\mathrm{c}}\int_0^\infty y\exp\left(-\frac{y^2}{15\pi z}\right)\frac{\mathrm{d}y}{\sinh\left(\frac{\pi y\tau_{\mathrm{c}}}{2}\right)}=1. \tag{8}$$

The equation for the critical concentration of impurities can be obtained from (8) at $\tau_{\mathrm{c}}\to 0$. It reads

$$\frac{2}{\pi}\int_0^\infty\exp\left(-\frac{y^2}{15\pi z_{\mathrm{cr}}}\right)\mathrm{d}y=1,\quad\text{or } z_{\mathrm{cr}}=\frac{1}{15}\cdot \tag{9}$$

Equations (8, 9) determine the phase diagram of the system under consideration. It is shown in Figure 1.

The theorem of Yang and Lee states that the zeros of the partition function Z lie on the unit circle $h=\mathrm{i}\theta$

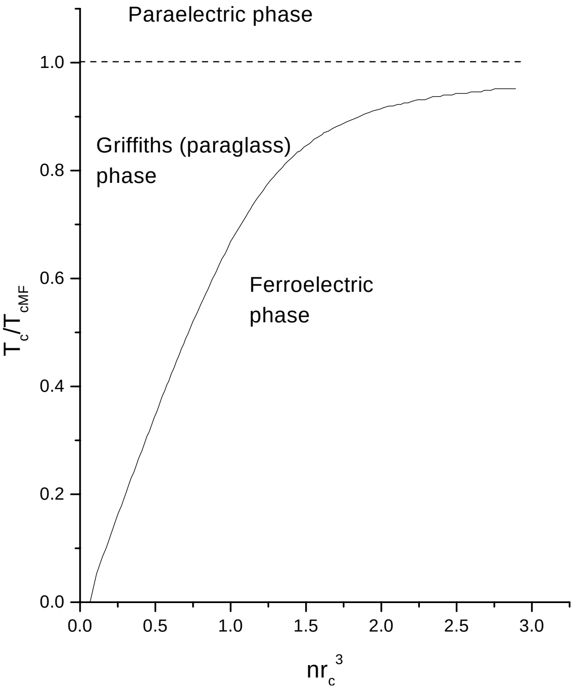

Fig. 1. Phase diagram of the substances under consideration.

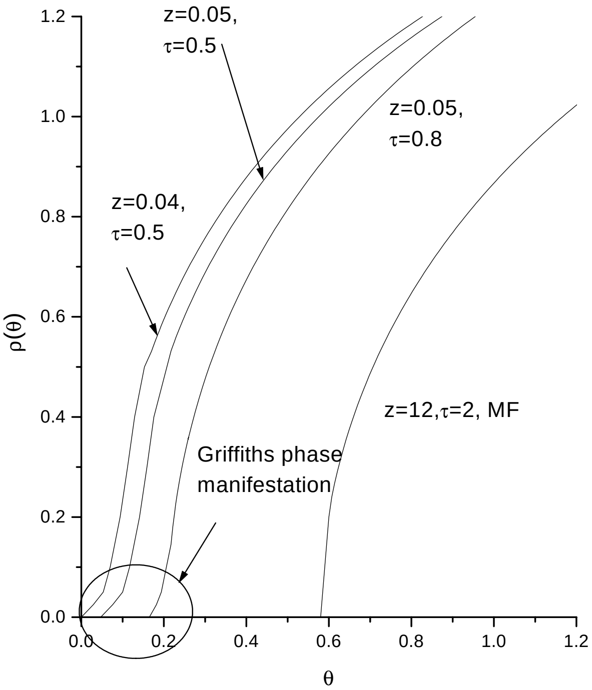

Fig. 2. Density of YL-zeros. Characteristic "tails" inherent to the Griffiths phase are shown. The curve labeled "MF" is also realized in mean field approximation (see Eq. (19)).

in the plane of the complex variable $z = \exp(-2\beta H)$ [7]. To calculate the density of YL-zeros, we put in (7)

$$h = \mathrm{i}\theta,\ L = L_1 + \mathrm{i}L_2. \tag{10}$$

We have from (7)

$$\begin{aligned} L_1 &= \tau \int_0^\infty \exp\left(-\frac{y^2}{15\pi z}\right) \frac{\sin(L_1 y)\cosh\left(y(\theta + L_2)\right)}{\sinh\left(\frac{\pi y \tau}{2}\right)} \mathrm{d}y, \\ L_2 &= \tau \int_0^\infty \exp\left(-\frac{y^2}{15\pi z}\right) \frac{\cos(L_1 y)\sinh(y(\theta + L_2))}{\sinh\left(\frac{\pi y \tau}{2}\right)} \mathrm{d}y. \end{aligned} \tag{11}$$

The density of YL-zeros $\rho(\theta)$ equals [8]

$$\rho(\theta) = \frac{L_1}{\pi} \cdot \tag{12}$$

Equations (11, 12) are the main theoretical results of this paper. To find $\rho(\theta)$ from (12), we should find (at a given temperature and concentration) L_1 and L_2 from (11). The Griffiths phase is realized in the substances under consideration if $\rho(\theta)$ has "tails" near $\theta = 0$ at $\tau_c < \tau < 1$. This is because, in the language of equations (8, 9), the phase transition temperature of a nondilute system $T_c(1)$ corresponds to the quantity E_0 determining the phase transition temperature in a mean field approximation T_{cMF}, *i.e.* $T_c(1) \equiv E_0 = T_{\mathrm{cMF}}$.

We plot the dependence $\rho(\theta)$ for different τ and z in Figure 2. First of all, one sees the presence of tails inherent to the Griffiths phase of dilute systems. For nondilute (completely ordered systems) there is no Griffiths singularities. This clearly demonstrates the occurrence of a Griffiths phase in dielectrics with a concentrational crossover between dipole glass and ferroelectricity. Figure 2 shows the region of a existence of a Griffiths phase in the phase diagram of these substances.

Since a Griffiths phase occurs at temperatures higher than that of the ferroelectric phase transition of the disordered system, but lower than that of the ordered (nondilute) system, we can call this phase a "para-glass". Glassy behaviour is due to clusters of impurity dipoles (see [2,8–10]). The manifestation of these clusters is indeed "tails" in $\rho(\theta)$. It is seen from Figure 2 that at temperatures higher than T_{cMF} there are no more "tails" in $\rho(\theta)$, and the para-glass phase becomes a conventional paraelectric phase.

Another peculiar feature of all curves is the existence of some threshold value θ_e, below which there are no YL-zeros ($\rho(\theta) \equiv 0$). This is the so-called YL edge, which is the manifestation of the ordered state of the system (paramagnetic phase of a nondilute system, see [8–10]). The "tail-like" approach to θ_e at smaller z is due to disorder (glassy effects) in the system. Thus at sufficiently small z ($z = 0.05$ in Fig. 2) the system is in a mixed ferro-glass phase, exhibiting both "order" and "disorder" features. The difference between ferro-glass and para-glass is that in the former an overall long-range order exists, while in the latter it does not exist. Our supposition is that the para-glass phase corresponds to superparamagnetism, well-known in spin glasses.

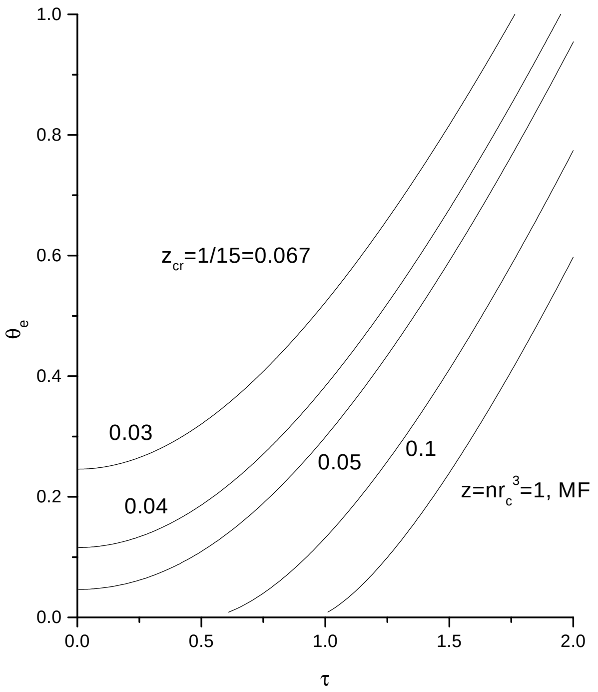

Fig. 3. Temperature dependence of $\theta_{\rm e}$ at different impurity concentrations. The curve labeled "MF" is also realized in the mean field approximation (see Eq. (20)).

To find the equation for $\theta_{\rm e}$ we put $L_1 = 0$ in (11).

$$L_2 = \tau \int_0^\infty \exp\left(-\frac{y^2}{15\pi z}\right) \frac{\sinh(y(\theta_{\rm e}+L_2))}{\sinh\left(\frac{\pi y\tau}{2}\right)}{\rm d}y. \quad (13)$$
$$1 = \tau \int_0^\infty \exp\left(-\frac{y^2}{15\pi z}\right) \frac{y\cosh(y(\theta_{\rm e}+L_2))}{\sinh\left(\frac{\pi y\tau}{2}\right)}{\rm d}y.$$

The dependence $\theta_{\rm e}(\tau)$ is shown in Figure 3. It is seen that at $z > z_{\rm cr} = 1/15$ (ferroelectric and ferro-glass phase) $\theta_{\rm e} = 0$ at $\tau = \tau_{\rm c}$, while at $z < z_{\rm cr}$, $\theta_{\rm e} \neq 0$ for all temperatures. To trace the transition from the ordered phase to the Griffiths phase it is instructive to investigate the concentrational dependence of $\theta_{\rm e}$ at zero temperature.

We have from (13)

$$L_2 = \frac{2}{\pi}\int_0^\infty \exp\left(-\frac{y^2}{15\pi z}\right) \frac{\sinh(y(\theta_{\rm e}+L_2))}{y}{\rm d}y, \quad (14)$$
$$1 = \frac{2}{\pi}\int_0^\infty \exp\left(-\frac{y^2}{15\pi z}\right) \cosh(y(\theta_{\rm e}+L_2)){\rm d}y. \quad (15)$$

The integral in (15) can be calculated analytically giving

$$\sqrt{15z}\exp\left[\frac{15\pi z}{4}(\theta+L_2)^2\right] = 1.$$

Denoting $\mu = \theta + L_2$, we obtain

$$\theta_{\rm e} = \mu - \frac{2}{\pi}\int_0^\infty \exp\left(-\frac{y^2}{15\pi z}\right)\frac{\sinh(\mu y)}{y}{\rm d}y,$$
$$\mu^2 = -\frac{2}{15\pi z}\ln(15z) \quad (16)$$

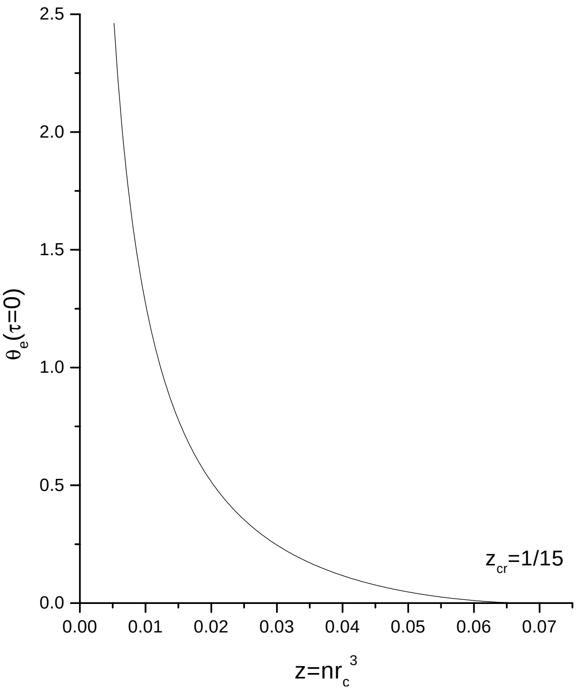

Fig. 4. Concentrational dependence of $\theta_{\rm e}$ at zero temperature.

or

$$\theta_{\rm e}(\lambda) = \frac{\lambda}{\sqrt{\pi}}\exp\left(\frac{\lambda^2}{4}\right) - \frac{2}{\pi}\int_0^\infty \exp(-t^2)\frac{\sinh(\lambda t)}{t}{\rm d}t,$$
$$\lambda^2 = -2\ln(15z). \quad (17)$$

The dependence (17) is reported in Figure 4. It can be shown that the equation $\theta_e(\lambda) = 0$ is satisfied at $z = z_{cr} = 1/15$.

Let us finally show that the para-glass phase cannot be realized in the ordered dielectric. To do so we demonstrate the absence of "Griffiths tails" for nondiluted systems. This corresponds to the mean field limit ($z \to \infty$) in the random field method. In this limiting case we have from (7)

$$L_{\rm MF} = \tanh\left(\frac{h + L_{\rm MF}}{\tau}\right). \quad (18)$$

This equation is indeed the mean field equation for the order parameter of the Ising model. In this case $\tau_{\rm cMF} = 1$. Substituting (10) for (18) gives:

$$L_{\rm 1MF} = \frac{\sinh(2L_{\rm 1MF}/\tau)}{2\left(\sinh^2(L_{\rm 1MF}/\tau) + \cos^2(\theta + L_{\rm 2MF}/\tau)\right)},$$
$$L_{\rm 2MF} = \frac{\sin\left(2\left(\theta + L_{\rm 2MF}/\tau\right)\right)}{2\left(\sinh^2(L_{\rm 1MF}/\tau) + \cos^2(\theta + L_{\rm 2MF}/\tau)\right)}\cdot \quad (19)$$

To calculate $\theta_{\rm e}(\tau)$ in this case we should put $L_{\rm 1MF} = 0$ in (11). This after some algebra yields

$$\theta_{\rm e} = \arccos\sqrt{Q} - \sqrt{Q(1-Q)}, Q = \frac{1}{\tau}\cdot \quad (20)$$

The dependences $\rho(\theta)$ and $\theta_e(\tau)$ for a nondiluted system are shown in Figures 2 and 3 (curves, labeled "MF") respectively. One sees the absence of "tails" in $\rho(\theta)$. This shows that random fields (*via* their distribution function $f(E,L)$) play a major role in the Griffiths phase formation.

In the present paper we have shown the existence of a Griffiths phase, inherent to disordered Ising magnets, in dielectrics with a concentrational crossover between dipole glass and ferroelectricity. We call this phase "para-glass" because it combines the paraelectric phase features (existence of YL-edge θ_e) and "disorder features" (tails in $\rho(\theta)$). This phase resembles very much the superparamagnetic phase, peculiar to many spin glasses.

Since the physical properties of the glass and ferroglass phases of these substances are different from those in the para-glass (Griffiths) phase, we can expect some peculiarities of the latter phase, which might be helpful in its experimental observation. One such feature may be the nonexponential relaxation of the polarization, different from that in the glass and ferro-glass phases. Its investigation is an interesting problem and can be done within the above formalism.

Unfortunately, we do not know of any direct experimental observation of the Griffiths phase in these substances. For the description of possible (direct or indirect) experiments our approach can be easily extended to the case of a nonGaussian distribution function of random fields, as well as to tunneling of the off-center impurities between their permissible orientations (*i.e.* between minima of their multi-well potentials) in the host dielectric.

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