Random-field smearing of the proton-glass transition

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Within a replica-symmetric mean-field theory we have studied the proton pseudo-spin-glass behavior of a random-bond classical Ising system in a homogeneous transverse field Ω and a random longitudinal field. This model is expected to describe some properties of the mixed hydrogen-bonded ferro- and antiferroelectric crystals such as $Rb_{1-x}(NH_4)_xH_2PO_4$ which have recently been investigated experimentally. It is shown that in the presence of Gaussian random fields with zero mean and variance Δ the proton-glass transition is smeared out, i.e., the cusp in the dielectric susceptibility is rounded off and the proton-glass order parameter remains finite at temperatures above the nominal freezing temperature. However, the average dielectric polarization is strictly zero for a symmetric bond distribution. We have also determined the limits of stability of the replica-symmetric solution for the case of a deuterated system ($\Omega=0$). The replica-symmetric proton-glass phase is separated from the phase with broken replica symmetry by a line of instability in the (T,Δ) plane. The crossing of this line is thus connected with a phase transition which persists in the presence of random fields. Finally, the distribution function of local parallel fields $P(h)$ determining the magnetic resonance line shape has been calculated within the random-field model and the results applied to interpret some recent experimental data.

I. INTRODUCTION

The infinite-range model of Sherrington and Kirkpatrick[1] (SK) and its subsequent solution by Parisi[2] has played a central role in modern understanding of magnetic spin glasses.[3] Recently,[4] an extension of this model has been proposed to describe the frozen proton pseudo-spin-glass (PG) phase observed in the mixed hydrogen-bonded ferro- and antiferroelectric crystals such as $Rb_{1-x}(NH_4)_xH_2PO_4$, commonly abbreviated as RADP.[5–7] In analogy to spin glasses, the frozen PG state is believed to be due to quenched random interactions between the pseudospin degrees of freedom which represent the equilibrium positions of the protons within the O—H $\cdots$ O bonds. The simplest prototype model of a PG is thus the tunneling model,[4] i.e., a random-exchange version of the Ising model with a transverse field Ω, which represents the tunneling frequency of the protons.[8] According to the tunneling model the transition from the paraelectric to the PG phase occurs at a freezing temperature $T_g(\Omega)$ which decreases with increasing Ω until a critical value Ω_c is reached such that $T_g(\Omega_c)\rightarrow 0$ and no PG phase exists for $\Omega \geq \Omega_c$. At the absolute zero of temperature the PG transition is controled solely by the transverse field Ω.

More recently, it has been suggested that the NH_4 groups in RADP, which are positioned nonsymmetrically with respect to the surrounding cations, tilt the proton double-well potential in a random manner, thus inducing an effective local random field. The essential difference between the magnetic spin glasses and the proton pseudo-spin-glasses is the fact that in this last group of materials an intrinsic random field generated by substitutional impurities always exists. The presence of this intrinsic random field adds new features to the PG case, which is, therefore, not just another analogue of the magnetic spin glass. It has been observed already by Courtens[5] using dielectric measurements that the PG transition in RADP is smeared out and no sharp cusp in the dielectric constant, as predicted by the SK theory, exists. Blinc *et al.*[7] have shown by NMR techniques applied to deuterated RADP that the assumption of local random fields is essential to the understanding of PG ordering in these systems.

The purpose of this work is to investigate the effects of Gaussian random fields on the PG phase using a replica-symmetric mean-field approach. Since we are interested in the general features of a PG system in the presence of random fields, we consider the simplest possible theoretical model, i.e., the random-bond transverse Ising model in a longitudinal random field. We do not treat in this paper any more realistic microscopic models of the Slater type.[9] We argue that already a weak random field can drastically change the PG behavior by (i) smearing out the cusp and shifting the peak in the dielectric susceptibility; (ii) maintaining a nonzero value of the PG order parameter well above the nominal freezing temperature. Since by assumption the random-bond distribution is symmetric around zero, the average spontaneous polarization remains zero at all temperatures. By considering small fluctuations of the order parameter around the symmetric solution we derive a line of instability in the (T,Δ) plane for the case of a deuterated PG ($\Omega=0$), which is analogous to the de Almeida–Thouless (AT) line in spin glasses,[10] below which only a solution involving broken replica symmetry is stable. The only phase transition in the system is thus the breaking of replica symmetry occurring as one crosses the line of instability which is characterized by a temperature $T_I(\Delta)$. In the region $T > T_I(\Delta)$ our symmetric solution is fully applicable. For this region we calculate the average probability distribution of local fields $P(h)$, where the total longitudinal field h can be decomposed into a local random field due to the impurities plus a random-exchange contribution from the other pseudospins. $P(h)$ can be measured directly by local techniques such as NMR (Ref. 7) and EPR (Ref. 11), and thus provides a crucial test of the theory.

The paper is organized as follows: In Sec. II we present the general formalism applicable to a PG in the presence of a random field and derive the replica-symmetric solution for the order parameter and the susceptibility. In Sec. III the stability of this solution against replica-symmetry breaking is discussed for the case of a deuterated PG and the instability line $T_I(\Delta)$ in the (T,Δ) plane is obtained. The local-field distribution $P(h)$ is derived in Sec. IV and evaluated for several representative cases. Finally, in Sec. V the results are discussed in the light of recent experimental data.

II. RANDOM-FIELD TUNNELING MODEL

We consider the tunneling model of a PG (Ref. 4) to which we add a term describing the coupling to local random longitudinal fields:

$$\mathcal{H}=-\tfrac{1}{2}\sum_{i,j}J_{ij}S_i^zS_j^z-\Omega\sum_i S_i^x-\sum_i(E+f_i)S_i^z\ . \tag{2.1}$$

As usual, J_{ij} denotes the infinite-range quenched random interactions between the pseudospins S_i^z, Ω is the tunneling frequency, whereas E and f_i represent the homogeneous and random local longitudinal field, respectively, at the site i. The random interactions J_{ij} and fields f_i are independently distributed according to their respective Gaussian probability densities

$$D(J_{ij})=(2\pi J^2)^{-1/2}\exp[-(J_{ij}-J_0)^2/(2J^2)]\ , \tag{2.2a}$$

$$D(f_i)=(2\pi\Delta)^{-1/2}\exp(-\tfrac{1}{2}f_i^2/\Delta)\ . \tag{2.2b}$$

In this work we will only consider the symmetric case $J_0=0$, which implies $[f_i]_d=[J_{ij}]_d=0$, where $[\cdots]_d$ means a random average with respect to both distributions (2.2). Both J and Δ depend on the concentration x characterizing the composition of the PG as in the case of $Rb_{1-x}(NH_4)_xH_2PO_4$. The simplest concentration dependence typically has the form

$$\Delta=4x(1-x)\Delta_{\max}\ , \tag{2.3}$$

and similar behavior can be assumed for the variance J^2.

The pseudospins $\mathbf{S}_i$ will be treated as classical m-component vectors $\mathbf{S}_i=(S_i^1,S_i^2,\ldots,S_i^m)$ with $S_i^1\equiv S_i^x$ and $S_i^m\equiv S_i^z$. It will be convenient to normalize the $\mathbf{S}_i$ to unity, i.e., $\mathbf{S}_i\cdot\mathbf{S}_i=1$. It should perhaps be noted in this context that for isotropic m-vector models the normalization $(\mathbf{S}_i)^2=m$ is more advantageous, since the freezing temperature then becomes m independent, and besides for $m\to\infty$ one recovers the results of the spherical model.[3] No such simple correspondence exists, however, in the transverse Ising case. As shown earlier,[4] the limit $m\to 1$ has special significance: namely, if one has solved the problem for general m with $\Omega\neq 0$, as well as $\Delta\neq 0$ for the present case, then for $m\to 1$ and $\Omega\to 0$, $\Delta\to 0$ one should recover the results of the SK theory.

Several authors have discussed the quantum transverse Ising glass,[12] which is described by model (2.1) without the random fields, and with S_i^x,S_i^z representing the Pauli matrices. It should be stressed, however, that in the usual so-called static approximation the quantum model leads to precisely the same behavior as the classical one in the $m\to 1$ limit. Moreover, in the case of a deuterated PG (i.e., $\Omega_D \ll \Omega_P$) on which we will concentrate in the following sections, the classical $m\to 1$ and the quantum model both effectively reduce to the same Ising limit. For $\Omega\neq 0$, quantum spin fluctuations—when treated in a better approximation—become important at low temperatures, as shown recently for a short-range PG model.[13]

The free energy averaged over the joint probability distribution $D(J_{ij})D(f_i)$ can be obtained via the well-known replica formalism for the partition function Z, i.e.,

$$\mathcal{F}_N=-k_BT\lim_{n\to 0}\frac{1}{n}(Z^n-1)\ ,$$

or

$$\mathcal{F}_N=-\frac{1}{\beta}\lim_{n\to 0}\frac{1}{n}\left[\int\prod_{i,j,k}dJ_{ij}df_kD(J_{ij})D(f_k)\mathrm{Tr}_n\exp\left[\tfrac{1}{2}\beta\sum_{i,j,\alpha}J_{ij}S_{i\alpha}^zS_{j\alpha}^z+\beta\sum_{i,\alpha}\mathbf{H}_i\cdot\mathbf{S}_{i\alpha}\right]-1\right]\ , \tag{2.4}$$

where $\beta\equiv 1/(k_BT)$, $\alpha=1,2,\ldots,n$ is the dummy replica label, and the limit $N\to\infty$ is implied. The m-component vector $\mathbf{H}_i$ is defined as $\mathbf{H}_i\equiv(\Omega,0,\ldots,E+f_i)$.

Our analysis is a generalization of that of Ref. 4 to the case $\Delta\neq 0$. By carrying out the integrations over J_{ij} and f_k in (2.4), and by subsequently linearizing the quadratic forms in $S_{i\alpha}^z$ through use of the identity

$$\exp(\lambda a^2)=(2\pi)^{-1/2}\int_{-\infty}^{+\infty}dv\,\exp[-\tfrac{1}{2}v^2+(2\lambda)^{1/2}av]\ , \tag{2.5}$$

we find

$$\mathcal{F}_N=-\frac{1}{\beta}\lim_{n\to 0}\frac{1}{n}\left[\int\prod_{\alpha,\beta}(N/2\pi)^{1/2}dv_{\alpha\beta}\times\exp\left[-\tfrac{1}{4}N\sum_{\alpha,\beta}v_{\alpha\beta}^2+N\ln Z_n\right]-1\right]\ , \tag{2.6}$$

where

$$Z_n = \mathrm{Tr}_n \exp(\beta \mathcal{H}_n) , \tag{2.7a}$$

$$\mathcal{H}_n = \tfrac{1}{2}\tilde{J} \sum_{\alpha,\beta} v_{\alpha\beta} S^z_\alpha S^z_\beta + \tfrac{1}{2}\beta\Delta \sum_{\alpha,\beta} S^z_\alpha S^z_\beta + \sum_\alpha \mathbf{B}\cdot\mathbf{S}_\alpha , \tag{2.7b}$$

with $\tilde{J} \equiv \sqrt{N} J$ and $\mathbf{B} \equiv (\Omega, 0, \ldots, E)$.

As usual, we assume that the order of the limits $n \to 0$ and $N \to 0$ in (2.6) can be interchanged and the integral thus evaluated by the saddle-point method. The saddle point occurs at

$$v_{\alpha\beta} = \beta\tilde{J}\langle S^z_\alpha S^z_\beta \rangle_n \equiv \begin{cases} \beta\tilde{J} q_{\alpha\beta} & \text{for} \quad \alpha \neq \beta \\ \beta\tilde{J} r_\alpha & \text{for} \quad \alpha = \beta \end{cases} . \tag{2.8}$$

Here $\langle\ \rangle_n$ means a statistical average weighted over $\exp(\beta\mathcal{H}_n)$, and a limit $n \to 0$ is implied. The quantities $q_{\alpha\beta}$ and r_α represent the off-diagonal and diagonal components, respectively, of the PG order parameter. In fact, r_α must be α independent, i.e., $r_\alpha = r$.

The replica-symmetric solution of a SK-type is then obtained by setting all $q_{\alpha\beta}$ equal to one another, say,

$$q = \langle S^z_\alpha S^z_\beta \rangle_n \text{ for all } \alpha \neq \beta . \tag{2.9}$$

Linearizing the quadratic forms $(\sum_\alpha S^z_\alpha)^2$ and $\sum_\alpha (S^z_\alpha)^2$ in (2.7) by repeated use of formula (2.5) we obtain the free-energy density

$$\mathcal{F} = \min_r \max_q \left[\tfrac{1}{4}\beta\tilde{J}^2(r^2 - q^2) - \frac{1}{\beta}\int_{-\infty}^{\infty} \frac{dx\, e^{-x^2/2}}{\sqrt{2\pi}} \ln Z(x) \right] , \tag{2.10}$$

$$Z(x) = \int_{-\infty}^{\infty} dy \frac{e^{-y^2/2}}{\sqrt{2\pi}} \mathrm{Tr} \exp(\beta \mathbf{H}\cdot\mathbf{S}) , \tag{2.11}$$

with $\mathbf{H} \equiv (\Omega, 0, \ldots, H_z)$ and

$$H_z \equiv H_z(x,y) = (\tilde{J}^2 q + \Delta)^{1/2} x + \tilde{J}(r - q)^{1/2} y + E .$$

The trace can now be evaluated as an integral over the m-dimensional solid angle, and after taking the limit $m \to 1$ we finally have

$$Z(x) = \int_{-\infty}^{\infty} dy \frac{e^{-y^2/2}}{\sqrt{2\pi}} 2\cosh(\beta H) \tag{2.12}$$

with $H \equiv [\Omega^2 + H_z(x,y)^2]^{1/2}$.

The variational conditions $\partial\mathcal{F}/\partial r = \partial\mathcal{F}/\partial q = 0$ now yield

$$q = \int_{-\infty}^{\infty} dx \frac{e^{-x^2/2}}{\sqrt{2\pi}} \left[\frac{2}{Z(x)} \int_{-\infty}^{\infty} dy \frac{e^{-y^2/2}}{\sqrt{2\pi}} \frac{H_z}{H} \sinh(\beta H) \right]^2 , \tag{2.13a}$$

$$r = \int_{-\infty}^{\infty} dx \frac{e^{-x^2/2}}{\sqrt{2\pi}} \frac{2}{Z(x)} \int_{-\infty}^{\infty} dy \frac{e^{-y^2/2}}{\sqrt{2\pi}} \left[\left[\frac{H_z}{H} \right]^2 \cosh(\beta H) + \frac{\Omega^2}{\beta H^3} \sinh(\beta H) \right] . \tag{2.13b}$$

The polarization $p \equiv p(E) = -\partial\mathcal{F}/\partial(\beta E)$ is given by

$$p = \int_{-\infty}^{\infty} dx \frac{e^{-x^2/2}}{\sqrt{2\pi}} \frac{2}{Z(x)} \int_{-\infty}^{\infty} dy \frac{e^{-y^2/2}}{\sqrt{2\pi}} \frac{H_z}{H} \sinh(\beta H) , \tag{2.14}$$

and the dielectric susceptibility in zero field $\chi = \partial p / \partial E \mid_{E=0}$ by

$$\chi = \beta(r - q) . \tag{2.15}$$

In the following we will only consider the case of zero external field ($E = 0$). Since by assumption also $J_0 = 0$ in (2.2a), the polarization p will be strictly zero at all temperatures.

The behavior of the PG order parameter q and the dielectric susceptibility χ has been obtained numerically from Eqs. (2.13) and (2.15). In Figs. 1 and 2, $q(T)$ and $\chi(T)$ are plotted for two different values of the transverse field Ω, and for five values of the random-field distribution variance $\Delta/\tilde{J}^2$. In the absence of any random fields ($\Delta = 0$), the susceptibility has a cusp at $T = T_g(\Omega)$.[4] For $\Omega \to 0$, one has $r \to 1$, and $q(T)$, $\chi(T)$ reduce to the well-known SK solutions. For a finite value of Δ, however, the PG transition is smeared out and the order parameter q remains nonzero at all temperatures. One might argue that the random-field variance Δ acts as an effective ordering "field" for the PG order parameter q without inducing an average polarization p. This is the main difference between the transition smearing by a random-field Δ and a homogeneous field E.[1] To further illustrate the onset of the PG state under the influence of random fields, q is plotted in Fig. 3 as a function of Δ at various temperatures above the nominal freezing temperature.

III. STABILITY LIMIT

It is well-known that in Ising spin-glasses the SK replica-symmetric solution in generally unstable against replica-symmetry breaking.[3,10] In the presence of a homogeneous external field, a borderline separating the regions of stable and unstable replica-symmetric solutions can be drawn, known as the AT line.[10] As indicated in Sec. II, the presence of Gaussian random fields in a PG has similar effects as a homogeneous field, i.e., the transition is smeared out and a nonzero value of the order parameter q is induced at all temperatures. However, the average polarization p is strictly zero in the present case. Thus it is not clear how on lowering the temperature the symmetric solution becomes stable against replica-symmetry breaking. To answer this question, we will in the following consider the simple case of a deuterated PG, i.e., we will set $\Omega=0$ in (2.1). Furthermore, we will choose the Ising case $m=1$ and write $S_i \equiv S_i^z = \pm 1$ for the remaining pseudospin component.

Following de Almeida and Thouless[10] we investigate the stability of the free-energy density against small Gaussian fluctuations around the symmetric solution $q_{\alpha\beta}=q$. Thus we write (notice that $r=1$ now):

$$q_{\alpha\beta}=q+\delta q_{\alpha\beta}\ , \tag{3.1}$$

where $\delta q_{\alpha\beta}$ represents small deviations from the replica-symmetric saddle-point value $q=q(\Delta)$.

From (2.6) the free-energy density is now given by

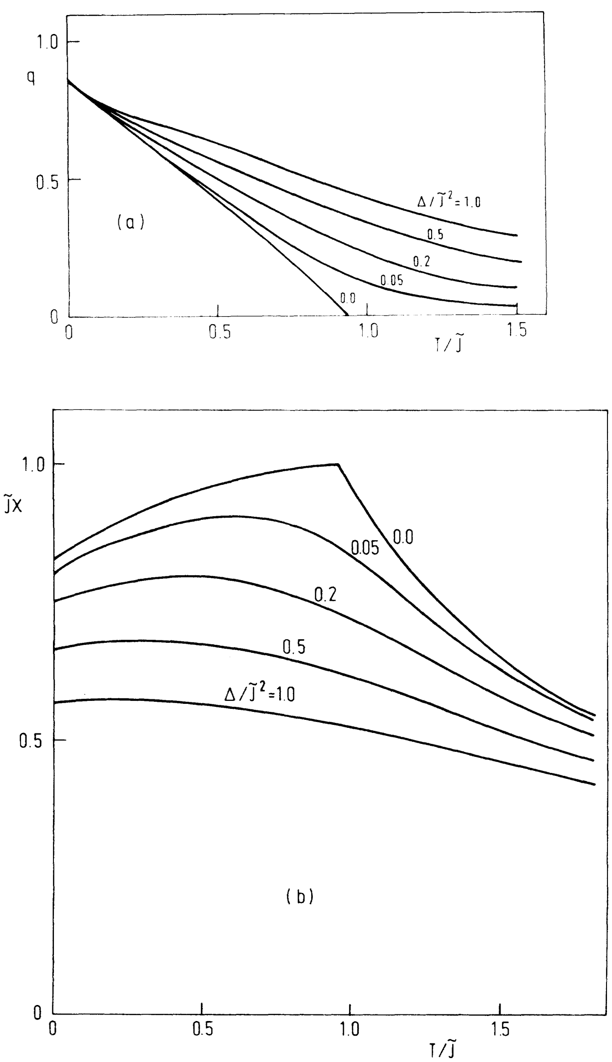

FIG. 1. Replica-symmetric solutions for (a) proton-glass order parameter q and (b) susceptibility χ, plotted vs $T/\tilde{J}$ for $\Omega/\tilde{J}=0.5$ and various values of the random-field variance $\Delta/\tilde{J}^2$.

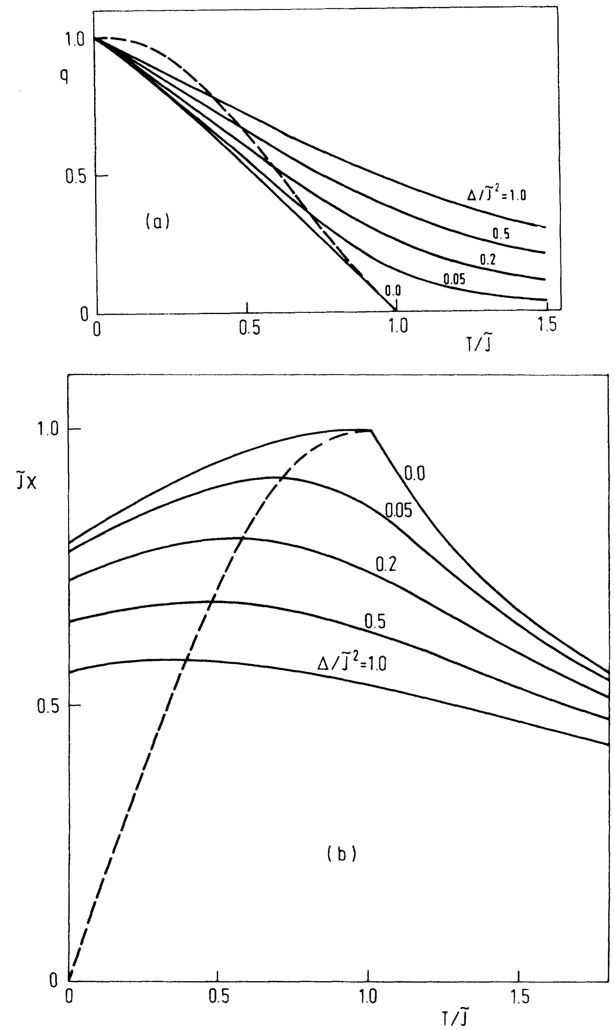

FIG. 2. Same as Fig. 1, but for a deuterated PG ($\Omega=0$). The dashed lines represent q and χ along the line of stability in the (T,Δ) plane (see Fig. 4).

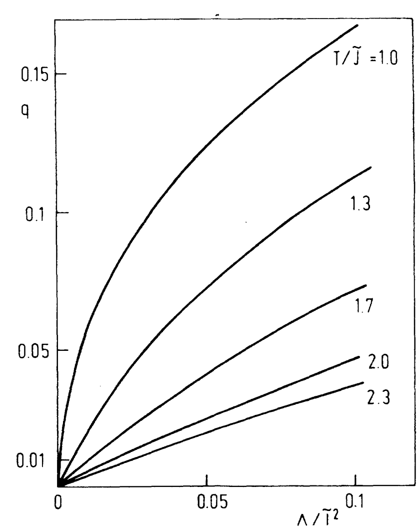

FIG. 3. PG order parameter q plotted vs $\Delta/\tilde{J}^2$ for $\Omega/\tilde{J}=1$ and various values of $T/\tilde{J}$ above the nominal freezing temperature $T_g=\tilde{J}$.

$$\mathcal{F}=\max_{\{q_{\alpha\beta}\}}\lim_{n\to 0}\frac{1}{n}\left[\tfrac{1}{4}\beta\tilde{J}^2\left[n-\sum_{\alpha,\beta\neq\alpha}q_{\alpha\beta}^2\right]-\frac{1}{\beta}\ln Z_n\right], \tag{3.2}$$

where Z_n is defined by (2.7) with $\Omega=0$, $v_{\alpha\beta}=\beta\tilde{J}q_{\alpha\beta}$ ($\alpha\neq\beta$), and $v_{\alpha\alpha}=\beta\tilde{J}$. Expanding $\mathcal{F}$ up to second order in $\delta q_{\alpha\beta}$ we have

$$\mathcal{F}=\mathcal{F}_0+\lim_{n\to 0}\frac{1}{n}\beta\tilde{J}^2\tfrac{1}{2}\sum_{(\alpha,\beta)}\sum_{(\gamma,\delta)}G_{\alpha\beta,\gamma\delta}\delta q_{\alpha\beta}\delta q_{\gamma\delta}+\cdots, \tag{3.3}$$

with $\mathcal{F}_0$ representing the saddle-point value of the free energy, and $G_{\alpha\beta,\gamma\delta}$ the Hessian matrix

$$G_{\alpha\beta,\gamma\delta}=\delta_{(\alpha\beta)(\gamma\delta)}-(\beta\tilde{J})^2(\langle S_\alpha S_\beta S_\gamma S_\delta\rangle_0-\langle S_\alpha S_\beta\rangle_0\langle S_\gamma S_\delta\rangle_0). \tag{3.4}$$

The symbol $(\alpha\beta)$ means that the pair α,β is to be counted only once, and the averages $\langle\ \rangle_0$ are now weighted over $\exp(\beta\mathcal{H}_0)$, i.e., the saddle-point value of (2.7b) with $\Omega=0$, $v_{\alpha\beta}=\beta\tilde{J}q$, but $\Delta\neq 0$.

As discussed in detail in Refs. 3 and 10 the problem of stability reduces to the requirement that all eigenvalues of the Hessian matrix (3.4) must be positive. In our case, it is easily shown that the replica-symmetric solution is stable if

$$\int_{-\infty}^{\infty}dx\frac{e^{-x^2/2}}{\sqrt{2\pi}}\operatorname{sech}^4[\beta\tilde{J}(q+\Delta/\tilde{J}^2)^{1/2}x]\leq\frac{1}{(\beta\tilde{J})^2}. \tag{3.5}$$

The order parameter q is again given by Eq. (2.13a), which now simplifies to

$$q=\int_{-\infty}^{\infty}dx\frac{e^{-x^2/2}}{\sqrt{2\pi}}\tanh^2[\beta\tilde{J}(q+\Delta/\tilde{J}^2)^{1/2}x]. \tag{3.6}$$

The borderline of stability is given by the simultaneous solution of Eq. (3.6) and the equality in (3.5), and represents a line in the (T,Δ) plane as shown in Fig. 4. It plays a role similar to that of the AT line in spin-glasses in a homogeneous field, i.e., for all values (T,Δ) above the line the replica-symmetric solution is stable. Below the instability line $T_I(\Delta)$ only a solution with broken replica symmetry provides a correct description of the PG state.

Approximate analytic expressions for the PG order parameter q and the dielectric susceptibility χ on the instability line can be derived for the regions of large or small values of $\Delta/\tilde{J}^2$. For $\Delta\gg\tilde{J}^2$, implying $T/\tilde{J}\ll 1$ and $q\to 1$, the appropriate expansions of Eqs. (3.5) and (3.6) yield $T/\tilde{J}\approx\tilde{J}/\sqrt{\Delta}$, and thus

$$q=1-\tfrac{3}{2}(T/\tilde{J})^2+\cdots, \tag{3.7}$$

as well as

$$\chi\tilde{J}=\tfrac{3}{2}T/\tilde{J}+O((T/\tilde{J})^2). \tag{3.8}$$

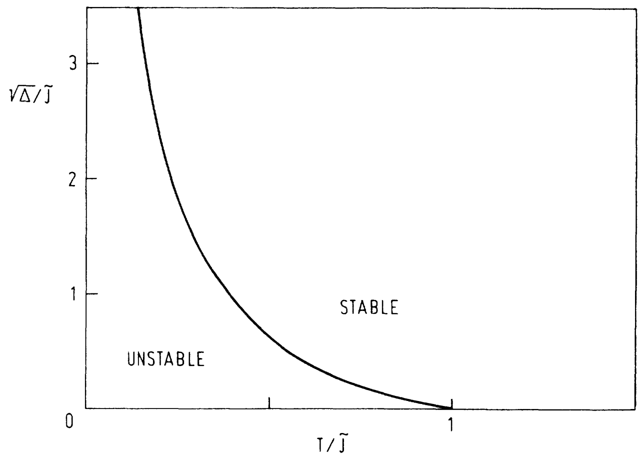

FIG. 4. Phase diagram showing the limit of stability of the replica-symmetry solution in the presence of a random field with variance Δ in the case $\Omega=0$. The phase boundary is analogous to the AT line for an Ising system in a longitudinal field.

Similarly, for $\Delta\ll\tilde{J}^2$, i.e., near the transition temperature in zero field $T_g=\tilde{J}$, we find that $\Delta/\tilde{J}^2\approx\frac{2}{7}\tau^2$, where $\tau\equiv 1-T/\tilde{J}$, leading to

$$q\approx\tau+\tfrac{3}{14}\tau^2+\cdots, \tag{3.9}$$

$$\chi\tilde{J}=1-\tfrac{3}{14}\tau^2+\cdots. \tag{3.10}$$

The behavior of the order parameter q and the susceptibility χ along the entire instability line is shown in Figs. 2(a) and 2(b) in the form of two dashed lines. Clearly, only those parts of the solid curves $q(T)$ and $\chi(T)$ which lie to the right of the dashed line represent stable solutions. It should be stressed, however, that already for small values of the parameter $\Delta/\tilde{J}^2$ the replica-symmetric solutions are stable well below the nominal freezing temperature $T_g=\tilde{J}$.

One can use Eq. (3.6) to calculate the so-called PG susceptibility, analogous to the spin-glass susceptibility χ_{SG},[3]

$$\chi_{PG}=\tilde{J}^2\frac{\partial q}{\partial\Delta}. \tag{3.11}$$

It is easily shown that χ_{PG} diverges on the instability line, indicating the onset of replica-symmetry breaking which occurs for $T\leq T_I(\Delta)$.

IV. LOCAL-FIELD DISTRIBUTION

It has recently been pointed out[14] that the distribution of local magnetic fields in pure and random spin systems provides useful information about the static thermal properties. Here we will discuss the local-field distribution for a PG described by model (2.1), where we will again limit ourselves to the case $\Omega=0$ and $m=1$, and also set $E=0$.

The total field acting on the ith pseudospin S_i contains in addition to the static random field f_i induced by substitutional impurities a contribution due to the interaction with the other pseudospins, i.e.,

$$h_i = f_i + \sum_j J_{ij} S_j \; . \tag{4.1}$$

The average local-field distribution $P(h)$ is defined as

$$P(h) = \frac{1}{N} \sum_i P_i(h), \quad P_i(h) = \langle \delta(h - h_i) \rangle \; , \tag{4.2}$$

where $\langle\ \rangle$ is a thermal average. A convenient way to evaluate $P(h)$, which in the thermodynamic limit becomes equal to $[P_i(h)]_d$, is by means of the generating function

$$G(k) = \frac{1}{N} \sum_i [\exp(ikh_i)]_d \; , \tag{4.3}$$

from which it follows that

$$P(h) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dk \exp(-ikh) G(k) \; . \tag{4.4}$$

Applying the identity[14]

$$\langle \hat{O} \rangle = \lim_{n \to O} \mathrm{Tr}_n \left[\hat{O}_1 \exp \left[-\beta \sum_{\alpha=1}^{n} \mathcal{H}_\alpha \right] \right] , \tag{4.5}$$

which holds for any operator $\hat{O}$ and replica label (chosen as 1) to (4.3), we have

$$G(k) = \lim_{n \to 0} \frac{1}{N} \sum_i \mathrm{Tr}_n \exp \left[ik \left[f_i + \sum_j J_{ij} S_{jl} \right] + \beta \sum_{(i,j)} \sum_\alpha J_{ij} S_{i\alpha} S_{j\alpha} + \beta \sum_i \sum_\alpha f_i S_{i\alpha} \right] . \tag{4.6}$$

By (i,j) we denote all pairs of different sites i and j.

Performing the random averages over the distributions (2.2) we obtain

$$\begin{aligned} G(k) = \exp[-\tfrac{1}{2}(\tilde{J}^2 + \Delta) k^2] \lim_{n \to 0} \frac{1}{N} \sum_i \mathrm{Tr}_n \exp & \left[ik\beta\Delta \sum_\alpha S_{i\alpha} + \tfrac{1}{2}\beta^2 \Delta \sum_j \sum_{\alpha\beta} S_{j\alpha} S_{j\beta} + ik\beta \tilde{J}^2 \frac{1}{N} \sum_l \sum_\alpha S_{l1} S_{l\alpha} S_{i\alpha} \right. \\ & \left. + \tfrac{1}{2}\beta^2 \tilde{J}^2 \frac{1}{N} \sum_{(j,l)} \sum_{\alpha\beta} S_{i\alpha} S_{l\beta} S_{j\alpha} S_{j\beta} \right] . \end{aligned} \tag{4.7}$$

We proceed in close analogy with Ref. 14, the only difference being the presence of the Δ terms in the exponent of (4.7). Linearizing the quadratic forms in the exponent by repeated use of formula (2.5), and using the fact that the trace is site independent, we thus find

$$\begin{aligned} G(k) = \exp[-\tfrac{1}{2}(\tilde{J}^2 + \Delta) k^2] \lim_{n \to 0} \int \prod_{(\alpha,\beta)} \frac{\beta \tilde{J}}{2} \sqrt{N/\pi}\, dq_{\alpha\beta} \exp & \left[-\tfrac{1}{2}\beta^2 \tilde{J}^2 N \sum_{(\alpha,\beta)} q_{\alpha\beta}^2 \right] \\ \times \mathrm{Tr}_n \exp & \left\{ N \left[\beta^2 \tilde{J}^2 \sum_{(\alpha,\beta) \neq (\alpha,1)} Q_{\alpha\beta} S_\alpha S_\beta \right. \right. \\ & \left. \left. + ik\beta \tilde{J}^2 \left[\sum_{\alpha(\neq 1)}' Q_{\alpha 1} S_\alpha + S_1 \right] + ik\beta\Delta S_1 \right] \right\} , \end{aligned} \tag{4.8}$$

where

$$Q_{\alpha\beta} \equiv g_{\alpha\beta} + \Delta / \tilde{J}^2 \; . \tag{4.9}$$

The integrals in (4.8) can be evaluated by the saddle-point method under the same conditions as in Eq. (2.6). Let us assume that the replica-symmetric solution is applicable. The maximum of the exponent then occurs at $q_{\alpha\beta} = q$, which is equivalent to $Q_{\alpha\beta} = Q \equiv q + \Delta / \tilde{J}^2$, where q is given by Eq. (3.6). Applying once more the linearization formula (2.5), we find

$$G(k) = \exp[-\tfrac{1}{2}(\tilde{J}^2 + \Delta) k^2] \lim_{n \to 0} \int_{-\infty}^{\infty} dx \frac{e^{-x^2/2}}{\sqrt{2\pi}} \mathrm{Tr}_n \exp \left\{ \beta(\tilde{J} x \sqrt{Q} + ik\tilde{J}^2 Q) \sum_{\alpha(\neq 1)} S_\alpha + \beta[\tilde{J} x \sqrt{Q} + ik(\tilde{J}^2 + \Delta)] S_1 \right\} . \tag{4.10}$$

Introducing a new integration variable $y=x+ik\tilde{J}\sqrt{Q}$ performing the trace and the $n\to 0$ limit, and inserting the expression for $G(k)$ into (4.4), we obtain the final result for the local-field probability distribution:

$$P(h)=\frac{\exp[-\frac{1}{2}\beta^2\tilde{J}^2(1-q)]}{2\pi\tilde{J}(1-q)^{1/2}}\cosh(\beta h)\times\int_{-\infty}^{\infty}dy\frac{e^{-y^2/2}}{\cosh(\beta\tilde{J}y\sqrt{Q})}\times\exp\left[-\frac{(h-\tilde{J}y\sqrt{Q})^2}{2\tilde{J}^2(1-q)}\right]. \tag{4.11}$$

For $\Delta\to 0$, the local-field distribution (4.11) reduces to the result of Thomsen *et al.*[14] At high temperatures $P(h)$ approaches asymptotically a Gaussian distribution with the variance $\tilde{J}^2+\Delta$, which is the sum of the variances of the local random-field distribution and the random-exchange distribution, respectively.

In Fig. 5(a), $P(h)$ is displayed for $T/\tilde{J}=1.2$ and for several values of the random-field distribution width $\Delta/\tilde{J}^2$. Similarly, in Fig. 5(b) the local-field distribution is plotted for $\Delta/\tilde{J}^2=0.5$ and several values of the relative temperature. All these cases refer to the region where the replica-symmetric solution is valid. Notice that on increasing the value of Δ or lowering the temperature, $P(h)$ flattens around $h=0$, and subsequently a double-peak structure of $P(h)$ appears.

It is further interesting to observe that the values of $P(0)$ evaluated at the instability line $T_I(\Delta)$ are very nearly located on a straight line, i.e.,

$$\tilde{J}P(0)\approx\frac{e^{-1/2}}{\sqrt{2\pi}}T/\tilde{J}\ . \tag{4.12}$$

This is indicated in Fig. 6 as a dashed line, which represents the exact values of $P(0)$ on the line of instability.

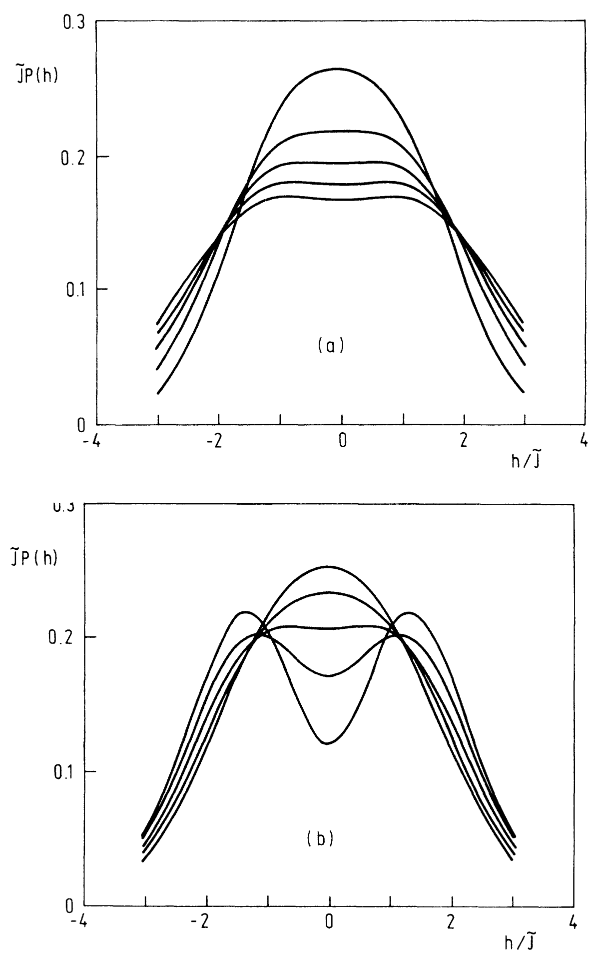

FIG. 5. Local-field distribution $P(h)$ plotted vs $h/\tilde{J}$ for two cases: (a) $T/\tilde{J}=1.2$ and $\Delta/\tilde{J}^2=$ (top to bottom) 0.0, 0.5, 1.0, 1.5, 2.0; (b) $\Delta/\tilde{J}^2=0.5$ and $T/\tilde{J}=$ (top to bottom) 1.5, 1.25, 1.0, 0.75, 0.5.

V. DISCUSSION AND CONCLUSIONS

The transverse Ising model with Gaussian random-exchange interactions and parallel random fields investigated in this paper describes some properties of mixed hydrogen-bonded ferroelectric-antiferroelectric crystals such as RADP, which are qualitatively different from magnetic spin glasses:

(i) The cusp in the dielectric susceptibility is rounded off, reflecting the random-field smearing of the proton glass transition.

(ii) The pseudo-spin-glass order parameter remains finite at temperatures far above the nominal freezing temperature.

(iii) The average local-field distribution determining the magnetic-resonance line shape is temperature dependent and changes from a single-peaked structure to a

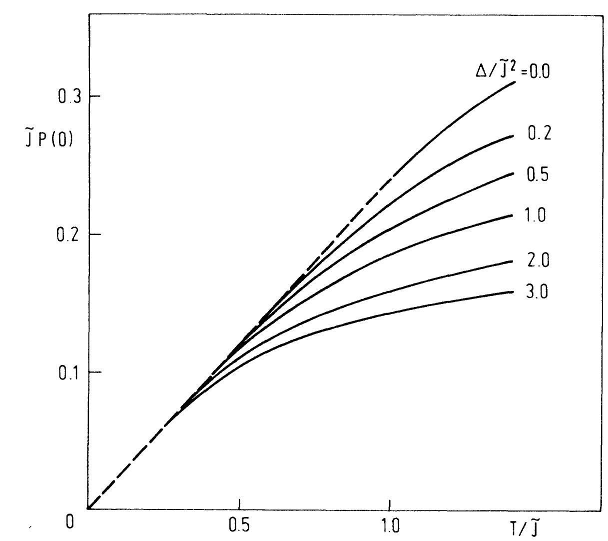

FIG. 6. Zero-field value of the distribution $P(h)$ plotted vs $T/\tilde{J}$ in the region where the replica-symmetric solution is valid, for various values of $\Delta/\tilde{J}^2$, as indicated. The dashed line connects values of $P(0)$ corresponding to T and Δ on the line of instability (see Fig. 4), and appears to be a nearly straight line.

double-peaked structure far above the nominal freezing temperature if the random field is strong enough.

(iv) There is a large isotope effect in the dielectric response of the system and in the nominal transition temperature on replacing hydrogen by deuterium, i.e., on changing the tunneling integral Ω.

Compared to magnetic systems there is a basic difference in the origin of the random fields. In proton glasses the random fields are generated by the substitutional disorder, i.e, they are due to the microscopic properties of the interactions in the systems and not generated by external fields as in dilute magnetic systems.

In our treatment we have assumed infinite-range interactions of SK type. We have obtained the spin-glass order parameter and the static dielectric susceptibility within a replica-symmetric theory both for a nonzero tunneling frequency ($\Omega \neq 0$), and for vanishing Ω. This latter case is appropriate for the deuterated samples, where tunneling is severely reduced.

The main effect of random fields is the smearing of the SK type of transition and the extension of the validity of the replica-symmetric solution for all temperatures and concentrations $[\Delta \sim x(1-x)]$ above the line of instability $T_I(\Delta)$, where the proton-glass susceptibility χ_{PG} diverges. For $\Omega=0$ we have explicitly calculated the line of instability $T_I(\Delta)$ which plays a role similar to the de Almeida–Thouless line in the case of magnetic glasses in the presence of homogeneous external parallel fields. This line separates the replica-symmetric phase from the phase with broken replica symmetry. The crossing of this line is thus connected with a phase transition which persists in the presence of random fields.

A number of the features discussed above can be verified experimentally. The existence of a static random field induced by the substitutional disorder of the ND_4^+ (or Rb^+) ions has been verified in RADP by observing the asymmetric ^{87}Rb $\frac{1}{2} \rightarrow -\frac{1}{2}$ quadrupole perturbed NMR line shapes.[7] The random-field distribution deduced from the room-temperature line shape data is indeed a Gaussian.[7] At lower temperatures the line shape significantly changed demonstrating that the total field acting on a given lattice site indeed contains, in addition to the static random field induced by substitutional disorder, still another contribution due to the interactions with the other pseudospins. The change from a single-peaked average local-field distribution to a double-peaked distribution predicted by the above model has been as well observed by ^{87}Rb and O—D $\cdots$ O deuteron line-shape data at lower temperatures which are, however, still higher than the nominal glass transition temperature.[15] The same effect has been seen as well by Tl^{2+} EPR line-shape data in doped RADP.[11]

The rounding of the cusp in the dielectric susceptibility has been observed experimentally by several authors.[16] Some evidence that the order parameter is nonzero far above the maximum in the dielectric susceptibility has been derived from Brillouin scattering data.[17] Recent NMR line-shape[15] measurements allowed for a quantitative determination of the order parameter q at temperatures which are much higher than the nominal glass transition temperature. From the ND_4^+ deuteron NMR linewidth data in deuterated RADP sample with $x=0.44$, for instance, the high-temperature tail of the q versus temperature curve has been obtained. The experimental q values vary from $q=0.03$ at 293 K to $q=0.18$ at 161 K. The observed temperature dependence of q can be fitted to the one predicted by Eq. (3.6) if one assumes that $\Delta=0.5\tilde{J}^2$ and $\tilde{J}=90$ K. These values of Δ and $\tilde{J}$ were independently obtained by fitting the experimentally observed $^{87}\mathrm{Rb}\frac{1}{2} \rightarrow -\frac{1}{2}$ NMR line shape[7] for $c \| H_0$ to $P(h)$ as given by expression (4.11).

Isotope effects on replacing hydrogen by deuterium have been observed as well. Whereas in KH_2PO_4-type systems the ferroelectric or antiferroelectric transition temperature shifts on deuteration by a factor $T_c(D)/T_c(H)=1.4$ to 1.9 the corresponding isotope shifts in the maxima of the dielectric constant in proton, respectively, deuteron glasses[16] lie in the range $T_G(D)/T_G(H)=3$ to 4.

We may thus conclude that the above model indeed describes some properties of mixed hydrogen-bonded ferro- and antiferroelectrics of the $Rb_{1-x}(NH_4)_xH_2PO_4$-type and that the predicted random-field smearing of the proton-glass transition has been verified experimentally.

[1]D. Sherrington and S. Kirkpatrick, Phys. Rev. Lett. **35**, 1792 (1975).

[2]G. Parisi, J. Phys. A **13**, 1101 (1980); **13**, 1887 (1980).

[3]For a recent review see K. Binder and A. P. Young, Rev. Mod. Phys. **58**, 801 (1986).

[4]R. Pirc, B. Tadić, and R. Blinc, Z. Phys. B **61**, 69 (1985).

[5]E. Courtens, J. Phys. (Paris) Lett. **43**, L199 (1982); Jpn. J. Appl. Phys. **24**, Suppl. **24**, (2), 70 (1985).

[6]J. Slak, R. Kind, R. Blinc, E. Courtens, and S. Žumer, Phys. Rev. B **30**, 85 (1984).

[7]R. Blinc, D. C. Ailion, B. Günther, and S. Žumer, Phys. Rev. Lett. **57**, 2826 (1986).

[8]P. G. de Gennes, Solid State Commun. **1**, 132 (1963); R. Blinc and B. Žekš, *Soft Modes in Ferroelectrics and Antiferroelectrics* (North-Holland, Amsterdam, 1974).

[9]P. Prelovšek and R. Blinc, J. Phys. C **15**, L985 (1982); E. Matsushita and T. Matsubara, Prog. Theor. Phys. (Japan) **71**, 235 (1984); W. Selke and E. Courtens, Ferroelectrics Lett. **5**, 173 (1986).

[10]J. R. L. de Almeida and D. J. Thouless, J. Phys. A **11**, 983 (1978).

[11]P. Cevc (unpublished).

[12]B. K. Chakrabarti, Phys. Rev. B **24**, 4062 (1981); R. R. dos Santos, R. Z. dos Santos, and M. Kischinhevsky, Phys. Rev. B **31**, 4694 (1985); K. D. Usadel, Solid State Commun. **58**, 629 (1986).

[13]V. Dobrosavljevič and R. M. Stratt (unpublished).
[14]M. Thomsen, M. F. Thorpe, T. C. Choy, D. Sherrington, and H. J. Sommers, Phys. Rev. B **33**, 1931 (1986).
[15]J. Dolinšek (unpublished); R. Kind (private communication).
[16]M. Takashige, H. Terauchi, Y. Miura, S. Hoshino, and T. Nakamura, Jpn. J. Appl. Phys. **24**, Suppl. **24**, (2), 947 (1986); E. Courtens, Phys. Rev. B **33**, 2975 (1986); Phys. Rev. Lett. **52**, 69 (1984); V. H. Schmidt and R. W. Mehlhose, Bull. Am. Phys. Soc. **31**, 603 (1986).
[17]E. Courtens, F. Huard, and R. Vacher, Phys. Rev. Lett. **55**, 722 (1985).