PHYSICAL REVIEW B VOLUME 37, NUMBER 1 1 JANUARY 1988

# Isotope effect and pressure dependence of the freezing temperature in proton glasses

B. Tadić, R. Pirc, and R. Blinc
*Jožef Stefan Institute, E. Kardelj University of Ljubljana, 61111 Ljubljana, Yugoslavia*

(Received 8 September 1987)

The phase diagram of the substitutionally disordered proton glass $Rb_{1-x}(NH_4)_xH_2PO_4$ has been evaluated as a function of pressure, composition, and deuteration content using the random-bond version of the Ising model in a transverse tunneling field. The results are compared with recent experimental data.

Recent experimental studies[1,2] have revealed that the proton-glass phase in $Rb_{1-x}(NH_4)_xH_2PO_4$ (RADP) at $x=0.5$ can be completely suppressed by the hydrostatic pressure $P_c=5$ kbar, and a quasilinear variation of the freezing temperature $T_g$ has been found in the range $0<P<P_c$. Moreover, a large isotope effect on $T_g$ and its pressure derivative has been observed on replacing hydrogen by deuterium. The purpose of this paper is to demonstrate that these effects can be understood in terms of the recently proposed tunneling model of proton glasses.[3] This model is a random-bond version of the Ising model in a transverse tunneling field,[4] which can be regarded as a simple prototype model for hydrogen-bonded ferroelectrics of the $KH_2PO_4$ family.

The Hamiltonian for a mixed RADP system is written[3] as

$$\mathcal{H}=-\tfrac{1}{2}\sum_{ij}J_{ij}S_i^zS_j^z-\Omega\sum_i S_i^x \ , \tag{1}$$

where $\Omega$ is the tunneling frequency for the O—H ⋯ O proton intrabond motion, and the $J_{ij}$ are chosen, in the spirit of the Sherrington-Kirkpatrick (SK) theory[5] of magnetic spin glasses, to be infinitely ranged with a Gaussian random distribution of mean $J_0=\tilde{J}_0/N$ and variance $J=\tilde{J}/N^{1/2}$. Since we are mainly interested in the variation of the nominal freezing temperature $T_g$ with pressure and composition here, and not in the detailed shape of the susceptibility versus temperature curves, we do not include in Eq. (1) the random-field term.[6] As argued in Ref. 3, within a mean-field theory the pseudospin variables $S_i^z=\pm 1$ can be treated as components of a classical $m$-dimensional unit vector. The phase diagram, obtained in the limit $m\rightarrow 1$, then reduces to that of a SK spin glass for $\Omega\rightarrow 0$, whereas for $\tilde{J}\rightarrow 0$ and $\Omega\neq 0$, one recovers the results of the mean-field theory of pure KDP-type ferroelectrics.[4]

According to the tunneling model, the transition from the disordered (paraelectric) into the ordered ferro- (FE), antiferroelectric (AFE), or proton glass (PG) phase can be induced either by lowering the temperature or by decreasing the transverse field $\Omega$. The exact nature of the transition depends on the relative magnitudes of the parameters $\tilde{J}_0$ and $\tilde{J}$: For $|\tilde{J}_0|>\tilde{J}$ the transition is into a FE ($\tilde{J}_0>0$) or AFE ($\tilde{J}_0<0$) phase, whereas for $\tilde{J}\geq|\tilde{J}_0|$ a PG phase appears. In each case, the transition temperature depends on $\Omega$. For $\Omega\geq 2\tilde{J}$, one finds $T_g(\Omega)=0$, i.e., no PG ordering is possible at any temperature. (Similarly, $T_c=0$ for $\Omega\geq|\tilde{J}_0|$ when $\tilde{J}=0$.)

Using the general replica formalism of Parisi,[7] one can show that the static dielectric susceptibility for the tunneling model (1) in the case $\tilde{J}_0=0$ is given by

$$\chi=T^{-1}\left[r-\int_0^1 q(x)dx\right] \ , \tag{2}$$

where $q(x)$, $0\leq x\leq 1$, is the Parisi order-parameter function, and $r=\langle (S_\alpha^z)^2\rangle$ represents the diagonal part of the PG order parameter in replica space.[3] $\chi$ exhibits a cusp at $T=T_g$ and has the value $\chi=1/\tilde{J}$ for $T\leq T_g$. The freezing temperature is obtained from the condition that $q(x)\rightarrow 0$ at $T=T_g$. i.e., $\chi(\Omega,T_g)=r/T_g=1/\tilde{J}$. This relation remains unchanged for $\tilde{J}_0\neq 0$ as long as $|\tilde{J}_0|\leq\tilde{J}$. For $|\tilde{J}_0|>\tilde{J}$, however, one obtains the critical temperature $T_c$ from $\chi(\Omega,T_c)=r/T_c=1/|\tilde{J}_0|$. The total susceptibility is given by $\chi_{\rm tot}=\chi/(1-|\tilde{J}_0|\chi)$, which diverges at the transition point $T_c(\Omega)$.

The order parameter $r$ at the phase boundary can be calculated within a replica-symmetric theory.[3] Thus the transition temperature $T$ (i.e., $T_c$ or $T_g$) is determined by the coupled equations

$$T=r\max\{\tilde{J},|\tilde{J}_0|\} \ , \tag{3a}$$

$$r=[\langle\cosh(H/T)\rangle_z]^{-1}[\langle(\Omega^2T/H^3)\sinh(H/T)\rangle_z+r\langle(\tilde{J}z/H)^2\cosh(H/T)\rangle_z] \ , \tag{3b}$$

with $H\cong(\Omega^2+r\tilde{J}^2z^2)^{1/2}$ and

$$\langle f\rangle_z\equiv(2\pi)^{-1/2}\int_{-\infty}^{+\infty}dz\exp(-z^2/2)f(z) \ .$$

Equations (3) can be rewritten as a single implicit equation for the reduced transition temperature $\hat{T}\equiv TW/\tilde{J}$, namely,

$$\langle\cosh(\hat{H}/\hat{T})\rangle_z=\langle(Wz/\hat{H})^2\cosh(\hat{H}/\hat{T})\rangle_z+\langle(\hat{\Omega}^2/\hat{H}^3)\sinh(\hat{H}/\hat{T})\rangle_z \tag{4}$$

with further reduced variables $\hat{\Omega} \equiv \Omega W/\tilde{J}$ and $\hat{H} \equiv [\hat{\Omega}^2 + \hat{T}(Wz)^2]^{1/2}$. The parameter $W$ is defined as

$$W = \begin{cases} \tilde{J}/|\tilde{J}_0| & \text{for}\,|\tilde{J}_0| > \tilde{J} \ , \\ 1 \ \text{for} \ |\tilde{J}_0| \leq \tilde{J} \ . \end{cases} \tag{5}$$

We now discuss solutions to Eq. (4) in these two cases.

(i) FE and AFE phase ($|\tilde{J}_0| > \tilde{J}$). The limiting case of a pure FE or AFE system is obtained by setting $\tilde{J} \rightarrow 0 (W \rightarrow 0)$ in (4) and (5). The transition temperature is then given by

$$\Omega/|\tilde{J}_0| = \tanh(\Omega/T_c) \ , \tag{6}$$

where $T_c$ corresponds to $T_c$ ($T_N$) for $\tilde{J}_0 > 0$ ($\tilde{J}_0 < 0$), respectively.[4]

When $\tilde{J} \neq 0$ but $|\tilde{J}_0| > \tilde{J}$, $T_c$ is lowered; however, long-range order persists for $W$ in the range $0 \leq W < 1$. Numerical solutions of Eq. (4) for several values of $W$ are shown in Fig. 1. Notice that for each $W$ a critical transverse field $\Omega_c$ is found such that $T \rightarrow 0$ as $\Omega \rightarrow \Omega_c$ and no FE (AFE) order exists for $\Omega \geq \Omega_c$. We obtain $\hat{\Omega}_c \equiv \Omega_c W/\tilde{J} = 1 + W^2$. For $\Omega$ close to $\Omega_c$ (i.e., $1/\hat{T} \gg 1$), as asymptotic expansion applied to Eq. (4) yields

$$\hat{T} = (\hat{\Omega}_c - \hat{\Omega}) \frac{8}{3W^2} \frac{\hat{\Omega}(\hat{\Omega} - W^2)^2}{4\hat{\Omega} + W^2 - W^2(\hat{\Omega} - W^2)} \ .$$

Thus the slope with which $T_c$ goes to zero at $\Omega_c$ is found as

$$s(W) = (\partial T_c/\partial \Omega)_{\Omega_c} = -2/(3W^2) \ .$$

In pure systems ($W = 0$) the slope becomes infinite, $s(0) \rightarrow -\infty$, in accordance with earlier results.[4,8] For finite $\tilde{J}$, however, one has $0 < W < 1$, and the slope is finite (cf. Fig. 1).

(ii) PG phase ($|\tilde{J}_0| \leq \tilde{J}$): Here $W = 1$, and the transition temperature is not affected by the actual value of $\tilde{J}_0$ as long as $|\tilde{J}_0| \leq \tilde{J}$. The solution for $W = 1$ represents the PG freezing temperature $T_g/\tilde{J}$ as a function of $\Omega/\tilde{J}$. The critical transverse field is now given by $\Omega_c = 2\tilde{J}$, and the slope $(\partial T_g/\partial \Omega)_{\Omega_c}$ has the value $s(1) = -\frac{2}{3}$. The line $T_g(\Omega)$ separates the paraelectric (PE) from the PG phase with broken replica symmetry, and is thus analogous to the de Almeida-Thouless line in spin glasses.[9]

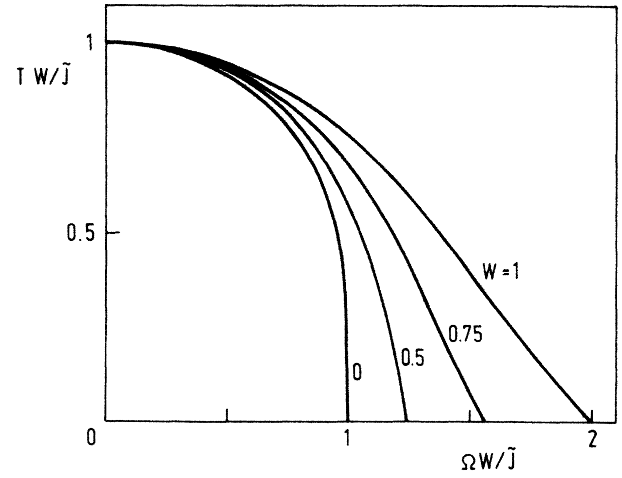

FIG. 1. Reduced transition temperature $TW/\tilde{J}$ plotted vs tunneling frequency $\Omega W/\tilde{J}$ for several values of the parameter $W$ [see Eq. (5)]. $T$ represents $T_c$ for $0 \leq W < 1$ and $T_g$ for $W = 1$, respectively.

We now turn to the concentration and pressure dependence of the transition temperature. We adopt a simple model for the concentration dependence of the coupling parameter $\tilde{J}_0$:

$$\tilde{J}_0(x,P) = -\tilde{J}_0^A(P)x + \tilde{J}_0^F(P)(1-x) \ , \tag{7}$$

where $\tilde{J}_0^A(P) > 0$ and $\tilde{J}_0^F(P) > 0$ are parameters appropriate to pure ADP and RDP at a given pressure $P$, and similarly,

$$\tilde{J}(x,P) = 2[x(1-x)]^{1/2}\tilde{J}(P) \ , \tag{8}$$

with $\tilde{J}(P)$ characterizing the 50% ADP-RDP system. We neglect, however, the variation of $\Omega$ with $x$, assuming that the tunneling frequency of protons in RDP is nearly the same as in ADP. There is, however, a strong isotope effect on $\Omega$ if protons are substituted by deuterons, i.e., $\Omega_{\text{deut}} \ll \Omega_{\text{proton}}$ or $\Omega_{\text{deut}} \approx 0$.

Following an earlier analysis for the case of pure ferroelectrics[4,8] we assume a linear variation of $\Omega$ and $\tilde{J}$, $\tilde{J}_0^{A,F}$ with $P$ at low pressures and write

$$\Omega(P) = \Omega(0) \ \alpha P \ , \tag{9}$$

$$\tilde{J}(P) = \tilde{J}(0)[1 + \gamma P/\tilde{J}(0)]^{-1} \ , \tag{10}$$

and, similarly ($k = A,F$)

$$\tilde{J}_0^k(P) = \tilde{J}_0^k(0)[1 + \gamma_k P/\tilde{J}_0^k(0)]^{-1} \ . \tag{11}$$

If $\gamma_k > 0$, this implies $\tilde{J}_0^k(P) > 0$ for all $P > 0$.

The parameters $\Omega(0)$, $\tilde{J}(0)$, and $\tilde{J}_0^k(0)$, as well as the coefficient $\alpha$, $\gamma$, $\gamma_k$, can be determined from the experimental data of Refs. 1 and 2. For the deuterated sample at $x = 0.5$ and atmospheric pressure ($P = 1$ bar $\approx 0$) we set $\Omega = 0$,[10] and thus $T_{g,\text{deut}} = \tilde{J}(0) = 56.5$ K.[2] The measured slope $dT_g/dP = -2$ K/kbar is due entirely to the decrease in $\tilde{J}(P)$, since $(\partial T_g/\partial \Omega)_{\Omega = 0} = 0$ (see Fig. 1). Thus we find $\gamma = 2$ K/kbar.

Turning next to the undeuterated sample $x = 0.5$, the decrease of the freezing temperature $T_g(P = 0)$ from 56.5 to 17.4 K may be attributed to a nonzero value of the tunneling frequency $\Omega$, but with the same $\tilde{J}(0)$. The ratio $T_g/\tilde{J}(0) = 0.308$ corresponds to $\Omega(0)/J(0) = 1.596$ *via* Eq. (4), thus $\Omega(0) = 90.23$ K. Finally, $\alpha$ is determined from the condition that at the critical pressure $P_c = 5$ kbar $\Omega$ reaches its critical value $\Omega_c \equiv \Omega(P_c) = 2\tilde{J}(P_c)$, which with the help of Eqs. (9) and (10) yields $\alpha = 1.156$ K/kbar.

Using these parameters we can calculate from Eq. (4) ($W = 1$) the pressure dependence of the freezing temperature $T_g(P)$ in the entire range $0 < P < P_c$. The result (curve *a* in Fig. 2) is a quasilinear variation of $T_g$ with $P$, in fair agreement with the experimental data of Samara and Terauchi.[2]

In a similar manner we can analyze the behavior in the range of concentration where AFE or FE order exists. To determine $\tilde{J}_0^k(0)$ in (11) we consider the cases of pure ADP ($x = 1$) and RDP ($x = 0$). Since $\tilde{J}(x,P) = 0$ in both

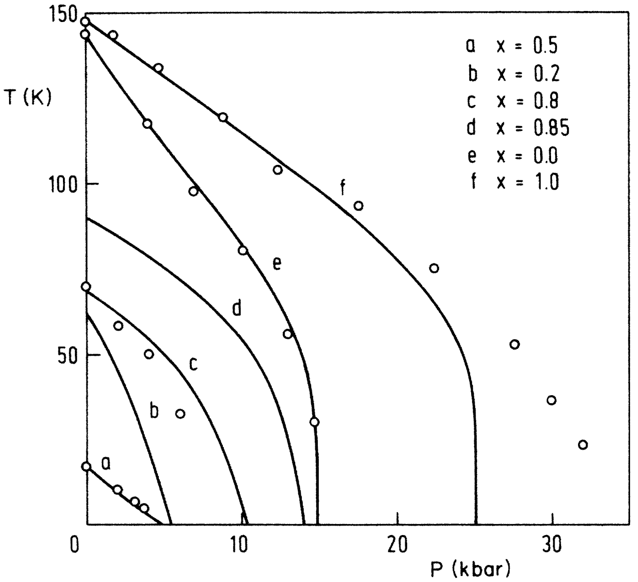

FIG. 2. Calculated pressure dependence of the transition temperature for $Rb_{1-x}(NH_4)_xH_2PO_4$. ○: data from Ref. 2.

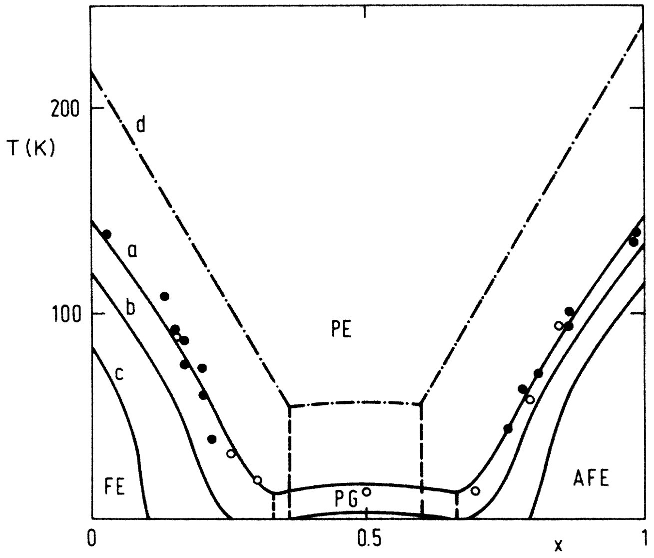

FIG. 3. Calculated phase diagram for $Rb_{1-x}(NH_4)_xH_2PO_4$. (a) atmospheric pressure ($P=0$), (b) $P=4$ kbar, (c) 10 kbar, (d) deuterated system ($P=0$). ●: data from Ref. 11; ○: Ref. 12.

limits, we can simply solve Eq. (6) with $\Omega$ known from the PG case. From known values of $T_N$ and $T_c$ at $P=0$,[2] we obtain $\tilde{J}_0^A(0)=165.9$ K and $\tilde{J}_0^F(0)=162.4$ K. To estimate the coefficients $\gamma_k$ in (11) we have tried to fit the measured[2] pressure dependences of $T_N(P)$ and $T_c(P)$, using the solutions of Eq. (6) with $\Omega(P)$ and $\tilde{J}_0^{A,F}(P)$ as given by (10) and (11), respectively. A reasonably good fit could be achieved in the range $0<P<15$ kbar with $\gamma_A=2.568$ K/kbar and $\gamma_F=5.587$ K/kbar (curves f and e in Fig. 2). For $P>15$ kbar the calculated $T_N(P)$ deviates from the experimental data. Obviously, the one-parameter approximants (9)–(11) cannot be extrapolated into the high-pressure region $P>15$ kbar.

We can now predict from Eq. (4) the pressure and concentration dependence of the transition temperature $T(x,P)$ for all values of $x$ and $P$. The results for three representative cases $x=0.2$, 0.8, and 0.85 are displayed in Fig. 2 (curves b, c, and d). The experimental points[2] lie close to the calculated $T_N(P)$ at $x=0.8$. No experiments are available at present to test our predictions for other concentrations.

Applying Eqs. (7) and (8) we can evaluate the phase diagram $T$ vs $x$ for a fixed value of the pressure, which is shown in Fig. 3. The apparent asymmetry around $x=0.5$ at $P=4$ and 10 kbar is due to the large difference between $\gamma_A$ and $\gamma_F$. There is no PG phase at $P=10$ kbar since $P>P_c$ ($P_c=5$ kbar at $x=0.5$). The vertical lines separating the PG and FE or AFE phases appear as a consequence of broken replica symmetry[7] in the ordered phases. The experimental points from the recent reviews of Courtens[11] and Hayase, Sakashita, and Terauchi[12] seem to support the predicted phase diagram at atmospheric pressure.

In Fig. 3 we also show the predicted phase diagram for the fully deuterated system $Rb_{1-x}(NH_4)_xD_2PO_4$ (or DRADP) at atmospheric pressure (curve d). It should be noted that the isotope effect in the proton-glass versus deuteron-glass freezing temperature $T_g(x)$ can be well described by assuming that in the deuterated system $\Omega=0$, whereas $\tilde{J}$ remains unchanged on deuteration. Thus it seems that $\tilde{J}$, which is essentially a measure of the amount of randomness in the system, is not affected by the "geometric" isotope effect in the O–H···O bond.[13] This effect is responsible, however, for the increase of $\tilde{J}_0^A(0)$ and $\tilde{J}_0^F(0)$ by factors of 1.46 and 1.34, respectively, which is necessary to account for the huge increase in $T_N$ and $T_c$ on deuteration. More experiments on the pressure and concentration dependence of $T_c$ and $T_g$ in mixed DRADP systems are needed to test these assumptions.

In conclusion, the above analysis provides strong support to the tunneling model of proton glasses[3] and, in a broader context, the tunneling model of hydrogen-bonded ferroelectrics.[4,14] A crucial prediction, which seems confirmed by experiments on RADP at finite temperature, is the slope of the temperature versus pressure curves. Within our approach, this slope remains finite at the critical pressure $P_c$ in a mixed system, but diverges in the pure ADP or RDP case.[4,8] It has recently been argued[15] that quantum fluctuations may be important in the PG transition at low temperatures, giving rise to a shift in $\Omega_c$ and an infinite slope $\partial/T_g/\partial\Omega$ as $\Omega\rightarrow\Omega_c$. Thus $\partial T_g/\partial P$ may also eventually become infinite as $P\rightarrow P_c$, where $T_g$ approaches absolute zero. Unfortunately, the existing data[1,2] on $T_g(P)$ have not been obtained at temperatures low enough to check these predictions. However, further refinements of the present model are clearly necessary, and should include the quantum effects, short-range correlations of the Slater type[4] as well as random-field effects.[6]

[1] G. A. Samara and H. V. Schmidt, Phys. Rev. B **34**, 2035 (1986).

[2] G. A. Samara and H. Terauchi, Phys. Rev. Lett. **59**, 347 (1987).

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

[4] R. Blinc and B. Žekš, *Soft Modes in Ferroelectrics and Antiferroelectrics* (North-Holland, Amsterdam, 1974).

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

[6] R. Pirc, B. Tadić, and R. Blinc, Phys. Rev. B **36**, 8607 (1987).

[7] G. Parisi, J. Phys. A **13**, 1101 (1980).

[8] G. A. Samara, Phys. Rev. Lett. **27**, 103 (1971).

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

[10] Actual;ly, the amount of deuteration is only 72%, leaving the possibility of a small nonzero average value of $\Omega$. However, since $|(\partial T_g/\partial \Omega)| \ll 1$ for $\Omega \ll \tilde{J}$, we can, to a good approximation, also set $\Omega = 0$ in this case.

[11] E. Courtens, Ferroelectrics **72**, 229 (1987).

[12] S. Hayase, H. Sakashita, and H. Terauchi, Ferroelectrics **72**, 245 (1987).

[13] R. Blinc and B. Žekš, Ferroelectrics **72**, 193 (1987).

[14] R. Blinc, J. Phys. Chem. Solids 13, 204 (1960); P. G. de Gennes, Solid State Commun. **1**, 132 (1963).

[15] V. Dobrosavljević and R. M. Stratt, Phys. Rev. B **36**, 8484 (1987).