

LETTER TO THE EDITOR

The Slater model of  $K(H_{1-x}D_x)_2PO_4$  in two dimensions

F Y Wu†‡ and Z R Yang||§

‡ Department of Physics, Northeastern University, Boston, Massachusetts 02115, USA

§ Department of Physics, Boston University, Boston, Massachusetts 02215, USA

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**Abstract.** The Slater model for the  $K(H_{1-x}D_x)_2PO_4$  crystal is considered, and solved in two dimensions, by assuming an annealed proton–deuteron distribution. The transition is found to be of first order, with the Curie temperature and the entropy jump both varying almost linearly with the deuterium concentration. These results are in good agreement with experiments.

It has long been known that deuteration of  $KH_2PO_4$  (potassium dihydrogen phosphate or KDP) crystals introduces an isotope effect in causing significant changes of its thermal and electrical properties (see e.g. Strukov *et al* 1972). Particularly, the Curie temperature of the ferroelectric transition increases almost linearly with the deuteron concentration, from 122 K for  $KH_2PO_4$  to 229 K for  $KD_2PO_4$  (DKDP) (Loiacono *et al* 1974). While attempts in elucidating the isotope effect starting from the Slater (1941) model of KDP have met with some success (Selsbee *et al* 1964, Blinc and Svetina 1966, Tokunaga and Matsubara 1966), there has been no definite results on solving any statistical mechanical model of the KDP–DKDP mixture. However, Lieb (1967) has solved the two-dimensional Slater model, correctly predicting, among other results, the nature of the transition in the pure (KDP or DKDP) case. It therefore seems to be of interest to see to what extent Lieb's solution can be extended to include the effect of deuteration.

In this Letter we consider a model of the KDP–DKDP mixture by regarding the deuterons as randomly distributed. This two-dimensional random Slater model is then solved by assuming an annealed random distribution of the protons and deuterons. We obtain from our analysis, among other results, a phase diagram which is extremely close to the experimental findings.

Consider the  $K(H_{1-x}D_x)_2PO_4$  crystal, a deuterated KDP with a fixed deuterium concentration  $x$ . As in the Slater model we assume that the ions (protons and deuterons) are distributed such that there is always one ion (proton or deuteron) per lattice bond and two ions (2 protons, 2 deuterons, or 1 proton and 1 deuteron) close to each lattice site (vertex). Therefore, we can specify the ionic positions by attaching arrows to the bonds. There are again two arrows pointing in and the two arrows pointing out at each vertex (the ice rule). However, each incoming arrow, say, which denotes an ion close by to a vertex, can now be in one of two (H or D) states and, consequently, each vertex can

† Supported in part by the National Science Foundation.

|| Present address: Department of Physics, Beijing Normal University, Beijing, China.

be in one of four ( $H_2$ , HD, DH or  $D_2$ ) ionic states. Thus we have a *random* Slater model with a random proton–deuteron distribution.

The randomness in real systems are presumably quenched, or fixed, in positions. But in view of the ionic tunnellings known to exist in hydrogen-bonded crystals, it is not too unrealistic to regard the randomness in the KDP–KDKP crystal as annealed, i.e. in thermal equilibrium with the surroundings. This assumption greatly simplifies the problem and renders the model soluble, if it can be solved in the pure case.

Consider now a square lattice of  $N$  sites. In figure 1 we show the six ice rule configurations together with their energies assigned according to the ionic state of the vertex. Here, for simplicity, the vertices of types (1) and (2) are assumed to have the same (zero) energy for all four ionic states. We further associate a fugacity  $z$  to each

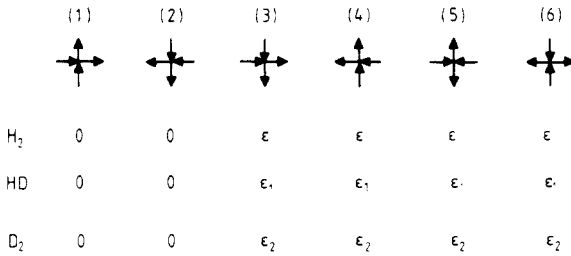


Figure 1. The six ice rule configurations and the associated energies.

deuteron. Now, for a given arrow configuration the ionic states of the vertices are mutually independent. We can therefore sum over the four possible ionic states at each vertex, and arrive at the following expression for the grand partition function:

$$\Xi(\beta, z) = \sum_{\text{arrow configurations}} \prod_{i=1}^6 w_i^{n_i} \tag{1}$$

where

$$\begin{aligned} w_1 &= w_2 = (1 + z)^2 \\ w_3 &= w_4 = w_5 = w_6 = u + 2u_1z + u_2z^2 \\ u &= \exp(-\beta\epsilon), u_1 = \exp(-\beta\epsilon_1), u_2 = \exp(-\beta\epsilon_2) \\ n_i &= \text{the number of the } i\text{th type vertex} \\ \beta &= 1/kT. \end{aligned} \tag{2}$$

Here the fugacity  $z$  is determined by fixing the overall deuterium concentration at

$$x = \frac{1}{2N} z \frac{\partial}{\partial z} \ln \Xi(\beta, z). \tag{3}$$

The internal energy per site is

$$U(\beta, x) = -\frac{1}{N} \frac{\partial}{\partial \beta} \ln \Xi(\beta, z) \tag{4}$$

where  $z = z(\beta, x)$  obtained from (3) is to be substituted after taking the differentiation.

Equations (1)–(4) completely determine the thermodynamics of the system.

Equation (1) can be written as

$$\Xi(\beta, z) = (1 + z)^{2N} Z(u^*) \tag{5}$$

where  $Z(u^*)$  is the partition function of the Slater KDP model containing a single parameter

$$u^* = \exp(-\beta\epsilon^*) = (u + 2u_1z + u_2z^2)/(1 + z)^2. \tag{6}$$

Substituting equation (5) into equations (3) and (4), we obtain

$$x = \frac{z}{1 + z} + f'(u^*)[(u_1 - u)z + (u_2 - u_1)z^2]/(1 + z)^3 \tag{7}$$

$$U(\beta, x) = f'(u^*)(\epsilon u + 2\epsilon_1u_1z + \epsilon_2u_2z^2)/(1 + z)^2 \tag{8}$$

where

$$f(u^*) = \frac{1}{N} \ln Z(u^*) \tag{9}$$

is the ‘free energy’ per site of the Slater model.

Now  $f(u^*)$  in the thermodynamic limit has been explicitly computed by Lieb (1967) in the form of an integral. The integral has since been evaluated by Glasser (1969), yielding after further simplifications (Lieb and Wu 1972)

$$\begin{aligned} f(u^*) &= 0, & u^* < \frac{1}{2} \\ &= \ln \left| \frac{2\mu}{\pi \sin \mu} \cot \left( \frac{\pi^2}{2\mu} \right) \right| & (u^* > \frac{1}{2}) \end{aligned} \tag{10}$$

where

$$\cos \mu = -(2u^*)^{-1}.$$

Properties of  $f(u^*)$  are summarised as follows. The function  $f(u^*)$  is continuous at  $u^* = \frac{1}{2}$ , while its derivative has a jump discontinuity with the limiting values

$$\begin{aligned} f'(u^*) &= 0 & u^* < \frac{1}{2} \\ &= 1 & u^* = \frac{1}{2}+. \end{aligned} \tag{11}$$

The singular part of  $f'(u^*)$  behaves as

$$f'(u^*) \sim (u^* - \frac{1}{2})^{1/2} \quad (u^* \approx \frac{1}{2}+) \tag{12}$$

implying the specific heat exponent  $\alpha = \frac{1}{2}$  for the Slater model.

The thermodynamics of the KDP–DKDP model is now obtained from (8) and (10) where  $z$  is to be eliminated using (7). Particularly, we observe that  $U(\beta, x)$  can be non-analytic (in  $\beta$ ) only when  $f'(u^*)$  is singular. But this can occur only at  $u^* = \frac{1}{2}$ ; the latter now determines the phase boundary. The explicit expression for the phase boundary is obtained by eliminating  $z$  between

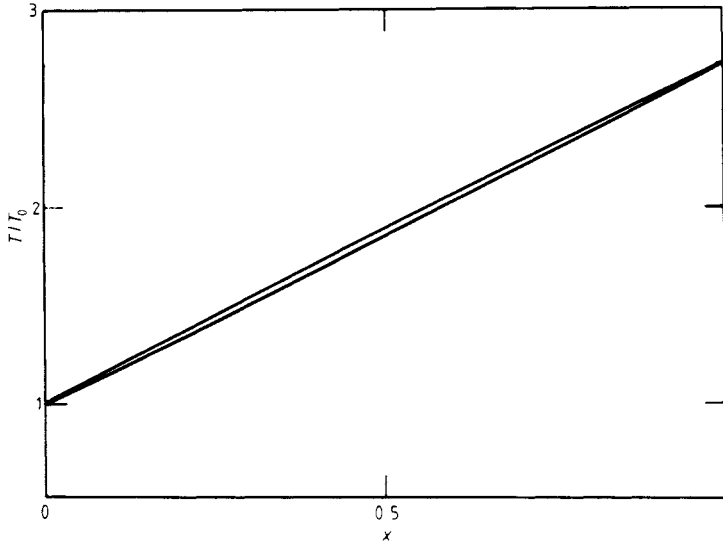
$$u^* = (u + 2u_1z + u_2z^2)/(1 + z)^2 = \frac{1}{2} \tag{13}$$

and equation (7). The two different limiting values of  $f'(u^* = \frac{1}{2})$  given by (11) now give rise to two branches of the phase boundary.

Results of a calculation of the phase boundary for the choice of

$$\begin{aligned} \epsilon_2 &= \frac{229}{122} \epsilon = 1.88\epsilon \\ \epsilon_1 &= \frac{1}{2} (\epsilon_2 + \epsilon) = 1.44\epsilon \end{aligned} \tag{14}$$

are plotted in figure 2. Here the value of  $\epsilon_2$  has been chosen by fitting the experimental Curie temperature for  $x = 1$ . The upper and lower branches of the phase boundary in figure 2 are obtained by taking  $f'(u^*) = 1$  and 0 respectively. Here the occurrence of a two-phase region between the two branches is reminiscent of that occurring in the



**Figure 2.** The phase diagram obtained for  $\epsilon_2 = 1.88\epsilon$ ,  $\epsilon_1 = 1.44\epsilon$ . Here  $T_0 \equiv \epsilon/\ln Z$  is the Curie temperature of pure KDP ( $x = 0$ ).

annealed dilute Potts models for  $q > 4$  (Wu 1980, Sarbach and Wu 1981), and is an artifact of the annealed randomness (Ramshaw 1979). The fact remains that the two branches lie very close to each other, and appear to be experimentally indistinguishable in practice. Both curves give an almost linear dependence of the Curie temperature on the deuterium concentration, a well known experimental fact (Strukov *et al* 1972, Samara 1973, Loiacono *et al* 1974).

The specific heat is obtained by further differentiating the internal energy  $U(\beta, x)$  given by equation (8). However, it is known (Fisher 1968) that the singular part of the specific heat in this case possesses the renormalised exponent

$$\alpha^A = -\alpha/(1 - \alpha) \tag{15}$$

or  $\alpha^A = -1$  after using  $\alpha = \frac{1}{2}$ . This implies that the specific heat is finite, and has a cusp with a finite slope at (and above) the upper branch of the phase boundary. Below the lower branch of the phase boundary the specific heat is identically zero due to our particular choice of the energies for the vertices of types (1) and (2) in figure 1. The specific heat can be made nonzero in this region if the vertices (1) and (2) are given different energies.

The internal energy  $U(\beta, x)$  has a jump discontinuity across the two-phase region. Consequently, there is a latent heat and the transition is first order for all deuterium concentrations. We have also calculated  $\Delta S$ , the entropy jump, at the transition point, and our result shows that  $\Delta S$  remains practically constant for all deuterium concentrations  $0 \leq x \leq 1$ . This is again consistent with the experimental indication that  $\Delta S$  varies linearly with  $x$  (Strukov *et al* 1972), since in the present model the pure crystals (KDP and DKDP) have identical entropy jumps. Presumably, the solution of a further refined model in which the energies of vertices (3), (4), and (5), (6) are assigned differently (Lieb and Wu 1972) will yield the observed linear rise of  $\Delta S$  with  $x$ .

In summary, we have considered, and solved in two dimensions, a Slater model for  $K(H_{1-x}D_x)_2PO_4$  in which the protons and deuterons are randomly distributed. The Curie temperature is found to rise linearly with the deuterium concentration, the transition is of first order with a latent heat and the specific heat possesses a cusp at the Curie point. The entropy jump at the Curie point also varies linearly (in this case a constant) with the deuterium concentration. These results are in good agreement with the experimental findings.

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