

below 26 atm is  $|n_e - n_o| = (2.6 \pm 0.1) \times 10^{-6}$ . Rather large single crystals of solid helium can be grown quickly by increasing the pressure over superfluid helium to slightly above the freezing pressure.

Note added in proof.—We have recently received preprints of papers by J. E. Vos, R. Veenenga Kingma, F. J. van der Gaag, and B. S. Blaisse of Delft, The Netherlands, which have been accepted for publication by Phys. Letters and Physica. They performed similar measurements on small (2-mm linear dimension) solid-helium crystals using a somewhat different technique and their results at 30 atm are in good agreement with the present results. Using crossed beams they were able to show that  $n_e - n_o$  is positive for hcp solid helium and to measure the direction of the  $c$  axis for sever-

al arbitrary crystals.

We wish to acknowledge many helpful discussions with Professor G. V. Chester, Professor P. L. Hartman, Professor H. Mahr, and Dr. F. P. Lipschultz. We are grateful to Dr. Bernard Bertman for useful suggestions during the preparation of the manuscript.

\*Work supported by the National Science Foundation and the Advanced Research Projects Agency through the Materials Science Center of Cornell University.

†John Simon Guggenheim Memorial Fellow on leave at Brookhaven National Laboratory during the academic year 1966-1967.

<sup>1</sup>F. P. Lipschultz and D. M. Lee, Phys. Rev. Letters **14**, 1017 (1965).

<sup>2</sup>J. H. Vignos and H. A. Fairbank, Phys. Rev. **147**, 185 (1966).

<sup>3</sup>B. Bertman, H. A. Fairbank, C. W. White, and M. J. Crooks, Phys. Rev. **142**, 74 (1966).

## EXACT SOLUTION OF THE TWO-DIMENSIONAL SLATER KDP MODEL OF A FERROELECTRIC

Elliott H. Lieb\*

Physics Department, Northeastern University, Boston, Massachusetts

(Received 31 May 1967)

The Slater KDP model is solved for all temperatures and with an electric field. Above  $T_C$  the specific heat behaves like  $(T - T_C)^{-1/2}$  and the polarizability like  $(T - T_C)^{-1}$ . There is a first-order phase transition at  $T_C$  (latent heat). Below  $T_C$  the free energy is simply  $-|\mathcal{E}|d$  ( $\mathcal{E}$  = electric field,  $d$  = dipole moment).

Slater<sup>1</sup> introduced a model of hydrogen-bonded ferroelectrics known as the KDP model, since it was supposed to account for  $\text{KH}_2\text{PO}_4$  and similar substances. He treated the model by mean field theory and obtained a first-order phase transition (latent heat). The position of the critical temperature  $T_C$  and the value of the latent heat were shown to be correct by Takahashi.<sup>2</sup> The model has been widely discussed.<sup>3</sup>

Recently, Wu<sup>4</sup> gave an exact treatment of a modified version of the two-dimensional Slater model. He obtained the same  $T_C$  as Slater but found a second-order phase transition (no latent heat). Wu also found that the specific heat  $C$  was 0 for all  $T < T_C$  and  $C \sim (T - T_C)^{-1/2}$  near and above  $T_C$ . This contrasts with Slater's result that  $C$  is finite at  $T_C$ .

In this paper we give an exact solution of the original Slater model in two dimensions. We also wish to emphasize that the analysis is somewhat different above and below  $T_C$  and that we have solved the model in both temperature ranges. Our results are the following:

(1) Below  $T_C$ ,  $C = 0$  as found by Wu. (2) There is a latent heat at  $T_C$  which agrees with Slater's value. (3)  $C \sim (T - T_C)^{-1/2}$  near and above  $T_C$ , which agrees with Wu. (4) Near and above  $T_C$  the polarizability goes like  $(T - T_C)^{-1}$ , which agrees with Slater's treatment (Wu did not discuss the polarizability of his model).

The mathematical statement of the problem is to place arrows on the bonds of a square  $N \times N$  net so that precisely two arrows point into each vertex. Associated with the six allowed vertices (Fig. 1) are energies  $e_1 = e_2 = 0$ ,  $e_3 = e_4 = e_5 = e_6 = \epsilon > 0$ . In the  $F$  model of an antiferroelectric discussed previously,<sup>5</sup> the assignments were  $e_1 = e_2 = e_3 = e_4 = \epsilon > 0$ ,  $e_5 = e_6 = 0$ .

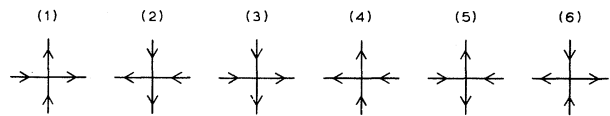


FIG. 1. The six allowed vertex configurations for the Slater KDP model in two dimensions. The energies are  $e_1 = e_2 = 0$ ;  $e_3 = e_4 = e_5 = e_6 = \epsilon > 0$ .

In Wu's version of KDP, vertex 1 was not allowed.

We find the partition function  $Z$  by the transfer-matrix method originally introduced for the the "ice" problem<sup>6</sup>:

$$Z = \max_y Z(y),$$

where

$$Z(y) = [\Lambda(y)]^N \exp[N^2 E y], \quad (1)$$

and where  $E = \mathcal{E}d/kT$  ( $\mathcal{E}$  = electric field,  $d$  = dipole moment),  $y = 1 - 2n/N$  ( $n$  = number of down arrows), and  $\Lambda$  is the maximum eigenvalue of the transfer matrix

$$A(\varphi, \varphi') = \sum \exp(-Km), \quad (2)$$

where  $K = \epsilon/kT$  and  $m$  = number of types (3)-(6) vertices, and where the sum is over the allowed arrangements of horizontal arrows. The notation in (2) has been fully explained in Refs. 5 and 6. The eigenvalue equation in a given  $n$  subspace is [cf. Eq. (1) of Ref. 6]

$$\Lambda f(x_1, \dots, x_n) = \sum_{y_1=1}^{x_1} \dots \sum_{y_n=x_{n-1}}^{x_n} f(y_1, \dots, y_n) D_1(\vec{X}, \vec{Y}) + \sum_{y_1=x_1}^{x_2} \dots \sum_{y_n=x_n}^{x_n} f(y_1, \dots, y_n) D_2(\vec{X}, \vec{Y}), \quad (3)$$

where

$$D_1(\vec{X}, \vec{Y}) = e^{-KN} U(y_2 - x_1) U(y_3 - x_2) \dots U(y_1 + N - x_n),$$

$$D_2(\vec{X}, \vec{Y}) = e^{-KN} U(y_1 - x_1) U(y_1 - x_2) \dots U(y_n - x_n), \quad (4)$$

with

$$U(x) e^{K(x-1)} [1 + \delta(x)(e^{2K} - 1)] \quad (5)$$

( $\delta$  = Kroenecker delta). It is instructive to compare (4) with the corresponding equation in Ref. 5, whence it will be seen that the KDP model has lost the left/right symmetry inherent in the  $F$  model.

Again we make the plane-wave Ansatz

$$f(x_1, \dots, x_n) = \sum_P a(P) \exp\left[i \sum_{j=1}^n k_{P(j)} x_j\right], \quad (6)$$

and we find (for  $n$  even) the following:

If  $P = \dots p, q, \dots$  and  $Q = \dots q, p, \dots$ , then  $a(P) = a(Q)B(p, q)$  with

$$B(p, q) = -[1 + e^{i(p+q)} - 2\Delta e^{ip}] [1 + e^{i(p+q)} - 2\Delta e^{iq}]^{-1},$$

where  $\Delta = \frac{1}{2}e^K$ .

For all  $i = 1, \dots, n$ ,

$$\exp(ik_i N) = \prod_{j \neq i} B(k_i, k_j).$$

$$\Lambda = \left\{ \prod_{j=1}^n [1 - \exp(ik_j + K)]^{-1} \right\} \left\{ \exp\left(i \sum_{j=1}^n k_j\right) + e^{-KN} \prod_{j=1}^n [\exp(ik_j) - \exp(ik_j + 2K) + e^K] \right\}. \quad (7)$$

Again, we have constructed the eigenvectors of the Heisenberg chain

$$H = - \sum_{i=1}^N S_i^x S_{i+1}^x + S_i^y S_{i+1}^y + \Delta S_i^z S_{i+1}^z, \quad (8)$$

although with a different eigenvalue. This time, however, the properties of the ground state of (8) are understood completely only for  $\Delta \leq 1$ . Nevertheless, we can solve the problem completely for all  $\Delta$ . It is worth noting that this problem is in some sense the mirror image of the  $F$  model.<sup>5</sup> For both models  $\Delta = \frac{1}{2}$  corre-

sponds to  $T = \infty$ . As  $T$  decreases,  $\Delta$  decreases monotonically for the  $F$  model with the critical point at  $\Delta = -1$ . For KDP  $\Delta$  increases monotonically with  $\Delta = +1$  being the critical point. This corresponds to a critical temperature  $e^K = 2$ . The two models are completely different, however, because the singularities at the two values of  $\Delta$  are different.

We discuss the high- and low-temperature cases separately:

High temperature ( $\frac{1}{2} < \Delta \leq 1$ ). - Following the standard development,<sup>7</sup> we change variables to  $e^{ik} = (e^{i\mu} - e^{-\alpha})(e^{i\mu} + \alpha - 1)^{-1}$  with  $\Delta = -\cos \mu$ .

The distribution in  $\alpha$  space,  $R(\alpha)$ , satisfies

$$R(\alpha) = \xi(\alpha) - \int_{-b}^b K(\alpha - \beta) R(\beta) d\beta, \quad (9)$$

$$\pi(1-y) = \int_{-b}^b R(\alpha) d\alpha, \quad (10)$$

with

$$\xi(\alpha) = \sin \mu [\cosh \alpha - \cos \mu]^{-1}, \quad (11)$$

$$K(\alpha) = (2\pi)^{-1} \sin 2\mu [\cosh \alpha - \cos 2\mu]^{-1}. \quad (12)$$

Since the  $k$ 's are real (with  $\sum k = 0$ ) and since  $n < \frac{1}{2}N$  (i.e.,  $y \geq 0$ ), the second term in (7) vanishes relative to the first (in the bulk limit). Hence

$$\begin{aligned} N^{-2} \ln Z(y) \\ = Ey - \frac{1}{4\pi} \int_{-b}^b R(\alpha) \ln \left( \frac{\cosh \alpha - \cos 3\mu}{\cosh \alpha - \cos \mu} \right) d\alpha. \end{aligned} \quad (13)$$

Since both  $b$  and  $R(\alpha)$  decrease with increasing  $y$  (with  $b = \infty$  at  $y = 0$ ) and since the log factor in (13) is negative, it follows that  $y$  is an increasing function of  $E$  with  $y = 0$  at  $E = 0$ .

For  $y = 0$ ,  $R(\alpha) = \pi [2\mu \cosh(\pi\alpha/2\mu)]^{-1}$  and hence, for  $E = 0$ ,

$$N^{-2} \ln Z = -\frac{1}{4} \int_{-\infty}^{\infty} \frac{d\alpha}{\cosh \pi\alpha} \ln \left( \frac{\cosh 2\mu\alpha - \cos 3\mu}{\cosh 2\mu\alpha - \cos \mu} \right). \quad (14)$$

For  $T \sim T_c$ ,  $\mu \approx \pi$  and we can expand the integral in (14) to obtain the internal energy/vertex  $= \frac{1}{2}\epsilon$  at  $T = T_c$ . We also find for  $T \sim T_c$  that

$$C \sim (\epsilon^2 / 4\pi k T^2) (2 - e^K)^{-\frac{1}{2}}. \quad (15)$$

To compute the polarizability for  $T \sim T_c$  we expand the logarithm in (13) in powers of  $(\cos \mu - \cos 3\mu)(\cosh \alpha - \cos \mu)^{-1}$ . The first term so obtained is the same as for the ground-state energy of the Heisenberg chain (8). The dependence of this term on  $y$  is known [Ref. 7, Eq. (69)] and we find that

$$\begin{aligned} N^{-2} \ln [Z(y)/Z(0)] \\ = Ey - \Delta \pi (\pi - \mu) (8\mu)^{-1} (\sin \mu) y^2 + O(y^4) \end{aligned} \quad (16)$$

to leading order in  $1 - \Delta$ . This leads to a polarizability

$$\chi \sim 2d^2 [k \ln 2 (T - T_c)]^{-1}. \quad (17)$$

Low temperature ( $\Delta \geq 1$ ).—We are able to derive the partition function in this case without recourse to (7). Set  $E = 0$  and observe that since all energies are non-negative,  $Z(y)$  is

a convex, continuous, monotonically decreasing function of  $\beta = (kT)^{-1}$  (for  $N$  finite). Since  $z(y) \equiv Z(y)^{1/N^2}$  is bounded above by (4), it follows<sup>8</sup> that as  $N \rightarrow \infty$ ,  $\lim z$  is a bounded, continuous, convex, nonincreasing function of  $\beta$ . For  $N = \infty$  and all  $y$ ,  $z(y) = 1$  at  $\beta \epsilon = \ln 2$  [from (13)]. Furthermore, at  $\beta = \infty$ ,  $z(y) = 1$  for all  $y$  because the completely ordered state has zero energy. [To be precise, if  $y = 0$ ,  $Z(0) \geq 2$  (two ordered states). If  $y \neq 0$ ,  $Z(y) \geq 2e^{-2\beta \epsilon N}$  which is obtained by placing all the up arrows on a row of vertical bonds next to each other and then placing rows on top of each other in a spiral structure. This introduces two "dislocations" running the length of the lattice. In the bulk limit the factor  $\epsilon^{-2\beta \epsilon N}$  is of no consequence.] Now, since  $z$  is nonincreasing, we conclude that  $z(y) = 1$  for all  $y$  and all  $T < T_c$ . Hence

$$N^{-2} \ln Z(y) = Ey, \text{ or } N^{-2} \ln Z = |E| \quad (18)$$

(for  $T < T_c$ ).

It is fortunate that we are able to solve the problem this way because it is difficult to obtain the solution from (7). Clearly  $\Lambda(0) = 1$  because the product in (7) is vacuous for  $n = 0$ . When  $\Delta > 1$ , the appropriate  $k$ 's are complex and this solution has not yet been found. However, we can evaluate (7) when  $n$  is fixed  $\gg 1$  and  $N \rightarrow \infty$ . In this case, it is known<sup>9</sup> that  $ik_j \equiv p_j$  is real and, as  $j \rightarrow \infty$ ,  $\cosh p_j$  approaches  $\frac{1}{2}\Delta$  rapidly.  $N^{-2} \ln \Lambda$  is therefore 0, as required.

\*Work supported by National Science Foundation Grant No. GP-6851.

<sup>1</sup>J. C. Slater, J. Chem. Phys. **9**, 16 (1941).

<sup>2</sup>H. Takahasi, Proc. Phys. Math. Soc. (Japan) **23**, 1069 (1941).

<sup>3</sup>J. F. Nagle, J. Math. Phys. **7**, 1492 (1966); E. A. Uehling, in Lectures in Theoretical Physics, edited by Wesley E. Brittin et al. (Interscience Publishers, Inc., New York, 1963), Vol. 5; F. Jona and G. Shirane, Ferroelectric Crystals (The Macmillan Company, New York, 1962).

<sup>4</sup>F. Y. Wu, Phys. Rev. Letters **18**, 605 (1967).

<sup>5</sup>E. H. Lieb, Phys. Rev. Letters **18**, 1046 (1967).

<sup>6</sup>E. H. Lieb, Phys. Rev. Letters **18**, 692 (1967).

<sup>7</sup>C. N. Yang and C. P. Yang, Phys. Rev. **150**, 327 (1966).

<sup>8</sup>G. H. Hardy, J. E. Littlewood, and G. Polya, Inequalities (Cambridge University Press, Cambridge, England, 1964).

<sup>9</sup>C. N. Yang and C. P. Yang, Phys. Rev. **151**, 258 (1966).