

The Spontaneous Magnetization of a Two-Dimensional Ising Model

C. N. YANG

Institute for Advanced Study, Princeton, New Jersey

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The spontaneous magnetization of a two-dimensional Ising model is calculated exactly. The result also gives the long-range order in the lattice.

IT is the purpose of the present paper to calculate the spontaneous magnetization (i.e., the intensity of magnetization at zero external field) of a two-dimensional Ising model of a ferromagnet. Van der Waerden¹ and Ashkin and Lamb² had obtained a series expansion of the spontaneous magnetization that converges very rapidly at low temperatures. Near the critical temperature, however, their series expansion cannot be used. We shall here obtain a closed expression for the spontaneous magnetization by the matrix method which was introduced into the problem of the statistics of a two-dimensional Ising model by Montroll³ and Kramers and Wannier.⁴ Onsager gave in 1944 a complete solution⁵ of the matrix problem. His method was subsequently greatly simplified by Kaufman,⁶ and the result has been used to calculate the short-range order in the crystal lattice.⁷

The Onsager-Kaufman solution of the matrix problem will be used in the present paper to calculate the spontaneous magnetization. In Sec. I we define the specific magnetization I and express it as an off diagonal element in the matrix problem. By introducing an artificial limiting process its calculation is reduced to an eigenvalue problem in Sec. II. This is solved in the next three sections and the final result given in Sec. VI. The relation between I and the usual long-range order is discussed in Sec. I.

It will be seen that the final expression for the spontaneous magnetization is surprisingly simple, although the intermediate steps are very complicated. Attempts to find a simpler way to arrive at the same result have, however, failed.

I. SPONTANEOUS MAGNETIZATION

Using Kaufman's notation⁶ we have for the two-dimensional square lattice the following expression for the partition function:

$$Z = (2 \sinh 2H)^{n/2} \text{trace}(\mathbf{V}_2 \mathbf{V}_1)^m, \quad (1)$$

¹ B. L. van der Waerden, *Z. Physik* **118**, 473 (1941).

² J. Ashkin and W. E. Lamb, Jr., *Phys. Rev.* **64**, 159 (1943).

³ E. Montroll, *J. Chem. Phys.* **9**, 706 (1941).

⁴ H. A. Kramers and G. H. Wannier, *Phys. Rev.* **60**, 252, 263 (1941).

⁵ L. Onsager, *Phys. Rev.* **65**, 117 (1944).

⁶ B. Kaufman, *Phys. Rev.* **76**, 1232 (1949).

⁷ B. Kaufman and L. Onsager, *Phys. Rev.* **76**, 1244 (1949).

where

$$\mathbf{V}_1 = \exp\{H^* \sum_1^n \mathbf{C}_r\}, \quad (2)$$

and

$$\mathbf{V}_2 = \exp\{H \sum_1^n \mathbf{s}_r \mathbf{s}_{r+1}\}. \quad (3)$$

H^* and H are given by

$$e^{-2H} = \tanh H^* = \exp[-(1/kT)\{V_{\uparrow\downarrow} - V_{\uparrow\uparrow}\}]. \quad (4)$$

The following abbreviation will be useful:

$$x = e^{-2H}. \quad (5)$$

If a weak magnetic field is introduced the partition function becomes

$$Z_{\mathcal{H}} = (2 \sinh 2H)^{n/2} \text{trace}(\mathbf{V}_3 \mathbf{V}_2 \mathbf{V}_1)^m, \quad (6)$$

where

$$\mathbf{V}_3 = \exp\{\mathcal{H} \sum_1^n \mathbf{s}_r\}. \quad (7)$$

For a large crystal only the eigenvector of $\mathbf{V} = \mathbf{V}_3 \mathbf{V}_2 \mathbf{V}_1$ with the largest eigenvalue is important. We shall be interested in the limiting form of this eigenvector as $\mathcal{H} \rightarrow 0$.

It has been shown by Onsager⁵ that below the critical temperature, i.e., for

$$x < \sqrt{2} - 1,$$

the largest eigenvalue of $\mathbf{V}_2 \mathbf{V}_1$ is doubly degenerate. This is evidently also true of the symmetrized matrix $\mathbf{V}_1^{\frac{1}{2}} \mathbf{V}_2 \mathbf{V}_1^{\frac{1}{2}}$. Let ψ_+ and ψ_- be the even and odd eigenvectors corresponding to the largest eigenvalue λ .

$$\mathbf{V}_1^{\frac{1}{2}} \mathbf{V}_2 \mathbf{V}_1^{\frac{1}{2}} \psi_+ = \lambda \psi_+, \quad \mathbf{V}_1^{\frac{1}{2}} \mathbf{V}_2 \mathbf{V}_1^{\frac{1}{2}} \psi_- = \lambda \psi_-. \quad (8)$$

The even eigenvector remains unchanged when the spins of all atoms are reversed while the odd eigenvector changes sign. Introducing the operator

$$\mathbf{U} = \mathbf{C}_1 \mathbf{C}_2 \cdots \mathbf{C}_n,$$

that reverses the spins of all atoms we have

$$\mathbf{U} \psi_+ = \psi_+, \quad \mathbf{U} \psi_- = -\psi_-. \quad (9)$$

With the introduction of the magnetic field \mathcal{H} the degeneracy is removed. Since we are only interested in the limit as $\mathcal{H} \rightarrow 0$, we may perform a perturbation cal-

ulation and consider the largest eigenvalue of

$$\begin{aligned} \mathbf{V}_1^{\frac{1}{2}} \mathbf{V} \mathbf{V}_1^{-\frac{1}{2}} &= \mathbf{V}_1^{\frac{1}{2}} \mathbf{V}_3 \mathbf{V}_2 \mathbf{V}_1^{\frac{1}{2}} \\ &= \mathbf{V}_1^{\frac{1}{2}} \mathbf{V}_2 \mathbf{V}_1^{\frac{1}{2}} + \mathcal{J} \mathcal{C} \mathbf{V}_1^{\frac{1}{2}} \left(\sum_1^n \mathbf{s}_r \right) \mathbf{V}_2 \mathbf{V}_1^{\frac{1}{2}}. \end{aligned} \quad (10)$$

The last term is a matrix that anticommutes with \mathbf{U} . It has, therefore, no diagonal matrix element with respect to either ψ_+ or ψ_- . It is, besides, a real symmetrical matrix. Ordinary perturbation theory shows immediately that the eigenvector of (10) with the largest eigenvalue approaches, as $\mathcal{J} \mathcal{C} \rightarrow 0$

$$\psi_{\max} = (1/\sqrt{2})(\psi_+ + \psi_-), \quad (11)$$

if the phases of ψ_+ and ψ_- are so chosen that they are real and that⁸

$$\psi_+ \mathbf{V}_1^{\frac{1}{2}} \left(\sum_1^n \mathbf{s}_r \right) \mathbf{V}_2 \mathbf{V}_1^{\frac{1}{2}} \psi_- \geq 0. \quad (12)$$

The average magnetization per atom is, from the general definition of the matrix method,

$$\begin{aligned} I &= \frac{1}{mn} \frac{\text{trace}(\mathbf{V}_3 \mathbf{V}_2 \mathbf{V}_1)^m \sum_1^n \mathbf{s}_r}{\text{trace}(\mathbf{V}_3 \mathbf{V}_2 \mathbf{V}_1)^m} \\ &= \frac{1}{n} \frac{\text{trace}(\mathbf{V}_1^{\frac{1}{2}} \mathbf{V}_3 \mathbf{V}_2 \mathbf{V}_1^{\frac{1}{2}})^m \left(\mathbf{V}_1^{\frac{1}{2}} \sum_1^n \mathbf{s}_r \mathbf{V}_1^{-\frac{1}{2}} \right)}{\text{trace}(\mathbf{V}_1^{\frac{1}{2}} \mathbf{V}_3 \mathbf{V}_2 \mathbf{V}_1^{\frac{1}{2}})^m} \\ &= -\frac{1}{n} \psi_{\max} \mathbf{V}_1^{\frac{1}{2}} \left(\sum_1^n \mathbf{s}_r \right) \mathbf{V}_1^{-\frac{1}{2}} \psi_{\max}. \end{aligned}$$

As $\mathcal{J} \mathcal{C} \rightarrow 0$ this becomes by (11)

$$I = \frac{1}{2n} (\psi_+' + \psi_-') \mathbf{V}_1^{\frac{1}{2}} \left(\sum_1^n \mathbf{s}_r \right) \mathbf{V}_1^{-\frac{1}{2}} (\psi_+ + \psi_-).$$

But $\mathbf{V}_1^{\frac{1}{2}} \left(\sum_1^n \mathbf{s}_r \right) \mathbf{V}_1^{-\frac{1}{2}}$ anticommutes with \mathbf{U} , and therefore has no diagonal matrix element with respect to either ψ_+ or ψ_- . Besides, by the use of (8), one shows easily that

$$\begin{aligned} \psi_- \mathbf{V}_1^{\frac{1}{2}} \left(\sum_1^n \mathbf{s}_r \right) \mathbf{V}_1^{-\frac{1}{2}} \psi_+ &= -\frac{1}{\lambda} \psi_- \mathbf{V}_1^{\frac{1}{2}} \left(\sum_1^n \mathbf{s}_r \right) \mathbf{V}_2 \mathbf{V}_1^{\frac{1}{2}} \psi_+, \\ \psi_+ \mathbf{V}_1^{\frac{1}{2}} \left(\sum_1^n \mathbf{s}_r \right) \mathbf{V}_1^{-\frac{1}{2}} \psi_- &= -\frac{1}{\lambda} \psi_+ \mathbf{V}_1^{\frac{1}{2}} \left(\sum_1^n \mathbf{s}_r \right) \mathbf{V}_2 \mathbf{V}_1^{\frac{1}{2}} \psi_-, \end{aligned} \quad (13)$$

which are obviously equal. Hence at zero magnetic field the spontaneous magnetization is

$$I = -\frac{1}{n} \psi_- \mathbf{V}_1^{\frac{1}{2}} \left(\sum_1^n \mathbf{s}_r \right) \mathbf{V}_1^{-\frac{1}{2}} \psi_+, \quad (14)$$

which is always positive by (13) and (12).

⁸ We use the notation $A' \equiv A$ transposed.

Intuitively one would infer that the summation $\sum \mathbf{s}_r$ in (14) can be replaced by $n \mathbf{s}_1$ so that

$$I = \psi_- \mathbf{V}_1^{\frac{1}{2}} \mathbf{s}_1 \mathbf{V}_1^{-\frac{1}{2}} \psi_+. \quad (15)$$

This can also be shown in detail by introducing the orthogonal operator \mathbf{L} that is equivalent to the cyclic permutation of the n spins:

$$\mathbf{L} \sigma_i \mathbf{L}^{-1} = \sigma_{i+1}, \quad \mathbf{L} \sigma_n \mathbf{L}^{-1} = \sigma_1.$$

Evidently \mathbf{L} commutes with \mathbf{V}_1 , \mathbf{V}_2 , and \mathbf{U} . Therefore $\mathbf{L} \psi_+$ is also an even eigenvector of $\mathbf{V}_2 \mathbf{V}_1$ with eigenvalue λ . Hence

$$\mathbf{L} \psi_+ = a \psi_+.$$

\mathbf{L} and ψ_+ are real. Therefore a is real. Since further $\mathbf{L}^n = 1$, we have $a = 1$, and

$$\mathbf{L} \psi_+ = \psi_+. \quad (16)$$

Similarly

$$\mathbf{L} \psi_- = \psi_-.$$

Now

$$\mathbf{s}_r = \mathbf{L}^{(r-1)} \mathbf{s}_1 \mathbf{L}^{-(r-1)}.$$

Substituting this into (14) and using (16) we obtain (15).

The spontaneous magnetization I per atom is exactly the usual long-range order parameter s which may be defined as the average of the absolute value of the total spin of the lattice divided by the number of atoms. That I is equal to s is easily seen from the fact that the introduction of a vanishingly weak positive magnetic field merely cuts out all states of the lattice for which the total spin is negative.

One may ask, as Zernike⁹ did, what is the average value of the total spin of the lattice if it is known that at a given lattice point the spin is $+1$. We can show that the answer is NI^2 in the following way: The total spin is either $+NI$ or $-NI$. If a given lattice point has a spin $+1$, it assumes the former value more frequently than the latter in the ratio of $\frac{1}{2}(1+I) : \frac{1}{2}(1-I)$. Hence the average total spin is

$$NI(1+I)/2 - NI(1-I)/2 = NI^2.$$

The long-distance order can also be investigated as the limit of the short-distance order which has been studied by Kaufman and Onsager. Onsager¹⁰ has done this and obtained the correlation of the spins of two atoms in one row at an infinite distance from each other. It can be shown that the long-distance order can be obtained from this, and the result agrees with the findings of this paper.

II. REDUCTION TO EIGENVALUE PROBLEM

A.

To calculate the spontaneous magnetization as given by (15) we notice that it is the off-diagonal ele-

⁹ F. Zernike, *Physica* 7, 565 (1938).

¹⁰ L. Onsager, unpublished; see also *Nuovo cimento* 6, Suppl. p. 261 (1949). The author wishes to thank Bruria Kaufman for showing him her notes on Onsager's work.

ment of the matrix $V_1^{\frac{1}{2}}s_1V_1^{-\frac{1}{2}}$ between the vectors ψ_+ and ψ_- . Onsager and Kaufman⁷ have shown how to calculate diagonal elements by reducing the $2^n \times 2^n$ matrix problem to one of $2n \times 2n$. Their method, however, does not apply to off-diagonal elements. To resolve this difficulty we shall in the present section introduce an artificial limiting process and reduce the problem to an eigenvalue problem of an $n \times n$ matrix.

From Kaufman's⁶ Eq. (60) we have, except for a multiplicative phase factor:

$$\psi_- = S^{-1}(T_-)\tau, \quad (17)$$

where

$$\tau = \mathbf{g} \begin{pmatrix} 1 \\ 0 \\ 0 \\ \vdots \\ 0 \end{pmatrix} = 2^{-n/2} \begin{pmatrix} 1 \\ 1 \\ \vdots \\ 1 \end{pmatrix}. \quad (18)$$

Similarly

$$\psi_+ = S^{-1}(T_+)\tau.$$

Now since T_- is real it follows that $S(T_-)$ is unitary. Hence taking the complex conjugate transposed of Eq. (17) we obtain

$$\psi_-' = \tau' S(T_-).$$

The reality condition of ψ_- has been used. Eq. (15) therefore assumes the form

$$I = \tau' S(T_-) V_1^{\frac{1}{2}} s_1 V_1^{-\frac{1}{2}} S^{-1}(T_+) \tau. \quad (19)$$

As we have just mentioned, if the expression were of the form

$$\tau' S(T_-) \cdots S^{-1}(T_-) \tau,$$

it would have been easy to reduce because $S(T_-) \cdots \times S^{-1}(T_-)$ induces a rotation in the $2n$ dimensional space formed by the Γ 's.¹¹ We could, however, in the present case still utilize this reduction by first writing

$$I = \text{trace} V_1^{\frac{1}{2}} s_1 V_1^{-\frac{1}{2}} S^{-1}(T_+) \tau \tau' S(T_-). \quad (20)$$

Now

$$\tau \tau' = (1/2^n)(1 + C_1)(1 + C_2) \cdots (1 + C_n), \quad (21)$$

does not induce a rotation. But we notice that

$$\begin{aligned} 1 + C_1 &= \lim_{a \rightarrow i\infty} (\cos a)^{-1} (\cos a - i C_1 \sin a) \\ &= \lim_{a \rightarrow i\infty} (\cos a)^{-1} \exp(-ia C_1), \end{aligned} \quad (22)$$

and $\exp(-ia C_1)$ does induce a rotation. Write

$$\mathbf{M} = \begin{pmatrix} \cos 2a & \sin 2a & & 0 \\ -\sin 2a & \cos 2a & & \\ & & \cos 2a & \sin 2a \\ & & -\sin 2a & \cos 2a \\ 0 & & & \ddots \end{pmatrix} \quad (23)$$

so that

$$\exp(-ia \sum_1^n C_r) \Gamma_\alpha \exp(ia \sum_1^n C_r) = \sum_\beta M_{\beta\alpha} \Gamma_\beta. \quad (24)$$

¹¹ The Γ 's are defined in Kaufman's paper (see reference 6). There is a mistake of sign in her Eq. (11) which should read

$$\Gamma_{2r} = -C \times C \times \cdots \times i s C \times 1 \times 1 \times \cdots = Q_r.$$

We have from (21) and (22)

$$\begin{aligned} \tau \tau' &= \lim_{a \rightarrow i\infty} (2 \cos a)^{-n} \exp(-ia \sum_1^n C_r) \\ &= \lim_{a \rightarrow i\infty} (2 \cos a)^{-n} \mathbf{S}(\mathbf{M}). \end{aligned}$$

Substitution back into (20) gives

$$I = \lim_{a \rightarrow i\infty} (2 \cos a)^{-n} \text{trace} V_1^{\frac{1}{2}} s_1 V_1^{-\frac{1}{2}} S(T_+^{-1} \mathbf{M} T_-). \quad (25)$$

B.

This can easily be calculated if we know the eigenvalues and eigenvectors of the $2n$ -dimensional rotation $T_+^{-1} \mathbf{M} T_-$. The rotations T_+ and \mathbf{M} have determinants equal to 1 while T_- has a determinant equal to -1 . Thus $T_+^{-1} \mathbf{M} T_-$ is an improper rotation and must have eigenvalues $1, -1, e^{\pm i\theta_2}, e^{\pm i\theta_3}, \dots, e^{\pm i\theta_n}$. Let ζ be an orthogonal matrix that transforms $T_+^{-1} \mathbf{M} T_-$ into the canonical form

$$\zeta T_+^{-1} \mathbf{M} T_- \zeta^{-1} = \begin{pmatrix} 1 & & & & 0 \\ & -1 & & & \\ & & \cos \theta_2 & \sin \theta_2 & \\ & & -\sin \theta_2 & \cos \theta_2 & \\ & & & & \cos \theta_3 & \sin \theta_3 \\ & & & & -\sin \theta_3 & \cos \theta_3 \\ 0 & & & & & \ddots \end{pmatrix} = \mathbf{W}. \quad (26)$$

\mathbf{W} is evidently orthogonal. We shall compute, first, instead of (25), the more general expression

$$\text{trace} \Gamma_j S(T_+^{-1} \mathbf{M} T_-), \quad (27)$$

where Γ_j is as defined in Kaufman's paper.¹¹ By (26)

$$\begin{aligned} \text{trace} \Gamma_j S(T_+^{-1} \mathbf{M} T_-) &= \text{trace} \Gamma_j S(\zeta^{-1} \mathbf{S}(\mathbf{W}) \mathbf{S}(\zeta)) \\ &= \text{trace} \mathbf{S}(\zeta) \Gamma_j S(\zeta^{-1} \mathbf{S}(\mathbf{W})). \end{aligned} \quad (28)$$

Now

$$\mathbf{S}(\zeta) \Gamma_j S(\zeta^{-1}) = \sum \zeta_{\alpha j} \Gamma_\alpha,$$

where $\zeta_{\alpha j}$ are the matrix elements of ζ . Moreover, the explicit form of $\mathbf{S}(\mathbf{W})$ is known:

$$\mathbf{S}(\mathbf{W}) = i P_1 (P_2 Q_2) (P_3 Q_3) \cdots (P_n Q_n) \exp\left(\frac{1}{2} \sum_2^n \theta_\beta P_\beta Q_\beta\right).$$

(28) therefore reduces to

$$\begin{aligned} &\text{trace} \Gamma_j S(T_+^{-1} \mathbf{M} T_-) \\ &= i \text{trace} \left(\sum \zeta_{\alpha j} \Gamma_\alpha \right) P_1 \left(\prod_2^n P_\alpha Q_\alpha \right) \exp\left(\frac{1}{2} \sum \theta_\beta P_\beta Q_\beta\right) \\ &= i \zeta_{1j} \text{trace} \prod_2^n P_\alpha Q_\alpha \exp\left(\frac{1}{2} \sum \theta_\alpha P_\alpha Q_\alpha\right) \\ &= i (-1)^{n-1} \zeta_{1j} \prod_2^n \sin(\theta_\alpha/2). \end{aligned} \quad (29)$$

Returning to (25) we notice that

$$V_1^{\frac{1}{2}} s_1 V_1^{-\frac{1}{2}} = P_1 \cosh H^* - i Q_1 \sinh H^*. \quad (30)$$

(25), (29), and (30) give

$$I = \left(\prod_2^n \lambda_\alpha \right) i (\xi_{11} \cosh H^* - i \xi_{12} \sinh H^*), \quad (31)$$

where

$$\lambda_\alpha = \text{Lim}_{a \rightarrow i\infty} (-\cos a)^{-1} \sin(\theta_\alpha/2), \quad (32)$$

and

$$\xi_{\alpha\beta} = \text{Lim}_{a \rightarrow i\infty} (\cos a)^{-1} \zeta_{\alpha\beta}. \quad (33)$$

C.

In this subsection we shall derive a formula for λ_α as the eigenvalue of an $n \times n$ matrix.

The matrices \mathbf{T}_+ and \mathbf{T}_- are real, so that we can write

$$\mathbf{T}_+^{-1} \mathbf{M} \mathbf{T}_- = \frac{1}{2} \mathbf{G} \exp(-2ia) + \frac{1}{2} \mathbf{G}^* \exp(2ia), \quad (34)$$

where * means complex conjugate, and \mathbf{G} is independent of a and is given by

$$\mathbf{G} = \mathbf{T}_+^{-1} \begin{pmatrix} 1 & i & & 0 \\ -i & 1 & & \\ & & 1 & i \\ & & -i & 1 \\ 0 & & & \ddots \end{pmatrix} \mathbf{T}_-. \quad (35)$$

Now in Eq. (34) the eigenvalues of the left-hand side are $1, -1, e^{\pm i\theta_2}, e^{\pm i\theta_3}, \dots, e^{\pm i\theta_n}$. As $a \rightarrow i\infty$, the second term of the right-hand side becomes negligible, and we see that

$$\text{Lim}_{a \rightarrow i\infty} 2e^{2ia} e^{i\theta} \alpha = l_\alpha,$$

where l_2, l_3, \dots, l_n are the nonvanishing eigenvalues of \mathbf{G} . A relation between the l 's and the λ 's is found by squaring (32):

$$\begin{aligned} \lambda_\alpha^2 &= \text{Lim}_{a \rightarrow i\infty} (\cos a)^{-2} \sin^2(\theta_\alpha/2) = \text{Lim}_{a \rightarrow i\infty} 4e^{2ia} \sin^2(\theta_\alpha/2) \\ &= -\frac{1}{2} l_\alpha. \end{aligned} \quad (36)$$

We therefore want to find the eigenvalues of the $2n \times 2n$ matrix \mathbf{G} defined by (35). Now explicit matrix elements of \mathbf{T}_+ and \mathbf{T}_- have been exhibited by Kaufman.⁶ Using these matrix elements and rearranging the rows and columns of all $2n \times 2n$ matrices so that the order of the \mathbf{T} 's is changed into $\mathbf{P}_1, \mathbf{P}_2, \dots, \mathbf{P}_n, \mathbf{Q}_1, \mathbf{Q}_2, \dots, \mathbf{Q}_n$, we arrive at the following expression for \mathbf{G} :

$$\mathbf{G} = \begin{pmatrix} \mathbf{D}_+^{-1} & 0 \\ 0 & -i\mathbf{D}_+^{-1} \end{pmatrix} \begin{pmatrix} \mathbf{p}_+^{-1} \\ \mathbf{p}_+ \end{pmatrix} \begin{pmatrix} \mathbf{p}_- & \mathbf{p}_-^{-1} \end{pmatrix} \begin{pmatrix} \mathbf{D}_- & 0 \\ 0 & i\mathbf{D}_- \end{pmatrix}, \quad (37)$$

where

$$\mathbf{D}_- = n^{-1} \begin{pmatrix} \epsilon^2 & \epsilon^4 & \dots & \epsilon^{2n} \\ \epsilon^4 & \epsilon^8 & \dots & \epsilon^{4n} \\ \dots & \dots & \dots & \dots \\ \epsilon^{2n} & \epsilon^{4n} & \dots & \epsilon^{2nn} \end{pmatrix}, \quad \epsilon = \exp(\pi i/n), \quad (38)$$

$$\mathbf{D}_+ = \mathbf{D}_- \begin{pmatrix} \epsilon^{-1} & & 0 \\ & \epsilon^{-2} & \\ & & \ddots \\ 0 & & & \epsilon^{-n} \end{pmatrix}, \quad (39)$$

$$\mathbf{p}_- = \begin{pmatrix} e^{i\delta_2'/2} & & 0 \\ & e^{i\delta_4'/2} & \\ & & \ddots \\ 0 & & & e^{i\delta_{2n}'/2} \end{pmatrix}, \quad (40)$$

and

$$\mathbf{p}_+ = \begin{pmatrix} e^{i\delta_1'/2} & & 0 \\ & e^{i\delta_3'/2} & \\ & & \ddots \\ 0 & & & e^{i\delta_{2n-1}'/2} \end{pmatrix}. \quad (41)$$

The quantities δ' are defined in Kaufman's paper. Explicit expressions for them will be given later in Eq. (60). The four matrices $\mathbf{D}_-, \mathbf{D}_+, \mathbf{p}_-$, and \mathbf{p}_+ are all unitary. Writing the eigenvector of \mathbf{G} as $\begin{pmatrix} \phi \\ \eta \end{pmatrix}$ and by the use of (37) one obtains the following eigenvalue problem

$$\mathbf{D}_+^{-1} \mathbf{p}_+^{-1} (\mathbf{p}_- \mathbf{D}_- \phi + i \mathbf{p}_-^{-1} \mathbf{D}_- \eta) = l \phi, \quad (42)$$

$$-i \mathbf{D}_+^{-1} \mathbf{p}_+ (\mathbf{p}_- \mathbf{D}_- \phi + i \mathbf{p}_-^{-1} \mathbf{D}_- \eta) = l \eta. \quad (43)$$

If $l \neq 0$, this shows that

$$\mathbf{p}_+ \mathbf{D}_+ \phi = i \mathbf{p}_+^{-1} \mathbf{D}_+ \eta.$$

With the aid of this, η could be eliminated and the eigenvalue problem is finally reduced to

$$(\mathbf{D}_+ \mathbf{p}_+^{-2} \mathbf{D}_+ \mathbf{p}_+^2) \phi_1 = l (\mathbf{p}_-^{-1} \mathbf{p}_+) \phi_1, \quad (44)$$

where

$$\phi_1 = \mathbf{D}_+ \phi,$$

and

$$\mathbf{D} = \mathbf{D}_- \mathbf{D}_+^{-1}. \quad (44a)$$

D.

The calculation of $\xi_{1\beta}$ will be reduced in this subsection to the eigenvector problem of an $n \times n$ matrix.

From the definition of ζ in (26) we see that the column matrix

$$\zeta_1 = \begin{pmatrix} \zeta_{11} \\ \zeta_{12} \\ \vdots \end{pmatrix}$$

which is the first column of ζ^{-1} is an eigenvector of $\mathbf{T}_+^{-1} \mathbf{M} \mathbf{T}_-$ with the eigenvalue $+1$:

$$(\mathbf{T}_+^{-1} \mathbf{M} \mathbf{T}_-) \zeta_1 = \zeta_1. \quad (45)$$

It is easily shown that if a column matrix ξ_1 could be found such that

$$\mathbf{G} \xi_1 = 0, \quad (46a)$$

and

$$\mathbf{G} \xi_1^* = 2 \xi_1, \quad (46b)$$

then in virtue of (34)

$$\zeta_1 = \frac{1}{2} (e^{-a} \xi_1 + e^{a} \xi_1^*) \quad (47)$$

does satisfy (45). It is to be emphasized that the ξ_1

defined by (46) is independent of a so that as $a \rightarrow i\infty$ (47) shows that ζ_1 becomes proportional to ξ_1 , and the first column of the matrix $\|\xi_{\alpha\beta}\|$ is exactly ξ_1 .

We now tackle Eqs. (46). Equations (37) and (46a) lead to

$$\begin{bmatrix} \mathbf{p}_- \mathbf{p}_-^{-1} \\ \mathbf{D}_- \quad 0 \\ 0 \quad i\mathbf{D}_- \end{bmatrix} \xi_1 = 0,$$

showing that there exists an $n \times 1$ column matrix y such that

$$\begin{bmatrix} \mathbf{D}_- \quad 0 \\ 0 \quad i\mathbf{D}_- \end{bmatrix} \xi_1 = \begin{bmatrix} \mathbf{p}_-^{-1} \\ -\mathbf{p}_- \end{bmatrix} y, \quad (48)$$

which is both necessary and sufficient for the fulfillment of (46a). Solving (48) for ξ_1 and substituting into (46b) one obtains

$$\mathbf{D}_+^{-1} \mathbf{p}_+^{-1} (\mathbf{p}_- \mathbf{D}_-^2 \mathbf{p}_- + \mathbf{p}_-^{-1} \mathbf{D}_-^2 \mathbf{p}_-^{-1}) y^* = 2\mathbf{D}_-^{-1} \mathbf{p}_-^{-1} y, \quad (49)$$

$$-\mathbf{D}_+^{-1} \mathbf{p}_+ (\mathbf{p}_- \mathbf{D}_-^2 \mathbf{p}_- + \mathbf{p}_-^{-1} \mathbf{D}_-^2 \mathbf{p}_-^{-1}) y^* = 2\mathbf{D}_-^{-1} \mathbf{p}_- y. \quad (50)$$

We shall show that

$$\mathbf{p}_- \mathbf{D}_-^2 \mathbf{p}_- = \mathbf{p}_-^{-1} \mathbf{D}_-^2 \mathbf{p}_-^{-1}. \quad (51)$$

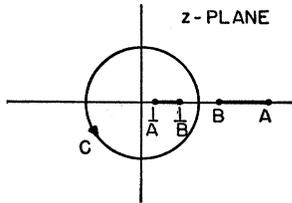


FIG. 1. Cuts in z -plane.

First, from (38)

$$\mathbf{D}_-^{-2} = \begin{bmatrix} 0 & 1 & 0 \\ & & 1 \\ & \dots & \\ 1 & & \\ 0 & & 1 \end{bmatrix}. \quad (51a)$$

But from Kaufman's definition of δ' ,

$$\delta_{2r}' = -\delta_{2n-2r}', \quad (52)$$

and

$$\exp(i\delta_{2n}') = -1, \quad T < T_C. \quad (53)$$

Hence by (40) $\mathbf{D}_-^2 \mathbf{p}_-^2 \mathbf{D}_-^2 = \mathbf{p}_-^{-2}$; and using $\mathbf{D}_-^4 = 1$ one immediately proves (51). (49) and (50) now simplify to

$$\mathbf{D} \mathbf{p}_+^{-1} \mathbf{p}_- \mathbf{D}_-^2 \mathbf{p}_- y^* = \mathbf{p}_-^{-1} y, \quad (54)$$

$$-\mathbf{D} \mathbf{p}_+ \mathbf{p}_- \mathbf{D}_-^2 \mathbf{p}_- y^* = \mathbf{p}_- y. \quad (55)$$

Elimination of y^* and simplification leads finally to

$$(\mathbf{D}^{-1} + \mathbf{p}_+^{-2} \mathbf{D}^{-1} \mathbf{p}_-^2) (\mathbf{p}_-^{-1} y) = 0. \quad (56)$$

Equations (54) and (56) together determine y , which in turn gives ξ_1 through (48).

The normalization of ξ_1 is determined by substitution of (47) into

$$\zeta_1' \zeta_1 = 1. \quad (57)$$

This results in

$$\xi_1' \xi_1 = 0, \quad (58)$$

and

$$\xi_1' \xi_1^* = 2. \quad (59)$$

(58) is automatically satisfied by virtue of (48), (51), and the fact that \mathbf{D}_- and \mathbf{p}_- are symmetrical matrices.

E.

To summarize the results of this section: The spontaneous magnetization I is given by (31), in which the λ 's are related through Eq. (36) to the eigenvalues l of Eq. (44), and in which ξ_{11} and ξ_{12} are the first and the $(n+1)$ th element of the column matrix ξ_1 calculated through (48) from the column matrix y which in turn is determined by (54) and (56). ξ_1 is to be normalized according to (59).

III. LIMIT FOR INFINITE CRYSTAL

A.

The procedure just outlined simplifies greatly when we approach the limit of an infinite crystal. To show this let us first introduce the variable

$$z = e^{i\omega} \quad (\omega = r\pi/n, r = 1, 2, \dots, n). \quad (59a)$$

The relationship between δ' and ω is given by Kaufman's Eq. (52). In terms of z this can be reduced to

$$e^{2i\delta'} = \frac{\tanh^2 H^* (z - \coth H \coth H^*) (z - \tanh H \coth H^*)}{(z - \coth H \tanh H^*) (z - \tanh H \tanh H^*)}. \quad (60)$$

From this we obtain $e^{i\delta'}$ and we shall write it as

$$\Theta(z) = e^{i\delta'} = (1/AB)^{\frac{1}{2}} [(z-A)(z-B)/(z-A^{-1})(z-B^{-1})]^{\frac{1}{2}} \quad (61)$$

where

$$\begin{aligned} A &= \coth H \coth H^* = [(1+x)/x(1-x)], \\ B &= \tanh H \coth H^* = [(1-x)/x(1+x)]. \end{aligned} \quad (62)$$

For $T < T_C$, $A > B > 1$. $\Theta(z)$ is analytic everywhere except at the points $z = A, B, 1/A$, or $1/B$ where it has branch points. The square root in (61) is defined to be that branch of the function that takes the value -1 at $z = 1$, in accordance with (53). (See Fig. 1.)

Consider Eq. (44). For a very large crystal

$$\mathbf{p}_- = \mathbf{p}_+ = \mathbf{p},$$

and we have

$$(\mathbf{D} + \mathbf{p}^{-2} \mathbf{D} \mathbf{p}^2) \phi_1 = l \phi_1. \quad (63)$$

By the definition of \mathbf{D} , Eq. (44a), the matrix elements of \mathbf{D} are

$$(\mathbf{D})_{rs} = \frac{1}{n} \sum_{t=1}^n e^{2rt} \epsilon^t \epsilon^{-2ts} = -\frac{2}{n} \frac{1}{1 - e^{2s-2r-1}}.$$

Hence \mathbf{D} operating on any vector ϕ gives

$$\begin{aligned}
 (\mathbf{D}\phi)_r &= \sum (\mathbf{D})_{rs} \phi_s = -\frac{2}{n} \sum_{s=1}^n \phi_s \left[1 - \exp \frac{\pi i}{n} (2s - 2r - 1) \right]^{-1} \\
 &= -\frac{2}{n} \sum_{s=1}^n \frac{\phi_s}{1 - z_{2s}/z_{2r}\epsilon}, \quad (64)
 \end{aligned}$$

where z is the variable defined in (59a). For $s = 1, 2, \dots, n$ the values assumed by z_{2s} are the n n th roots of unity. As $n \rightarrow \infty$ the summation in (64) therefore becomes an integral around the unit circle:

$$(\mathbf{D}\phi)_r = -2 \int_C \frac{1}{2\pi i} \frac{dz}{z} \frac{\phi(z)}{1 - (z/z_r)}, \quad (65)$$

where

$$z = \exp(2\pi i s/n) \quad \text{and} \quad z_r = \exp(2\pi i r/n).$$

The contour C is the unit circle. At the point $z = z_r$ the principle value of the integral is to be taken. This is necessary because of the factor ϵ in the expression (64) which prevents the denominator from assuming the value zero. Alternately, we might make a detour around the point z_r and make up the difference by adding a term to (65):

$$(\mathbf{D}\phi)_r = -\frac{1}{\pi i} \int_{C'} \frac{dz}{z} \frac{\phi(z)}{1 - (z/t)} + \phi(t). \quad (66)$$

We have here used the more convenient notation t for z_r . With this definition it is evident that the point t does not have to be on the unit circle. If, however, t is inside the unit circle, it is more convenient to use the following equivalent of (66):

$$(\mathbf{D}\phi)_r = -\frac{1}{\pi i} \int_{C''} \frac{dz}{z} \frac{\phi(z)}{1 - (z/t)} - \phi(t), \quad (66a)$$

where C'' is as shown in Fig. 2.

The definitions (66) and (66a) for \mathbf{D} are valid when \mathbf{D} operates on any function $\phi(z)$ that is analytic in a region that contains the circumference of the unit circle in its interior. It is important to notice that this region does not have to be singly connected.

We quote a few interesting properties of the operator \mathbf{D} :

$$\begin{aligned}
 \mathbf{D}z^m &= t^m \quad \text{for } m = \text{integer} \geq 1, \\
 \mathbf{D}z^m &= -t^m \quad \text{for } m = \text{integer} \leq 0,
 \end{aligned} \quad (67)$$

$$\mathbf{D}^2 = 1. \quad (68)$$

Now return to Eq. (63). Since \mathbf{p}^2 is a diagonal matrix with diagonal element $\Theta(z)$ given by (61), it is evident that (63) reduces to

$$2\phi_1(t) - \frac{1}{\pi i} \int_{C'} \frac{dz}{z} \frac{\phi_1(z)}{1 - (z/t)} \left(1 + \frac{\Theta(z)}{\Theta(t)} \right) = l\phi_1(t). \quad (69)$$

This integral equation will be solved in the next two sections.

B.

There still remains, according to the results of the last section, the problem of solving (54) and (56). By virtue of (68), (56) reduces to the same form as (63) with $l=0$. Thus $p_-^{-1}y$ is proportional to that eigenvector $\phi_1 = \Phi$ of (69) belonging to the eigenvalue $l=0$:

$$2\Phi(t) - \frac{1}{\pi i} \int_{C'} \frac{dz}{z} \frac{\Phi(z)}{1 - (z/t)} \left(1 + \frac{\Theta(z)}{\Theta(t)} \right) = 0. \quad (70)$$

For the convenience of normalization we shall write

$$\mathbf{p}_-^{-1}y = n^{-1/2}\Phi. \quad (71)$$

Then by virtue of (48), Eq. (59) reduces to

$$(1/n)\Phi' \Phi^* = 1,$$

or

$$\frac{1}{2\pi i} \int_C |\Phi(z)|^2 \frac{dz}{z} = 1. \quad (72)$$

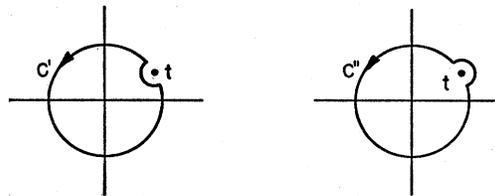


FIG. 2. Contours in z -plane.

The first and $(n+1)$ th elements of ξ_1 are, according to (48) and (71):

$$\begin{aligned}
 \xi_{11} &= \frac{1}{n} \sum_{s=1}^n \epsilon^{-2s} \Phi_s = \frac{1}{2\pi i} \int_C \frac{dz}{z^2} \Phi(z), \\
 \xi_{12} &= \frac{i}{n} \sum_{s=1}^n \epsilon^{-2s} \Theta(\epsilon^{2s}) \Phi_s = \frac{1}{2\pi} \int_C \frac{dz}{z^2} \Theta(z) \Phi(z).
 \end{aligned} \quad (73)$$

The question of the fulfillment of Eq. (54), which now reduces to

$$\mathbf{D}\mathbf{D}_-^2\Phi^* = \Phi,$$

is best discussed with the aid of the introduction of the function $\Phi^\dagger(z)$ defined by

$$\Phi^\dagger(z) = [\Phi(z^*)]^*. \quad (74)$$

If Φ is analytic in a region containing the circumference of the unit circle in its interior, Φ^\dagger would be analytic in a similar region. Equation (51a) shows that

$$(\mathbf{D}_-^2\Phi^*)_z = [\Phi(z^*)]^* = \Phi^\dagger(z).$$

Thus (54) is fulfilled if

$$\Phi^\dagger(t) - \frac{1}{\pi i} \int_{C'} \frac{dz}{z} \frac{\Phi^\dagger(z)}{1 - z/t} = \Phi(t). \quad (75)$$

C.

The integral equation (70) is easily solved by inspection:

$$\Phi(z) = Fz[(A-z)(B-z)]^{-\frac{1}{2}}, \quad (76)$$

where F is a normalization factor. F will turn out to be real, so that according to (74)

$$\Phi^\dagger(z) = \Phi(z).$$

It is easy to prove that (75) is satisfied. This completes the verification that (73) does indeed give the correct matrix elements of ξ_1 .

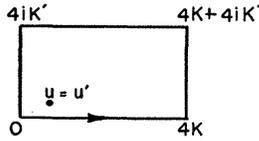


FIG. 3. Contour in u -plane.

To find F we substitute (76) into (72) and obtain

$$\frac{F^2}{2\pi i} \int_C \frac{dz}{[(A-z)(B-z)(Az-1)(Bz-1)]^{\frac{1}{2}}} = 1. \quad (76a)$$

In the integrand the sign of the square root is to be so taken that at $z=1$ the integrand is positive. The integral is a complete elliptic integral and can be reduced to the standard form by a projective transformation. The result is

$$F^{-2} = -\frac{4}{\pi} \frac{1}{A-B} k_{-1}^{\frac{1}{2}} K(k_{-1}),$$

where

$$k_{-1} = \left[\frac{(A^2-1)^{\frac{1}{2}} - (B^2-1)^{\frac{1}{2}}}{A(B^2-1)^{\frac{1}{2}} + B(A^2-1)^{\frac{1}{2}}} \right]^2, \quad (77)$$

and K is the complete elliptic integral of the first kind.¹² It is convenient to change the modulus and define¹³

$$k = 2k_{-1}^{\frac{1}{2}} / (1+k_{-1}) = 4x^2 / (1-x^2)^2 = \sinh^{-2} 2H. \quad (78)$$

Then

$$F^{-2} = 2kK(k) / \pi(A-B). \quad (79)$$

The values of ξ_{11} and ξ_{12} are obtained from (73) and (76):

$$\xi_{11} = F(AB)^{-\frac{1}{2}}, \quad \xi_{12} = 0.$$

Substitution of these into (31), with the use of (36), leads to

$$I^4 = \prod_2^n [(l_\alpha^2/4)] F^4 A^{-2} B^{-2} \cosh^4 H^*.$$

We have here taken the fourth power of I to eliminate the undetermined phase factor that was introduced into the expression for I as early as Eq. (17). When the

¹² E. T. Whittaker and G. N. Watson, *Modern Analysis* (Cambridge University Press, London, 1927), fourth edition.

¹³ The modulus k is the same as that used in references 5 and 7.

explicit expressions for A , B , F , and H^* are introduced, the expression for I^4 further simplifies to

$$I^4 = \left(\prod_2^n \frac{l_\alpha^2}{4} \right) \frac{\pi^2}{4} \left[\frac{1}{K(k)} \right]^2. \quad (80)$$

IV. ELLIPTIC TRANSFORMATION

It remains to find the eigenvalues l from (69) and substitute into (80). To do this we first introduce an elliptic transformation¹² that was essentially the one used in evaluating the integral in (76a):

$$z = - (cnu - i[1+k]^{\frac{1}{2}} snu) (dnu - i[k+k^2]^{\frac{1}{2}} snu) / (1+k sn^2u), \quad (81)$$

the modulus k being given by (78).¹³ This is the same transformation as was used by Onsager,⁵ and Kaufman and Onsager⁷ in their calculations. It serves to eliminate the square root in the function Θ :

$$\Theta = e^{i\psi} = cnu + i snu. \quad (82)$$

It is easy to verify that

$$\frac{1}{z} \frac{dz}{du} = -i \frac{1-k^2}{(1+k)^{\frac{1}{2}} dnu - k^{\frac{1}{2}} cnu}. \quad (83)$$

We shall need the following properties of the transformation (81): (A) z is doubly periodic in u with periods $4K$ and $4iK'$.

(B) z is everywhere analytic, except at $u = iK'/2, 3iK'/2 \pmod{4K, 4iK'}$, where $z = \infty$.

(C) In a unit cell in the complex u -plane, to every value of z there correspond exactly two values of u , except for $z = A, B, 1/B$ or $1/A$ for which there corresponds only one value of u , namely, $u = +iK', 2K+iK', 2K-iK'$ or $-iK' \pmod{4K, 4iK'}$.

(D) If for a value of z there correspond in a unit cell two values of u , then at those two values Θ assume equal values but have different signs. Thus a unit cell of the u plane corresponds to both sheets of the Riemann surface in the z plane of Fig. 1 with respect to the function $\Theta(z)$.

The substitution, suggested by (76), into (69), of

$$\phi_1(z) = z[(z-A)(z-B)]^{\frac{1}{2}} \phi$$

gives, with the use of (81), (82), and (83)

$$2\phi(u') + \int_0^{4K} J(u', u) \phi(u) du = l\phi(u'), \quad (84)$$

where

$$J = \text{I II III IV}; \quad (85)$$

and

$$\text{I} = [1 - z(u)/z(u')]^{-1}, \quad (86)$$

$$\text{II} = 1 + \Theta(z)/\Theta(z') = 1 + (cnu + i snu)/(cnu' + i snu'), \quad (87)$$

$$\text{III} = \frac{z(u) \left[\{z(u') - A\} \{z(u') - B\} \right]^{\frac{1}{2}}}{z(u') \left[\{z(u) - A\} \{z(u) - B\} \right]^{\frac{1}{2}}}, \quad (88)$$

and

$$IV = -\frac{1}{\pi} \frac{1-k^2}{(1+k)^{\frac{1}{2}} \operatorname{dn}u - k^{\frac{1}{2}} \operatorname{cn}u},$$

V. SOLUTION OF INTEGRAL EQUATION (84)

We proceed by investigating the analytic behavior of $J(u', u)$ with respect to the variable u .

(A) **I**, **II**, and **IV** are all doubly periodic with periods $4K$ and $4iK'$. But **III** is doubly periodic with periods $4K$ and $8iK'$. It changes sign at periods $4iK'$:

$$III(u+4iK) = -III(u). \tag{89}$$

(B) **III** is analytic everywhere except at $z=A$ or $z=B$, i.e., $u=iK'$ or $2K+iK'$ (mod. $4K, 4iK'$) where **III** has simple poles.

(C) **II** is analytic everywhere except at $u=-iK'$ or $2K-iK'$ (mod. $4K, 4iK'$) where it has simple poles.

(D) **IV** is analytic everywhere except at

$$u = \pm iK'/2, \pm 3iK'/2 \pmod{4K, 4iK'},$$

where it has simple poles.

(E) **I** is analytic everywhere except at $z(u)=z(u')$. According to the last section in each cell there are, in general, two values of u where this exception occurs. At these two points **I** has simple poles.

However, there is *only one pole* for J in each unit cell ($4K$ by $4iK'$). This is so because of the following considerations:

(F) At $u = \pm iK', \pm iK'+2K$ (mod. $4K, 4iK'$), **IV** has simple zeros.

(G) At $u = iK'/2, 3iK'/2$ (mod. $4K, 4iK'$), $z(u) = \infty$, so that **I** has simple zeros.

(H) At $u = -iK'/2, -3iK'/2$ (mod. $4K, 4iK'$), $z(u) = 0$, so that **III** has simple zeros.

(I) According to property *D*, Sec. IV, in a unit cell ($4K$ by $4iK'$) at one of the solutions of $z(u)=z(u')$, $\Theta(u)=\Theta(u')$ so that **II**=2. At the other solution, **II** has a zero.

Thus inside the rectangle in Fig. 3, J has only one pole at $u=u'$ which we assume to be inside of the rectangle. In the neighborhood of this pole **II**=2, **III**=1, and **I-IV**= $i\pi^{-1}(u-u')^{-1}$. Hence the residue of J at $u=u'$ is $2i/\pi$.

The solution of (84) is given by

$$\phi = \exp(im\pi u/2K), \quad m = \pm \text{integer}. \tag{90}$$

To show that this is indeed a solution we note that ϕ is periodic with period $4K$. Hence calling

$$g = \int_0^{4K} J(u', u)\phi(u)du,$$

one obtains by performing a contour integration around the rectangle of Fig. 3:

$$2\pi i(2i/\pi)\phi(u') = g[1 + \exp(-2m\pi K'/K)]. \tag{91}$$

[The integration along the two vertical sides cancel

each other and that along the top reduces to g multiplied by a factor, in virtue of (89).] This gives

$$g = -4\phi(u')/(1+q^{2m}), \tag{92}$$

where

$$q = \exp(-\pi K'/K). \tag{93}$$

(84) is therefore satisfied with

$$l = 2 - 4/(1+q^{2m}) = 2(q^{2m}-1)/(q^{2m}+1). \tag{94}$$

For $m=0$ this gives, as expected, the solution $l=0$ which was already found by inspection in Sec. IIIC.

Knowing all the nonvanishing eigenvalues we can now calculate

$$\prod_2^{\infty} \frac{l_{\alpha}^2}{4} = \prod_{\substack{m=-\infty \\ m \neq 0}}^{\infty} \left(\frac{1-q^{2m}}{1+q^{2m}} \right)^2 = \prod_1^{\infty} \left(\frac{1-q^{2m}}{1+q^{2m}} \right)^4.$$

This infinite product can be¹⁴ expressed in terms of the ϑ functions which are related to K . We get finally

$$\prod_2^{\infty} \frac{l_{\alpha}^2}{4} = \frac{4}{\pi^2} [K(k)]^2 (1-k^2)^{\frac{1}{2}} = \frac{4}{\pi^2} \frac{1+x^2}{(1-x^2)^2} (1-6x^2+x^4)^{\frac{1}{2}}. \tag{95}$$

VI. FINAL RESULTS

The spontaneous magnetization I is obtained from (95) and (80) as

$$I = \left[\frac{1+x^2}{(1-x^2)^2} (1-6x^2+x^4)^{\frac{1}{2}} \right]^{\frac{1}{2}}. \tag{96}$$

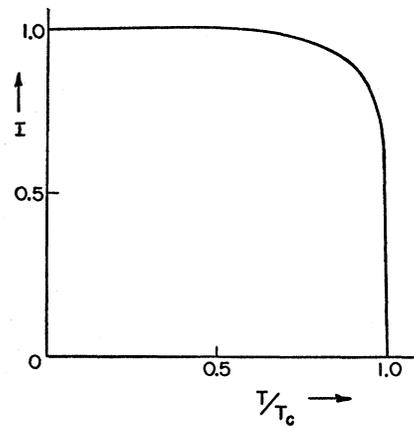


FIG. 4. Spontaneous magnetization.

At low temperatures this gives the same expansion in powers of x as obtained in previous works of Van der Waerden¹ and Ashkin and Lamb:²

$$I = 1 - 2x^4 - 8x^6 - 34x^8 - 152x^{10} - 714x^{12} - \dots$$

This series is convergent all the way up to the critical

¹⁴ See reference 11, especially p. 472.

point, where

$$x = x_c = \sqrt{2} - 1.$$

Near the critical point, I has a branch point:

$$I \cong [4(\sqrt{2} + 2)(x_c - x)]^{1/8}.$$

In Fig. 4, I is plotted against the temperature.

This work was completed in the summer of 1951 while the author was at the University of Illinois. He wishes to take this opportunity to thank the staff of the Department of Physics, University of Illinois for the hospitality extended him during his stay. He also wishes to thank Bruria Kaufman for many stimulating discussions.

High Energy Induced Fluorescence in Organic Liquid Solutions (Energy Transport in Liquids). III*†

MILTON FURST AND HARTMUT KALLMAN

Physics Department, New York University, New York, New York

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Experimental results on the fluorescence of a large number of efficient solutions under both gamma-ray and alpha-particle excitation are presented. These results are compared with the theory to be found in Part I, and very good agreement is obtained in almost all cases. The physical efficiencies of some of these solutions under gamma-ray excitation are found to be quite high when compared with an anthracene crystal. The light output for the same amount of absorbed energy is considerably less for alpha-particle excitation than for gamma-rays in all of the solutions. The experimental data are discussed in conjunction with the theoretical considerations, and the physical processes involved in the large fluorescence of the solutions are analyzed.

A. EXPERIMENTAL RESULTS

SOME experimental and theoretical results on the fluorescence of organic liquid solutions using gamma-ray excitation have previously been reported.¹⁻³ This paper presents results under alpha-particle excitation in addition to further findings with gamma-ray bombardment. The light intensities of all the solutions were measured as a function of the solute concentrations, using mainly a RCA 1P28 photomultiplier with both types of excitation. In most cases, in order to minimize errors, the identical solutions were used for both excitations in comparing their effects. The light emission in the case of gamma-ray excitation is referred to the emission of an anthracene crystal of the same mass and in the same geometrical setting. Such relative fluorescence values at the optimum concentration are described here by the term relative physical efficiencies. These efficiencies differ somewhat from the practical efficiencies published previously,³ as a consequence of the use of a nonreflecting container in the present measurements to minimize effects caused by different amounts of reflection at the walls of the container because of the spectral differences in the emission of the solutions. The values listed in Table I still depend to some extent on the spectral distribution of the emitted light because of the non-uniform spectral response of the photomultiplier. To determine the im-

portance of such effects, measurements were made using two photomultipliers with different spectral responses (RCA 1P28 and 1P21), after the emission spectra of many of the solutions were determined.² A measure of the importance of this spectral effect is given in the last column of Table I, where the ratios of the intensities in the two photomultipliers for the different solutions are presented. The gamma-ray results for all the solutions are referred to the same mass, which means approximately the same amount of absorbed gamma-ray energy since the number of electrons per gram is essentially the same for all these organic solutions (see below).

It is to be noted that some of the light emission efficiencies are quite high; this is particularly the case for *p*-terphenyl which in phenylcyclohexane and xylene has an efficiency about half as great as an anthracene crystal. Since an anthracene crystal converts about 15 percent of the absorbed energy into light (measurements on a naphthalene crystal show about 5 percent conversion and anthracene is better by a factor of about 3),⁴ this indicates that with the solutions as much as about 7 percent of the absorbed gamma-energy may be transformed into light. Another feature to be noted is that fairly generally a solute showing a relatively high efficiency in one solvent exhibits a rather high light emission in the other efficient solvents.

For alpha-particles the values are also referred to a standard measurement with an anthracene crystal or a zinc sulfide powder. Here there is the difficulty that the anthracene crystal surface deteriorates rather quickly under the alpha-particle bombardment (a 10-mC

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† This is part of a dissertation (M.F.) in partial fulfillment of the requirements for the PhD degree at New York University.

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⁴ Broser, Kallmann, and Martius, *Z. Naturforsch.* **4a**, 204 (1949).