Bogoliubov-Tyablikov approximation for the ferromagnet, but the fact that this solution is consistent with the decoupling of the Green's functions that gives the self-energy of the conduction electrons to second order in g allows us to find an expression for the resistivity, Eq. (39), valid for all temperatures, and, in particular, the low-temperature result of Eq. (40).

A detailed comparison with experiments would require a precise knowledgment of the parameter ω_m, but an approximate plot of the resistivity versus temperature is given in Fig. 2. It shows the qualitative features of the resistivity of gadolinium as measured by Colvin, Legvold, and Spedding.[11] Gadolinium metal has localized spins and approximates best the assumptions of the theory.

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Ising Model with Antiferromagnetic Next-Nearest-Neighbor Coupling: Spin Correlations and Disorder Points*

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The existence of a *disorder point* T_D is established for some one- and two-dimensional Ising lattices with antiferromagnetic next-nearest-neighbor interactions. Within the disordered phase, the decay of axial next-nearest-neighbor pair correlations with increasing spin separation is positive monotonic exponential below T_D and oscillatory with exponential envelope above T_D. A general definition of a disorder point is formulated, and a method of estimating T_D described.

This paper summarizes some exact calculations performed recently to determine the nature of pair correlations between two spins on an axis of an Ising lattice when next-nearest-neighbor interactions are present. The primary result concerns the existence of a disorder point T_D in one- and two-dimensional Ising lattices with ferromagnetic nn[1] and antiferromagnetic nnn[1] exchange. The results also hold when the nn interaction is antiferromagnetic, at least when the nn lattice is loose packed. A definition of T_D is framed and a procedure indicated for its estimation on lattices for which exact solutions are not yet available. Figure 1 illustrates the lattices considered, and Fig. 2 shows the dependence of the disorder point T_D and the critical point T_C (Curie point) on the ratio of nnn to nn interactions for the "union-jack" lattice.[2]

Consider an Ising model with spin variables $\sigma_{\vec{r}} = \pm 1$ at lattice sites $\vec{r}$, and Hamiltonian

$$\mathcal{H} = -J_1 \sum_{nn} \sigma_{\vec{r}} \sigma_{\vec{r}'} - J_2 \sum_{nnn} \sigma_{\vec{r}} \sigma_{\vec{r}''}, \qquad J_2 < 0 < J_1 \qquad (1)$$

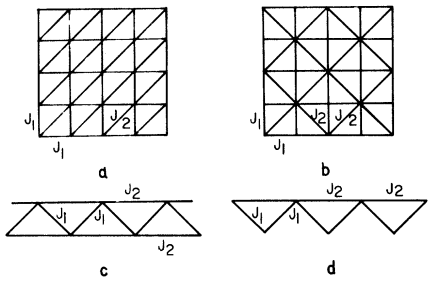

FIG. 1. (a) Triangular lattice, (b) union-jack lattice, (c) linear chain with both nnn interactions, (d) decorated chain with alternate nnn interactions.

where the first sum is over all nn pairs of spins, and the second sum over all nnn pairs of spins. The nn interaction J_1 is chosen to be positive so that the nn lattice is coupled ferromagnetically. The nnn interaction J_2 is chosen to be negative, so nnn spins are coupled antiferromagnetically. J_1 is supposed to be sufficiently strong relative to J_2 so that the ground state of the lattice is that of the ferromagnetic nn lattice. The notion "sufficiently strong" may be made precise for the lattice structure in question.[3] The choice of a negative J_2 is deliberately designed to introduce a nnn interaction which inhibits the ferromagnetic ordering process. In this sense the lattice is less stable when an antiferromagnetic nnn interaction is present.[4] The pair correlation between spins at sites $\vec{0}$ and $\vec{r}$ is defined by $\omega_2(\vec{r}) = \langle \sigma_{\vec{0}}\sigma_{\vec{r}} \rangle$ in which we assume translational symmetry of an infinite lattice. For lattices which exhibit an ordered phase, the situation will, as we argue below, be as follows:

(i) At temperatures below the critical point T_C there is ferromagnetic long-range order and $\lim |\vec{r}| \to \infty |\omega_2(\vec{r})| \neq 0$.

(ii) For a certain range of temperatures above the critical point there is ferromagnetic short-range order, and the pair correlation decays *monotonically* to zero as the spin separation increases.

(iii) The ferromagnetic short-range order breaks down at the disorder point T_D above which pair correlations in the nnn direction decay in an *oscillatory* manner.

For the one-dimensional systems we consider there is no ordered phase, but (ii) and (iii) continue to be valid. The existence of an ordered phase for the two-dimensional systems is evident from the exact solutions. The nature of the oscillation in (iii) above the T_D point depends on lattice structure. Thus we are led to distinguish two kinds of disorder point according as the wavelength of oscillation is temperature dependent (first kind) or independent (second kind). Let $K_l = J_l/k_B T$, $l = 1, 2$.

(*a*) *Triangular lattice.* We regard the triangular lattice as a square lattice with nn ferromagnetic interaction J_1 and a single nnn antiferromagnetic J_2 along one set of diagonal bonds. The salient features of the axial pair correlations[5] are a ferromagnetic short-range-order region above the Curie point T_C up to the disorder point T_D which is determined by

$$\tanh K_2 + (\tanh K_1)^2 = 0 \text{ or } \cosh 2K_1 = e^{-2K_2}, \qquad (2)$$

provided $-|J_1| < J_2 < 0$. The dependence of T_c and T_D on the ratio $J_2/|J_1|$ is qualitatively similar to that indicated in Fig. 2, for the union-jack lattice.[2,5] The monotonic decay of the axial pair correlations below T_D changes over to oscillatory decay with exponential envelope above T_D, the wavelength of oscillation being *temperature dependent.* We shall call this a T_D point of the first kind. Above T_D the axial pair correlation between spins separated by asymptotically large distance $r = |\vec{r}|$ is

$$\omega_2(\vec{r}) \sim (\tfrac{1}{2}\pi \sin\theta_l)^{-1/2} v_l^k k^{-1/2} \cos(k\theta_l + \tfrac{1}{2}\theta_l - \tfrac{1}{4}\pi - \phi_l), \qquad (3)$$

where $l = 1$ and $\vec{r} = (k, 0)$ or $(0, k)$ for nn axial directions, and $l = 2$ and $\vec{r} = (k, k)$ for the nnn direction. Here $v_l = \tanh K_l$, and ϕ_l and θ_l are temperature-dependent angles, explicit expressions for which are given in Ref. 5. The oscillation is determined by the cosine factor. θ_1 is zero at T_D and at $T = \infty$, and rises to a maximum value, which must be less than $\frac{1}{3}\pi$ in between. Also $0 < \theta_2 < \pi$, θ_2 being π at T_D and decaying monotonically to zero as T increases without bound. At T_D the nn-axis pair correlations are exactly $\omega_2(k, 0) = \omega_2(0, k)$

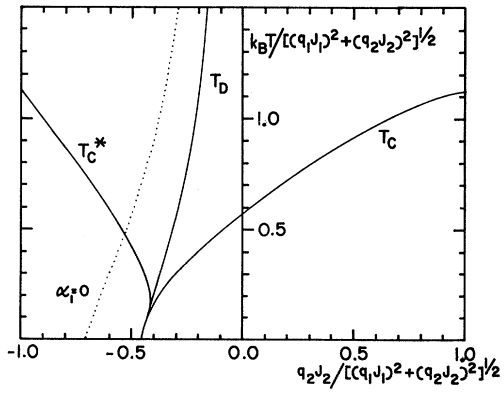

FIG. 2. Graphs of Curie point T_C, disorder point T_D, and second critical temperature T_C^*, suitably scaled, versus the nnn interaction, also scaled, for the union-jack lattice. $q_1 = 4$ is the nn coordination number. $q_2 = 2$ is the effective nnn coordination number. The dotted line is the locus $\alpha_1 = 0$.

$= (\tanh K_1)^k$, and the nnn-axis pair correlations $\omega_2(k,k) = (-\tanh K_2)^k$.

(b) *Union-jack lattice.* The union-jack lattice is constructed out of a square lattice by introducing nnn bonds along alternate diagonals. The average coordination number is 6, the same as that of the triangular lattice. The basic square lattice will be taken as the nn lattice with ferromagnetic interaction J_1. The diagonal bonds, which themselves form a square lattice, will have antiferromagnetic interaction J_2. Vaks, Larkin, and Ovchinnikov[2] have constructed a generating function for the elements of the Toeplitz determinant representing pair correlations along the diagonal direction containing nnn bonds. They showed that the form of the correlation is determined by two parameters α_1 and α_2, the relevant mathematical properties of which are given in parentheses in the following:

$$\alpha_1 = e^{2K_2}(\cosh 4K_1 - e^{-2K_2})/(1+e^{-2K_2}) ,$$

$$\alpha_2 = e^{-2K_2}(1-e^{-2K_2})/(\cosh 4K_1 + e^{-2K_2}) .$$

The usual critical temperature T_C is determined by $\alpha_1 = 1$, or $\cosh 4K_1 = e^{-4K_2} + 2e^{-2K_2}$, which has solutions when $-|J_1| < J_2$. A second critical temperature T_C^* is determined by $\alpha_2 = -1$ or $\cosh 4K_1 = e^{-4K_2} - 2e^{-2K_2}$, which has solutions when $J_2 < -0.907|J_1|$ (see Fig. 2). Analysis of the formulas given by Vaks *et al.*[2] for correlations along the diagonals with nnn interaction only, when $-|J_1| < J_2 < 0$, shows that below T_C there is ferromagnetic long-range order ($\alpha_1 > 1$ and $-1 < \alpha_2 < 0$). Above T_C there is ferromagnetic short-range order up to a disorder temperature T_D determined by $\alpha_1 = -\alpha_2$ or

$$\cosh 4K_1 = e^{-4K_2}, \qquad (4)$$

$$\text{or} \quad \tanh 2K_2 + (\tanh 2K_1)^2 = 0 .$$

Thus T_D for the union-jack lattice is exactly twice T_D for the triangular lattice. (Between T_C and T_D, $-1 < \alpha_2 < 0 < \alpha_1 < 1$ and $|\alpha_2| < |\alpha_1|$.) In a range of temperatures above T_D there is antiferromagnetic short-range order along an axis containing the nnn bonds, the sign of the correlation $\omega_2(k,k)$ being $(-)^k$, independent of temperature. We shall call this a T_D point of the second kind. (Above T_D, $\alpha_2 < 0 < |\alpha_1| < 1$ and $|\alpha_1| < |\alpha_2|$.) If the interaction J_2 satisfies $-0.907|J_1| < J_2 < 0$, the antiferromagnetic short-range-order region extends to $T = \infty (-1 < \alpha_2 < 0)$. But if $-|J_1| < J_2 < -0.907|J_1|$, there is an intervening antiferromagnetic long-range-order phase between lower and upper critical points T_C^* ($\alpha_2 < -1$). At T_D the nnn axis correlations are zero (exactly) if k is odd, and decay for even k as $\omega_2(k,k) \sim (\frac{1}{2}\pi k)^{-1/2}(\tanh K_2)^k$. The pair correlations in the nnn direction remain antiferromagnetic above T_D. It is also feasible to construct a determinant representation for the nn axial correlations, though Vaks *et al.* did not do so.

(c) *Linear chain with both nnn interactions.* The lattice is illustrated in Fig. 1(c). Using the techniques developed by Kramers and Wannier,[6] and Marsh,[7] and Dobson,[8] it is straightforward, though tedious, to calculate pair correlations on the infinite chain with all nnn interactions present. The essential result is that a T_D point of the first kind is located by

$$\tanh K_2 + (\tanh \tfrac{1}{2}K_1)^2 = 0 , \qquad (5)$$

provided $-\frac{1}{2}|J_1| < J_2 < 0$. For temperatures below T_D the pair correlations decay exponentially with temperature-dependent oscillatory envelope. At T_D, $\omega_2(k) \sim \text{const} \times k(\mu_+/\lambda_+)^k$, with $0 < \mu_+/\lambda_+ < 1$.

(d) *Decorated chain with alternate nnn interactions.* The lattice is illustrated in Fig. 1(d). There are two types of spins: those coupled by nnn interactions and those with nn coupling only. The split-bond decoration transformation of Syozi[9] may be adapted for calculation of pair correlations. The essential result is that a T_D point of the second kind is located by

$$\tanh K_2 + (\tanh K_1)^2 = 0 \qquad (6)$$

provided $-|J_1| < J_2 < 0$. In fact, nnn correlations are given by

$$\omega_2(k) = \left(\frac{\cosh 2K_1 - e^{-2K_2}}{\cosh 2K_1 + e^{-2K_2}}\right)^{k/2}, \quad k \text{ even} \qquad (7)$$

from which it is clear that there is ferromagnetic short-range order below T_D, and antiferromagnetic short-range order above T_D, between nnn spins. The pair correlations vanish at T_D. More details of the calculations on the one-dimensional lattices will be presented elsewhere.[10]

(e) *General definition of T_D point.* Consider the class of Ising lattices with ferromagnetic nn interaction J_1 and antiferromagnetic nnn interaction J_2, i.e., $J_2 < 0 < J_1$. Suppose that J_1 is sufficiently strong to ensure that the ground state is ferromagnetic, so all pair correlations are positive at sufficiently low temperatures. We shall show that some pair correlations are negative at sufficiently high temperatures, and thence construct the highest temperature below which spins that are far apart cannot have a vanishing pair correlation. This will be the disorder point. From the Kac-Ward graphical interpretation of the Ising model, it follows that the leading term in the power-series expansion of the pair correlation between two spins separated by k nnn links (along a nnn axis with interaction J_2) is proportional to $(\tanh K_2)^k$.

So for fixed k as $T \to \infty$, $\omega_2 \sim \text{const} \times (\tanh K_2)^k$, which is negative for odd k when $J_2 < 0$. Therefore ω_2 vanishes at some finite temperature. Let $\omega(\vec{r})$ vanish at some temperature $T(\vec{r})$ for general $\vec{r}$. [Note that for some $\vec{r}$, $T(\vec{r})$ may be infinite, and for some other $\vec{r}$, $\omega_2(\vec{r})$ may vanish at more than one temperature.] Let $T_0(\vec{r})$ be the lowest of the temperatures at which $\omega_2(\vec{r})$ vanishes ("lowest"—one may need to take an infimum). Now we are interested in the breakdown of the ferromagnetic (probably short-range) order at large spin separation. $T_0(\vec{r})$, as a function of $\vec{r}$, is bounded below, and so has an infimum (greatest lower bound) for all values of $r = |\vec{r}|$ greater than some fixed value R. Let this infimum be $T^*(R)$. Then $T^*(R)$ is a monotonic increasing function of R. So as $R \to \infty$, either $T^*(R) \to \infty$ or $T^*(R)$ tends to a finite limit temperature. In either case we set $\lim R \to \infty\, T^*(R) = T_D$. Formally, $T_D = \liminf |\vec{r}| \to \infty\, [T\colon\ \omega_2(\vec{r}) = 0]$.

(i) It is probably sufficient to consider only nnn axis correlations. Then it is clear that our definition of T_D works for the disorder points of the second kind on the union-jack lattice and on the decorated chain with alternate nnn interactions considered previously.

(ii) For the triangular lattice, consideration shows that, for any fixed k, the argument of the cosine in the expression (3) for pair correlations along the nnn axis can always be set equal to an odd multiple of $\frac{1}{2}\pi$ by appropriate choice of θ_2, $0 < \theta_2 < \pi$. Take the value of θ_2 closest to π which does this to obtain the lowest temperature $T_0(\vec{r})$ at which $\omega_2(\vec{r})$ vanishes for a given $\vec{r} = (k, k)$. Then as $k \to \infty$, $\theta_2 \to \pi$ and $T_0(\vec{r}) \to T_D$ as located previously.

(iii) Our definition of a disorder point does not immediately provide an easy means of calculating T_D. To calculate $T^*(R)$ one would need to know the properties of all pair correlations. In practice, for three-dimensional lattices, information is usually available only for pair correlations between spins separated by a few (e.g., 12) lattice spacings.[11] As a practical method of estimating T_D, one may proceed as in (ii) for the triangular lattice. For fixed spin separation $\vec{r}$, estimate the lowest temperature $T_0(\vec{r})$ at which the pair correlation vanishes. Then extrapolate the sequence $[T_0(\vec{r})]$ for large $r = |\vec{r}|$ to estimate T_D. For example, in the triangular lattice, one finds a steadily decreasing sequence $[T_0(\vec{r})]$ from pair correlations along the nnn axis when $\vec{r} = (k, k)$, which may be extrapolated for large k, by plotting T_0 versus $1/k^2$, to yield estimates of T_D in close agreement (0.1%) with the exact values.

(iv) The preceding discussion shows that the pair correlation between two nnn spins separated by *one* nnn lattice vector must vanish at some (lowest) temperature T_E, which we will call the energy temperature, because at T_E the contribution to the internal energy from the nnn interaction will change sign, being positive below T_E and negative above. Intuitively one would expect that $T_E \geq T_D > T_C$ (if present) > 0. In the soluble examples $T_E = T_D$ for T_D points of the second kind. For the triangular lattice $T_E = 2T_D$ and for the linear chain with both nnn interactions $2T_D < T_E < 4T_D$. For these T_D points of the first kind, the first change of sign of each of the pair correlations along the nnn axis occurs between T_D and T_E as the temperature rises.

(v) The disorder point T_D and energy point T_E, defined above for interacting spin systems confined to a lattice, characterize the change in the nature of the short-range order, which must occur within the disordered phase when certain antiferromagnetic interactions are present. Now many recent developments in the theory of phase transitions have revealed a close analogy between magnetic and fluid systems, particularly in the neighborhood of the critical point.[12,13] Accordingly, it is of some interest to see whether there is any feature of a fluid system which corresponds to the disorder point in the magnetic system. In a recent article Fisher and Widom[14] have argued that the pair-correlation function in a fluid should have different asymptotic behavior on either side of a definite line in the phase diagram. On the high-temperature side of this line, the decay is monotonic for large intermolecular separations, whereas on the low-temperature side the decay is oscillatory. Such a behavior is to be expected, because at sufficiently high temperatures the fluid behaves as an ideal gas, and at sufficiently low temperatures it undergoes transition to the solid state, in general, with oscillatory long-range order. Insofar that the Fisher-Widom line borders regions of the disordered phase in which the fluid pair-correlation function has different modes of decay, it is analogous to a locus of disorder points, which would be in the magnetic field temperature diagram of the corresponding magnetic system. (The existence of such a locus follows by an argument similar to that for the phase boundary of an antiferromagnet.[15]) However, the modes of decay are opposite at temperatures above and below the relevant line in the fluid and magnetic systems, which may be attributed to the differences in the physical mechanisms responsible. Most models of fluids use a pair potential with a strongly repulsive core (cf. antiferromagnetic interactions) with a weakly attractive tail (cf. ferromagnetic interactions), whereas in the magnetic systems considered above, the sign of the nn interaction is unimportant on loose-packed lattices, but the nnn interactions must be antiferromagnetic.

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[1]The abbreviations nn for nearest neighbor and nnn for next nearest neighbor are used throughout.

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Phase Transitions and Soft Librational Modes in Cubic Crystals*†

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Landau's theory of second-order phase transitions and the theory of lattice dynamics are combined in a presentation of an approach to the understanding of the crystallographic phase transitions of complex fcc crystals. The approach is applied to the antifluorite-type crystal K_2ReCl_6, which exhibits four phase transitions. The results of a series of crystallographic and spectrographic experiments are described, and are interpreted in light of the developed theory. Finally, a model based on the theory is constructed and is shown to describe the spectral observations. The resultant model leads to the conclusion that two of the phase transitions are driven by a single branch of a "soft" phonon.

INTRODUCTION

This paper attempts to provide a single consistent theoretical picture for the understanding of all the experimental results related to the lattice dynamics and crystallographic phase transitions of crystals possessing the antifluorite (R_2MX_6) structure. This theoretical picture centers around the establishment that these materials exhibit phase transitions that are driven by a new type of soft mode. In fact, most of the observed transitions can be described in terms of the temperature dependence of a single branch of the phonon spectrum, the longitudinal rotary mode which involves librational motion of the $MX_6^=$ octahedron as a solid body. This mode is unique in the respect that it is a *gerade* phonon unlike the *ungerade* transverse optic mode that is responsible for the $BaTiO_3$ ferroelectric transition.[1-5] The system R_2MX_6 is singular in that a single branch of the spectrum can describe transitions involving no change in the number of molecules per unit cell and also transitions involving doubling or quadrupling of the number of molecules per cell.

In developing a model for this system, we were spurred on by the belief that it is possible to obtain a rather detailed understanding of the lattice dynamics and phonon spectrum of a relatively complicated structure via imaginative use of traditional and readily available experimental techniques. In order to glean the maximum amount of information from these techniques, however, it is necessary to utilize a combined theoretical and experimental approach. We will be attempting to show here that a description of such a system is possible when a theoretical calculation is carried out in close connection with experiment. Thus, theoretical and experimental results will be interspersed in an attempt to demonstrate the close relationship between the two that is all important in such an undertaking.

The particular antifluorite structure that we are concerned with here is essentially the same as CaF_2, except for the replacement of the F^- by a positive ion R^+, and the Ca^{++} by the octahedral anion $MX_6^=$, indicated in Fig. 1. The extra degrees