

Spin-Wave Theory of a Finite Concentration of Impurities in a Ferromagnet; Effects to c^2 [†]

Eugene Shiles

Department of Physics, Florida State University, Tallahassee, Florida 32306

(Received 21 March 1972)

Green's functions are used to study a simple-cubic Heisenberg ferromagnet containing a small finite concentration of randomly oriented substitutional magnetic impurities, including effects to second order in the concentration. The results involve the effects of spin-wave scattering from one impurity or coherently from two, and reflect the properties of single isolated impurities and distinct impurity pairs. Impurity excitations at energies within the host spin-wave energy band are emphasized. Several types of experiments are discussed, and a simple numerical comparison shows that the magnitude of the deviation from pure-crystal behavior due to the pairs as compared to that due to single isolated impurities depends essentially only on the relative concentrations of the various species. Only zero temperature is considered.

I. INTRODUCTION

There has been considerable recent interest in systems containing a finite concentration of substitutional impurities, where the perturbation due to individual impurities is of the type described by Lifshitz.¹ Essentially the finite spatial extent of the perturbation, which is not restricted to be small in magnitude, makes an expansion in powers of the concentration valid if one is not concerned with the nature of the Van Hove critical points of the excitation spectral density. An ordered magnetic insulator containing substitutional magnetic impurities is a system of this type. It has not yet proved possible to carry out an explicit calculation for arbitrary concentrations, and the recent work has essentially been restricted to small concentrations. Izyumov² and Jones,³ for example, have considered the problem to first order in the concentration and obtained results that may be described as spin-wave scattering by single isolated impurities. Jones initially uses a "mean-lattice" approximation to make the formalism symmetric in both types of ion, but completes the calculation only for small impurity concentrations, whereas Izyumov begins with a calculation not symmetric in the two components. Murray⁴ considered a combined perturbation theory and variational calculation valid for arbitrary concentrations in the limit of low-energy spin waves. The latter work included, for arbitrary energies, a calculation linear in the concentration, and quadratic in the concentration for the special case of nonmagnetic impurities. The present paper contains a calculation similar to that of Izyumov or of Jones but carried out to second order in the concentration of impurities; this includes the coherent scattering of spin waves by impurity pairs. The theory is valid for arbitrary impurity spin and for the full range of

spin-wave energies.

When experiments are done on crystals containing 1-3% impurities, the effects of impurity pairs should be observable since the pairs will be present in substantial numbers. Effects of groups of three or more impurities, proportional to third and higher powers of the concentration, will be small in this concentration range. Therefore, the accurate interpretation of the experimental results and the extraction of all the useful information contained in the data require that the pair effects be considered. For example, one may wish to learn more about the superexchange mechanism in a given material by determining experimentally the exchange coupling strength between two host ions, a host ion and an impurity ion, and two impurity ions. The theory of the impurity modes associated with a single impurity pair in a face-centered-cubic ferromagnet has been considered by Frikkee,⁵ and the local modes due to impurity pairs in a simple-cubic ferromagnet, for which the isolated-pair problem is adequate at low concentrations and at energies well separated from the host energy band, have been examined by Shiles and Hone.⁶ White and Hogan⁷ have also studied the problem of two impurities in a magnetic lattice and discussed the splitting of the single-impurity states due to impurity-impurity interactions. Since a theory that considers only a single impurity or impurity pair is inadequate for energies near or within the pure-host continuum when the concentration is large enough for the pair effects to be observable, the present paper in effect extends some of the calculations of Ref. 6 to all energies; this includes the resonance modes associated with impurities, which are at energies within the host spin-wave energy band and have important effects on the thermodynamics of the system. Resonance modes have been seen, for example, in inelastic

neutron scattering.^{8,9} The preliminary results of Ref. 6 are utilized in the present work, as a theory quadratic in the impurity concentration leads to results that reflect the properties of isolated single impurities and impurity pairs.

To keep algebraic difficulties to a minimum, we have chosen to examine an impure simple-cubic Heisenberg ferromagnet with only isotropic nearest-neighbor exchange interactions. While this simple model cannot be expected to allow a detailed study of the real crystals, the qualitative features of the problem will not be greatly affected. The ferromagnetic salts EuO, EuS, and EuSe may be useful host crystals for eventual study; they have cubic, although not simple-cubic, magnetic structure, but may have important exchange interactions beyond nearest neighbors in the pure crystal as well as more complex impurity exchange.¹⁰ To examine the spin dynamics of the system we employ the method of two-time Green's functions, expressing these functions directly in terms of the spin operators. Only the low-temperature limit is considered, so that our calculation is equivalent to that of the simple spin-wave approximation. We initially express the Green's-function equation of motion in terms of a definite, although not specified, impurity configuration (for experimental purposes, the impurities are randomly oriented). Averaging over all possible impurity configurations restores translational invariance, making the calculation tractable. A diagrammatic technique due originally to Edwards¹¹ is utilized to extract the single-impurity and impurity-pair effects, ignoring coherent scattering from more than two impurities.

An approximate dispersion relation is obtained from the resulting Green's function. The behavior of the spectral weight function, as well as scattering cross sections, may be determined from the imaginary part of this Green's function. As our Green's function is defined directly in terms of the spin operators instead of using the simple spin-wave approximation in the Holstein-Primakoff transformation, we avoid the introduction of the square-root spin factor found in the results of Izyumov.² This difference was pointed out by Jones.³ Our results, to terms in the self-energy quadratic in the impurity concentration, reflect the effects of the resonances and/or local modes associated with single isolated impurities and with the distinct impurity pairs, that is, those pairs which have their own distinct perturbation scheme. The perturbation is limited, in our approximation, to the impurities and their nearest neighbors, so that the distinct pairs are those that are nearest neighbors themselves or share one or two common nearest neighbors.

We develop the Green's-function formalism and calculate the configuration-averaged Green's func-

tion in Sec. II. In Sec. III we discuss the result, make a simple numerical comparison of some impurity-pair effects to the effects of single isolated impurities, and comment on experimental applications.

II. GREEN'S-FUNCTION FORMALISM

The Heisenberg Hamiltonian for the ferromagnet containing substitutional impurities, including a Zeeman term that may involve both an external magnetic field and an effective single-ion anisotropy field, is

$$\mathcal{H} = -\mu_B \sum_i g_i H_i S_i^z - \sum_{\langle i,l \rangle} J_{il} \vec{S}_i \cdot \vec{S}_l. \quad (2.1)$$

We consider only nearest-neighbor exchange, so that the exchange integral J_{il} takes on the values J , J' , and J'' for i and l two-nearest-neighbor host ions, an impurity and a host ion that are nearest neighbors, and two-nearest-neighbor impurities, respectively, and is zero otherwise. For simplicity the values of the various exchange parameters are chosen so as to give a ground state with all spins "up."

The two-time Green's functions are defined¹²:

$$G_{il}(t) = -i\theta(t) \langle [S_i^+(t), S_l^-(0)] \rangle, \quad (2.2)$$

where $\theta(t)$ is the unit step function and the angular brackets denote the thermal expectation value.

Following standard procedures we first write the equations of motion for the $G_{il}(t)$ and decouple the resulting set of equations via the random-phase approximation (RPA); only a low-temperature limit equivalent to the simple spin-wave approximation is considered in this discussion, so that the operator S_l^z , which appears in higher-order Green's functions that describe spin-wave-spin-wave interactions, is in effect replaced by its maximum value S for l a host ion or S' for l an impurity ion. The finite temperature notation will be retained. We then take the time Fourier transform and obtain a set of algebraic equations for the energy Green's functions $G_{il}(E)$. Defining the reduced Green's functions $\Gamma_{il} = (12JzS/S_l)G_{il}(E)$, where z is the number of nearest neighbors to an ion, the set of equations becomes, when written in terms of the pure-crystal Green's functions Γ^0 ,

$$\Gamma_{il} = \Gamma_{il}^0 + \sum_n (\Gamma^0 V)_{in} \Gamma_{nl}, \quad (2.3)$$

where Γ_{il}^0 is the familiar expression

$$\Gamma_{il}^0 = (1/N) \sum_{\vec{k}} e^{i\vec{k} \cdot (\vec{r}_i - \vec{r}_l)} / (\omega - \omega_{\vec{k}} + i0^+). \quad (2.4)$$

The \vec{k} summation is over the first Brillouin zone of the crystal, N is the total number of ions in the crystal, $\omega = E/2JzS$ is the energy in natural units, $\omega_{\vec{k}} = 1 - (1/z) \sum_{\vec{\Delta}} e^{i\vec{k} \cdot \vec{\Delta}} + h$ is the dispersion relation for the pure host, $\vec{\Delta}$ is summed over all nearest-

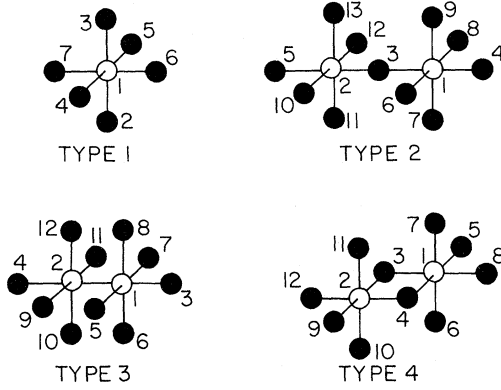


FIG. 1. Four distinct impurity clusters. Types 2 and 3 have three possible orientations, with the interimpurity axis parallel to the x , y , and z axes, respectively, and type 4 has six orientations, along the six (110) directions. The labeling conventions for the impurities (open circles) and host neighbors (dark circles) are indicated.

neighbor vectors, and $h = g\mu_B H/2JzS$ is the Zeeman energy for the pure host. V is the perturbation matrix of the crystal containing a particular configuration of cN impurities and is of block-diagonal form due to the finite extent of the perturbation due to each impurity. Ignoring c^3 and higher effects, the elements of V_{mn} for the simple-cubic crystal are

$$V_{mn} = \sum_{\eta} \sum_{\beta_{\eta}} \sum_{\substack{\Delta_{\eta} \\ \Delta'_{\eta}}} V_{\Delta'_{\eta}\Delta_{\eta}}^{(\eta)} \delta_{m, \beta_{\eta} + \Delta'_{\eta}} \delta_{n, \beta_{\eta} + \Delta_{\eta}}, \quad (2.5)$$

where the primed sum is over all the clusters, as shown in Fig. 1, of types $\eta = 1, 2, 3, 4$, including all possible orientations of the pairs. Types 2 and 3 have each three possible orientations, with the interimpurity axis along the x , y , and z axes, respectively, and type 4 has six orientations, with the interimpurity axis along the six (110) directions. The site index β_{η} is summed over the sites labeled 1 of all clusters of type η , and the indices Δ_{η} and Δ'_{η} over all sites of the type η cluster. The vectors $\vec{\Delta}_{\eta}$, included in later expressions, have their origin at the site labeled 1 of a given cluster (thus $\vec{l}_{\eta} = 0$ in all cases). $V^{(\eta)}$ is the perturbation matrix associated with the type- η cluster, and these matrices are listed in the Appendix. Equation (2.3) describes the impure crystal in terms of four distinct kinds of scattering centers, the impurity clusters of types 1, 2, 3, and 4. Reference 6 discusses the various impurity excitations associated with each type of cluster; in the present calculation these may be local modes and/or resonance modes. We point out that the energy of a given mode associated with a given type of pair cluster is independent of the orientation of that cluster.

We next transform Γ to wave-vector space. Lack of translational invariance in the impure crystal precludes a simple Fourier representation of Γ_{ii} , that is, $\Gamma_{ii} \neq \Gamma(\vec{i} - \vec{l})$. We may make the following transformation, retaining in the Green's function one of the spatial indices,²

$$\Gamma_{ii} = (1/N) \sum_{\vec{k}} G_i(\vec{k}) e^{i\vec{k} \cdot (\vec{i} - \vec{l})}. \quad (2.6a)$$

For the pure crystal, the corresponding expression is

$$\Gamma_{ii}^0 = (1/N) \sum_{\vec{k}} G^0(\vec{k}) e^{i\vec{k} \cdot (\vec{i} - \vec{l})}, \quad (2.6b)$$

so that we have the familiar result $G^0(\vec{k}) = (\omega - \omega_{\vec{k}})^{-1}$. The scattering equation becomes

$$G_i(\vec{k}) = G^0(\vec{k}) + \sum_n (\Gamma^0 V)_{in} G_n(\vec{k}) e^{i\vec{k} \cdot (\vec{i} - \vec{l})}. \quad (2.7)$$

By iteration this expression is expanded to give, where we choose $l = \beta_{\mu} + \Delta_{\mu}$ restricted to be the index of any perturbed site,

$$\begin{aligned} G_{\beta_{\mu} + \Delta_{\mu}}(\vec{k}) &= G^0(\vec{k}) + G^0(\vec{k}) \sum'_{\eta} \frac{1}{N} \sum_{\vec{k}'} \sum_{\substack{\Delta'_{\eta} \\ \Delta_{\eta}}} G^0(\vec{k}') \\ &\quad \times V_{\eta}^{\Delta_{\mu} \Delta'_{\eta}}(\vec{k}, \vec{k}') e^{-i(\vec{k} - \vec{k}') \cdot \vec{\beta}_{\mu}} \rho_{\eta}(\vec{k}' - \vec{k}) \\ &\quad + G^0(\vec{k}) \sum'_{\eta, \nu} (1/N^2) \sum_{\vec{k}', \vec{k}''} \sum_{\substack{\Delta'_{\eta} \\ \Delta_{\nu}}} G^0(\vec{k}') \\ &\quad \times V_{\eta}^{\Delta_{\mu} \Delta'_{\eta}}(\vec{k}, \vec{k}') G^0(\vec{k}'') V_{\nu}^{\Delta'_{\eta} \Delta_{\nu}}(\vec{k}', \vec{k}'') \\ &\quad \times e^{-i(\vec{k} - \vec{k}') \cdot \vec{\beta}_{\mu}} \rho_{\eta}(\vec{k}' - \vec{k}'') \rho_{\nu}(\vec{k}'' - \vec{k}) + \dots, \end{aligned} \quad (2.8)$$

where

$$\begin{aligned} V^{\Delta_{\mu} \Delta'_{\eta}}(\vec{k}, \vec{k}') &= \sum_{\Delta'_{\eta}} V_{\Delta'_{\eta} \Delta_{\eta}}^{(\eta)} e^{-i\vec{k} \cdot (\vec{\Delta}'_{\eta} - \vec{\Delta}_{\eta})} \\ &\quad \times e^{-i(\vec{k} - \vec{k}') \cdot (\vec{\Delta}_{\mu} - \vec{\Delta}'_{\eta})} \end{aligned} \quad (2.9)$$

and

$$\rho_{\eta}(\vec{k}) = \sum_{\beta_{\eta}} e^{-i\vec{k} \cdot \vec{\beta}_{\eta}}. \quad (2.10)$$

We seek the quantity $\langle G_i(\vec{k}) \rangle$, where the angular brackets denote an average over all possible impurity configurations, noting that, for a large crystal, $G \sim \langle G \rangle$ for the overwhelming majority of possible configurations.¹³ The l dependence of $\langle G_i(\vec{k}) \rangle$ vanishes after the averaging is carried out, as the translational invariance introduced by averaging implies it must. The average involves only the products of $\rho_{\eta}(\vec{k})$ in Eq. (2.8); the explicit expressions are discussed, for example, by Kohn and Luttinger,¹³ by Yonezawa,¹⁴ and by Izyumov,² and we will not reproduce the results here. We may apply the earlier results to our crystal by averaging over the different types of clusters

separately, for example,

$$\sum_{\eta, \nu}' \langle \rho_{\eta}(\vec{k}) \rho_{\nu}(\vec{k}') \rangle \rightarrow \sum_{\eta}' \langle \rho_{\eta}(\vec{k}) \rho_{\eta}(\vec{k}') \rangle + \sum_{\substack{\eta, \nu \\ \eta \neq \nu}}' \langle \rho_{\eta}(\vec{k}) \rangle \langle \rho_{\nu}(\vec{k}') \rangle .$$

This expression includes unphysical terms that involve two clusters of different types that are counted as occupying the same sites, but these contribute to order c^3 and higher and are neglected.

In general, the scattering equation for the Green's function can be written in the familiar form

$$\langle G \rangle = G^0 + G^0 \Sigma G^0 + G^0 \Sigma G^0 \Sigma G^0 + \dots = G^0 + G^0 \Sigma \langle G \rangle , \tag{2.11}$$

where Σ is the "proper self-energy." The solution is, of course, $\langle G \rangle = (1 - G^0 \Sigma)^{-1} G^0$. The expression (2.11) is easily expressed in diagram form, as is shown in Fig. 2. In these diagrams the double line refers to the perturbed Green's function $\langle G \rangle$, the single line to the unperturbed Green's function G^0 , and the square to the proper self-energy. The single horizontal lines thus describe the free propagation of a particle (spin wave in our case), and the self-energy parts describe all possible interactions or scatterings due to the perturbations; the expression can be interpreted as the sum of the contributions from any number of alternating interactions and free propagations. The advantage of the diagrammatic technique is that it provides a systematic means of keeping track of the terms (or processes) contributing to Σ and retaining only those we wish to consider. In this calculation we want the self-energy terms linear and quadratic in the impurity concentration c , which are the terms that describe the scattering from one impurity or coherently from two.

The dominant physical processes, the scattering from single isolated impurities and the coherent scattering from impurity pairs that form clusters of types 2, 3, and 4, are described by the proper self-energy diagrams linear in the concentration c_{η} of each of the clusters of type η . For a large crystal c_{η} has the expected values, to order c^2 , $c_1 = c - 24c^2$, and $c_2 = c_3 = c_4 = c^2$ for each of the various orientations of the pair clusters. These processes are described by the diagrams of Fig. 3(a), where we keep all orders in the perturbations $V_{\eta}^{(\mu)}$. X_{η} carries concentration c_{η} , the labels \vec{k} on the horizontal lines indicate the argument of the $G^0(\vec{k})$, the dashed interaction lines represent $V_{\eta}^{\Delta \mu \Delta'}(\vec{k}, \vec{k}')$ where \vec{k}' is the label on the solid line immediately to the left of the interaction line, and all internal

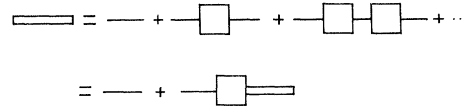


FIG. 2. Diagrammatic representation of Eq. (2.11).

\vec{k}' s and $\vec{\Delta}'$ s are summed. The \vec{k} sums also include the factors $1/N$. The papers by Edwards¹¹ and by Izyumov² describe the graphs and their relationships to the expressions more fully. Wave vector \vec{k} is conserved in the scattering in the translationally invariant crystal, as expected. There are other diagrams that contribute terms in the self-energy proportional to c^2 . These describe the coherent scattering from pairs of impurities more widely separated than those forming the types 2, 3, and 4 clusters. Their diagrams are shown in Figs. 3(b) and 3(c). Each of these diagrams is assumed to include all possible separations $l\hat{x} + m\hat{y} + n\hat{z}$, of the two impurities, for which $|l| + |m| + |n| > 2$ (for unit-lattice constant). The significant difference between the two sets is that in the first the initial and final interactions are with the same impurity and in the second with different impurities; this introduces different phase factors, and we found it necessary to sum the two types of terms separately. These contributions to the self-energy are less important than those linear in the c_{η} , due to the decrease in communication between spins as they find themselves farther apart. This is evidenced by the fact that the pure-crystal Green's function Γ_{ii}^0 , which describes the free propagation of a spin wave from site i to site l , is a sum over the first Brillouin zone of a function proportional to $e^{i\vec{k} \cdot (\vec{i} - \vec{l})}$. As $|\vec{i} - \vec{l}|$ gets larger, the oscillations in this factor cause cancellations that greatly decrease the value of the sum; this can be seen from the tabulated numerical values of Γ_{ii}^0 given in Ref. 15. These less important terms in the self-energy will not significantly affect the general discussion of this paper, and they will not be included. The analytical expressions, which reflect the properties of the type-1 cluster, may be found in Ref. 15.

Including only the dominant self-energy contributions, to order c^2 , the Green's function has the diagrammatic representation of Fig. 4. Then we may write

$$\langle G(\vec{k}) \rangle = G^0(\vec{k}) + G^0(\vec{k}) \Sigma(\vec{k}, \omega) \langle G(\vec{k}) \rangle , \tag{2.12}$$

where $\Sigma(\vec{k}, \omega)$ is the self-energy term. Solving for $\langle G(\vec{k}) \rangle$ then gives, using $G^0(\vec{k}) = (\omega - \omega_{\vec{k}})^{-1}$,

$$\langle G(\vec{k}) \rangle = \{ \omega - [\omega_{\vec{k}} + \Sigma(\vec{k}, \omega)] \}^{-1} , \tag{2.13}$$

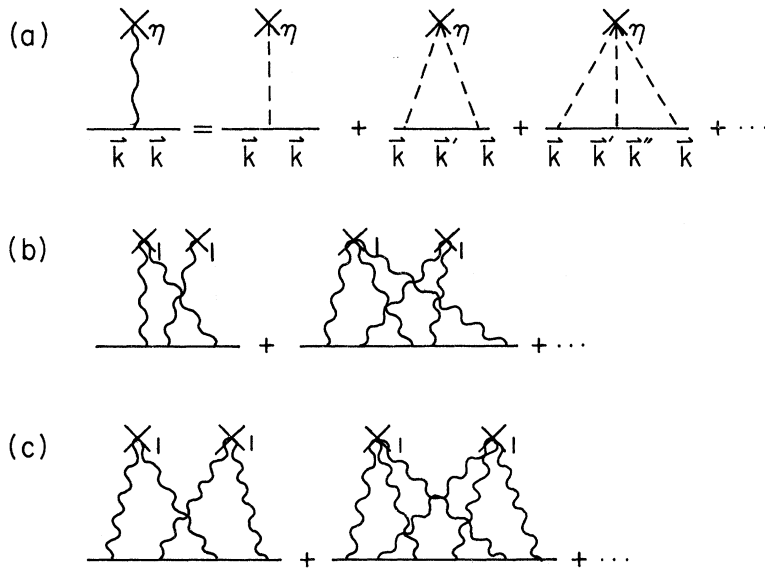


FIG. 3. (a) Diagrammatic representation of the self-energy terms linear in the concentration c_η ; (b) and (c) diagrams that describe the coherent scattering from pairs of impurities farther apart than the distinct pairs of types $\eta=2, 3, 4$.

which describes the average spin correlations in the crystal. We note that additional diagrams, similar to those called interference diagrams in the work of Jones,³ do not arise here. This is due to the fact that we have used Γ_{it} rather than G_{it} , where a factor of S_i/S has been removed. The dispersion relation is not affected by this procedure. The factor S_i/S must be reinserted when calculating such quantities as the neutron scattering cross section.

As (2.13) clearly shows, if $\Sigma(\vec{k}, \omega)$ were independent of ω it would simply represent a correction to the spin-wave energy $\omega_{\vec{k}}$. This self-energy

expression may be written in terms of functions W_η describing scattering from a single cluster of type η ,

$$\Sigma(\vec{k}, \omega) = \sum'_\eta c_\eta W_\eta(\vec{k}, \omega). \quad (2.14)$$

The $W_\eta(\vec{k}, \omega)$ are lengthy and will not be given here. They are given explicitly in Ref. 15. Each term in $W_\eta(\vec{k}, \omega)$ is of the same simple form: a product of an impurity perturbation parameter, a phase factor describing coherence in scattering, an energy denominator $D_{t\eta}^{-1}(\omega)$ associated with modes of

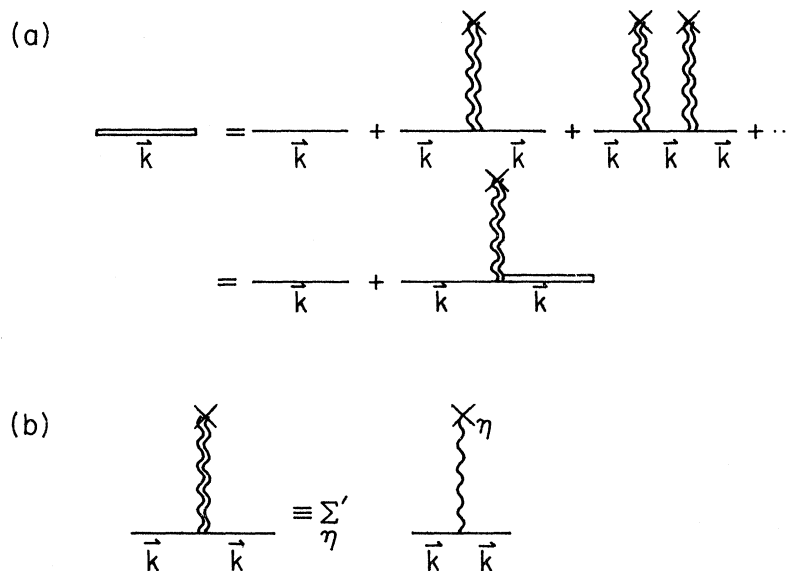


FIG. 4. (a) Diagrammatic representation of the Green's function, including only the dominant self-energy parts; (b) definition of the self-energy diagram.

symmetry t relative to clusters of the type η , and a minor of the matrix whose determinant is $D_{t\eta}(\omega)$. [We note here that, as discussed in Ref. 6, the impurity modes of symmetry t for a single cluster of type η are found at the energy zeros of the real part of $D_{t\eta}(\omega)$; the expressions for the $D_{t\eta}(\omega)$ are given in Ref. 15.] There is a term in $\Sigma(\vec{k}, \omega)$ for each impurity mode associated with each cluster type, and these contributions are proportional to the concentration of that cluster. Simplified cases are examined numerically in Sec. III. Separating the real and imaginary parts of $\Sigma(\vec{k}, \omega)$, the expression (2.13) becomes

$$\langle G(\vec{k}) \rangle = \{ \omega - [\omega_{\vec{k}} + \text{Re}\Sigma(\vec{k}, \omega)] - i \text{Im}\Sigma(\vec{k}, \omega) \}^{-1}. \quad (2.15)$$

In the pure and really translationally invariant crystal, where $\Sigma(\vec{k}, \omega)$ vanishes, this function has a simple pole at the pure-crystal spin-wave energy $\omega_{\vec{k}}$ (we recall that the normal modes of the system are at the poles of the Green's functions). In our averaged impure crystal we can obtain approximately the spin-wave energies from the real part of the denominator of (2.15), and we write the dispersion relation as

$$\omega \approx \omega_{\vec{k}} + \text{Re}\Sigma(\vec{k}, \omega). \quad (2.16)$$

Of special interest are the energy regions near the impurity-resonance energies in the host band, where $\text{Re}D_{t\eta}(\omega) = 0$. [We comment that $\text{Re}D_{t\eta}(\omega)$ may also vanish elsewhere in the band, at the anti-resonances; Wolfram and Callaway¹⁶ discuss the resonance modes for a single impurity.] The function $\text{Re}\Sigma(\vec{k}, \omega)$ changes rapidly in these regions and the imaginary part, which defines a damping due to resonance scattering by the impurities, has peaks. Section III discusses the results in more detail.

III. DISCUSSION

The configuration-averaged Green's function describing the propagation of spin waves in a cubic ferromagnetic insulator containing a finite concentration of randomly oriented magnetic impurities, including the effects of scattering from one impurity or coherently from two, has been calculated in Sec. II. The neglect of groups of three or more impurities, a c^3 effect, should be valid for concentrations up to about 3%. In this section we discuss the results in more detail, and make a simple quantitative estimate on the magnitude of the effects, comparing the impurity-pairs contribution with that of single isolated impurities. Of course, our simplified model cannot give a detailed prediction of the results of experiments on actual

crystals, but a reasonable estimate on the size of the effects can be made if the numerical values of various parameters are chosen from those expected in actual crystals. A quantitative study of our results also requires numerical evaluation of the pure-crystal Green's functions Γ_{it}^0 for various energies and various pairs of indices i, l . These universal functions of dimensionless energy ω , which are purely real outside the host-spin-wave band but have finite imaginary parts for energies within the band, have been tabulated^{16,17} for those pairs of indices i, l related to the single impurity problem. To study the pair clusters, the Γ_{it}^0 for other sets i, l are needed; we have calculated and tabulated in Ref. 15 all the necessary cases. Our method of calculation of the pure-crystal Green's functions was similar to that of Wolfram and Callaway.¹⁶

Equation (2.16) gives an approximate dispersion relation for the crystal. The total spin of the system commutes with the Hamiltonian even in the impure crystal, so we require that the spin-wave energy vanish at $\vec{k} = 0$ when the Zeeman term is absent. It is, of course, true that in this case $\omega_{\vec{k}=0} = 0$, and it is easy to show that each contribution to $\Sigma(\vec{k} = 0, \omega)$, from each of the impurity modes of each cluster type, also vanishes. As has been pointed out by Izyumov,² this correct result is obtained only if all orders of the perturbation terms V are retained in the diagram sums.

When local modes exist, the dispersion relation (2.16) describes the impurity band, correct to order c^2 if all pair effects are included. The structure of the band will include the splitting of the single impurity states due to interactions between pairs of impurities. We will not discuss the local modes in any detail here as a study of a crystal containing a single cluster, as is given in Ref. 6, should be adequate for many problems when the modes are well localized and the impurity concentration is small.

Let us consider the situation where the impurity parameters are such that impurity modes exist inside the host-spin-wave band, and examine the self-energy $\Sigma(\vec{k}, \omega)$. $\text{Re}\Sigma(\vec{k}, \omega)$ gives an energy shift (though ω dependent) from the pure-crystal energy $\omega_{\vec{k}}$ for a spin wave of wave vector \vec{k} , while $\text{Im}\Sigma(\vec{k}, \omega)$ defines the damping due to impurity scattering of the spin wave. To obtain a rough estimate of the energy shift and the damping due to the impurity pairs as compared to that due to isolated impurities, we take $\omega = \omega_{\vec{k}}$ in $\Sigma(\vec{k}, \omega)$. Then the dispersion relation becomes

$$\omega \approx \omega_{\vec{k}} + \text{Re}\Sigma(\vec{k}, \omega_{\vec{k}}) \quad (3.1)$$

and the damping term becomes $\text{Im}\Sigma(\vec{k}, \omega_{\vec{k}})$. The energy shift and the damping are most important

near the resonance mode energies, where the various energy denominators $\text{Re}D_{tn}(\omega)$ vanish, so we examine their values in these regions. We consider first the single-impurity (type-1) effects; the expression $W_1(\vec{k}, \omega_{\vec{k}})$, from which the contribution of the type-1 clusters to $\Sigma(\vec{k}, \omega_{\vec{k}})$ is obtained, is similar to that given by Izyumov,² so we will not include it here. Choosing a typical set of impurity parameters $S'/S=0.5$ and $J'/J=0.25$, and assuming no external or anisotropy fields, we have an S-type resonance associated with the type-1 cluster at $\omega \approx 0.24$. Near this energy the contribution of the type-1 impurity cluster to the energy shift $\text{Re}\Sigma$ and the damping $\text{Im}\Sigma$ is about (3-5)% of $\omega_{\vec{k}}$ for $c=0.03$. For the pairs case, since the expressions for Σ are very complicated algebraically, we choose a simplifying set of parameters. For $J'/J=1.0$, $S'/S=1.0$, and $J''/J \neq 1.0$, only a p-type mode of the type-3 pair cluster contributes to Σ . The contribution comes from the term $W_3(\vec{k}, \omega_{\vec{k}})$ which, for this special case, has the simple form

$$W_3(\vec{k}, \omega_{\vec{k}}) = (\text{Re}D_{p3} - i \text{Im}D_{p3}) \times \frac{(J''/J - 1) \frac{1}{3} [1 - \cos[\vec{k} \cdot (\vec{1} - \vec{2})]]}{(\text{Re}D_{p3})^2 + (\text{Im}D_{p3})^2}, \quad (3.2a)$$

where

$$\text{Re}D_{p3} = \frac{1}{3}(J''/J - 1)[1 - \omega_{\vec{k}} \text{Re}\Gamma_{11}^0(\omega_{\vec{k}})] + 1, \quad (3.2b)$$

$$\text{Im}D_{p3} = -\frac{1}{3}(J''/J - 1)\omega_{\vec{k}} \text{Im}\Gamma_{11}^0(\omega_{\vec{k}}). \quad (3.2c)$$

$\vec{1} - \vec{2}$ is the vector connecting the two impurities, and the expression must be summed over the three orientations, so that the cosine term becomes $1 - (1/z)\sum_{\Delta} e^{i\vec{k} \cdot \vec{\Delta}} = \omega_{\vec{k}}$. Choosing $J''/J = -1.0$, where the resonance is at $\omega \approx 0.30$, we find that $\text{Re}\Sigma$ and $\text{Im}\Sigma$ are about 1% of $\omega_{\vec{k}}$ near the resonance for $c=0.03$. Examination of these numbers for the singles and the pairs indicates that the average contribution from *each* of the $3c^2N$ type-3 pairs (three orientations, but resonance energy does not depend on orientation) is approximately equal in magnitude to the contribution from *each* of the $(c - 24c^2)N$ isolated impurities, that is, the deviation from pure-crystal behavior near a resonance essentially depends only on the concentration of the relevant cluster. The effects are found to be roughly of the same size for other sets of parameters that produce impurity modes in the same region of the band.

A function that is useful in predicting many experimental results in a system, for example the specific heat, is the spectral weight, which is essentially the smoothed distribution of excitations

as a function of energy. This function may be obtained from the imaginary part of the Green's function and is given by

$$A(\omega) = -(1/\pi) \text{Im} \sum_t G_{tt}. \quad (3.3)$$

This is equivalent to a sum over the Brillouin zone of the imaginary part of the \vec{k} -dependent Green's function. Also the scattering cross section for spin waves, which is used, for example, to study the thermal conductivity at low temperatures (where impurity resonance-mode scattering is important), as well as the cross section for inelastic neutron scattering by creation or annihilation of spin waves, are determined by the imaginary part of the spin Green's functions. Of course in these calculations the S_t/S term left out in calculating $\langle G(\vec{k}) \rangle$ (as well as other terms, in the case of neutron scattering, that derive from the neutron-crystal interaction Hamiltonian) must be inserted, so that other diagrams similar to the interference diagrams of Jones³ will be added to the results. This will not change the denominator of $\langle G(\vec{k}) \rangle$ and the behavior discussed briefly here. The imaginary part of $\langle G(\vec{k}) \rangle$ has the form

$$\text{Im} \langle G(\vec{k}) \rangle = \frac{\text{Im}\Sigma(\vec{k}, \omega)}{[\omega - \omega_{\vec{k}} - \text{Re}\Sigma(\vec{k}, \omega)]^2 + [\text{Im}\Sigma(\vec{k}, \omega)]^2}. \quad (3.4)$$

For a pure crystal, this expression is simply the δ function $\delta(\omega - \omega_{\vec{k}})$, that is, it has a peak of zero width at the host spin-wave energy $\omega_{\vec{k}}$. When impurities are present the resonance scattering broadens this peak; the width is determined by $\text{Im}\Sigma(\vec{k}, \omega)$, which has its peaks at precisely the resonance energies. As a function of energy $\text{Im}\langle G(\vec{k}) \rangle$ has, for a given wave vector \vec{k} , a peak of width $\text{Im}\Sigma(\vec{k}, \omega)$ at $\omega = \omega_{\vec{k}} + \text{Re}\Sigma(\vec{k}, \omega)$. There are additional peaks at each resonance energy, due to the peaks in $\text{Im}\Sigma(\vec{k}, \omega)$, which exhibit the concentration dependence of the respective impurity clusters. The deviation from pure-crystal behavior at a specified energy therefore depends on the various contributions to the self-energy term $\Sigma(\vec{k}, \omega)$, and will be greatest at the resonance energies (and proportional to the concentration of the relevant cluster types). To examine the spectral weight we add together the functions $\text{Im}\langle G(\vec{k}) \rangle$ for all \vec{k} in the first Brillouin zone. The result, for large N , is approximately a smooth function, with peaks at the resonance energies where the density of states has increased. Since the number of states remains constant, this requires that the density be reduced elsewhere (at the antiresonances). The size of the peaks, that is, the magnitude of the deviation from pure-crystal behavior, is propor-

tional to the probability c_n of finding the relevant impurity clusters. Experimental resolvability of the various effects, of course, requires that the resonances be sufficiently separated.

The inelastic neutron scattering cross section, including effects to c^2 , is calculated in Ref. 15. This calculation proceeds from an expression given by Van Hove,¹⁸ where the cross section is expressed in terms of the imaginary parts of two-time spin correlation functions, which may be written in terms of the Green's functions.¹² The results are very complicated algebraically, and we will include only a simple case here. For $S' = S$ and $F'_q = F_q$, where F'_q and F_q are the neutron-scattering form factors at scattering vector \vec{q} for impurity ions and host ions, respectively, the inelastic neutron differential cross section for creation of a spin wave of energy ω and wave vector $\vec{q} - \vec{G}$ (\vec{G} is a reciprocal lattice vector, keeping $\vec{q} - \vec{G}$ in the first Brillouin zone), to first order in the neutron-crystal interaction, is, at zero temperature,

$$\frac{d^2\sigma}{d\Omega d\omega} = \frac{N(r_0\eta_0)^2}{24\pi J} \frac{p'}{p} [1 + (\hat{e} \cdot \hat{z})^2] F_q^2 \text{Im}\langle G(\vec{q}, \omega) \rangle. \quad (3.5)$$

r_0 is the classical electron radius, η_0 is the magnetic moment of the neutron, \vec{p} and \vec{p}' are the initial and final momenta of the neutron ($\vec{q} = \vec{p} - \vec{p}'$), $\hat{e} = \vec{q}/q$, \hat{z} is the unit vector in the direction of spontaneous magnetic moment of the crystal, and ω is the energy change of the neutron upon scattering (we have indicated the energy dependence of the Green's function for clarity). We have assumed that the incident neutrons are unpolarized and that the slow neutrons do not create electronic orbital excitations. The cross section is just proportional to $\text{Im}\langle G(\vec{q}) \rangle$ and the neutron scattering will reflect the behavior of this function. As we have discussed in Ref. 6 with respect to scattering by local modes, the effects of pairs will be difficult to observe with present neutron technology due to the lack of resolution. Our result in Ref. 6 was essentially that the cross section for scattering by a single impurity pair was comparable to that for scattering by a single isolated impurity, so that the difference in intensity will be due only to the concentration factors; the same will be true for scattering by resonance modes when comparing impure-crystal data to pure-crystal data. It may be feasible to use neutron scattering to detect the p -type mode, discussed earlier in a special case, that involves the two impurities that are themselves nearest neighbors. This is the only mode in our theory whose energy is dependent upon the impurity-impurity exchange coupling J'' , so it may be possible to have the mode well separated from other resonance

(or local) modes. This was pointed out by Frikke⁵ in reference to the nearest-neighbor impurity pair in a face-centered-cubic ferromagnet. We note that the Eu salts mentioned earlier are not good candidates for neutron-scattering experiments, due to the high absorption in these materials.

In conclusion we comment that it would be algebraically prohibitive to attempt to carry out this theory to higher orders in the concentration. The next step involves impurity triples, for which there are many possible distinct arrangements, each of which has a large perturbation matrix and many possible impurity modes. Impurity banding becomes important, and a new model is needed to discuss experiments on the substitutionally disordered systems such as those examined in the neutron-scattering experiments of Buyers *et al.*,¹⁹ where the "impurity" concentration is in the range of 20–30%.

ACKNOWLEDGMENTS

The author wishes to thank Dr. Daniel Hone, who suggested the problem, for his valuable assistance, and Dr. Douglas Scalapino for several helpful discussions. Grants of computer time from the UCSB Computer Center and the FSU Computer Center are gratefully acknowledged.

APPENDIX

The perturbation matrix $V^{(n)}$ is determined from the equation of motion for the energy-dependent Green's function $G_{ii}^{(n)}$ characteristic of a crystal containing a single type- η impurity cluster. The site numbering is as shown in Fig. 1, and the symbols are defined $\epsilon = J'/J - 1$, $\rho = (J'/J)(S'/S) - 1$, $\rho' = (J''/J)(S'/S) - 1$, $\sigma = 6(\nu + \epsilon) + (\rho' - \epsilon)$, and $\nu = \mu_B \times (H'g' - Hg)/2zJS$. For the type-1 cluster, that of the single isolated impurity, where seven ions are involved,

$$V^{(1)} = \frac{1}{6} \begin{pmatrix} 6(\nu + \epsilon) & -\rho & -\rho & -\rho & -\rho & -\rho & -\rho \\ -\epsilon & \rho & 0 & 0 & 0 & 0 & 0 \\ -\epsilon & 0 & \rho & 0 & 0 & 0 & 0 \\ -\epsilon & 0 & 0 & \rho & 0 & 0 & 0 \\ -\epsilon & 0 & 0 & 0 & \rho & 0 & 0 \\ -\epsilon & 0 & 0 & 0 & 0 & \rho & 0 \\ -\epsilon & 0 & 0 & 0 & 0 & 0 & \rho \end{pmatrix}. \quad (A1)$$

This expression was given by Hone.²⁰ The type-2 cluster, where the two impurities share one common nearest neighbor located on the interimpurity axis, has 13 ions:

†Supported in part by the National Science Foundation (U. C. Santa Barbara) and in part by the Air Force Office of Scientific Research under Grant No. AFOSR-70-1940.

¹I. M. Lifshitz, *Usp. Fiz. Nauk* **83**, 617 (1964) [*Sov. Phys. Usp.* **7**, 549 (1965)].

²Yu. Izyumov, *Proc. Phys. Soc. (London)* **87**, 505 (1966).

³R. C. Jones, *J. Phys. C* **4**, 2903 (1971).

⁴G. A. Murray, *Proc. Phys. Soc. (London)* **89**, 87 (1966).

⁵E. Frikkee, *J. Phys. C* **2**, 345 (1969).

⁶E. Shiles and D. Hone, *Phys. Rev.* **5**, 1915 (1972).

⁷R. M. White and C. M. Hogan, *Phys. Rev.* **167**, 480 (1968).

⁸N. Kroð and L. Bata, *Phys. Letters* **24A**, 22 (1967).

⁹N. Kroð and L. Pål, *J. Appl. Phys.* **39**, 453 (1968).

¹⁰W. J. DeBonte and H. Callen, *Phys. Rev.* **188**, 831 (1969).

¹¹S. F. Edwards, *Phil. Mag.* **3**, 1020 (1958).

¹²D. N. Zubarev, *Usp. Fiz. Nauk* **71**, 71 (1959) [*Sov. Phys. Usp.* **3**, 320 (1960)].

¹³W. Kohn and J. M. Luttinger, *Phys. Rev.* **108**, 590 (1957).

¹⁴T. Yonezawa, *Progr. Theoret. Phys. (Kyoto)* **31**, 357 (1964).

¹⁵E. Shiles, thesis (University of California, Santa Barbara, 1970) (unpublished).

¹⁶T. Wolfram and J. Callaway, *Phys. Rev.* **130**, 2207 (1963).

¹⁷D. Hone, H. Callen, and L. R. Walker, *Phys. Rev.* **144**, 283 (1966).

¹⁸L. Van Hove, *Phys. Rev.* **95**, 1374 (1954).

¹⁹W. J. L. Buyers, T. M. Holden, E. C. Svensson, R. A. Cowley, and R. W. H. Stevenson, *Phys. Rev. Letters* **27**, 1442 (1971).

²⁰D. Hone, in *Localized Excitations in Solids*, edited by R. F. Wallis (Plenum, New York, 1968), p. 335.

Phase Transition in a Sixteen-Vertex Lattice Model*

F. Y. Wu

Department of Physics, Northeastern University, Boston, Massachusetts 02115

(Received 31 January 1972)

We consider a sixteen-vertex ferroelectric model defined on a square lattice and deduce the nature of the phase transition in this model from its equivalence with an Ising model with a non-zero magnetic field. We find that, as the value of a parameter which occurs linearly in the Hamiltonian is varied, the model may exhibit a first-order transition, a second-order transition with an infinite specific heat, or no phase transition.

INTRODUCTION

There has been considerable recent interest in the eight-vertex lattice model which is a generalization of the Ising and ice-rule ferroelectric models of phase transitions.¹ In view of the unexpected behavior of a variable exponent found to exist in the eight-vertex model,² it seems appropriate to investigate a further generalization of these models, the sixteen-vertex model. The sixteen-vertex model can be defined on any lattice of coordination number 4, and encompasses, among others, the eight-vertex model and the Ising model in a nonzero magnetic field as special cases.¹ Very little is known about the behavior of this general lattice model, except in a few special cases in which the model can be shown to be directly equivalent to an Ising model, hence exhibiting the usual Ising-type transition.³ Any result which leads to different types of phase transition would be very useful and illuminating.

In this paper some new findings are reported in this connection. A certain class of the sixteen-vertex model is considered and the behavior of this model at the transition point is deduced. It

is found that, as the value of a parameter which occurs linearly in the Hamiltonian is varied, the model may exhibit a first-order transition, a second-order transition with an infinite specific heat, or no phase transition. It is of interest to note that a first-order transition results and persists in a region in the parameter space. In the potassium-dihydrogen-phosphate (KDP) model of a ferroelectric which also exhibits a first-order transition,⁴ the transition becomes a second-order one when an infinitesimal electric field is present.¹

DEFINITION OF THE MODEL

We first define the sixteen-vertex problem. Consider a lattice of coordination number 4, which has N vertices. Each of the $2N$ lattice edges (assuming periodic boundary conditions) may or may not be covered by a bond. A definite bond covering of the lattice will be called a state so that there are 2^{2N} distinct states. A fixed energy is assigned to each of the $2^4 = 16$ bond configurations that may occur at a vertex, and the energy E of a state is taken to be the sum of all vertex energies. The partition function of the sixteen-ver-