

Density of States of an Insulating Ferromagnetic Alloy*

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An algorithm is developed for the calculation of the density of states for an arbitrary ferromagnetic insulating alloy. The procedure is based upon enumerating the number of negative eigenvalues associated with a large matrix. While the theory is developed to treat any number of magnetic components in an arbitrary lattice, numerical results are presented for a binary alloy of the simple cubic type. The spectra are related to previously calculated isolated local magnetic excitations, and the effect of such spectra on the magnetization and specific heat is indicated.

I. INTRODUCTION

THE energy spectra of ferro- and antiferromagnetic insulating alloys have been investigated primarily in the limit in which the minor constituents are quite small in concentration. Experimenters have thus examined the energy levels induced by dilute doping of a magnetic host using neutron spectroscopy,¹ optical fluorescence,² magnetic sidebands of electronic transition spectra,^{3,4} and infrared Raman spectroscopy.^{5,6} Theoretically, several authors⁷⁻¹⁰ have calculated the excitation energies and resulting thermodynamic properties for the case of an isolated magnetic impurity; more recently^{11,12} the interaction between two magnetic impurities has been treated and indicates significant coupling even at a range of several lattice spacings. In one dimension a calculation for arbitrary alloy ratio has been carried out using a diagrammatic Green's-function method to calculate the moments of the energy spectrum.¹³ This is a most elegant formalism, although the convergence of individual moments is not established, and the ability to reconstruct typical spectra from even as many as ten moments is in serious question.¹⁴

On the other hand, *vibrational* energy spectra of two-dimensional alloys have been calculated using a matrix formalism.¹⁴ These results show that the spectrum of an alloy can change radically with the alloying ratio. Specifically, it was shown that the energy spectrum of an alloy can be related to the component spectra of the two pure crystals, but superposition is not applicable. The latter is to be expected for both vibrational and magnetic spectra, since the interaction between two impurities is a nonlinear function of concentration.^{15,16}

The present study gives a method for calculation of magnetic energy spectra of arbitrary alloys in three dimensions using the microscopic spin and exchange values. Section II explicates the matrix technique used in calculation, and Sec. III presents the Hamiltonian matrix for the case of a ferromagnet. Section IV reports numerical results for a binary alloy in a simple cubic lattice.

II. MATRIX EVALUATION OF ENERGY SPECTRUM

The treatment is essentially that used in the calculation of vibrational spectra¹⁴; in particular, one considers the eigenvalue spectrum of an arbitrary symmetric matrix $H^{(1)}$:

$$H^{(1)}|\Psi\rangle = E|\Psi\rangle. \quad (1)$$

An equivalent problem is to seek the number of negative eigenvalues n of the matrix $H^{(1)} - E$ for arbitrary E , since n represents the number of eigenvalues of $H^{(1)}$ less than the value E . Taking successive differences in n for incremental E 's reconstructs the spectrum of $H^{(1)}$ to arbitrary accuracy.

One now pursues this alternative problem and relies upon a theorem for calculating n . It can be shown¹⁴ that the number of negative eigenvalues of $H^{(1)} - E$ is

$$n(H^{(1)} - E) = n(X^{(1)}) + n(H^{(2)} - E), \quad (2)$$

where formally

$$H^{(1)} - E = \begin{bmatrix} X^{(1)} & Y^{(1)} \\ Y^{T(1)} & Z^{(1)} \end{bmatrix}. \quad (3)$$

¹⁵ E. W. Montroll and R. B. Potts, Phys. Rev. **102**, 72 (1956).

¹⁶ C. M. Hogan, Ph.D. thesis, Stanford University, Stanford, Calif., 1969 (unpublished).

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¹ W. J. L. Buyers, R. A. Cowley, P. M. Holden, and R. W. H. Stevenson, J. Appl. Phys. **39**, 1118 (1968).

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⁵ A. Oseroff and P. S. Pershan, Phys. Rev. Letters **21**, 1593 (1968).

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⁷ T. Wolfram and J. Callaway, Phys. Rev. **130**, 2207 (1963).

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¹⁰ D. Hone, H. Callen, and L. R. Walker, Phys. Rev. **144**, 283 (1966).

¹¹ R. M. White and C. M. Hogan, Phys. Rev. **167**, 480 (1968).

¹² R. M. White and C. M. Hogan, *Localized Excitations in Solids* (Plenum Press, Inc., New York, 1968), p. 350.

¹³ H. Hartman, *Localized Excitations in Solids* (Plenum Press, Inc., New York, 1968), p. 619.

¹⁴ P. Dean and M. D. Bacon, Proc. Roy. Soc. (London) **A283**, 64 (1965).

Here $X^{(1)}$ is a 1×1 submatrix, and

$$H^{(2)} - E = Z^{(1)} - Y^{T(1)} Y^{(1)} / X^{(1)}. \quad (4)$$

Obviously, $X^{(1)}$ is its own eigenvalue, so that $n(X^{(1)})$ is either plus or minus unity depending upon the sign of $X^{(1)}$. Iteration of Eq. (2) reduces the calculation to the examination of the signs of consecutive scalars $X^{(i)}$; in fact,

$$n(H^{(1)} - E) = \sum_{i=1}^M n(X^{(i)}), \quad (5)$$

where

$$H^{(i+1)} - E_i = Z^{(i)} - Y^{T(i)} Y^{(i)} / X^{(i)}, \quad i = 1, 2, \dots, N-1 \quad (6)$$

and N is the order of the matrix $H^{(1)}$. Equations (5) and (6) follow from iteration of (2)–(4). The above procedure is formally equivalent to Gaussian elimination, which is a common technique in numerical analysis.

III. ADAPTATION TO FERROMAGNETIC ALLOY

In this section one establishes the Hamiltonian for an arbitrary ferromagnetic alloy in three dimensions, so that the technique of Sec. II can be applied.

The magnetic Hamiltonian will be taken as the nearest-neighbor Heisenberg interaction and Zeeman term:

$$H = - \sum_{j,\Delta} J(j, j+\Delta) \mathbf{S}(j) \cdot \mathbf{S}(j+\Delta) - h_z g \beta \sum_j S_z(j), \quad (7)$$

where j sums all of the atoms in the lattice and Δ sums the nearest neighbors. S and J are the usual spin and exchange constants, while h_z is the magnetic field taken in the z direction, g is the spectroscopic splitting factor, and β is the Bohr magneton. Using a basis formed by the

N orthogonal single-spin deviation states $S^-(j)|0\rangle$, one finds

$$\begin{aligned} \langle i | H | k \rangle = & \delta_{ik} [E_0 + 2 \sum_{\Delta} J(i, i+\Delta) S(i+\Delta)] \\ & - 2 \sum_{\Delta} \delta_{i, k+\Delta} J(k, k+\Delta) [S(i) S(k)]^{1/2}, \quad (8) \end{aligned}$$

where the constant diagonal term

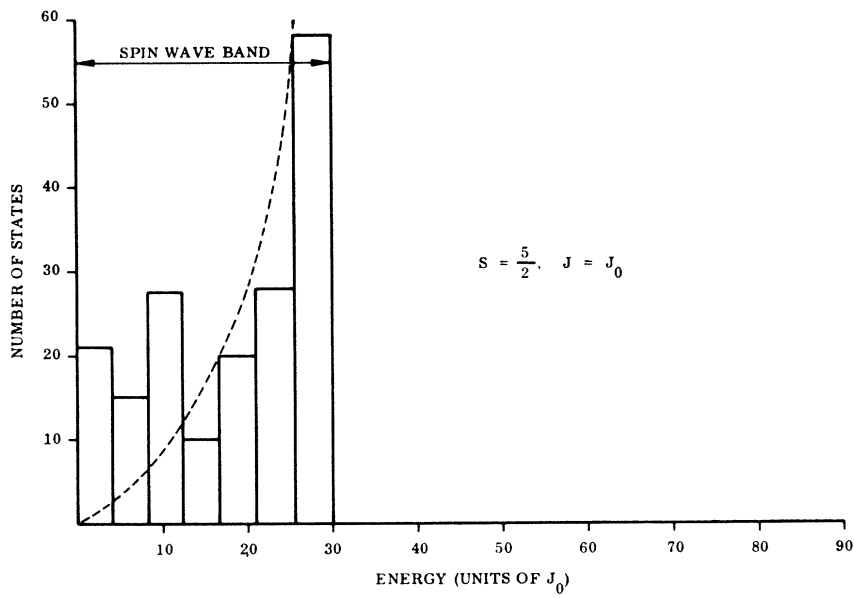
$$E_0 = - \sum_{j,\Delta} J(j, j+\Delta) S(j) S(j+\Delta) - h_z g \beta \times \sum_j S(j) + h_z g \beta. \quad (9)$$

Because of the short-range nature of the exchange interaction, most of the off-diagonal terms of H will vanish under the representation chosen. It is, in fact, crucial to the subsequent numerical calculations to know the locations of the zeros of H ; to this end the structure of H is elaborated. This entire procedure is tractable only when the crystal atoms are labeled in a judicious manner. Assume that the crystal is divided into nonoverlapping groups of atoms such that appropriate subgroups form nonintersecting lines and larger subgroups form nonintersecting planes. In essence, a superlattice of the simple cubic form is being simulated. The technique, however, is not restricted to simple cubic lattices, although in that case one finds the fundamental groups to be single atoms. It will be assumed in the following that the groups have been chosen such that magnetic interactions extend only to neighboring groups. This is not an inherent limitation, and excursions from this course would merely result in a few more off-diagonal terms in the following matrix forms. Naturally, total absence of a spatial cutoff for interactions would invalidate the utility of the entire analysis. The crystal is taken to have M planes, each having Q lines of K groups. Now one can write

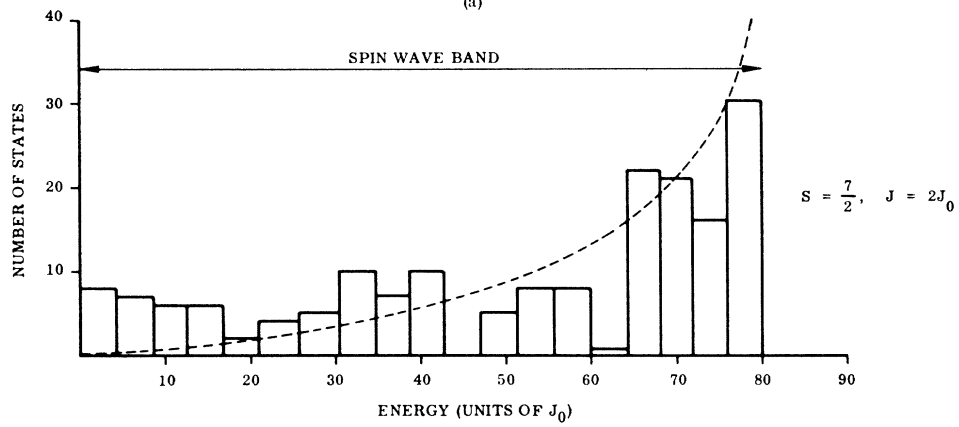
$$\langle i | H | k \rangle = \begin{pmatrix} P_{11} & P_{12} & 0 & \cdot & \cdot & \cdot & \cdot & 0 \\ P_{21} & P_{22} & P_{23} & 0 & \cdot & \cdot & \cdot & 0 \\ 0 & P_{32} & P_{33} & & & & & \cdot \\ \cdot & 0 & & \cdot & & & & \cdot \\ \cdot & \cdot & & & & & & 0 \\ \cdot & \cdot & & & & P_{M-1, M-1} & P_{M-1, M} & \\ 0 & 0 & \cdot & \cdot & \cdot & P_{M, M-1} & P_{MM} & \end{pmatrix}, \quad (10)$$

where diagonal elements P_{mm} represent all the interactions within the m th plane of the crystal. Furthermore, the super- and subdiagonals $P_{mm'}$ represent all the interactions between planes m and m' . The matrices P_{mm} can be written, in turn,

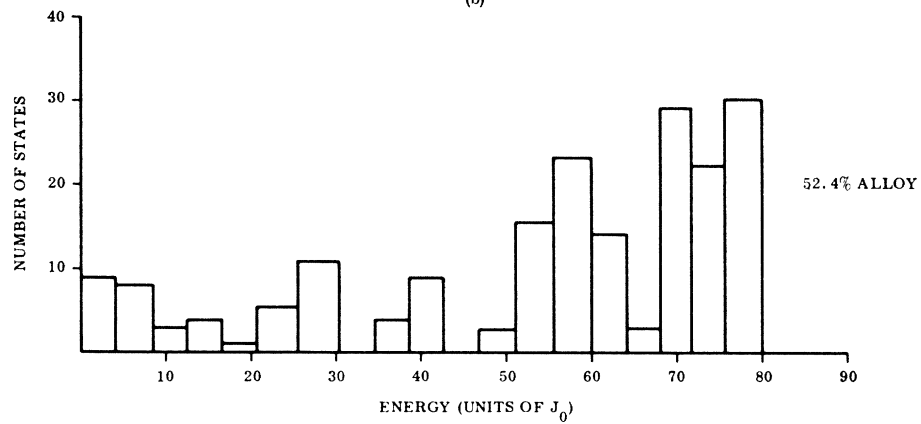
$$P_{mm} = \begin{pmatrix} L_{11}^m & L_{12}^m & 0 & \cdot & \cdot & \cdot & \cdot & 0 \\ L_{21}^m & L_{22}^m & L_{23}^m & 0 & \cdot & \cdot & \cdot & 0 \\ 0 & L_{32}^m & L_{33}^m & & & & & \cdot \\ \cdot & 0 & & \cdot & & & & \cdot \\ \cdot & \cdot & & & & & & \cdot \\ \cdot & \cdot & & & & & & 0 \\ 0 & 0 & \cdot & \cdot & \cdot & 0 & L_{Q-1, Q-1}^m & L_{Q-1, Q}^m \\ & & & & & & L_{Q, Q-1}^m & L_{QQ}^m \end{pmatrix}. \quad (11)$$



(a)



(b)



(c)

FIG. 1. Density of states for two pure ferromagnets and a 52.4% alloy.

The diagonal elements L_{qq}^m include all interactions within the q th line of the m th plane. The super- and subdiagonal $L_{qq'}^m$ represent interactions between lines q and q' of plane m . The L matrices and off-diagonal P matrices will be given for a special case in Sec. IV.

IV. SIMPLE CUBIC LATTICE

For the sake of arriving at definite spectra, assume that the planes and lines of Sec. III are formed merely from atoms which comprise a simple cubic magnetic

$$L_{qq}^m = \begin{pmatrix} L_{qq}^m(1,1) & L_{qq}^m(1,2) & 0 & \cdots & 0 \\ L_{qq}^m(2,1) & L_{qq}^m(2,2) & L_{qq}^m(2,3) & 0 & \cdots & 0 \\ 0 & L_{qq}^m(3,2) & L_{qq}^m(3,3) & \cdot & \cdot & \cdot \\ \cdot & 0 & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ 0 & 0 & \cdots & 0 & L_{qq}^m(K-1, K-1) & L_{qq}^m(K-1, K) \\ & & & & L_{qq}^m(K, K-1) & L_{qq}^m(K, K) \end{pmatrix}, \quad (13)$$

where the diagonals

$$L_{qq}^m(k, k) = E_0 + \sum_{\Delta} J(\mathbf{m}, \mathbf{q}, \mathbf{k}; \mathbf{m}, \mathbf{q}, \mathbf{k} + \Delta) S(\mathbf{m}, \mathbf{q}, \mathbf{k} + \Delta). \quad (14)$$

The symbolic notation $\mathbf{m}, \mathbf{q}, \mathbf{k}$ has been used to emphasize that Δ is added vectorially. Next the off-diagonals

$$L_{qq}^m(k, k') = -2[\delta(k - k' - 1) + \delta(k' - k - 1)] \times J(\mathbf{m}, \mathbf{q}, k; \mathbf{m}, \mathbf{q}, k') [S(\mathbf{m}, \mathbf{q}, k) S(\mathbf{m}, \mathbf{q}, k')]^{1/2}. \quad (15)$$

Finally, the interactions between lines $q = q'$ of the m th plane are given by

$$L_{qq}^m(k, k') = -2[\delta(q - q' - 1) + \delta(q' - q - 1)] \times \delta_{kk'} [J(\mathbf{m}, \mathbf{q}, k; \mathbf{m}, \mathbf{q}', k) S(\mathbf{m}, \mathbf{q}', k)]^{1/2}. \quad (16)$$

Equations (10)–(16) now comprise an explicit designation for $\langle i | H | k \rangle$. In order to find the spectrum of H , one merely sets $H^{(1)} = H$ and uses the algorithm outlined above.

Computer programs were developed to carry out this task for small crystals of binary alloys. A random lattice filing technique was employed to fill each site with atom type A with probability Y_A , where Y_A is *a priori* a fraction of A in the crystal; therefore, no artifacts due to periodicity or chemical order are present in the results.

Resultant energy spectra for a simple cubic lattice of 180 atoms are represented by histograms in Fig. 1, the crystal dimensions being $9 \times 5 \times 4$. Figures 1(a) and 1(b) are spectra of pure crystals, and the dashed lines illustrate the density of states for a lattice of infinite extent. Departure from the dashed lines shows the greater number of surface and edge modes that arise in a crystal of only 180 atoms; indeed, 84 of the atoms reside on the surface. Previous investigators have cal-

culated¹⁷ the surface spin-wave energies of a ferromagnet and have demonstrated those energies to be systematically lower than the bulk modes. As is seen in Figs. 1(a) and 1(b), there are additional modes appearing at lower energies and compensatingly fewer modes near the band maximum. Figure 1(c) shows the spectrum of an alloy of composition 52.4% of $S = \frac{7}{2}$ and 47.6% of $S = \frac{5}{2}$, the exchange constant between two different spins being taken as $\frac{3}{2}J_0$. It is clear that alloying produces marked changes in the spectrum, and the results cannot be explained by mere superposition of the pure component spectra.

V. CONCLUSIONS

Although a workable method for computing the energy spectra of arbitrary magnetic insulating alloys has been developed, the length of computing time, even using high-speed digital computers, limits application to rather small crystals. Therefore, the role of surface modes is prominent and bulk properties may be obscured. Obviously, the present technique is highly desirable if one wishes to study the behavior of surface modes themselves, since a crystal in which every atom is on the surface can be examined; in fact, a two-dimensional system can be studied using the identical algorithms.

It should be emphasized that all of the above procedures can be extended to arbitrary crystal structures and an arbitrary number of components in a straightforward fashion. One should also remark that the reason for choosing a rather elongated sample was to minimize computing time for a fixed number of atoms.

As mentioned above, the spectra of the pure hosts resemble the infinite crystal result except for an excess

¹⁷ J. R. Eshbach and R. W. Damon, Phys. Rev. **118**, 1208 (1960).

of lower-energy modes caused by the advent of surface states. The alloy spectrum [Fig. 1(c)] shows interesting peaks near $60J_0$, which is the range in which local s modes are predicted to arise when an $S=\frac{7}{2}$ impurity is placed in $S=\frac{5}{2}$ host (with a doubling of J). In fact, the exact prediction for an isolated impurity⁷ is $57J_0$.

The specific heat and magnetization can be calculated readily using the prescriptions given by previous authors.^{9,10} Dramatic specific-heat changes, for example, would not be expected¹⁶ in the alloy treated numerically above, since $\epsilon(=J'/J-1)$ had the value $\frac{1}{2}$ or -1 ; the low-lying resonance modes which enhance the specific

heat greatly are present for $0 < |\epsilon| < 0.2$, the latter inequality being approximate. Combining the condition for low-lying resonances with the ability to calculate detailed magnetic spectra of alloys allows one to design materials with substantially altered specific heats and theoretically predict that property.

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Localized Correlations in Narrow Conduction Bands. I

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We have studied the effects of an exchange-enhanced substitutional impurity on a host metal by double-time Green's functions. We have used a simplification of the Wolff model to describe this system, i.e., a one-band model in which Coulomb interactions in the host lattice are neglected, and the impurity is represented by $Un_\sigma n_\sigma + V(n_\sigma + n_\sigma)$, where n_σ is the electron occupation number for spin σ at the impurity site. A decoupling scheme is used in which operators on the exchange-enhanced site are never separated from each other in the process of decoupling. This leads to a singular integral equation for the localized Green's function of the exchange-enhanced site, in terms of which all the one-electron properties of the system are expressible. The integral equation, assuming essentially a Lorentzian density of states for the host lattice, is exactly solvable in the U -infinite, V -finite limit, as well as for the special case of electron-hole symmetry, $U+2V=0$. Numerical results for the U -infinite, V -zero limit for zero temperature are obtained for n_0 , the number of electrons on the impurity site, and for the one-electron t matrix as a function of energy. n_0 has a value of 0.4, which may be compared with the values $n_0=0$ predicted by the Hartree-Fock theory and $n_0=\frac{2}{3}$ obtained by using a determinantal wave function from which the doubly occupied state is projected out. The t matrix is found to exhibit a characteristic Kondo-like resonance at zero energy, and indicates a resistivity which falls rapidly with increasing temperature, as well as a specific-heat anomaly.

I. INTRODUCTION

THE purpose of this paper is to establish the basis for a new approach to the problem of a magnetic impurity in a narrow energy band.

Until a few years ago, it was generally believed that the localized Coulomb interaction associated with magnetic impurities in metals and heavily doped semiconductors could be understood within the context of Hartree-Fock theory.^{1,2} The inadequacy of this point of view became clear with the now famous work of Kondo³ on the logarithmic divergence in the host conduction-electron t matrix. In the model studied

by Kondo, the s - d Hamiltonian, strong localized correlations enter indirectly through the assumption that a local spin exists in the electron gas. In order to study the strong Coulomb interactions present on certain impurities a model which explicitly exhibits these interactions is obviously needed. The extraorbital model of a magnetic impurity due to Anderson meets this requirement, and considerable effort has been expended⁴ during the past few years in studying correlations in this system. It appears clear that for certain situations, namely, for transition-metal impurities in transition metals and particularly for heavily doped semiconductors,⁵ a one-band model such as was studied within

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