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Point-Group Symmetry and the Impurity Problem

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It is shown that in a pure crystal the density of states of a given point-group symmetry (that is, belonging to a given row of a given irreducible representation of the point group) is simply $(d_\Gamma/p)g^0(E)$, where $g^0(E)$ is the familiar over-all density of states, d_Γ is the dimensionality of the representation, and p is the order of the group. Point-group symmetry is incorporated into Green's-function theory to define Green's functions which propagate excitations of particular symmetries from shell to shell (rather than from site to site). Both simple crystal Green's functions and two-time thermodynamic Green's functions are considered, and the ferromagnetic-impurity problem is formulated in terms of such Green's functions (at $T=0$ and at arbitrary temperatures, respectively). The analysis is illustrated explicitly for a fcc ferromagnet with first- and second-nearest-neighbor exchange.

I. INTRODUCTION

The theory of the localized-impurity problem (in Heisenberg ferromagnets, in electronic semiconductors, in phonon systems, etc.) has been investigated extensively,[1-5] but the lack of appropriate tabulated Green's functions has hindered applications. In a companion paper by Swendsen and Callen,[6] extensive tabulations have been given for fcc next-nearest-neighbor ferromagnets, permitting calculations for real systems (such as the europium chalcogenides). As such real calculations become practical it seems useful now to present certain additional observations which simplify and facilitate the theory of the general impurity problem.[7]

The rationale of the work lies in the observation that translational symmetry generally is emphasized over point-group symmetry in pure crystalline systems, primarily because the translational group is both large and simple in structure (Abelian). Introduction of an impurity destroys the translational symmetry, but (at least for many structures) it does not alter the point-group symmetry. Hence it is advantageous to recast the theory into a form which fully exploits the point-group symmetry. Appropriately defined Green's functions propagate excitations of given symmetry from shell to shell (rather than from site to site). The impurity problem is automatically factored and the matrix elements are greatly simplified.

In the investigation of the pure crystal we find a curious and interesting theorem on the partial densities of states. That is, the density in energy of states of any given symmetry (i.e., belonging to a given row of a given irreducible representation) is simply proportional to the over-all density of states. More specifically, let $g^0(E)$ be the conventional density of states in the pure crystal, and let $g^0_{\Gamma m}(E)$ be the density of states of those states which belong to the mth row of the irreducible representation Γ of the crystal point group. Let d_Γ be the dimensionality of the representation Γ, and let p be the order of the point group. Then we shall show that

$$g^0_{\Gamma m}(E)=(d_\Gamma/p)\,g^0(E)\,. \qquad (1)$$

Furthermore, we shall see that introduction of an impurity with short-range interactions perturbs only certain of these states, others remaining totally unaffected. Again, this is in contrast with Bloch states, all of which are perturbed by any impurity.

As we subsequently discovered, symmetry-classified Green's functions had been introduced first by Lehman and De Wames,[8] and later by Gautier and Lenglart.[9] Lehman and De Wames[8] analyzed the vibrational spectrum of an impurity in the aluminum or germanium lattices, in a nearest-neighbor approximation. They adapted their Green's functions to the "molecular-vibration symmetry coordinates" of the impurity and its first-shell neighbors, which are precisely the projections of our point-group eigenfunctions. The work of Gautier and Lenglart[9] was on the electron tight-binding approximation. Their work contains the additional complexity that the localized Wannier states of an electron may have different internal symmetries (s states, p states, etc.), whereas our emphasis on the ferromagnetic impurity problem is based on localized-spin deviations which have only s-like internal symmetry. On the other hand, the complexity of spin commutation relations requires consideration of two-time thermodynamic Green's functions in some decoupling approximation, such as the random-phase approximation (RPA). The theorem on the density of states of particular symmetries is not contained in previous work, at least to our knowledge. In presenting the work now we retain the full discussion of zero-temperature symmetry-based Green's functions for completeness and clarity, fully acknowledging the priority of Lehman and De Wames[8] and of Gautier and Lenglart.[9]

II. DENSITY OF STATES OF GIVEN SYMMETRY IN A PURE CRYSTAL

For simplicity of discussion consider a single band of excitations, such as spin waves, phonons, or s-band electrons. Assume that the space group $\mathcal{S}$ of the crystal is symmorphic—a direct product of a translational group $\mathcal{T}$ and a point group $\mathcal{P}$. The familiar eigenstates are of Bloch form, corresponding to irreducible representations of the translational group $\mathcal{T}$; these states are labeled by a wave vector $\vec{k}$ which takes values within the first Brillouin zone.

Consider a particular wave vector $\vec{k}$. The star of $\vec{k}$, denoted by k^*, consists of all the wave vectors into which $\vec{k}$ is carried by the operations of the point group $\mathcal{P}$. All the corresponding Bloch states are degenerate.

For general $\vec{k}$ there are p vectors in the star (recall that p is the order of the point group $\mathcal{P}$). However, there are particular values of $\vec{k}$ which lie on symmetry planes or symmetry axes and which therefore generate smaller stars; these values of $\vec{k}$ are of measure zero in reciprocal space. We focus on the preponderant majority of p-fold stars. The p Bloch eigenfunctions associated with such a general star are basis functions for a p-dimensional irreducible representation of the space group $\mathcal{S}$. Fully analogous to the Bloch functions which reduce the subgroup $\mathcal{T}$, there are particular linear combinations of the Bloch functions which reduce $\mathcal{P}$ (but not $\mathcal{T}$). That is, particular linear combinations of the Bloch functions of a general star form basis functions of the irreducible representations of the point group $\mathcal{P}$. Denote these linear combinations of Bloch states by $|\Gamma m\lambda, k^*\rangle$. Here k^* designates the particular star, Γ denotes a particular irreducible representation of $\mathcal{P}$ (of dimensionality d_Γ), m denotes a row of Γ, and finally the additional index λ is required because there generally is more than one linear combination of the Bloch states in the star k^* which transforms according to the mth row of Γ. In fact, we shall demonstrate that λ can take the values $1, 2, \ldots, d_\Gamma$.

Consider now the density in energy of states belonging to the mth row of Γ. This density is denoted, in the pure crystal, by $g^0_{\Gamma m}(E)$. That is, $g^0_{\Gamma m}(E)\,dE$ is the number of states $|\Gamma m\lambda, k^*\rangle$ with given Γ and m and with energy E in the range dE. Then the conventional over-all density-of-states function $g^0(E)$ is

$$g^0(E)=\sum_\Gamma \sum_{m=1}^{d_\Gamma} g^0_{\Gamma m}(E)\,. \tag{2}$$

Now to prove the theorem enunciated in Eq. (1), we first observe that because special stars have zero measure we need only consider the contributions to the density of states arising from general (p-fold) stars. As is well known,[10] the Bloch functions in such a star are basis functions for the "regular representation" of the group $\mathcal{P}$; the regular representation can be defined as that representation generated by the operations of the group, considered themselves as "basis functions." Since the Bloch functions of the star are in one-to-one correspondence with the operations of the group (by definition of the star), it follows that the Bloch functions also generate the regular representation. Now the regular representation contains each irreducible representation a number of times equal to the dimensionality of the irreducible representation.[10] That is, reducing the star k^* we obtain states $|\Gamma m\lambda, k^*\rangle$ with d_Γ different values of λ for each given value of Γ and m. Since each star k^* therefore contributes d_Γ states to $g^0_{\Gamma m}(E)$, Eq. (1) follows immediately [the scale factor $1/p$ being determined by Eq. (2)].

An analytic formulation of the proof can be constructed by recalling that the density of states $g^0(E)$ is given by

$$g^0(E)=-(1/\pi)\,\mathrm{Im}\,\mathrm{Tr}\,(E^+-\mathcal{H}_0)^{-1}\,, \tag{3}$$

where $(E^+-H_0)^{-1}$ is the Green's operator of the pure crystal; E^+ denotes $E+i\delta$, and the limit $\delta\to 0$ is implicit. In a completely analogous fashion the partial density of states $g^0_{\Gamma m}(E)$ is given by

$$g^0_{\Gamma m}(E)=-(1/\pi)\,\mathrm{Im}\,\mathrm{Tr}\,P_{\Gamma m}\,(E^+-H_0)^{-1}\,P_{\Gamma m}\,, \tag{4}$$

where $P_{\Gamma m}$ is the operator which projects out of any state that part which is of symmetry Γ, m. Since the factors can be cyclically permuted in the trace, and since $P^2_{\Gamma m}=P_{\Gamma m}$, we can omit one projection operator in Eq. (4). Then taking the trace in $|k\rangle$ representation,

$$g^0_{\Gamma m}(E)=-\frac{1}{\pi}\,\mathrm{Im}\sum_{\vec{k}}\frac{\langle\vec{k}|P_{\Gamma m}|\vec{k}\rangle}{E^+-\epsilon(\vec{k})}\,. \tag{5}$$

Consider $\langle\vec{k}|P_{\Gamma m}|\vec{k}\rangle$. We insert the projection operator $P_{\Gamma m}$ as a sum over all operations $\mathcal{R}$ of the group

$$\langle\vec{k}|P_{\Gamma m}|\vec{k}\rangle=\frac{d_\Gamma}{p}\sum_{\mathcal{R}}\Gamma^*_{mm}(\mathcal{R})\langle\vec{k}|\mathcal{R}|\vec{k}\rangle=\frac{d_\Gamma}{p}\,. \tag{6}$$

Here the last equality follows because $\langle\vec{k}|\mathcal{R}|\vec{k}\rangle$

clearly vanishes for all $\mathcal{R}$ except the identity operator, for which it is unity. Inserting Eq. (6) into (5), and invoking Eq. (3), we again obtain the resultant theorem of Eq. (1).

III. SYMMETRY STATES IN REAL SPACE; SHELL-SYMMETRY GREEN'S FUNCTIONS

The symmetry states $|\Gamma m\lambda, k^*\rangle$ have useful analogs in real space. To define these states recall that the Bloch states $|\vec{k}\rangle$ are conjugate to a set of localized states $|\vec{R}\rangle$:

$$|\vec{R}\rangle = N^{-1/2}\sum_{\vec{k}} e^{-i\vec{k}\cdot\vec{R}}\,|\vec{k}\rangle\,. \tag{7}$$

For the electron case $|\vec{R}\rangle$ is a Wannier state but for definiteness we shall refer to the conceptually simpler case of a Heisenberg ferromagnet in which $|\vec{R}\rangle$ denotes a single spin deviation at the lattice site $\vec{R}$. For simplicity we also restrict the discussion to a Bravais lattice (with a single magnetic ion at each lattice point), although the formalism permits trivial generalization. The particular site to be occupied by the impurity (if such be the problem of interest) is chosen as the origin.

Consider a particular lattice site $\vec{R}$. The "shell of R" consists of all sites into which $\vec{R}$ is carried by the operations of the point group $\mathcal{P}$. By definition, then, the maximum number of sites in a shell is equal to p. The shell of $\vec{R}$ will be labeled by its radius R (two shells with the same radius would have to be distinguished by subscripts or some such device).

If a particular $\vec{R}$ in a shell is left invariant by a subgroup of $\mathcal{P}$, this subgroup is called the "group of the lattice vector $\vec{R}$"; in such a case the sites of the shell are in one-to-one correspondence with the cosets of the group of the lattice vector. It follows that the number of sites ν_R in the shell R must be a divisor of p, and, more stringently, it must be equal to the index of a subgroup of $\mathcal{P}$. The possible numbers of points in a shell for a cubic crystal with point groups T or T_h, accordingly, are 1, 6, 12, 24, or 48; for a cubic crystal with point group O_h the permissible numbers are 1, 6, 8, 12, 24, 48.

Whereas our interest is in *general* stars of $\vec{k}$, we are interested primarily in *special* shells of $\vec{R}$. This is so because the effect of an impurity is localized, and the shells of small radius usually contain a comparatively small number of sites. We note here a fundamental difference between the states in $\vec{k}$ space and those in real space; the sites $\vec{R}$, and therefore the shell radii R, are discrete, whereas the wave vectors $\vec{k}$ are quasicontinuous for large systems. It should also be observed that the states $|\vec{k}\rangle$ of a star are energy eigenstates, subject thereby to various quantum-mechanical theorems which are not applicable to the states $|\vec{R}\rangle$ of a shell. Analogies between $\vec{k}$ space and real space are helpful but limited.

The states $|\vec{R}_i\rangle$ $(i=1,2,\ldots,\nu_R)$ of a given shell R are basis functions of a ν-dimensional reducible representation of $\mathcal{P}$. Linear combinations of these states are basis functions for irreducible representations. We denote these linear combinations by $|\Gamma ml, R\rangle$, $m=1,2,\ldots,d_\Gamma$. For a p-fold shell the number of admissible l values is d_Γ, but for smaller shells we are not able to give a general rule for the number of l values. However, the completeness of the states $|\Gamma ml, R\rangle$ on any shell implies that the total number of such states for a given R is equal to ν_R.

By definition the basis states are orthogonal:

$$\langle\Gamma ml, R|\Gamma' m' l', R'\rangle = \delta(\Gamma,\Gamma')\,\delta(m,m')\,\delta(l,l')\,\delta(R,R')\,, \tag{8}$$

where $\delta(x,y)$ is zero unless x and y are equal, in which case it is unity.

For small shells, near the central shell, there is frequently only a single l value, which can therefore be dropped from the notation. In other cases the shell labeled R can be thought of as a composite label, specifying both R and l. Therefore we henceforth omit the index l, designating the states simply by $|\Gamma m, R\rangle$, except in a few rare cases where the l index must be reintroduced to avoid ambiguity.

Expressing the states $|\Gamma m, R\rangle$ as linear combinations of the states $|\vec{R}\rangle$, by a unitary transformation,

$$|\Gamma m, R\rangle = \sum_{R^*}\,[\Phi_R^{\Gamma m}(\hat{R})]\,|\vec{R}\rangle\,, \tag{9}$$

where $\hat{R}$ denotes the angular coordinates of $\vec{R}$. Inversely, we have

$$|\vec{R}\rangle = \sum_{\Gamma ml}\,[\Phi_R^{\Gamma m}(\hat{R})]^*\,|\Gamma m, R\rangle\,. \tag{10}$$

The coefficients $\Phi_R^{\Gamma m}(\hat{R})$ are orthonormal in both Γm and R:

$$\sum_{R^*}\,[\Phi_R^{\Gamma m}(\hat{R})]^*\,\Phi_R^{\Gamma' m'}(\hat{R}) = \delta(\Gamma,\Gamma')\,\delta(m,m')\,\delta(l,l')\,, \tag{11}$$

$$\sum_{\Gamma ml}\,[\Phi_R^{\Gamma m}(\hat{R})]^*\,\Phi_R^{\Gamma m}(\hat{R}') = \delta(\hat{R},\hat{R}')\,. \tag{12}$$

The coefficients $\Phi_R^{\Gamma m}$ are given for the first three shells of the simple-cubic (sc) and fcc structures in Tables I and II. A general expression for these coefficients in terms of crystal harmonics (such as the kubic harmonics of van der Laage and Bethe[11]) is given in the Appendix A.

Consider now the "shell-symmetry Green's function":

$$G_\Gamma(R,R';E) \equiv \langle\Gamma m, R|(E^+ - \mathcal{H})^{-1}|\Gamma m, R'\rangle$$

$$=\langle \Gamma m, R | \mathcal{G} | \Gamma m, R' \rangle . \qquad (13)$$

This Green's function is independent of m, as follows from a group-theoretical theorem[10] on the matrix elements of a fully symmetric operator. It is also a consequence of the physical significance of the Green's function as a propagator of excitations; different observers, in rotated coordinate systems, will interpret a given excitation as belonging to different m values, whereas the matrix element $G_\Gamma(R, R'; E)$ is observable and must therefore be independent of m.

The Green's function $G_\Gamma(R, R'; E)$ propagates an excitation of symmetry Γ, m from the shell R' to the shell R.

Equation (9) expresses the shell-symmetry Green's function in terms of the conventional site-to-site Green's functions $G(\vec{\mathrm{R}}, \vec{\mathrm{R}}', E) = \langle \vec{\mathrm{R}} | \mathcal{G} | \vec{\mathrm{R}}' \rangle$:

$$G_\Gamma(R, R'; E) = \sum_{R^*} \sum_{R'^*} [\Phi_R^{\Gamma m}(\hat{R})]^* \, \Phi^{\Gamma m}(\hat{R}') \, G(\vec{\mathrm{R}}, \vec{\mathrm{R}}'; E) , \qquad (14)$$

or inversely,

$$G(\vec{\mathrm{R}}, \vec{\mathrm{R}}'; E) = \sum_{\Gamma m l} \Phi_R^{\Gamma m}(\hat{R}) [\Phi_{R'}^{\Gamma m}(\hat{R}')]^* \, G_\Gamma(R, R'; E) . \qquad (15)$$

Thus the shell-symmetry Green's functions are simple linear combinations of the conventional site-to-site Green's functions. The shell-symmetry Green's functions for the first three shells of a pure fcc lattice are listed in Table III; in this compilation we have exploited the fact that $G^0(\vec{\mathrm{R}}, \vec{\mathrm{R}}'; E)$ is a function only of $\vec{\mathrm{R}} - \vec{\mathrm{R}}'$, with cubic symmetry, so that many of the Green's functions on the right-hand side of Eq. (14) are equivalent.

IV. IMPURITY PROBLEM

Suppose a single impurity to be introduced in a crystal in such a way that the point-group symmetry is maintained. Then the energy eigenstates can again be classified by the indices Γm, but they no longer can be associated with particular stars in reciprocal space. Accordingly, we designate the energy eigenstates by $|\Gamma m \lambda, E\rangle$, where E denotes the energy and λ distinguishes the (possibly) degenerate states corresponding to a given energy. These states form a quasicontinuum or "band," although one or more discrete states may be split off the band.

There are several distinctive types of problems of interest. In this section we inquire as to the spatial structure of the state $|\Gamma m \lambda, E\rangle$; given the symmetry and the energy, what is the amplitude of the perturbed eigenstate $|\Gamma m \lambda, E\rangle$ on any given shell or on any given site?

In Sec. V we explore the effect of the impurity on the general and local density in energy of the states of a particular symmetry. This analysis is applied to a fcc ferromagnet in Sec. VI. And finally, in Sec. VII we consider thermodynamic properties such as the magnetization (or the local magnetization), extending the analysis to double-time thermodynamic Green's functions in the RPA. Again the formalism is illustrated specifically for a fcc next-nearest-neighbor ferromagnet at nonzero temperature.

Let the Hamiltonian of the impurity problem be

TABLE I. Shell symmetry states in sc and fcc crystals. Columns correspond to the localized states in the second shell of a sc, or in the first shell of a fcc crystal. For sc, R is $\sqrt{2}$ times the lattice constant; for fcc, R is half the lattice constant (throughout applications to fcc we measure distance in units of half the lattice constant, so that $R=1$). For the zeroth, or central, shell $\Phi_R^{\Gamma m}(\hat{R}) = 1$ for $\Gamma = A_{1g}$; this is the only nonzero coefficient.

	$\lvert R0R\rangle$	$\lvert 0RR\rangle$	$\lvert \bar{R}0R\rangle$	$\lvert 0\bar{R}R\rangle$	$\lvert RR0\rangle$	$\lvert \bar{R}R0\rangle$	$\lvert \bar{R}\bar{R}0\rangle$	$\lvert R\bar{R}0\rangle$	$\lvert R0\bar{R}\rangle$	$\lvert 0R\bar{R}\rangle$	$\lvert \bar{R}0\bar{R}\rangle$	$\lvert 0\bar{R}\bar{R}\rangle$
$\lvert A_{1g}, 1, 0; R\rangle$	$12^{-1/2}$	$12^{-1/2}$	$12^{-1/2}$	$12^{-1/2}$	$12^{-1/2}$	$12^{-1/2}$	$12^{-1/2}$	$12^{-1/2}$	$12^{-1/2}$	$12^{-1/2}$	$12^{-1/2}$	$12^{-1/2}$
$\lvert T_{1u}, 1, 1; R\rangle$	$2^{-3/2}$	0	$-2^{-3/2}$	0	$2^{-3/2}$	$-2^{-3/2}$	$-2^{-3/2}$	$2^{-3/2}$	$2^{-3/2}$	0	$-2^{-3/2}$	0
$\lvert T_{1u}, 2, 1; R\rangle$	0	$2^{-3/2}$	0	$-2^{-3/2}$	$2^{-3/2}$	$2^{-3/2}$	$-2^{-3/2}$	$-2^{-3/2}$	0	$2^{-3/2}$	0	$-2^{-3/2}$
$\lvert T_{1u}, 3, 1; R\rangle$	$2^{-3/2}$	$2^{-3/2}$	$2^{-3/2}$	$2^{-3/2}$	0	0	0	0	$-2^{-3/2}$	$-2^{-3/2}$	$-2^{-3/2}$	$-2^{-3/2}$
$\lvert E_{g}, 1, 2; R\rangle$	$2^{-3/2}$	$-2^{-3/2}$	$2^{-3/2}$	$-2^{-3/2}$	0	0	0	0	$2^{-3/2}$	$-2^{-3/2}$	$2^{-3/2}$	$-2^{-3/2}$
$\lvert E_{g}, 2, 2; R\rangle$	$2^{-1}6^{-1/2}$	$2^{-1}6^{-1/2}$	$2^{-1}6^{-1/2}$	$2^{-1}6^{-1/2}$	$-6^{-1/2}$	$-6^{-1/2}$	$-6^{-1/2}$	$-6^{-1/2}$	$2^{-1}6^{-1/2}$	$2^{-1}6^{-1/2}$	$2^{-1}6^{-1/2}$	$2^{-1}6^{-1/2}$
$\lvert T_{1g}, 1, 2; R\rangle$	0	2^{-1}	0	-2^{-1}	0	0	0	0	0	-2^{-1}	0	2^{-1}
$\lvert T_{2g}, 2, 2; R\rangle$	2^{-1}	0	-2^{-1}	0	0	0	0	0	-2^{-1}	0	2^{-1}	0
$\lvert T_{2g}, 3, 2; R\rangle$	0	0	0	0	2^{-1}	-2^{-1}	2^{-1}	-2^{-1}	0	0	0	0
$\lvert T_{2u}, 1, 3; R\rangle$	$-2^{-3/2}$	0	$2^{-3/2}$	0	$2^{-3/2}$	$-2^{-3/2}$	$-2^{-3/2}$	$2^{-3/2}$	$-2^{-3/2}$	0	$2^{-3/2}$	0
$\lvert T_{2u}, 2, 3; R\rangle$	0	$2^{-3/2}$	0	$-2^{-3/2}$	$-2^{-3/2}$	$-2^{-3/2}$	$2^{-3/2}$	$2^{-3/2}$	0	$2^{-3/2}$	0	$-2^{-3/2}$
$\lvert T_{2u}, 3, 3; R\rangle$	$2^{-3/2}$	$-2^{-3/2}$	$2^{-3/2}$	$-2^{-3/2}$	0	0	0	0	$-2^{-3/2}$	$2^{-3/2}$	$-2^{-3/2}$	$2^{-3/2}$

TABLE II. Shell-symmetry states in sc and fcc crystals. Columns correspond to the localized states in the first shell of a sc or in the second shell of a fcc crystal. In each case R is to be taken as the cube edge.

	$\lvert R00\rangle$	$\lvert \bar{R}00\rangle$	$\lvert 0R0\rangle$	$\lvert 0\bar{R}0\rangle$	$\lvert 00R\rangle$	$\lvert 00\bar{R}\rangle$
$\lvert A_{1g}, 1, 0; R\rangle$	$6^{-1/2}$	$6^{-1/2}$	$6^{-1/2}$	$6^{-1/2}$	$6^{-1/2}$	$6^{-1/2}$
$\lvert T_{1u}, 1, 1; R\rangle$	$2^{-1/2}$	$-2^{-1/2}$	0	0	0	0
$\lvert T_{1u}, 2, 1; R\rangle$	0	0	$2^{-1/2}$	$-2^{-1/2}$	0	0
$\lvert T_{1u}, 3, 1; R\rangle$	0	0	0	0	$2^{-1/2}$	$-2^{-1/2}$
$\lvert E_g, 1, 2; R\rangle$	2^{-1}	2^{-1}	-2^{-1}	-2^{-1}	0	0
$\lvert E_g, 2, 2; R\rangle$	$-12^{-1/2}$	$-12^{-1/2}$	$-12^{-1/2}$	$-12^{-1/2}$	$3^{-1/2}$	$3^{-1/2}$

written in the form $\mathcal{H} = \mathcal{H}_0 + V$, where $\mathcal{H}_0$ is the Hamiltonian of the pure crystal. [Additive constants can also be absorbed in $\mathcal{H}_0$; it is convenient to absorb the change in energy of the ground state of the perturbed crystal (relative to the energy of the ground state of the pure crystal) as an additive constant in $\mathcal{H}_0$.] Suppose further that the matrix elements $\langle \vec{R} \lvert V \rvert \vec{R}'\rangle$ are nonzero only if $\vec{R}$ and $\vec{R}'$ are in the first few shells.

Suppose that there is some representation Γ which is not supported by any of the shells within the range of V. Then the unperturbed state $\lvert \Gamma m\lambda; E\rangle_0$ has no amplitude of any of these shells, and it follows that the impurity cannot perturb this state. *Impurities with a range of n shells do not perturb states of any irreducible representation which is not contained in the first n shells.*

As an example, an impurity spin in a Heisenberg ferromagnet with nearest-neighbor interactions perturbs only those states belonging to the irreducible representations of the central ion and the nearest-neighbor shell. For a sc crystal, therefore, only states of A_{1g}, T_{1u}, and E_g are perturbed by the impurity (see Table II), whereas the seven other representations of the cubic group are unperturbed. The fractional density of states so affected is $\frac{1}{48}(1 + 3^2 + 2^2) = \frac{7}{24}$, whereas $\frac{17}{24}$ of the states of the crystal are totally unaffected.

The Green's-function formalism of Lifshitz[2] directly demonstrates the above conclusion and provides an explicit solution for the perturbed states. The Schrödinger equation

$$(E - \mathcal{H}_0)\lvert \Gamma m\lambda; E\rangle = V\lvert \Gamma m\lambda; E\rangle \tag{16}$$

is solved formally:

$$\lvert \Gamma m\lambda; E\rangle = \lvert \Gamma m\lambda; E\rangle_0 + (E^+ - \mathcal{H}_0)^{-1} V\lvert \Gamma m\lambda; E\rangle \; , \tag{17}$$

where $\lvert \Gamma m\lambda; E\rangle$ and $\lvert \Gamma m\lambda; E\rangle_0$ are the perturbed and unperturbed states, respectively.[12] The usual procedure is to multiply by $\langle \vec{R}\rvert$ and to introduce complete sets of intermediate states $\lvert \vec{R}'\rangle\langle \vec{R}'\rvert$; this gives a secular equation which must then be diagonalized by symmetry considerations. The diagonalization is automatic if we use the shell-symmetry states $\lvert \Gamma m, R\rangle$. Multiplying Eq. (17) by $\langle \Gamma m, R\rvert$, introducing complete sets of intermediate states, and noting that $(E^+ - \mathcal{H}_0)^{-1}$ and V are each diagonal in Γ and m, we find

$$\begin{aligned}\langle \Gamma m, R \vert \Gamma m\lambda; E\rangle = {} & \langle \Gamma m, R \vert \Gamma m\lambda; E\rangle_0 \\ & + \sum_{R', R''} \langle \Gamma m, R \vert \mathcal{G}_0 \vert \Gamma m, R'\rangle \langle \Gamma m, R' \vert V \vert \Gamma m, R''\rangle \\ & \times \langle \Gamma m, R' \vert \Gamma m\lambda; E\rangle \, .\end{aligned} \tag{18}$$

Let

$$\psi^{\lambda}_{\Gamma m}(R, E) \equiv \langle \Gamma m, R \vert \Gamma m\lambda; E\rangle \, , \tag{19}$$

$$\bar{\psi}^{\lambda}_{\Gamma m}(R, E) \equiv \langle \Gamma m, R \vert \Gamma m\lambda; E\rangle_0 \, , \tag{20}$$

and

$$V^{\Gamma}_{RR'} \equiv \langle \Gamma m, R \vert V \vert \Gamma m, R'\rangle \, ; \tag{21}$$

then we have

$$\begin{aligned}\psi^{\lambda}_{\Gamma m}(R, E) = {} & \bar{\psi}^{\lambda}_{\Gamma m}(R, E) \\ & + \sum_{R' l'} \sum_{R'' l''} G^0_{\Gamma}(R, R'; E)\, V^{\Gamma}_{R' R''}\, \psi^{\lambda}_{\Gamma m}(R'', E) \, .\end{aligned} \tag{22}$$

Equation (22) is of a form familiar in the impurity problem. But only a single symmetry enters into the equation, so that no further factorization of a secular equation is required. The order of the secular equation obtained from Eq. (22) is equal to the number of distinct amplitudes $\psi^{\lambda}_{\Gamma m}(R, E)$ (for fixed Γ and m) in the first n shells. Thus we see

TABLE III. Shell-symmetry Green's functions for a pure fcc lattice. The Green's functions $G^0(\vec{R}, E)$ appearing in the right-hand members are the conventional site-to-site Green's functions (depending only on coordinate differences). The vector $\vec{R}$ is indicated by (R_x, R_y, R_z), with distance measured in units of half the cube edge. The dependence on the energy variable is suppressed in the notation; $G^0(\vec{R}) \equiv G^0(\vec{R}; E)$.

A_{1g}

$G^0_{A1g}(R_0, R_0) = G^0([000])$

$G^0_{A1g}(R_0, R_1) = \sqrt{12}\, G^0([110])$

$G^0_{A1g}(R_0, R_2) = \sqrt{6} G^0([200])$

$G^0_{A1g}(R_1, R_1) = G^0([000]) + 2G^0([200]) + 4G^0([110]) + 4G^0([211]) + G^0([220])$

$G^0_{A1g}(R_2, R_2) = G^0([000]) + G^0([400]) + 4G^0([220])$

$G^0_{A1g}(R_1, R_2) = 2\sqrt{2} G^0([110]) + 2\sqrt{2} G^0([211]) + 2\sqrt{2} G^0([310])$

T_{2g}

$G^0_{T2g}(R_1, R_1) = G^0([000]) - 2G^0([200]) + G^0([220])$

T_{2u}

$G^0_{T2u}(R_1, R_1) = G^0([000]) - 2G^0([110]) - G^0([220]) + 2G^0([211])$

T_{1u}

$G^0_{T1u}(R_1, R_1) = G^0([000]) + 2G^0([110]) - G^0([220]) - 2G^0([211])$

$G^0_{T1u}(R_2, R_2) = G^0([000]) - G^0([400])$

$G^0_{T1u}(R_1, R_2) = 2G^0([110]) - 2G^0([310])$

E_g

$G^0_{Eg}(R_1, R_1) = G^0([000]) + 2G^0([200]) + G^0([220]) - 2G^0([110]) - 2G^0([211])$

$G^0_{Eg}(R_2, R_2) = G^0([000](+ G^0([400]) - 2G^0([220])$

$G^0_{Eg}(R_1, R_2) = \sqrt{2} G^0([110]) + \sqrt{2} G^0([310]) - 2\sqrt{2} G^0([211])$

from Tables I and II that for both fcc and sc ferromagnets with nearest- and next-nearest-neighbor exchange we get a third-order secular equation for A_{1g} symmetry (zeroth, first, and second shells); a second-order equation for T_{1u} symmetry; a second-order equation for E_g symmetry; and first-order equations for T_{2u} and T_{2g} symmetries.

The matrix elements of the perturbation have a simple form. From (21) and (9) we have

$$V^{\Gamma}_{RR'} = \sum_{R*} \sum_{R'*} [\Phi^{\Gamma m}_{R}(\hat{R})]^* \, \Phi^{\Gamma m}_{R'}(\hat{R}') \langle \vec{\mathrm{R}} | V | \vec{\mathrm{R}}' \rangle . \qquad (23)$$

In most cases the matrix element $\langle \vec{\mathrm{R}} | V | \vec{\mathrm{R}}' \rangle$ is nonzero only if $\vec{\mathrm{R}}$ and $\vec{\mathrm{R}}'$ are identical (and within the range of interaction of the impurity ion),[13] or if one of them is the impurity site. The matrix element $\langle \vec{\mathrm{R}} | V | \vec{\mathrm{R}} \rangle$ is the change in energy of a spin deviation (or electron, etc.) on the site $\vec{\mathrm{R}}$, due to the impurity at the origin; the matrix element $\langle 0 | V | \vec{\mathrm{R}} \rangle$ is the change in the transfer integral between the impurity and the site $\vec{\mathrm{R}}$. The presence of the impurity generally does *not* alter the transfer integral between two other sites, since such an effect would require a three-site interaction in the Hamiltonian.

Consider first the case in which neither of the shells R nor R' in Eq. (23) is the central shell. Then the matrix elements $\langle \vec{\mathrm{R}} | V | \vec{\mathrm{R}}' \rangle$ are diagonal, and if Γ is supported by the shell R the orthogonality relation (11) leads immediately to

$$V^{\Gamma}_{RR'} = \langle \vec{\mathrm{R}} | V | \vec{\mathrm{R}} \rangle \, \delta(R, R') \, \delta(l, l') \equiv V_R \, \delta(R, R') \, \delta(l, l'), \qquad R, R' \neq 0 . \qquad (24)$$

If, however, $R = 0$, then $\Phi^{\Gamma m}_{0}$ is zero unless Γ is the fully symmetric representation, in which case it is unity. Then $\Phi^{\Gamma m}_{R'}$ is simply $\nu_{R'}^{-1/2}$, where $\nu_{R'}$ is the number of sites in the shell R'. That is,

$$V^{\Gamma}_{0R'} = \sum_{R'*} \nu_{R'}^{-1/2} \langle 0 | V | \vec{\mathrm{R}}' \rangle = \nu_{R'}^{1/2} \langle 0 | V | \vec{\mathrm{R}}' \rangle \equiv V_{0R'} . \qquad (25)$$

Summarizing, for all symmetries other than the fully symmetric representation, $V^{\Gamma}_{RR'}$ is diagonal in R (and l); its diagonal value is equal to the change in energy of a site in the given shell due to the presence of the impurity. For the fully symmetric representation, $V^{\Gamma}_{RR'}$ has additional off-diagonal matrix elements connecting the central site to other shells; the value of the matrix element is $V_{0R} \equiv \nu_R^{1/2} \langle 0 | V | \vec{\mathrm{R}} \rangle$, where ν_R is the number of sites in the shell R.

Because the matrix elements of V have such restricted form, and because of the low order to the secular equation, Eq. (22) is easily solved. There will generally be more than one solution, corresponding to different indices λ. The solutions $\psi^{\lambda}_{\Gamma m}(R, E)$ are the amplitudes of the perturbed states $| \Gamma m \lambda; E \rangle$ on the shell symmetry states $| \Gamma m, R \rangle$:

$$| \Gamma m \lambda; E \rangle = \sum_R \psi^{\lambda}_{\Gamma m}(R, E) \, | \Gamma m, R \rangle . \qquad (26)$$

Of course the state can be resolved further into amplitudes on individual sites by Eq. (9), if desired.

V. PERTURBED DENSITIES OF STATES

Turning to the second class of problems, we consider the change in the density of states of a given symmetry, caused by the introduction of an impurity. As in Eq. (4), we have

$$g_{\Gamma m}(E) = -\frac{1}{\pi} \, \mathrm{Im} \, \mathrm{Tr} P_{\Gamma m} (E^+ - \mathcal{H}_0)^{-1} P_{\Gamma m}$$
$$= -\frac{1}{\pi} \, \mathrm{Im} \, \mathrm{Tr}_{\Gamma m} (E^+ - \mathcal{H}_0)^{-1} , \qquad (27)$$

where $\mathrm{Tr}_{\Gamma m}$ denotes a trace over all states of symmetry Γ, m. Then following the procedures of Callaway,[14]

$$g_{\Gamma m}(E) = -\frac{1}{\pi} \, \mathrm{Im} \, \frac{d}{dE} \, \mathrm{Tr}_{\Gamma m} \ln (E^+ - \mathcal{H})$$
$$= -\frac{1}{\pi} \, \mathrm{Im} \, \frac{d}{dE} \ln \det{}_{\Gamma m} (E^+ - \mathcal{H}) , \qquad (28)$$

where $\det_{\Gamma m}$ denotes the determinant in the basis of states of symmetry Γ, m. To isolate the unperturbed density of states one invokes the identity

$$(E^+ - \mathcal{H}) = (E^+ - \mathcal{H}_0)[1 - (E^+ - \mathcal{H}_0)^{-1} V] , \qquad (29)$$

or symbolically,

$$\mathcal{G}^{-1} = \mathcal{G}_0^{-1} (1 - \mathcal{G}_0 V) , \qquad (30)$$

hence

$$g_{\Gamma m}(E) = \frac{d_\Gamma}{p} \, g^0(E) - \frac{1}{\pi} \, \mathrm{Im} \, \frac{d}{dE} \ln \det{}_{\Gamma m} (1 - \mathcal{G}_0 V). \qquad (31)$$

As we shall see in Sec. VI, Eq. (31) is very simple to evaluate because of the highly restricted matrix elements of V in the shell-symmetry representation.

Localized states outside the spin-wave band occur when $\det_{\Gamma m}(1 - \mathcal{G}_0 V)$ has a zero for some value of energy outside the band [in which case $g_{\Gamma m}(E)$ has a singularity]. Such states have been investigated in detail,[3] particularly for the sc lattice.[1]

Frequently we are interested in the *local* density of states, as perturbed by the impurity. In the case of a ferromagnet the local density of states is related to the local magnetization. In simple spin-wave theory this connection is direct; in more complicated theories (as discussed in Sec. VII) the connection is less straightforward. But temporarily, for purposes of illustration, we assume that the density of excitations is so low (low temperature) that the spin waves can be considered as simple bosons.

Then the significance of each boson state $| \Gamma m \lambda; E \rangle$

is that it corresponds to one boson (one-spin deviation), distributed over various shells with the distribution $\sum_l |\psi^\lambda_{\Gamma m}(R,E)|^2$. The statistical weight of each state is $(e^{\beta E}-1)^{-1}$. Then the local excitation density, or the local magnetization deviation, is

$$\delta S^z(\vec{\mathrm{R}}) = \int_0^\infty \frac{g_{\vec{\mathrm{R}}}(E)}{e^{\beta E}-1}\, dE\,, \tag{32}$$

where the local density of states $g_{\vec{\mathrm{R}}}(E)$ is

$$\begin{aligned} g_{\vec{\mathrm{R}}}(E) &= -\frac{1}{\pi}\,\mathrm{Im}\langle \vec{\mathrm{R}}\,|\,\mathcal{G}\,|\vec{\mathrm{R}}\rangle \\ &= -\frac{1}{\pi}\,\mathrm{Im}\sum_{\Gamma m l l'} [\Phi_R^{\Gamma m}(\hat{R})]^* \,\Phi_R^{\Gamma m}(\hat{R})\, G(Rl, Rl'; E)\,. \end{aligned} \tag{33}$$

The local density of states $g_{\vec{\mathrm{R}}}(E)$ must be identical for every site in the same shell. Therefore we can sum the right-hand member of (36) over all sites in the shell and divide by ν_R. The orthogonality relation (11) then requires that $l=l'$, giving

$$g_{\vec{\mathrm{R}}}(E) = \nu_R^{-1}\sum_{\Gamma m} g_{\Gamma m}(R,E)\,, \tag{34}$$

where $g_{\Gamma m}(R,E)$ is the density in energy of states of symmetry Γm, on the shell R:

$$g_{\Gamma m}(R,E) = -\frac{1}{\pi}\,\mathrm{Im}\sum_l G_\Gamma(Rl, Rl';\; E)\,. \tag{35}$$

We note that $g_{\Gamma m}(R,E)$ is independent of m, so that the sum over m in Eq. (34) merely multiplies by d_Γ.

Correspondingly, the spin deviation at a given site is a sum of contributions [through Eqs. (32) and (34)] from each symmetry separately.

To calculate the partial density of states $g_{\Gamma m}(R,E)$ we employ the Dyson equation for the Green's-function operator

$$\mathcal{G} = \mathcal{G}_0 + \mathcal{G}_0 V \mathcal{G} = \mathcal{G}_0 + \mathcal{G}_0 V(1-\mathcal{G}_0 V)^{-1}\,\mathcal{G}_0\,, \tag{36}$$

where

$$\begin{aligned} g_{\Gamma m}(R,E) &= g^0_{\Gamma m}(R,E) \\ &\quad - \frac{1}{\pi}\,\mathrm{Im}\sum_l \langle \Gamma m l, R|\mathcal{G}_0 V(1-\mathcal{G}_0 V)^{-1}\mathcal{G}_0|\Gamma m l, R\rangle\,. \end{aligned} \tag{37}$$

The last term in Eq. (37) is evaluated by introducing summations over intermediate states. Again suppressing the l indices (which are superfluous in any case for our fcc next-nearest neighbor model),

$$\begin{aligned} g_{\Gamma m}(R,E) &= g^0_{\Gamma m}(R,E) - \frac{1}{\pi}\sum_{R' R'' R'''} G^0_\Gamma(R,R') \\ &\quad \times V_{\Gamma R' R''}(1-\mathcal{G}_0 V)^{-1}_{\Gamma m R'' R'''}\, G^0_\Gamma(R''', R)\,. \end{aligned} \tag{38}$$

We shall now apply the foregoing analysis to a fcc ferromagnet to illustrate the simplicity by which all equations can be evaluated in the shell-symmetry representation.

VI. FACE-CENTERED-CUBIC FERROMAGNET AT LOW TEMPERATURES

The definitions of the shell-symmetry states for a fcc structure have been given in Tables I and II. The unperturbed Green's functions have been given in terms of the conventional site-to-site Green's functions in Table III.

Consider now an Heisenberg ferromagnet with the Hamiltonian

$$\mathcal{H} = -\sum_{i,j} J_{ij}\,\vec{\mathrm{S}}_i\cdot\vec{\mathrm{S}}_j - 2j_1\vec{\mathrm{S}}_0\cdot\sum_{\vec{\mathrm{R}}}\vec{\mathrm{S}}_{\vec{\mathrm{R}}} - 2j_2\vec{\mathrm{S}}_0\cdot\sum_{\vec{\mathrm{R}}'}\vec{\mathrm{S}}_{\vec{\mathrm{R}}'}\,. \tag{39}$$

Here J_{ij} is the unperturbed exchange, and it is assumed to have the value J_1 for nearest neighbors and J_2 for next-nearest neighbors. Similarly, j_1 and j_2 are the changes in nearest- and next-nearest-neighbor exchange of the impurity, relative to the host ions. The summation over $\vec{\mathrm{R}}$ in Eq. (39) is over all sites of the first shell; the summation over $\vec{\mathrm{R}}'$ is over sites of the second shell. We must also note that the magnitude S_0 of the impurity spin may be different from the magnitude of the host spins.

The energy of the ground state is shifted by the impurity, by an amount

$$\delta E = -2(S_0 - S)S(12J_1 + 6J_2) - 2S_0S(12j_1 + 6j_2)\,. \tag{40}$$

We absorb this term in the unperturbed Hamiltonian. Then we easily find the following diagonal matrix elements of the perturbing potential:

$$V_0 = \langle \vec{\mathrm{R}}_0\,|\,V\,|\,\vec{\mathrm{R}}_0\rangle = 2S(12j_1 + 6j_2)\,, \tag{41}$$

$$V_1 = \langle \vec{\mathrm{R}}_1\,|\,V\,|\,\vec{\mathrm{R}}_1\rangle = 2(S_0 - S)J_1 + 2S_0 j_1\,, \tag{42}$$

$$V_2 = \langle \vec{\mathrm{R}}_2\,|\,V\,|\,\vec{\mathrm{R}}_2\rangle = 2(S_0 - S)J_2 + 2S_0 j_2\,. \tag{43}$$

As discussed below Eq. (23), these matrix elements describe the change in energy required to produce a spin deviation on a site in the zeroth, first, and second shell, respectively. The off-diagonal matrix elements are conveniently defined with a factor $\nu_R^{1/2}$ as in Eq. (25):

$$\begin{aligned} V_{01} &= \sqrt{12}\,\langle \vec{\mathrm{R}}_0\,|\,V\,|\vec{\mathrm{R}}_1\rangle \\ &= 4\sqrt{3}\,\{[(S_0S)^{1/2} - S]\,J_1 + (S_0S)^{1/2} j_1\}\,, \end{aligned} \tag{44}$$

$$\begin{aligned} V_{02} &= \sqrt{6}\,\langle \vec{\mathrm{R}}_0\,|\,V\,|\,\vec{\mathrm{R}}_2\rangle \\ &= 2\sqrt{6}\,\{[(S_0S)^{1/2} - S]\,J_2 + (S_0S)^{1/2} j_2\}\,, \end{aligned} \tag{45}$$

Thus V_{01} is $\sqrt{12}$ times the change in the transfer matrix element taking a spin deviation from the origin to a site in the first shell.

As indicated in Eq. (25), V_{01} and V_{02} are also the matrix elements between the indicated *shells*, in the symmetry A_{1g}. And from Eq. (24), V_0, V_1, and V_2 are the matrix elements *within* the indicated shells for every symmetry supported by the given shell.

Summarizing, then, the only nonzero matrix elements are

$$V_{A1g,R_0,R_0}=V_0\,, \tag{46}$$

$$V_{A1g,R_1,R_1}=V_{T1u,R_1,R_1}=V_{Eg,R_1,R_1}=V_{T2g,R_1,R_1}=V_{T2u,R_1,R_1}=V_1, \tag{47}$$

$$V_{A1g,R_2,R_2}=V_{T1u,R_2,R_2}=V_{Eg,R_2,R_2}=V_2\,, \tag{48}$$

$$V_{A1g,R_0,R_1}=V_{01}\quad, \tag{49}$$

$$V_{A1g,R_0,R_2}=V_{02}\,. \tag{50}$$

With the matrix elements identified we can turn to physical problems. If we wish to calculate the change in the density of states of a given symmetry by Eq. (31) we must consider the matrix $(1-\mathcal{G}_0V)_{\Gamma m}$. We also recall that discrete states exist outside the spin-wave band if $\det_{\Gamma m}(1-\mathcal{G}_0V)$ has a zero for some energy outside the spin-wave band. Calculation of the *local* density of states by Eq. (38) also requires knowledge of $(1-\mathcal{G}_0V)_{\Gamma m}$. We examine this matrix for each symmetry.

The symmetries T_{2g} and T_{2u} are supported only by the first shell, so that

$$(1-\mathcal{G}_0V)_{\Gamma m}=1-G^0_\Gamma(R_1,\ R_1)V_1\,,\quad \Gamma=T_{2g},T_{2u}. \tag{51}$$

The symmetries T_{1u} and E_g are supported only by the first and second shells, so that $(1-\mathcal{G}_0V)_{\Gamma m}$ is of rank two:

$$(1-\mathcal{G}_0V)_{\Gamma m}=\begin{pmatrix}1-G^0_\Gamma(R_1,R_1)V_1 & -G^0_\Gamma(R_1,R_2)V_2\\ -G^0_\Gamma(R_2,R_1)V_1 & 1-G^0_\Gamma(R_2,R_2)V_2\end{pmatrix},\quad \Gamma=T_{1u},\ E_g\,. \tag{52}$$

Finally the symmetry A_{1g} leads to a matrix of rank three:

$$\{1-\mathcal{G}_0V\}_{A1g}=\begin{Bmatrix}1-G^0(00)V_0-G^0(01)V_{10}-G^0(02)V_{20} & -G^0(01)V_1-G^0(00)V_{01} & -G^0(02)V_2-G^0(00)V_{02}\\ -G^0(10)V_0-G^0(11)V_{10}-G^0(12)V_{20} & 1-G^0(11)V_1-G^0(10)V_{01} & -G^0(12)V_2-G^0(00)V_{02}\\ -G^0(20)V_0-G^0(21)V_{10}-G^0(22)V_{20} & -G^0(21)V_1-G^0(20)V_{01} & 1-G^0(22)V_2-G^0(20)V_{02}\end{Bmatrix}, \tag{53}$$

where we have omitted the subscript A_{1g} (and the argument E) in $G^0_{A1g}(R,R';E)$.

With the shell-symmetry Green's function assumed known, and with the matrix elements V_0, V_{01}, etc., given by Eqs. (41)–(45), it is now trivial to evaluate the various matrices $\{1-\mathcal{G}_0V\}_{\Gamma m}$. The local magnetization deviations and the changes in the partial densities of states follow directly from the appropriate equations of Sec. V.

At this point it is well to stress that the final equations that we have obtained are equivalent to those obtained by Wolfram and Callaway[1] and others.[3] The virtue of our approach is threefold. First, the factorization of $(1-\mathcal{G}_0V)$ into matrices for each separate symmetry has been automatic in our approach. Second, the form of Eqs. (51)–(53) is transparent, so that these equations can be written easily and directly (whereas their form is quite obscure when written in the representation of localized states). And finally, the *evaluation* of the matrices is quite simple if the various shell-symmetry Green's functions are known. In Ref. 6 the site-to-site Green's functions have been approximated by simple Tchebyshev polynomial representations. The coefficients in these polynomials need only to be combined according to Table III to obtain polynomial representations of the shell-symmetry Green's functions. This convenient polynomial approximation permits matrices such as those in Eqs. (52) or (53) to be evaluated *analytically*. One can thereby obtain approximate analytic criteria for the appearance of discrete states of particular symmetries, of the functional form of in-band resonances, or of other physical solutions.

VII. THERMODYNAMIC CONSIDERATIONS, RANDOM-PHASE APPROXIMATION

Finally we consider the case of interacting spin waves, necessitating the introduction of double-time temperature-dependent Green's functions. As might be expected, these Green's functions can be accommodated to the point-group symmetry in a manner which is formally identical to the crystal Green's function. We exhibit the procedure within the simple and convenient RPA, as has been employed by Wolfram and Hall[4] and by Hone, Callen, and Walker.[5]

The conventional retarded Green's function for a ferromagnet is defined by[15]

$$\overline{G}(\vec{\mathrm{R}},\ \vec{\mathrm{R}}';t)\equiv -i\,\Theta(t)\,\langle[S^{+}_{\vec{\mathrm{R}}}(t),\ S^{-}_{\vec{\mathrm{R}}'}(0)]\rangle\,, \tag{54}$$

where $\Theta(t)$ is the unit step function, the square brackets indicate a commutator, and the angular brackets designate a canonical average. The Fourier transform of $\overline{G}(\vec{\mathrm{R}},\vec{\mathrm{R}}';t)$ will be designated by $\overline{G}(\vec{\mathrm{R}},\vec{\mathrm{R}}';E)$, the bar distinguishing this thermodynamic Green's function from the crystal Green's function. Given the Green's function $\overline{G}(\vec{\mathrm{R}},\vec{\mathrm{R}}';E)$ one can calculate the local magnetization $\langle S^z_{\vec{\mathrm{R}}}\rangle$ by the following algorithm.[16] One first defines a "quasi-boson" energy $\Omega(\vec{\mathrm{R}})$ by

$$(e^{\beta\Omega(\vec{R})}-1)^{-1}=-\int_{-\infty}^{\infty}dE\,\frac{(e^{\beta E}-1)^{-1}\,\mathrm{Im}\bar{G}(\vec{R},\vec{R};E)}{\langle S^z_{\vec{R}}\rangle}\ , \tag{55}$$

then we have

$$\langle S^z_{\vec{R}}\rangle=S_{\vec{R}}B_s(\beta\Omega)\ , \tag{56}$$

where B_s is the Brillouin function.

The calculation of the Green's function proceeds through the equation of motion[1]:

$$i\frac{d}{dt}\bar{G}(\vec{R},\vec{R}';t)=\langle[S^+_{\vec{R}},S^-_{\vec{R}'}]\rangle\,\delta(t)$$

$$-i\Theta(t)\langle[S^+_{\vec{R}}(t),\mathcal{H}],\ S^-_{\vec{R}'}(0)]\rangle. \tag{57}$$

In the RPA, furthermore, the Green's function on the right-hand side is "decoupled":

$$\langle[S^z_{\vec{R}}(t)S^+_{\vec{R}'}(t),S^-_{\vec{R}''}(0)]\rangle\to\langle S^z_{\vec{R}}\rangle\langle[S^+_{\vec{R}'}(t),\ S^-_{\vec{R}''}(0)]\rangle\ . \tag{58}$$

In this way one obtains the following equation of motion of the Green's function[15]:

$$(E-2\sum_{\vec{R}}\mathcal{J}_{\vec{R}'\vec{R}}\ \langle S^z_{\vec{R}}\rangle)\bar{G}(\vec{R}',\vec{R};\ E)+2\sum_{\vec{R}}\mathcal{J}_{\vec{R}'\vec{R}}\langle S^z_{\vec{R}'}\rangle$$

$$\times\bar{G}(\vec{R},\vec{R}'';E)=\frac{1}{\pi}\langle S^z_{\vec{R}'}\rangle\,\delta(\vec{R}',\vec{R}''). \tag{59}$$

Here $\mathcal{J}_{\vec{R}'\vec{R}}$ is the actual exchange integral between the ions at $\vec{R}'$ and $\vec{R}$; it differs from the host exchange if either $\vec{R}'$ or $\vec{R}$ is the impurity site. Now, let $J_{\vec{R}'\vec{R}}$ be the exchange interaction between sites $\vec{R}'$ and $\vec{R}$ in the pure crystal, and let

$$j_{\vec{R}'\vec{R}}\equiv\mathcal{J}_{\vec{R}'\vec{R}}-J_{\vec{R}'\vec{R}}\ . \tag{60}$$

Also, let $\langle S^z\rangle$ be the magnetization of a site in the pure crystal, and

$$\mu_{\vec{R}}\equiv(\langle S^z_{\vec{R}}\rangle-\langle S^z\rangle)/\langle S^z\rangle. \tag{61}$$

Then equation (59) can be rewritten[5]

$$(E-2\langle S^z\rangle\sum_{\vec{R}}J_{\vec{R}'\vec{R}})\bar{G}(\vec{R}',\vec{R}'';E)$$

$$+2\langle S^z\rangle\sum_{\vec{R}}J_{\vec{R}'\vec{R}}\bar{G}(\vec{R},\vec{R}'';E)$$

$$=\frac{1}{\pi}\langle S^z_{\vec{R}'}\rangle\delta(\vec{R}',\vec{R}'')+2\sum_{\vec{R}}j_{\vec{R}'\vec{R}}\langle S^z_{\vec{R}}\rangle\bar{G}(\vec{R}',\vec{R}'';E)$$

$$-2\sum_{\vec{R}}j_{\vec{R}'\vec{R}}\langle S^z_{\vec{R}}\rangle\bar{G}(\vec{R},\vec{R}'';\ E)$$

$$+2\langle S^z\rangle\sum_{\vec{R}}J_{\vec{R}'\vec{R}}\mu_R\bar{G}(\vec{R}',\vec{R}'';E)$$

$$-2\langle S^z\rangle\sum_{\vec{R}}J_{\vec{R}\vec{R}}\mu_{R'}\bar{G}(\vec{R},\vec{R}'';E)\ \ . \tag{62}$$

However, the classical-crystal Green's function satisfies the equation[6]

$$(E-2\langle S^z\rangle\textstyle\sum_{\vec{R}}J_{\vec{R}'\vec{R}})\,G^0(\vec{R}',\vec{R}'';E)$$

$$+2\langle S^z\rangle\textstyle\sum_{\vec{R}}J_{\vec{R}'\vec{R}}G^0(\vec{R},\vec{R}'';E)=\delta(\vec{R}',\vec{R}''). \tag{63}$$

This Green's function is identical to that defined previously, by the equation

$$G^0(\vec{R},\vec{R}';E)=\langle\vec{R}|(E^+-\mathcal{H}_0)^{-1}|\vec{R}'\rangle\ \ ,$$

except that the spin magnitude S is understood to be replaced (self-consistently) by the thermal average $\langle S^z\rangle$. To avoid needless complexity of notation we shall *not* signify this replacement in the notation. The solution of Eq. (62) is, then[6]

$$\bar{G}(\vec{R}',\vec{R}'';E)=\textstyle\sum_{\vec{R}}G^0(\vec{R}',\vec{R};\ E)\ Q(\vec{R},\vec{R}''), \tag{64}$$

where

$$Q(\vec{R},\vec{R}'')=\frac{1}{\pi}\langle S^z_{\vec{R}}\rangle\,\delta(\vec{R},\vec{R}'')+2\sum_{\vec{R}'}j_{\vec{R}\vec{R}'}\langle S^z_{\vec{R}'}\rangle\bar{G}(\vec{R},\vec{R}'';E)$$

$$-2\sum_{\vec{R}'}j_{\vec{R}\vec{R}'}\ \langle S^z_{\vec{R}}\rangle\,\bar{G}(\vec{R}',\vec{R}'';E)$$

$$+2\langle S^z\rangle\sum_{\vec{R}'}J_{\vec{R}\vec{R}'}\ \mu_{\vec{R}'}\bar{G}(\vec{R},\vec{R}'';E)$$

$$-2\langle S^z\rangle\sum_{\vec{R}'}J_{\vec{R}\vec{R}'}\mu_{\vec{R}}\bar{G}(\vec{R}',\vec{R}'';E). \tag{65}$$

At this point we introduce the shell-symmetry Green's functions. For this purpose we define the operator

$$S^-_{\Gamma mR}=\sum_{R^*}\Phi^{\Gamma m}_R(\hat{R})S^-_{\vec{R}}\ \ . \tag{66}$$

Then the two-time thermodynamic shell-symmetry Green's function is defined by

$$\bar{G}_\Gamma(R,R';t)=-i\Theta(t)\langle[S^+_{\Gamma mR}(t),S^-_{\Gamma mR'}(0)]\rangle\ . \tag{67}$$

Again the Green's function is independent of m, as in Eq. (13). The physical significance[15] of the Green's function is the probability of finding the set of spin deviations (66) on the R shell at time t, after applying a set of instantaneous spin deviations (of the same symmetry) to the shell R' at time $t=0$. That is, the Green's function is a propagator, at temperature T, of spin deviations of a definite pattern, from shell to shell.

The definitions (66) and (67) lead to the analog of Eq. (14) for either $\bar{G}(R,R';t)$ or for its Fourier transform $\bar{G}_\Gamma(R,R';E)$:

$$\bar{G}_\Gamma(R,R';E)=\sum_{R^*}\sum_{R'^*}\ [\Phi^{\Gamma m}_R(\hat{R})]^*\,\Phi^{\Gamma m}_{R'}(\hat{R}')\bar{G}(\vec{R},\vec{R}';E). \tag{68}$$

Similarly, this equation can be inverted, precisely as in Eq. (15). Consequently, knowledge of $\bar{G}_\Gamma(R,R';E)$ would enable us to calculate $\bar{G}(\vec{R},\vec{R}';E)$, and then $\langle S^z_{\vec{R}}\rangle$ by Eqs. (55) and (56).

We now show that the equation of motion (64) permits us to calculate $\bar{G}_\Gamma(R,R';E)$. We insert equation (64) into (66), to find

$$\bar{G}_\Gamma(R',R'';E)=\sum_R\sum_{R'^*}\sum_{R''^*}[\Phi^{\Gamma m}_{R'}(\hat{R}')]^*$$

$$\times\Phi^{\Gamma m}_{R''}(\hat{R}'')G^0(\vec{R}',\vec{R}\ ;\ E)\,Q(\vec{R},\vec{R}'') \tag{69}$$

or

$$\bar{G}_\Gamma(R',R'';E)=\textstyle\sum_R G^0_\Gamma(R',R;E)Q_\Gamma(R,R'';E), \tag{70}$$

where

$$Q_\Gamma(R,R'';E) \equiv \sum_{R^*} \sum_{R''^*} [\Phi_R^{\Gamma m}(\hat{R})]^* \, \Phi_{R''}^{\Gamma m}(\hat{R}'') Q(\vec{R},\vec{R}''). \tag{71}$$

Inserting Eq. (65) we obtain

$$\begin{aligned} Q_\Gamma(R,R'';E) = \frac{1}{\pi}\langle S^z_{\vec{R}}\rangle \delta(R,R'') &+ 2\Big(\sum_{\vec{R}'} j_{\vec{R}\vec{R}'}\langle S^z_{\vec{R}'}\rangle \\ &+ \langle S^z\rangle \sum_{\vec{R}'} J_{\vec{R}\vec{R}'}\,\mu_{\vec{R}'}\Big)\overline{G}_\Gamma(R,R'';E) \\ &- 2\sum_{R'}\big(\langle S^z_R\rangle j_\Gamma(R,R') \\ &+ 2\langle S^z\rangle \mu_R J_\Gamma(R,R')\big)\overline{G}_\Gamma(R',R'';E). \end{aligned} \tag{72}$$

The coefficients of the Green's functions are to be evaluated for any $\vec{R}$ in the shell R. The quantities $j_\Gamma(R,R')$ and $J_\Gamma(R,R')$ are defined by equations precisely analogous to Eq. (14), the relevant exchange constants replacing the Green's functions in that equation.

Since $Q_\Gamma(R,R'';E)$ in Eq. (70) is a function of the Green's function itself, and also of the magnetization $\langle S^z_{\vec{R}}\rangle$ on the various shells, this equation leads to a set of self-consistent equations. Although they are considerably more complicated than those obtained in simple spin-wave theory, they are fully factored and fully explicit. In particular cases they lead to explicit analytic solutions. To demonstrate this we explicitly demonstrate the solution of a spin impurity in a fcc ferromagnet. Throughout the paper we have referred to the fcc, next-nearest-neighbor ferromagnet as an illustrative example of the method. We need only to assemble the appropriate facts required to evaluate Eq. (60).

Consider first the quantities $J_\Gamma(R,R')$ appearing in Eq. (61). As noted immediately below Eq. (72), these quantities are defined by equations isomorphic to Eq. (14). However, $J_{\vec{R}\vec{R}'}$ takes only two values; J_1 if $\vec{R}$ and $\vec{R}'$ are nearest neighbors ($\vec{R}-\vec{R}'=[110]$ or equivalent), and J_2 if $\vec{R}$ and $\vec{R}'$ are next-nearest-neighbors ($\vec{R}-\vec{R}'=[200]$ or equivalent). Hence we transcribe Table III as shown in Table IV.

At this point all procedures are quite straightforward. We illustrate by writing Eqs. (70) and (72) for the case of T_{2g} symmetry:

$$\begin{aligned} \overline{G}_{T2g}(R_1,R_1) = G^0_{T2g}(R_1,R_1)\Big(\frac{1}{\pi}\langle S^z_1\rangle &+ 2\big[j_1\langle S^z_1\rangle \\ &+ J_1\langle S^z\rangle(\mu_0+4\mu_1+2\mu_2+4\mu_3+\mu_4) \\ &+ 2J_2\langle S^z\rangle(\mu_1+\mu_3+\mu_5)\big]\overline{G}_{T2g}(R_1,R_1) \\ &- 4\langle S^z\rangle\,\mu_1(-2J_2)\overline{G}_{T2g}(R_1,R_1)\Big). \end{aligned} \tag{73}$$

Solving for $\overline{G}_{T2g}$, we have

$$\overline{G}_{T2g}(R_1,R_1) = \frac{1}{\pi}\,\frac{\langle S^z_1\rangle G^0_{T2g}(R_1,R_1)}{1-G^0_{T2g}(R_1R_1)[2j_1\langle S^z_1\rangle + 2J_1\langle S^z\rangle(\mu_0+4\mu_1+2\mu_2+4\mu_3+\mu_4)+4J_2\langle S^z\rangle(\mu_1+\mu_3+\mu_5)-8J_2\langle S^z\rangle\mu_1]}\,. \tag{74}$$

We observe that $\overline{G}_{T2g}$ depends on $\langle S^z_1\rangle$, $\langle S^z_2\rangle$, ..., $\langle S^z_5\rangle$ (or $\mu_1 \cdots \mu_5$). These quantities must be calculated self-consistently. A practical solution is to first assume that all μ_i vanish beyond some low-ordered shell (usually the first or even the zeroth), to find the magnetizations of all shells from this, and if necessary, to iterate this solution once again.

The Green's function $\overline{G}_{T2u}(R_1,R_1)$ is determined by a single self-consistent equation, analogous to Eq. (73).

For the symmetry T_{1u} (or for E_g) there are three Green's functions which are coupled by Eq. (70); $\overline{G}_{T1u}(R_1,R_1)$, $\overline{G}_{T1u}(R_1,R_2)$, and $\overline{G}_{T1u}(R_2,R_2)$. Hence these Green's functions must be obtained from the solution of three simultaneous equations. Fortunately, these equations are truncated if we assume $\mu_2=0$, as in the approximation above. Nevertheless, it is evident that the structure of the equations is considerably more complicated than in the zero-temperature case. The full prior exploitation of symmetry is correspondingly more nearly essential.

APPENDIX

We here derive an analytic expression for the coefficients $\Phi^{\Gamma m}_{Rl}$ of Eq. (9). Let us first recall the definitions of the "crystal harmonics" $\Phi^{\Gamma m}_l(\hat{r})$;

TABLE IV. Symmetry combinations of the exchange constants for a fcc crystal.

$J_{A1g}(R_0,R_0)=0$	$j_{A1g}(R_0,R_0)=0$
$J_{A1g}(R_0,R_1)=\sqrt{12}J_1$	$j_{A1g}(R_0,R_1)=\sqrt{12}j_1$
$J_{A1g}(R_0,R_2)=\sqrt{6}J_2$	$j_{A1g}(R_0,R_2)=\sqrt{6}j_2$
$J_{A1g}(R_1,R_1)=4J_1+2J_2$	$j_{A1g}(R_1,R_1)=0$
$J_{A1g}(R_2,R_2)=2\sqrt{2}J_1$	$j_{A1g}(R_2,R_2)=0$
$J_{T2g}(R_1,R_1)=-2\ J_2$	$j_{T2g}(R_1,R_1)=0$
$J_{T2u}(R_1,R_1)=-2J_1$	$j_{T2u}(R_1,R_1)=0$
$J_{T1u}(R_1,R_1)=2J_1$	$j_{T1u}(R_1,R_1)=0$
$J_{T1u}(R_2,R_2)=0$	$j_{T1u}(R_2,R_2)=0$
$J_{T1u}(R_1,R_2)=2J_1$	$j_{T1u}(R_1,R_2)=0$
$J_{Eg}(R_1,R_1)=-2J_1+2J_2$	$j_{Eg}(R_1,R_1)=0$
$J_{Eg}(R_2,R_2)=0$	$j_{Eg}(R_2,R_2)=0$
$J_{Eg}(R_1,R_2)=\sqrt{2}J_1$	$j_{Eg}(R_1,R_2)=0$

these are linear combinations of the spherical harmonics $Y_l^{m'}(\hat{r})$ of degree l, such that they transform according to the mth row of the Γ irreducible representation of the given point group. For the cubic group O_h the crystal harmonics are the "kubic harmonics" of van der Laage and Bethe.[11] If $\mathcal{R}$ is a rotation operator of the point group, then, by definition,

$$\Phi_l^{\Gamma m}(\mathcal{R}^{-1}\hat{r}) = \mathcal{R}\Phi_l^{\Gamma m}(\hat{r}) = \sum_{m'} \Phi_l^{\Gamma m}(\hat{r})\Gamma_{m'm}(\mathcal{R}) \ . \qquad \text{(A1)}$$

It is then evident that

$$|\Gamma ml, R\rangle = (A_{Rl}^{\Gamma m})^{-1/2} \sum_{R^*} \Phi_l^{\Gamma m}(\hat{R}) |\vec{\mathrm{R}}\rangle \ , \qquad \text{(A2)}$$

where $A_{Rl}^{\Gamma m}$ is a normalization constant, and where $\Phi_l^{\Gamma m}(\hat{R})$ is the crystal harmonic $\Phi_l^{\Gamma m}$ evaluated at the angular coordinates of an ion in the shell R. To corroborate Eq. (A2) we apply the operator $\mathcal{R}$, invoke Eq. (A1), and find

$$\mathcal{R} \,|\, \Gamma ml; R\rangle = \sum_{m'} \Gamma_{m'm}(\mathcal{R}) \,|\, \Gamma m'l; R\rangle, \qquad \text{(A3)}$$

which defines the functions $|\Gamma ml; R\rangle$.

To evaluate the normalization constant $A_{Rl}^{\Gamma m}$ we infer from (A1) that

$$A_{Rl}^{\Gamma m} = \sum_{R^*} |\Phi_l^{\Gamma m}(\hat{R})|^2 \ . \qquad \text{(A4)}$$

The sum over the shell R can be replaced by a sum over all operations applied to a single site vector $\vec{\mathrm{R}}$, but we must then correct it by the ratio ν_R/p (the ratio of the number of sites in the shell to the number of operations in the point group). We have

$$A_{Rl}^{\Gamma m} = \frac{\nu}{p} \sum_{\mathcal{R}} |\mathcal{R}\,\Phi_l^{\Gamma m}(\hat{R})|^2 \qquad \text{(A5)}$$

$$= \frac{\nu}{p} \sum_{\mathcal{R}} \sum_{m'm''} \Gamma^*_{m'm}(\mathcal{R}) \Gamma_{m''m}(\mathcal{R}) [\Phi_l^{\Gamma m'}(\hat{R})]^* \, \Phi_l^{\Gamma m''}(\hat{R}) \ , \qquad \text{(A6)}$$

but

$$\sum_{\mathcal{R}} \Gamma^*_{m'm}(\mathcal{R}) \Gamma_{m''m}(\mathcal{R}) = \frac{p}{d_\Gamma} \, \delta(m', m''), \qquad \text{(A7)}$$

hence

$$A_{Rl}^{\Gamma m} = \frac{\nu_R}{d_\Gamma} \sum_{m'} |\,\Phi_l^{\Gamma m}(\hat{R})\,|^2 \ , \qquad \text{(A8)}$$

and finally

$$\Phi_{Rl}^{\Gamma m}(\hat{R}) = \left(\frac{\nu_R}{d_\Gamma} \sum_{m'} |\,\Phi_l^{\Gamma m}(\hat{R})\,|^2 \right)^{-1/2} \Phi_l^{\Gamma m}(\hat{R}). \qquad \text{(A9)}$$

It should now be noted that the index l was introduced merely as an index in the states $|\Gamma ml, R\rangle$, to distinguish states corresponding to the same Γ, m, and R. We have now associated l with the degree of the cubic harmonics in an equation such as (A2). It does *not* follow that all l values are acceptable. In fact, higher values of l in the right-hand member of Eq. (A2) merely reproduce the same values of the crystal harmonics at the discrete ionic position $\vec{\mathrm{R}}$, giving the *same* states $|\Gamma ml, R\rangle$ as do lower values of l. This phenomenon is completely analogous to the fact that values of $\vec{\mathrm{k}}$ outside the first Brillouin zone merely repeat Bloch states inside the zone, again because of the discrete nature of the lattice. It is in this sense that the states $|\Gamma ml, R\rangle$ are orthogonal in l (Eq. 8); the orthogonality does *not* extend to hypothetical higher values of l which merely repeat equivalent states. In the body of the paper the index l is generally suppressed.

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[1] T. Wolfram and J. Callaway, Phys. Rev. 130, 2207 (1963).

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

[3] Yu. A. Izyumov, Advan. Phys. 14, 569 (1965).

[4] T. Wolfram and W. Hall, Phys. Rev. 143, 284 (1966).

[5] D. Hone, H. Callen, and L. R. Walker, Phys. Rev. 144, 283 (1966).

[6] R. H. Swendsen and H. Callen, Phys. Rev. B (to be published).

[7] These observations were developed in 1968 during an extended visit to the University of Pennsylvania by Professor Victor Baryakhtar, under a Soviet-American scientific-exchange program.

[8] G. H. Lehman and R. E. De Wames, Phys. Rev. 131, 1008 (1963).

[9] F. Gautier and P. Lenglart, Phys. Rev. 139, A705 (1965).

[10] M. Tinkham, *Group Theory and Quantum Mechanics* (McGraw-Hill, New York, 1964).

[11] F. C. van der Laage and H. A. Bethe, Phys. Rev. 71, 612 (1947).

[12] The unperturbed state $|\Gamma m\lambda;\ E\rangle_0$ is identical to a state $|\Gamma m\lambda,\ k^*\rangle$ as discussed in Sec. II, although that notation is no longer convenient for our present applications.

[13] Recall the comment in the third paragraph of Sec. IV; the mere shift of the ground-state energy is absorbed into $\mathcal{H}_0$.

[14] J. Callaway, J. Math. Phys. 5, 783 (1964).

[15] See, D. N. Zubarev, Usp. Fiz. Nauk 71, 71 (1960) [Sov. Phys. Usp. 3, 320 (1960)].

[16] H. Callen and S. Shtrikman, Solid State Commun. 3, 5 (1965).