Thermodynamic Properties of Spin Impurities in Heisenberg Ferromagnets*

DANIEL HONE AND HERBERT CALLEN
Department of Physics, University of Pennsylvania, Philadelphia, Pennsylvania

AND

LAURENCE R. WALKER
Bell Telephone Laboratories, Murray Hill, New Jersey

(Received 17 November 1965)

Thermodynamic properties of an isolated spin impurity in a Heisenberg ferromagnet are calculated as functions of the magnitude of the impurity spin and of the strength of its exchange coupling to the host spins. The magnetization of the impurity, the energy and weight of its s-state localized mode (when one exists), and the shape of the local spectral weight function are all obtained as functions of temperature.

I. INTRODUCTION

THE properties of systems containing impurities is a pervasive problem in many fields of solid-state physics. Of the various types of such systems the particular case of spin impurities in ferromagnets is uniquely convenient for experimental investigation. Nuclear magnetic resonance, Mössbauer techniques, and angular-correlation methods can probe the magnetization of the impurity, and neutron scattering can determine the distribution of magnetization in the vicinity of the impurity. In fact the results of NMR and Mössbauer measurements have been reported recently for several systems: for Fe in Ni,[1] Mn in Fe,[2] rare-earth ions in garnets,[3] and Fe in rare-earth manganates.[4]

Although many interesting single-particle[5] and two-particle[6] (transport) effects arise from the interactions of impurities at nonzero concentrations, we here consider only a single impurity, and we limit our attention to insulating (Heisenberg) ferromagnets. This impurity may be distinguished from the host by the magnitude of its spin, by its exchange interaction, or by both. The localized spin-excitation modes at zero temperature have been calculated by Wolfram and Calloway,[7] whereas we are interested in thermodynamic properties. In particular we shall calculate the magnetization of the impurity ion, and the energy and weight of the s-state localized mode, as a function of temperature. In addition, we calculate the spectral weight function or the distribution-in-energy of the single-spin-flip excitations on the impurity ion, again as a function of temperature. The work is an extension of heuristic and semi-quantitative discussions given previously by Jaccarino, Walker, and Wertheim[8] and by Callen, Hone, and Heeger.[9]

In several of the experiments cited above, the impurity magnetization is very accurately given by a molecular field theory, with an effective field proportional to the host magnetization. This result is given a fundamental rationale by the present work, as has been discussed in a preliminary way in Refs. 8 and 9. The molecular field dependence is by no means general, and we shall find criteria for its applicability.

The theory of impurities in one type of physical system has close formal relationships with theories for other types of systems. Unfortunately the original extensive work by Lifshitz[10] on the vibrational modes of impure crystal systems was for many years almost unrecognized outside the USSR. Much of the theory subsequently was developed independently and was extended by workers in this country and in England.[11] Similar methods were thereafter applied to other types of systems; by Koster and Slater[12] to the spectrum of conduction electrons in impure metals, and, as mentioned above, by Wolfram and Calloway[7] to impure ferromagnets. The exploitation of the short range of the perturbation (rather than the small magnitude, as in conventional perturbation theory) is applied in our theory to thermodynamic Green's functions, thereby extending the Lifshitz method to thermodynamic properties.

In Sec. II we formulate the equations of motion of the temperature-dependent, two-time, retarded Green's functions for the spins in the perturbed lattice. These Green's functions are decoupled by the random-phase

* Supported in part by the Advanced Research Projects Agency (D. H.) and by the U. S. Office of Naval Research (H. C.). This work is a contribution of the Laboratory for Research on the Structure of Matter, University of Pennsylvania.

[1] J. G. Dash, R. D. Dunlap, and D. G. Howard, Phys. Rev. **141**, 376 (1966).

[2] Y. Koi, A. Tsujimura, and T. Hihara, J. Phys. Soc. Japan **19**, 1493 (1964).

[3] M. E. Caspari, A. Koicki, S. Koicki, and G. T. Wood, Phys. Letters **11**, 195 (1964).

[4] J. Chappert, Phys. Letters **18**, 229 (1965).

[5] A. A. Maradudin and P. A. Dixon, J. Appl. Phys. **31**, 329S (1960); P. Vashishta and J. Mahanty, Proc. Phys. Soc. (London) **84**, 309 (1964).

[6] For electrical conductivity in an impure metal, e.g., see G. Rickayzen in *The Many Body Problem* (W. A. Benjamin, Inc. New York, 1962).

[7] T. Wolfram and J. Calloway, Phys. Rev. **130**, 2207 (1963).

[8] V. Jaccarino, L. R. Walker, and G. K. Wertheim, Phys. Rev. Letters **13**, 752 (1964).

[9] H. Callen, D. Hone, and A. Heeger, Phys. Letters **17**, 233 (1965).

[10] I. M. Lifshitz, Usp. Fiz. Nauk **83**, 617 (1964) [English transl.: Soviet Phys.—Uspekhi **7**, 549 (1965)] and references therein.

[11] See, e.g., E. W. Montroll and R. B. Potts, Phys. Rev. **100**, 525 (1955); **102**, 72 (1956); A. A. Maradudin, P. Mazur, E. W. Montroll, and G. H. Weiss, Rev. Mod. Phys. **30**, 175 (1958); W. M. Visscher, Phys. Rev. **129**, 28 (1963); P. G. Dawber and R. J. Elliott, Proc. Roy. Soc. (London) **273**, 222 (1963).

[12] G. F. Koster and J. C. Slater, Phys. Rev. **96**, 1208 (1954).

approximation (RPA). By assuming that the perturbation is influential over only a finite range, we find the Green's functions can be solved explicitly (and self-consistently). Successive approximations are achieved by assuming successively larger limits on the range of influence of the perturbation, but we demonstrate that the sequence converges extremely rapidly. Accurate results can be obtained by taking the range to be only the nearest-neighbor distance, and such results are presented for various values of host and impurity spins and of the associated exchange parameters.

An investigation very similar to the present one, by Izyumov and Medvedev,[13] has appeared recently. However, those authors introduce the simple boson representation of the spin operators, which simplifies the theory enormously but restricts it to the region of validity of simple (unrenormalized) spin-wave theory. In contrast the RPA form of Green's function theory has been found to be quite successful over the entire temperature range below the Curie temperature, although it admittedly fails to reproduce the niceties of spin-wave renormalizations at low temperatures. In particular, the RPA predictions of Curie temperatures of pure ferromagnets agree well with the "rigorous" Curie temperatures obtained by high-temperature Padé extrapolations.[14] And, perhaps more impressively, the real part of the temperature-dependent self-energy shift of the spin-wave frequencies agrees well with the results of inelastic-neutron-scattering experiments,[15] although the imaginary part (or spin-wave lifetime) is not properly accounted for. The thermodynamic properties are primarily determined by the energy shifts rather than by the lifetimes, so we believe that the theory given here is a reliable description of the thermodynamic properties of isolated impurities over the complete ferromagnetic temperature range.

It should be mentioned that our theory strictly applies only to insulating ferromagnets, but much of the available data is on metallic systems and it is irresistible to make a direct comparison. As pointed out by Dash, Dunlap, and Howard[1] part of the magnetization at an impurity in a metal may arise from the polarization of the conduction electrons, but those authors also find empirically that this conduction-electron contribution is fairly small. Therefore it is tempting to consider the metallic ferromagnet as a collection of localized moments, with the conduction electrons merely providing the mechanism for an effective exchange interaction. At low temperatures this is clearly not an adequate model, but there is at least suggestive evidence[16] that this model may be increasingly satisfactory at higher temperatures. To the extent that such a model may be reasonable, our theory may in fact have relevance to metals.

II. THE GREEN'S FUNCTIONS

Consider a system of localized spins, each of magnitude S except for a single impurity of spin S_I. The exchange interaction between host spins at sites g and l is denoted by $2J_{gl}$, and it is assumed to depend only on the distance between g and l. The position of the impurity is denoted by the subscript c (the "central" ion), and its exchange interaction with a host spin at g is denoted by $2(J_{gc}+j_{gc})$.

Accordingly the Hamiltonian is

$$\mathcal{H}=-h\sum_g S_g{}^z-\sum_{g,l} J_{gl}\mathbf{S}_g\cdot\mathbf{S}_l-2\sum_g j_{gc}\mathbf{S}_g\cdot\mathbf{S}_c, \quad (2.1)$$

where h is the product of the g factor, the Bohr magnetron, and the externally applied magnetic field.

A quantity of primary interest is the thermodynamic expectation value of the z component of spin at site g.

$$\langle S_g{}^z\rangle=\frac{1}{Z}\sum_\alpha e^{-\beta E_\alpha}\langle\alpha|S_g{}^z|\alpha\rangle$$

$$=\frac{1}{2Z}\sum_\alpha e^{-\beta E_\alpha}\langle\alpha|S_g{}^+S_g{}^--S_g{}^-S_g{}^+|\alpha\rangle$$

$$=\frac{1}{2Z}\sum_{\alpha,\gamma} e^{-\beta E_\alpha}(|\langle\gamma|S_g{}^-|\alpha\rangle|^2-|\langle\gamma|S_g{}^+|\alpha\rangle|^2), \quad (2.2)$$

where Z is the partition function, β is the inverse temperature, and α and γ label the exact eigenstates of the system. By rewriting this equation in a spectral representation we find the natural emergence of the appropriate Green's function:

$$\langle S_g{}^z\rangle=\frac{1}{2}\int dE[A_g(\beta,E)-B_g(\beta,E)]$$

$$=\frac{1}{2}\int dE(1-e^{-\beta E})\mathrm{A}_g(\beta,E), \quad (2.3)$$

where

$$A_g(\beta,E)=\frac{1}{Z}\sum_{\alpha,\gamma} e^{-\beta E_\alpha}|\langle\gamma|S_g{}^-|\alpha\rangle|^2\delta(E-E_\gamma+E_\alpha) \quad (2.4)$$

and

$$B_g(\beta,E)=\frac{1}{Z}\sum_{\alpha,\gamma} e^{-\beta E_\alpha}|\langle\gamma|S_g{}^+|\alpha\rangle|^2\delta(E-E_\alpha+E_\gamma)$$

$$=e^{-\beta E}A_g(\beta,E). \quad (2.5)$$

$A_g(\beta,E)/2\langle S_g{}^z\rangle$ measures the probability that a single spin-flip excitation of energy E, occurring with the system at temperature $1/\beta$, will flip the particular spin at the site g: The initial state $|\alpha\rangle$ occurs with weight $e^{-\beta E_\alpha}$, all final states $|\gamma\rangle$ with the correct energy E above E_α are summed over, and $S_g{}^-$ just projects out

[13] Yu. A. Izyumov and M. V. Medvedev, Zh. Experim. Teor. Fiz. 48, 574 (1965) [English transl. Soviet Phys.—JETP 21, 381 (1965)].
[14] Geogre A. Baker, Jr., Phys. Rev. 136, A1376 (1964), and references therein.
[15] K. C. Turberfield, A. Okazaki, and R. W. H. Stevenson, Proc. Phys. Soc. (London) 85, 743 (1965).
[16] T. Moriya, Progr. Theoret. Phys. (Kyoto) 33, 159 (1965).

(with weight $2\langle S_g{}^z\rangle$) that part of $|\gamma\rangle$ which differs from $|\alpha\rangle$ only by a spin flip at g. With this interpretation in mind, henceforth we shall call $A_g(\beta,E)$ the "spectral weight function" at site g.[17] The argument of the integral in Eq. (2.3) is (-2) times the imaginary part of the retarded Green's function $G_{gg}(E)$:

$$G_{gg}(E)=\int \frac{dE'}{2\pi}\frac{(1-e^{-\beta E'})A_g(\beta,E')}{E-E'+i0^+}, \tag{2.6}$$

$$(1-e^{-\beta E})A_g(\beta,E)=-2\,\mathrm{Im}G_{gg}(E). \tag{2.7}$$

It is natural to consider the slightly more general function $G_{gl}(E)$, which is the Fourier transform of the double-time, retarded, thermodynamic Green's function[18] $G_{gl}(t)$:

$$G_{gl}(t)=-i\langle\langle S_g{}^+(t);S_l{}^-(0)\rangle\rangle \equiv -i\theta(t)\langle[S_g{}^+(t),S_l{}^-(0)]\rangle. \tag{2.8}$$

Here $\theta(t)$ is the unit step function. The quantity $G_{gl}(E)$ is the transfer admittance function,[18] measuring the response of the g'th spin to a small applied magnetic field acting only on the lth spin and rotating in the x-y plane with angular frequency $E/\hbar$. This interpretation is transparent in Eq. (2.7), which relates the energy absorption (the imaginary part of the response) to the difference in the probabilities of turning a spin down (and absorbing a photon from the driving field) and of turning a spin up (and of emitting a photon to the field).

Given the Green's function, and thence the spectral weight function $A_g(\beta,E)$, one could calculate $\langle S_g{}^z\rangle$ by Eq. (2.3). However, it is preferable to use an independent relationship proved by Callen[19] and recast in a more convenient form by Callen and Shtrikman.[20] For this purpose one first defines a "quasiboson energy" $\Omega(g)$, such that

$$1/[e^{\beta\Omega(g)}-1]=\int_{-\infty}^{\infty}dE A_g(\beta,E)e^{-\beta E}/2\langle S^z\rangle. \tag{2.9}$$

Then the Green's-function formalism implies that

$$\langle S_g{}^z\rangle=S_g B_{s_g}(\beta\Omega(g)), \tag{2.10}$$

where B_s is the Brillouin function corresponding to the spin magnitude S

$$SB_s(\beta\Omega)=(S+\tfrac{1}{2})\coth\frac{\beta\Omega(2S+1)}{2S}-\tfrac{1}{2}\coth\frac{\beta\Omega}{2S}. \tag{2.11}$$

If the quasiboson energy were to be proportional to $\langle S_g{}^z\rangle$ then the solution of Eq. (2.10) would correspond to a molecular field theory. But, of course, the solution of Eq. (2.9) for $\Omega(g)$ will not generally be of this simple form.

In order to calculate the Green's functions we employ the equation of motion

$$i(d/dt)G_{gl}(t)=\langle[S_g{}^+,S_l{}^-]\rangle\delta(t) +\langle\langle[S_g{}^+(t),\mathcal{H}];S_l{}^-(0)\rangle\rangle \tag{2.12}$$

and we invoke the random-phase approximation,[21]

$$\langle\langle S_m{}^z(t)S_g{}^+(t);S_l{}^-\rangle\rangle\rightarrow\langle S_m{}^z\rangle\langle\langle S_g{}^+(t);S_l{}^-\rangle\rangle \tag{2.13}$$

from which we directly find

$$[E-h-2\sum_m J_{gm}\langle m^z\rangle]G_{gl}(E)+2\sum_m J_{gm}\langle g^z\rangle G_{ml}(E) =\frac{1}{\pi}\langle g^z\rangle\delta_{gl}+2\sum_m j_{gm}\langle m^z\rangle G_{gl}(E) -2\sum_m j_{gm}\langle g^z\rangle G_{ml}(E). \tag{2.14}$$

We have abbreviated $\langle S_g{}^z\rangle$ as $\langle g^z\rangle$, and we interpret j_{gm} as zero unless either g or m is equal to c, the central ion. The expectation values $\langle g^z\rangle$ (or $\langle m^z\rangle$) are actually unknown at this point, but they are to be carried as parameters in the calculation, ultimately to be determined self-consistently.

We now seek to isolate to the right-hand side of the equation all terms explicitly involving the perturbation. We therefore define

$$\langle\delta m\rangle=\langle m^z\rangle/\langle S^z\rangle-1, \tag{2.15}$$

where $\langle S^z\rangle$ is the magnetization per ion in the pure host crystal (or in the impure crystal at great distances from the impurity). Then Eq. (2.14) is rewritten as

$$[E-h-2\langle S^z\rangle\sum_m J_{gm}]G_{gl}(E)+2\langle S^z\rangle\sum_m J_{gm}G_{ml}(E) =\delta_{gl}\langle g^z\rangle/\pi+2\sum_m j_{gm}\langle m^z\rangle G_{gl}(E)-2\sum_m j_{gm}\langle g^z\rangle G_{ml}(E) +2\langle S^z\rangle\sum_m J_{gm}\langle\delta m\rangle G_{gl}(E)-2\langle S^z\rangle\sum_m J_{gm}\langle\delta g\rangle G_{ml}(E). \tag{2.16}$$

Consider l fixed, taking it specifically to be c. The first and second summations on the right-hand side of the equation actually involve only a very few terms, because of the factors j_{gm}. If $\langle\delta m\rangle$ were also limited in range, being appreciable only in the vicinity of c, then the last two summations would be similarly limited. We proceed on the general assumption that this is in fact true; the accuracy of this approximation will be central to our method. Then we invert Eq. (2.16) by defining

[17] The quantity $\frac{1}{2}(1-e^{-\beta\omega})A_c(\omega)$ is commonly referred to as "the spectral weight function of the Green's function $G_{cc}(\omega)$," whereas $A_c(\omega)$ is the "spectral weight function of $\langle S_c{}^+S_c{}^-\rangle$."

[18] See D. N. Zubarev, Usp. Fiz. Nauk **71**, 71 (1960) [English transl.: Soviet Phys.—Uspekhi **3**, 320 (1960)].

[19] Herbert B. Callen, Phys. Rev. **130**, 89 (1963).

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

[21] S. V. Tyablikov, Ukr. Matem. Zh. **11**, 287 (1959). A review may be found in Ref. 18.

the classical Green's functons $L_{gn}(E)$ by

$$[E-h-2\langle S^z\rangle\sum_m J_{gm}]L_{gn}(E) +2\langle S^z\rangle\sum_m J_{gm}L_{mn}(E)=\delta_{gn} \quad (2.17)$$

and writing Eq. (2.16) in the form

$$[E-h-2\langle S^z\rangle\sum_m J_{gm}]G_{gc}(E) +2\langle S^z\rangle\sum_m J_{gm}G_{mc}(E)=R_g, \quad (2.18)$$

where

$$R_g=\delta_{gc}\langle g^z\rangle/\pi+2\sum_m[J_{gm}\langle\delta m\rangle\langle S^z\rangle+j_{gm}\langle m^z\rangle G_{gc}(E) -2\sum_m[J_{gm}\langle\delta g\rangle\langle S^z\rangle+j_{gm}\langle g^z\rangle]G_{mc}(E). \quad (2.19)$$

The solution of Eq. (2.18) is

$$G_{gc}(E)=\sum_n L_{gn}R_n. \quad (2.20)$$

The Green's function $L_{gn}(E)$ is $(\pi/\langle S^z\rangle)G_{gn}{}^0(E)$, where $G_{gn}{}^0(E)$ is the Green's function of the pure host, as can be seen by comparing Eq. (2.17) with Eq. (2.16) and taking $j_{gn}=\langle\delta m\rangle=0$. Accordingly, Eq. (2.17) can be diagonalized by spatial Fourier transformation and $L_{gn}(E)$ is obtained as the propagator of RPA-renormalized spin waves in the pure host,

$$L_{gn}(E)=\frac{1}{N}\sum_{\mathbf{k}}\frac{\exp[-i\mathbf{k}\cdot(\mathbf{g}-\mathbf{n})]}{E-h-2\langle S^z\rangle[J(0)-J(\mathbf{k})]} =\frac{1}{N}\sum_{\mathbf{k}}\frac{\exp[-i\mathbf{k}\cdot(\mathbf{g}-\mathbf{n})]}{E-E(\mathbf{k})}, \quad (2.21)$$

where $\mathbf{g}$ denotes the vector position of ion g, and $J(\mathbf{k}')$ is the Fourier transform of J_{gm}

$$J(\mathbf{k})=\sum_g J_{gm}\exp[i\mathbf{k}\cdot(\mathbf{g}-\mathbf{m})]. \quad (2.22)$$

Let us suppose that the range of j_{gc} and the range of $\langle\delta m\rangle$ were such that only some small number (N_0) of Green's functions appeared in Eq. (2.19). Then writing N_0 equations of the form of Eq. (2.20) we would obtain N_0 simultaneous equations for the N_0 functions—a soluble problem. Undoubtedly, $\langle\delta m\rangle$ falls rapidly toward zero as $|m-c|$ increases, but it never rigorously vanishes. Nevertheless it is clear that increasingly accurate approximations can be made by neglecting $\langle\delta m\rangle$ beyond increasingly greater distances from the impurity ion. We shall explicitly study two approximations. In the first, we neglect $\langle\delta m\rangle$ unless $m=c$. In the second, we neglect $\langle\delta m\rangle$ unless $m=c$ or f, where f denotes a nearest neighbor of c. Both give very nearly the same results for $\langle\delta c\rangle$, and $\langle\delta f\rangle$ is found to be very small indeed in the second approximation. This convergence encourages us to believe that the second approximation is a fully satisfactory one.

III. THE SIMPLE-CUBIC NEAREST-NEIGHBOR MODEL

In order to exhibit numerical results we must explicate our model, and we henceforth assume a simple cubic Bravais array of spins interacting by nearest-neighbor interactions only. The central impurity ion is indicated by c, its six first-neighbor ions at $\langle 100\rangle$ by f (or, when these must be distinguished, by f', f'',$\cdots$), its twelve second-neighbor ions at $\langle 100\rangle$ by s, and its third-neighbor ions at $\langle 200\rangle$ by t.

An enormous simplification occurs in the thermodynamic theory, as contrasted with the zero-temperature theory of Wolfram and Calloway. In their theory the amplitude of the wave function at f plays the role of G_{fc}, and $\Psi_{f'}$ need not be equal to $\Psi_{f''}$. But the symmetry of the thermodynamic state ensures that G_{fc} (as well as $\langle f^z\rangle$ and L_{fc}) is identical for all the six first-neighbor ions f. Of course, we pay heavily for this advantage, for the analogs of the last two troublesome terms in Eq. (2.16) are absent in the zero-temperature theory.

We denote the single nonvanishing host-host exchange integral by J, and j_{fc} by j.

It is convenient now to adopt a system of units in which all energies are measured in units of $2zJ\langle S^z\rangle$:

$$\frac{E}{12J\langle S^z\rangle}=\mathcal{E}, \text{ or } \omega, \qquad \frac{\Omega(g)}{12J\langle S^z\rangle}=\omega(g)$$
$$12J\langle S^z\rangle G=\mathcal{G}, \qquad 12J\langle S^z\rangle L=\mathcal{L}. \quad (3.1)$$

In these units the spin-wave band of the unperturbed host lattice extends from $\omega=0$ to $\omega=2$.

The crystal Green's functions $L_{lj}(\omega)$ for a simple-cubic structure have been studied, and several functions (of low indices) have been tabulated,[7,22] but not all those required are available. We have therefore tabulated the necessary functions, the values being given in Table I. Details of the evaluation procedure are given in Appendix A.

For the simple-cubic nearest-neighbor model the following useful identities can be proved directly from the definition (2.21) of L_{gn}.

$$\tfrac{1}{6}\sum_f \mathcal{L}_{fl}(\omega)=\delta_{lc}-(\omega-1)\mathcal{L}_{cc}, \quad (3.2)$$

$$\sum_{l^*}\mathcal{L}_{fl}(\omega)=\delta_{lc}-(\omega-1)N_l\mathcal{L}_{lc}, \quad (3.3)$$

$$4\sum_{l^*}\mathcal{L}_{sl}(\omega)=6[\delta_{lf}-(\omega-1)\delta_{lc}] +[6(\omega-1)^2-1]N_l\mathcal{L}_{lc}-\sum_{l^*}\mathcal{L}_{tl}. \quad (3.4)$$

[22] M. Yussouff and J. Mahanty, Proc. Phys. Soc. (London) 85, 1223 (1965).

TABLE I. The functions $\mathfrak{L}_{ij}(\omega)$. These are proportional to the pure-crystal Green's functions: $\mathfrak{L}_{ij}(\omega)=\pi\mathcal{G}_{ij}(\omega)/\langle S^z\rangle$. The running index i in the first column for in-band frequencies labels the "Gaussian frequency" ω_i, defined by Eq. (A2). For $1<\omega<2$, $\mathfrak{L}_{ij}(\omega)=-\mathfrak{L}_{ij}(2-\omega)$.

i	ω	$\mathfrak{L}_{cc}(\omega)$	$\mathfrak{L}_{sc}(\omega)$	$\mathfrak{L}_{tc}(\omega)$	$\bar{\mathfrak{L}}_{tt'}(\omega)$
1	0.0086790	$-1.51877-0.09526i$	$-0.31400-0.09423i$	$-0.23349-0.09133i$	$-2.13235-0.52526i$
2	0.0412512	$-1.53040-0.24324i$	$-0.25260-0.22335i$	$-0.14914-0.20412i$	$-1.56575-1.02718i$
3	0.0837488	$-1.55199-0.35990i$	$-0.17838-0.30111i$	$-0.05651-0.24790i$	$-1.10506-1.02348i$
4	0.1163210	$-1.56850-0.43915i$	$-0.12112-0.33987i$	$0.00639-0.25690i$	$-0.89959-0.90372i$
5	0.1336790	$-1.57864-0.47384i$	$-0.09222-0.35286i$	$0.03542-0.25002i$	$-0.84449-0.78979i$
6	0.1662512	$-1.59283-0.54548i$	$-0.03481-0.37297i$	$0.08940-0.23673i$	$-0.77832-0.61784i$
7	0.2087488	$-1.61492-0.63538i$	$0.03732-0.38656i$	$0.14493-0.20429i$	$-0.82444-0.40022i$
8	0.2413210	$-1.63328-0.70679i$	$0.09199-0.38951i$	$0.17734-0.17421i$	$-0.93101-0.27846i$
9	0.2586790	$-1.64329-0.74109i$	$0.12004-0.38797i$	$0.19109-0.15198i$	$-1.00736-0.20260i$
10	0.2912512	$-1.66009-0.81471i$	$0.17364-0.38106i$	$0.21306-0.11529i$	$-1.15943-0.13625i$
11	0.3337488	$-1.68480-0.91289i$	$0.24167-0.36378i$	$0.22682-0.06221i$	$-1.40589-0.09995i$
12	0.3663210	$-1.70602-0.99467i$	$0.29324-0.34424i$	$0.22568-0.02307i$	$-1.62059-0.13341i$
13	0.3836790	$-1.71642-1.03548i$	$0.31958-0.33193i$	$0.22247+0.00219i$	$-1.73285-0.13929i$
14	0.4162512	$-1.73590-1.12603i$	$0.36944-0.30329i$	$0.21019+0.03837i$	$-1.94190-0.23833i$
15	0.4587488	$-1.76388-1.25226i$	$0.43278-0.25746i$	$0.17850+0.08233i$	$-2.23046-0.41222i$
16	0.4913210	$-1.78932-1.36277i$	$0.48112-0.21425i$	$0.14003+0.10558i$	$-2.47530-0.61346i$
17	0.5086790	$-1.79961-1.41982i$	$0.50507-0.18959i$	$0.11898+0.12100i$	$-2.58889-0.69954i$
18	0.5412512	$-1.82200-1.55468i$	$0.55081-0.13272i$	$0.06959+0.12405i$	$-2.82288-1.00461i$
19	0.5837488	$-1.85294-1.76062i$	$0.60848-0.04259i$	$-0.01087+0.10216i$	$-3.16196-1.51971i$
20	0.6163210	$-1.88745-1.97244i$	$0.65454+0.04911i$	$-0.09441+0.03516i$	$-3.51570-2.17450i$
21	0.6336790	$-1.89007-2.09216i$	$0.67300+0.10309i$	$-0.12758-0.00515i$	$-3.62990-2.53072i$
22	0.6662512	$-1.82058-2.60546i$	$0.68212+0.30662i$	$-0.12286-0.36063i$	$-3.43371-4.81916i$
23	0.7087488	$-1.24603-2.70722i$	$0.51099+0.39427i$	$0.31458-0.24609i$	$-0.76755-4.31100i$
24	0.7413210	$-1.01445-2.70664i$	$0.43735+0.43013i$	$0.41134-0.09950i$	$-0.16595-3.69066i$
25	0.7586790	$-0.92979-2.71021i$	$0.40845+0.44893i$	$0.41721-0.03262i$	$-0.09606-3.45706i$
26	0.7912512	$-0.76630-2.69926i$	$0.34892+0.47448i$	$0.42234+0.09739i$	$0.05737-3.01958i$
27	0.8337488	$-0.58588-2.69489i$	$0.27640+0.50471i$	$0.38010+0.23091i$	$0.09105-2.67755i$
28	0.8663210	$-0.45631-2.69341i$	$0.22038+0.52349i$	$0.32959+0.31146i$	$0.10238-2.51991i$
29	0.8836790	$-0.39910-2.69373i$	$0.19364+0.53226i$	$0.28825+0.34619i$	$0.05218-2.46727i$
30	0.9162512	$-0.28140-2.68858i$	$0.13870+0.54332i$	$0.21716+0.40399i$	$0.04456-2.36653i$
31	0.9587488	$-0.13736-2.68702i$	$0.06839+0.55324i$	$0.10967+0.44844i$	$0.01733-2.31153i$
32	0.9913210	$-0.02598-2.68855i$	$0.01343+0.55695i$	$0.02608+0.46003i$	$0.02028-2.30873i$
	2.1	1.13044	0.10291	0.06307	1.21184
	2.2	0.97934	0.06190	0.03537	1.00785
	2.3	0.87494	0.04353	0.02399	0.89181
	2.4	0.79373	0.03049	0.01689	0.80259
	2.5	0.72835	0.02380	0.01248	0.73298
	2.6	0.67428	0.01848	0.00984	0.67835
	2.7	0.62779	0.01412	0.00749	0.62945
	2.8	0.58819	0.01234	0.00627	0.59030
	2.9	0.55373	0.00982	0.00545	0.55625
	3.0	0.52307	0.00866	0.00450	0.52388
	3.1	0.49606	0.00774	0.00393	0.49659
	3.2	0.47177	0.00642	0.00330	0.47156
	3.3	0.44980	00.0627	0.00255	0.44802
	3.4	0.43097	0.00510	0.00283	0.43230
	3.5	0.41354	0.00436	0.00251	0.41447
	3.6	0.39760	0.00403	0.00207	0.39797
	3.7	0.38312	0.00306	0.00169	0.38353
	3.8	0.36971	0.00293	0.00115	0.36902
	3.9	0.35771	0.00239	0.00097	0.35705
	4.0	0.34700	0.00179	0.00120	0.34764

In the latter two equations the summations over l^* denote summations over the "star of l", or over all sites equivalent to l under the operations of the cubic group. The number of such sites is denoted by N_l.

With all these preliminaries disposed of we can proceed to the first approximation, in the following section. We note in passing, however, that the simplest possible approximation (the "zeroth" approximation) can be obtained by relaxing the requirement of self-consistency, and taking $\langle\delta m\rangle=0$ for *all* m. This zeroth approximation, with the additional simplification $S_I=S$, was reported in a preliminary account of the present work.[9]

IV. FIRST APPROXIMATION: ZERO RANGE OF SPIN DEVIATION

We tentatively assume that all spin deviations $\langle\delta m\rangle$ except $\langle\delta c\rangle$ are negligible, and proceed to evaluate this single unknown spin deviation. Writing Eqs. (19)–(20) successively for G_{cc} and G_{fc} we obtain two coupled linear equations, which are trivially solved to give

$$\mathcal{G}_{cc}=\frac{\langle c^z\rangle}{\pi}\,\frac{\mathfrak{L}_{cc}+\mathfrak{L}_{fc}(j/J)+\langle\delta c\rangle(1+j/J)\mathfrak{L}_{cf}}{1+(j/J)(1+\omega-\omega^2\mathfrak{L}_{cc})+\omega\langle\delta c\rangle(1+j/J)\mathfrak{L}_{fc}}. \tag{4.1}$$

The zeros of the denominator give all but one of the single-spin-excitation frequencies because the poles of the numerator [at $\omega=\mathcal{E}(\mathbf{k})$] are cancelled by corresponding poles in the denominator. The exceptional case is the pole of the numerator at $\omega=0$, which is not cancelled and which remains as an eigenfrequency of the perturbed system. This mode is the uniform precession of all spins, which is unaffected by spin magnitude or exchange interaction.

The poles of $\mathcal{G}_{cc}$ are spaced in a way which is familiar in other impurity problems,[21] being interleaved between the unperturbed eigenvalues $\mathcal{E}(\mathbf{k})$, except for one possible pole which is split off the band. Thus, the density of states in the band is unchanged (to order $1/N$) from that in the pure crystal. To see that this is so we examine the denominator of $\mathcal{G}_{cc}$, which is given explicitly by

$$\left(1+\frac{j}{J}\right)(1+\omega\langle\delta c\rangle)+\frac{j}{J}\omega-\left[\langle\delta c\rangle(\omega-1)\left(1+\frac{j}{J}\right)+\frac{j}{J}\omega\right]\times\frac{\omega}{N}\sum_{\mathbf{k}}\frac{1}{\omega-\mathcal{E}(\mathbf{k})}. \quad (4.2)$$

As ω varies between two successive values of $\mathcal{E}(\mathbf{k})$, which are separated by $O(1/N)$,the sum goes monotonically from plus to minus infinity. If the quantity in brackets does not have a zero in this small interval, the entire last term in Eq. (4.2) behaves similarly. The first three terms of Eq. (4.2) are simply linear in ω, and the corresponding straight line intersects the nearly vertical curve at some point in the interval. Thus, the poles of $\mathcal{G}_{cc}$ alternate with the unperturbed spin-wave poles $\mathcal{E}(\mathbf{k})$.

In addition to the interleaved poles, one pole can be split off the top of the band. The values of the parameters necessary for the appearance of such a localized mode can be determined by setting (4.2) equal to zero for ω just above the top of the spin-wave band ($\omega=2$). At this energy $\mathcal{L}_{cc}$ is equal[7] to 1.48. Thus the marginal condition for a localized mode is

$$(1+j/J)(1+2\langle\delta c\rangle)+2j/J-[\langle\delta c\rangle(1+j/J)+2j/J](2.96)=0 \quad (4.3)$$

or

$$\frac{j}{J}>\frac{1-0.96\langle\delta c\rangle}{2.92+0.96\langle\delta c\rangle}. \quad (4.4)$$

At zero temperature $\langle\delta c\rangle$ is simply $(S_I-S)/S$, and Eq. (4.4) then reproduces the criterion found by Wolfram and Calloway. In particular j/J must be greater than 0.34 for $S_I=S$.

If j/J is positive, we expect $\langle\delta c\rangle$ to be greater than $(S_I-S)/S$ at higher temperatures. Thus, the requirement on j/J becomes less stringent as temperature increases.[22] We shall subsequently see that a localized mode can appear at elevated temperatures even though it does not exist at zero temperature.

It should be noted that only a single localized mode appears when we study $\mathcal{G}_{cc}$, whereas Wolfram and Calloway found seven, of s, p, and d symmetry. Obviously this is a result of the fact that only the s-like mode has a nonzero amplitude at the central ion. The other localized modes would appear as poles of the Green's function $\mathcal{G}_{ff}$.

Comparison of Eqs. (2.6) and (4.1) reveals that the spectral weight function $A_c(\beta,\omega)$ consists of a set of delta functions at the poles of $\mathcal{G}_{cc}(\omega)$. As $N\to\infty$ the poles of $\mathcal{G}_{cc}(\omega)$ crowd together quasidensely, except for the possible isolated pole above the spin-wave band. If we then examine $G_{cc}(\omega+i\epsilon)$ for fixed small positive ϵ we will not be able to distinguish the effects of the separate poles when the eigenvalue separation becomes much less than ϵ, and the distribution of poles will appear like a cut along the real ω axis. Thus taking the limit $N\to\infty$ first, and then $\epsilon\to 0$, we effectively average over the quasidense poles. In the language of many-body theory, a "quasiparticle" is formed as a superposition of neighboring eigenstates. The dephasing of these states in time gives an apparent imaginary part to the energy, or appears as a lifetime of the quasiparticle.

In the limiting process defined above, the quantity $\mathcal{L}_{cc}(\omega)$ is

$$\lim_{\epsilon\to 0^+}\lim_{N\to\infty}\mathcal{L}_{cc}(\omega+i\epsilon)=P\int\frac{d^3k}{(2\pi)^3}\frac{1}{\omega-\mathcal{E}(\mathbf{k})}-i\pi\int\frac{d^3k}{(2\pi)^3}\delta(\omega-\mathcal{E}(\mathbf{k}))\equiv P_{cc}(\omega)-i\pi N(\omega)/N, \quad (4.5)$$

where $P_{cc}(\omega)$ is defined by the principal value integral, and $N(\omega)/N$ is the density of states per site in the unperturbed crystal.

For ω within the band we now have, by Eqs. (2.7), (4.1), and (4.5), and the identity (3.2),

$$A_c(\beta,\omega)=\frac{\langle c^z\rangle^2/\langle S^z\rangle}{1-e^{-\beta\omega}}\frac{N(\omega)}{N}\xi^2/[\{\xi(1+\langle\delta c\rangle)+[\omega+\xi\langle\delta c\rangle(\omega-1)][1-\omega P_{cc}]\}^2+\omega^2[\omega+\xi\langle\delta c\rangle(\omega-1)]^2\pi^2N^2(\omega)/N^2], \quad (4.6)$$

where

$$\xi\equiv 1+J/j. \quad (4.7)$$

We recall that Eq. (2.3) provides us with a sum rule which, in our reduced units, is

$$\int d\omega(1-e^{-\beta\omega})A_c(\beta,\omega)/\langle c^z\rangle=2. \quad (4.8)$$

This can be used as a check of self-consistency when there is no localized mode, or it can be used to evaluate the weight of the localized mode when it exists. In

Fig. 2 of Ref. 9 we plotted the integrand of Eq. (4.8), divided by $N(\omega)/N$, as a function of ω. Recalling the interpretation of $A_c(\beta,\omega)$ given in Sec. II, we see that this removal of the density-of-states factor [which, to $O(1/N)$ can be taken to be the perturbed density of states] leaves a function describing the probability for a *single* excitation of energy ω to flip the impurity spin. Any deviations from the pure host value of unity are readily observed in such a plot. By Eq. (4.8) the product of these curves and $N(\omega)/N$ should be normalized to 2 when no localized mode is present; even in this crude approximation we found excellent normalization.

At this point we should evaluate $\langle c^z\rangle$ by Eqs. (2.9)–(2.11), but as that requires considerable labor we proceed directly to the second approximation, which will be evaluated fully and explicitly.

V. SECOND APPROXIMATION: NUMERICAL ANALYSIS

Returning to Eqs. (2.19) and (2.20) assuming only $\langle\delta c\rangle$ and $\langle\delta f\rangle$ to be nonzero, we find we can write four simultaneous equations for the Green's functions $\mathcal{G}_{cc}$, $\mathcal{G}_{fc}$, $\mathcal{G}_{sc}$, and $\mathcal{G}_{tc}$. These are most succinctly written in matrix notation

$$\mathcal{C}\begin{bmatrix}\mathcal{G}_{cc}\\ \mathcal{G}_{fc}\\ \mathcal{G}_{sc}\\ \mathcal{G}_{tc}\end{bmatrix}=\frac{\langle c^z\rangle}{\pi}\begin{bmatrix}\mathcal{L}_{cc}\\ \mathcal{L}_{fc}\\ \mathcal{L}_{sc}\\ \mathcal{L}_{tc}\end{bmatrix} \tag{5.1}$$

or

$$\sum_j \mathcal{C}_{ij}\mathcal{G}_{jc}=\frac{\langle c^z\rangle}{\pi}\mathcal{L}_{ic}, \tag{5.2}$$

where

$$\mathcal{C}=\begin{bmatrix}1+(\mathcal{L}_{cf}-\mathcal{L}_{cc})+(j/J+\eta\langle\delta f\rangle) & (j/J+\eta\langle\delta c\rangle)(\omega\mathcal{L}_{cc}-1) & 4(\mathcal{L}_{cf}-\mathcal{L}_{cs})\langle\delta f\rangle & (\mathcal{L}_{cf}-\mathcal{L}_{ct})\langle\delta f\rangle\\ -\omega\mathcal{L}_{fc}(j/J+\eta\langle\delta f\rangle) & 1+(j/J+\eta\langle\delta c\rangle)\omega\mathcal{L}_{fc} & \tfrac{1}{3}(2\sum_{f'}\mathcal{L}_{ff'}-\sum_{s}\mathcal{L}_{fs})\langle\delta f\rangle & \tfrac{1}{6}[\sum_{f'}\mathcal{L}_{ff'}-\sum_{t}\mathcal{L}_{ft}]\langle\delta f\rangle\\ -\omega\mathcal{L}_{sc}(j/J+\eta\langle\delta f\rangle) & \omega\mathcal{L}_{sc}(j/J+\eta\langle\delta c\rangle) & 1+\tfrac{1}{3}(2\sum_{f}\mathcal{L}_{sf}-\sum_{s'}\mathcal{L}_{ss'})\langle\delta f\rangle & \tfrac{1}{6}[\sum_{f}\mathcal{L}_{sf}-\sum_{t}\mathcal{L}_{st}]\langle\delta f\rangle\\ -\omega\mathcal{L}_{tc}(j/J+\eta\langle\delta f\rangle) & \omega\mathcal{L}_{tc}(j/J+\eta\langle\delta c\rangle) & \tfrac{1}{3}(2\sum_{f}\mathcal{L}_{tf}-\sum_{s}\mathcal{L}_{ts})\langle\delta f\rangle & 1+\tfrac{1}{6}[\sum_{f}\mathcal{L}_{tf}-\sum_{t'}\mathcal{L}_{tt'}]\langle\delta f\rangle\end{bmatrix}, \tag{5.3}$$

and we have defined

$$\eta=1+j/J. \tag{5.4}$$

Solving for $\mathcal{G}_{cc}(\omega)$, we find

$$\mathcal{G}_{cc}=(\mathfrak{N}/\mathfrak{D})\langle c^z\rangle/\pi, \tag{5.5}$$

where

$$\mathfrak{D}=\det\mathcal{C},$$

and $\mathfrak{N}$ is the determinant of the same matrix except for the replacement of $\mathcal{C}_{lc}$ by $\mathcal{L}_{lc}$. By judicious subtraction of rows or columns these determinants can be reduced by one order, so that

$$\mathfrak{N}=\begin{bmatrix}\eta(1+\langle\delta c\rangle)-1+\alpha\mathcal{L}_{cc} & 4\langle\delta f\rangle(\mathcal{L}_{tc}-\mathcal{L}_{sc}) & \langle\delta f\rangle[1-(\omega-1)\mathcal{L}_{cc}-\mathcal{L}_{tc}]\\ \alpha\mathcal{L}_{cc} & 1-[(5/4)\bar{\mathcal{L}}_{tt'}+\Lambda(\mathcal{L}_{sc}-5\mathcal{L}_{tc}/4)]\langle\delta f\rangle & -\langle\delta f\rangle[\bar{\mathcal{L}}_{tt'}+\Lambda(\mathcal{L}_{sc}-\mathcal{L}_{tc})+(\omega-1)\mathcal{L}_{sc}]\\ \alpha(\mathcal{L}_{tc}+4\mathcal{L}_{sc}) & 0 & 1-\langle\delta f\rangle(\omega-1)(\mathcal{L}_{tc}+4\mathcal{L}_{sc}-\Lambda\mathcal{L}_{cc})+\Lambda]\\ -\Lambda[\eta(1+\langle\delta c\rangle)-1+\alpha\mathcal{L}_{cc}] & & \end{bmatrix}, \tag{5.6}$$

$$\mathfrak{D}=\begin{bmatrix}\omega\mathfrak{N}_{11}+\eta(1+\langle\delta f\rangle)(1-\omega\mathcal{L}_{cc}) & \mathfrak{N}_{12} & \mathfrak{N}_{13}\\ \alpha-\eta(1+\langle\delta f\rangle)\omega\mathcal{L}_{sc} & \mathfrak{N}_{22} & \mathfrak{N}_{23}\\ \omega-\mathfrak{N}_{31}-\eta(1+\langle\delta f\rangle)\{\omega\mathcal{L}_{tc}+4\omega\mathcal{L}_{sc}+\Lambda[1-(\omega-1)\mathcal{L}_{cc}]\} & 0 & \mathfrak{N}_{23}\end{bmatrix}, \tag{5.7}$$

where $\bar{\mathcal{L}}_{tt'}$ denotes $\frac{1}{6}\sum_{t'}\mathcal{L}_{tt'}$, and where

$$\alpha\equiv(1-\omega)\eta(1+\langle\delta c\rangle)+\omega, \tag{5.8}$$

$$\Lambda\equiv 6(1-\omega)^2-1. \tag{5.9}$$

Discussion of the poles of the Green's function parallels that in the preceding section, with similar conclusions. We proceed directly to the evaluation of $\langle c^z\rangle$ and $\langle f^z\rangle$. We then calculate $A_c(\beta,\omega)$ by Eqs. (2.7) and (5.6)–(5.7). This spectral weight function in turn yields a quasiboson energy $\omega(c)$ after integration according to Eq. (2.9); the numerical integrations have been carried out by Gaussian-quadrature methods, as discussed in Appendix A. Finally $\langle c^z\rangle$ is calculated by Eq. (2.10), to be used again as the starting approximation for a repetition of the complete cycle, until self-consistency is obtained.

For complete self-consistency, we should, of course,

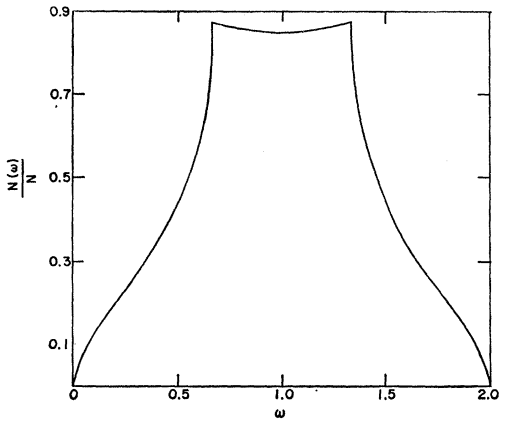


FIG. 1. The density of states per spin, $N(\omega)/N$, within the spin-wave band. This density of states is the same (to order $1/N$) for impure and pure host crystals.

calculate G_{ff}, to evaluate $\langle f^z\rangle$ by an analogous procedure. Instead we have resorted to the relatively simple molecular field theory, which should be sufficient for the small quantity $\langle\delta f\rangle$. Consider a spin in the first shell. In our approximation, it has five normal neighbors with magnetization $\langle S^z\rangle$, and one abnormal neighbor, with magnetization $\langle c^z\rangle$. The increment in the molecular field acting on this f-shell spin is then

$$\Delta h=2(J+j)\langle c^z\rangle-2J\langle S^z\rangle=2J\langle S^z\rangle[j/J+\eta\langle\delta c\rangle]. \quad (5.10)$$

The increment in magnetization of the f-site ion is therefore

$$\langle S^z\rangle\langle\delta f\rangle=\chi\Delta h, \quad (5.11)$$

where χ is the molecular field susceptibility. Inserting this susceptibility explicitly, we find

$$\langle\delta f\rangle=\frac{1}{6}\left[\frac{j}{J}+\eta\langle\delta c\rangle\right]\times\left[1-\frac{4\langle S^z\rangle/\beta\omega_0}{(2S+1)^2\,\mathrm{csch}^2[(S+\tfrac{1}{2})\beta\omega_0]-\mathrm{csch}^2(\tfrac{1}{2}\beta\omega_0)}\right], \quad (5.12)$$

where ω_0 is the quasiboson frequency of the pure host at the given temperature $1/\beta$.

At each stage in the iteration we have simply related $\langle\delta f\rangle$ to $\langle\delta c\rangle$ by Eq. (5.12). The first guess of $\langle c^z\rangle$ was taken as S_I/S.

Our criterion of self-consistency was a rather stringent one, requiring that the difference in the values of $\langle c^z\rangle$ on successive iterations be less than 0.01. In almost all cases the required convergence was obtained in less than five iterations, being slowest, of course, at high temperatures and for large disparity between host and impurity parameters. At each iteration we have also checked the sum rule [Eq. (4.8)] when no localized mode existed, and we have found it to be satisfied always to within 2%. The spectral weight function, magnetization, and the quasiboson energies of the pure host and the impurity ion are shown in Figs. 2–4.

To locate the position of the localized mode at each temperature requires a numerical search for the isolated root of the denominator. This in turn requires knowledge of the unperturbed propagators above the band. These were calculated in the required region, as described in Appendix A, and the position of the localized mode was obtained at each temperature, using the self-consistent values of $\langle c^z\rangle$ and $\langle f^z\rangle$. However, instead of evaluating the residue of G_{cc} at this pole we have determined the weight of the δ function by the sum rule for $A_c(\beta,\omega)$. The position and weight of the localized modes, as a function of temperature, are also shown in Figs. 6 and 7.

VI. RESULTS AND DISCUSSION

In order to examine the quantitative predictions of our theory and, in particular, to investigate the effects of varying impurity parameters, we have carried out a rather extensive series of calculations. Representative results are shown in Figs. 1–8, in which we present, as functions of temperature, both host and impurity magnetization ($\langle S^z\rangle$ and $\langle c^z\rangle$), effective boson energy [ω_0 and $\omega(c)$], and the frequency and weight (ω_s and W) of a localized mode (when it exists). In addition we show the dependence of the spectral weight function on frequency, at very low temperature and just below T_c. All these data are shown for various values of host spin S, impurity spin S_I, and $\eta=(J+j)/J$.

A. The Spectral Weight Function

In the unperturbed crystal the spectral weight function $A_0(\beta,\omega)$ is proportional to the density of states per spin:

$$(1-e^{-\beta\omega})A_0(\beta,\omega)/2\langle S^z\rangle=N(\omega)/N.$$

This curve is shown in Fig. 1. Accordingly we plot the reduced spectral weight function

$$\mathfrak{A}(\omega)=A_c(\beta,\omega)\langle S^z\rangle/A_0(\beta,\omega)\langle c^z\rangle=-\frac{\mathrm{Im}G_{cc}(\omega)}{\langle c^z\rangle}\Big/\frac{N(\omega)}{N}. \quad (6.1)$$

Any deviation of $\mathfrak{A}(\omega)$ from unity then represents a discrimination (by spin excitations of energy ω) between the impurity and other sites. By the sum rule (4.8) $\mathfrak{A}(\omega)$ is normalized to two, so an enhanced probability of flipping the impurity spin by excitations in one energy region [$\mathfrak{A}(\omega)>1$] must be compensated by a reduced probability [$\mathfrak{A}(\omega)<1$] elsewhere in the band.

As discussed in Ref. 9, the shape of $\mathfrak{A}(\omega)$ can be understood qualitatively on the basis of simple physical considerations. Consider first the case in which host and impurity spins are equal, but $\eta<1$, as in Figs. 2(a) ($\eta=0.8$) and 2(b) ($\eta=0.4$). A localized deviation (or

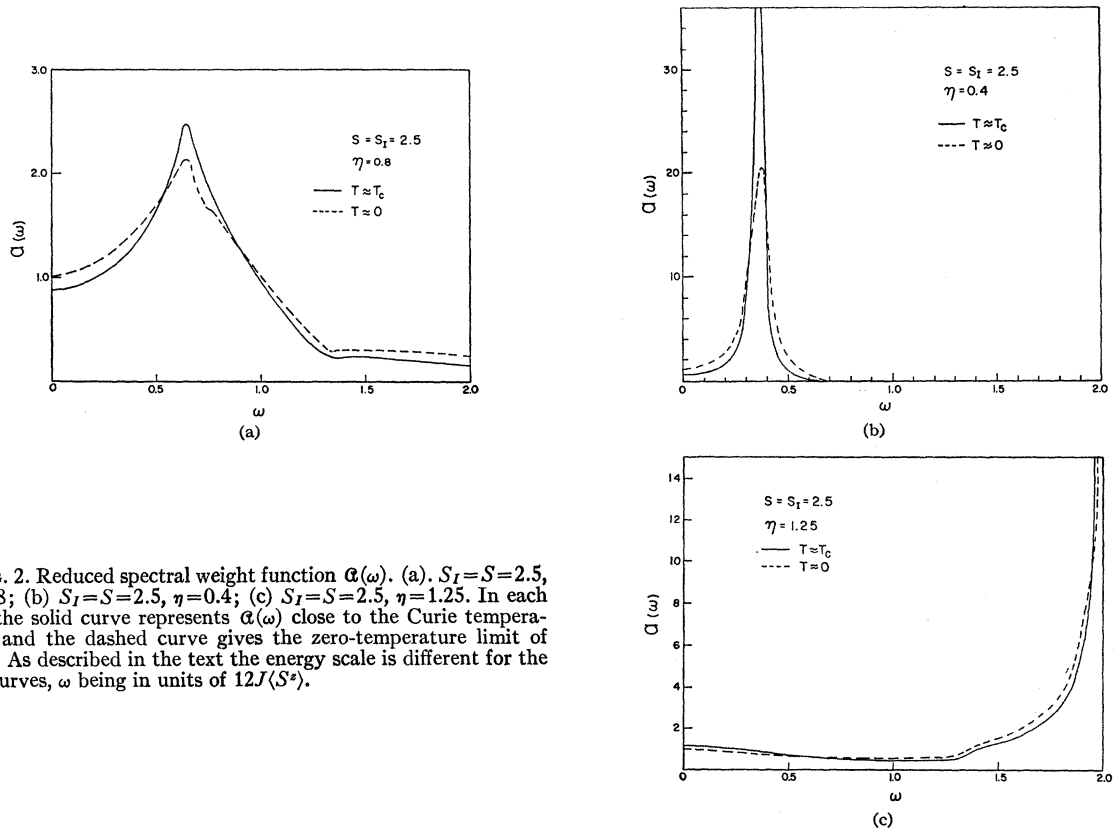


FIG. 2. Reduced spectral weight function $\mathcal{A}(\omega)$. (a). $S_I=S=2.5$, $\eta=0.8$; (b) $S_I=S=2.5$, $\eta=0.4$; (c) $S_I=S=2.5$, $\eta=1.25$. In each case the solid curve represents $\mathcal{A}(\omega)$ close to the Curie temperature, and the dashed curve gives the zero-temperature limit of $\mathcal{A}(\omega)$. As described in the text the energy scale is different for the two curves, ω being in units of $12J\langle S^z\rangle$.

"spin flip") introduced into the lattice has lower energy at the impurity than elsewhere, so the impurity acts as an attractive center. Nevertheless, a long-wavelength spin wave simply sweeps over this local potential well without appreciable modification, as any wave is insensitive to a perturbation of range small compared to its wavelength. Consequently, $\mathcal{A}(\omega)$ is equal to unity in the limit $\omega \rightarrow 0$. As ω increases, the wavelength of the excitation becomes comparable with the width of the attractive potential well, the spin deviation is resonantly trapped, and the spectral weight function becomes large. The compensating reduction required by the sum rule occurs near the top of the band, where the spin wave can be treated as a localized-spin-deviation packet. As this packet approaches the attractive center it loses potential energy and correspondingly increases its kinetic energy; it therefore spends an abnormally small time on the impurity, so that $\mathcal{A}(\omega)<1$. This picture suggests that with decreasing values of η the peak should move to lower energies and become sharper, and these effects are indeed observed in the figures. Incidentally, the sudden changes of slope in these curves are reflections of the Van Hove singularities in the density of states.

The opposite tendencies are found for a strongly bound impurity, as shown in Fig. 2(c) for $\eta=1.25$. The impurity now acts as a repulsive center. Long-wavelength, low-energy excitations are again unperturbed. Near the top of the band the spin-deviation packet slows down near the impurity, spending an abnormally long time there and peaking $\mathcal{A}(\omega)$. The required reduction in $\mathcal{A}(\omega)$ elsewhere now occurs near the middle of the band, corresponding to the repulsive scattering of these spin waves from the impurity.

When the repulsive potential becomes of the order of the bandwidth this suppression extends to the top of the band, squeezing the spectral weight out into a high-energy δ function. This δ function corresponds, of course, to the localized mode which appears for these strong couplings.

Comparison of the reduced spectral weight function at low temperature (dashed curves) with that just below T_c (solid curves) indicates that the peak sharpens with increasing temperature. This effect occurs for all values of the parameters S, S_I, and η. We see no transparent argument which would lead us to anticipate this result of the numerical analysis.

One of the most striking results of our calculations is the lack of any appreciable shift in peak position with temperature. Since the energy units we have chosen are proportional to $\langle S^z\rangle$ this result demonstrates the very accurate scaling of the peak frequency with the host magnetization. The result undoubetdly depends to some extent on the use of the random-phase approximation, but it is *not* tautologically equivalent to the RPA.

In Fig. 3 we examine the behavior of $\mathcal{A}(\omega)$ for the

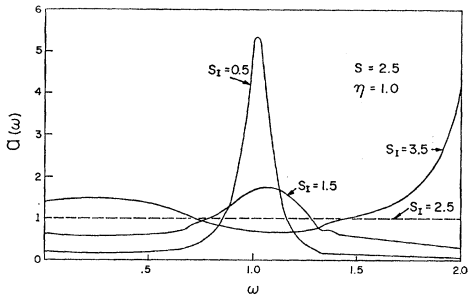


FIG. 3. Reduced spectral weight function $\mathcal{A}(\omega)$ for a series of impurity spins, $S_I=\frac{1}{2}, \frac{3}{2}, \frac{5}{2}$ (pure host, shown dashed), $\frac{7}{2}$, in a host of spins, $S=\frac{5}{2}$. The exchange ratio η is maintained at unity. The temperature is the same in all cases, $T\approx T_c$.

case of unequal spins but equal exchange integrals ($\eta=1$). A decrease in the magnitude of S_I is qualitatively similar to a decrease in η, in that it gives a peak in $\mathcal{A}(\omega)$ at intermediate band energies. However, only the height of the peak—not its location—seems to depend on the value of S_I. This determination of the peak frequency by exchange parameters alone is found to hold as well, to a good approximation, for values of η other than unity. Similarly, an increase in S_I is qualitatively like an increase in η, in that it shifts spectral weight to the upper part of the band. However, even small changes in η produce very prominent peaking of $\mathcal{A}(\omega)$, whereas changes in S_I are relatively ineffective. Thus, a reduction of η from 1.0 to 0.4 gives a maximum in $\mathcal{A}(\omega)\sim 20$, while double this fractional reduction in S_I—from 2.5 to 0.5—produces a peak height only of the order of 5.

B. Magnetization and Quasiboson Energy

Magnetization curves for the impurity with $S_I=S$ and various η are shown in Fig. 4(a), and with $\eta=1.0$ and various S_I in Fig. 4(b). The magnetization of the unperturbed host is shown dashed, for comparison.

We expect more tightly coupled spins to be more difficult to flip, and we indeed find that increasing either η or S_I tends to raise the value of $\langle c^z\rangle_{S_I}$ at a given temperature. Again variations of η are considerably more effective than the same fractional changes in S_I.

As we remarked in the Introduction, a common feature of the empirical observations is that the magnetization of the impurity is well represented by a Brillouin function with argument proportional to the host magnetization. In our language this is equivalent to the statement that the quasiboson energy, in reduced units, is approximately independent of temperature [see Eq. (2.10)]. We have therefore included plots of the quasiboson energies for impurity and host, normalized in each case to the value at T_c, in Figs. 4(a) ($S_I=S$, various η) and 4(b) ($\eta=1.0$, various S_I). We do observe that for weakly coupled impurities the quasiboson energy $\omega(c)$ of the impurity becomes nearly constant over a wide temperature range.

For the two cases ($S_I=S$, $\eta=1.4$, 2.0) in which the coupling is sufficiently strong for a localized mode to exist $\omega(c)$ departs from its value at T_c even faster than does ω_0. Although in each case the δ function contributes an appreciable fraction of the spectral weight the Boltzmann factor diminishes its importance in determining $\omega(c)$.

Finally there remains the case of coupling not sufficiently strong to split off a localized mode. The peak in $\mathcal{A}(\omega)$ at the top of the band is still at a low enough energy to be thermally effective; $\omega(c)$ for the case $\eta=1.0$, $S_I=3.5$ is virtually indistinguishable from $\omega(c)$ for $\eta=1.0$, $S_I=1.5$ (in fact, the former curve lies slightly above the latter).

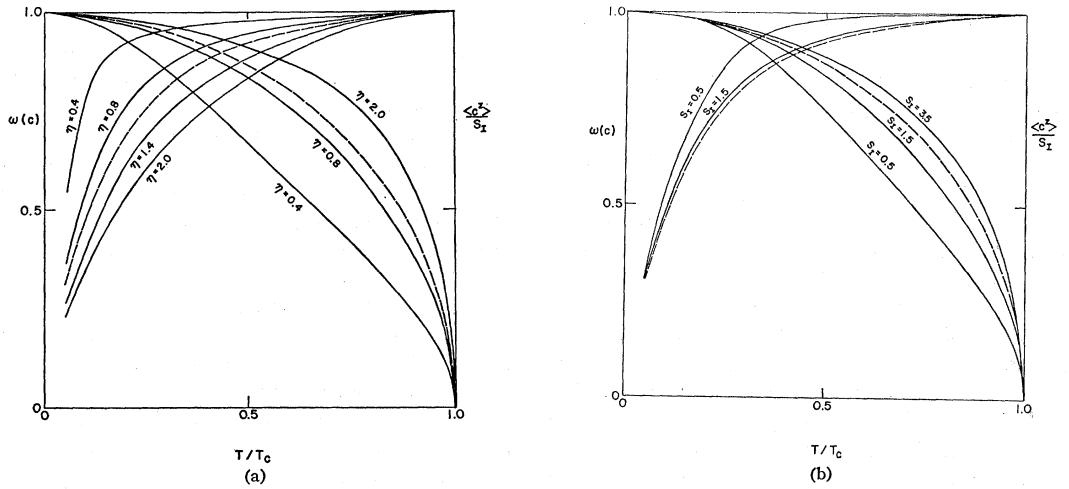


FIG. 4. Reduced impurity magnetization $\langle c^z\rangle/S_I$ and quasiboson energy $\omega(c)$ (normalized to its value at $T/T_c=1$), as functions of reduced temperature T/T_c. (a). The effects of varying the ratio of exchange integrals: $\eta=0.4$, 0.8, 2.0, for $S_I=S=2.5$; (b) the effects of varying the impurity spin: $S_I=\frac{1}{2}, \frac{3}{2}, \frac{7}{2}$ in a host, $S=\frac{5}{2}$, and $\eta=1$. For reference in both (a) and (b) the corresponding curves for the pure host are shown dashed.

In order to illustrate the comparison with experiment more directly (although less elegantly) we turn to the recent results of Koi, Tsujimara, and Hihara[2] on the magnetization of Mn in Fe (keeping in mind our remarks in the Introduction concerning applicability of our theory to metallic systems). In Fig. 5 we show the empirical host and impurity magnetizations as well as the theoretical curves for these functions (as obtained from the Green's function within the RPA and in our simple-cubic, nearest-neighbor exchange model). Clearly the RPA and the nearest-neighbor model are inadequate for the host, for well understood reasons. To correct crudely for this deficiency we have also "renormalized" our result to the empirical host magnetization by multiplying $\omega(c)$ at each temperature by the ratio of the measured to the theoretical value of $\langle S^z\rangle$ [that, is, $\omega(c)\rightarrow\omega(c)\langle S^z\rangle_{\text{meas.}}/\langle S^z\rangle_{\text{theor.}}$]. The resultant "renormalized" impurity magnetization is also shown in Fig. 5. As anticipated in the article[8] by Jaccarino, Walker, and Wertheim, the agreement with experiment is excellent.

In cases such as rare-earth ions in garnets, which are very weakly bound, the constancy of the quasiboson energy [Fig. 4(a)] guarantees excellent agreement with the observed molecular-field behavior. The strong-coupling experimental results[1,4] are also reasonably well described by molecular-field theory, even though $\omega(c)$ for these cases is only slightly flatter (as a function of temperature) than ω_0. However, the impurity magnetization is so nearly constant in these strongly coupled cases that it does not provide a critical test of the molecular-field model.

C. The Effective Molecular-Field Coefficient

An alternative interpretation can be given to the quasiboson energy, providing helpful insight into the impurity problem. We define an effective host-impurity coupling constant $J'(\beta)$ by the usual form of the molecular-field equation

$$\langle c^z\rangle = S_I B_{S_I}(\beta 2zJ'(\beta)\langle s^z\rangle). \tag{6.2}$$

Then we observe that $2zJ'(\beta)\langle S^z\rangle=\Omega(c)$, or $\omega(c)$ is simply proportional to $J'(\beta)$: $\omega(c)=J'(\beta)/J$, whence

$$J'(\beta)/(J+j)=\omega(c)/\eta. \tag{6.3}$$

In Fig. 6 we plot $J'(\beta)/(J+j)=\omega(c)/\eta$ as a function of η for each of the values $S_I=1.5$, 2.5, and 3.5, and for two temperatures. Even when the molecular-field type of solution is valid we see that the usual assumption that the effective coupling constant $J'(\beta)$ is simply equal to $J+j$ is not necessarily correct, although this relation is approached in the weak-coupling limit.

D. Localized Modes

The s-wave localized-mode frequency (when it exists) is given by the one zero of the Green's-function denominator [Eq. (5.7)] which occurs above the band

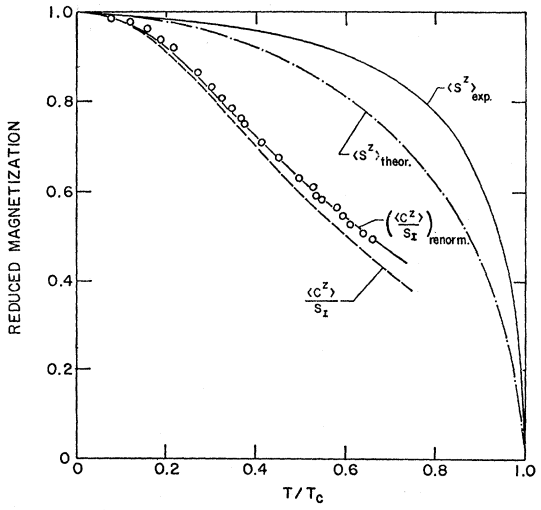


FIG. 5. Empirical (Ref. 2) values of the impurity magnetization are indicated by circles, of the host by the upper solid curve, for dilute Mn in Fe. The theoretical curves for these functions, as obtained within our model, are also shown (dashed for the impurity, dot-dashed for the host). The solid curve represents the theoretical impurity magnetization as corrected by an approximate accounting for the discrepancy between the empirical and theoretical values for the host (see text). As in Ref. 8 we have taken $S=1$ and $S_I=\frac{3}{2}$. The value of η required to obtain a high-temperature value of $\omega(c)$ consistent with their value of $H_0^{\text{Mn}}(\omega(c)\approx 0.23)$ is $\eta=0.25$. This very weak host-impurity exchange coupling explains the observed accuracy of molecular-field theory.

$(\omega>2)$. Its qualitative behavior is more readily ascertained from Eqs. (4.2)–(4.4), obtained from the "first approximation." A preliminary discussion on this basis was presented[23] by two of us at the 1965 Conference on Magnetism and Magnetic Materials.

Consider the criterion (4.4) for the first emergence of a localized mode as the impurity-host coupling is increased. At $T=0$ we can take $\langle\delta c\rangle=(S_I-S)/S$, and Eq. (4.4) reduces to the condition found by Wolfram and

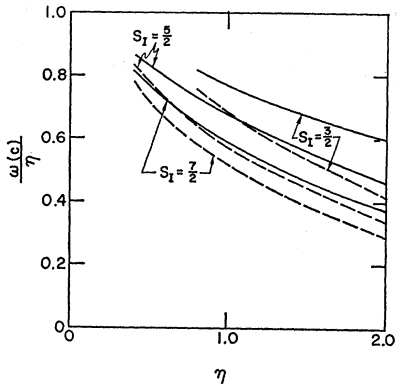


FIG. 6. The effective relative exchange parameter $J'(\beta,\eta)/(J+j)=\omega(c)/\eta$ as a function of η. The solid curves are for a temperature $T\approx T_c$; the dashed curves are for $T\approx 0.37T_c$. For each of these temperature values the lowest curve corresponds to an impurity spin $S_I=\frac{7}{2}$, the middle curve to $S_I=\frac{5}{2}$ and the highest to $S_I=\frac{3}{2}$. In all cases $S=\frac{5}{2}$.

[23] D. Hone and H. Callen, J. Appl. Phys. (to be published).

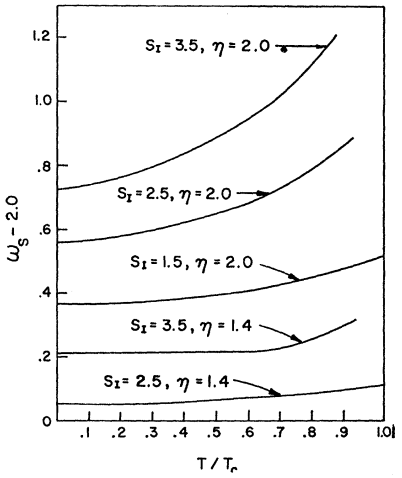
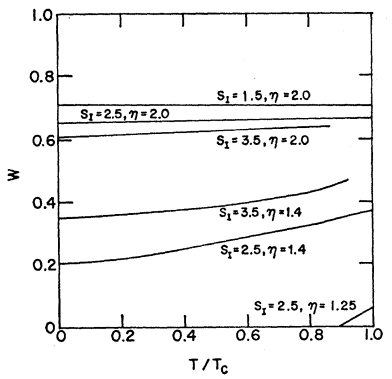


FIG. 7. The energy of the localized mode above the top of the band, $\omega_s - 2.0$, as a function of temperature, for $\eta = 1.4$ and 2.0 and for several values of S_I. Note that $(\omega_s - 2.0)$ is expressed in reduced units, or in units of $12J\langle S^z\rangle$.

Calloway. These strongly coupled impurity spins are more difficult to flip than a typical host spin (spectral weight is concentrated at high energies), so $\langle c^z\rangle$ de-decreases less rapidly than $\langle S^z\rangle$, and δc therefore increases as the temperature is raised. Hence the requirements set by (4.4) for a minimum value of j/J become less stringent with rising temperature. It is, in fact, sometimes possible for a localized mode to split off the top of the band at some nonzero temperature in a system where no such mode exists at $T=0$. This conclusion strongly suggests that all localized-mode frequencies ω_s increase as a function of temperature. In unreduced units this implies that the energy of such a mode decreases less rapidly than $\langle S^z\rangle$. This expectation is corroborated by the numerical results, as shown in Fig. 7. The two values $\eta = 1.4$ and $\eta = 2.0$ are shown for various S_I.

We have examined one system for which the localized mode appears only at high temperatures. In Fig. 2(c) we have plotted the reduced spectral weight function



for $S_I = 2.5$, $\eta = 1.25$. Although the function as drawn satisfies the sum rule (4.8) at low temperatures, the solid curve ($T \simeq T_c$) is found to be about 7% deficient. Indeed, above about 0.9 T_c we find that a localized mode appears, with energy ω_s which rises to the value 2.019 just below T_c.

The spectral weight W contained in the δ function at ω_s tends to increase with the value of ω_s; except for the case discussed in the preceding paragraph it is found not to be highly temperature-dependent. This behavior of the weight W is shown in Fig. 8.

The ideas and techniques which have been explored here have application to a number of related problems. At the expense of relative algebraic, rather than conceptual, complexity, the restrictions to simple-cubic crystals and nearest-neighbor interactions can be relaxed. Work is in progress on the impure antiferromagnet and on concentration-dependent effects.

APPENDIX A: SIMPLE-CUBIC-CRYSTAL GREEN'S FUNCTIONS

As shown by Slater and Koster[12] (see also the Appendix of Wolfram and Calloway[7]) the crystal Green's functions of a simple-cubic structure can be reduced from the three-dimensional integral of Eq. (2.21) to a one-dimensional integral

$$\mathcal{L}_{gj}(\omega) = -3i^{(1+l+m+n)} \int_0^\infty dt\, e^{3i(\omega-1)t} J_l(t) J_m(t) J_n(t)\,, \tag{A1}$$

where $\mathbf{r}_g - \mathbf{r}_j = (l,m,n)$ and J_l is the Bessel function of (integral) order l.

Because of the great reduction in required computer time we have chosen to do all numerical integrations by the Gaussian-quadrature method, based on Legendre polynomials.[24] Integrations over ω, involving $\mathcal{L}_{gj}(\omega)$, were carried out by 16 four-point quadratures spanning the spin-wave band ($0 \leq \omega \leq 2$), and, when necessary, by extension of this net above the band. The net of points within the band is given by

$$\omega_p \equiv \omega_{4n+m} = (2n+1+x_m)/16, \quad n=0,1,\cdots,15; \quad m=1,2,3,4, \tag{A2}$$

where

$$x_1 = -x_4 = -0.86113631; \quad x_2 = -x_3 = -0.33998104. \tag{A3}$$

It is at these energies that we have evaluated the unperturbed propagators $\mathcal{L}_{gj}(\omega_p)$, given in Table I.

To carry out the numerical integration of equation (A1) we have used polynomial approximations[25] for the Bessel functions, accurate to 10^{-8}. We have also

[24] Zdenek Kopal, *Numerical Analysis* (John Wiley & Sons, Inc.,

followed the procedure of others[7,22] in truncating the integration at $t=50$. However, instead of using Simpson's rule, which is both time consuming and subject to troublesome round-off errors, we again employed the Gaussian-quadrature method, with 64 four-point quadrature intervals in the range $0\leq t\leq 50$.

To estimate the errors accumulated in the numerical integrations we have calculated the redundant propagator $\mathfrak{L}_{fc}$, and checked its value by the identity (3.5) $\mathfrak{L}_{fc}(\omega)-1+(\omega-1)\mathfrak{L}_{cc}(\omega)=0$. The real and imaginary parts of this quantity were each found to be consistently less in absolute value than 2×10^{-4}. In addition we checked the exactly integrable propagator[26]

$$\mathfrak{L}_{fc}(1)=\int_0^1 J_0^2(t)J_1(t)\,dt=\tfrac{1}{3},$$

finding 0.33327.

All numerical calculations were carried out on an IBM 7040 computer.

[26] G. N. Watson, *Theory of Bessel Functions* (Cambridge University Press, Cambridge, England, 1922), p. 412.

PHYSICAL REVIEW VOLUME 144, NUMBER 1 8 APRIL 1966

Determination of Electron Energy Losses in Rubidium*

B. M. Hartley and J. B. Swan
Physics Department, University of Western Australia, Nedlands, Australia
(Received 1 November 1965)

Surface and volume plasmon energies of 2.4 and 3.45 eV, and energy losses of 25 and 55 eV, are measured in the characteristic electron energy-loss spectra of rubidium. A computer program used to determine peak positions and evaluate energy losses is described.

INTRODUCTION

MEASUREMENTS of the characteristic loss spectra of the alkali metals are of interest for comparison with the theoretical values of the plasmon energy.[1] Several measurements have been made of the loss spectra of lithium,[2,3] sodium,[2,4,5] and potassium,[2,4,5] but no studies of the optical loss function or the energy losses of electrons have been reported previously for rubidium.

APPARATUS AND EXPERIMENTAL PROCEDURE

The apparatus employed in these measurements of the characteristic electron energy-loss spectra of rubidium has been described previously.[5] The multichannel analyzer was used as a multi-scalar, with appropriate circuitry installed to synchronize the channel-advance signals with the energy sweep. The rubidium target was maintained with a clean surface by continuous evaporation of the pure metal direct from the glass ampoule in which it was supplied.[6] The energy spread of the primary electrons prevented resolution of the surface and volume components of the loss spectrum of rubidium, and the method previously employed to separate these components in the case of potassium[5] was again used. Many loss spectra were obtained, in the range of primary energies 250 to 2500 eV, and the data comprising each spectrum was analyzed by computer methods described below.

The energy scale of each spectrum was determined as previously described, by shifting the zero-loss peak successively by measured energy decrements, as determined by a potentiometer and standard cell.

DATA-ANALYSIS PROGRAM

Processing of Data

The procedure used for determining the position of the peaks in each loss spectrum relied on the assumption that the background under each peak has constant curvature, while the peak itself is characterized by a relatively rapid variation in curvature. On this basis, the second derivative of the spectrum will in general be negative in the region occupied by a peak, with the background contributing only a relatively small positive or negative constant value to this second derivative. The position of the peak, in terms of channel number, may then be calculated as $n=\sum n_i f_i''/\sum f_i''$, where f_i'' is the value of the second derivative determined for channel number n_i, and each summation extends over the range for which $f_i''<0$.

The required calculations were written as a program in FORTRAN II, and were run on an IBM 1620 computer.[7]

* Work supported by the U. S. Army Research Office and the University of Western Australia.

[1] R. A. Ferrell, Phys. Rev. **101**, 554 (1956). D. Pines, Rev. Mod. Phys. **28**, 184 (1956).
[2] C. Kunz, Phys. Letters **15**, 312 (1965).
[3] H. Fellenzer, Z. Physik **165**, 419 (1961).
[4] J. L. Robins and P. E. Best, Proc. Phys. Soc. (London) **79**, 110 (1962).
[5] J. B. Swan, Phys. Rev. **135**, A1467 (1964).
[6] L. Light & Company, England.
[7] I. B. M. (Australia).