Impure Heisenberg systems with biquadratic interactions

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The purpose of the present paper is to study an impure Heisenberg ferromagnet governed by the Hamiltonian $H=-J\sum_{i,\Delta}[\vec{S}_i\cdot\vec{S}_{i+\Delta}+\alpha(\vec{S}_i\cdot\vec{S}_{i+\Delta})^2]-2J_0\sum_\Delta[\vec{S}_0\cdot\vec{S}_\Delta+\alpha_0(\vec{S}_0\cdot\vec{S}_\Delta)^2]$, where J is the host-host bilinear exchange constant, $2(J+J_0)$ is the host-impurity bilinear exchange constant, α and α_0 being the corresponding biquadratic coupling parameters, and Δ, a nearest-neighbor vector. $\vec{S}$ and $\vec{S}_0$ are the host and the impurity spins, respectively. Through utilization of the Dyson transformation, it is shown that at low temperatures the effect of the biquadratic terms is simply to renormalize the bilinear exchange constants J and J_0 by $1+2\alpha S(S-1)$ and $1+\alpha_0(2SS_0-S-S_0)$, respectively. Some qualitative discussions on the scattering processes are presented. The method of Green's function is then employed to discuss the criteria for the existence of localized modes in the system. The situations appearing in $KMnF_3$, $RbMnF_3$, $KNiF_3$, and MnF_2 doped by impurities are critically examined. Some numerical estimates of the biquadratic parameters α and α_0 are also made which are found to agree satisfactorily with those obtained by previous authors.

I. INTRODUCTION

The effect of impurities on the spectrum of elementary excitations of a magnetically ordered crystal lattice has been studied in great detail using a bilinear-type exchange Hamiltonian.[1–15] But there exist some experimental data in the literature which clearly point to the fact that the host system should have, in addition, an appreciable biquadratic exchange. When the impurities Ni^{++} are embedded in the host lattice of $KMnF_3$, it would be clearly incorrect to examine their data on the basis of bilinear exchange only since $KMnF_3$ does have some biquadratic exchange in appreciable magnitude.[1] It may be noted that in the above example, only the host-host interaction may contain a significant biquadratic part, while the host-impurity interaction may still be regarded as a bilinear type, since $KNiF_3$ does not contain any biquadratic exchange.[16] In similar manner, one finds that in $KNiF_3$:Mn^{++} the host-host interaction is a pure bilinear isotropic type, but the host-impurity interaction should contain both bilinear and biquadratic exchange. An approximate theory based on random-phase approximation (RPA) Green's function approximation was developed by the author[17] where it was shown that the presence of biquadratic exchange sometimes enhances and sometimes hinders the formation of localized modes. But due to the oversimplifications involved in the theory this general result should be critically examined in the light of more realistic and reasonably accurate formalism.

In order to discuss the effects of impurities in both of the two kinds of situations stated above, we include biquadratic exchange in both the host-host and host-impurity interactions so that one may write down the following Hamiltonian:

$$H=-J\sum_{i,\Delta}[\vec{S}_i\cdot\vec{S}_{i+\Delta}+\alpha(\vec{S}_i\cdot\vec{S}_{i+\Delta})^2]-2J_0\sum_\Delta[(\vec{S}_0\cdot\vec{S}_\Delta)+\alpha_0(\vec{S}_0\cdot\vec{S}_\Delta)^2]\ , \tag{1}$$

where J is the host-host interaction, $2(J+J_0)$ is the host-impurity interaction and α and α_0 are the corresponding biquadratic coupling parameters. $\vec{S}_i$ is the spin operator at the ith lattice site and $\vec{S}_{i+\Delta}$ is the same at the neighboring site, Δ being a nearest-neighbor vector. The impurity is assumed to be situated at the origin and the impurity spin is denoted by S_0, while the host spin is denoted by S. In Ref. 17 it was assumed $J=2J_0$ and $\alpha_0=0$ and these approximations are mainly responsible for crude oversimplifications in the theory.

We utilize the Dyson transformations for both the host and the impurity spins to express the above Hamiltonian in terms of boson creation and annihilation operators. The transformed Hamiltonian is found to convey some important information regarding the physical properties of the system. These are elaborately studied in Secs. II and III. The method of two-time thermodynamic Green's function is then employed in Sec. IV to discuss the localized impurity modes appearing in the system. The higher-order Green's functions are decoupled by a Hartree-Fock approximation, and the linearized equations of motion are solved to find the criteria for the existence of S_0 modes. The existence of localized modes in $KMnF_3$, $KNiF_3$, $RbMnF_3$, and MnF_2 is then discussed on the basis of present theory and compared with the existing observed data of literature.

II. TRANSFORMED HAMILTONIAN

The Dyson transformations for both the host and the impurity spins may be written in the following forms:

$$S_i^z = S - a_i^\dagger a_i, \quad S_0^z = S_0 - a_0^\dagger a_0 ,$$
$$S_i^+ = (2S)^{1/2} a_i, \quad S_0^+ = (2S_0)^{1/2} a_0 ,$$
$$S_i^- = (2S)^{1/2} a_i^\dagger [1-(1/2S) a_i^\dagger a_i] ,$$
$$S_0^- = (2S_0)^{1/2} a_0^\dagger [1-(1/2S_0) a_0^\dagger a_0] , \quad (2)$$

where $a_i^\dagger$, a_i create and destroy bosons at the lattice site i and are the corresponding operators attached to the impurity spin situated at 0.

We shall reexpress our basic Hamiltonian in terms of boson operators using the transformations written above. Utilizing the usual boson commutation relations successively, we rearrange the boson operator products in such form that all the creation operators stand in the left and the annihilation operators stand in the right. The procedure is indeed very lengthy and tedious. The result obtained is

$$H = R_1 JS \sum_{i,\Delta} (a_i^\dagger a_i + a_{i+\Delta}^\dagger a_{i+\Delta} - a_i^\dagger a_{i+\Delta} - a_{i+\Delta}^\dagger a_i)$$
$$+2R_1^0 J_0 \sum_{\Delta} [S a_0^\dagger a_0 + S_0 a_\Delta^\dagger a_\Delta - (SS_0)^{1/2} a_0^\dagger a_\Delta - (SS_0)^{1/2} a_\Delta^\dagger a_0] + V + V_0 , \quad (3)$$

where the first two terms refer to the low-temperature region and R_1 and R_1^0 are two renormalization factors given by

$$R_1 = 1 + 2\alpha S(S-1) ,$$
$$R_1^0 = 1 + \alpha_0 (2SS_0 - S - S_0) . \quad (4)$$

The third and the fourth terms of Eq. (3) refer to magnon scattering processes. The involved interactions V and V_0 are given by

$$V = -J \sum_{i,\Delta} [R_2 V_1(i,\Delta) + R_3 V_2(i,\Delta)] ,$$
$$V_0 = -2J_0 \sum_{\Delta} [R_2^0 V_1(0,\Delta) + R_3^0 V_2(0,\Delta)] , \quad (5)$$

where

$$V_1(i,\Delta) \equiv (i,i+\Delta,i,i+\Delta) - \tfrac{1}{2} A_1^i (i+\Delta,i+\Delta,i,i+\Delta) - \tfrac{1}{2} A_2^i (i,i,i,i+\Delta) , \quad (6)$$

$$V_2(i,\Delta) \equiv (i,i,i,i) + M_i (i+\Delta,i+\Delta,i+\Delta,i+\Delta) + N_i (i,i,i+\Delta,i+\Delta) + Q_i (i+\Delta,i+\Delta,i,i) - 2m_i (i,i+\Delta,i+\Delta,i+\Delta) - 2q_i (i,i+\Delta,i,i) . \quad (7)$$

The symbol $(i,i+\Delta,i,i+\Delta)$ stands for the product $a_i^\dagger a_{i+\Delta}^\dagger a_i a_{i+\Delta}$. For $i \neq 0$, it is implied that

$$A_1^i = A_2^i = 1, \quad M_i = Q_i = N_i = m_i = q_i = 1$$

but for $i=0$,

$$A_1^0 = A_1, \quad A_2^0 = A_2, \quad M_0 = (S_0/S)\phi, \quad N_0 = \phi,$$
$$Q_0 = S_0/S, \quad m_0 = \phi (S_0/S)^{1/2}, \quad q = 2(S_0/S)^{1/2} ,$$

where all the symbols are explained as follows:

$$R_2 = 1 + \alpha(2S-1)(3S-1) ,$$
$$R_3 = \tfrac{1}{2}\alpha S(2S-1) ,$$
$$R_2^0 = 1 + \alpha_0 (6SS_0 - \tfrac{5}{2}S - \tfrac{5}{2}S_0 + 1) ,$$
$$R_3^0 = \tfrac{1}{2}\alpha_0 S(2S-1) , \quad (8)$$
$$\phi = (2S_0 - 1)/(2S-1) ,$$
$$A_1 = (1/R_1^0)(S_0/S)^{1/2}[1 + \alpha_0(2S_0-1)(3S-1)] ,$$
$$A_2 = (1/R_1^0)(S_0/S)^{1/2}[1 + \alpha_0(2S-1)(3S_0-1)] .$$

III. LOW-TEMPERATURE EFFECT

The transformed Hamiltonian as shown by Eq. (3) conveys some important basic physical information regarding the effects of biquadratic exchange. In the present section we shall mention the important effects at low temperatures. Since the magnon scattering is insignificant at very low temperatures the transformed Hamiltonian would correspond to

$$H_{\text{low}} = -R_1 J \sum_{i,\Delta} (\vec{S}_i \cdot \vec{S}_{i,\Delta}) - 2R_1^0 J_0 \sum_{\Delta} (\vec{S}_0 \cdot \vec{S}_\Delta) , \quad (9)$$

which implies that the presence of biquadratic terms simply renormalizes the bilinear exchange constants at low temperatures where the magnon scattering processes can be ignored, the renormalization factors being R_1 and R_1^0 in the case of host-host and host-impurity interactions, respectively. It is relevant to remark that in the case of a pure system with bilinear and biquadratic coupling the effect of the biquadratic term, at low temperatures, is to renormalize the bilinear exchange constant J by the same factor R_1, provided the interaction between two spins becomes isotropic.

We conclude this section by pointing out some interesting effects of biquadratic exchange on the localized modes in the system described by Eq. (9). Following Wolfram and Calloway[1] or Hone and Callen[4] one can have the following condition for the existence of a localized mode:

$$\frac{R_1^0 J_0}{R_1 J} > \frac{1.96S - 0.96S_0}{1.96S + 0.96S_0} .$$

If $S = \frac{5}{2}$, $S_0 = 1$ one therefore gets the condition for the localized mode

$$\frac{J_0}{J} > \frac{0.67+5.025\alpha}{1+1.5\alpha_0} . \quad (10)$$

When $\alpha_0=0$, which corresponds to the situations in $KMnF_3{:}Ni^{++}$ one finds that a negative α enhances the possibility of formation of a localized mode and a positive α hinders it. In the case $\alpha_0 \neq 0$ which may correspond to the situations in $KMnF_3{:}Eu^{++}$ the effects of α and α_0 would be reverse. If $S=1$, $S_0=\frac{5}{2}$ the condition for the appearance of a localized excitation at $T=0$ K becomes

$$|J_0/J| > 0.2/2+3\alpha_0 , \quad (11)$$

which is free from α, but depends on α_0. The increase (decrease) of α_0 enhances (hinders) the possibility of appearance of a localized mode. This condition may correspond to the case $KNiF_3{:}Mn^{++}$. The above two conditions are valid at 0 K but localized excitation is also found to split off the spin-wave band at finite temperatures, and therefore the effects of scattering terms have to be considered. We shall discuss these effects in subsequent sections.

IV. GENERAL STUDY OF SCATTERING PROCESSES

Before discussing the effects of scattering terms on the localized modes we shall present some general study of different scattering processes so as to elucidate their implications on impure biquadratic systems. The emphasis is given to the discussion of translational invariance of the system due to the presence of biquadratic terms in the scattering matrix.

Equation (3) can be written in the form

$$H=\sum_{ij}\epsilon_{ij}a_i^{\dagger}a_j+\sum_{ijmn}V_{ijmn}a_i^{\dagger}a_j^{\dagger}a_m a_n , \quad (12)$$

where ϵ_{ij} is the dominant interaction at low temperatures given by

$$\epsilon_{ij}=2R_1JS\sum_{\Delta}\left\{(\delta_{ji}-\delta_{j,i+\Delta})+(c_1-1)\delta_{i0}\delta_{j0}+\left[c_1\frac{S_0}{S}-1\right]\delta_{i\Delta}\delta_{j\Delta}-\left[c_1\left(\frac{S_0}{S}\right)^{1/2}-1\right](\delta_{i0}\delta_{j\Delta}+\delta_{i\Delta}\delta_{j0})\right\} \quad (13)$$

and V_{ijmn} is the magnon scattering matrix

$$\begin{aligned}V_{ijmn}=&-R_2J\sum_{\Delta}[(\delta_{j,i+\Delta}\delta_{mi}\delta_{n,i+\Delta}-\delta_{ji}\delta_{m,i+\Delta}\delta_{n,i+\Delta})+2(C_2-1)\delta_{i0}\delta_{j\Delta}\delta_{m0}\delta_{n\Delta}\\&-(C_2A_1-R_2/R_1)\delta_{i\Delta}\delta_{j\Delta}\delta_{m\Delta}\delta_{n\Delta}-(C_2A_2-R_2/R_1)\delta_{i0}\delta_{j0}\delta_{m0}\delta_{n\Delta}]\\&-2R_3J\sum_{\Delta}\{(\delta_{ji}-\delta_{j,i+\Delta})(\delta_{mi}\delta_{ni}+\delta_{m,i+\Delta}\delta_{n,i+\Delta})+(C_3-1)\delta_{i0}\delta_{j0}\delta_{m0}\delta_{n0}\\&+[C_3(S_0/S)-1]\delta_{i\Delta}\delta_{j\Delta}\delta_{m\Delta}\delta_{n\Delta}+[C_3(S_0/S)-1]\delta_{i\Delta}\delta_{j\Delta}\delta_{m0}\delta_{n0}+(C_3\phi-1)\delta_{i0}\delta_{j\Delta}\delta_{m\Delta}\delta_{n\Delta}\\&-2[C_3(S_0/S)^{1/2}-1]\delta_{i0}\delta_{j\Delta}\delta_{m\Delta}\delta_{n\Delta}-2[C_3\phi(S_0/S)^{1/2}-1]\delta_{i0}\delta_{j\Delta}\delta_{m\Delta}\delta_{n0}\} ,\end{aligned} \quad (14)$$

where

$$C_1=\frac{R_1^0J_0}{R_1J},\quad C_2=\frac{R_2^0J_0}{R_2J},\quad C_3=\frac{R_3^0J_0}{R_3J} . \quad (15)$$

Various possible diagrams representing magnon scattering processes may be discussed in terms of creation and annihilation of magnons at two adjacent sites. Restricting only to nearest neighbors one can draw the diagrams representing two-magnon, three-magnon, four-magnon, and higher-order scattering processes. These are shown in Fig. 1. In relevance with the present problem we suppose $i=0, j=\Delta$ so the two-magnon scattering diagrams are those in Fig. 2. The matrix elements for different interactions shown in Figs. 2(a) and 2(b) can easily be found out from Eq. (5) or from Eq. (14). These are shown in Table I. An inspection of the table exposes some salient features of the problem. We find that if 0 and

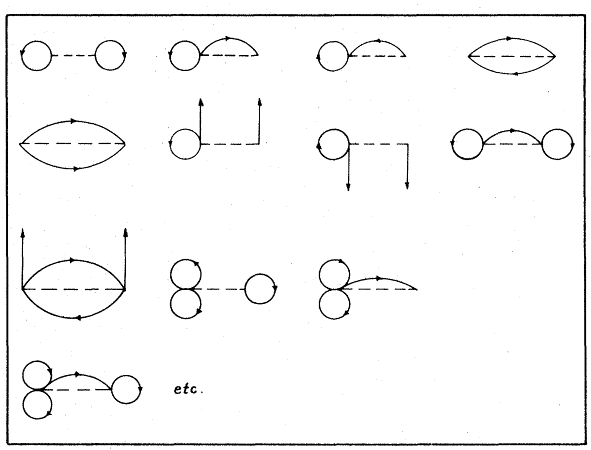

FIG. 1. Diagram representation of various two-magnon, three-magnon, and four-magnon scattering processes.

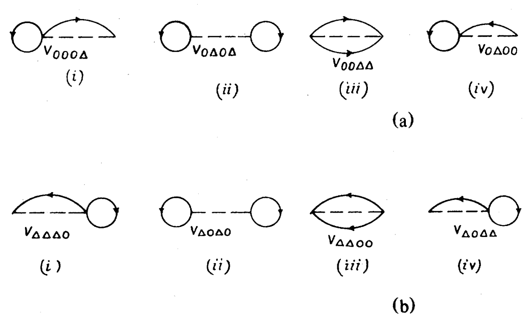

FIG. 2. (a) Typical two-magnon scattering diagrams. Only the magnon creation and annihilation occurring at the impurity site 0 and its neighboring site Δ are considered. $V_{000\Delta}$, $V_{0\Delta0\Delta}$, $V_{00\Delta\Delta}$, and $V_{0\Delta00}$ are the respective interactions. (b) Two-magnon scattering diagrams reverse of (a).

Δ are both host sites the situations represented by the diagrams of (i)–(iv) of Fig. 2 become identical, since the interactions in each case are equal. This is what one expects from the symmetry of the lattice. However, when 0 happens to be an impurity site two classes of diagrams become possible: (i) symmetry class, as a result of interchange of 0 and Δ the diagrams of Fig. 2(a) and those of Fig. 2(b) remain identical; (ii) asymmetry class, as a result of interchange of 0 and Δ the diagrams do not remain identical.

In the case of two-magnon scattering which is our present consideration the diagrams (i) of Fig. 2(a) and 2(b) correspond to the symmetry class since one finds $V_{0\Delta0\Delta}=V_{\Delta0\Delta0}=V_{0\Delta\Delta0}$. All other diagrams drawn in Figs. 2(a) and 2(b) correspond to the asymmetry class if the biquadratic coupling is taken into account. When $\alpha=\alpha_0=0$ all the diagrams fall to the symmetry class since then one would find one-to-one correspondence between the diagrams of Figs. 2(a) and 2(b). The inclusion of biquadratic interactions destroys this correspondence in certain cases. It is found that the diagrams of the symmetry class remain unaffected. We find that in these diagrams no exchange takes place between the host and the impurity sites, bosons being created and annihilated at 0 and Δ independently. But in the diagrams of the asymmetry class the exchange of bosons occurs between the host and the impurity sites. Topologically equivalent diagrams of the symmetry class demonstrates the translational invariance of the lattice, whereas it breaks down in the case of the diagrams of the asymmetry class. This breakdown of translational invariance is clearly due to the perturbation caused by the impurity spin on the neighboring host spin and we therefore categorize the diagrams of the asymmetry class as strong-coupling cases. The diagrams of the symmetry class may conversely be regarded as those representing the weak-coupling case. To discuss the effects of these diagrams on the spin-wave modes we may follow the arguments of Hone *et al.*[7] We note that the diagrams of the symmetry class (weak-coupling case) cause additional small perturbation of the spin-wave band downward in the vicinity of the impurity, the top of the band remaining practically unchanged, while the diagrams of the asymmetry class (strong-coupling case) provide an additional small distortion of the spin-wave band upward in the vicinity of the impurity, but the spin waves at the bottom of the band are not appreciably influenced. Furthermore, it is interesting to note that if $\alpha_0=0$ all the diagrams of Fig. 2 fall to the symmetry class, thus decreasing the perturbing potential at the impurity, and thereby distorting the spin-wave band downward. We see also that for spin-half case the effect of biquadratic exchange on the scattering process is nill and in all other spins the effect of increase (decrease) of α is to increase (decrease) the perturbing potential at the impurity which renders additional small distortion of the spin-wave band upward (downward).

TABLE I. The matrix elements for different interactions corresponding to Figs. 2(a) and 2(b). We have units in which $JZ=1$.

Two-magnon scattering matrix	Matrix elements
$V_{000\Delta}$	$\frac{1}{2}R_2+R_2^0A_2$
$V_{0\Delta0\Delta}$, $V_{\Delta00\Delta}$	$-R_2-2R_2^0$
$V_{00\Delta\Delta}$	$-2R_3$
$V_{0\Delta00}$	$4R_3[1+C_3(S_0/S)^{1/2}]$
$V_{\Delta\Delta\Delta0}$	$\frac{1}{2}R_2+R_2^0A_1$
$V_{\Delta0\Delta0}$, $V_{0\Delta\Delta0}$	$-R_2-2R_2^0$
$V_{\Delta\Delta00}$	$-2R_3-2R_3^0(S_0/S)$
$V_{\Delta0\Delta\Delta}$	$4R_3[1+C_3\phi(S_0/S)^{1/2}]$

V. LOCALIZED SPIN-WAVE MODES

In order to examine the effects of biquadratic coupling on the spin-wave impurity modes we employ the method of Green's function which may still be regarded as a convenient tool for such a description. We shall work with the following Green's functions:

$$G_{00}(E)=\langle\langle a_0;a_0^\dagger\rangle\rangle_E\ ,$$

$$G_{\Delta0}(E)=\langle\langle a_\Delta;a_0^\dagger\rangle\rangle_E\ ,$$

where the symbols bear conventional meaning. Henceforth we shall omit the subscript E occurring in the right-hand side.

The equations of motion for the Green's functions

$G_{00}(E)$ and $G_{\Delta 0}(E)$ are

$$EG_{00}(E)=\frac{\langle S_0^z\rangle}{\pi}+R_1[b_1G_{00}(E)-g_1G_{\Delta 0}(E)]-R_2\langle\langle(b_2a_\Delta^\dagger a_\Delta a_0-a_2a_0^\dagger a_0a_\Delta);\,a_0^\dagger\rangle\rangle$$
$$-R_3\langle\langle(b_3a_0^\dagger a_0a_0+\phi_1a_0^\dagger a_\Delta a_\Delta-g_3a_\Delta^\dagger a_0a_0-\phi_2a_\Delta^\dagger a_\Delta a_\Delta);\,a_0^\dagger\rangle\rangle\ , \quad (16)$$

$$EG_{\Delta 0}(E)=R_1[h_1G_{\Delta 0}(E)-g_1G_{00}(E)]-R_2\langle\langle(b_2a_0^\dagger a_0a_\Delta-a_1a_\Delta^\dagger a_\Delta a_0);\,a_0^\dagger\rangle\rangle$$
$$-R_3\langle\langle(\phi_3a_\Delta^\dagger a_\Delta a_\Delta+h_3a_\Delta^\dagger a_0a_0-\phi_2a_0^\dagger a_\Delta a_\Delta-g_3a_0^\dagger a_0a_0);\,a_0^\dagger\rangle\rangle\ , \quad (17)$$

where we have written R_1, R_2, and R_3 for $2JZ\langle S^z\rangle R_1$, $2JZ\langle S^z\rangle R_2$, and $2JZ\langle S^z\rangle R_3$, respectively. The symbols a, b, g, and h are given by

$$\begin{aligned}b_n&=1+C_n\ ,\\ g_n&=1+C_n(S_0/S)^{1/2}\ ,\\ a_n&=1+A_nC_2\ ,\\ h_n&=1+C_n(S_0/S)\ ,\end{aligned}\quad (18)$$

where n runs through the values 1, 2, and 3. The symbols ϕ_1 and ϕ_2 are given by

$$\begin{aligned}\phi_1&=1+C_3\phi\ ,\\ \phi_2&=1+C_3\phi(S_0/S)^{1/2}\ .\end{aligned}\quad (19)$$

In order to linearize Eqs. (16) and (17), we decouple the higher-order Green's functions appearing on the right-hand side of these equations. It is convenient for the present purpose to use the Hartree-Fock approximation which may be stated in the forms:

$$\langle\langle a_g^\dagger a_ma_l;\,a_0^\dagger\rangle\rangle\underset{g\neq m\neq l}{=}\langle a_g^\dagger a_m\rangle\langle\langle a_l;\,a_0^\dagger\rangle\rangle+\langle a_g^\dagger a_l\rangle\langle\langle a_m;\,a_0^\dagger\rangle\rangle\ ,$$
$$\langle\langle a_g^\dagger a_ga_g;\,a_0^\dagger\rangle\rangle=2\langle a_g^\dagger a_g\rangle\langle\langle a_g;\,a_0^\dagger\rangle\rangle\ . \quad (20)$$

We restrict our calculations to the low-temperature zone so that the following approximations can be employed:

(i) The differences $S-\langle S^z\rangle$ and $S_0-\langle S_0^z\rangle$ are small;

(ii) $f_{gm}\equiv\langle a_g^\dagger a_m\rangle=0$ for $g\neq m$;

(iii) $f_{gm}=0$ for $g=m=\Delta$ and $f_{gm}\neq 0$ for $g=m=0$. We now express the correlation $\langle a_0^\dagger a_0\rangle$ in terms of the polarization deviation parameter

$$d_m=\langle S_m^z\rangle/\langle S^z\rangle-1$$

such that $d_m\neq 0$ for $m=0$ and zero otherwise.

The second condition for the approximation mentioned in (iii) therefore gives $f_{00}=\langle a_0^\dagger a_0\rangle=-d_0\langle S^z\rangle$.

Thus the equations of motion are reduced to the following simple forms:

$$[E-(R_1b_1+2R_3b_3d_0)]G_{00}(E)=\langle S_0^z\rangle/\pi-(R_1g_1+R_2a_2d_0)G_{\Delta 0}(E)\ , \quad (21)$$

$$[E-(R_1h_1+R_2b_2d_0)]G_{\Delta 0}(E)=-(R_1g_1+2R_3g_3d_0)G_{00}(E)\ . \quad (22)$$

Eliminating $G_{\Delta 0}(E)$, one gets readily

$$G_{00}(E)=\frac{\langle S^z\rangle}{\pi}(1+d_0)\frac{E-A_1}{(E-A_1)(E-A_2)-A_3}\ , \quad (23)$$

where A_1, A_2, and A_3 stand for the following expressions:

$$\begin{aligned}A_1&=R_1h_1+R_2b_2d_0\ ,\\ A_2&=R_1b_1+2R_3b_3d_0\ ,\\ A_3&=(R_1g_1+R_2a_2d_0)(R_1g_1+2R_3g_3d_0)\ .\end{aligned}\quad (24)$$

The zeros of the denominator of Eq. (23) gives the localized spin-wave modes. One gets after simplifications (restoring the units of R_1, R_2, and R_3) the following expression

$$\frac{E_q}{E_0}=\tfrac{1}{2}\Psi\left[1+\left(1-\frac{4\Psi_0}{\Psi^2}\right)^{1/2}\right]\ , \quad (25)$$

where E_0 is the spin-wave energy for the unperturbed host and is given by $E_0=2Jz\langle S^z\rangle$. The symbols Ψ and Ψ_0 are

$$\Psi=\alpha_1+\gamma_1+d_0(\alpha_2+4\alpha_3)\ , \quad (26)$$

$$\Psi_0=(\alpha_1+4\alpha_3d_0)(\alpha_1+\alpha_2d_0)-(\beta_1+d_0\gamma_2)(B_1+4d_0\beta_3)\ . \quad (27)$$

The symbols α_1, α_2, α_3, β_1, β_3, γ_1, and γ_2 are given by

$$\begin{aligned}\alpha_1&=R_1+x_0R_1^0\ ,\\ \alpha_2&=R_2+x_0R_2^0\ ,\\ \alpha_3&=R_3+x_0R_3^0\ ,\\ \beta_1&=R_1+x_1R_1^0\ ,\\ \beta_3&=R_3+x_1R_3^0\ ,\\ \gamma_1&=R_1+x_2R_1^0\ ,\\ \gamma_2&=R_2+A_2x_0R_2^0\ ,\end{aligned}$$

where

$$x_n=\left(\frac{S_0}{S}\right)^{n/2}\left(\frac{J_0}{J}\right)\ ,$$

the integer n running through 0, 1, and 2.

Since Eq. (25) was obtained as a solution from a quadratic equation, there would occur a negative sign in front of the parentheses. This negative sign has been discarded since in that case one would find that it would lead to an unphysical result for $\alpha=0$, $J_0 >> J$, and $S_0 > S$.

We shall now discuss the effects of biquadratic exchange on the localized spin-wave modes with the help of Eq. (25). We first study a simple situation: $J_0/J=1$, $S_0/S=1$, and $\alpha_0=0$. Equation (25), in this case, reduces to

$$E_q/E_0=2+d_0+2\alpha S(S-1)+\tfrac{1}{2}\alpha d_0(2S-1)(SS-1) \; . \tag{28}$$

This equation shows that if $\alpha=0$ the localized modes depend on d_0. At $T=0$ K since $d_0=0$, one thus finds that a localized excitation just tends to split off the spin-wave band and as the temperature increases, since $\langle S_0^z \rangle$ does not decrease rapidly as $\langle S^z \rangle$ does, d_0 becomes greater than zero so that at any finite temperature a "well-localized" excitation mode splits off the spin-wave continuum.

The presence of nonzero host-host biquadratic exchange complicates the problem. We shall present some simple observations from Eq. (28). For the spin-half case one finds that at $T=0$ K, $E_q/E_0 =2-\frac{1}{2}\alpha$ which implies that a negative α enhances the possibility of the appearance of a localized mode while a positive α hinders it. In other words, the decrease of α renders the situation more favorable for the formation of a localized mode. This conclusion was also reached previously by the author[17] for a general spin pattern which is not true. From Eq. (28) one may find that for $S > \frac{1}{2}$ the effects of an increase or a decrease in α become different. For $S=1$ at $T=0$ K, $E_q/E_0=2$ and for $S=\frac{3}{2}$, $E_q/E_0=2+\frac{3}{2}\alpha$. In the spin-1 case the biquadratic exchange has, therefore, no effect, while in the latter as α increases the situations become favorable for a localized excitation to split-off the spin-wave band. Similar results are also obtained for spins greater than $\frac{3}{2}$.

However, one obtains distinctly different results when $J_0/J \neq 1$ and $S_0/S \neq 1$. We first consider the case where $S_0/S < 1$ and $J_0/J < x_0^c$ so that no localized mode can be observed at 0 K, x_0^c being the critical value of J_0/J for which a localized mode is possible when the biquadratic interactions are absent. x_0^c has been calculated by different authors using different methods with slightly different results. Hone and Callen found

$$x_0^c=\frac{1.96-0.96(S_0/S)}{1.96+0.96(S_0/S)} \; . \tag{29}$$

In the present treatment we get for a localized mode

$$(2\Psi-\Psi_0-4)>0$$

which yields the value

$$x_0^c=[1-(S_0/S)^{1/2}]^{-1} \times\{1-[4(S/S_0)^{1/2}-2(S/S_0)-1]^{1/2}\} \; . \tag{30}$$

The comparison of Eqs. (29) and (30) will readily show that the value of x_0^c becomes greater in the present formalism. This is due to the consideration of the scattering effects. In the case $S=\frac{5}{2}$, $S_0=1$ one gets from Eq. (29) $x_0^c \simeq 0.67$ and from Eq. (30) $x_0^c \simeq 1.04$.

We now examine the effect of positive α (but $\alpha_0=0$) on the localized modes when $S_0/S<1$ and $x_0 < x_0^c$. Computations show that as α increases from zero, E_q/E_0 increases from 1.68 (approximately) for $J_0/J=0.5$, $S_0/S=0.4$ but as α crosses 0.05 we have found that E_q turns out to be complex and the excitation rapidly decays into the spin-wave continuum.

However, the above situation does not arise in the case where $S_0/S>1$ and $J_0/J > x_0^c$. It is quite evident that these conditions are favorable for the appearance of a localized mode at 0 K even in the absence of biquadratic coupling. In this case it has been found that the effect of increase of α in the positive side is simply to diminish the magnitude of E_q.

Interesting results are obtained when the magnitude of α increases in the negative side. When the situation happens to be such that it does not favor

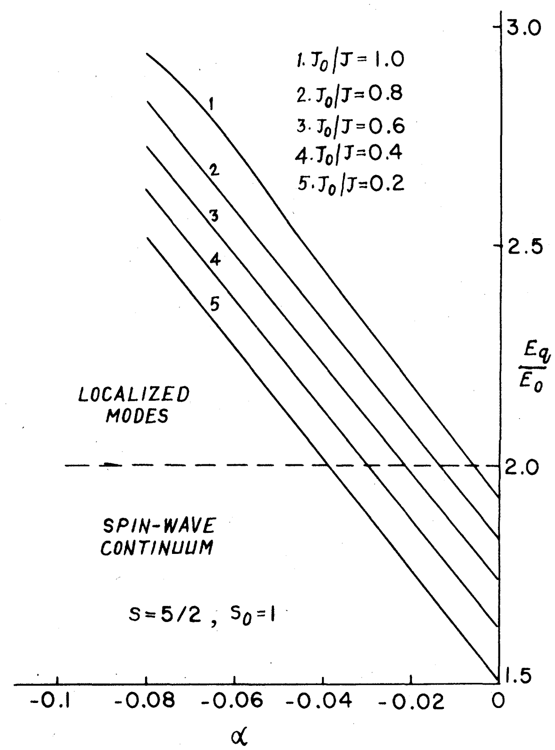

FIG. 3. Localized modes for negative α and for various positive values of J_0/J. Here $S=\frac{5}{2}$, $S_0=1$.

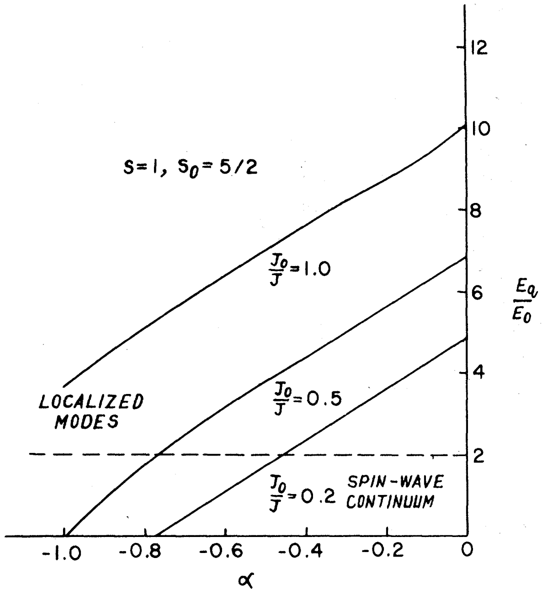

FIG. 4. Localized modes for $S=1$, $S_0=\frac{5}{2}$.

any localized excitation at 0 K in the absence of biquadratic coupling, one may find in that case that a certain negative α will render a favorable situation for an excitation mode to split off the spin-wave continuum. Conversely, when the conditions become such that these are favorable for the appearance of a localized mode even in the absence of biquadratic coupling, the increase of α in the negative side compels the excitation to decay into the spin-wave continuum. That is to say, the increase of α in the negative side acts adversely with the existing behavior of the system. This is clearly demonstrated in Figs. 3 and 4.

We conclude this section by making some comments on the influence of α on the localized excitations. Computations show that for $S_0/S < 1$ the effect of α_0 resembles closely the behavior mentioned above, but the changes in α_0 alter the magnitude of E_q/E_0 appreciably. For example, when $J_0/J=1$ we find that E_q/E_0 decreases rapidly as α_0 increases in the negative side and at about $\alpha_0=-0.4$, E_q vanishes which is markedly different from the result shown in Fig. 4.

VI. COMPARISON WITH OBSERVED DATA

Although it is not possible to verify all the theoretical results obtained in the preceding sections in view of the unavailability of proper experimental data, we point out some definite examples where some of our conclusions can be shown to be valid qualitatively, if not semiquantitatively. In the present section we shall discuss the situations which appear in the systems $KMnF_3$, $RbMnF_3$, $KNiF_3$, and MnF_2 doped by impurities. The exchange parameters and other physical constants are tabulated in Table II[18–21] where the values of S, S_0, J, $J+J_0$, and x_0 are collected from literature. The table shows that except for $RbMnF_3:Ni^{++}$ no localized mode can appear in other systems at 0 K in absence of biquadratic coupling. One, therefore, feels it necessary to include biquadratic exchange in all such cases. We shall attempt to make the estimates of the biquadratic coupling parameters α and α_0 in all these cases.

In $KMnF_3:Ni^{++}$ a localized mode is found to split off the band at very low temperatures. The host-host bilinear exchange and host-impurity bilinear exchange constants were estimated by Johnson *et al.* and their values are shown in the Table II. In view of the spin-wave result and the calculation of Hone

TABLE II. Exchange parameters and other physical constants for several impure Heisenberg systems are shown. Only the bilinear interactions are taken into account. The sign + (−) denotes that a localized mode exists (does not exist) at $T=0$ K. The values of J, $J+J_0$ are collected from literature (Refs. 18–21).

System	S	S_0	J	$J+J_0$	x_0 (observed)	x_0^c	Inference
$KMnF_3:Ni^{++}$	$\frac{5}{2}$	1	5.05	8.7	0.72	1.04	−
$KMnF_3:Eu^{++}$	$\frac{5}{2}$	1	5.05	1.52	−0.6	1.04	−
$RbMnF_3:Ni^{++}$	$\frac{5}{2}$	1	3.4	8.1	1.38	1.04	+
$RbMnF_3:Eu^{++}$	$\frac{5}{2}$	1	3.4	1.52	−0.55	1.04	−
$KNiF_3:Mn^{++}$	1	$\frac{5}{2}$	43	8.7	−0.98	−0.22	−
$MnF_2:Ni^{++}$	$\frac{5}{2}$	1	1.76	3.2	0.81	1.04	−

and Callen, one finds a J_0/J ratio which may favor a localized mode. But since the present treatment yields a larger critical ratio, a localized mode cannot be possible. In order to introduce biquadratic coupling, we first note that the host-impurity biquadratic coupling should not be very significant in such case so that $\alpha_0=0$ and only a small negative α may be found to be sufficient for the appearance of a localized mode. An estimate of α is seen to be -0.014 (approximately). Incidentally this value coincides excellently with that obtained by Joseph, who found that a value of $\alpha \simeq -0.015$ is necessary for good high-temperature-susceptibility data. Also this value is consistent with that calculated by Shrivastava[22] for linear T_{2g} system $V^{++}-F^{-}-V^{++}$ in cubic $KMgF_3$. Recently, the author[23] has performed a Green's-function calculation and obtained a value $\alpha \simeq -0.016$ for a good fit for the susceptibility data of $KMnF_3$.

In $KMnF_3:Eu^{++}$ we note that $x_0 < x_0^c$ and calculations show that the above value of α together with $\alpha_0=0$ would result in the appearance of a localized mode.

We now discuss the situations appearing in $RbMnF_3$ and $KNiF_3$ doped by impurities. Various measurements show that these two systems have negligible second-neighbor exchange and anisotropy and that the properties of pure systems can be satisfactorily understood on the basis of simple bilinear exchange. So $\alpha=0$ in these cases can be assumed. In $RbMnF_3:Ni^{++}$ we thus find $\alpha=0$, $\alpha_0=0$, $x_0 > x_0^c$, and a localized mode is possible, which agrees with the observation of Johnson *et al.* But we find that in $RbMnF_3:Eu^{++}$ since $x_0 < x_0^c$ no localized mode becomes possible. As $\alpha=0$, $\alpha_0=0$ in this case no question of modification of this result by biquadratic exchange arises. However, due to the lack of experimental data this conclusion cannot be verified.

Regarding $KNiF_3:Mn^{++}$ it was remarked by Parkinson that the large host spin of the Mn salts and the large host exchange in $KNiF_3$ tend to favor the resonance impurity modes within the spin-wave band rather than the localized excitation above the band. Table II demonstrates $x_0 < x_0^c$ and so no localized mode is possible when biquadratic exchange is absent. But in this case we note that although $\alpha=0$, α_0 is not zero since there should exist an appreciable biquadratic coupling part in host-impurity interaction. Considering the estimate we have found $E_q/E_0 < 2$ and thus no localized excitation is possible.

Lastly, in the case of Ni^{++} doping in MnF_2 one finds an estimate: $\alpha \simeq -0.013$ for the appearance of a localized mode. This estimate agrees with that obtained by Rodbell *et al.*[24] In Table III,[25] we have put $\alpha_0=0$ for $MnF_2:Ni^{++}$. A very small value of α_0 is possible since NiF_2 may have some small biquadratic exchange.

TABLE III. The values of the bilinear and biquadratic exchange constants for the host and impure spins estimated from the present treatment.

System	From literature	α	α_0
$KMnF_3:Ni^{++}$	-0.015[a] -0.01[b] -0.016[c]	-0.017	0
$KMnF_3:Eu^{++}$	...	-0.017	0
$RbMnF_3:Ni^{++}$	0[a]	0	0
$RbMnF_3:Eu^{++}$	...	0	0
$KNiF_3:Mn^{++}$	0[a]	0	-0.017
$MnF_2:Ni^{++}$	-0.005[d]	-0.013	0

[a]Reference 25.
[b]Reference 22.
[c]Reference 23.
[d]Reference 24.

VII. CONCLUSION

A theory of the impure Heisenberg system with both bilinear and biquadratic interactions has been elaborately studied and the results are found to be consistent with the observed data. The theory is, however, valid at low temperatures and the criteria for the existence of localized modes are duly modified when their temperature dependence is more rigorously considered. Indeed, a localized mode which feels harder to split off the spin-wave band at 0 K may appear at some high temperature where the scattering effects should be appropriately included. It becomes, furthermore, necessary to study the temperature variations of the host magnetization and the impurity magnetization, giving proper consideration of the scattering effects. However, it may be believed that more rigorous consideration of the scattering effects can only alter the numerical results, without affecting the qualitative results too seriously. We also point out that the theory only presents the discussion of the appearance of *s*-type localized excitation. The conditions for the appearance of *p* and *d* modes should also be studied. All these aspects along with those related to more complicated magnetic systems give rise to great mathematical complexities and enormous computational labor. The problem of inclusion of biquadratic exchange related to more complicated systems can be studied easily at low temperatures by simply extending the existing theory. Complication arises at high temperatures where such simple extension cannot work well.

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