

Effect of  $S_z$ -nonconserving interactions on local-mode dynamics in  $\text{FeF}_2:\text{Mn}$ 

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(Received 27 September 1982)

In Mn-doped  $\text{FeF}_2$  a localized excitation exists below, but close to, the magnon continuum. With the application of an external magnetic field along the anisotropy axis, both the magnon band and the local mode undergo Zeeman splitting. When, with increasing field, the upgoing local mode becomes degenerate with the downgoing band, it broadens because of the opening of scattering channels into the continuum through  $S_z$ -nonconserving terms in the Hamiltonian (dipolar and orthorhombic anisotropy interactions). The contribution of each of these interactions to the local-mode linewidth is calculated, using standard Green-function techniques. Although comparison with the single available experimental point indicates that much of the linewidth arises from magnon-phonon decay, the signature of the field dependence of the contribution calculated here makes separate identification readily possible, once field-dependent experiments have been made.

## I. INTRODUCTION

The usefulness of substitutional impurities, with excitations spatially localized because they lie outside of the continuous energy bands of the host, as local probes in solids, has long been recognized.<sup>1</sup> A particularly interesting case is the impure antiferromagnet with a localized magnon excitation below, but close to, the magnon continuum (such as  $\text{Mn}:\text{FeF}_2$ , studied in Ref. 2 or  $\text{Mn}:\text{CoF}_2$ , which is discussed in Ref. 3), where the dynamics are particularly sensitive to an applied magnetic field. The nature of the elementary excitation spectrum, as a function of magnetic field strength along the principal anisotropy axis, is illustrated in Fig. 1 for  $\text{Mn}:\text{FeF}_2$ , where the host band in zero field extends from 1.58 to 2.35 THz and the local mode is at 1.507 THz. In this two sublattice uniaxial antiferromagnet, both the local mode and the host-magnon continuum split under the application of the field, depending on whether the spin-flip excitation lies primarily on the sublattice with spins parallel to, or the one with spins antiparallel to, the field direction. For either local or band modes, we will refer to the branch with energies increasing with the field as "upgoing" and with energies decreasing with the field as "downgoing."

Because of the proximity of the local mode to the band edge, this excitation is relatively extended spatially, involving substantial participation of the Fe neighbors to a Mn spin, so the magnetic field dependence of the local-mode energy is intermediate between those of Fe and Mn. Although this dependence need not be linear in the field, it is found to be so (both experimentally and theoretically) to a good

approximation, with an effective  $g$  factor of approximately 2.05, less than the value  $g=2.22$  for the Fe spins, so the downgoing local mode approaches the downgoing band edge (they cross near  $H_0 \approx 250$  kOe). Thus, the spatial extent of the local mode, and therefore the overlap of such modes centered on different impurities and the resulting impurity bandwidth, increase with the applied field. The impact on the local-mode magnetic resonance linewidth with increasing field has been explored in Ref. 4. Here, we will be concerned with the dynamics of the upgoing local mode, as it enters and passes through

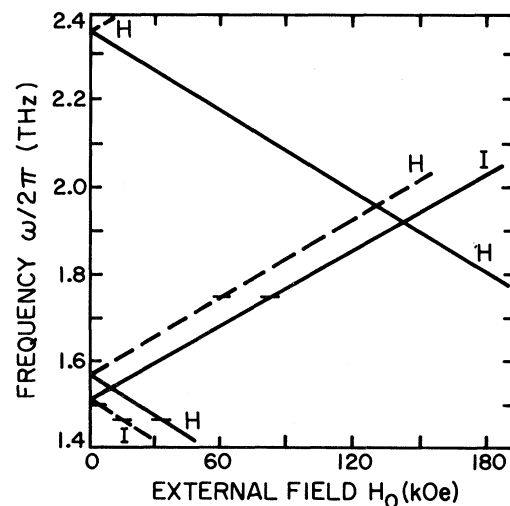


FIG. 1. Predicted positions of the host band edges ( $H$ ) and the impurity local modes ( $I$ ) in  $\text{FeF}_2:\text{Mn}$ , from a linear fit to the data, indicated by horizontal bars. The branches of concern here (upgoing local mode and downgoing host band) are shown by the solid lines.

the downgoing continuum with increasing applied field; a brief discussion of this was presented earlier.<sup>5</sup> Were there complete rotational symmetry about the  $z$  axis (the direction of the applied field, as well as the principal anisotropy axis), so that total  $S_z$  was conserved, then the degenerate local and continuum modes would be orthogonal by symmetry, and they would not mix. However, both the dipolar and orthorhombic anisotropy interactions, although relatively small, break this symmetry, and decay into the continuum becomes a source of linewidth for the local mode. Here we present a calculation of this effect. We will find that, although perhaps as much as 80% of the linewidth arises from other sources (probably dominantly from spin-lattice effects), the remaining linewidth contribution from the sources calculated here exhibit significant field (or frequency) dependence and should easily be separately identifiable in the experimental results, once these become available as a function of field.

## II. CALCULATIONS

Since the experimental quantity of interest here is the magnetic resonance linewidth of the local mode, we should calculate the response of the system to a spatially uniform field at the relevant frequency. In fact, as long as we require only the linewidth and not the intensity and detailed shape of the resonance line, it will be adequate (and simpler in this system without translational symmetry) to calculate the local susceptibility of the impurity itself. For this purpose we will make use of standard Green-function techniques. We will first calculate the propagators for the pure crystal, including the effects of the rotational symmetry-breaking terms, a calculation in which the wave vector is a good quantum number. A single impurity will be introduced; if the corresponding perturbation is sufficiently localized, then the dynamical equations couple only a few Green functions in a lattice-site representation, with propagation expressed in terms of the solutions to the pure-crystal problem.

The Hamiltonian of the pure rutile-structure crystal is conveniently written as

$$H = H_e + H_z + H_{ua} + H_{0a} + H_d, \quad (2.1)$$

referring, respectively, to Heisenberg exchange, Zeeman, uniaxial anisotropy, orthorhombic anisotropy, and dipolar interaction terms. With the magnetic field applied along the direction defining uniaxial anisotropy (the "z axis"), the first three terms retain rotational symmetry about the  $z$  axis and therefore commute with the total  $z$  component of spin

$$H_e + H_z + H_{ua} = \sum J_{ij} \vec{S}_i \cdot \vec{S}_j - \gamma H_0 \sum S_i^z - D \sum (S_i^z)^2, \quad (2.2)$$

where  $S$  is the  $\text{Fe}^{2+}$  spin magnitude. The dominant exchange interaction  $J_{ij}$  is between spins at next-nearest-neighbor sites  $i$  and  $j$ . Although there exist weaker exchange couplings between nearest and third neighbors, we will incorporate all such effects into a single next-nearest-neighbor exchange constant  $J$ , which simplifies the algebraic manipulations without altering any of the essential physics (note, in particular, that all Heisenberg exchange terms commute with total  $S_z$ ).

The magnetocrystalline anisotropy arises from the electrostatic fields of the ions surrounding a  $\text{Fe}^{2+}$  site. The dominant uniaxial term is associated with the tetragonal distortion of the cell from cubic symmetry. But there is, in addition, a small orthorhombic anisotropy in the  $x$ - $y$  plane which can be represented as

$$H_{0a} = -\frac{E}{2S} \sum_i \eta_i [(S_i^x)^2 - (S_i^y)^2], \quad (2.3)$$

where  $\eta_i$  equals  $+1$  for  $i$  on the up sublattice and  $-1$  for  $i$  on the down sublattice, because the  $F^-$  cage is rotated by  $\pi/2$  about the  $z$  axis in going from a magnetic site on one sublattice to one on the other. Thus, there is local, but not global, orthorhombic anisotropy. Although this term is small, it breaks the uniaxial rotational symmetry and can therefore play an essential role in properties relying on this broken symmetry—in particular, the local-mode linewidth considered here. The same remark holds for the magnetic dipole-dipole interaction,

$$H_d = \frac{1}{2} \hbar \gamma^2 \sum [\vec{S}_i \cdot \vec{S}_j - 3(\vec{S}_i \cdot \hat{r}_{ij})(\vec{S}_j \cdot \hat{r}_{ij})] r_{ij}^{-3}. \quad (2.4)$$

For simplicity, we consider temperatures far below the antiferromagnetic ordering temperature  $T_N$  (as was, in fact, the case for the experiments with which we will compare our results). If no temperature-dependent renormalization effects then are involved, we can avoid the complications of the spin commutation relations in the dynamical equation by making use of the boson representation of the Holstein-Primakoff transformation<sup>6</sup>:

$$S_{aj}^+ = \sqrt{2S_j} \left[ 1 - \frac{a_j^\dagger a_j}{2S} \right]^{1/2} a_j = (S_{aj}^-)^\dagger, \quad (2.5)$$

$$S_{bl}^+ = \sqrt{2S_l} b_l^\dagger \left[ 1 - \frac{b_l^\dagger b_l}{2S} \right]^{1/2} = (S_{bl}^-)^\dagger,$$

where the boson annihilation operators  $a$  and  $b$  refer to up and down sublattices, respectively, and  $j, l$  label the sites.

We define the usual zero-temperature retarded Green function  $G^{AB}(t)$  for two Heisenberg operators

$A(t)$  and  $B(t)$ :

$$G^{AB}(t) = -i\Theta(t)\langle [A(t), B(0)] \rangle \equiv \langle \langle A(t); B(0) \rangle \rangle, \quad (2.6)$$

where  $\Theta(t)$  is the unit step function and the single angular brackets denote the ground-state expectation value. In the familiar case of a two sublattice antiferromagnet with a Hamiltonian which conserves total  $S_z$ , the equation of motion of  $G^{AB}$ , with  $A$  a spin operator (e.g.,  $S_l^-$ ), introduces only other operators producing the same net spin deviation ( $S_m^-$  for other sites  $m$ ). In a translationally invariant system, where wave vector is a good quantum number, the equations of motion then mix only two Green functions  $G_\alpha(\vec{q}, t)$  one for each sublattice. But when  $S_z$  is no longer conserved, four such functions are dynamically coupled. Then for any pair of sites  $m$  and  $l$  it is convenient to define the four Green functions

$$\begin{aligned} G_{ml}^{+-}(t) &= \langle \langle \xi O_m(t), O_l^\dagger(0) \rangle \rangle, \\ G_{ml}^{++}(t) &= \langle \langle \xi O_m(t), O_l(0) \rangle \rangle, \\ G_{ml}^{-+}(t) &= \langle \langle \xi O_m^\dagger(t), O_l^\dagger(0) \rangle \rangle, \\ G_{ml}^{-+}(t) &= \langle \langle \xi O_m^\dagger(t), O_l(0) \rangle \rangle, \end{aligned} \quad (2.7)$$

$$\begin{pmatrix} G_{\uparrow\uparrow}(\vec{q}, \omega) & G_{\uparrow\downarrow}(\vec{q}, \omega) \\ G_{\downarrow\uparrow}(\vec{q}, \omega) & G_{\downarrow\downarrow}(\vec{q}, \omega) \end{pmatrix} = \begin{pmatrix} \omega_- - \nu & B_-^*(\vec{q}) & -B_x^*(\vec{q}) & A(\vec{q}) \\ -B_-(\vec{q}) & \omega_+ + \nu & -A(\vec{q}) & B_x(\vec{q}) \\ -B_x(\vec{q}) & A(\vec{q}) & \omega_+ - \nu & B_+(\vec{q}) \\ -A(\vec{q}) & B_x^*(\vec{q}) & -B_+(\vec{q}) & \omega_- + \nu \end{pmatrix}^{-1}, \quad (2.10)$$

where the asterisk indicates complex conjugation,  $\omega_\pm \equiv \omega \pm \omega_0$ , with  $\omega_0 \equiv \gamma H_0$  the Zeeman frequency,  $\nu = 2S(D + 8J)$ , and

$$A(\vec{q}) = 2JS \sum_{\vec{\delta}} \exp(i\vec{q} \cdot \vec{\delta}),$$

summed over the eight next-nearest-neighbor vectors connecting exchange-coupled sites. More precisely,  $\nu$  also contains small  $S_z$ -conserving  $\vec{q}$ -dependent terms arising from dipole sums. At  $\vec{q}=0$  these describe demagnetization effects; at all  $\vec{q}$  the corrections are small and we shall neglect them. The coefficients  $B(\vec{q})$  arise from the  $S_z$  nonconserving terms in the Hamiltonian:

$$B_\pm(\vec{q}) = B_s(\vec{q}) \pm E, \quad (2.11)$$

$$B_s(\vec{q}) = -\frac{3}{2}S\gamma^2 h \sum_{j(s)} \frac{(x_{0j} - iy_{0j})^2}{r_{0j}^5} e^{i\vec{q} \cdot \vec{r}_{0j}}, \quad (2.12)$$

with  $j(s)$  summed over all sites on the same sublattices as the reference site, here labeled 0. Similarly,

where  $O_s \equiv a_s(b_s^\dagger)$  if site  $s$  is on the up (down) sublattice (so it always flips a spin up, increasing  $S_z$  by one unit), and  $\xi = \pm 1$  is defined so that the equal time commutator of the operators in  $G$  is  $+1$  or zero:  $\xi = +1$  if it is followed by a destruction operator ( $a$  or  $b$ ) and  $\xi = -1$  if followed by a creation operator ( $a^\dagger$  or  $b^\dagger$ ). Then, if we introduce the  $2 \times 2$  matrix  $G_{ml}^{\alpha\beta}(t)$  of Green functions for each pair of sites  $m$  and  $l$ , with  $\alpha\beta$  taking the values  $+$  and  $-$ , the frequency Fourier transform of these matrix Green functions obeys equations of motion

$$\omega G_{ml}^{\alpha\beta}(\omega) = \delta_{ml} \delta_{\alpha\beta} + M_{mn}^{\alpha\gamma}(\omega) G_{nl}^{\gamma\beta}(\omega), \quad (2.8)$$

where repeated indices are to be summed. As always, translational symmetry block diagonalizes these matrices, with each block labeled by a wave vector  $\vec{q}$ :

$$G_{\sigma\sigma'}^{\alpha\beta}(\vec{q}, \omega) \equiv \sum_m G_{m(\sigma)l(\sigma')}^{\alpha\beta}(\omega) e^{i\vec{q} \cdot (\vec{r}_m - \vec{r}_l)}, \quad (2.9)$$

where  $\sigma, \sigma'$  label the sublattices on which the sites  $m$  and  $l$  are located. Then the solution of Eq. (2.8) is reduced to inversion of a  $4 \times 4$  matrix:

$B_x(\vec{q})$  is defined by Eq. (2.12) but with the sum  $j(x)$  now taken over all sites on the opposite sublattice from the site 0. Of course, in the absence of these coefficients  $B(\vec{q})$ , the problem factors into the usual  $2 \times 2$  matrix structure, where a Green function  $G(\vec{q}, \omega)$  is connected to a single other one, associated with the other sublattice.

The magnon energies are the poles of the Green function, or zeros of the determinant  $\Delta(\vec{q}, \omega)$  of the matrix whose inverse is the right-hand side of Eq. (2.10). In the absence of the long-range dipolar interactions this determinant takes the simple form

$$\Delta(\vec{q}, \omega) = [\Omega_+^2 - \nu^2 + A^2(q)][\Omega_-^2 - \nu^2 + A^2(\vec{q})], \quad (2.13)$$

where  $\Omega_\pm = (\omega^2 + E^2)^{1/2} \pm \omega_0$ . Clearly the zeros of  $\Delta(\vec{q}, \omega)$  arising from these two factors form the upgoing and downgoing host bands. The dispersion relation reduces to the form familiar for uniaxial antiferromagnets if the orthorhombic anisotropy  $E$  is

also set equal to zero. Although the fourth-order secular equation does not readily factor into a similar intuitively obvious form in the presence of the dipole interactions, the resultant band structure is, of course, very similar both qualitatively and quantitatively; the dipole interactions are relatively small. The important alteration of the pure-system spin dynamics by the symmetry-breaking terms is not in the spectral range but rather in the introduction of new nonvanishing correlation functions  $G^{++}(\vec{q}, \omega)$  and  $G^{--}(\vec{q}, \omega)$ , which imply spectral density for a given direction of spin flip where it did not exist before, which will permit the decay of the local mode of interest here, as anticipated.

We now introduce a single substitutional Mn impurity on the up sublattice, on a site henceforth labeled 0. This impurity has both a different spin magnitude and different exchange couplings with its neighbors than the host Fe spin which it replaces. However, the net exchange mean field is *not* much changed, and these Heisenberg interactions conserve total  $S_z$  in any case, so the effect of altered exchange interactions is unimportant for our purposes. On the other hand, inclusion of these terms as perturbations, off-diagonal in a lattice-site representation, would greatly increase the algebraic complexity of the calculation, so we shall neglect them. The site-diagonal perturbations of the impurity which we will keep include the much smaller uniaxial anisotropy ( $D' \ll D$ , where the prime denotes the value

associated with the Mn impurity), a different  $g$  value ( $g'=2.00$ ,  $g=2.22$ ), and the near absence of an orthorhombic anisotropy term for the orbital  $S$ -state ion ( $E' \approx 0$ ). These perturbations then take the form

$$H' = -P(H_0)a_0^\dagger a_0 + \frac{1}{2}E(a_0 a_0 + a_0^\dagger a_0^\dagger), \quad (2.14)$$

where  $P(H_0)$  includes the difference in both uniaxial anisotropy and Zeeman energy terms. This term is larger than the other (proportional to  $E$ ) in Eq. (2.14), and it primarily controls the energy of the local mode; the parameters of  $P(H_0)$  are chosen to reproduce the experimental local-mode energy:

$$P(H_0)/16JS = 0.38 + 2 \times 10^{-4} H_0 (\text{kOe}). \quad (2.15)$$

The dynamical equation for the Green functions of the impure system  $\mathcal{G}$  can now be written in the lattice-site representation as

$$\mathcal{G}_{ij}^{\alpha\beta}(\omega) = G_{ij}^{\alpha\beta}(\omega) + G_{i0}^{\alpha\gamma}(\omega) V^{\gamma\delta} \mathcal{G}_{0j}^{\delta\beta}(\omega), \quad (2.16)$$

where again repeated indices imply summation. The  $2 \times 2$  perturbation matrix  $V$  has diagonal elements  $\pm P(H_0)$  and off-diagonal elements  $\pm E$ , with elements of the matrix labeled only by the superscripts (which take values  $+$  and  $-$ ), since it is localized on the impurity site. Further, since we have indicated that we are only interested in the local function  $\mathcal{G}_{00}(\omega)$ , we can immediately set  $i=j=0$  in (2.16) to obtain

$$\mathcal{G}_{00}(\omega) = \begin{pmatrix} 1 + PG_{00}^{+-} - EG_{00}^{++} & EG_{00}^{+-} - PG_{00}^{++} \\ PG_{00}^{--} - EG_{00}^{+-} & 1 - PG_{00}^{++} + EG_{00}^{--} \end{pmatrix}^{-1} G_{00}(\omega). \quad (2.17)$$

The singularities of  $\mathcal{G}_{00}$ , in addition to a quasicontinuum coinciding with that of  $G_{00}$ , include isolated poles at the zeros of the determinant of the  $2 \times 2$  matrix in Eq. (2.17), the local-mode frequencies. We recall that  $G^{++}$  and  $G^{--}$  vanish with  $E$ , so neglecting terms of order  $E^2$  we find the local-mode frequency  $\omega_l$  is given by the condition

$$1 + P(H_0)G_{00}^{+-}(\omega_l) = 0. \quad (2.18)$$

(The other factor in the secular determinant,  $1 - PG_{00}^{--}$ , does not vanish for positive  $\omega$ .) It is clear from Eqs. (2.17) and (2.18) that near  $\omega = \omega_l$  the

Green function takes the form

$$\mathcal{G}_{00}(\omega) \simeq \frac{C}{\omega - \omega_l - \Sigma - i\Gamma}, \quad (2.19)$$

where  $C$ ,  $\Sigma$ , and  $\Gamma$  are approximately independent of frequency  $\omega$ , and  $\Sigma$  and  $\Gamma$  vanish with the  $S_z$ -nonconserving interactions. That is, the response of the impurity spin itself near the local-mode frequency is approximately Lorentzian in shape, with a small frequency shift  $\Sigma$  from  $\omega = \omega_l$  and a half-width  $\Gamma$ , given approximately by

$$\Gamma = \left[ \frac{d}{d\omega} G_{00}^{+-}(\omega) \right]^{-1} \text{Im} \left[ G_{00}^{+-} + \frac{(E^2/P)G_{00}^{+-}G_{00}^{--} + PG_{00}^{++}G_{00}^{--} + (E/P)(G_{00}^{--} - G_{00}^{++})}{1 - PG_{00}^{++}} \right], \quad (2.20)$$

where the right-hand side is evaluated at  $\omega = \omega_l$ . Corrections to  $\Gamma$  are of higher order in the dipolar and orthorhombic anisotropy coupling constants  $V_d$  and  $E$ .

For explicit evaluation of  $\Gamma$  we require the local pure-crystal Green functions, the spatial Fourier transforms of the solution (2.10),

$$G_{00}^{\alpha\beta}(\omega) = \frac{1}{N} \sum_q C_{\uparrow\uparrow}^{\alpha\beta}(\vec{q}, \omega) / \Delta(\vec{q}, \omega), \quad (2.21)$$

where  $\Delta(\vec{q}, \omega)$  is the determinant of the matrix whose inverse is the right-hand side of Eq. (2.10), and

$$C_{\uparrow\uparrow}^{+-}(\vec{q}, \omega) = -C_{\uparrow\uparrow}^{-+}(\vec{q}, -\omega) \\ = (\omega_- + \nu)[\omega_+^2 - \nu^2 + A^2(q)] + |B_+|^2(\omega_+ + \nu) - |B_x|^2(\omega_+ - \nu) - A(q)(B_x B_+^* + B_x^* B_+), \quad (2.22)$$

$$C_{\uparrow\uparrow}^{--}(\vec{q}, \omega) = -C_{\uparrow\uparrow}^{++}(\vec{q}, \omega) \\ = B_- [\omega^2 - (\nu - \omega_0)^2 + |B_+|^2] - A^2(q)B_+ + 2A(q)B_x(\nu - \omega_0) - B_x^2 B_+^*. \quad (2.23)$$

It is clear from these explicit expressions that the leading terms in  $C_{\uparrow\uparrow}^{+-}$  and  $C_{\uparrow\uparrow}^{-+}$  are constants plus corrections of order  $V_d^2$  and  $E^2$ , while in  $C_{\uparrow\uparrow}^{++}$  and  $C_{\uparrow\uparrow}^{--}$  they are of order  $V_d$  and  $E$ . Although  $V_d$  is only a few percent of  $E$ , the dipolar interaction is long ranged, while the orthorhombic anisotropy is local, so their effects can be comparable, and we retain both. In fact, to second order their effects are simply additive and we can examine them separately: The terms in Eq. (2.23) which are linear in  $B_\pm$  and  $B_x$  [see the definitions (2.11) and (2.12)] involve dipolar sums of the form

$$\sum_j \frac{(x_{0j} - iy_{0j})^2}{r_{0j}^5} \sum_q \frac{[a + bA(q)]}{\Delta(\vec{q}, \omega)} e^{i\vec{q} \cdot \vec{r}_{0j}}, \quad (2.24)$$

which vanishes by symmetry (since the sum over  $q$  itself retains the full lattice symmetry as a function of  $\vec{r}_{0j}$ ). Therefore, terms linear in  $V_d$  in  $G_{00}$  vanish, as do terms of order  $EV_d$ , for the same reason. Thus to second order we can evaluate the orthorhombic and dipolar contributions separately.

We first consider the orthorhombic contribution. The Green function takes the form

$$G_{00}^{\alpha\beta}(\omega) = \frac{1}{4\omega_0\Omega} \sum_q C_{\uparrow\uparrow}^{\alpha\beta}(\vec{q}, \omega) \left[ \frac{1}{\Omega_-^2 - \nu^2 + A^2(\vec{q})} - \frac{1}{\Omega_+^2 - \nu^2 + A^2(\vec{q})} \right], \quad (2.25)$$

where  $\Omega = (\omega^2 + E^2)^{1/2}$  and, as before,  $\Omega_\pm = \Omega \pm \omega_0$ . In the absence of dipolar interactions the  $\vec{q}$  dependence of  $C(\vec{q}, \omega)$  is contained in terms proportional either to a constant or to a simple phase factor, so the  $q$  sums are all of the form

$$U_{ij}(\epsilon) = \frac{1}{N} \sum \frac{\exp(i\vec{q} \cdot \vec{r}_{0j})}{\epsilon^2 - \nu^2 + A^2(\vec{q})}, \quad (2.26)$$

which has been tabulated<sup>7</sup> for small  $|r_{ij}|$  (all that is needed here), since it is just what is required for the Green function when  $E=0$ . We note that the imaginary part of the retarded function is to be interpreted as the limit of the vanishing positive imaginary part of  $\omega$  at the cut along the real axis explicitly exhibited in Eqs. (2.25) and (2.26).

Some simplification in the form of the orthorhombic contribution  $\Gamma_E$  to the halfwidth results because of the relation

$$G_{00}^{++}(\omega) = (E/2\omega)[G_{00}^{+-}(\omega) + G_{00}^{-+}(\omega)] \quad (2.27)$$

in the absence of dipolar contribution. To lowest nonvanishing order in  $E$  we find

$$\Gamma_E = \frac{(E/P)^2 [G_{00}^{-+}(\omega_l)]_0}{|1 - P[G_{00}^{+-}(\omega_l)]_0|^2} \left[ \frac{d}{d\omega} G_{00}^{+-}(\omega = \omega_l) \right]^{-1}, \quad (2.28)$$

where the subscript 0 on the brackets around the Green functions indicates that they are to be evaluated to zero order in the  $S_2$ -nonconserving in-

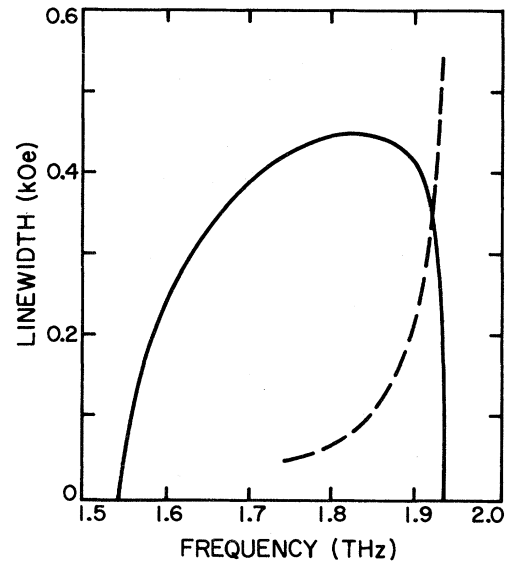


FIG. 2. Predicted linewidth of the upgoing local mode as a function of its frequency. The solid line shows the width due to orthorhombic anisotropy, the dotted line due to dipolar interactions.

teraction. The linewidth  $2\Gamma_E$  is plotted as a function of resonance frequency (effectively, as a function of applied magnetic field) in Fig. 2, with the orthorhombic anisotropy strength taken as  $E=2.68 \text{ cm}^{-1}$ . This value of  $E$  was obtained from measurements<sup>8</sup> on the optical spectrum of  $\text{Fe}^{2+}$  in nonmagnetic  $\text{ZnF}_2$ . Although  $E$  is very sensitive to the lattice parameters, a crude calculation of the change in the electric quadrupole field strengths using a point-charge model with the known lattice parameters of  $\text{ZnF}_2$  and  $\text{FeF}_2$  suggests an increase in  $E$  of order 10% or less.

We turn now to the dipole contribution, setting  $E=0$ . Then, since the site-diagonal Green functions  $G_{00}^{\alpha\beta}$  contain no term linear in  $V_d$ , as discussed above, to second order in  $V_d$  the expression (2.20) for the linewidth takes the simple form

$$\Gamma_d \approx \left[ \frac{d}{d\omega} \text{Re}G_{00}^{+-}(\omega=\omega_l) \right]^{-1} \text{Im}G_{00}^{+-}(\omega_l). \quad (2.29)$$

In contrast to the contribution from orthorhombic anisotropy considered above, the necessary Green functions here are not immediately expressible in terms of the same sums over wave vector  $\vec{q}$  which define the tabulated Green functions of the  $S_z$ -conserving Hamiltonian. Algebraically, the missing simplification is the factorized structure (2.13) for

$$\text{Im}G_{00}^{+-}(\omega) = V_d^2 \text{Im} \sum_{j,k} \left[ \left[ A_1 \frac{(r_{0j(s)}^+ r_{0k(s)}^-)^2}{r_{0j}^5 r_{0k}^5} + A_2 \frac{(r_{0j(x)}^+ r_{0k(x)}^-)^2}{r_{0j}^5 r_{0k}^5} \right] U_{jk}(\omega_+) + A_3 \frac{(r_{0j(s)}^+ r_{0k(x)}^-)^2}{r_{0j}^5 r_{0k}^5} V_{jk}(\omega_+) \right], \quad (2.31)$$

where  $r^\pm \equiv x \pm iy$  and, as before,  $j(s)$  and  $j(x)$  imply sums over the same and opposite sublattices, respectively, as the reference site 0. The coefficients  $A_1, A_2, A_3$  depend only on  $\omega, \omega_0$ , and the parameters of the  $S_z$ -conserving Hamiltonian, and the lattice function  $V_{jk}(\epsilon)$  is related to  $U_{jk}(\epsilon)$ , defined in Eq. (2.26), by

$$V_{jk}(\epsilon) = \frac{1}{8} \sum U_{j+\delta, k}(\epsilon), \quad (2.32)$$

where the sum is over the eight nearest-neighbor vectors  $\vec{\delta}$  on the body-centered lattice. The functions  $U_{\vec{R}}(\omega)$  have been tabulated only out to the lattice point  $\vec{R}=(2,2,2)$ , and so the sums of Eq. (2.31) are easily done numerically only when they have already converged by the time the lattice vectors reach this size. This causes problems only for frequencies  $\omega_l$  near the lower band edge (of the downgoing continuum), so in Fig. 2 we have plotted the results for  $\Gamma_d$  only well away from this point. Of course,

the orthorhombic contribution of the secular determinant  $\Delta(\vec{q}, \omega)$ , which appears in the denominator of the  $q$  sum defining  $G_{00}$  [see Eq. (2.21)]. However, such a form is approximately correct:

$$\Delta(\vec{q}, \omega) \approx [\omega_-^2 - \nu^2 + A^2(\vec{q})] \times \left[ \omega_+^2 - \nu^2 + A^2(\vec{q}) + \frac{\alpha V_d^2}{\omega_-^2 - \nu^2 + A^2(\vec{q})} \right], \quad (2.30)$$

where we recall  $\omega_\pm = \omega \pm \omega_0$  and  $\alpha$  is a constant of order unity. At  $\omega = \omega_l(H_0)$  we find  $\omega_-$  is nearly field independent [it would be exactly so if  $g'$  were equal to  $g$ , so that  $\omega_l(H_0)$  was  $\omega_l(0) + \omega_0$ ]. As always,  $\nu^2 - A^2(\vec{q})$  is the square of the band-magnon energy of wave vector  $q$ , in the absence of a field. Therefore, the last term in the second set of large parentheses of (2.30) represents a correction (effectively a shift in the poles of the Green function) of the order of the square of the ratio of the dipolar coupling to the separation of the local mode from the band at zero field. This can be neglected in all cases considered here (note that the width  $\Gamma_d$  is already proportional to  $V_d^2$  from the numerator of  $\text{Im}G_{00}$ ), and we have approximately

$\Gamma_d=0$  exactly at that band minimum frequency and it is clear by continuity that it remains small up to the point where we can be confident of the numerical convergence of our sums.

### III. DISCUSSION, COMPARISON WITH EXPERIMENT

The results of the above calculation, as summarized in the graph of Fig. 2, reflect the linewidth of the upgoing local mode in  $\text{FeF}_2:\text{Mn}$  associated with decay of that mode into the downgoing continuum. This contribution vanishes, of course, when the local mode lies outside the band:  $\omega_l < 1.54 \text{ THz}$  or  $\omega_l > 1.93 \text{ THz}$  (see Fig. 1). Because both destruction of the upgoing local mode and creation of a downgoing band magnon correspond in lowest order to increase of  $S_z$  by one unit, axial-symmetry-breaking terms of the form  $S_i^+ S_j^+$  play an important role.

The transition matrix elements are largest when  $i$  and  $j$  are on opposite sublattices (since the local-mode wave-function amplitude is large on one sublattice, and the band-mode amplitude on the other). Thus for the dipolar interactions the intersublattice terms [proportional to  $A_2$  in Eq. (2.31)] play a dominant role. The linewidth contribution  $\Gamma_d$  is of the order of the square of the dipolar coupling constant times the density of states for excitation by a single spin flip in the direction of the field, at positive frequencies. This density of states, which in the pure axially symmetric system has a singularity at the upper band edge, no longer is singular, though it does have a large peak there, as indicated in the figure.

The orthorhombic coupling constant is intrinsically more than an order of magnitude larger than the dipolar coupling constant, but its contribution to local-mode broadening is reduced by two important features. First it is site local, and  $S_i^+ S_i^+$  couples strongly either only to the local magnon (if  $i$  is on the up sublattice) or to the continuum (if  $i$  is on the down sublattice). Second, the sign of  $E$  alternates between the two sublattices; there is no global orthorhombic anisotropy. If the impurity felt the same anisotropy as did the atom which it replaced, then this alternation of sign would lead to complete cancellation of terms in the local-mode linewidth to second order in  $E$ . Effectively, the relative amplitude (to first order in  $E$ ) for a spin flip in the "wrong" sense (e.g., up on the up sublattice) in the local mode, as perturbed by  $E$ , is equal and opposite to the corresponding amplitude for a band mode at that frequency; it is the sum of these amplitudes times a factor representing the overlap between the local and extended modes which determines the local-mode decay amplitude to first order in  $E$ , and this vanishes. Thus the lowest-order contribution to the local-mode decay rate, or linewidth, arises from the contrast between the orthorhombic anisotropy for the Mn impurity (approximately zero) and that for the Fe atom which it has replaced in the lattice. The effective density of the final states is associated with  $G_{00}^{-+} = \langle \langle S_0^-(t); S_0^+(0) \rangle \rangle$ , rather than with  $G_{00}^{+-} = \langle \langle S_{00}^+(t); S_0^-(0) \rangle \rangle$ , which at the positive frequencies of interest no longer exhibits a peak near the band maximum<sup>9</sup> [the peak is now found at nega-

tive frequencies, as  $G_{00}^{-+}(\omega) = G_{00}^{+-}(-\omega)$ ]. The shape of the predicted local-mode linewidth as a function of frequency closely mirrors the density of states associated with  $G_{00}^{-+}(\omega)$ .

To date, there is, to our knowledge, only a single experimental measurement with which our theory can be compared. Data taken at  $\omega_l/2\pi = 1.75$  THz and extrapolated to zero sample volume (to eliminate the radiation damping contribution to the linewidth) and to vanishing impurity concentration (to eliminate the effect of impurity-impurity interactions) show a residual linewidth of about 3 kOe. The above theory predicts a value which is only about one-sixth of this value. Similarly, an earlier calculation<sup>4</sup> of the linewidth of the downgoing local mode associated with impurity banding effects left unexplained an observed concentration-independent contribution of about 1 kOe. Calculations by Rezende<sup>10</sup> and by Motokawa<sup>11</sup> suggest that in both cases the difference between theory and experiment can be eliminated by including spin-lattice relaxation decay of the local mode into a phonon. The one-magnon-one-phonon term in the Hamiltonian, associated with expansion of the magnetostriction to lowest (first) order in the strain,<sup>12</sup> involves a coupling constant proportional to  $(\hbar q^2/2M\omega_{q\lambda})^{1/2} \propto \omega^{3/2}$  (from the expansion of the strain in boson operations), so the local mode to phonon decay transition rate is predicted to be proportional to  $\omega_l^3$ . Then if this mechanism is responsible for the 1-kOe residual width of the downgoing mode at  $\omega_l = 1.36$  THz, we would expect a contribution of  $(1.75/1.36)^3 = 2.1$  kOe to the upgoing mode linewidth, bringing that theory also into essential agreement with experiment. Clearly at this stage it would be very instructive to have experimental measurements of the local-mode linewidth as a function of applied field (i.e., of local-mode frequency  $\omega_l$ ).

#### ACKNOWLEDGMENTS

We gratefully acknowledge the communications from Professor S. Rezende and Professor M. Motokawa of their results on spin-phonon relaxation prior to publication. This work was supported in part by the National Science Foundation through Grant No. DMR-80-08004.

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