Light scattering by nuclear magnons*

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The possibility of the use of inelastic light scattering to investigate nuclear magnons is analyzed theoretically. The mechanisms for coupling photons with nuclear spins in Raman processes are identified and compared. In addition to one-nuclear-magnon scattering, second-order processes involving nuclear and electronic magnons in antiferromagnets are feasible.

To explain the linewidth of the nuclear magnetic resonance (NMR) of nonmagnetic ions is paramagnetic iron-group fluorides, Nakamura[1] and Suhl[2] proposed an indirect coupling between nuclear spins through the hyperfine interaction with electronic spin waves. de Gennes *et al.*[3] showed that this coupling gives rise to collective excitations of the nuclear spins with small admixture of the electronic magnons. These nuclear spin waves or magnons have a well-defined k-dependent energy spectrum. Conventional NMR measurements give information only about the uniform precession ($k=0$) nuclear excitation. In recent years microwave photon[4-6] and phonon[7,8] nonlinear pumping techniques have been used to probe $k\neq 0$ modes in the antiferromagnets $RbMnF_3$ and $CsMnF_3$. These techniques lead only to indirect information about the nuclear modes and have several limitations.[4-10] Among others, they can be used only in materials with relaxation times that yield sufficiently low threshold powers for the nonlinear processes. In the present work we show that the technique of inelastic light scattering can also be used to study nuclear spin waves. Three mechanisms can be envisaged which allow the coupling of light photons with nuclear magnons, namely, (a) direct magnetic-dipole interaction analogous to the case of electronic magnons[11] (b) indirect coupling of the nuclear spins with the electric field of the radiation via the electric-dipole interaction with the electrons combined with the hyperfine interaction and (c) indirect coupling via virtual electronic magnons. In usual situations mechanism (c) is much stronger than the others.

As in the electronic case[12] one can show that interaction (a) is negligible compared to (b). To calculate interactions (b) and (c) we use the single-ion model of Fleury and Loudon, [12] except that we allow for the presence of the hyperfine splitting in the energy levels. Consider a crystal with S-ground-state magnetic ions with electronic spin S and nuclear spin I. The electric-dipole interaction connects an initial state $S_z^i I_z^i$ with intermediate P states and these with a final state $S_z^f I_z^f$. The spin-orbit and the hyperfine interactions mix different S_z and I_z in the intermediate states allowing the flip of the electronic and nuclear spins. One can therefore calculate the transition probabilities for different Raman processes, involving changes in I_z and/or S_z. With $I_z^f = I_z^i$ and $S_z^f = S_z^i \pm 1$ the calculation is identical to that of Fleury and Loudon. [12] With third-order perturbation theory one obtains an electronic-spin Hamiltonian, [12]

$$H_{S\,\mathrm{rad}} = \Gamma_S \sum_i (E_L^z E_S^+ - E_L^+ E_S^z) S_i^- - \mathrm{H.c.}, \qquad (1)$$

where Γ_S is proportional to the spin-orbit constant λ of the excited state, [12] and the other symbols have their usual meanings. Now, setting $S_z^f = S_z^i$ and $I_z^f = I_z^i \pm 1$ and following the same steps which led to (1) we find for the nuclear-spin case

$$H_{I\,\mathrm{rad}} = \Gamma_I \sum_i (E_L^z E_S^+ - E_L^+ E_S^z) I_i^- - \mathrm{H.c.}, \qquad (2)$$

where $\Gamma_I = (A_L/\lambda)\Gamma_S$; A_L being the orbital hyperfine constant of the excited states. In this relation we have neglected λ in comparison with the energy separation between the ground state and the lowest allowed intermediate state. The Hamiltonian (2) represents a process analogous to the one of Eq. (1). In (1) the spin-orbit interaction allows the flipping of the electronic spin by the electric field of the radiation. Here the hyperfine coupling needed to flip the nuclear spins proceeds through the orbital angular momentum of excited non-S states of the magnetic ions which serve as intermediate states in the Raman process.

Mechanism (b) referred to previously arises from the interaction Hamiltonian (2). In ferromagnets the nuclear-spin-deviation operators I_i^- and I_i^+ can be expressed directly in terms of nuclear-magnon creation and destruction operators. Therefore (2) leads to Stokes and anti-Stokes scattering processes very much analogous to the electronic case. [12] Due to the relation for Γ_I the intensity of this scattering process for nuclear magnons is smaller than for electronic magnons by

a factor of $(A_L/\lambda)^2$. For Mn ions for instance this ratio is of the order of 10^{-10} and mechanism (b) is too weak.

Finally, mechanism (c) arises from the interaction between the radiation fields and the electron spins represented by (1). Due to the presence of the hyperfine coupling with the nuclear spins, an electron-spin deviation is necessarily accompanied by a disturbance of the nuclear system. This results in the fact that in order to diagonalize the Hamiltonian of a spin system with electrons and nuclei coupled by the hyperfine interaction, one must use collective operators which are combinations of both electronic and nuclear-magnon operators. In the case of a ferromagnet the transformation from the electron-spin operator to the diagonal operators is, [5]

$$S_i^- = (2S/N)^{1/2} \sum_k e^{i\vec{k}\cdot\vec{R}_i} (\alpha_k \cos\theta_k + \beta_k^\dagger \sin\theta_k), \quad (3)$$

where

$$\sinh\theta_k \approx -(\gamma H_N \omega_N)^{1/2}/(\Omega_k + \omega_N) \approx (\omega_N \delta_F/\Omega_k)^{1/2}, \quad (4)$$

N is the number of magnetic ions, γ is the electronic gyromagnetic ratio, H_N is the hyperfine field, Ω_k is the electronic-magnon frequency, ω_N is the "unpulled" NMR frequency, δ_F is the fractional frequency pulling, and α_k and β_k are the normal-mode operators of the electron-nuclei spin system. Under typical conditions in ferromagnetics $\sinh\theta_k$ is small. Therefore the admixture of electronic and nuclear modes is small and α_k approximates the pure-electronic-magnon operator, whereas β_k approximates the nuclear-excitation operator. This admixture completes the mechanism of Raman scattering by nuclear spin waves. Replacing the spin operator in (1) by (3) we obtain the interaction Hamiltonian for the first-order Stokes scattering process by nuclear magnons,

$$H_{N\,\mathrm{rad}}^S = \left(\frac{(2\pi)\hbar(2\omega_L\omega_S SN)^{1/2}}{\eta_L\eta_S V}\right)\Gamma_S \sinh\theta_k \times \sum_{k_N} (\epsilon_L^x \epsilon_S^+ - \epsilon_L^+ \epsilon_S^x) a_L a_S^\dagger \beta_k^\dagger \delta(\vec{k}_L - \vec{k}_S - \vec{k}_N), \quad (5)$$

where $\eta_{L,S}$ and $\epsilon_{L,S}$ are, respectively, the refractive indices and the polarizations of the incident and scattered radiations, a_L and $a_S^\dagger$ are their photon destruction and creation operators, and V is the interaction volume.

Comparison between (5) and (1) shows that in ferromagnets the intensity of the scattering by nuclear magnons in the present process is smaller than by electronic magnons by the factor $\sinh^2\theta_k$. In typical ferromagnets this factor can be as large as 10^{-3}. Therefore mechanism (c) is much stronger than the others. The polarization selection rules for scattering by nuclear magnons are the same as for electronic magnons. [12]

While in ferromagnets the fractional NMR frequency change is $\delta_F = \gamma H_N/\Omega_k$, in a two-sublattice antiferromagnet it is approximately $\delta_{AF} = \gamma^2 H_E H_N/\Omega_{1k}\Omega_{2k}$ in the unflopped state and $\delta_{AF}^i = \gamma^2 H_E H_N/\Omega_{ik}^2$ for the ith mode in the flopped state. As the exchange field H_E is large in low-anisotropy antiferromagnets such as $RbMnF_3$ and $CsMnF_3$, the electronic frequencies Ω_{ik} at low k lie in the low microwave range and the nuclear frequency pulling is much larger than in ferromagnets. In fact only in this class of materials nuclear magnons have been observed indirectly in microwave nonlinear pumping experiments. [6-10] In antiferromagnets the Hamiltonian for scattering based on mechanism (c) can be obtained by allowing the summation in (1) to run over the different magnetic sublattices and by the use of the appropriate transformations from the spin to the normal mode operators. [4,5] With the Hamiltonian obtained in this manner we arrive at the differential cross section for Stokes scattering by the ith-mode nuclear spin wave in a two-sublattice unflopped antiferromagnet,

$$\frac{d\sigma}{d\Omega} = \frac{2MV\eta_S\omega_L\omega_S^3(n_k^i+1)\Gamma_S^2(S_{pi}+S_{qi})^2}{g\mu_B\eta_L c^4} \times |\epsilon_L^x\epsilon_S^- - \epsilon_L^-\epsilon_S^x|^2, \quad (6)$$

where M is the sublattice magnetization, $g\mu_B$ is the elementary electronic magnetic moment and n_k^i is the ith-mode nuclear magnon occupation number. S_{pi} and S_{qi} are the transformation coefficients from the Fourier transforms of the two sublattice electronic spin deviation operators to the ith-mode nuclear magnon creation operator. Using the notation and results of Ninio and Keffer[5] for an unflopped antiferromagnet, the scattering cross section (6) is shown to be proportional to $\Gamma_S^2(S_{41}-S_{43})^2$. With the approximations $H_N \ll H_0$ and $H_A \ll H_E$, where H_0 is the applied field, this factor reduces to

$$V_N = \Gamma_S^2\omega_N\delta_{AF}^2(H_0-H_A)^2/\gamma H_N(H_E+H_0-H_A)^2. \quad (7)$$

This is to be compared with the factor for scattering by electronic magnons[12] $V_e = (H_A/2H_E)^{1/2}\Gamma_S^2$. For $RbMnF_3$ in which nuclear magnons were first observed, with $H_0 = 2$ kOe along a $\langle 111\rangle$ axis, $T = 4.2$ °K ($\delta_{AF} = 0.14$), one has $V_N \sim 10^{-5}\Gamma_S^2 \sim 10^{-2}V_e$. This low intensity, together with the small frequency shift of the Brillouin signal (the unpulled NMR frequency of Mn^{55} is $\omega_N \simeq 680$ MHz) should make the scattering by thermal nuclear magnons very difficult to observe. However, one has the possibility of increasing the population of nuclear magnons by many orders of magnitude with microwave pumping, [4-10] leading to strong signals which may be resolved with the high-resolution experi-

mental methods recently developed.[13] This combined rf-pumping light-scattering experiment may be used to better clarify the existing measurements of nuclear-magnon relaxation times in $RbMnF_3$ and $CsMnF_3$.

There are other magnetic systems in which first-order light scattering by nuclear magnons may prove more useful. One example is a uniaxial antiferromagnet such as MnF_2. In this material the transverse anisotropy is low enough that the application of a high magnetic field brings the down-going electronic magnon branch to the low microwave range. Therefore with a field just above the spin-flop value, which is 93 kOe at $T = 4.2$ °K in MnF_2, both electronic frequencies are low[14] and the coupling with nuclear magnons is strong. Under these conditions calculations similar to (7) give $V_N \sim 8\times10^{-3}\Gamma_S^2 \sim 10^{-1}V_e$. The larger intensity in this material might make it possible to use light scattering to study nuclear magnons directly. Another possible application is in the study of nuclear magnons in spiral and conical spin structures, such as found in certain rare-earth metals.[15] In these materials the coupling between nuclear and electronic magnons is due to the fact that there is no gap in the electronic spin wave spectrum and that the hyperfine fields are large. In addition to the stronger scattering the large NMR frequency (e.g. $\omega_N \simeq 6.5$ GHz in holmium) makes the resolution no longer critical for the experiments. Again the new techniques may circumvent the problem created by the fact that one has to scatter light from the surface of the rare-earth metal.

In addition to one-nuclear-magnon scattering it is possible to have in antiferromagnets second-order Raman scattering involving the creation or destruction of a pair of nuclear magnons or a mixed electronic-nuclear magnon pair. As in the one-nuclear-magnon case the origin of the mechanism here is based on the coupling of light photons with the electronic spins. The interaction of light with two electronic spins in an antiferromagnet in a Raman process can be written as[16]

$$\sum_{\substack{id\\ \alpha\beta\gamma\delta}} E_L^{\alpha}E_S^{\beta}B(d)S_i^{\gamma}S_{i+d}^{\delta}, \tag{8}$$

where d indicates the neighbors to site i. The origin of interaction (8) resides on a coupling through virtual phonons or on an exchange mechanism via electronic excitations.[12] Regardless of this, one can determine the form of the B tensor from the symmetry of the magnetic crystal. In the terms $S_i^+S_{i+d}^-$ and $S_i^-S_{i+d}^+$, where i and $i+d$ refer to the down-spin and up-spin sublattices. One can now replace the electronic spin operators in $RbMnF_3$[16] the interaction is proportional to $\vec{S}_i \cdot \vec{S}_{i+d}$ and the largest contributions come from these terms by the electron-nuclei normal mode operators. The resulting expression contains in addition to terms which give the scattering by electronic magnons of different branches,[12] terms with creation and destruction operators for pairs of nuclear magnons of different modes and mixed electronic-nuclear magnon pairs. For a normal two-sublattice antiferromagnet, using the notation of Ninio and Keffer,[5] the ratio of the interactions for Stokes scattering by two nuclear magnons to Stokes scattering by two electronic magnons becomes $(S_{21}S_{43}+S_{23}S_{41})/(S_{11}S_{33}+S_{31}S_{13})$, which, with the approximations appropriate for $RbMnF_3$, reduces to

$$\omega_N\delta_{AF}^2(1+\gamma_k^2)\{(u_k^2+v_k^2)[\gamma H_N+(1-\gamma_k^2)\omega_N\delta_{AF}^2]\}^{-1}, \tag{9}$$

where γ_k, u_k, and v_k are the usual coefficients used in the transformation which diagonalize the electronic spin Hamiltonian in an antiferromagnet.[12] At low k, $\gamma_k \simeq 1$ and the ratio (9) is of the order of unity. Therefore in this region the scattering by nuclear-magnon pairs is comparable to the scattering by electronic-magnon pairs. This fact may be used to probe nuclear-magnon pairs excited for instance in parallel pumping experiments.[4-6] The spontaneous scattering by nuclear pairs, however, is expected to be much smaller than the electronic analog. The reason is that since the wave vectors of the light photons are very small compared with the Brillouin-zone edge value of k, the wave vectors of the magnons excited are nearly equal and opposite and can assume any value. As the density of states increases rapidly with k the largest contribution to the scattering comes from the neighborhood of the Brillouin-zone edge. This has been clearly observed in the electronic-magnon scattering.[12] Here as k_N increases the electronic frequency Ω_k increases rapidly and the admixture of the nuclear-electron spin-wave modes, expressed by the frequency pulling δ_{AF}, vanishes quickly. At the edge of the Brillouin zone $\delta_{AF} \simeq H_N/H_E \approx 10^{-6}$ and the ratio (9) is of the order 10^{-10}.

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