Raman Scattering by Four Magnons in NiO and $KNiF_3$

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We have observed Γ_3^+ excitations by Raman scattering in $KNiF_3$ at 1270 cm^{-1} (17.9J), and in NiO at 2800 cm^{-1} (18.9J). These excitations are identified as four-magnon excitations by agreement of the peak frequencies with calculated values, and in the case of NiO by the temperature shift. Scattering by four magnons is the highest-order nonresonant Raman scattering yet observed. The excitation of four magnons is interpreted in terms of excited-state propagation effects.

Raman scattering by two magnons has been observed in a number of materials in the past few years. Because of the large exchange interaction, the two-magnon scattering recently observed in NiO[1] and $KNiF_3$[2] is exceptionally strong. We have examined the higher-energy-loss regions of the Raman spectra of NiO and $KNiF_3$ and have discovered peaks which we have identified as four-magnon scattering.

Raman scattering was observed from polished (100) faces of NiO crystals grown epitaxially on MgO by vapor transport of the halide. Crystals from different sources were used, which gave identical results except for differences in signal-to-noise ratio due to strong sample-dependent absorption at both the laser and scattered radiation frequencies. A "reflection" geometry was used for the scattering experiments in which the laser beam was incident on the crystal at the Brewster angle (65°). A typical Raman spectrum is shown in Fig. 1(a) for 500 mW of 4880-Å excitation at 1.5°K (with the sample immersed in liquid helium). The scattering below 1200 cm^{-1} is due to first- and second-order phonon processes, while the strong peak at 1560 cm^{-1} arises from two magnons. Both the phonon and two-magnon (2M) processes are discussed elsewhere in detail.[1] While the temperature dependence of the 2M process could be studied at low incident laser power levels (<50 mW at the sample), in order to observe the relatively weak line peaking at 2800 cm^{-1} we were obliged to use >500 mW which resulted in local heating of the sample. As the temperature is raised from 1.5°K, the 2M and 2800-cm^{-1} scattering peaks both broaden and shift to lower frequencies. The solid line in Fig. 2 shows the temperature shift of the 2M peak observed with low power, while the points represent high-power data. The temperature of the high-power experiment was established by

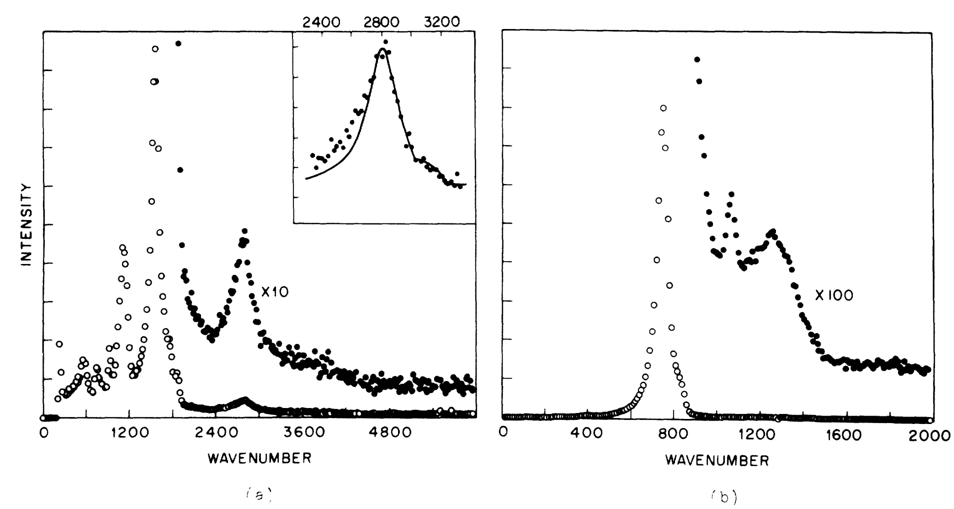

FIG. 1. (a) Raman scattering from NiO at 1.5°K using 500-mW 4880-Å argon laser light. The ordinate for the region beyond 1800 cm^{-1} is expanded by a factor of 10. The spectral slit width was approximately one channel. Adjacent channels are uncorrelated except by noise. The solid line superposed on the data in the inset is the 2M Γ_3^+ Green's function scaled as discussed in the text. (b) Raman scattering from $KNiF_3$ under similar conditions as in (a) except that the spectral slit was approximately three channels. The ordinate for the region beyond 900 cm^{-1} is also shown expanded by a factor of 100.

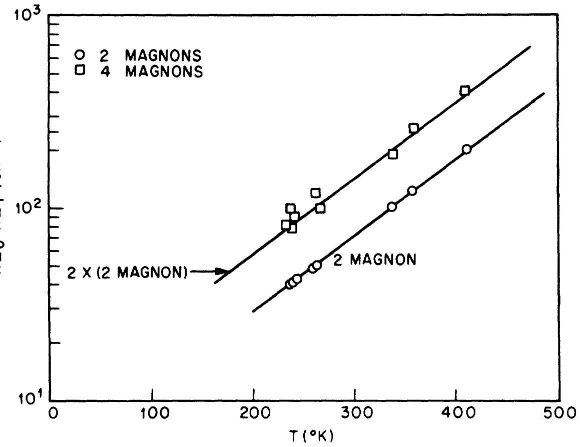

FIG. 2. The shift of the 2M and the 4M scattering peaks with temperature. The lower solid line represents the shift of 2M peaks using <50 mW laser power to avoid sample heating (Ref. 1). The points are high-power data where the temperature was determined by comparing the observed 2M shift with that measured at low power. The upper curve is arbitrarily drawn a factor of 2 higher in the peak shift than the 2M line.

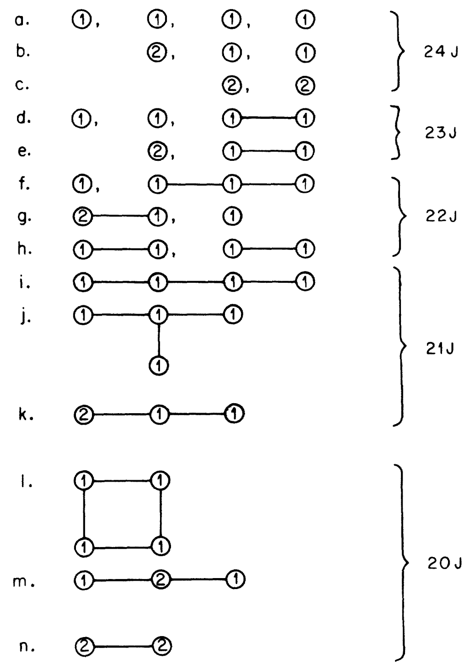

FIG. 3. A schematic listing of all possible four spin-deviation Ising states in a simple cubic lattice of $s=1$ spins interacting only via a nearest-neighbor exchange. The circles indicate sites; the numbers give the number of spin deviations on each site, while the linkages denote exchange interactions, i.e., that the sites are nearest neighbors. The Ising states are arranged in order of descending energy, as indicated on the right.

calibrating the 2M shift using the low-power line. It is seen that the upper set of points, representing the shift of the 2800-cm^{-1} scattering peak, lie along a line scaling the 2M shift by a factor of 2.

By correcting for absorption, refraction, and reflection by the NiO, we were able to estimate the extinction coefficient for the 2800-cm^{-1} line: $\epsilon \sim 10^{-8}$ cm^{-1} sr^{-1}, a factor of 20 smaller than for the 2M peak.[1]

We have also studied scattering using 5145-Å excitation, and find a similar scattering peak at 2800 cm^{-1}, except that the high-frequency side of the line is attenuated by a strong absorption peak.

Scattering was also observed from single, oriented crystals of $KNiF_3$ using both 4880 and 5145 Å lines in the usual way. Figure 1(b) shows scattering of 4880-Å light from $KNiF_3$ at 1.5°K for *yxyx* polarization, where x, y, and z were only approximately ⟨100⟩. The strong ($\epsilon \sim 10^{-8}$ cm^{-1} sr^{-1}) peak at 750 cm^{-1} is due to 2M scattering.[2] A temperature-dependent peak is observed at 1270 cm^{-1}, and a generally stronger, sharper temperature-independent Γ_1^+ peak is observed at 1060 cm^{-1}. This latter peak is apparently two-phonon scattering, while the 1270-cm^{-1} peak which lies above the two-phonon density-of-states cutoff[3] must arise from a higher-order process. Detailed polarization studies indicate that it has the same symmetry Γ_3^+ as in 2M scattering, and has a cross section roughly 150 times weaker than in 2M scattering. Since there is neligible absorption in $KNiF_3$ in the bandwidth of the Raman scattering frequencies at low temperatures, this scattering is nonresonant. Unfortunately we could not observe the 1270-cm^{-1} peak at higher temperatures since it apparently broadens and moves under the two-phonon line.

The data on the high-energy-loss scattering peaks suggest that they are 4M excitations. The value of the exchange integral in NiO[1] is 148 cm^{-1} and that of $KNiF_3$[2] is 71 cm^{-1} so that the peaks of the 4M excitations lie at $18.9J$ and $17.9J$, respectively. We shall argue below that this is approximately where the peak is to be expected because of magnon-magnon interaction effects. The behavior of these lines as a function of temperature is also consistent with this assignment.

Detailed calculations of the 2M scattering have been performed for both NiO[1] and $KNiF_3$.[2] In both cases, a simple cubic, Γ_3^+ 2M Green's function gave an excellent fit to the shape and position of the 2M scattering peak. There is little hope of performing a fully interacting Green's-function calculation of 4M processes.

On the other hand, simple calculations based on the Ising model plus second-order perturbation theory have been shown to be useful in estimating peak frequencies of various one- and two-magnon excitations.[4,5] The various possible 4M Ising states are listed in Fig. 3. The number in the circle represents the number of spin deviations on that site and the bars indicate nearest neighbors. If we assume the matrix element for creation of four magnons to be such that the spin deviations must be on sites connected by strong exchange interactions, then we need consider only states of the type i through n. Furthermore, states of type j and k are difficult to create using the excitation mechanisms discussed below. Thus, three of the four states which remain have an Ising energy of $20J$ while states of type i have an energy of $21J$. That the 4M peaks are $\sim J$ below the lowest 4M Ising states is consistent with the fact that the 2M peak is $\sim\frac{1}{2}J$ below its Ising estimate.[6] The ratio of the Ising energies of these 4M states to that of the 2M state is a factor of 20/11. If we scale the $\Gamma_3{}^+$ density of 2M states for NiO by 20/11.1, we find a good fit to the shape of the 4M peak at low temperatures as shown in the inset in Fig. 1(a) (but we can give no good argument that these shapes should scale). This scaling is also consistent with the factor of 2 in the ratio of the temperature dependence of the 2M and 4M lines. For $KNiF_3$ the corresponding scattering factor would be 20/11.8. However, the influence of the background severely distorts the line shape so that a fit as for NiO is not possible. The peak frequency does appear to be slightly lower in $KNiF_3$ than in NiO relative to the 2M scattering, and we do not at present have an explanation for this effect.

There appear to be several possible ways of creating four magnons. The first is a propagation effect in the virtual excited-state mechanism discussed for the 2M process by Fleury and Loudon.[7] A second possibility is a kinematical effect which arises because the products such as $S_i{}^+S_j{}^-$ occurring in the 2M excitation operator are not exactly equal to the product of two-magnon creation operators. A third possible explanation for the intensity we have considered is the second-order effect of the creation process of two magnons plus one LO phonon seen in absorption.[1,8-10] If the optical phonon is virtually created in the Raman process, the final excitation could result in four magnons. By using the integrated absorption coefficient in NiO we have estimated an extinction coefficient of 10^{-14}–10^{-16} cm^{-1} which should be compared with the observed value of 10^{-8} cm^{-1}. Since the cross section for the 2M + one-phonon process in $KNiF_3$ is some 70 times smaller than in NiO, the extinction coefficient for the 4M process would be some 10^3 times smaller than predicted for NiO. Experimentally the observed 4M scattering in $KNiF_3$ is about 75 times weaker than in NiO.

The propagation effect goes as follows. Suppose that in NiO the incident light virtually excites one of the e_g electrons up into a p orbital. This state is relatively spread out except that it is bound to the hole left behind. Now, before this particle-hole pair recombines, the hole may propagate to several sites. The hole moves by electrons hopping onto the vacant site. Since all the electrons surrounding the hole are of opposite spin, the hop by the hole creates a spin deviation. Thus one or two hops by the hole before recombination creates a 2M state while three hops create a 4M state. In this case the matrix element for the 4M process is proportional to $[t/(E-\omega_0)]^2$ times the second-order matrix element. Here t is the effective hopping integral for the hole plus the excited electron, ω_0 is the incident light frequency, and E is the energy necessary to excite the electron into the p state. In NiO, $E-\omega_0\sim 2$ eV. If $t\sim 0.1$–0.5 eV, this mechanism gives an intensity for the 4M process of order 10^{-3}–10^{-4} of that for the 2M process. If we consider a slightly different process in which instead of hopping three times the electrons only hop twice, but after the first hop invoke a spin flip via Hund's rule coupling between the excited electron and the other e_g electron, we obtain a matrix element $tJ_H/(E-\omega_0)^2$. If $J_H\sim 1$ eV this process gives an intensity of approximately 1% of the 2M intensity. If the hole is unable to move, then one can still create four magnons via exchange between the excited electron and the other atoms of the crystal. This effect could be important since the electron in the excited state may not be strongly bound to the hole. However, such a mechanism would not discriminate between 4M excitations on one of the simple cubic sublattices of the fcc structure of NiO from 4M excitations on a mixture of the simple cubic sublattices. Four magnons created on different simple cubic sublattices would not interact strongly enough to produce the observed frequency lowering so that it appears that there must be some propagation of the hole.

The kinematical effect can be estimated as follows: One takes a quadratic operator like $S_i^+S_j^-$ and expresses this operator in terms of boson operators via the Dyson-Maleev transformation or the Holstein-Primakoff expansion, and then expresses these operators in terms of spin-wave operators obtained by a Bogoliubov transformation. Such a series of steps have been carried out for the simple Heisenberg Hamiltonian by Harris,[11] and four-magnon creation terms appear. The final expressions are quite complicated, and it is difficult to determine the size of the 4M terms. A much simpler method is to again start with the Ising states listed in Fig. 3 and calculate via perturbation theory the admixture of two spin-deviation states with these states and with the ground states. Assuming that the light introduces a perturbation of the form $S_i^+S_j^-$, where i and j are nearest neighbors, the 4M states all have the spin deviations grouped in pairs as in states h, i, l, m, or n, and the matrix element is zero for the states of type h. For a state of type l the matrix element is $\frac{2}{10}-\frac{2}{11}\sim 1/2z^2$ times the matrix element of 2M creation, where z is the number of nearest neighbors. Thus the total intensity is $\sim z^{-4}\sim 10^{-3}$ of the 2M peak. If the kinematical effect made the dominant contribution to the matrix element, this ratio of the 4M intensity should be the same for both NiO and $KNiF_3$. Experimentally, the ratio is 7 times larger in NiO than in $KNiF_3$ and this is only consistent with some form of excited-state exchange mechanism as discussed in the previous paragraph. Since in $KNiF_3$ the ratio of 4M to 2M intensities $\sim\frac{1}{150}$, it is possible that some kinematical effect is important for this case.

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Eu^{153} Indirect Spin-Spin Interaction and Inhomogeneous Line Broadening in Ferromagnetic EuO

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The transverse relaxation rate of Eu^{153} in EuO, caused by the indirect Suhl-Nakamura interaction, has been calculated and measured. The results confirm the validity of a theoretical model that was developed recently to treat inhomogeneously broadened NMR lines. The local variation of the Eu^{153} hyperfine field is determined and interpreted in terms of a local strain.

Various aspects of the indirect nuclear spin-spin interaction[1]—the so-called Suhl-Nakamura (SN) interaction—have been examined recently by several groups.[2-6] However, as yet no study has been reported of the SN interaction in a ferromagnetic system for which the theory is directly applicable, namely, a Heisenberg-type ferromagnet. The present report describes the calculation and the experimental determination of the Eu^{153} SN interaction in EuO. It will be demonstrated that recently developed theory[2] can account accurately for the observed SN interaction, and that the SN interaction is essentially the only source for the Eu^{153} dynamic linewidth manifested by the transverse relaxation rate $1/T_2$.