

NONLINEAR OPTICAL EFFECTS IN ANTIFERROMAGNETIC KNiF_3

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Frequency broadening and self-focusing of optical pulses are observed in antiferromagnetic KNiF_3 under intense picosecond laser excitation. Below the Néel temperature considerable enhancement of the frequency broadened intensity is observed which is attributed to the spin dependent part of the third order susceptibility.

An intense monochromatic optical pulse propagating through a material can give rise to a variety of nonlinear optical effects depending on the medium's nonlinear susceptibility tensor. For a centrosymmetric solid the lowest order effect occurs through the third-order susceptibility [1] $\chi^{(3)}$. Such effects as self-phase modulation [2], four-wave mixing [3], stimulated Raman scattering [4], etc. have received much attention over the past several years. In general the mechanisms underlying all of the nonlinear optical effects observed to date have been considered to arise from either "electronic" or "nuclear" degrees of freedom, that is, (a) nonlinear distortion of electron orbits around the average nuclear positions, and (b) changes in motion of the nuclei, as in configurational degrees of freedom, respectively. Considerable effort has gone into separating the relative contributions of these mechanisms [5] to the various $\chi^{(3)}$ related effects.

Several nonlinear optical effects induced or enhanced by the application of a magnetic field on nonmagnetic solids have been reported [6,7]. In this paper we report the first observation of nonlinear optical (NLO) effects associated with the onset of magnetic order in a solid. KNiF_3 exhibits the cubic perovskite

(O_h^1), at all temperatures and develops anti-ferromagnetic order below ~ 260 K. Its spontaneous Raman spectrum shows no first-order and negligible second-order phonon contributions; but rather is dominated by a strong and temperature dependent magnon pair scattering [8]. At $T \ll T_N$ the magnon pair spectral peak lies at a frequency shift of 746 cm^{-1} . Although a complicated phenomenon for which at present we have only a qualitative understanding, the NLO behavior of this material appears dominated by the magnon (spinwave) contribution to $\chi^{(3)}$. The principle evidence for this conclusion appears in fig. 1 showing the temperature dependence of the spectrally broadened intensity excited by intense monochromatic picosecond optical pulses. This temperature dependence follows closely that of the peak intensity of the spontaneous magnon pair Raman scattering [8,9] in this material, clearly implying the importance of the spin related contributions to $\chi^{(3)}$.

The samples were grown by a Bridgman technique and analyzed by standard chemical methods. The crystal placed in a dewar was temperature controlled by adjusting the flow rate of cold N_2 gas. Temperatures between 297 K and 77 K were easily achieved within an accuracy of ± 2 K.

The 5300Å pulses were derived by passing a Nd-glass mode locked laser beam (Q -switched and mode-locked with 9860 Kodak dye) through a 2 cm KDP

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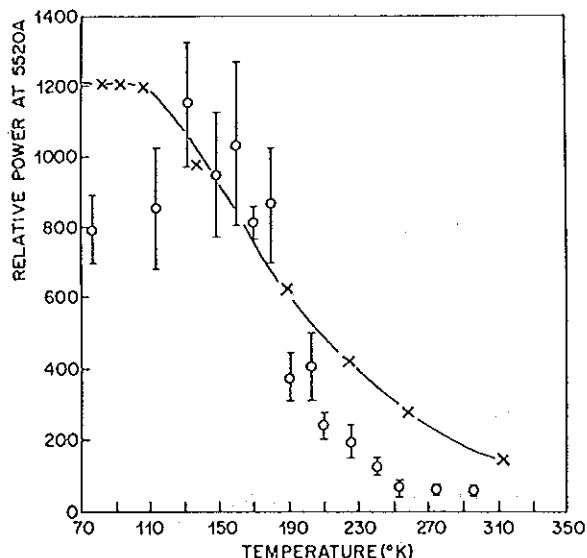


Fig. 1. Intensity of the frequency broadened emission from KNiF_3 as function of temperature at fixed pump intensity at 5520 Å; the apparent decrease at low temperatures (barely outside experimental error) may be associated with the slight temperature dependence of the optical absorption [10] in this range. X - relative peak intensity for spontaneous magnon pair Raman scattering.

second harmonic generator crystal. Use of 5300 Å light is well suited to KNiF_3 because it exhibits a broad minimum in its optical absorption [10] between 4800 Å and 6100 Å. The laser output at 1.06 μm typically consisted of ~ 100 intense pulses ($\sim 1 \times 10^9$ W peak) 9 psec in duration and ~ 80 cm^{-1} in frequency width, separated from each other by the cavity round trip time of 9 nsec. After second harmonic generation (SHG) the pulse peak power at 5300 Å was $\sim 2 \times 10^8$ W. An amplified single pulse was also used in the experiment with a power of 10^9 W at 5300 Å. The results obtained were essentially the same using a train or single pulse excitation.

The SHG beam emerging from KDP was reduced in size to a collimated ~ 2 -mm diam beam by an inverting telescope. The intensity distribution of light emitted from the exit face of the KNiF_3 sample was imaged onto the 1-mm slit of a Jarrell-Ash grating 1/2-m spectrograph. Spectra were recorded on Polaroid Type 57 film.

Typical spectra from an unoriented 5 cm long KNiF_3 single crystal are displayed in fig. 2. The spectra are characterized by extensive spectral broadening

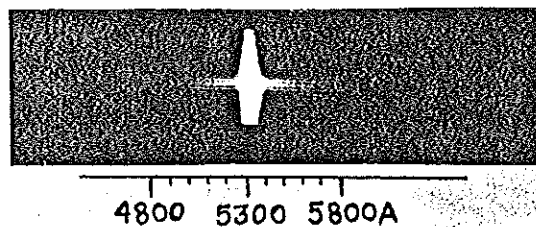


Fig. 2. Stokes and anti-Stokes spectra from 5 cm long KNiF_3 under picosecond excitation.

ranging up to ~ 3000 cm^{-1} to either side of the laser frequency. The intensity, although not the spectral broadening, of the output exhibited the large temperature dependence illustrated in fig. 1. Note particularly the absence of any sharp feature at 5520 Å, the position expected for simple stimulated Raman scattering by the 746 cm^{-1} magnon pair excitation. Usually the spectra were smooth; however, occasionally structure was observed. Less frequently a periodic structure with modulation frequencies of tens to hundreds of wave numbers was evident. The frequency broadened light is polarized in the same direction as the 0.53 μm pulse. This type of behavior has been observed in glasses, crystals and liquids and associated with self-phase modulation of the optical beam [2,11]. We have observed self-focussing, usually in the form of ten to forty small self-focussed spots of 5 – 20 μm diameter at the exit face of the crystal. Using a focussed beam optical damage could also be produced. While all these effects complicate interpretation and make difficult any quantitative conclusions, we emphasize that the spectral broadening was always observed even in the absence of self-focussing, damage or periodic spectral intensity modulation. We therefore consider these effects peripheral and concentrate on the temperature and pump intensity dependence of the forward directed broadened spectrum.

In fig. 3 we show the output intensity at 5700 Å as a function of input intensity (at 5300 Å) for two temperatures: above and below the Néel temperature. The pump intensity is quoted as an area average - ignoring any self-focussing effects, which may be partly responsible for the scatter in the data. Note that the output intensity is approximately exponential in the input intensity at both temperatures. However, the slope is more than a factor of two larger at 77 K than at 300 K.

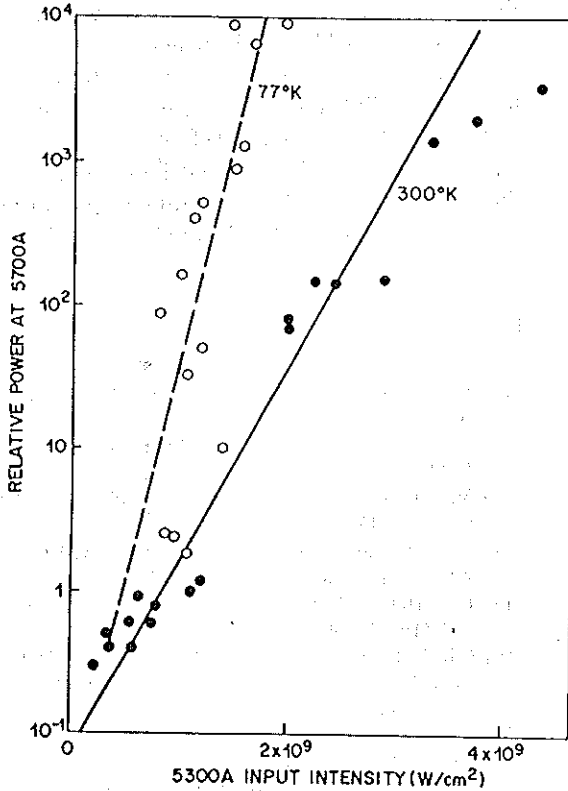


Fig. 3. Intensity dependence of the frequency broadened emission at 5700 Å from KNiF₃ as function of laser pump intensity at fixed lattice temperature.

The rapid rise in conversion efficiency of four orders of magnitude within a small interval of input intensity is indicative of an amplification process with very large gain. Identical curves were obtained at 5520 Å and 6000 Å output wavelengths. The similarity in results for several output frequencies shows that simple stimulated magnon pair scattering is not the dominant process observed here. If it were, one would expect the behavior at 5520 Å to differ considerably from that at other wavelengths ($\bar{\nu}_{5520} = \bar{\nu}_{5300} - 746 \text{ cm}^{-1}$).

As mentioned earlier the most novel experimental results are shown in fig. 1: the large ($\sim 20\times$) intensity increase below T_N . Spectra at 5520 Å, 5700 Å and 6000 Å behave identically — within experimental error — consistent with the observations in fig. 3. The temperature dependence of the relative peak intensity for the spontaneous magnon pair scattering in our KNiF₃ sample (using 5145 Å laser light) was measured and is plotted in fig. 1. For KNiF₃ the magnon pair scatter-

ing accounts for the entire inelastic light scattering, and therefore for the non- σ electronic contribution to $\chi^{(3)}$ [5]. The correlation of the two temperature dependences is compelling evidence for the magnetic origin of the low temperature enhanced NLO spectral broadened intensity.

Our observations may be semi-quantitatively accounted for in terms of a temperature dependent spin contribution to the overall nonlinear susceptibility $\chi_{ijkl}^{(3)}$ which governs four photon parametric mixing as the primary process. In general $\chi^{(3)}$ may be written as a sum of electronic and Raman contributions [3]. For KNiF₃ we may consider the latter to consist solely of the magnon pair Raman scattering contribution [8,9] which we can approximate as a Lorentzian:

$$\chi_{ijkl}^{(3)}(-\omega_3, \omega_1, \omega_1, -\omega_2) = \chi_E^{(3)} + K \frac{\alpha_{ij}^m \alpha_{kl}^m + \alpha_{il}^m \alpha_{jk}^m}{\omega_m - (\omega_1 - \omega_2) + i\Gamma_m} \quad (1)$$

Here ω_m and Γ_m denote the temperature dependent frequency and linewidth respectively of the magnon pair excitations, and α_{ij}^m is the magnon pair polarizability. $\chi_E^{(3)}$ is the usual non-resonant, temperature independent "electronic" contribution from nonlinear distortion of electronic orbits. The second term in eq. (1) is called $\chi_M^{(3)}$. Since the integrated intensity of the spontaneous magnon pair Raman spectrum, which is $\sim |\alpha^m|^2$, has been measured to be essentially temperature independent [8,9], the only quantities in eq. (1) which vary significantly with temperature are ω_m and Γ_m . The observed temperature independence for the extent of spectral broadening, $\delta\omega$, may be explained by noting that $\delta\omega \sim 2\Delta\omega n_2 k E_1^2 l$ due to self-phase modulation [2]. Here $\Delta\omega$ is the spectral width of the input pulse, k its propagation constant, E_1 the field amplitude and l the path length. n_2 is the nonlinear refractive index which contains a purely electronic contribution, σ , and a contribution proportional to the integrated Raman scattering cross section [5]. Since neither σ nor $|\alpha^m|^2$ are temperature dependent in KNiF₃, n_2 and therefore $\delta\omega$ should not vary either, in agreement with observations.

The observed strong temperature dependence for the intensity of the frequency broadened spectrum (see fig. 1) arises from the resonant term in eq. (1) through the primary process $2\omega_1 \rightarrow \omega_2 + \omega_3$ which is strongest when $\omega_2 = \omega_1 + \omega_m$ and increases as Γ_m decreases (upon cooling below the Néel temperature [8,9]).

That is, the resonant contribution to $\chi^{(3)}$ in eq. (1) varies with temperature in the same way as the peak spontaneous magnon pair cross section: $\Gamma_m^{-1}(T)$. However, the individual contributions to $\chi^{(3)}$ cannot be directly inferred from the temperature dependence of the broadened spectrum. This is because the latter receives significant contributions from secondary processes of the form $\omega_1 + \omega_2 \rightarrow \omega_3 + \omega_4$, etc. in which products of the primary process interact with the pump to smooth the spectral distribution and wash out the sharp features which the resonant spin non-linearity produce in the primary process. The large values of pump intensity and the source spectral width* make possible strong amplification in spite of imprecise phase matching in the forward direction. Such behavior (washing out of stimulated Raman features by spectral broadening processes) has frequently been observed in both liquids and crystals [2]. Thus a full quantitative description of the NLO processes in KNiF_3 is not yet possible. Some idea of the complexity involved and additional information required can be gained from the work of Penzkofer et al. on resonant contributions to $\chi^{(3)}$ in water [12].

In conclusion we have presented observations of the first nonlinear optical effects associated with the

* A large spectral width causes a wide range of k -values for the pump laser, i.e. $\delta\nu \sim 80 \text{ cm}^{-1}$ gives rise to a wide range of $\delta k \sim 750 \text{ cm}^{-1}$. This allows the material to select the possible pump photons in the k -band which satisfies the k -matching condition best to stimulate the other photons in a collinear four-photon parametric process.

onset of magnetic order in a solid. Our results suggest that the primary NLO process is a four wave parametric mixing dominated below the magnetic transition temperature by the spin wave contribution to the nonlinear susceptibility $\chi^{(3)}$. KNiF_3 is well suited to an investigation of magnetic NLO effects because of the absence of vibrational Raman contributions to $\chi^{(3)}$ and should serve as a standard for future studies of magnetic NLO effects in related and more complex systems.

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