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Nonlinear mixing spectroscopy of $Fe_xZn_{1-x}F_2$ and $Fe_{1-x}Mn_xF_2$

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We report the first observation of electronic Raman-resonant four-wave mixing (4WM) in magnetic materials. The coherent anti-Stokes Raman spectroscopy is used to measure the frequency dispersion of the $\chi^{(3)}$ components in $Fe_{1-x}Zn_xF_2$ and $Fe_{1-x}Mn_xF_2$. Energy, width, and polarization characteristics of the excitations of the Fe^{2+} ion within the $^5T_{2g}$ orbital levels manifold are studied as a function of the temperature. Below the Néel temperature an enhancement of the 4WM signal is observed which is due to the spin-dependent part of $\chi^{(3)}_{ijkl}(2\omega_1-\omega_2,\omega_1,\omega_1,-\omega_2)$.

Four-wave-mixing (4WM) techniques in condensed matter have been traditionally employed to investigate vibrational and electronic transitions in nonmagnetic materials.[1-3] This type of experiment yields the determination of a number of different resonances in the ground and excited states which have been studied by several authors leading to interesting information on gases, liquids, and solids.[1-3]

In this paper we report for the first time the results of a study using a 4WM technique [electronic CARS (coherent anti-Stokes Raman spectroscopy)] to investigate the effect of the magnetic phase transition on the generated emission.

The materials studied in this work ($Fe_{1-x}Zn_xF_2$ and $Fe_{1-x}Mn_xF_2$) are important systems where an extensive study of their magnetic and electronic properties may lead to the comprehension of a whole class of problems since they exemplify a class of three-dimensional antiferromagnetic alloys of high anisotropy. In the past few years interesting observations based on a large variety of techniques have been reported for this class of materials.[4-7] These compounds have the rutile structure D^{14}_{4h} in which the cations are located on a body-centered tetragonal lattice. The point symmetry at the position of the Fe^{2+} ions is D_{2h} in the paramagnetic phase. The octahedral crystalline field splits the five orbital states of the Fe^{2+} into a lower $^5T_{2g}$ orbital triplet consisting of states with symmetry $^5A_{1g}$, $^5B_{1g}$, and $^5B_{2g}$, and an upper ^5E_g doublet consisting of two orbital states with $^5A_{1g}$ and $^5B_{3g}$ symmetry. Below the Néel temperature these compounds become antiferromagnetically ordered with spins parallel and antiparallel to the c axis. In the present experiments we used the CARS technique[1-3] to study the electronic transition between the ground $^5A_{1g}$ and the excited $^5B_{1g}$ states of the Fe^{2+} ion. The generation of light at the frequency $\omega_4=2\omega_1-\omega_2$ by two incident laser beams at ω_1 and ω_2, was studied as a function of $\omega_1-\omega_2$, of the samples temperature, of the Zn and Mn concentration, and of the lasers' polarizations. The results yield the energy, the width, and a symmetry assignment of the resonances for the several concentrations.

The lasers used were two homemade dye lasers of the grazing incidence type[8] pumped by the second harmonic of a NdYAG (yttrium aluminum garnet) laser (Quanta Ray), operating in the range of 5600–6130 Å, with linewidths of ≤ 0.1 cm^{-1}. The dye laser beams with 8-nsec duration were overlapped temporally and spatially inside the sample using a 20-cm focal length lens and properly located mirrors. The typical peak laser power was 1–20 kW. The beams propagated along the c axis and were linearly polarized with an adjustable angle (ϕ) between their electric fields. Phase matching was accomplished adjusting the angle between beams $E_1(\omega_1)$ and $E_2(\omega_2)$ so that $\vec{k}_4=2\vec{k}_1-\vec{k}_2$. The maximum output occurred when the angle between $\vec{k}_1$ and $\vec{k}_2$ was approximately 1° in the sample. The generated signal was spatially filtered, sent through a Glan Prism analyzer and a 0.5-m spectrometer (Spex-Doublemate) to a photomultiplier followed by a boxcar integrator (P.A.R. model 162), and plotted using a recorder. The apparatus allows a study of the polarization of the anti-Stokes beam.

The experiments were performed with well-polished crystals grown by N. Nighman of University of California at Santa Barbara. The single crystals of good optical quality were mounted in a cold finger Dewar which allows the temperature of the samples to be varied in the range 15–300 K.

The measurements have been done for different values of ϕ in order to analyze the selection rules of the $^5A_{1g}\rightarrow {}^5B_{1g}$ transition. The polarization of beam ω_1 was parallel to a crystallographic a direction and the polarization of beam ω_2 was adjusted in the range 0°–90° with respect to the other beam.

The intensity of ω_4 as a function of $\omega_1-\omega_2$ and the temperature, is shown in Fig. 1 for $Fe_{0.995}Mn_{0.005}F_2$. The spectra were obtained with both laser fields $E_1(\omega_1)$ and $E_2(\omega_2)$ parallel ($\phi=0°$). Notice that at high temperature there is no sharp resonance in the frequency range 975 cm^{-1} $<\omega_1-\omega_2<1200$ cm^{-1}. Below the Néel temperature, a resonant behavior in the generated beam at $2\omega_1-\omega_2$ is observed when $\hbar(\omega_1-\omega_2)$ equals the energy difference between states $^5A_{1g}$ and $^5B_{1g}$ (1082 cm^{-1}). At 15 K the signal on resonance is ≈ 10 times larger than the nonresonant background at 100 K. As the temperature increases up to T_N the peak intensity decreases but its linewidth (28 cm^{-1}) remains constant. A calibration was made relative to the 992-cm^{-1} line of benzene which is a very strong Raman mode. The magnitude of $|\chi^{(3)}|^2$ has been found to be about 10% of the squared modulus of the resonant susceptibility of benzene. Thus, we obtain for $Fe_{0.995}Mn_{0.005}F_2$ at resonance, $\chi^R_{xxxx}\cong 5\times 10^{-14}$ esu.

Other experiments have been performed for different values of ϕ. For perpendicular fields, the 4WM intensity for $\omega_1-\omega_2=\omega_A=1082$ cm^{-1} decreases by more than one order of magnitude and a new resonance at $\omega_1-\omega_2=\omega_B=1115$ cm^{-1} is observed. The spectrum for $\phi=85°$ and 15 K is shown in Fig. 2. In this figure the line splitting

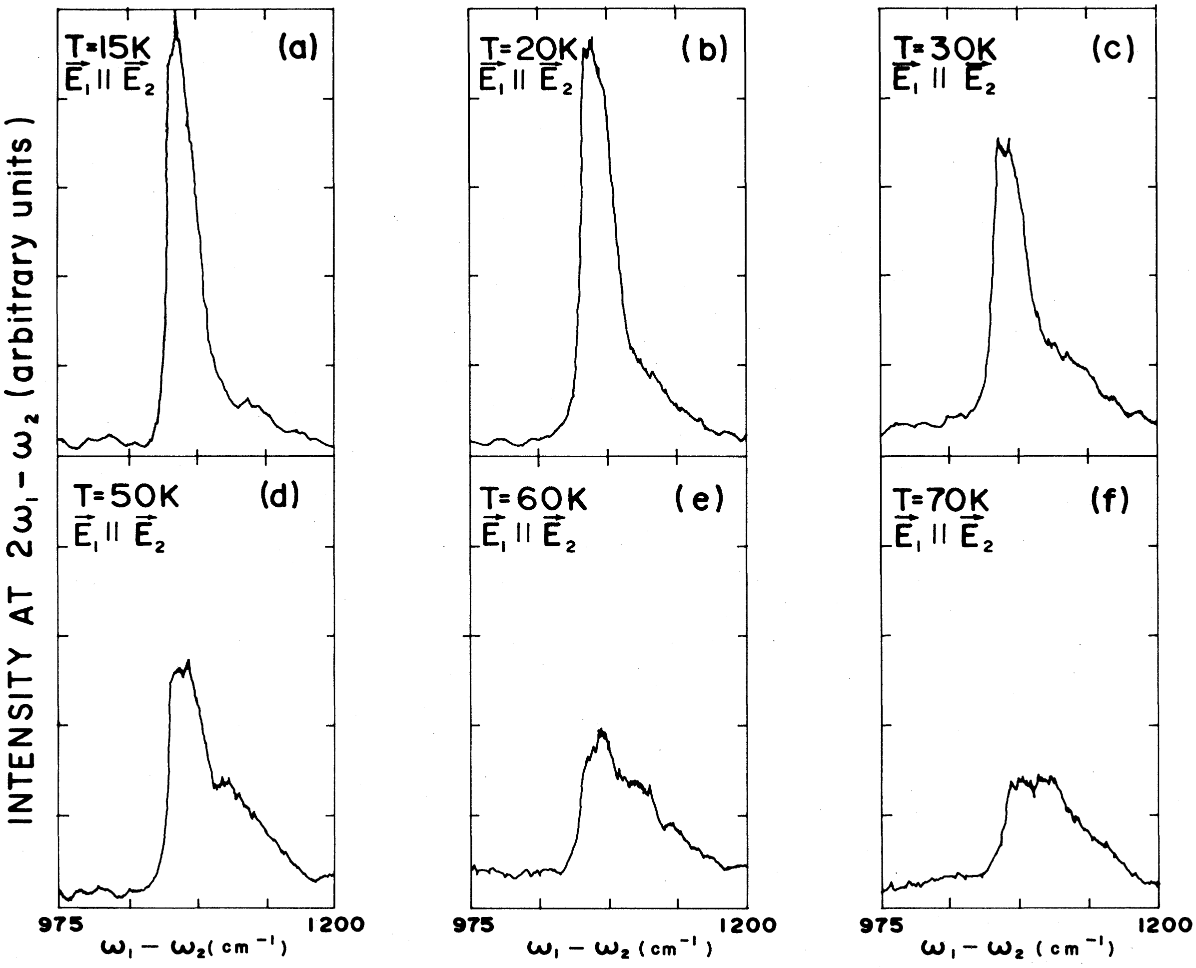

FIG. 1. (a)–(f) Four-wave-mixing spectra of $Fe_{0.995}Mn_{0.005}F_2$ as a function of the temperature. The laser fields $E_1(\omega_1)$ and $E_2(\omega_2)$ are parallel and propagate along the c axis. The Néel temperature is 78 K.

can be interpreted considering the spin orbit and the magnetic interactions which play an important role below the Néel temperature. In the antiferromagnetic phase the magnetic point group is $D_{4h}(D_{2h})$, where D_{2h} is the unitary group which generates the corepresentations of the magnetic group D_{4h}. Thus, the first excited manifold will be spread around the B_{1g} crystal-field level and the low electronic levels are excitons of symmetry $\Gamma_i^+ (i=1,2,3,4)$.[9] Accordingly, the resonances ω_A and ω_B are identified as the $k \cong 0$ Γ_1^+ and Γ_2^+ excitons and the spectrum of the Fig. 2 is the first evidence for the Davidov splitting in FeF_2, first proposed in Ref. 9. The splitting of the orbitally nondegenerate levels occurs because the magnetic unit cell contains two translationally nonequivalent magnetic ions. The resonance ω_B has also been observed in Refs. 10 and 11 by infrared absorption measurements. However, it was not observed in the Raman experiments by Chinn and Zeiger.[10] Although those authors suggest that the resonance at 1082 cm^{-1} would be the Davidov split partner of the Γ_2^+ exciton at 1115 cm^{-1}, they could not be sure of the existence of both resonances. The spectrum of Fig. 2 displays both resonances and the energy difference $\omega_B-\omega_A \cong 30$ cm^{-1} is a measurement of the Davidov splitting for $Fe_{0.995}Mn_{0.005}F_2$. The appearence of the Γ_2^+ resonance is in agreement with the expected selection rules.[9] The spectrum obtained in the $\phi=90°$ configuration and the one of Fig. 1(a) with $\phi=0$, indicate that the electronic polarizability associated to the resonance ω_B has matrix elements $\alpha^B_{xx}=\alpha^B_{yy}=0$ and $\alpha^B_{xy}\neq 0$. For the $\phi=0°$ configuration, the spectrum of Fig. 1(a) indicates that only the ω_A resonance contributes, in agreement with the selection rules ($\alpha^A_{xx}=-\alpha^A_{yy}\neq 0$). Comparing the 4WM signal intensity at $\phi=0°$ and 90°, we have $|\chi^{(3)}_{xxxx}(\omega_1-\omega_2=\omega_A)|^2 \cong 10|\chi^{(3)}_{yxxy}(\omega_1-\omega_2=\omega_B)|^2$ and assuming the same linewidths for both Davidov's levels, we obtain for the electronic polarizabilities an approximate relation, $|\alpha^A_{xx}|^2 \cong \sqrt{10}|\alpha^B_{xy}|^2$. A curve similar to Fig. 2 can be obtained by spontaneous Raman scattering measuring the spectrum in the xy configuration.

The behavior of the 4WM signal with the Zn and Mn concentration is very similar to the one already reported in Ref. 6. Namely, the peaks move to lower energy and broaden with increasing Zn or Mn concentration. The linewidth becomes inhomogeneously broadened due to the effect of strains and clustering of magnetic ions and the 4WM peak signal displays a linear dependence with the Fe^{2+} concentration. The details will be discussed in a more

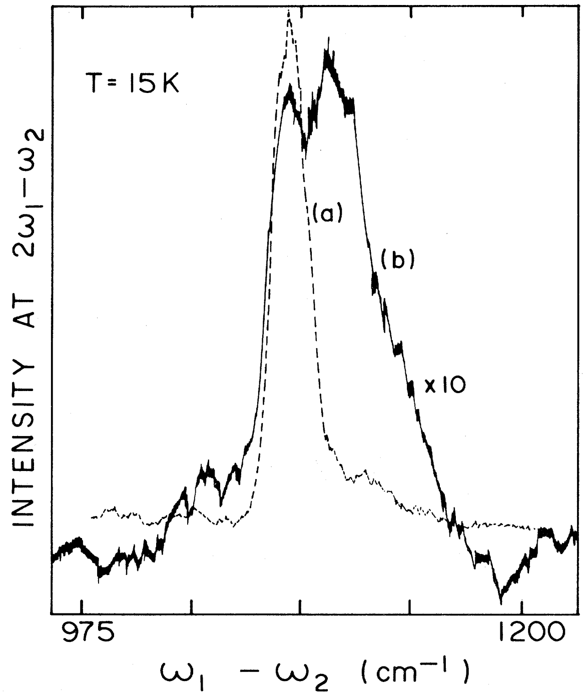

FIG. 2. Four-wave-mixing spectra of $Fe_{0.995}Mn_{0.005}F_2$ at low temperature (15 K). (a) $E_1(\omega_1)$ and $E_2(\omega_2)$ are parallel ($\phi=0°$). (b) The laser fields $E_1(\omega_1)$ and $E_2(\omega_2)$ are almost perpendicular ($\phi=85°$). The two peaks are an evidence for the Davidov splitting (~ 30 cm^{-1}) of the lowest excited crystal-field level of Fe^{2+} ion. When $\phi=90°$ only the resonance at 1115 cm^{-1} is observed.

TABLE I. Nonresonant third-order susceptibility elements.

Crystal	$\chi^{(3)}_{1122}/\chi^{(3)}_{1221}$	$\chi^{(3)}_{1122}/\chi^{(3)}_{1111}$	σ
$Fe_{0.50}Mn_{0.50}F_2$	0.86	0.44	0.39 ±0.06
$Fe_{0.80}Mn_{0.20}F_2$	1.10	0.52	0.51 ±0.08
$Fe_{0.995}Mn_{0.005}F_2$	1.32	0.62	0.70 ±0.10
$Fe_{0.90}Zn_{0.10}F_2$	1.36	0.54	0.48 ±0.07
$Fe_{0.81}Zn_{0.19}F_2$	0.85	0.49	0.56 ±0.08

detailed future paper.[12]

The nonresonant part of $\chi^{(3)}_{ijkl}$ has also been measured at room temperature using the method of Ref. 13. The results are shown in Table I where the anisotropy ratio $\sigma=(\chi^{(3)}_{xyyx}+2\chi^{(3)}_{xxyy}-\chi^{(3)}_{xxxx})/\chi^{(3)}_{xxxx}$ is also reported. The results on Table I show deviation from the Kleinman's symmetry which may be attributed to the proximity between the laser frequencies and exciton levels associated with an excited configuration, or with two photon absorption processes. Concerning the diagonal element of the nonresonant susceptibility in FeF_2, an order of magnitude estimate based on the intensity of the nonresonant signal, gives the value of $\chi^{NR}_{xxxx}=0.61\times10^{-14}$ esu which is about one order of magnitude smaller than the nonresonant susceptibility of liquid benzene. This result is in agreement with the theoretical value ($\chi^{NR}_{xxxx}=10^{-14}$ esu) which we have obtained using a simple model[14] consisting in neglecting the anharmonicity of the short-range forces between ions and taking into account the anharmonicity of the Coulomb interactions.

In conclusion, we emphasize that the present results clear up the origin of the infrared resonances of $Fe_{1-x}Mn_xF_2$ and $Fe_{1-x}Zn_xF_2$ in the region of 10^3 cm^{-1}. The behavior of the 4WM signal with the temperature and the lasers' polarizations indicates the dependence of $\chi^{(3)}$ on intermediate virtual magnetically ordered states and provides a clear evidence that the mixing process is associated to the spin-dependent part of $\chi^{(3)}(2\omega_1-\omega_2,\omega_1,\omega_1,-\omega_2)$. In addition, the present results help to rule out the alternative explanation of Ref. 10 based on the possibility of the resonance at 1082 cm^{-1} to be related with the presence of Fe^{3+} impurities since the 4WM intensity varies linearly with the Fe^{2+} concentration.

As the first observation of 4WM in magnetic materials this work is a first step in applying the nonlinear spectroscopy for magnetism studies. Further extensions of the present research may include the study of the 4WM signal enhancement by magnon resonances and resonant energy-transfer processes between magnetic ions.

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