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FAST TRACK COMMUNICATION

Resonant excitation of Mn local vibrational modes in the higher order Raman spectra of nanocrystalline $\text{Ga}_{1-x}\text{Mn}_x\text{N}$ films

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Abstract

The effect of manganese on the vibrational properties of $\text{Ga}_{1-x}\text{Mn}_x\text{N}$ ($0 \leq x \leq 0.18$) films has been investigated by Raman scattering using 488.0 and 632.8 nm photon excitations. The first-order transverse and longitudinal optical GaN vibrational bands were observed in the whole composition range using both excitations, while the corresponding overtones, as well as a prominent peak located in 1238 cm^{-1} (153.5 meV) were only observed in the Mn-containing films under 488.0 nm excitation. We propose that the peak observed at 1238 cm^{-1} is due to resonant Mn local vibrational modes, the excitation process being related to electronic transitions involving the Mn acceptor band.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The $\text{Ga}_{1-x}\text{Mn}_x\text{N}$ compound has been the focus of several research groups in the last few years due to its ferromagnetic behaviour above room temperature, as well as to its potential applications in spin-based devices and quantum computation [1–3]. Actually, the interaction between the Mn ion and the free carriers and its role in the dynamics of the lattice is a central issue concerning the magnetic behaviour and the control of the material's properties [2–4]. Amongst many different spectroscopic attempts to address this question, Raman scattering has been shown to be particularly useful [4–6].

The analysis of the first-order Raman scattering spectra of $\text{Ga}_{1-x}\text{Mn}_x\text{N}$ compounds, prepared by different techniques [3–8], displays general progressive modifications with Mn incorporation. However, no specific modes directly

associated with Mn can be clearly and unambiguously identified [4–9], even when resonant excitation is used. The only exception to this trend, is the identification of a well-defined band attributed to the Mn local vibration mode (LVM) using a polarized excitation–detection combination [6].

Motivated by the above issues, and looking for additional information about the $\text{Ga}_{1-x}\text{Mn}_x\text{N}$ system, we have investigated the Mn-related LVMs via Raman spectroscopy. The experiments were carried out on nanocrystalline $\text{Ga}_{1-x}\text{Mn}_x\text{N}$ ($0 \leq x \leq 0.18$) films by using different excitation wavelengths: 488.0 nm (in resonance with the Mn-related transitions), 632.8 nm (out of resonance). In both cases the spectral resolution was around 1.5 cm^{-1} .

2. Experimental details

The films were deposited on crystalline GaAs substrates by planar radio frequency magnetron sputtering using a

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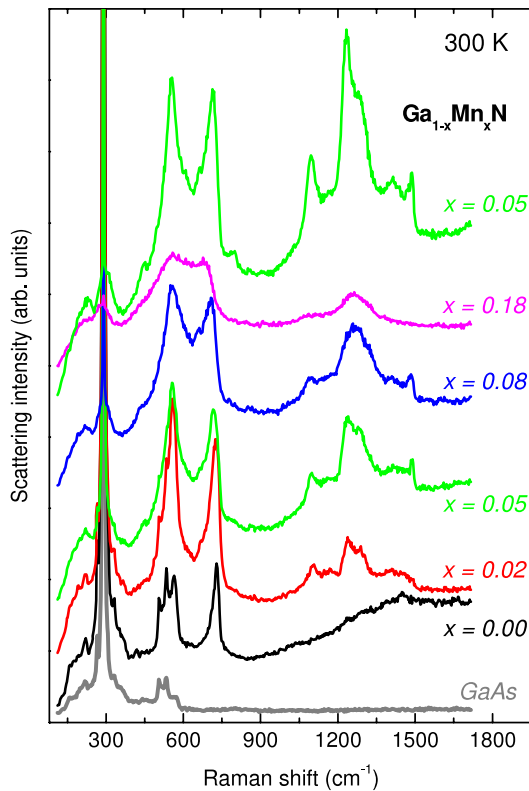


Figure 1. Room temperature (300 K) Raman scattering spectra of $\text{Ga}_{1-x}\text{Mn}_x\text{N}$ ($0 \leq x \leq 0.18$) films under 488.0 nm photon excitation. The spectra have been vertically shifted for clarity. Except for the film at the top of the figure, which is 2 μm thick, the thicknesses of all films are 0.7 μm . The substrate (GaAs) spectrum is also shown.

(7N (99.9999%) pure) Ga target in (6N (99.9999%) pure) N_2 atmosphere. The insertion of Mn was achieved during deposition by adding small pieces of metallic Mn onto the Ga target. Further details on the sample preparation and characteristics can be found elsewhere [10].

The films are polycrystalline with crystallites typically ~ 25 nm large. They exhibit wurtzite structure, and strong orientation texture with the c -axis oriented perpendicular to the substrate surface [8]. No other crystalline phase was detected by x-ray diffraction.

Raman scattering experiments have been carried out in a commercial micro-Raman probe setup (Renishaw RM2000) equipped with 1200 lines mm^{-1} diffraction gratings and optical microscope, rendering a spatial resolution of $\sim 1 \mu\text{m}^2$, and a spectral resolution of 1.5 cm^{-1} . The experiments were performed under the back-scattering geometry. The films were excited either by the 488.0 nm (2.54 eV) or 632.8 nm (1.96 eV) lines of Ar^+ and HeNe lasers respectively, and no preferential polarization was adopted. In spite of the 3.4 eV optical band gap of the GaN, the 488.0 nm photons have enough energy to excite electronic states associated with the Mn centres, due to the location of the electronic deep Mn impurity inside the gap located ~ 1.3 eV above the valence band [11].

3. Results and discussion

The Raman spectra of the present $\text{Ga}_{1-x}\text{Mn}_x\text{N}$ films excited with the 488.0 Ar^+ laser line are shown in figures 1 and 2 as

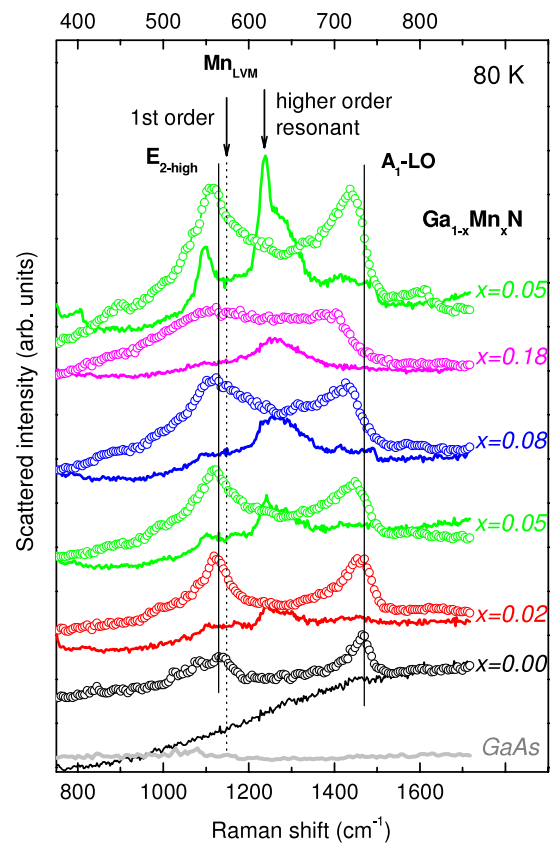


Figure 2. Low temperature (80 K) Raman scattering spectra of $\text{Ga}_{1-x}\text{Mn}_x\text{N}$ ($0 \leq x \leq 0.18$) films after excitation with 488.0 nm photons. The top axis corresponds to the first-order Raman spectra (open symbols). The solid lines refer to the high-frequency Raman spectra (overtone region) and their phonon frequencies are indicated in the bottom axis. The spectra have been vertically shifted for comparison reasons. The top spectra correspond to a thicker (2 μm) $\text{Ga}_{0.95}\text{Mn}_{0.05}\text{N}$ film. The frequency position corresponding to the one phonon optical modes of crystalline GaN and Mn-LVM are indicated by vertical solid and dotted lines, respectively.

obtained at 300 and 80 K, respectively. The Raman spectra of the $\text{Ga}_{1-x}\text{Mn}_x\text{N}$ films measured at 80 K (figure 2) are very similar to those observed at 300 K (figure 1). For this reason figure 2 was plotted mainly for comparison of the first-order (open symbols, top scale) with the second-order peaks (full lines, bottom scale). The films are 0.7 μm thick. For comparison, the spectra of a thicker film (2 μm) are included at the top of the figures. In figure 1, two clear peaks at approximately 570 and 720 cm^{-1} are evident. These peaks, slightly modified by the nanostructure and by the presence of Mn, are well known and correspond to the transverse (TO) and longitudinal (LO) optical modes of wurtzite GaN, which present, respectively, E_2 (high) and A_1 symmetries [6, 11]. In the undoped film ($x = 0$), the line shapes of the first-order Raman peaks are intermediary between those of the GaN crystal and its amorphous counterpart [13]. Moreover, the Raman signal coming from the GaAs substrate adds two small peaks (at $\sim 520 \text{ cm}^{-1}$) to the spectrum of the undoped film. In the ~ 150 – 450 cm^{-1} range, corresponding to the acoustic modes, the spectrum resembles the phonon density of states of GaN [6, 9].

In terms of the Mn content of the films, it can be observed that the first-order optical Raman peaks tend to broaden and to red-shift [4, 6, 8, 9]. Besides, there is a considerable increase in the Raman intensity between the TO and LO peaks with the increase of the Mn concentration.

Based on a light impurity model, it is common to attribute the frequency of the Mn-LVM to values a little above those typically found in the TO of GaN [3, 6, 7, 9]. Since the reduced mass of the Ga–N and Mn–N pairs are basically determined by the much lighter N atom, and the bond strengths are considered equal in the model, the expected peak position results are very close to the ones corresponding to the TO GaN peak [4, 6, 9, 12]. As a consequence, with the broadening of the E_2 (high) TO peak due to disorder [13], it is generally not possible to identify in the Raman spectrum of $\text{Ga}_{1-x}\text{Mn}_x\text{N}$ a specific peak that can be associated with Mn—albeit the spectra can be compatible with the existence of such a peak encompassed by the spectrum broadening.

Analysing the room temperature Raman spectra above 900 cm^{-1} (figure 1), it is evident that no clear peaks appear in the spectrum of the undoped film. Only a small kink in the frequency region corresponding to the overtone of the LO mode at about 1449 cm^{-1} can be noticed. This is an expected result due to the much lower efficiency in generating higher order phonons, particularly with the use of below gap excitation [14]⁴. Concerning the Mn-containing films, the presence of weak peaks in the positions corresponding to the two-TO and LO phonons of GaN in addition to a strong band at $\sim 1238\text{ cm}^{-1}$ ($\sim 153.5\text{ meV}$) can be clearly noticed. While the peaks, associated with the TO and LO overtones, tend to reduce their intensities as the Mn concentration increases, the peak at 1238 cm^{-1} tends to keep its intensity, increasing its relative importance in the higher frequency region. This behaviour makes improbable the assignment of this peak to a non-resonant combination of one TO and one LO phonon. In the following, we will consider some possibilities concerning the identification of this peak.

Surface plasmons [4–6] could also be the origin of the signal at 1238 cm^{-1} , particularly in nanostructured materials due to the enhancement of the effective surface. Nevertheless, the plasmon frequency is expected to be highly susceptible to the carrier density in these surfaces, and a significant shift in its peak position is expected to occur with variations in the Mn content and, under certain circumstances, with the measurement temperature. Also, the plasmon peak should be present in the undoped film, as the surface of the nanocrystallites is rich in native defects. Considering that the frequency of the contribution at 1238 cm^{-1} remains unchanged with the Mn concentration, and since this peak is absent in the undoped film, it is rather improbable that it refers to surface plasmons.

It is worth noting that the peak width at $\sim 1238\text{ cm}^{-1}$ is only $\sim 12\text{ meV}$ (100 cm^{-1}). As the host material is nanocrystalline, with lots of substitutional Mn sites ($0.02 \leq x \leq 0.18$), the material is expected to present considerable disorder effects in its electronic structure. In such a case,

luminescent transitions are expected to produce much broader bands so the assignment of the contribution at $\sim 1238\text{ cm}^{-1}$ to such transitions can be discarded. Once more, the nanostructured nature of the films and increasing contents of Mn should influence the main characteristics of this peak.

Another possibility is that the 1238 cm^{-1} band can be related to some impurity due to contamination of the material. Analysing the set of spectra, we can see that the band shows up only after Mn inclusion. Its association with the presence of Mn in the deposition chamber was also confirmed by later experiments in which the Mn was removed and the band is again not present. So the only possibility is that the impurity responsible for the band can be introduced in the films with the Mn, as for example an oxide layer in the surface of the Mn pieces. In this case the band should weaken with the film thickness, since the plasma process tends to clean away the oxide layer from the Mn pieces placed in the target. That was not observed since the thicker films presented more prominent peaks. Therefore, the peak at $\sim 1238\text{ cm}^{-1}$ is clearly not associated with any contaminant.

Taking into account the above discussion, we have assigned the peak at 1238 cm^{-1} to the excitation of higher order local mode phonons involving the Mn ions through a resonance associated with the electronic transitions related to the Mn impurity band. In the following we present the basic ideas that support this statement and its consequences to the existing models.

The previous arguments clearly show that the 1238 cm^{-1} peak cannot be attributed to GaN-related defects or to lattice modes, since it is completely absent in the undoped film, so we discuss its association to the electronic Mn transitions. The below band gap optical absorption of the Mn doped films [11] presents two broad absorption bands located at ~ 1.3 and $\sim 2.3\text{ eV}$. Similar absorption bands in crystalline $\text{Ga}_{1-x}\text{Mn}_x\text{N}$ were associated with the presence of an electronic Mn^{2+} acceptor band, located 1.4 eV above the valence band [3, 15–17]. In our samples, in which the band gap is somewhat smaller ($\sim 3.2\text{ eV}$), the acceptor band seems to be red-shifted. According to this picture, the exciting transition observed here should be due to the excitation of electrons from the occupied levels of the Mn deep acceptor band to the conduction band. This trend is consistent with the fine absorption structure observed in the reports of Korotkov *et al* (in which the first- and second-order phonon-related peaks are clearly seen with a separation of 73 meV) [17], and to the fact that in our experiments using the 632.8 nm excitation, the Raman overtones are hardly seen (in a clear indication of an off-resonant condition). In this way both the vibrational second-order spectra and the excitation condition of the 488.0 nm Ar^+ laser line are consistent with the resonance or quasi-resonance in the Raman spectra, produced by the electronic transition involving the Mn impurity band.

The 1238 cm^{-1} (153.5 meV) peak is slightly above the one expected for the two Mn-LVM phonons (1130 cm^{-1} , 140.1 meV) and slightly below the sum of the frequencies of one TO and one LO phonons (1291 cm^{-1} , 160.1 meV). Considering the assignment of the peak to two Mn-LVM, each phonon is expected to have an energy of 76.7 meV (619 cm^{-1})

⁴ The closeness can be seen in figure 2, where we represent the Raman shift of this mode by a vertical dotted line.

instead of the 71.6 meV (577 cm^{-1}) predicted by the light impurity model [4, 6–8]. We suggest that the energy difference may be due to the changes in the force constants related to the Mn and a more complex local environment of the Mn ion in the lattice than that predicted by the LVM [4–6] model. In a previous structural analysis of this compound [8], we have observed that the presence of Mn induced some increase in the bond length and ionicity of the Mn–N bonds along the c -axis. Furthermore, the bond distance shrinks and the covalent character increases in the plane perpendicular to the c -axis, indicating that the force constants and the local symmetry of the lattice are effectively changing with the presence of the Mn impurity.

The observed increase in the intensity of TO and LO bands of the first-order Raman spectra of the $\text{Ga}_{1-x}\text{Mn}_x\text{N}$ films, as compared to the undoped sample, may also be possibly attributed to the (quasi-)resonance effect—even though the Mn local mode peaks do not become evident in the position expected to the first order. Possible reasons for this observation are discussed below.

As the atomic movements related to E_2 (high) vibrations are in directions perpendicular to the c -axis, it is likely that stronger covalent character and shorter distances of the bonds outside the c -axis will generate higher vibration frequencies, thus favouring the attribution of the peak to a pair of Mn-LVMs. This explanation also favours the interpretation of the overall increase in the inter-peak scattering observed in the first-order spectra, upon the assignment of a disorder broadened Mn-LVM to frequencies ($\sim 619\text{ cm}^{-1}$) above those expected ($\sim 577\text{ cm}^{-1}$) by the current LVM model. Nevertheless, as the band with the maximum at 1238 cm^{-1} is asymmetric and encompasses also a higher frequency tail, it can in principle contain also a component due to the combination of one TO and one LO phonon, with a basis in the same bond strengthening explanation.

The frequencies of the signals related to the first-order TO and LO modes of hexagonal GaN are indicated by solid vertical lines in figure 2 [12]. The expected frequency of the LVM associated with Mn impurity centres (as calculated by the light impurity approximation) is represented by a dotted vertical line. Just like the results obtained at 300 K, the undoped film exhibits only a smoothly increasing signal in the Raman overtone region. The spectra of the Mn-containing films, on the contrary, clearly display weak overtones of the TO and LO modes and the 1238 cm^{-1} asymmetric peak. According to our tentative assignment, the development of the peak at 1238 cm^{-1} involves the electronic excitation of Mn sites and the associated higher order local vibrational modes. In principle, this mechanism could also produce a resonance in the first-order Raman spectra, however this is not supported by the present and by other experimental results [6]. Also, the effects of the resonance on the first-order phonon modes could be a small enhancement of the LO and TO peaks, and an overall increase in the light scattering, but no specific feature related to the Mn-LVM excitation can be observed. We propose that this can be related to asymmetries of the first-order Mn local vibration mode, the excitation of which possibly involves significant momentum transfer, not allowed by photon

excitation in the single phonon spectra. So we attribute the presence of the 1238 cm^{-1} peak to higher order symmetric local vibration excitations of the Mn sites.

The present results indicate that the Raman activity of the first-order local vibration modes of Mn should be very weak, unlike what was expected in previous reports [4, 6–8]. This suggests that the Mn sites in GaMnN do not bring the exact symmetry of the Ga sites as proposed by the Mn-LVM, and also that the symmetry of the Raman active vibration modes can possibly be recovered when two optical phonons are created in the process. Also, the second-order excitation of the Mn-LVM is placed at higher energy than that predicted by the model, indicating that the force constant of the Mn–N bonds in the bond axis out of the c -direction is bigger than that observed in the equivalent Ga–N bonds. Even though the present results refer to vibrations involving nanometric crystallites, the resemblance of the Raman spectra obtained here with the ones reported for Mn-containing crystals [6] suggests that the results may also be applied to single-phase crystalline material.

4. Conclusions

The second-order Raman scattering of $\text{Ga}_{1-x}\text{Mn}_x\text{N}$ films using below band gap excitation was investigated in detail. In addition to the TO and LO overtones, the experimental spectra (488.0 nm excitation only) exhibit a phonon contribution at $\sim 1238\text{ cm}^{-1}$, which was attributed to a higher order resonant scattering associated with Mn local vibration modes in the lattice. The individualization of a characteristic vibration mode due to Mn in $\text{Ga}_{1-x}\text{Mn}_x\text{N}$ compounds is important since, in most cases, only the global effects of Mn are apparent from spectroscopic characterization. In this respect, the use of the 1238 cm^{-1} peak can provide a more detailed understanding of the role of Mn in the $\text{Ga}_{1-x}\text{Mn}_x\text{N}$ lattice.

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