Magnons and acoustic phonons in $Y_{3-x}Bi_xFe_5O_{12}$

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(Received 1 May 2000; revised manuscript received 16 March 2001; published 13 August 2001)

We use Brillouin light scattering (BLS) to study a series of single-crystal Bi-doped yttrium iron garnet $Y_{3-x}Bi_xFe_5O_{12}$ (Bi-YIG) prepared with $x = 0, 0.14, 0.36, 0.54$, and 0.92. BLS shows that the optimal laser power should be as low as possible, $\leq 5$ mW. BLS manifests the Bi-concentration dependence of the magnetic and mechanic properties of Bi-YIG. Two bulk magnons are observed. One is the thermally excited magnon and another is the uniform magnetostatic mode. The stiffness constant $D_{xx}$, the relative intensity and bandwidth (full width at half maximum) of the thermally excited bulk magnon all increase linearly with $x$, while $4\pi M_s$ is insensitive to doping. On the contrary, the scattering intensity and the sound velocity of the acoustic phonon decreases.

DOI: 10.1103/PhysRevB.64.094421 PACS number(s): 75.50.Gg, 78.35.+c

I. INTRODUCTION

$Y_3Fe_5O_{12}$ (YIG) is a typical collinear ferrimagnet. The unit cell of YIG contains eight molecules and is made up of connected oxygen tetrahedrons and octahedrons with $Fe^{3+}$ at centers, denoted as the $d$ (24 $Fe^{3+}$) and $a$ sites (16 $Fe^{3+}$), respectively. In their interstices are distorted oxygen cubes (dodecahedrons) with $Y^{3+}$ at centers, denoted as $c$ sites (24 $Y^{3+}$). Diamagnetic bismuth ions ($Bi^{3+}$) partly substitute $Y^{3+}$ at the $c$ sublattice in yttrium iron garnet (YIG) crystal. The site distribution of Bi-YIG is denoted as $Y_{3-x}Bi_x[Fe^3]_{y}(Fe^3)_{6-y}O_{12}$, where the superscripts denote the pertinent sublattice in YIG structure. There is an extensive literature on defect structure in YIG.

Bismuth induces large magneto-optic (MO) effects in iron garnets—the Faraday rotation $\theta_F$ and the Kerr rotation $\theta_K$ increase drastically. The Curie temperature also increases with the Bi concentration. The unique magnetic and MO properties make the Bi-YIG crystal widely applied and arouses interests. Theoretical and experimental research is performed to clarify the physical origins of the large bismuth-enhanced MO activity. Progress was made by x-ray diffraction, spectroscopic investigations (MO, Mössbauer, Brillouin, and Raman). The understanding of the functions of Bi ions in YIG is being acquired. Early Brillouin light scattering (BLS) work on Bi-YIG observed a new mode of magnon may appear. Recently, we obtained the understanding of new magnon modes.

In this paper, we report a detailed BLS study on a series of single-crystal Bi-YIG. We prepared samples with several Bi concentrations $x$, some of which are higher than Ref. 9. We investigated the influence of exciting power on the BLS first and determined that the optimal power range is below 25 mW. From the measured BLS spectra, it is shown that the spin-wave exchange stiffness constant $D_{xx}$, bulk magnon intensity and bandwidth increase linearly with $x$, whereas the scattering intensity and sound velocity of the acoustic phonon decreases. We identified an additional signal that also appeared in previous works.

II. EXPERIMENT

Bi-YIG single crystals were grown by the flux method. The melt of constituent oxides with $Bi_2O_3$-$PbO$-$B_2O_3$ as flux was slowly cooled in a Pt crucible. The composition of as-grown crystals was determined by chemical analyses. Five slab samples with $x = 0.00, 0.14, 0.36, 0.54$, and 0.92, re-
respectively, all of size ~2.0×2.0×0.5 mm³, are selected for BLS experiments. They exhibit natural rhomboid facets of, e.g., (110) planes with the [001] and [110] axes bisecting its obtuse and acute angles, respectively,17 (determined by x-ray diffraction). The facets were shiny, suitable for optical experiment, but we polished them with diamond paste of size 1 μm for cleaning and to reduce Rayleigh scattering.

A JRS tandem Fabry-Perot interferometer was used for BLS. The 514.5 nm line of an Ar ion laser (Coherent INNOVA 308) in a single-longitudinal-mode-track operation served as the excitation. The optic axis of a focusing and collecting lens is taken to be the x axis. The sample slab stands vertically on the holder in the gap of a magnet and its surface normal coincides with the x axis. The horizontal [110] direction is the z axis, along which the external magnetic field \( H_0 \) is applied. The [001] direction is the vertical y axis. The origin is the light spot on the sample. The laser beam was incident along the negative x direction through a 3.6 cm Nikkor lens, 4 cm from the sample and focused onto the sample surface. The scattered light was collected along the x direction through the same lens.

A pseudobackscattering geometry was adopted with the actual incident angle \( \theta_i \) equal to 20° instead of 0° so as to remove direct reflection from the entrance aperture. Taking the refractive index \( n \) of YIG equal to 2.44 at 514.5 nm, the refractive angel was only 8° from the normal (vertical to \( H_0 \)), close to backscattering.

III. RESULTS

A. The broadening and downshift effect of laser power on magnon

Wettling, Cottam, and Sanderock investigated the bulk magnon and LA phonon in single-crystal YIG with a three-pass Brillouin spectrometer.12 In this paper, we intend to use the same BLS rather than Raman scattering to study Bi-YIG. Whether BLS is more sensitive than Raman scattering in showing spectral subtleties depends on the excitation power. Besides, the scattering intensity and the one-magnon line shape show a strong dependence on the excitation wavelength but any meaningful interpretation of the wavelength dependence of the line shape has to exclude the effect of excitation power first. Significant heating of samples should be prevented so as to keep the accuracy of measured magnetic parameters.

Figure 1 shows the scattering spectra of the Bi-YIG (\( x = 0.14 \)) sample with different laser powers. When the power exceeds 25 mW, the spectra deteriorate drastically; the scattering peaks weaken and widen markedly with decreasing frequency shift and intensifying anti-symmetry. The incident power should therefore be less than 25 mW. It shows that large-power excitation could affect the magnetic order of the crystal Bi-YIG and produce widening of spectral lines. Low power of 5 mW, the lowest in BLS for Bi-YIG, was used and the results were good, showing the development in interferometry (compared to Refs. 11,12).

B. Effect of bismuth concentration on sound velocity

In Ref. 12 LA phonon of YIG was observed only in the red region (\( \lambda > 6328 \text{ Å} \)) because of strong absorption in visible region. To our knowledge, no BLS study of the Bi-YIG mechanical properties has been reported. We use green excitation (\( \lambda = 514.5 \text{ nm} \)) here. BLS spectra of a series of Bi-YIG are measured as the external magnetic field \( H_0 = 0 \). The measurements were made under identical conditions, i.e., the counting rate of scattering from organic glass reaches about 5000 counts/channel (mW) (s). The scattered light was recorded without analyzing its polarization so as to observe both the phonon and magnon. Two pairs of Stokes and anti-Stokes lines, \( \omega_m \) and LA, are observed as shown in Fig. 2. The peak \( \omega_m \) shifts towards higher frequency as \( H_0 \) increases (see following paragraphs) and has been identified as the thermal bulk acoustic magnon.12 The frequency of LA is not affected by \( H_0 \) and the peak is polarized parallel to the incident direction. It is concluded that the peak LA is due to scattering from longitudinal-acoustic (LA) phonons. LA phonons propagating in the [110] direction for a series of Bi-YIG (\( 0 < x < 0.54 \)) at 514.5 nm excitation are observed. The frequency shift and intensity of the LA phonon decrease with increasing bismuth concentration. LA can no longer be observed for \( x > 0.54 \) because of strong optical absorption.

The LA sound velocity \( V_L \) follows the usual linear dispersion

\[
V_L = \omega_p / K, \tag{1}
\]

where \( \omega_p \) is the measured Brillouin frequency shift. \( K \) is the wave number involved in the scattering process, given in our scattering geometry as follows:
where $n$ is the refractive index of Bi-YIG. The wave vector of both the phonon and magnon are the same. We obtain the value $V_L = 7.18 \times 10^5$ cm/s for YIG, in agreement with the value $7.15 \times 10^5$ cm/s. $V_L$ as a function of $x$ is shown in Fig. 3 by solid triangles. $V_L$ decreases linearly with increasing bismuth concentration.

\[ K = \frac{4\pi n}{\lambda}, \tag{2} \]

FIG. 2. BLS spectra of Bi−YIG with different $x$ at $H_0=0$ (without polarization analysis for observing both the LA phonon and thermally excited magnon) at 5 mW excitation. The spectra show that the intensity and frequency of the LA phonon decrease with $x$ while the magnon intensity and frequency increase with $x$.

FIG. 3. Bi−concentration dependences of the sound velocity of the LA phonon propagating along [110] (solid triangles) and the lattice constant of single-crystal Bi−YIG from Ref. 8 (solid circles).

FIG. 4. (a) BLS spectra of magnons of Bi−YIG ($x=0.92$) as the external magnetic field $H_0=0$, 1.2, 1.8, and 2.4 kOe. A weak peaks $\omega_s$ on the lower-frequency side is well resolved. (b) BLS spectra of magnons of Bi−YIG ($x=0.54$) at $H_0=0$, 0.7, 1.3, 1.9, and 2.5 kOe.

Now the scattered light was recorded with the polarization rotated by 90° from the incident light. Only one strong $\omega_m$ occurs and the peak shifts with $H_0$. Its intensity lowers with increasing frequency shift. Figure 4 shows the typical BLS spectra vs the external magnetic field $H_0$ under excitation of 5 mW for the Bi-YIG samples of (a) $x=0.92$ and (b) $x = 0.54$, respectively. When $H_0$ is applied, another weak peak $\omega_s$ appears at the low-frequency side and it also shifts to-

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wards high frequency with $H_0$. The peak $\omega_m$ is very weak as compared with $\omega_m$ but is well resolved and clearly manifested. The $\omega_m$ peak is identified as a thermally excited bulk magnon based on its characteristics. It depends on Bi concentration.

### C. Scattered intensity of bulk magnon

The effect of Bi doping can be clearly manifested in Fig. 2 at $H_0 = 0$. The condition of zero external field is selected in order to exclude its effect on intensity and bandwidth of scattering. The increase of Bi concentration $x$ not only increases the magnon frequency but also increases the scattering intensity. The scattered intensity of Bi-YIG at $x = 0.92$ is taken as the reference. The relative intensity of Bi-YIG vs the concentration $x$ is shown in Fig. 5. The scattered intensity increases linearly with $x$.

### D. The band width of bulk magnons

The bandwidth of bulk magnons at $\sim 1.8$ kOe is fitted using the standard Lorentzian line shape. $\Delta f$ increases from 0.60 GHz at $x = 0$ to 1.51, 1.12, 0.80, and 0.54 GHz, all in unit of GHz, for $x = 0.14$, 0.36, 0.54, and 0.92, respectively. Figure 5 also shows that the bandwidth is linearly proportional to $x$. In the meantime, the magnon band becomes more antisymmetric. The high frequency side of the peak is normal but the low-frequency side shows certain mixture with the Rayleigh scattering.

The most important relation to describe a spin wave is its dispersion. The field dependence is shown in the accurately understood dispersion of the bulk magnons in ferrimagnetic with in-plane magnetization as the magnon wave-vector $K \perp H_0$.\textsuperscript{11,12}

$$\omega_m = \gamma \sqrt{(H_0 + D_{ex}K^2)(H_0 + D_{ex}K^2 + 4\pi M_s)},$$  

where $\omega_m$ is the frequency of the excited bulk magnons, $\gamma = g(e/2mc) = 1.76 \times 10^7$ Oe$^{-1}$sec$^{-1}$ is the gyromagnetic ratio. $H_0$ should include the external field and both the anisotropic field and demagnetizing field

$$H_0 = H_{appl} + H_{an} + H_{demag},$$

as in Ref. 11 so it needs justification to approximate it by the external field only. $D_{ex}$ is the spin-wave exchange stiffness constant and $4\pi M_s$ the saturation magnetization. $D_{ex}$ and $4\pi M_s$ are taken as parameters fitted to the experimental data.

The external field is in the order of kOe and $(2\pi M_s)^2$ is comparatively small. The radical sign in the dispersion relation can be removed. The magnon frequency $\omega_m$ is approximately proportional to $H_0 + D_{ex}K^2 + 2\pi M_s$. In $H_0$ the anisotropy field $H_{an} = 0$ or $-90$ Oe for $H_{appl}$ parallel to [110] or [100]. The demagnetization field $H_{demag} = -N(4\pi M_s)$, where $N$ is the demagnetizing factor ($N = 1/3$ for a sphere) and is difficult to calculate owing to nonuniform magnetization in a platelet. $H_{demag}$ is on the order of a hundred Oe, much smaller than the demagnetizing field of a sphere ($\sim 590$ Oe). Neglecting $H_{an}$ causes an error less than 1% for $H_0 = [110]$. After combining $H_{demag}$ with $4\pi M_s$,

$$\omega_m = \gamma [H_0 + D_{ex}K^2 + (1 - 2N)2\pi M_s].$$

This is a straight line with a slope $\gamma$ and an intercept $\gamma [D_{ex}K^2 + (1 - 2N)2\pi M_s]$. This approximation gives an explanation of Eq. (3) as we only take $H_{appl}$ into account in $H_0$ and the spin-wave dispersion assumes a form identical to that of a thin-film sample. The term $4\pi M_s$ should now be related to $(1 - 2N)2\pi M_s$.

The half collecting angle is 24.22° in air that reduces to 9.68° inside YIG. The $K$ values spread from 1 to 0.982 times the backscattering value that produces 1.8% error in the wave number.

Under 5 mW excitation and for Bi-YIG ($x = 0.36$, 0.54, and 0.92), the data points of $\omega_m$ and the straight line of $\omega_m$ vs $H_0$ are shown in Fig. 6, which follows Eq. (3). This agreement provides a method for obtaining basic magnetic parameters by BLS. The fitted parameters of Bi-YIG with different $x$ are listed in Table I. The value of $D_{ex}$ of YIG ($x = 0$) is $5.58 \times 10^{-9}$ Oe(cm)$^2$, slightly larger than the value $5.4 \times 10^{-9}$ Oe(cm)$^2$ obtained under 25 mW and that of Ref. 11. The value 1753 G of $4\pi M_s$ is similar to the value 1750 G of Ref. 12 but the real value should be larger since there is a factor $(1 - 2N)$ now. The results at 25 mW are consistent to Ref. 9 as $x = 0.54$ and all others are new. The least squares fitting has standard deviation of $\Delta \omega = 0.1$ GHz. The fitting errors for $D_{ex}$ and $4\pi M_s$ are 3% and 7%, respectively. The standard deviation of $4\pi M_s$ is always the largest.

### E. The stiffness constant $D_{ex}$

Table I shows how the stiffness $D_{ex}$ and saturation magnetization $4\pi M_s$ depend on the excitation power. It is $D_{ex}$ instead of $4\pi M_s$, which is sensitive to excitation power. The magnon frequency $\omega_m$ decreases notably as the excitation power increases, which is usually ascribed to decreasing $4\pi M_s$ in heating. However, the variance of $D_{ex}$ in the intercept term is magnified by a factor $K^2 (3.55 \times 10^{11})$ which
excludes any significant effect of change in \(4\pi M_s\) in fitting, (even assuming it to be zero does not help). Smaller value of \(D_{ex}\) for fitting smaller frequencies becomes necessary. It shows that the exchange interaction proportional to \(D_{ex}\) is very sensitive to temperature, probably associated to that the increasing mobility of oxygen ions in heating weakens the superexchange interaction between iron ions.

In fact, even the spectrum at 5 mW shows peak widening so that it is recommended that experiments should be performed at even lower excitation power, for example, 1 mW so as to prevent the heating effect and to make use of the high sensitivity of the Sanderock tandem Fabry-Perot interferometer. This improvement will be made in a further investigation.

It is apparent that \(4\pi M_s\) remains constant in heating. With increasing laser power, temperature rises so that both the magnetization and demagnetizing fields decrease. \(N\) becomes smaller, together with \(4\pi M_s\), but \((1-2N)4\pi M_s\) can still remains constant. We have

\[
\frac{\Delta(4\pi M_s)}{4\pi M_s} = \frac{2}{1-2N}\Delta N.
\]

TABLE I. The stiffness constant \(D_{ex}\) and saturation magnetization \(4\pi M_s\) of Bi-YIG.

<table>
<thead>
<tr>
<th>Concentration (x)</th>
<th>Stiffness Constant (D_{ex}) (10^{-9}) Oe cm(^2)</th>
<th>Saturation Magnetization (4\pi M_s) /G</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5 mW</td>
<td>25 mW</td>
</tr>
<tr>
<td>0.00</td>
<td>5.58</td>
<td>5.40</td>
</tr>
<tr>
<td>0.14</td>
<td>6.03</td>
<td>5.87</td>
</tr>
<tr>
<td>0.36</td>
<td>6.48</td>
<td>6.23</td>
</tr>
<tr>
<td>0.54</td>
<td>6.98</td>
<td>6.75</td>
</tr>
<tr>
<td>0.92</td>
<td>8.06</td>
<td>7.66</td>
</tr>
</tbody>
</table>

Assuming the approximate demagnetizing factor of a uniformly magnetized square-section rectangular block,\(^{19}\) \((2/\pi)\arcsin(1/1+q)\) where \(q\) is the dimensional ratio \((2:0.5=4)\), we have \(2/(1-2N)\sim 3\). So \(4\pi M_s\) decreases together with \(N\): if \(N\) decreases from 0.16 to 0.14, \(4\pi M_s\) of 1760 G will reduces by 104 G.

The dependence of the stiffness constant \(D_{ex}\) on the Bi concentration \(x\) is shown in Fig. 7. The larger the stiffness constant \(D_{ex}\) is, the higher the magnon frequency \(v_m\) becomes. \(D_{ex}\) increases linearly with \(x\) (with essentially the same slope at different excitation powers). On the other hand, \(4\pi M_s\) increases only slightly with Bi concentration \(x\) and is insensitive to Bi doping. This is expected since the diamagnetic Bi ions only substitute the Y ions at the \(c\) sites.

However, there is a better method to measure \(D_{ex}\). To circumvent the uncertainty of the demagnetizing factor, different \(K\) values can be taken to change the term \(D_{ex}K^2\) while the \(4\pi M_s\) term in Eq. (3) remains more or less the same. It could be done by simply changing the excitation wavelength or normally changing the incident angle and make frequency measurements as a function of wavelength or angle. This provides more accurate measurement results for comparison.

Further experiments are, hence, carried out. In the first
experiment, the excitation of BLS changes from 514.5 to 457.9 nm. The second is with the same 514.5 nm excitation but the incident angle increased to 60°. All measurements have 5 mW excitation and $H_0=3.3$ kOe. The results of the first experiment are shown in Fig. 8. Besides strengthening and widening of peaks at 457.9 nm excitation, noticeable shifts in $\omega_m$ are observed but $\omega_s$ stays almost in the same position. As $\omega_m$ shifts from 19.15 to 21.54 GHz, as excitation changes from 514.5 to 457.9 nm, $\omega_s$ only changes 0.08 GHz. The second experiment cannot provide a large enough range of $K$ since the increase of the incident angle from 20° to 60° is fairly notable, but inside the crystal, the refractive angle only changes from 8.06° to 20.79°, which causes only a small change in the vertical component of the wave vector. Take the refractive index at 457.9 nm to be 2.49 by extrapolating the values in Ref. 12 and $K^2=4.67\times10^{11}$. The stiffness constant is, hence, estimated to be $-8\times10^{-9}$ Oe(cm)$^2$, which is identical to the value obtained before.

F. New weak peak $\omega_s$

A weak peak $\omega_s$ at the low-frequency side of the bulk magnon $\omega_m$ appears as the external magnetic field $H_0$ is applied (Fig. 4). Both shift by similar amount towards higher frequency with the field, while their intensity decreases. They disappear simultaneously when the scattering polarization is parallel to the incident direction. Their intensities decrease quickly as the crystal is heated by laser beam. It is thus determined that $\omega_s$ is scattering from magnon too.

Could it be a surface magnon? It is unlikely so, since $\omega_s$ lacks the signature of a surface magnon that its Stokes and anti-Stokes lines have very different intensities. The magnon $\omega_s$ is independent of $K$ as shown by the above-mentioned $K$-varying experiments, which also rejects this possibility. As $K$ increases drastically or the incident angle increases from 20° to 60° so that the component of $K$ parallel to the external field increases, there is no characteristic shift of a surface magnon and $\omega_s$ shifts little.

It is interesting to further examine the effect of bismuth doping on the frequency, scattering intensity, and bandwidth of the peak $\omega_s$. Figure 9 shows the BLS spectra of Bi-YIG crystals with different Bi concentrations as $H_0=2.5$ kOe. The scattering intensity and the bandwidth of the peak $\omega_s$ increase with Bi concentration $x$. One characteristic of the magnon $\omega_s$ is that it is independent of bismuth concentration. Its position remains the same for different $x$. However, the separation $\Delta \omega_{ms}$ between $\omega_m$ and $\omega_s$ is definite and the weak peak $\omega_s$ only emerges as $H_0$ increases large so that the strong peak $\omega_m$ shifts away from the Rayleigh peak, leaving space for $\omega_s$. $\Delta \omega_{ms}$ increases with Bi concentration: 4.09, 5.50 and 7.49 GHz for $x=0.36$, 0.54, and 0.92, respectively (Fig. 10). This implies that $\omega_s$ is independent of the spin-wave stiffness constant $D_{ex}$ but $\Delta \omega_{ms}$ is somehow associated with $D_{ex}$. The larger $D_{ex}$ is, the larger the separation becomes.

For comparison, one BLS spectrum of a rare-earth garnet \{Bi$_{0.72}$Ca$_{0.28}$\}[Fe$_{1.87}$In$_{0.13}$]O$_{12}$ (In-BiCaVIG) is also shown in Fig. 9. Its $\Delta \omega_{ms}$ is 14.68 GHz. The Raman study of acoustic magnon in Bi-YIG ($x=0.41$) \textsuperscript{10} also revealed a magnetic-field-related weak peak with 457.9 nm excitation. The magnon $\omega_s$ appears generally in light scattering. Why can $\omega_s$ be observed only with short-wavelength excitation in Raman scattering? This is associated not only with the low-resolution power of Raman scattering compared with BLS but also with the large excitation power in the Raman work.
making an angle $\theta$ with $H_0$. In fact, no component can produce a separate signal. All these small components only produce error to $\omega_n$ as shown by substituting a complete $K$ to the dispersion with $\sin^2 \theta$. From the geometry of experiments, the received signals of scattering from magnons have essentially a wave vector along the $x$ axis instead of any other directions. We conclude that the peak $\omega_s$ is a magnon with a wave vector in the $x$ direction but independent of it.

The magnetostatic approximation is valid for both spin waves and uniform-precession modes. The latter is usually named as magnetostatic modes in which the magnetization precesses in phase throughout the entire sample. They are, hence, independent of the exchange interaction and propagation factors (the wave vector $K$). The magnon $\omega_s$ just possesses these characteristics and it does not fit the description of spin waves. So it is reasonable that Eq. (7) is the rectangular-block-approximated form of the dispersion of the magnetostatic mode in a tangentially magnetized ferrite film described by Eq. (4.27) of Ref. 21:

$$\omega_s = \sqrt{H_0 (H_0 + \gamma^2 M_s^2)}$$

which describes a small-signal magnetization along the $x$ direction. More precisely, the magnetostatic mode has $k_y = k_z = 0$ but is “quite arbitrary in the $x$ direction within the slab” as described by Eq. (4.27) of Ref. 22 so that wave vector can still be conserved. Because of this consistent description, $\omega_s$ is identified as a magnetostatic mode.

IV. DISCUSSION

Bi doping in YIG causes linear increases of the stiffness constant, the scattered intensities and bandwiths of the magnons, the Curie temperature, and the magneto-optical rotation, as well as linear decreases of the scattered intensity and the sound velocity of the LA phonon. The diamagnetic $\text{Bi}^{3+}$ substitution for $\text{Y}^{3+}$ in YIG improves its magnetic properties while weakens its mechanical properties.

The structure changes and their effects are important. The linear decrease of $V_L$ with increasing bismuth concentration results from the linear decrease of the elastic parameters of Bi-YIG. These are attributed to the structure changes of Bi-YIG caused by the larger ionic radius of $\text{Bi}^{3+}$, 0.96 Å, compared with 0.89 Å of $\text{Y}^{3+}$ at the dodecahedral $c$ site. The lattice constant is 12.376 Å for pure YIG, whereas those of Bi-YIG at $x = 0.32$ and 0.57 are 12.390 and 12.420 Å, respectively. The lattice constant increases linearly with Bi substitution. The relationship of the lattice constant with the bismuth concentrations of Bi-YIG is also shown in Fig. 3. We found that the higher Bi concentration is, the softer Bi-YIG becomes. For achieving a suitable smooth finish, sample grinding becomes easier. Bi doping changes the binding energy of the crystal so that lowers the crystal hardness.

The effects of Bi doping in the magnetic properties of YIG are unusual. Dilution of magnetic Fe ions by nonmagnetic ions, such as Zn doping in lithium ferrite, lowers magnon frequency. The spin-wave stiffness constant even drops to zero at certain Zn concentration. Doping with diamagnetic trivalent ions such as Sc and Ga, Al in YIG, respectively, may dilute [Fe] and (Fe). Dilution of (Fe) reduces the net

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FIG. 10. The separation $\Delta \omega_{ms}$ between the bulk and weak magnons versus $x$.

Figure 6 also shows the dispersion of $\omega_s$. The bulk-magnon dispersions $a$, $b$, $c$ for different $x$ separate from each other but with essentially the same slope $\gamma$. However, the data points of $\omega_s$ as a function of $H_0$ for different $x$ all lie in only one straight dispersion line $d$, showing the dispersion relation Eq. (3) is not applicable. The line $d$ is parallel to lines $a$, $b$, $c$ and has an intercept of about 2.6 GHz (the coordinate axis starts from 2.5 GHz). Its equation is now

$$\omega_s = \gamma [H_0 + (1 - 2N)2\pi M_s]$$

which is independent of $D_{ex}$. There is a common saturation magnetization $4\pi M_s$ since its 2% increase from $x = 0$ to $x = 0.92$ is minute. On the other hand, the difference $\Delta \omega_{ms}$ is just the difference between Eq. (3) [approximated by Eq. (5)] and Eq. (7). $\Delta \omega_{ms} = \gamma D_{ex} K^2$, which increases with the doping density $x$. The slopes of Fig. 6 and 10 (a factor $\gamma K^2$ has to be considered) are, respectively, $2.6 \times 10^{-9}$ and $1.0 \times 10^{-9}$ Oe/(cm)$^2$. They are in the same order of magnitude but the former is more accurate since it has more data points and also since $\omega_s$ is weak.

Is this still Eq. (4.11) of Ref. 20 or Eq. (4.18) of Ref. 21 with angle $\theta$ there put equal to $\pi/2$ but with negligibly small $K$? At first it looks likely due to another component of $K$ vertical to $H_0$. Because of the finite collecting angle, there is a $y$-component of wave vector that is perpendicular to $H_0$, in addition to its $x$ component (the previous $K$). The maximum $K_y = (2\pi/n) \sin 9.68^\circ = 0.0841(4\pi n/\lambda)$, only 8 percent of $K$. Then the $D_{ex} K^2$ is less than 0.7 percent of $D_{ex} K^2$ and less than one percent of the $(1 - 2N)2\pi M_s$, so that its contribution is negligibly small. The dispersion is almost independent on the doping density $x$. The spreading of scattering is small so that the resulting signal is weak. The peak $\omega_s$ appears as scattering from magnons is strong enough.

Further considerations reject this identification because there are other components of $K$, e.g., $K_z$ parallel to $H_0$ or any projection of $K$ on the bottom of the receiving cone.
magnetization and Curie temperature of garnet. The Bi doping in YIG increases magnon frequency, which shows that Bi$^{3+}$ substitute for Y$^{3+}$ only. $T_C$ of rare-earth (RE) ion garnet is also affected by the size of the RE ion on the $c$ site. The larger the ionic radius and, hence, the lattice constant, the higher is $T_C$. Bi$^{3+}$ also behaves anomalously in that $T_C$ is higher than would be expected according to the lattice constant solely. It shows apparent increase in superexchange between [Fe] and (Fe) lattices.

The consistency of increases in both $D_{ex}$ and $T_C$ with $x$ in Bi-YIG is shown in Fig. 7 with an inset from Ref. 8. Following Ref. 21 $D_{ex} = 4\pi M_\lambda$ and the phenomenological exchange constant $\lambda_{ex}$ is determined to increase from 3.18 at $x = 0$ to 3.42, 3.67, 3.93, 4.50, all in unit of $10^{-12}$ cm$^2$, for $x = 0.14$, 0.36, 0.54, 0.92, respectively. ($\lambda_{ex} R^2$ is larger than unity so the excitons are properly named as the spin waves.)

For a simple-cubic ferromagnet, while taking the exchange interaction between the nearest neighbors, the magnetic dipole interaction and external field into consideration, the stiffness constant $D_{ex}$ is deduced from first principles:

$$D_{ex} = 2JR^2 s/(\mu_B g),$$

(9)

where $R$ is the nearest-neighbor distance, $J$ is the exchange integral, $\mu_B$ is the Bohr magneton, and $s$ is the spin quantum number of a single magnetic ion. It is also applicable to a cubic ferrimagnetic, but the relation to the microscopic parameters is more complicated. However, in the low-energy limit, YIG can be considered a ferromagnet with the magnetic moment $20\mu_B$ per unit cell. Approximately, Eq. (9) can be applied for estimation of $D_{ex}$ with the effective quantum number $s = 5/2$ (but for extracting more information, a thorough treatment is needed). In each octant of a cubic unit of YIG there is one (Fe) more than [Fe] and the magnetic dipole moment $5\mu_B$ locates at the center of each octant. The distance between the nearest neighbors is thus $a/2$ where $a$ is the lattice constant of a cubic unit. From $D_{ex} = 5.58 \times 10^{-9}$ Oe(cm)$^2$ for $x = 0$, the magnon stiffness $Ja^2$ can be estimated to be $82.8 \times 10^{-30}$ erg(cm)$^2$, consistent with the experimental values (e.g., the data from specific heat$^{27}$). We obtain $J = 5.40 \times 10^{-15}$ erg for YIG. In Bi-YIG, the lattice constant $a$ increases only slightly about 12.4 Å. The linear increase of $D$ (so the increase of the magnon stiffness $Ja^2$) is essentially attributed to the increase of the exchange integral $J$ shown as follows:

$$x \begin{pmatrix} 0.00 & 0.14 & 0.36 & 0.54 & 0.92 \\ D_{ex}/10^{-9} \text{ Oe(cm)}^2 & 5.58 & 6.03 & 6.48 & 6.98 & 8.06 \\ a/\AA & 12.376 & 12.384 & 12.400 & 12.413 & 12.442 \\ J/10^{-15} \text{ erg} & 5.41 & 5.83 & 6.25 & 6.72 & 7.73 \end{pmatrix}$$

So the exchange interaction $J$ is enhanced by Bi doping. However, it is premature to ascertain how much the superexchange interaction $J_{ad}$ between [Fe] and (Fe) strengthens because the ferromagnetic approximation in low-energy limit has to consider not only the nearest-neighbor exchange interaction $J_{ad}$ but also the next nearest-neighbor interaction $J_{dd}$ and the next after the $d-d$ interaction, $J_{aa}$.\footnote{The fact that Bi-enhanced magnon intensity is related to MO enhancement can be perceived by the Bi-induced drastic changes in the Kerr rotation$^{5,30}$ and greatly enhanced Faraday rotation.$^{2,31}$ There has been extensive investigation into the origin of the enhanced magneto-optic effects in Bi-substituted iron garnet and Scott and Lacklison have made a thorough review.$^{32}$ The increasing of $D_{ex}$ with $x$ confirms its assumption of enhanced exchange interaction. Bi-enhanced superexchange between [Fe] and (Fe) sublattices strengthens the intensity of transitions involving pairs of Fe$^{3+}$ ions, one.

$$J = \frac{5}{16} \left( -5J_{ad} + 3J_{dd} + 8J_{aa} \right).$$

(10)

Although $J_{ad} > J_{dd} > J_{aa}$, their cancelation will produce different $J$ as their relative values vary. Further work is necessary to distinguish individual change of $J_{ad}, J_{dd}$, and $J_{aa}$ with increasing $x$.

Besides the cell expansion, the Bi substitution in YIG also causes local distortion of Fe$^{3+}$ so as to affect the magnetic and mechanical properties. Geller and Colviller$^{3}$ revealed that it slightly increases the [Fe]-O distance and decreases the (Fe)-O distance as compared with YIG. Since the superexchange interaction is very sensitive to distance, $J_{ad}, J_{dd}$, and $J_{aa}$ do change individually. Another question is whether the increase in $T_C$ and $D_{ex}$ result from a change of electronic structure or from the local deformation around Bi$^{3+}$. Novák et al.$^{29}$ studied the temperature dependence of $^{57}$Fe NMR in Bi$_{0.3}$Y$_{2.7}$Fe$_5$O$_{12}$ and Lu$_{0.3}$Y$_{2.7}$Fe$_5$O$_{12}$ garnets. They conclude that the exchange interaction is enhanced by the change of electronic structure rather than local deformation.

BLS results provide direct evidence of the role of Bi played in increasing the magnon intensity and bandwidth. Wetting et al.$^{12}$ provided a theoretical interpretation to the about three orders of magnitude increase of scattering intensity of magnon as the incident wavelength decreases from 632.8 to 488.0 nm, despite the strengthening absorption. They also explained the variation of the Stokes and anti-Stokes intensities, which are markedly different at 632.8 nm but are nearly equal at 488.0 nm. Quadratic magneto-optic coupling is important at 632.8 nm excitation but only has a small effect at 488.0 nm as at 514.5 nm in this work. The wavelength dependence of the scattered intensity is given, in terms of the magneto-optic effects, by the factor

$$\frac{1}{\alpha h_0 g_0\omega_m} \left[ (\Psi_{MLB} - \Phi_{MCB})^2 + \left( \frac{1}{2} \Psi_{MLD} - \frac{1}{4} \Phi_{MCD} \right)^2 \right],$$

(11)

where $\alpha$ is the optical absorption, $\Psi_{MLB} - \Phi_{MCB}$, and $\Phi_{MCD}$ are magnetic linear (circular) birefringence and magnetic (circular) dichroism, respectively. The upper and lower signs refer to the Stokes and anti-Stokes scattering, respectively. If the magneto-optic data are available for Bi doping, the theory can be compared with experiment. There is no explicit linear relationship between intensity and Bi concentration. However, if all magneto-optic effects increase linearly with $x$ as Faraday rotation (MCR), the factor of Eq. (11) does give a linear increase of intensity since the linear increase of $\omega_m$ in the denominator reduces the power by one.
on each sublattice (biexciton excitation). The large spin-orbit coupling constant of the rather covalent bismuth ions also increase the excited state splitting via overlapping of their 6p wave functions with the 2p oxygen and 3d iron wave functions.\textsuperscript{5,33}

Assuming the Gilbert\textsuperscript{34} damping term that is equivalent to the Landau-Lifshitz form, the torque equation of motion is

$$\frac{dM}{dt} = -\gamma M \times H_{eff} + \frac{\alpha}{M} M \times \frac{dM}{dt},$$

where $\alpha$ is the damping coefficient of spin wave. The amplitude of the spin wave decays exponentially and this is related with Lorentzen line shape as pointed out by Abragam and Bleaney\textsuperscript{35} or Heys and Loudon.\textsuperscript{36} The linewidth of the spin wave is then

$$\Delta \omega_m = \gamma \Delta H = 2/\tau = 2 \alpha \omega_m.$$  \hspace{1cm} (13)

The increase of magnon linewidth corresponds to a decrease in relaxation times. The linewidths in Sec. III D corresponds $\tau \sim 5.31$, 3.98, 2.84, 2.15, and 1.54, all in unit of $10^{-10}$ s, for $x = 0$, 0.14, 0.36, 0.54, and 0.92, respectively. This shows that more impurity ions break the translational symmetry of the crystal. The damping coefficient increases with $x$. With $f_m = 1.186$, 13.26, and 15.22, all in unit of GHz, $\alpha = 0.048$, 0.056, and 0.068 for $x = 0.36$, 0.54, and 0.92, respectively. $\alpha^2 < 1$, the damping is small and $1/\omega_m < \tau$.\textsuperscript{37}

The appearance of the magnetostatic mode $\omega_s$ as an additional small peak in BLS from a rectangular-block Bi-YIG sample magnetized tangentially is similar to those additional small peaks appeared in ferromagnetic resonance (FMR).\textsuperscript{38} However, the uniform magnetostatic mode is the major absorption peak in FMR. This uniform precession of the entire spin system is due to purely magnetostatic forces arising from the externally applied dc magnetic field and the dipolar fields of the sample magnetization. As shown by Fig. 4, $\omega_s$ appears once $H$ is applied or becomes large enough. On the contrary, $\omega_m$ is thermally excited by laser beam and appears at $H = 0$. Both $\omega_m$ and $\omega_s$ strengthen as Bi concentration $x$ increases, owing to the strengthening of magneto-optic effects with $x$. Their linewidths widen, as $x$ increases owing to shorter relaxation times.

V. SUMMARY

The effects of Bi-doping on YIG properties are investigated by BLS for a series of single-crystal Bi-YIG. This paper presents detailed experimental results of the magnetic and mechanical properties of Bi-YIG. They show a close relationship between the increase of the superexchange interaction (the effective exchange integral $J$) between the magnetic ions and the enhanced magneto-optical effects in Bi-YIG.

In BLS, the spin-wave exchange stiffness constant $D_{ex}$ is very sensitive to the excitation power so that low power should be used. The behavior of the bulk magnon is opposite to LA phonons. Not only the spin-wave exchange stiffness constant, but also the relative intensity and the bandwidth (full width at half maximum) of the bulk magnon increase linearly with $x$. On the other hand, the substitution of $Y^{3+}$ with $Bi^{5+}$ softens the crystals and the measured sound velocities of the acoustic phonons decrease linearly with $x$. As an external dc magnetic field is applied, the uniform magnetostatic mode appears. These results provide useful information for studying the relationship between the Bi concentration, the microstructure of Bi-YIG crystals, and their magnetic and mechanical properties. Their significance can only be shown when relating to other studies as shown by the review.\textsuperscript{32}

ACKNOWLEDGMENTS

We owe the identification of $\omega_s$ to the enlightening discussion with Professor Carl E Patton. The work described in this paper was fully supported by a Grant from the City University of Hong Kong (Project No. 7000894).


