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Temperature dependent phonon Raman scattering of highly *a*-axis oriented CoFe₂O₄ inverse spinel ferromagnetic films grown by pulsed laser deposition

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Lattice vibrations of highly *a*-axis oriented CoFe₂O₄ (CFO) films have been investigated by Raman scattering in the temperature range of 80–873 K. The five phonon modes T_{1g}(2), T_{1g}(3), E_g, A_{1g}(1), A_{1g}(2), and their evolutions can be uniquely distinguished. It was found that an electron transfer between Co²⁺ and Fe³⁺ cations occurs in octahedral sites at about 173 K. The structure disorder in the CFO films appears with increasing the temperature, which indicates the cation migration between tetrahedral and octahedral sites. The phenomena suggest the structural transformation trend from inverse spinel to normal spinel at the elevated temperatures. © 2012 American Institute of Physics. [doi:10.1063/1.3683520]

The type of AB₂O₄, which is classified as spinel structure such as MgFe₂O₄, MnFe₂O₄, and ZnFe₂O₄ has recently attracted considerable attention and intensive researches due to the remarkable electronic and magnetic properties in electro-optic devices, ferrofluids, microwave devices, and high-density information storage.^{1–5} In particular, cobalt ferrite CoFe₂O₄ (CFO) is especially interesting owing to its unique physical properties. There are some potential applications in the field of magneto-optic recording and magnetic resonance imaging.^{6,7} The feature of normal spinels is representative of different positions of [A] (divalent elements) and [B] (trivalent elements) occupying the tetrahedral and octahedral sites, respectively.⁸ However, the CFO structure, considered as a cubic inverse spinel, is characterized with eight iron cations (Fe³⁺) occupying the tetrahedral sites, both eight cobalt (Co²⁺) and eight Fe³⁺ cations occupying the octahedral sites.^{9–11} The occupations of metals at T_d and O_h sites have an important effect on the properties of spinels, such as diffusivity, magnetic behaviors, and catalytic activity. Although there are many reports on the magnetic and electrical features of CFO films, nanoparticles, and powders, the identification and evolution of the phonon modes have rarely been studied. Recently, x-ray diffraction and pressure-dependent Raman spectroscopic studies indicate that tetragonal CFO transforms to an orthorhombic structure at a pressure of about 32.5 GPa and the cation distribution can be affected by the surface temperature.^{12,13} However, the detailed relationship among temperature, structure, and temperature-induced phase transformations of CFO materials have not been presented up to date.

Raman scattering is a nondestructive and available spectral characterization technique, which can provide some invaluable information on the order-disorder phenomena and lattice vibration of material. The scattering spectra of vibration modes in different frequencies could be a crucial tool in the research field of materials. Because there are not too many morphological requirements for measurement, Raman

scattering is widely used to characterize the properties of bulks, films, and nano-structured materials. Based on the spectral analysis, the phonon mode pattern can be explained by the variations of frequency, intensity, and full width at half maximum (FWHM). Therefore, the application of Raman spectroscopy by analyzing lattice vibration is acceptable include strain effects, textures, x-ray amorphous phases, and superlattice-related features, etc.^{14,15} In this letter, a complete set of temperature-induced optical phonon modes in spinel CFO films have been investigated by Raman spectroscopy.

The CFO film studied in this work was fabricated on single-side polished SrTiO₃ (STO) by pulsed laser deposition (PLD) method. The substrate was cleaned in pure ethanol with an ultrasonic bath to remove physisorbed organic molecules from the STO surface. Then, the substrate was rinsed several times with deionized water. Finally, the wafer was dried in a pure nitrogen stream before the deposition of the CFO films. A krypton fluoride (KrF) excimer laser was used for the deposition with the pulse frequency of 5 Hz. The crystallinity of the CFO crystals was examined by the XRD with Cu K α radiation (D/MAX-2550 V, Rigaku Co.) at room temperature (RT). Temperature-dependent Raman scattering experiments were carried out by a Jobin-Yvon LabRAM HR 800 micro-Raman spectrometer and a THMSE 600 heating/cooling stage (Linkam Scientific Instruments) in the temperature range from 80 to 873 K. A laser with the wavelength of 488 nm was used as the excitation source with a power of 20 mW and the spectral resolution was better than 1 cm⁻¹. The laser beam was focused through a 50 \times microscope with the numerical aperture of 0.35 and the working distance of 18 mm. An air-cooled charge coupled device (CCD) was used to collect the scattered signal dispersed on 1800 grooves/mm grating.

The result of XRD from θ -2 θ scan has been shown in the inset (a) of Fig. 1. The peaks at 43.739° and 47.402° can be identified as (400) and (200) reflections from the CFO film and STO substrate, respectively. The appearance of only (100) diffraction peak indicates that the film is preferentially oriented along the *a*-axis perpendicular to the substrate

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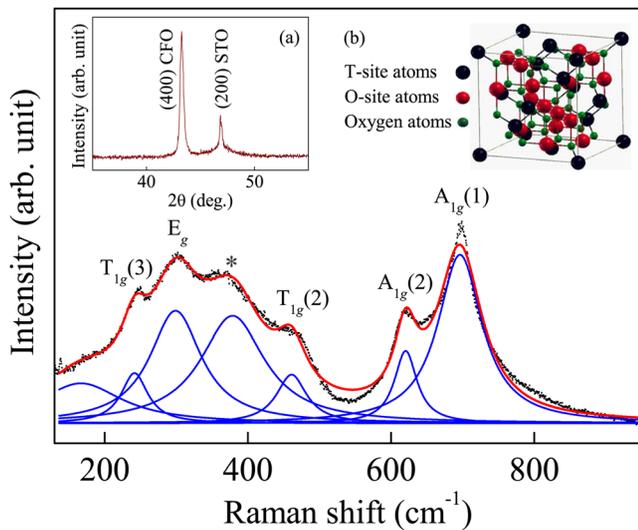


FIG. 1. (Color online) Raman spectra of the CoFe_2O_4 film at the room temperatures. Each vibration mode has been labeled corresponding to the respective Raman activities. The mode originated from the second-order mode of SrTiO_3 substrate has been marked by the symbol (*). The inset (a) shows x-ray diffraction pattern of the CoFe_2O_4 film at room temperature. The cubic cell of normal spinel structure has been shown in inset (b), tetrahedral sites (T-site), octahedral sites (O-site), and oxygen atoms are denoted by the spheres with different sizes, respectively.

surface. It should be noted that there are no extra peaks, humps or other detectable phases, confirming the single-phase structure of the film. Furthermore, the FWHM of the (400) diffraction peak is about 0.342° , suggesting good crystallinity of the CFO film. According to the cubic crystal system and well-known Scherrer equation,¹⁶ the lattice parameters and crystallite size of the CFO film were determined to 8.4 \AA and 28 nm , respectively. On the other hand, the thickness of the CFO film is evaluated to about 115 nm with the aid of profilometer and spectroscopic ellipsometry, which is closer to the nominal value. Thus, one can conclude that the residual stress in the CFO film could be tiny due to the relaxation effect.

Generally, the CFO crystallizes in cubic structures belong to the space group $\text{Fd}\bar{3}m$ (O_h^7 , No. 227).¹⁷ The normal spinel cubic cell structure has been shown in the inset (b) of Fig. 1, which contains two inequivalent cation sites, i.e., tetrahedrally coordinated A sites and octahedrally coordinated B sites. The 8a of Wyckoff position classified as T_d symmetry has been occupied by divalent cation at (0, 0, 0). On the other hand, the Wyckoff position 16d belonging to O_h symmetry has been occupied by the trivalent cation at (5/8, 5/8, 5/8). For inverse spinel, however, the trivalent cations replace the divalent cations and occupy tetrahedral sites (T-site) together with divalent and trivalent cations occupying octahedral sites (O-site). Although the full unit contains 56 atoms ($Z=8$), the smallest Bravais cell consists of only 14 atoms ($Z=2$). As a result, factor group analysis predicts the following phonon modes for the spinel structure: $A_{1g}(\text{R}) + E_g(\text{R}) + T_{1g} + 3T_{2g}(\text{R}) + 2A_{2u} + 2E_u + 4T_{1u}(\text{IR}) + 2T_{2g}$.¹³ Four of them are infrared active modes ($4F_{1u}$), and five Raman active modes namely A_{1g} , E_g , and $3T_{1g}$ have been shown in Fig. 1. The two peaks at 622 and 699 cm^{-1} are considered to represent A_{1g} symmetry, the peaks at 249 and 452 cm^{-1} are identified as T_{1g} symmetry, and E_g mode

is located at 302 cm^{-1} . As for cubic spinel, the modes of ferrite above 600 cm^{-1} usually correspond to the motion of oxygen in the tetrahedral AO_4 group involving symmetric stretching of oxygen atom with respect to metal ion in tetrahedral void and tetrahedral breath mode. The other low-frequency modes are characteristics of the octahedral site due to metal ion involved in octahedral void (BO_6), corresponding to the symmetric and anti-symmetric bending of oxygen atom in metal (M)-oxygen (O) bond at octahedral void. Hence, the A_{1g} modes at 622 and 699 cm^{-1} are assigned to T-site modes, which reflect the local lattice effect in tetrahedral sublattice. The other modes at 249 , 302 , and 452 cm^{-1} are concerned with the O-site modes, which indicate the local lattice effect in the octahedral sublattice. Note that an additional mode located at about 375 cm^{-1} can be observed at/below RT, which can be assigned to the second-order mode from the single crystal STO substrate.^{18,19} It should be emphasized that the mode cannot be owing to the crystalline distortion because there is no residual stress in the CFO film, as previously discussed.

Due to different exciting laser power, the surface temperature of sample can be heated, leading to the increasing anharmonic interactions.^{13,20} In order to confirm the stability of the CFO layer, the experiments at the laser power of 0.2 mW , 0.5 mW , 1.0 mW , and 2.0 mW have been done. The Raman spectra of these different optical excitation intensities at 300 K and 80 K have been shown in Figs. 2(a) and 2(b), respectively. When the laser power increases from 0.2 to 2.0 mW , the intensities of the vibration modes have been gradually enhanced. Nevertheless, the center frequencies of phonon modes are kept as constants at the present experimental temperatures. Taking the Raman features into account, the crystallographic structure and chemical composition of the

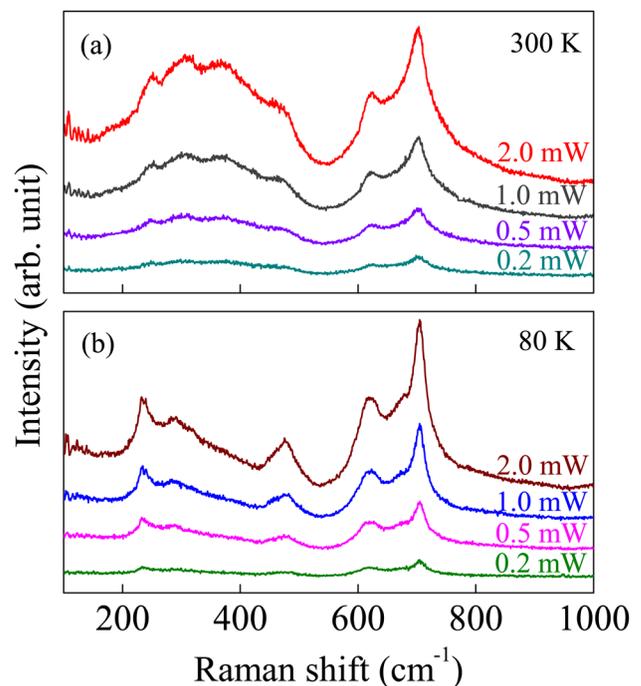


FIG. 2. (Color online) Raman spectra of the CoFe_2O_4 film recorded with increasing laser power from 0.2 mW to 2.0 mW at (a) 300 K and (b) 80 K , respectively. Note that the phonon frequencies are kept as constants with the incident power.

compound remains unaffected by increasing the incident laser power, indicating the stability of the CFO film in the present work. Therefore, the maximum power of 2.0 mW, which can provide the strong vibration signal, is applied to study the phonon evolutions with the temperature.

In order to observe the temperature effects on the spinel structure of the CFO film, Raman spectra were collected in the temperature range from 80 K to 873 K, as plotted in Fig. 3. It is found that the spectra present the softening and broadening trend of the vibration modes $A_{1g}(1)$ and $A_{1g}(2)$ as the temperature increases. However, other Raman bands below 600 cm^{-1} become more fuzzy since the widths are too wide to be recognized. The two vibration modes below 400 cm^{-1} [$T_{1g}(3)$ and E_g], which were influenced by the thermal effect, have shifted toward a higher-frequency side with increasing the temperature. It is worth noting that the phenomenon has rarely been mentioned in the previous literatures. In addition, the $T_{1g}(2)$ phonon mode disappears and/or is overlapped by the broadening band beyond 473 K.

The correlation between photomagnetism and structure in CFO nanoparticles has been studied by temperature dependent measurements based on an incident light intensity of 1.95 mW, which was similar to the laser power in the work.²¹ Analogous to the Verwey transition at 120 K in Fe_3O_4 , there is a metal-insulator transition phenomenon in CFO nanoparticles at about 170 K.^{9,21} Compared phonon spectra below 173 K with those recorded at higher temperatures in Fig. 3, the $T_{1g}(2)$ phonon mode at about 473 cm^{-1} has been overlapped by a broadening peak beyond 173 K. Meanwhile, there is a T_{1u} peak appearing at about 370 cm^{-1} beyond the temperature of 273 K. It should be emphasized that the peak has the frequency shift (about 10 cm^{-1}) with the temperature. It suggests that the structural/electronic transition appears at the temperature region. Considering that the particle size of CFO nanoparticles (about 30 nm) is closer to the crystallite size of the present CFO film, one can believe that the intrinsic mechanism is similar. The phenom-

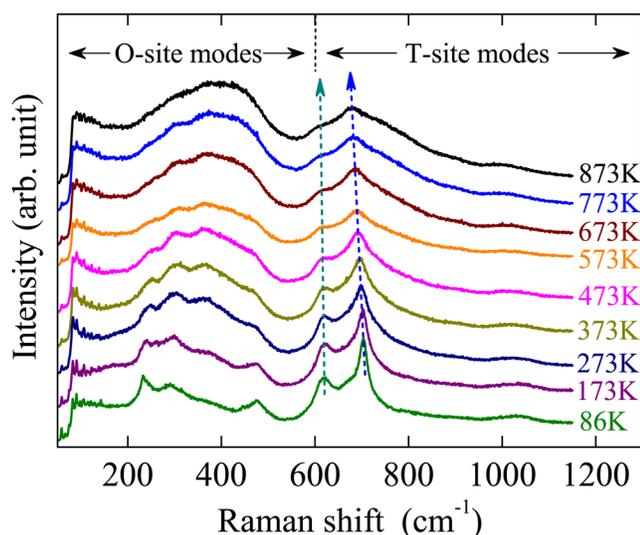


FIG. 3. (Color online) Raman spectra of the CoFe_2O_4 film with the temperatures from 86 K to 873 K. Note that “O-site” and “T-site” means octahedral and tetrahedral sites in the crystalline, respectively. The arrows are used to guide the eyes, which indicate the red shifts of two A_{1g} phonon modes with increasing the temperature.

ena indicate that the Co^{2+} cations in octahedral sites absorb the photon, inducing an electron transferred to a nearby Fe^{3+} ion, leaving Co^{3+} and Fe^{2+} after the illumination below 173 K. With the temperature further increasing, the charge can migrate easily and the film is recovered rapidly. Note that the charge transfer occurs only between the ions in octahedral sites. Hence, the phonon mode variations of octahedral sites are more obvious than the ones in tetrahedral sites, as seen in Fig. 3.

By fitting the Raman peaks $T_{1g}(3)$, E_g , $A_{1g}(1)$, and $A_{1g}(2)$ with a Lorentzian line shape, the band positions can be deduced, which are plotted in Fig. 4, respectively. The frequencies of the two vibration modes $A_{1g}(1)$ and $A_{1g}(2)$ with the temperature are shifted about 25 and 14 cm^{-1} in sequence. As described above, the lattice vibrations of tetrahedral structure could be characterized by Raman peaks above 600 cm^{-1} . The shift of these two modes is associated with the changes in T-site lattice structure. The cation distributions of CFO particles under different laser power have been reported by Chandramohan *et al.*,¹³ which agree well with the present observation. Due to the thermal effect, the red shift of the A_{1g} phonon modes in CFO spinel system indicates the sensitivity of cation distribution in ferrite systems with the temperature. Furthermore, the frequencies of the phonon modes A_{1g} decrease more rapidly with increasing the temperature beyond 373 K, especially for the $A_{1g}(1)$ phonon, which is associated with the cation migration in tetrahedral structure.^{22,23} The similar situation also appears in octahedral sites, which presents the blue-shift trend for the $T_{1g}(3)$ and E_g modes in Figs. 4(a) and 4(b), respectively. It can be explained in terms of the dislocation of Fe^{3+} cations from T-site to O-site, while the same number of Co^{2+} cations move from O-site to T-site. Therefore, the interchange results in the disorder of the whole inverse spinel structure for the CFO films at high temperatures owing to the imbalance of these two valences.

According to the Néel-type ferrimagnetic arrangement, the magnetic moments of tetrahedral and octahedral site cations are oriented antiparallel in inverse spinel. Therefore, the Fe^{3+} cations in T-site are offsetted by the ones in O-site,

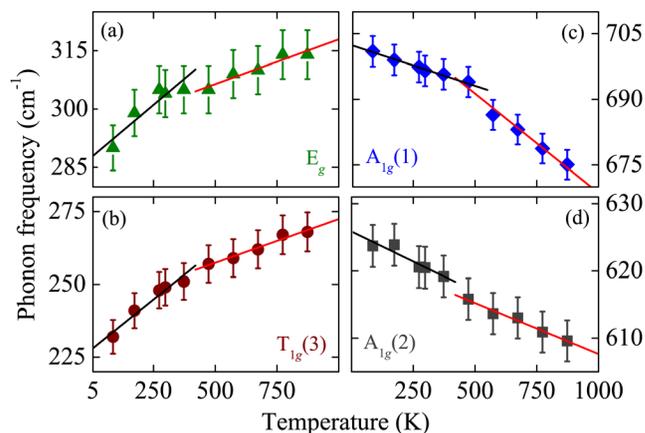


FIG. 4. (Color online) The phonon frequency variations of (a) E_g , (b) $T_{1g}(3)$, (c) $A_{1g}(1)$, and (d) $A_{1g}(2)$ modes as a function of temperature for the CoFe_2O_4 film, respectively. The solid lines are the linear fitting data below and above 373 K, respectively. Note that the error bars are taken from the fitting calculation.

indicating that the magnetic properties are originated from the divalent O-site cation Co^{2+} . As the temperature increases, the migration of Fe^{3+} and Co^{2+} cations gives rise to the structure transformation. Consequently, the long-range cation order has been broken, and the crystal magnetic field becomes complicated. In other words, the magnetic properties of spinel CFO might be changed due to cation disorder at elevated temperature. A recent study revealed that the Néel temperature is nearly 870 K.²⁴ It suggests that the magnetic moments in magnetic domain of CFO transforms from antiparallel arrangement to the same direction slowly with the temperature increasing toward 870 K. Hence, the structure of the CFO film undergoes an obvious trend from antiferromagnetic phase to paramagnetic phase in the present experiment. The Raman spectra of the CFO film match well with those from NiFe_2O_4 , exhibiting a similar structure between these two ferromagnets. Considered as inverse spinel structure, CFO and NiFe_2O_4 crystals can be seen as derivatives of Fe_3O_4 , substituting the Fe^{2+} cations in magnetite by a different divalent 3d transition metal cation.²⁵ As previously discussed, the mutual migration between tetrahedral and octahedral sites occurs in inverse spinel crystal with increasing the temperature, inducing the transformation from inverse spinel to normal spinel structure, in which the T-sites and O-sites are filled by trivalent cations and divalent cations, respectively.

In conclusion, structure and optical properties of inverse spinel CFO film have been investigated by x-ray diffraction, laser power-dependent, and temperature-dependent Raman scattering experiments. The electron transfer between Co^{2+} and Fe^{3+} has been probed at about 173 K. The shifts of tetrahedral and octahedral modes indicate the structural transition in both sites of the CFO film with the temperature. Due to the interchange of Fe^{3+} and Co^{2+} cations between tetrahedral and octahedral sites at high temperature, the cation migration breaks the long-range order and tends to transform from inverse spinel to normal spinel structure as a consequence.

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