


 Cite this: *RSC Adv.*, 2024, 14, 2727

# Phase transitions and spectral shifts: a quantum mechanical exploration of vibrational frequency in magnesium ferrite†

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Spinel ferrites represent an integral subset of magnetic materials, with their inherent properties largely influenced by cation occupancy and spin interaction. In this study, we present an in-depth theoretical exploration of the phase transition landscape of pure magnesium-ferrite, deploying hybrid functionals and a local Gaussian basis set to scrutinize the relaxed lattice structure, relative energy, magnetic properties, electronic characteristics, and vibrational frequencies. Our investigation reveals that the ground state of magnesium-ferrite is an open-shell system with an inverse structure. This is characterized by the complete occupancy of octahedral sites by magnesium atoms, with Iron atoms dispersed between both tetrahedral and octahedral sites. We found a relative energy difference of 0.41 eV between the antiferromagnetic ground configuration and the ferro arrangement within the inverse structure. Furthermore, our research also delved into the impact of spin rearrangement and inversion ( $X = 0.0, 0.5$  and  $1$ ) on Raman and infrared spectra. Notably, the lattice distortion from the cubic form, apparent in the optimized structure, resonates in the IR and Raman spectra, resulting in significant splitting. The frequencies calculated in this study align well with experimental values, suggesting that the literature's current assignments warrant reevaluation in light of this new data. The results presented herein can be instrumental in detecting the phase of Mg ferrites from experimental spectra, thereby paving the way for a more profound comprehension of their properties and possible uses.

 Received 27th October 2023  
 Accepted 9th January 2024

DOI: 10.1039/d3ra07339d

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## 1. Introduction

Ferrite materials ( $MFe_2O_4$ ) ( $M = Ni, Co, Mn, Mg$  or  $Zn$ ) have gained prominence as multifaceted materials in recent years, offering a myriad of applications in cutting-edge technology. These spinel-structured oxide materials demonstrate exceptional physical, chemical, and magnetic properties, making them an essential component in diverse areas, such as electronics, communications, energy, and environmental sectors.<sup>1–3</sup> As a versatile material, Mg ferrite possesses unique magnetic and physical properties that render it useful across a wide array of applications.<sup>4–7</sup> Its high magnetic permeability, minimal magnetic losses, and remarkable magnetic stability make it ideal for magnetic cores,<sup>8</sup> while its high electrical resistivity and low thermal conductivity render it a promising material for energy conversion applications.<sup>9</sup>

Mg ferrite can adopt spinel structures in which divalent metal ions and trivalent metal distributed over the octahedral and tetrahedral sites.<sup>10–12</sup> Various techniques are in place to manipulate Mg ferrite's crystal structure and composition,

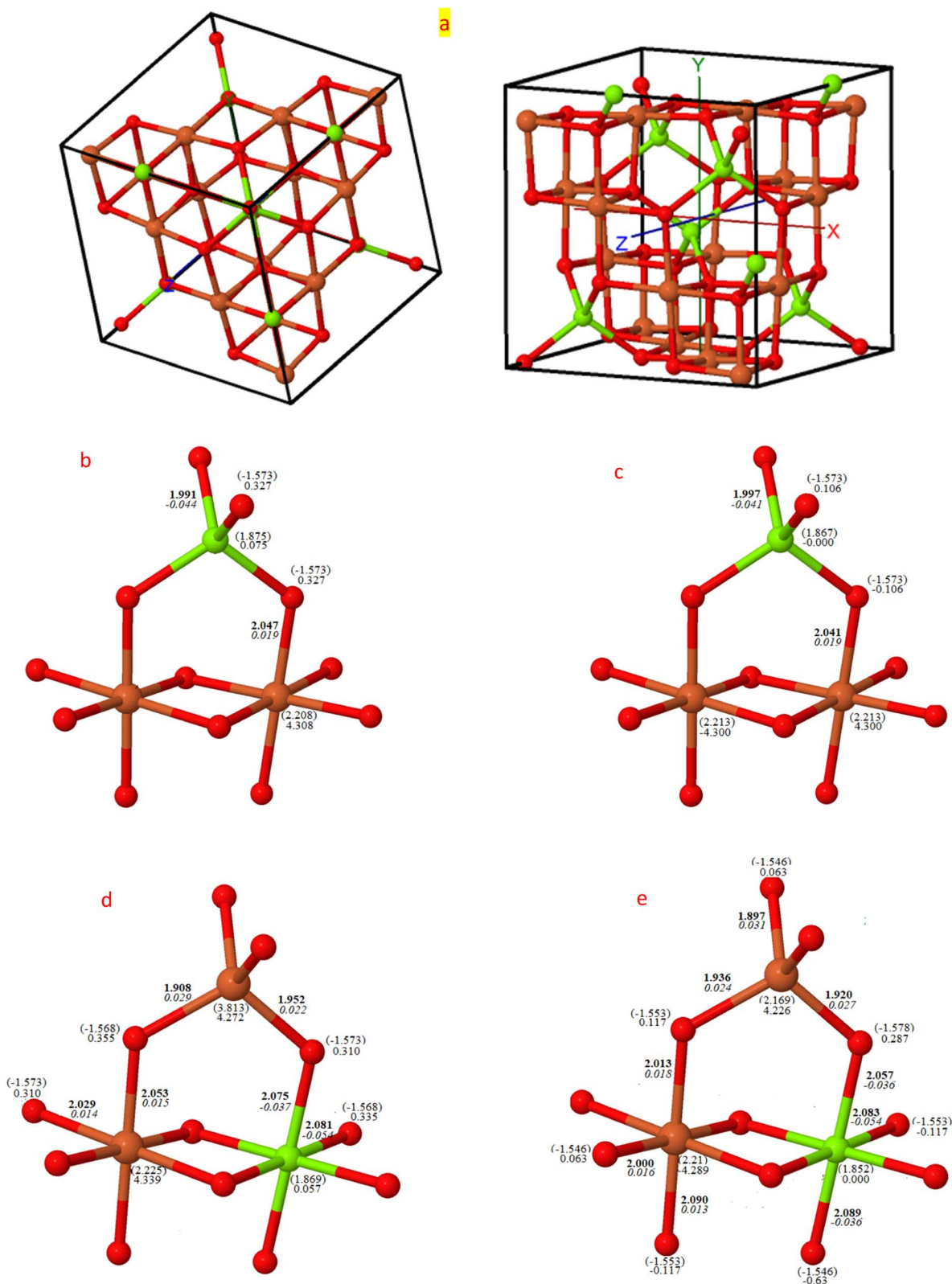
which subsequently influences its magnetic and electrical properties. These include synthesis methods, doping, processing conditions, post-processing treatments, and ligand functionalization.<sup>6,11,13–17</sup> Adjusting the crystal structure and composition of Mg ferrite requires a deep understanding of its inherent properties and the invention of innovative synthesis and processing methods to customize its properties for specific utilities.<sup>18,19</sup> Numerous studies have highlighted the profound influence of thermal treatment on Mg ferrite's magnetic properties, attributing it to the distribution and magnetic ordering of cations over tetrahedral and octahedral sites.<sup>20–22</sup>

The captivating world of vibrational spectra of ferrites is a field that has seen considerable attention in scientific literature, thanks to the theoretical foundations laid by Waldron.<sup>23,24</sup> Waldron's model interprets the vibrations of this system using the point group  $T_d$ 's irreducible representations. In principle, four IR active normal vibrations can be identified. The  $\nu_1$ , the highest frequency, is associated with vibrations along the tetrahedral bonds. Meanwhile, the  $\nu_2$  frequency relates to vibrations along the octahedral bonds. The  $\nu_3$  and  $\nu_4$ , on the other hand, represent the metal ion vibrations within their respective tetrahedral and octahedral environments. However, every model has its limitations. Waldron's model, as well as those proposed by White and De Angelis, have shown some challenges in interpreting certain characteristics observed in

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† Electronic supplementary information (ESI) available. See DOI: <https://doi.org/10.1039/d3ra07339d>





**Fig. 1** Visual depiction of bond metrics for normal and inverse configurations: this figure provides (a) the conventional cubic cell (with 8 f.u. of  $\text{MgFe}_2\text{O}_4$ , delimited by solid black lines), and a schematic illustration of bond lengths ( $\text{\AA}$ /bold), bond populations ( $|e|$ /italic), spin moment ( $|e|$ ), and Mulliken charges ( $|e|$  in brackets) of non-equivalent atoms by symmetry for normal, (b) ferromagnetic (FM) and (c) antiferromagnetic (AFM), and inverse (d) FM and (e) AFM configurations. Atoms in red, orange, and green are for oxygen, iron and magnesium, respectively. Data is derived using B3LYP.



experimentally obtained spectra.<sup>25</sup> For instance, variations and splitting in the  $\nu_1$  and  $\nu_2$  bands reported by different researchers for distinct ferrites are perplexing phenomena yet to be fully explained. Moreover, inverse spinals add another layer of complexity. In these instances, each degenerate vibration may undergo splitting, leading to three separate frequency vibrations. This splitting primarily happens due to symmetry reduction. Numerous factors have been proposed to explain the splitting observed in the main bands, such as the Jahn–Teller distortions, the presence of a divalent metal in the octahedral complex, and the varying synthesis conditions.<sup>25,26</sup> The assignment of Raman modes further complicates the scenario as there are discrepancies between different studies.<sup>10,27,28</sup> Interestingly, the splitting of the five modes predicted by group theory for the cubic structure has also been observed.<sup>16,29</sup> A particularly elusive area is the phase transformation between various Mg ferrite configurations and their impact on frequencies, a topic rarely explored in literature using density functional theory (DFT).<sup>7,30–33</sup> This study aims to bridge this gap by examining the influence of cation distribution and magnetic ordering on the infrared (IR) and Raman spectra through DFT and using a hybrid functional. The ultimate goal is to provide theoretical insight into the phase change landscape of Mg ferrite, shedding light on the complexities of this fascinating field.

## 2. Computational methods

Theoretical investigations were performed within the framework of density functional theory (DFT) using the CRYSTAL17 software.<sup>34</sup> The functionals utilized in the calculations include the global hybrid functional B3LYP (20% of HF exchange),<sup>35</sup> PBE0 (25% of HF exchange),<sup>36</sup> and range-separated HSE06 (the fraction of HF exchange varies based on the distance between electrons),<sup>37</sup> which largely rectify the self-interaction error of pure DFT functionals. The choice of functionals is essential in DFT, as they significantly affect the predicted relative energies and thereby influence the interpretation of system stability and vibrational properties. B3LYP, in particular, has garnered widespread acceptance for its consistent performance in modeling a diverse array of chemical systems.<sup>34,38,39</sup> It merges the Becke three-parameter exchange with the Lee–Yang–Parr correlation functional, offering an extensively benchmarked and experimentally validated balance of accuracy and computational tractability. This has cemented its status as a preferred choice for computational studies, particularly when a reliable depiction of crystal behavior is paramount. Furthermore, B3LYP's ability to predict vibrational frequencies and other electronic properties is well-documented in comparative literature, underscoring its reliability and the rationale for its selection in this study. Gaussian-type functions were utilized for

**Table 1** Comparative energy analysis of Mg ferrite spinel structure: this table details the total energy (in Hartree)  $E$  of Mg ferrite spinel structure ( $\text{Mg}_{1-x}\text{Fe}_x$ ) [ $\text{Mg}_x\text{Fe}_{2-x}\text{O}_4$ ] for inversion factor  $X = 0$  (normal), 0.5 (mixed), and 1 (inverse), calculated with different functionals. The bracketed  $E_R$  values signify the relative energy compared to the AFM inverse spinel structure

Functionals		$(X = 0)$		$(X = 0.5)$		$(X = 1)$	
		FM	AFM	FM	AFM	FM	AFM
B3LYP	$E$	−6057.0980	−6057.0950	−6057.0882	−6057.0988	−6057.0905	−6057.1059
	$E_R$	0.21	0.29	0.48	0.19	0.41	0.00
HSE06	$E$	−6055.9801	−6055.9767	−6055.9687	−6055.9784	−6055.9704	−6055.9845
	$E_R$	0.12	0.21	0.43	0.16	0.38	0.00
PBE0	$E$	−6055.9858	−6055.9823	−6055.9747	−6055.9841	−6055.9764	−6055.9901
	$E_R$	0.12	0.21	0.42	0.16	0.37	0.00

**Table 2** Thermodynamic properties of Mg ferrite systems: This table displays thermodynamic functions (eV per cell) at  $T = 298.15$  K and  $P = 0.10132500$  MPa for varied Mg ferrite systems.  $E_L$  signifies the energy per lattice cell (electronic energy),  $E_0$  is the zero-point energy,  $E_T$  represents the thermal contribution to the vibrational energy, and  $S$  indicates entropy. All energies were computed at the B3LYP level. Bracketed values showcase relative energy compared to the ground state (AFM,  $X = 1.0$ )

Energy	$X = 0$		$X = 0.5$		$X = 1$	
	FM	AFM	FM	AFM	FM	AFM
$E_L$	−164822.0184	−164821.9344	−164821.7512	−164822.0390	−164821.8142	−164822.2312
$E_0$	0.9533	0.9406	0.9544	0.9510	0.9580	0.9602
$E_T$	0.3613	0.3668	0.3608	0.3624	0.3589	0.35819
$S$ (meV per (cell K))	1.9515	1.9954	1.9414	1.9549	1.9208	1.9171
PV	0.0000975	0.0000974	0.0000968	0.0000961	0.0000958	0.0000957
TS	0.5818	0.5949	0.5788	0.5828	0.5727	0.5715
$E_T + PV - TS$	−0.2203	−0.2279	−0.2178	−0.2203	−0.2136	−0.2133
$E_L + E_0 + E_T + PV - TS$	−164821.2855 (0.20)	−164821.2218 (0.26)	−164821.0147 (0.47)	−164821.3083 (0.18)	−164821.0698 (0.41)	−164821.4843 (0.00)



the all-electron basis set for all atoms involved.<sup>40–42</sup> The optimized structure enabled us to derive the IR and Raman active frequencies and intensities. We employed spin-polarized computations to investigate the effect of spin ordering on electronic and structural properties. In the ferromagnetic (FM) configuration, all magnetic moments were initially oriented in one direction. Conversely, in the antiferromagnetic (AFM) configuration, the magnetic moments between two Fe atoms in the unit cell were set to be antiparallel. The five thresholds, denoted as  $T_i$ , which govern the truncation criteria for the Coulomb and exchange infinite series, were set to 8 ( $T_1$ – $T_4$ ) and 16 ( $T_5$ ). The self-consistent-field cycle used  $10^{-8}$  and  $10^{-10}$  Hartree energy convergence thresholds for optimization and vibration frequency calculations, respectively. The comprehensive optimization process, which involved lattice parameters and all atomic bases in the cell, used a root mean square (r.m.s.) displacement of  $10^{-5}$  Å. The shrinking factors dictating the count of independent  $k$ -points employed in the sampling of the Monkhorst–Pack grid were configured to 88. The frequencies (wavenumber)  $\omega_p$  were computed from second energy derivatives relative to atomic displacements  $u$  at the  $\Gamma$  point,<sup>43,44</sup> according to the following equations.

$$W_{ai,bj}^{\Gamma} = \frac{H_{ai,bj}^0}{\sqrt{M_a M_b}} \quad \text{where} \quad H_{ai,bj}^0 = \frac{\partial^2 E}{\partial u_{ai}^0 \partial u_{bj}^0} \quad (1)$$

In these equations,  $u$  denotes the atomic displacements of atom  $a$ , and  $b$  in the system, with the atomic mass, respectively. The  $i$ -th and  $j$ -th denote atomic coordinates. We were then able to determine the shift in frequencies due to isotopic substitutions at no additional computational cost by replacing the masses in eqn (1). The study used a coupled Perturbed–Hartree–Fock/Kohn–Sham method (CPHF/KS)<sup>45,46</sup> to calculate the integrated intensity for IR absorption and evaluated Raman intensities analytically.

### 3. Results and discussion

#### 3.1 Bond lengths, charge and spin distribution, energy, and band structure

The consolidated visualizations of the converged structures of both normal and inverse magnesium ferrite in their two spin configurations, ferromagnetic (FM) and antiferromagnetic (AFM), are depicted in Fig. 1. Under both FM and AFM conditions, the cubic symmetry is preserved when  $X = 0$ , as demonstrated by the Mg–O and Fe–O bond lengths of approximately  $4 \times 1.99$  Å and  $6 \times 2.04$  Å. These measurements align closely with the recorded values of 1.99 Å and 2.02 Å, respectively.<sup>19</sup> The charge and spin distribution data highlight the ionic properties of the system, with the oxygen atom gaining a charge of  $-1.57|e|$ , while magnesium and iron atoms lose charges of  $1.87|e|$  and  $2.21|e|$  respectively. Bond populations are reported as  $-0.04$  and  $0.02$  respectively. In the AFM configuration, there is a distinct alternating distribution of spin densities over the iron atoms in B-sites ( $4.3|e| \alpha$ ,  $-4.3|e| \beta$ ), thereby maintaining a net zero spin per cell. However, in the FM configuration, all spins align parallel ( $4.3 \alpha$ ).

With the complete transformation to inverse structure, there is a clear distortion from the cubic form, resulting in two and three non-equivalent Fe–O and Mg–O bond lengths for FM ( $X = 1$ ) and AFM ( $X = 1$ ) respectively. This alters both the charge and spin distributions, as indicated in Fig. 1. The magnetic moment of iron in the A-site is smaller than in the B-site by approximately  $0.06|e|$ , and inversely, the magnetic moment of Mg in the B-site is lower than in the A-site by  $0.02|e|$  in the FM configuration, but this becomes zero in both AFM structures. The FM

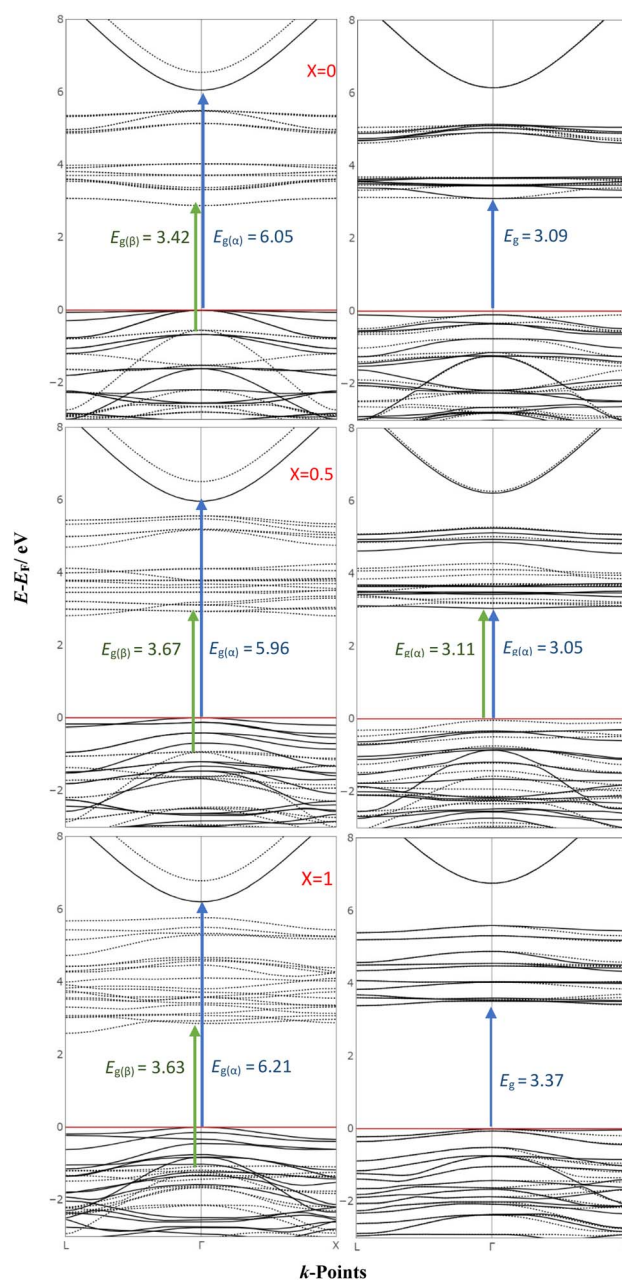


Fig. 2 Band structures of Mg ferrite in FM and AFM configurations: this figure shows the band structures of Mg ferrite in FM (left panel) and AFM (right panel) configurations as calculated with B3LYP for varying degrees of inversion. The red horizontal line denotes the Fermi level set to zero, while continuous and dotted black lines represent the  $\alpha$  and  $\beta$  energy bands, respectively.



lattice parameter when  $X = 0$  is 8.51 Å, which decreases to 8.46 Å when inverted to FM ( $X = 1$ ), closely matching the measured value of 8.44 Å.<sup>47</sup>

The relative energy difference among the six optimized structures was analyzed using three functionals and is presented in Table 1. The most stable configuration was determined to be the inverse structure with AFM arrangements.<sup>27,48</sup> MFO is an antiferromagnetic material, with magnetic moments aligned in an antiparallel orientation, resulting in a net magnetic moment of zero. This is consistent with experimental observations of zero magnetization at a Curie temperature of 738 K.<sup>49</sup> This antiferromagnetic behavior is attributed to its inverse spinel structure, where the magnetic moments of iron ions on tetrahedral sites are compensated by the magnetic moments of iron ions on octahedral sites due to the nonmagnetic nature of magnesium atoms. The energy difference between FM and AFM in the ( $X = 1$ ) arrangement was found to be notably high at 0.41 eV (B3LYP), even considering the free energy inclusive of zero-point energy (Table 2).

The band structures of MFO in their FM configurations were compared to their corresponding AFM configurations, as

illustrated in Fig. 2. The influence of inversion on the electronic structure was minimal, with the band gap increasing by 0.16 eV for  $\alpha$  bands and 0.21 eV for  $\beta$  bands in FM and by 0.28 eV in AFM upon transitioning from the normal to inverse structure. The band gaps of the AFM structures in this study closely match the measured value of 2.48 eV for samples calcinated at 700 °C,<sup>50</sup> and 2.38 eV (ref. 51) for those calcinated at 550 °C. The variations in band gaps with changing temperatures may be related to cation disorder within the crystal or existing defects such as oxygen vacancies.<sup>30,52</sup> In the FM configuration ( $X = 0$  and 1), the band gaps along the  $\alpha$  and  $\beta$  spins are open at the gamma point (direct band gap), while only the  $\alpha$  gap is direct for  $X = 0.5$ . In the AFM configuration, the shift between the  $\alpha$  and  $\beta$  bands is minor, resulting in virtually identical band gaps.

### 3.2 Spectroscopic characterization: investigating crystal structures *via* Raman and infrared spectroscopy

Raman and Infrared spectroscopy serve as robust methodologies for comprehensively probing vibrational properties in various materials. These techniques provide invaluable

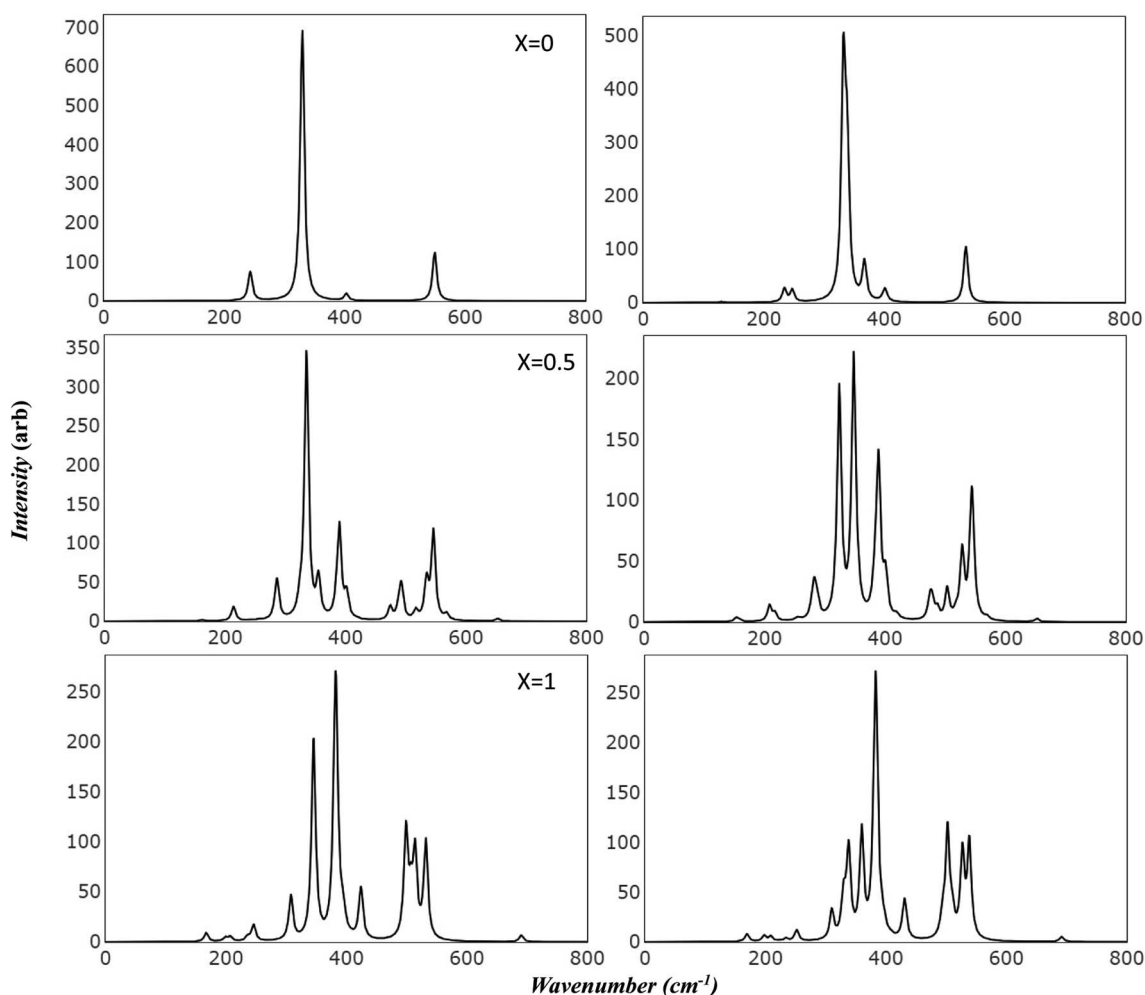


Fig. 3 Simulated infrared spectra of Mg ferrite by B3LYP: this figure displays B3LYP simulated infrared spectra of Mg ferrite ( $X = 0.0, 0.5, 1.0$ ) with its two-order magnetic configuration, where left panels refer to FM and right panels refer to AFM.



perspectives on the crystal structure, chemical composition, and defective characteristics by scrutinizing the frequency and intensity of the scattered light. Additionally, they can be employed to investigate the impact of extrinsic factors, such as temperature and pressure, on the vibrational characteristics of the material under study. Through meticulous observation of spectral changes under diverse conditions, researchers can achieve a more profound comprehension of the physical principles that govern the magnetic and electrical attributes of Mg ferrite. Importantly, the simulated spectra has introduced a powerful tool in scientific resources. This facilitates precise characterization of spectral features, effectively avoiding numerous confounding factors such as preparation methods, temperature variations, defects, and intrinsic structural disorder, which may otherwise make the analysis unclear.

Fig. 3 presents the simulated vibrational frequencies and intensities of Mg ferrite geometries ( $X = 0.0, 0.5, 1.0$ ) within two spin configurations: ferromagnetic (FM) and antiferromagnetic (AFM). All spectra are computed at the B3LYP level and visualized using a pseudo-Voigt function, a linear combination of Lorentzian and Gaussian functions, with a full width at half maximum of  $8 \text{ cm}^{-1}$ . For the FM configuration ( $X = 0.0$ ), four triply degenerate  $T_{1u}$  modes, predicted by group theory analysis for the  $Fd3m$  space group structure, are discerned. These four peaks are observed at 243, 330, 403, and  $550 \text{ cm}^{-1}$ , with the peak at  $330 \text{ cm}^{-1}$  showcasing an exceptionally high intensity compared with the others. The two lowest frequency peaks are subject to disagreement across different papers regarding their detection and precise location.<sup>10</sup> In its AFM counterpart, the intense peak is slightly affected by the new configuration ( $332 \text{ cm}^{-1}$ ), with a small peak appearing at  $338 \text{ cm}^{-1}$ . Additional minor peaks emerge at 129 and  $367 \text{ cm}^{-1}$ , and the low-frequency peak (243) splits into two peaks at 234 and  $247 \text{ cm}^{-1}$ . At higher frequencies, peaks are observed at 400 and  $403 \text{ cm}^{-1}$ , and one at  $536 \text{ cm}^{-1}$ , marking a shift of  $14 \text{ cm}^{-1}$  compared to  $550 \text{ cm}^{-1}$  in FM. The FM spectra analysis reveals that the peak at  $243 \text{ cm}^{-1}$  is associated with the bending mode of the Fe–O–Mg bond, and the subsequent two peaks at 330 and  $403 \text{ cm}^{-1}$  are connected to the bending bond of O–Mg–O and Fe–O–Mg. The highest frequency band at  $550 \text{ cm}^{-1}$  signifies a combination of the stretching mode of the Mg–O bond and the bending mode of the Fe–O–Mg bond.

In the AFM configuration, the peak at  $129 \text{ cm}^{-1}$  involves the bending modes of Fe–O–Mg and Fe–O–Fe, and the subsequent two peaks at 234 and  $247 \text{ cm}^{-1}$  entail the bending mode of Fe–O–Mg, sustaining the same modes as the  $243 \text{ cm}^{-1}$  in FM. The peak at  $332 \text{ cm}^{-1}$  and its shoulder at  $338 \text{ cm}^{-1}$  are more correlated than other modes, as they comprise the stretching mode of Fe–O–Fe and bending modes of O–Mg–O, Fe–O–Fe, and Fe–O–Mg. The final modes ( $400, 403, 536 \text{ cm}^{-1}$ ) involve the bending and stretching of O–Mg–O and Fe–O–Mg bonds.

The IR spectra reflect splitting upon transitioning from normal to complete inverse structure. For FM ( $X = 1.0$ ), low frequency region reveals a small peak at  $167 \text{ cm}^{-1}$ , followed by peaks at 199, 207, and  $246 \text{ cm}^{-1}$ , which correspond to the  $243 \text{ cm}^{-1}$  peak in FM ( $X = 0$ ). These peaks are associated with the bending mode of both cations, except for the modes at 207

and  $246 \text{ cm}^{-1}$ , which relate to the iron cation, O–Fe–O. The peak at  $246 \text{ cm}^{-1}$  appears with small shoulders at  $236 \text{ cm}^{-1}$ , signifying a combination of bending modes of O–Fe–O, FeO–Mg– and Fe–O–Fe. At moderate frequencies, high-intensity peaks appear at  $308 \text{ cm}^{-1}$ , encompassing the bending of all cations, and  $346 \text{ cm}^{-1}$ , marking the stretching mode of O–Fe–O. A peak at  $383 \text{ cm}^{-1}$  has the highest intensity and involves a complex mode of Mg–O stretching and Fe–O–Mg bending. The peak at  $424 \text{ cm}^{-1}$  exhibits stretching modes for Fe–O and Fe–O–Mg. In the high-frequency region, a group of split peaks are observed ( $499, 507, 514, \text{ and } 532 \text{ cm}^{-1}$ ), corresponding to the unsplit peak at  $550 \text{ cm}^{-1}$  in FM ( $X = 0$ ). The mode at  $499 \text{ cm}^{-1}$  is linked to the stretching of Fe–O and Mg–O bonds and the bending of Fe–O–Fe. The peaks at 507 and  $514 \text{ cm}^{-1}$  relate to the stretching of Mg–O and the bending of O–Mg–O, respectively, and the one at  $532 \text{ cm}^{-1}$  involves the stretching of Fe–O bonds.

The highest frequency peak at  $690 \text{ cm}^{-1}$  appears in an otherwise flat area in the normal spectra, making it a potential marker for identifying the inverted structure. This mode involves the stretching of Fe–O and the bending of Fe–O–Mg and Fe–O–Fe. Baraton *et al.* detected this high frequency peak for Mg ferrite at  $700 \text{ cm}^{-1}$ , alongside the two main peaks ( $\nu_1, \nu_2$ ) at 581 and  $424 \text{ cm}^{-1}$ , and found that it becomes more pronounced as the Mg content increases.<sup>10</sup>

Table 3 presents a comparison of the frequencies observed in FM and AFM orderings within an inverted structure. A marked shift is observed for AFM (where  $X = 1$ ) when compared to its FM counterpart. Specifically, the peaks observed at 252, 431, 527, and  $539 \text{ cm}^{-1}$  in AFM display an upward shift by 6, 7, 13, and  $7 \text{ cm}^{-1}$ , respectively, when compared to the corresponding FM frequencies (246, 424, 514 and  $532 \text{ cm}^{-1}$ ). In the FM

**Table 3** Frequency comparison of inverse structure with two-spin ordering: this table contrasts the simulated frequencies of an inverse structure with its two-spin ordering (FM and AFM)

Sy	Frequencies ( $\text{cm}^{-1}$ ) FM ( $X = 1$ )	Frequencies ( $\text{cm}^{-1}$ ) AFM ( $X = 1$ )	Shifts ( $\text{cm}^{-1}$ )
B <sub>2u</sub>	167	169	+2
B <sub>3u</sub>	199	198	–1
B <sub>2u</sub>	207	209	+2
B <sub>1u</sub>	236	234	–2
B <sub>3u</sub>	246	252	+6
B <sub>1u</sub>	308	310	+2
B <sub>2u</sub>	346	338	–8
		360	
B <sub>3u</sub>	381	382	–1
B <sub>1u</sub>	383	384	–1
B <sub>3u</sub>	394	394	0
B <sub>2u</sub>	395	397	+2
B <sub>1u</sub>	408	408	0
B <sub>3u</sub>	424	431	+7
B <sub>3u</sub>	499	494	–5
B <sub>1u</sub>	507	503	+4
		511	
B <sub>1u</sub>	514	527	+13
B <sub>1u</sub>	529	529	0
B <sub>2u</sub>	532	539	+7
B <sub>1u</sub>	690	692	+2



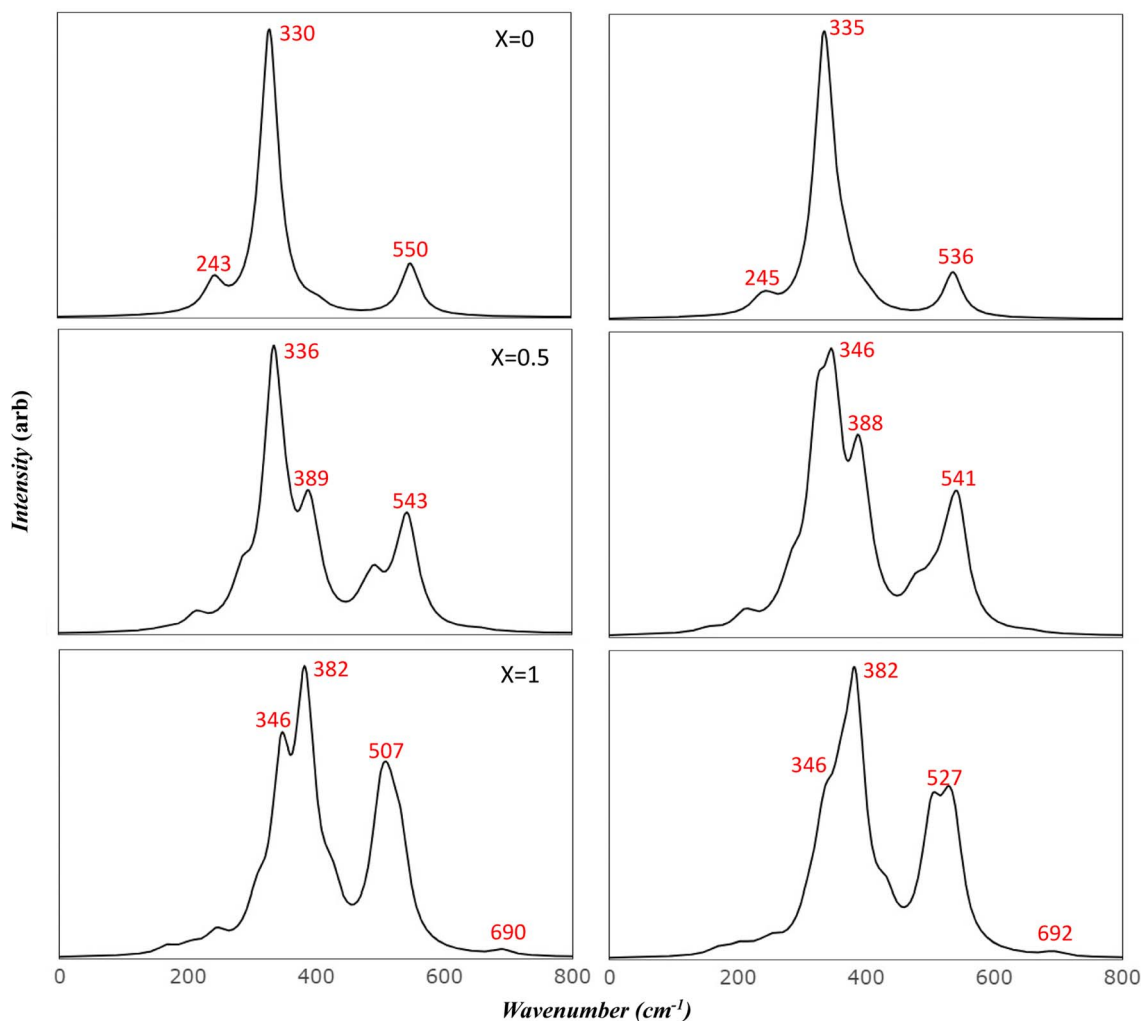


Fig. 4 Comparison of simulated IR spectra of Mg ferrite: this figure compares the simulated IR spectra of Mg ferrite ( $X = 0.0, 0.5, 1.0$ ) in its two-spin order using a Full Width at Half Maximum (FWHM) of  $35 \text{ cm}^{-1}$ .

Table 4 Analysis of normal Mg ferrite IR modes frequencies: this table compares the frequencies of the IR modes of normal Mg ferrite as previously documented in literature

Vibrational modes ( $\text{cm}^{-1}$ )	Ref. 23	Ref. 14	Ref. 47	Ref. 21	Ref. 54	Ref. 10	Ref. 28		Ref. 51	
							200 °C	1000 °C	550 °C	1000 °C
$\nu_1$	565	561	566	606	574	581	552	542	539	536
$\nu_2$	406	437	409	458	409	424	424	418	395	402
$\nu_3$									350	360
$\nu_4$										

spectrum, the peak at  $346 \text{ cm}^{-1}$  diminishes to half its original intensity when it shifts to  $338 \text{ cm}^{-1}$  in the AFM spectrum. This shift is accompanied by the emergence of a new peak at  $360 \text{ cm}^{-1}$ . The group of FM peaks at  $499, 507, 514, 532 \text{ cm}^{-1}$  exhibit a significant shift in the AFM spectrum, appearing at  $494, 511, 527$  and  $539 \text{ cm}^{-1}$ , respectively. Their intensities also decrease by half. A dominant peak emerges at  $503 \text{ cm}^{-1}$  in the AFM spectrum, displaying a high intensity. This peak is

associated with the stretching mode of both Fe–O and Mg–O bonds. The two modes at  $494$  and  $511 \text{ cm}^{-1}$  blend with the  $503 \text{ cm}^{-1}$  peak, resulting in a broad, dominant peak.

To more accurately mimic the experimental broadening of peaks and create a more representative image, we adjusted the full width half maximum value from  $8$  to  $35 \text{ cm}^{-1}$ . This was done using a linear combination of Lorentzian curves to derive the pseudo-Voigt functional form, as depicted in Fig. 4. The



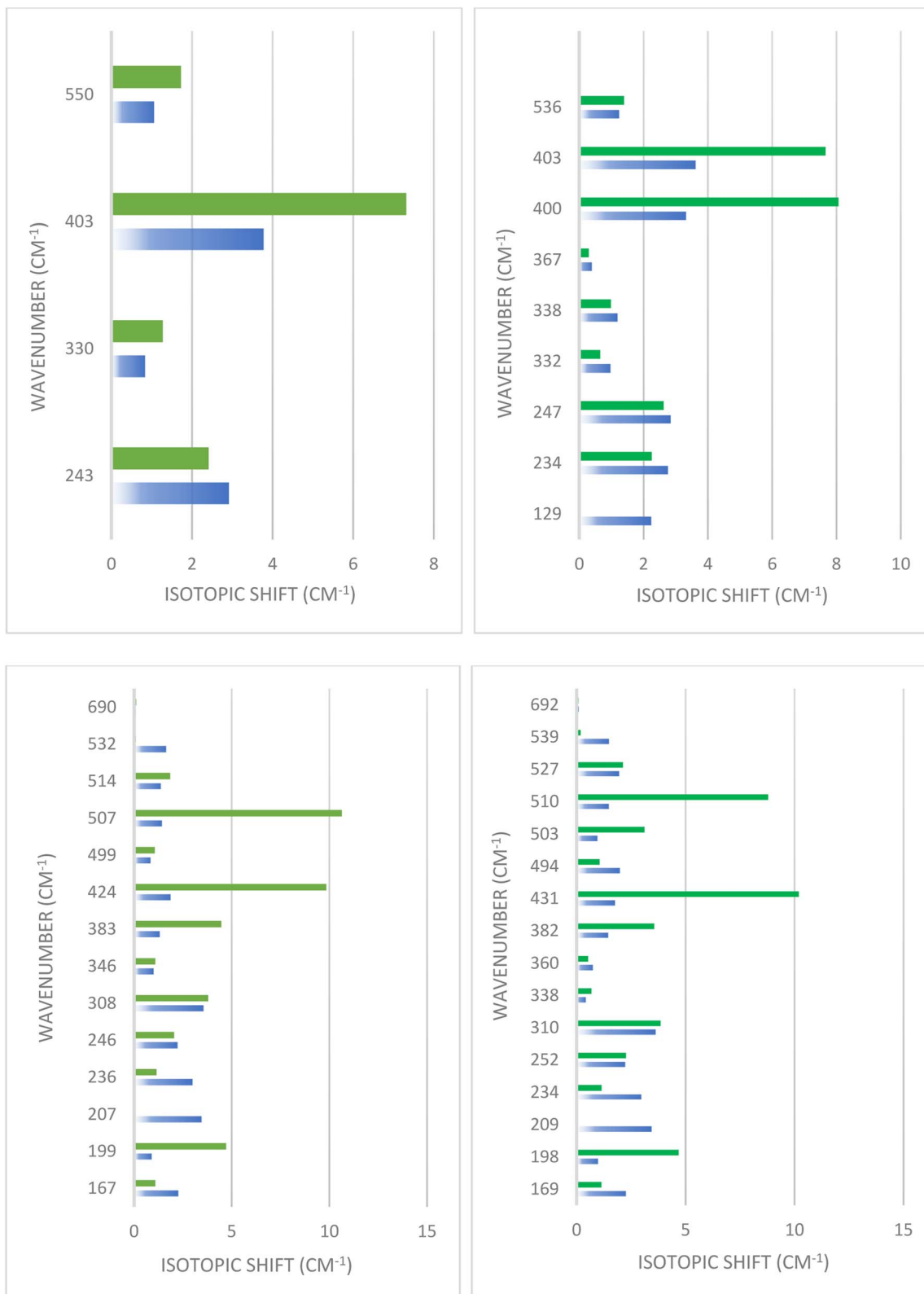


Fig. 5 Simulated isotopic shifts in Mg ferrite: this figure shows the simulated isotopic shifts resulting from  $^{56}\text{Fe} \rightarrow ^{58}\text{Fe}$  and  $^{24}\text{Mg} \rightarrow ^{26}\text{Mg}$  substitution for Mg ferrite ( $X = 0.0$  (top panel),  $1.0$  (below panel)) in its two-spin configuration. Blue bars represent Fe atom and green bars represent the Mg atom.



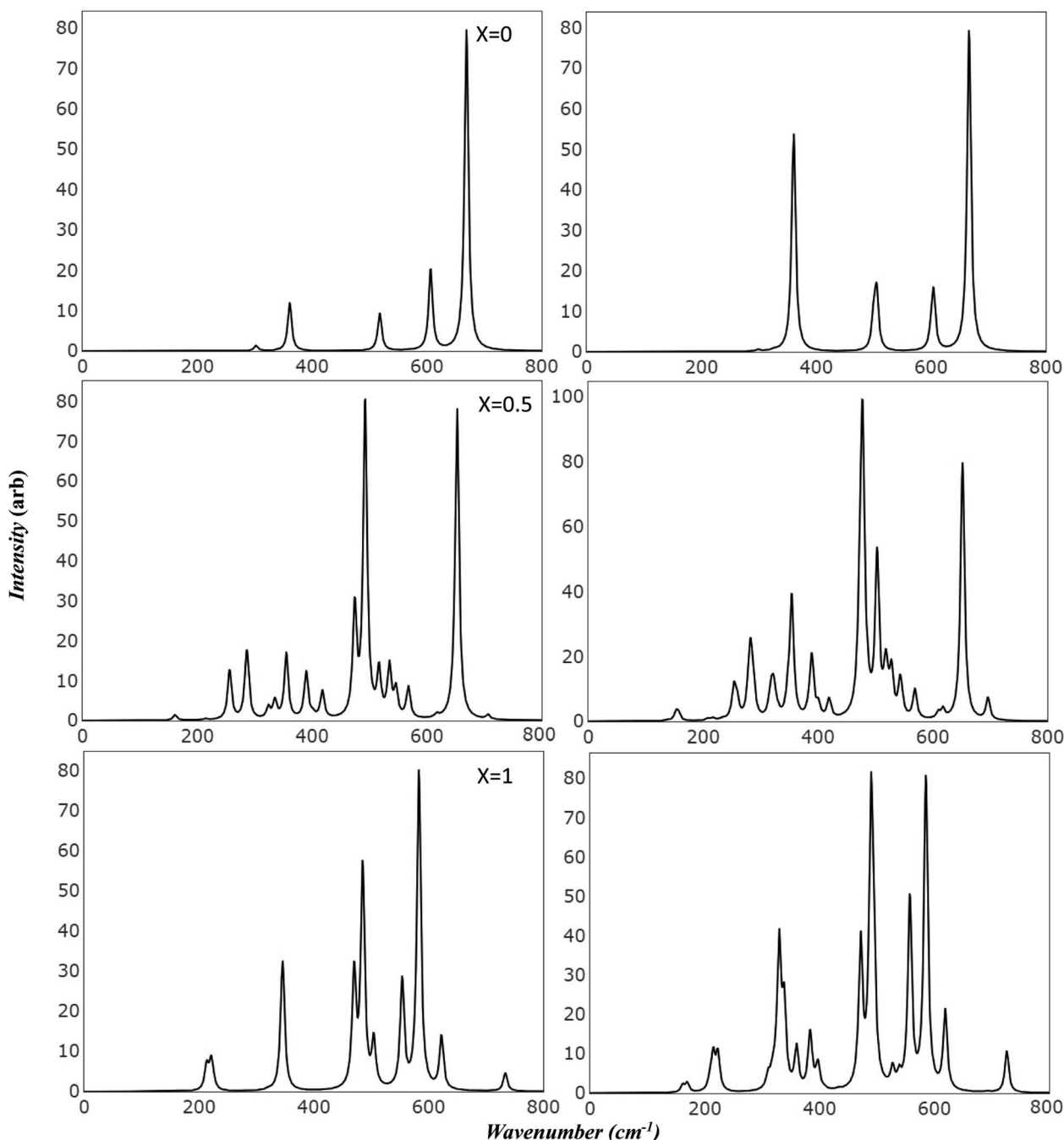


Fig. 6 Simulated Raman spectra of Mg ferrite by B3LYP: this figure presents B3LYP simulated Raman spectra of Mg ferrite ( $X = 0.0, 0.5, 1.0$ ) with its two-order magnetic configuration, where left panels refer to FM and right panels refer to AFM.

results we obtained showed a satisfactory agreement with the most commonly reported values for  $\nu_1$  and  $\nu_2$ , as listed in Table 4. These results also provided an explanation for the fewer features observed in the experimental data.

Previous studies have reported the splitting of IR peaks in MFO due to deformation from a cubic to a non-cubic structure. For instance, Waldron reported  $\nu_1$  and  $\nu_2$  at 565 and 406  $\text{cm}^{-1}$ , respectively, along with additional peaks at 380, 430, and 735  $\text{cm}^{-1}$ .<sup>23</sup> Heiba *et al.* also reported a split in the main  $\nu_1$  and  $\nu_2$  modes, with the seven frequencies in their study recorded at

406, 419, 436, 481, 493, 582, and 667  $\text{cm}^{-1}$ .<sup>53</sup> Their findings indicated that these frequencies were influenced by the ratio of cations. The frequency at 667  $\text{cm}^{-1}$ , which had a very low intensity, was not identified in some of their samples, aligning with our findings. Frequencies lower than 400  $\text{cm}^{-1}$  were not reported in their study due to the limitations of their instrument.

In order to delve deeper into the contribution of cations in the observed modes, we computed the spectra of isotopic substitutions ( $^{56}\text{Fe} \rightarrow ^{58}\text{Fe}$  and  $^{24}\text{Mg} \rightarrow ^{26}\text{Mg}$ ). As seen in Fig. 5,

**Table 5** Assignment of Raman modes in Mg ferrite: this table compares the Raman modes assignments for Mg ferrite as calculated in the current study and as previously reported

Sy	Ref. 55	Ref. 27	Ref. 10	Current study										
				Ref. 28		Ref. 16	(X = 0)			(X = 1)				
				200 °C	1000 °C	500 °C	Ref. 29	Sy	FM	AFM	Sy	FM	AFM	
T <sub>2g</sub> (1)	217	217	209	202	216	217	215	T <sub>2g</sub> (1)	302	298		B <sub>3g</sub>	213	215
												A <sub>g</sub>	221	222
												B <sub>2g</sub>	224	224
E <sub>g</sub>	333	329	326	307	331	326	335	E <sub>g</sub>	361	361		B <sub>1g</sub>	316	329
												B <sub>2g</sub>	320	338
												B <sub>3g</sub>	332	360
						367						B <sub>1g</sub>	345	384
												A <sub>g</sub>	346	397
T <sub>2g</sub> (2)	486	480	475	462	483	487	400	T <sub>2g</sub> (2)	518	505		B <sub>2g</sub>	470	472
												A <sub>g</sub>	485	490
							480					B <sub>3g</sub>	505	503
T <sub>2g</sub> (3)	554	548	535	499	546	550	560	T <sub>2g</sub> (3)	607	605		B <sub>2g</sub>	554	557
	646											A <sub>g</sub>	583	585
A <sub>1g</sub>	715	704	700	693	707	630	670	A <sub>1g</sub>	669	667		B <sub>3g</sub>	622	619
						703	715					A <sub>g</sub>	734	726

the vibrations of cations in their sites are highly correlated, making it challenging to interpret the spectra by categorizing the observed modes into A-site and B-site. In both FM and AFM ( $X = 0$ ), the most noticeable shift was observed for the normal mode at approximately 400  $\text{cm}^{-1}$ . The largest shift occurred with the  $^{26}\text{Mg}$  substitution, which was 7–8  $\text{cm}^{-1}$ , while the  $^{58}\text{Fe}$  substitution resulted in a shift of approximately 3.5  $\text{cm}^{-1}$ . In FM and AFM of ( $X = 1$ ), where all the Mg atoms transition to the octahedral site, a significant shift was also observed with the  $^{26}\text{Mg}$  substitution at 424 and 507  $\text{cm}^{-1}$  mode in FM and 431 and 510  $\text{cm}^{-1}$  modes in AFM. This shift was considerable, at about 10  $\text{cm}^{-1}$ . The modes at (199, 308, and 383  $\text{cm}^{-1}$ ) in FM and their corresponding modes at (198, 310, and 382  $\text{cm}^{-1}$ ) in AFM, shifted with  $^{26}\text{Mg}$  by 3.6–4.7  $\text{cm}^{-1}$ , indicating the influence of these modes by the lighter atom (Mg). Moreover, the  $^{58}\text{Fe}$  substitution also shifted the two modes at 308 and 207  $\text{cm}^{-1}$  in FM, and the modes at 310 and 209  $\text{cm}^{-1}$  in AFM by 3.5  $\text{cm}^{-1}$ .

In the examination of scattered Raman (Fig. 6), the five modes predicted by group theory are discerned in FM ( $X = 0.0$ ) at the following frequencies: 669  $\text{cm}^{-1}$  for A<sub>1g</sub>; 607, 518, and 302  $\text{cm}^{-1}$  for triply degenerate T<sub>2g</sub> symmetry; and 361  $\text{cm}^{-1}$  for doubly degenerate E<sub>g</sub> symmetry. Analysis of these modes reveals that the peaks at 302  $\text{cm}^{-1}$  and 607  $\text{cm}^{-1}$  encompass all the cations, specifically including the bending mode of O–Mg–O and Fe–O–Mg, in addition to the Fe–O–Fe bending detected at 606.6  $\text{cm}^{-1}$ .

The peak at 361  $\text{cm}^{-1}$  implicates the stretching mode of Fe–O–Fe, O–Fe–O, and Fe–O–Mg, along with the bending mode of O–Mg–O and Fe–O–Mg. The peak at 518  $\text{cm}^{-1}$  solely corresponds to the stretching mode of O–Mg–O and Fe–O–Mg bonds. The peak with the highest intensity and frequency, at 667  $\text{cm}^{-1}$ , is associated with the stretching mode of Mg–O and the bending mode of Fe–O–Mg. The impact of AFM spin ordering

on Raman spectra is evident in both frequencies and intensities. For example, the peak at 302  $\text{cm}^{-1}$  is shifted by 4  $\text{cm}^{-1}$  (to 298  $\text{cm}^{-1}$ ) and its intensity is halved, while the second peak at 361  $\text{cm}^{-1}$  remains stationary but its intensity increases fivefold. The most significant shift is observed with the 518  $\text{cm}^{-1}$  peak, which shifts to a lower frequency by 13  $\text{cm}^{-1}$  (to 505  $\text{cm}^{-1}$ ) with a doubling in intensity. This peak combines with a shoulder at 500  $\text{cm}^{-1}$ , leading to peak broadening. Minor shifts to lower frequencies are seen with 607 and 669  $\text{cm}^{-1}$ , by about 2  $\text{cm}^{-1}$ , accompanied by a minor decrease in their intensities.

Upon conversion to an inverse structure, the spectra undergo splitting over a broad region and show emerging new peaks, indicative of the deformation of the cubic structure. Starting with FM ( $X = 1$ ), the spectra display ten peaks appearing in the entire calculated region. New twin peaks emerge at 213 and 221  $\text{cm}^{-1}$ , with small intensities related to the bending mode of O–Mg–O, Fe–O–Fe, and O–Fe–O. The peak at 346  $\text{cm}^{-1}$ , shifted from the corresponding doubly degenerate peak in FM ( $X = 0$ ) at 361  $\text{cm}^{-1}$  by 15  $\text{cm}^{-1}$ , displays a high correlation between cations, involving similar modes to those found at 361  $\text{cm}^{-1}$ .

The mid-range features three split peaks at 470, 485, and 505  $\text{cm}^{-1}$ . The peaks at 470 and 485  $\text{cm}^{-1}$  are related to the stretching mode of Fe–O–Mg and O–Fe–O, and the second peak at 485  $\text{cm}^{-1}$  additionally involves the bending mode of O–Fe–O and Fe–O–Fe. The third peak at 505  $\text{cm}^{-1}$  is correlated to iron only, involving the stretching mode of both Fe–O–Fe and O–Fe–O. Another group of three peaks at 554, 583, and 622  $\text{cm}^{-1}$  appear in the high-frequency region, along with a small peak at the edge of the spectra at 734  $\text{cm}^{-1}$ . The peak at 554  $\text{cm}^{-1}$  resonates with the same stretching modes as the 470  $\text{cm}^{-1}$  peak, but also includes the bending of O–Fe–O. Meanwhile, the 583 and 622  $\text{cm}^{-1}$  peaks incorporate the same stretching modes as the 505  $\text{cm}^{-1}$  peak, but with the additional bending of Fe–O–



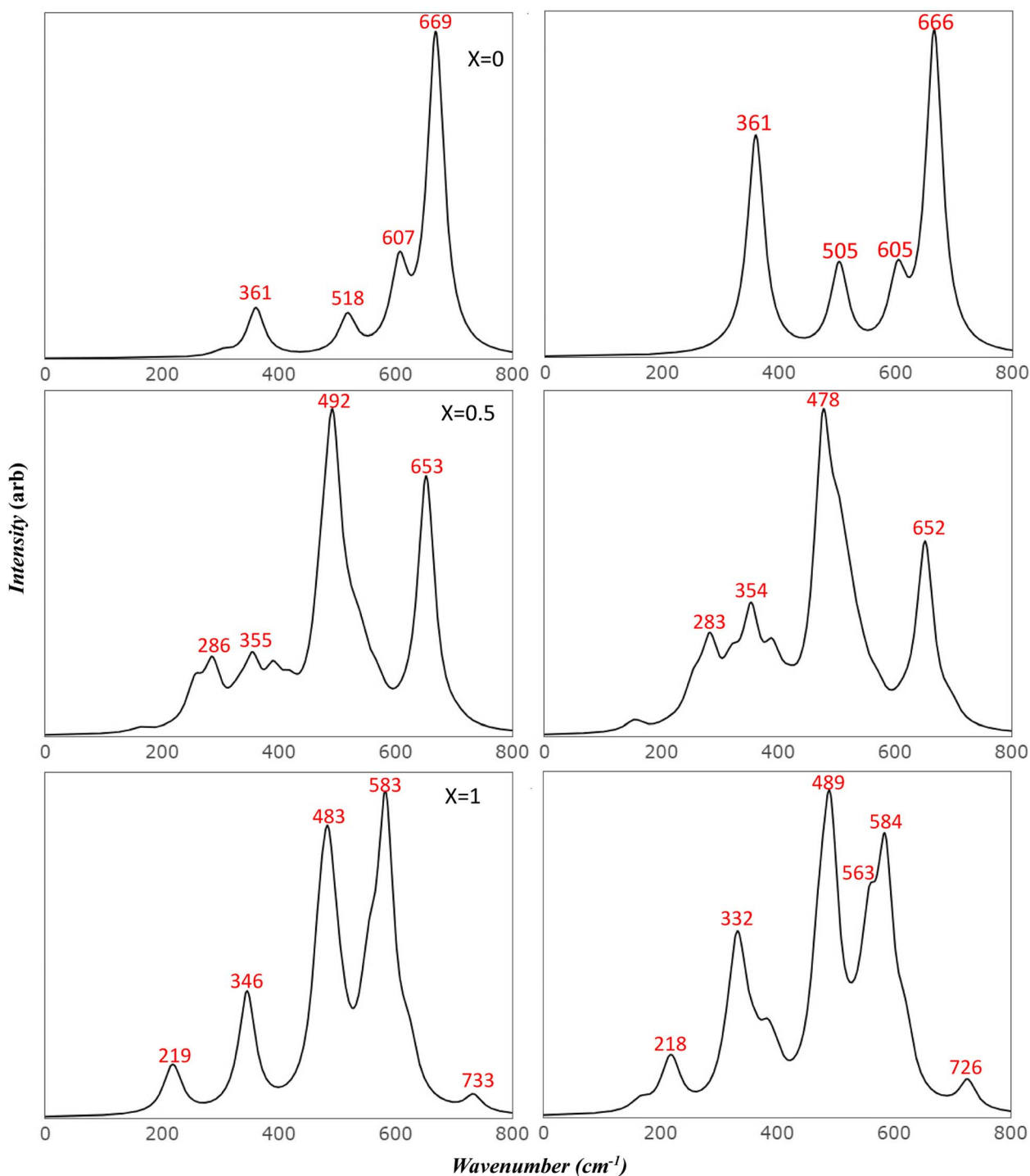


Fig. 7 Comparison of simulated Raman spectra of Mg ferrite: this figure contrasts the simulated Raman spectra of Mg ferrite ( $X = 0.0, 0.5, 1.0$ ) in its two-spin order using a Full Width at Half Maximum (FWHM) of  $35 \text{ cm}^{-1}$ .

Fe and O–Mg–O, respectively. The peak at  $734 \text{ cm}^{-1}$  is related to the bending of Fe–O–Mg and Fe–O–Fe and the stretching of the Fe–O bond.

Alterations in spin arrangement in AFM ( $X = 1$ ) also affect the Raman spectra, prompting shifts for most peaks and activating only three peaks due to slight deformation. Small new twin peaks appear at  $162$  and  $169 \text{ cm}^{-1}$ , and another at

$527 \text{ cm}^{-1}$ . No further splitting occurs for other peaks; instead, they undergo shifts as listed in Table 5. One of the most notable features in AFM spectra is the significant intensity increase of a group of peaks in the region of  $300 \text{ cm}^{-1}$  ( $329, 338, 360, 384,$  and  $397 \text{ cm}^{-1}$ ), four of which had almost zero intensity in FM. The small peak at  $503 \text{ cm}^{-1}$  merges with the  $490 \text{ cm}^{-1}$  peak to form one broad peak. The peak at  $734 \text{ cm}^{-1}$  in FM can be seen

as an indication of the present inverse structure as it stands in a flat region in the normal spectra. Its large shift ( $8\text{ cm}^{-1}$ ) with the change in spin order can be useful for tracking phase changes under experimental conditions. Most of the studies reported in Table 5 detected this peak.

The comparison of the obtained frequencies for both normal and inverted structures with available experimental data reveals a better alignment with the inverted structure. The breadth of the experimental peaks can be represented by resetting the full width half maximum value from 8 to  $35\text{ cm}^{-1}$ , as executed in the IR section (Fig. 7). Wang *et al.*<sup>55</sup> predicted seven modes at frequencies of 217, 333, 390, 486, 554, 646, and  $715\text{ cm}^{-1}$ . These predictions are detailed in Table 5. The researchers attributed the additional peak at  $646\text{ cm}^{-1}$  to the order–disorder effect within the structure. However, they provided no further explanation for the presence of the peak at  $390\text{ cm}^{-1}$ , which is also found in the simulated AFM Mg ferrite spectra (refer to Table 5). Our simulated spectra, with a FWHM of  $35\text{ cm}^{-1}$ , bear a significant resemblance to those of Wang *et al.* Frequencies of the modes are found at 218, 332, 489, 563, 584, 619, and  $727\text{ cm}^{-1}$ . The minor peak at  $618\text{ cm}^{-1}$  merges with the  $583\text{ cm}^{-1}$  peak in our study. The low intensity of these peaks could account for their absence in most of the studies listed in Table 5.<sup>10,27,28</sup> Nakagomi *et al.* predicted seven modes similar to those identified by Wang *et al.* Yet, they attributed the peak at  $670\text{ cm}^{-1}$  to the substitution of iron (Fe) atoms at tetrahedral sites with magnesium (Mg) atoms.<sup>29</sup> They proposed that the substantial mass difference between  $\text{Fe}^{3+}$  and  $\text{Mg}^{2+}$  ions cause the  $A_{1g}$  mode to split into two: one being attributable to  $\text{Mg}^{2+}$  ( $715\text{ cm}^{-1}$ ) and the other to  $\text{Fe}^{3+}$  ions ( $670\text{ cm}^{-1}$ ). They quantified the ion distribution at the tetrahedral sites based on the fluctuation in the integrated intensity of both modes relative to the total spectrum. Feng *et al.* identified a clear splitting into eight modes, including  $E_g$  and  $T_{2g}(3)$ , which further split into four peaks. They attributed the two highest peaks to  $A_{1g}$ .<sup>16</sup> Their frequency values align with our findings, but the assignments they reported do not. The peak at  $619\text{ cm}^{-1}$ , which resulted from the  $T_{2g}(3)$  split in our study, closely matches their value at  $630\text{ cm}^{-1}$ . It's evident that the deformation from the cubic structure in inverse spinel leads to the degeneration of most modes and activates new modes in the Mg ferrite spectra. This finding aligns with experimental results<sup>10</sup> and suggests that the assignments provided in existing literature need to be reassessed considering our simulated data.

## 4. Conclusion

This study delves into a comprehensive theoretical analysis based on density functional theory, examining the influence of inversion degree and spin arrangement of magnesium ferrite on multiple attributes including geometry, energy, electronic structure, and the frequencies and intensities of both IR and Raman spectra. We found that the inverse structure with anti-ferromagnetic order emerges as the ground structure, with relative energy being 0.21 and 0.41 eV (B3LYP) compared to the ferromagnetic order of ( $X = 0$ ) and ( $X = 1$ ), respectively. Our findings uncover the profound effect of inversion on the lattice

structure, leading to deformation that significantly impacts the calculated IR and Raman spectra, inducing noteworthy shifting and splitting. The four IR frequencies with  $T_{1u}$  symmetry calculated for the typical cubic structure of ( $X = 0$ ) (243, 330, 403, and  $550\text{ cm}^{-1}$ ) split over a wide spectral region upon inversion ( $X = 1$ ). These frequencies are further influenced by the spin order, leading to a significant shift that provides valuable insights into phase transition under varying experimental conditions. Our isotopic calculations reveal an intricate relationship between the Mg and Fe vibrational modes. Despite the large correlation detected, some specific modes are predominantly influenced by the lighter Mg atom rather than the Fe atom, attributable to the substantial mass discrepancy, irrespective of the degree of inversion. This results in a significant shift ( $7\text{--}10\text{ cm}^{-1}$ ) obtained by  $\text{Mg}^{26}$  substitution with ( $403\text{ cm}^{-1}$ ) in the normal structure and ( $424, 507\text{ cm}^{-1}$ ) alongside corresponding modes ( $431, 510\text{ cm}^{-1}$ ) in FM and AFM, respectively, in the inverse structure. This can be construed as evidence of this mode's correlation to the Mg cation. Even though the IR peak at  $690\text{ cm}^{-1}$  is of low intensity, its detection can be attributed to the inverse structure since no corresponding peak exists in this region in the normal phase. The simulated Raman spectra, which demonstrate splitting, elucidate a substantial amount of experimental data that detected more than five modes for Mg ferrite. Consequently, the provided assignments were reevaluated, taking into account the reduction in symmetry caused by lattice deformation. Similar to IR, the unique peak detected at the highest frequency region ( $727\text{ cm}^{-1}$ ) in Raman spectra can be considered as evidence for inverting the spinel structure. Unlike the  $690\text{ cm}^{-1}$  peak in IR, this peak has a detectable intensity and is observed in most of the experimental data. In summary, this study invites us into a world where the inversion degree and spin arrangement of magnesium ferrite display substantial impacts on the material's properties. The findings not only contribute to the scientific understanding of these materials but also open up new alleys for exploration, fostering future developments in material science.

## Author contributions

Dr Tahani Saad Almutairi contributed in conceptualizing and designing the study, curating data, performing the formal analysis, leading the investigation, drafting the manuscript, and revising it critically for important intellectual content.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

The author extends his thanks to Taibah University and the Deanship of Scientific Research for their generous support, offering both essential facilities and an encouraging research atmosphere that contributed to conducting this study within the Department of Chemistry.



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