

Raman scattering in substituted strontium orthoferrite $\text{La}_{0.5}\text{Sr}_{0.5}\text{FeO}_{3-\delta}$ at high pressure

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ABSTRACT

The Raman spectra of polycrystalline sample of antiferromagnetic orthoferrite $\text{La}_{0.5}\text{Sr}_{0.5}\text{FeO}_{3-\delta}$ with Néel temperature $T_N \approx 410$ K were measured in the temperature range 300–500 K as well as at room temperature and high pressure up to 18 GPa. Pressure dependence of the observed high-energy band at ~ 1400 cm^{-1} differs from the double frequency dependence of the strongest band at ~ 700 cm^{-1} , which indicates most likely the two-magnon nature of the former band, in agreement with temperature behavior of its intensity. Anomalies in the spectral width at $P > 15$ GPa points to a possible phase transition at high pressures.

1. Introduction

Perovskite orthoferrites $\text{R}_{1-x}\text{A}_x\text{FeO}_{3-y}$, where R is a rare earth element, A – Ba, Ca, or Sr, have unusual electrical, magnetic, and catalytic properties and are promising materials in a wide variety of fields, for example, as electrode materials for fuel cells, catalysts, chemical sensors, optoelectronic devices, magnetic memory, etc. [1–3]. Variations in synthesis conditions (atmosphere, temperature, cooling rate) can significantly change their properties [4]. Importantly, that ions of the transition metal Fe in these systems have mixed valence states, Fe^{3+} and Fe^{4+} , which can be caused by introduction of divalent ions (A) into the places of the trivalent element (R) or by formation of oxygen vacancies [4].

Lanthanum orthoferrite LaFeO_3 (LFO), belonging to these perovskite type oxides, is a very important *p*-type semiconducting material with a middle-range band gap ~ 2.5 eV and distinct optoelectronic properties [5]. This compound has an orthorhombic structure with the space group *Pbnm*. Doping at the La site with various metal ions such as Sr, Ca or Ba modifies LFO significantly and lattice parameters, structural, optical, catalytic, electrical properties can be changed considerably by doping [6–8]. Iron ions in LFO are in a trivalent state Fe^{3+} and have an octahedral oxygen environment FeO_6 , while the O^{2-} anions between the octahedra produce a superexchange antiferromagnetic (AFM) interaction between Fe^{3+} ions [9]. Strength of the superexchange interaction between Fe^{3+} ions increases with the angle θ of the $\text{Fe}^{3+}\text{--O}^{2-}\text{--Fe}^{3+}$ bond [5] and LFO has the largest bond angle in the orthoferrite family,

resulting in the highest Néel temperature $T_N \approx 750$ K [10]. Partial substitution of trivalent La by bivalent Sr leads to increase in the valence state of iron ions from Fe^{3+} to Fe^{4+} , resulting in the appearance of holes and significant decrease in the resistivity at room temperature. Substitution also leads to weakening of the AFM order in $\text{La}_{1-x}\text{Sr}_x\text{FeO}_{3-y}$ and T_N decreases strongly with increasing of the Sr content [11].

For studying of the magnetically ordered systems inelastic neutron scattering and optical Raman spectroscopy are the most informative methods [12,13]. One should note that the ideal ABO_3 perovskite has a cubic symmetry and thus should not have Raman-active phonon due to symmetry reasons [5]. However, in most real perovskites the ideal cubic structure is broken, which leads to appearance of Raman-active phonon modes in the Raman spectra [12–15]. The strong coupling of the electron system to such phonons in perovskites leads to the extreme sensitivity of the Raman-active phonon bands to the oxygen content and a significant temperature dependence of their energy [16,17]. Classification of phonon modes in the region below 1000 cm^{-1} was studied in numerous works and is quite well defined [14]. For example, modes below 200 cm^{-1} in LaFeO_3 are referred to lattice vibrations of heavy lanthanum. Modes in the range of 200–500 cm^{-1} (like bands Ω_0 and Ω_1 for the presented samples in Fig. 1) are attributed to various vibrations of light oxygen ions in inclined FeO_6 octahedra and a strong mode at $\sim 600\text{--}700$ cm^{-1} is usually referred to the in-phase stretching vibration of Fe–O bonds [15–19]. We emphasize that despite of more than two decades of studies still there is no consensus about the nature of some Raman modes in orthoferrites at present. Firstly, it concerns the mode in

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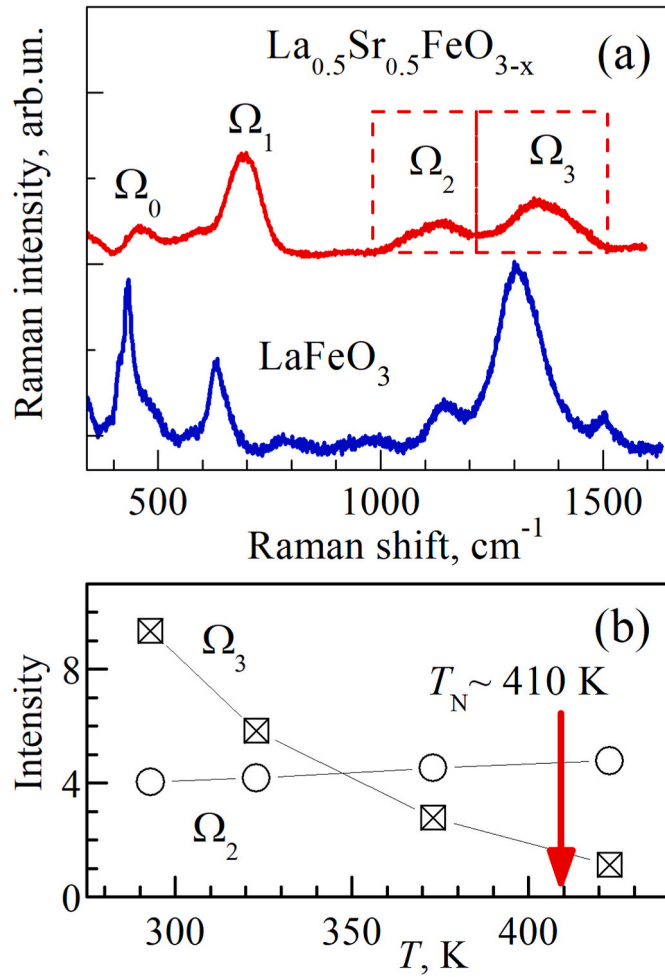


Fig. 1. (a) Raman spectra of LaFeO_3 and of the annealed in vacuum (see text) substituted orthoferrite $\text{La}_{0.5}\text{Sr}_{0.5}\text{FeO}_{3-\delta}$ with $T_N \approx 410$ K at ambient conditions ($T = 290$ K and $P = 1$ atm.). Broad and featureless background was subtracted manually. Spectra are shifted for clarity. (b). Temperature dependence of the spectrally integrated intensities for the Ω_2 and Ω_3 Raman bands in $\text{La}_{0.5}\text{Sr}_{0.5}\text{FeO}_{3-\delta}$. The lines are guides for eye.

the range of $\sim 600\text{--}700\text{ cm}^{-1}$, which is usually strong in intensity compare to others, like in the case of the studied substituted orthoferrite $\text{La}_{0.5}\text{Sr}_{0.5}\text{FeO}_{3-\delta}$ (Fig. 1). In some publications this band is concluded as not a first-order Raman mode [14] but rather supposed that it is caused by a two-phonon scattering or assigned to impurity-related scattering (see Ref. [12] and references therein).

At the same time, for orthoferrites there is still a principal uncertainty in interpretation of the high energy modes above 1000 cm^{-1} (Ω_2 and Ω_3 in Fig. 1). Because of their high energy, some authors attribute these modes to the magnetic two-magnon scattering [15,18], but another authors consider them as two-phonon combinations or defect scattering [5,19]. Only studies in a broad temperature range, below and above the Néel temperature T_N can clarify this situation, as in works [18–20]. For example, in work [19] LaFeO_3 was studied in a wide temperature range (80–873 K) below and above its $T_N \approx 750$ K. A significant decrease in the intensity of the pronounced high energy band at Raman frequency $\sim 1300\text{ cm}^{-1}$ (band Ω_3 in Fig. 1) was observed when heated up the sample but without complete disappearance of the band above T_N . Despite of such correlation, the authors of [19] concluded that this band has a two-phonon origin caused by the Fröhlich interaction, which activates infrared-active phonons and their combination scattering. On the other hand, it is well known that two-magnon scattering band in AFM perovskites can be observed not only below the Néel

temperature but also well above T_N due to correlations of magnetic moments [13]. Thus, studies in a broad temperature range, below and above the Néel temperature are quite necessary.

Interesting criteria for distinguishing of the two-phonon and two-magnon scattering bands was proposed in work [20] where different baric behavior under high-pressure was considered. Generally, pressure can be also used to tune the material's structure, electronic bands and other parameters. The pressure dependence of the two-phonon modes typically has a double slope as compared to the single phonon Raman-active modes. In contrast, pressure dependencies of the two-magnon scattering band may have completely different slope which is defined by a nature of scattering mechanism [20,21]. Unsuitable experimental conditions had not allowed to check this conclusion in Ref. [20] so it remains a challenge. Later it was found experimentally and discussed analytically that hydrostatic pressure produces strong relative shift for the magnetic constants which typically is much larger than that for phonons [21]. For example, the dependence of the superexchange interaction constant J on the distance d between the transition metal and anion scales as $J \propto d^{-n}$ in K_2NiF_4 with $n = 9.5 \pm 0.5$, $n = 7\text{--}8$ in NiO , $n = 5\text{--}6$ in La_2CuO_4 and Eu_2CuO_4 [21]. Contrary, much weaker dependence for phonon frequencies $\omega_{ph} \propto d^{-n}$ with $n \approx 1.5$ was observed in isostructural manganites, containing octahedral MnO_6 [22]. Phase transitions at high-pressures in LaFeO_3 were studied by Etter et al. using powder synchrotron X-ray diffraction measurements [23]. It was found that in this material a second-order structural phase transition from space group $Pbnm$ to $Ibmm$ takes place at ~ 21 GPa and then at ~ 38 GPa a first-order phase transition from the high-spin to low-spin Fe^{3+} ions occurs [23]. LaFeO_3 was studied in details as well using high-pressure Raman spectroscopy and a big progress was achieved in its understanding [24]. To the best of our knowledge there are no Raman scattering studies in the substituted orthoferrites at high-pressure.

In this paper, polycrystalline sample of AFM orthoferrite $\text{La}_{0.5}\text{Sr}_{0.5}\text{FeO}_{3-\delta}$ (orthorhombic phase $Pbnm$) was studied by Raman spectroscopy at room temperature in the pressure range up to 18 GPa and in a wide temperature range 300–500 K at ambient pressure. Strong suppression of the scattering intensity above $T_N \approx 410$ K and quite unusual pressure behavior were observed for the characteristic high-energy band $\sim 1300\text{--}1400\text{ cm}^{-1}$, pointing to its two-magnon scattering nature, in contrast to the band $\sim 1100\text{ cm}^{-1}$, which retains its intensity over the entire temperature range and thus ascribed to the two-phonon scattering.

2. Materials and methods

Polycrystalline $\text{La}_{1-x}\text{Sr}_x\text{FeO}_{3-\delta}$ ($x = 0$ and 0.5) samples were synthesized by the sol-gel method using Sr, Fe, and La nitrates in a stoichiometric ratio as initial reagents. Details of preparation of the samples, their composition and structure are described in Ref. [25]. The samples are conglomerates of fused particles ranging in size from fractions of a micron to tens of microns. Heat treatment does not significantly affect the particle size and shape. Absence of distinct faces in the microcrystals doesn't allow to perform polarization resolved measurements. Note that the $\text{La}_{1-x}\text{Sr}_x\text{FeO}_{3-\delta}$ family of strontium orthoferrites is a compound with an anion-deficient perovskite type structure (the symbol δ characterizes the oxygen vacancy content), and Fe cations can have a mixed valence state (Fe^{3+} or Fe^{4+}). The physical properties of these oxides are extremely sensitive to the oxygen content, which significantly depends on the synthesis and heat treatment conditions. In particular, lanthanum orthoferrite LaFeO_3 has complete oxygen stoichiometry, which is confirmed by Mössbauer spectroscopy. X-ray diffraction analysis indicates the initial orthorhombic phase of $Pbnm$ synthesized samples [25]. After synthesis, the $\text{La}_{1-x}\text{Sr}_x\text{FeO}_{3-\delta}$ samples were annealed in vacuum (10^{-3} torr) at a temperature of $T^\circ = 650^\circ\text{C}$ for 10 h to reduce the oxygen content and create oxygen vacancies in the immediate environment of iron ions, converting all of them to the trivalent state of Fe^{3+} . It is quite necessary because previously we found that significant

proportion of Fe^{4+} ions in non-annealed sample $\text{La}_{0.5}\text{Sr}_{0.5}\text{FeO}_{3-\delta}$ leads to complete suppression of phonon modes [26]. According to the Mössbauer spectroscopy data, the oxygen content in this annealed sample is 2.76 ± 0.05 . Magnetic studies give the Néel temperature of $T_N \approx 410$ K for the annealed sample $\text{La}_{0.5}\text{Sr}_{0.5}\text{FeO}_{3-\delta}$ [26].

Raman spectra were measured in the backscattering geometry on a setup with a home-made optical thermostat, designed to measure Raman scattering in micro-samples from room temperature to $T^\circ = 750$ K. The stabilization system ensures the accuracy of temperature maintenance $\pm 4^\circ\text{C}$. The optical part of the setup includes an Acton SpectraPro-2500i spectrograph with a -70°C cooled CCD Pixis2K detector and an Olympus BX51 microscope. A continuous solid-state single-mode laser with a wavelength of $\lambda^\circ = 532$ nm was used to excite Raman scattering. The laser beam was focused on the sample at a spot of $\sim 5\text{ }\mu\text{m}$ by Olympus SLMPLN lens with a magnification of $\times 50$, numerical aperture of 0.35 and working distance of 18 mm. The laser radiation line in the scattered beam was suppressed using an edge filter for $\lambda^\circ = 532$ nm with an optical density of $\text{OD}^\circ = 6$ and a bandwidth shift of $\sim 100\text{ cm}^{-1}$, and the intensity of laser excitation immediately in front of the sample was $\sim 1\text{ mW}$. In the high-pressure Raman scattering measurements unoriented crystallites with size of $\sim 100 \times 100\text{ }\mu\text{m}$ were loaded into a high-pressure diamond-anvil cell as was used in our previous publication [27]. Small ruby chips were included in the sample chamber to allow pressure calibration with accuracy to $\pm 0.1\text{ GPa}$ using the R_1 ruby fluorescence line. The pressure transmitting medium was a 4:1 mixture of methanol:ethanol.

One should note specially that in present study of polycrystalline samples the homogeneity of the samples was specially checked and reproducibility of the Raman spectra from different microcrystals was verified. Such verification allows us to reject the presence of the secondary phases in studied material with rather complex synthesis and annealing treatment, in accordance with X-ray diffraction analysis and Mössbauer spectroscopy [25]. For presentation were selected the most intense spectra with better signal-to-noise ratio and low scattered laser background.

3. Results

3.1. Raman scattering in lanthanum orthoferrites

Raman spectra of the lanthanum orthoferrite LaFeO_3 and strontium substituted orthoferrite $\text{La}_{0.5}\text{Sr}_{0.5}\text{FeO}_{3-\delta}$ at room temperature and atmospheric pressure are presented in Fig. 1. It can be seen that both samples show pronounced Raman bands below 1000 cm^{-1} with a strong spectral band Ω_1 at $\sim 650\text{--}700\text{ cm}^{-1}$ (Fig. 1a). In accordance with studies on structurally related compounds, this band usually is ascribed to the in-phase stretching of Fe–O bond [15–19]. As we mentioned in introduction, by now there is no unambiguous interpretation about origin of this mode and in present studies without polarization resolved measurements we cannot present a definite proof of any point of view. In this context we note that exact origin of this band is not significant for present study because the main interest concerns the nature of another band, namely of the high energy band Ω_3 (see later).

In LaFeO_3 lanthanum orthoferrite, which crystallizes in the orthorhombic phase, the phonon bands are pronounced. Similarly, in the substituted orthoferrite $\text{La}_{0.5}\text{Sr}_{0.5}\text{FeO}_{3-\delta}$ with orthorhombic structure as well, less intense Raman bands are clearly seen, but they are strongly broadened and blueshifted compared to LaFeO_3 (Fig. 1). Such a significant broadening of all Raman lines in $\text{La}_{0.5}\text{Sr}_{0.5}\text{FeO}_{3-\delta}$ is naturally attributed to the local disorder when Sr substitutes La. Also a strong microscopic inhomogeneity of the charge state of $\text{Fe}^{4+}/\text{Fe}^{3+}$ ions and the associated oxygen vacancies arising during vacuum annealing contributes additionally to disorder. In spectra of both orthoferrites, LaFeO_3 and lanthanum substituted orthoferrite $\text{La}_{0.5}\text{Sr}_{0.5}\text{FeO}_{3-\delta}$, one can see also two rather broad high energy bands Ω_2 and Ω_3 at $\sim 1100\text{--}1200\text{ cm}^{-1}$ and at $\sim 1300\text{--}1400\text{ cm}^{-1}$, respectively. Temperature dependencies of

intensity of these two bands for $\text{La}_{0.5}\text{Sr}_{0.5}\text{FeO}_{3-\delta}$ are shown in Fig. 1b. One can see striking difference between dependencies of different bands. These high energy bands and temperature dependence of their intensities will be discussed in details later.

3.2. Raman scattering at high-pressure

Fig. 2 shows Raman spectra $I(\omega)$ of the substituted orthoferrite $\text{La}_{0.5}\text{Sr}_{0.5}\text{FeO}_{3-\delta}$ at high-pressures and room temperature. Optical phonon of diamond anvils ($\sim 1332\text{ cm}^{-1}$ at ambient pressure) obscures the part of spectra in the range of $\sim 1100\text{--}1400\text{ cm}^{-1}$ at ambient pressure. However, the diamond line has relatively slow pressure dependence, so that the high energy part of spectra could be well resolved above $P = 2\text{ GPa}$, as shown in Fig. 2. Note, that the broad and featureless background caused by the fluorescence from the sample for clarity was subtracted manually from each spectrum. One can see that the Raman band Ω_1 as well as the high energy band Ω_3 show gradual blue-shift with pressure (Fig. 2). The spectral positions of both bands Ω_1 and Ω_3 , plotted as functions of pressure, are presented in Fig. 3a. Because of both bands are rather broad, their positions were calculated as first spectral moments, i.e. spectral weights of the corresponding band:

$$\omega_{av} = \frac{\int \omega I(\omega) d\omega}{\int I(\omega) d\omega} \quad (1)$$

Also the full width at half amplitude (FWHA) for both bands as a function of pressure is shown in Fig. 3b. Note, that contrary to the Raman band Ω_1 , the width FWHM for the high energy band Ω_3 changes considerably.

4. Discussion

Turning to discussion of the obtained results we remind at first, that for antiferromagnetic (AFM) orthoferrites the interpretation of the high energy modes above 1000 cm^{-1} (like wide bands Ω_2 and Ω_3 in Fig. 1a) is still controversial, as it was considered in introduction. In some works such high energy Raman bands were assigned to the two-phonon combination or defect scattering [5,19] while another authors attributed these bands to the magnetic two-magnon scattering [15,18], which is

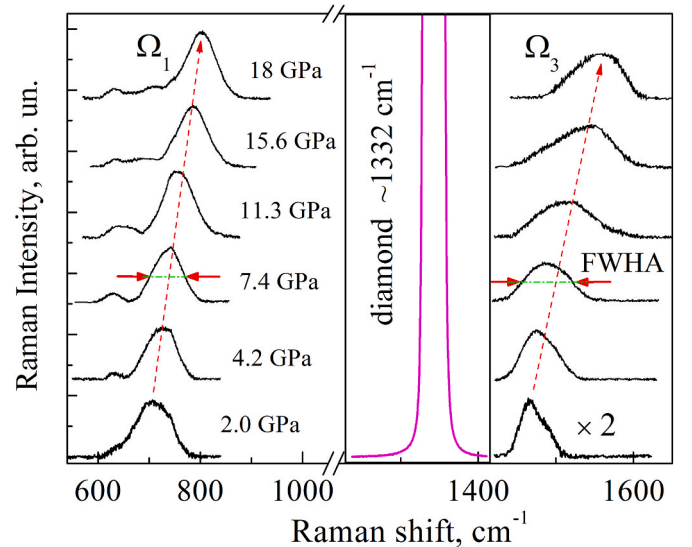


Fig. 2. Raman spectra $I(\omega)$ of the substituted orthoferrite $\text{La}_{0.5}\text{Sr}_{0.5}\text{FeO}_{3-\delta}$ at different -pressure and room temperature (sequentially shifted up vertically, background is subtracted). The inset shows the spectrum of diamond at normal pressure. The part of each spectrum at high energy above 1400 cm^{-1} was multiplied $\times 2$ for clarity. Arrows for bands Ω_1 and Ω_3 at $P = 7.4\text{ GPa}$ illustrate the width FWHM for both bands.

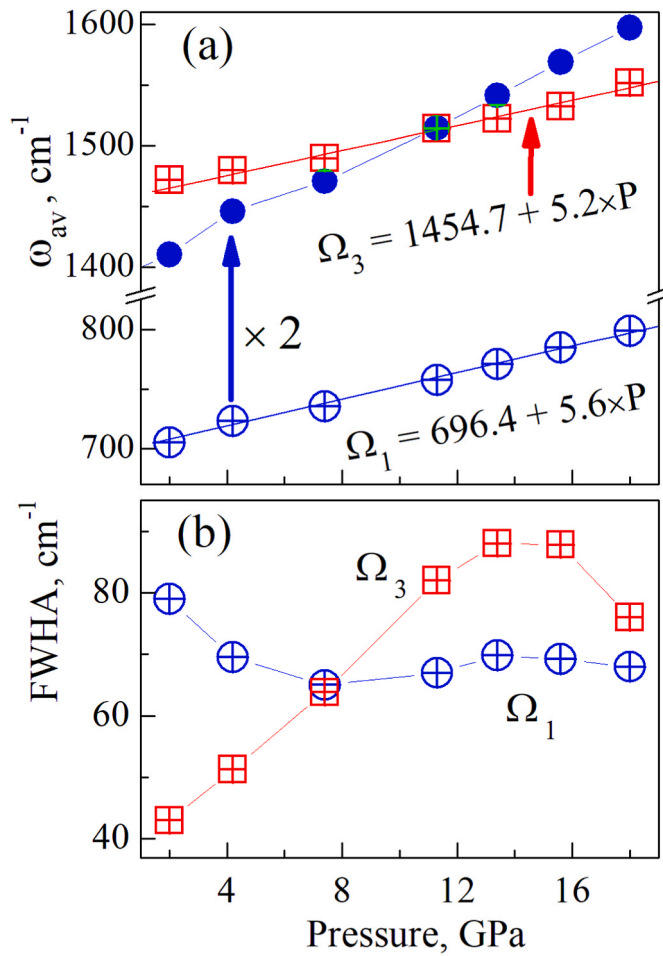


Fig. 3. (a) Pressure dependence of Raman frequencies ω_{av} for Raman band Ω_1 and high energy band Ω_3 at room temperature. Solid lines are linear fittings. The pressure coefficients for each mode are shown. Blue filled circles denote the pressure dependence of the multiplied twice Raman band $\Omega_1(P)$ as illustrated by arrow. (b). Spectral width (FWHA) of both bands as a function of pressure at room temperature. The lines are guides for eye.

supported by a significant drop of their intensity upon approaching Néel temperature T_N . On one hand, the presence of such weakened bands above T_N in the temperature dependent Raman spectra raises question on their magnetic origin, as it was emphasized by Andreasson et al. [19]. On the other hand, in accordance with different theoretical approaches, a role of the AFM fluctuations is still significant even above T_N so that the intensity of the two-magnon magnetic scattering may remain appreciable up to temperatures as high as twice T_N (see Refs. [12,13] and references there). As one can see in Fig. 1b, the band Ω_3 in $\text{La}_{0.5}\text{Sr}_{0.5}\text{FeO}_{3-\delta}$ shows strong intensity drop upon increasing temperature to $T_N \approx 410$ K while the band Ω_2 demonstrates completely opposite behavior and even slightly grows with temperature. This kind of temperature behavior is fully consistent with previously observed behavior of the two-magnon bands in AFM perovskites [13,18] and gives us the reasons to attribute the band Ω_3 to the two-magnon Raman scattering. As for the band Ω_2 at ~ 1150 cm^{-1} , it can be attributed to the two-phonon scattering as a combinations of two modes: Ω_0 (~ 460 cm^{-1}) and Ω_1 (~ 680 – 700 cm^{-1}) at ambient conditions (Fig. 1a).

Such an interpretation of the band Ω_3 for substituted orthoferrite $\text{La}_{0.5}\text{Sr}_{0.5}\text{FeO}_{3-\delta}$ is also supported by results of high-pressure Raman studies at room temperature, presented in Figs. 2 and 3. Pressure dependence of the two-phonon band has a double slope as compared to the single phonon Raman-active mode while the pressure dependencies of the two-magnon scattering bands have quite different slopes [20]. The

slope for the two-magnon band is defined by a nature of magnetic ordering mechanism and typically is much stronger than that for phonons [20,21]. On one hand, in the studied substituted orthoferrite $\text{La}_{0.5}\text{Sr}_{0.5}\text{FeO}_{3-\delta}$ the doubled pressure dependence of the Raman band Ω_1 , shown in Fig. 3a by the arrow, goes much steeper than the experimental dependence $\omega_{av}(P)$ of the band Ω_3 , thus rejecting interpretation of the band Ω_3 as a two-phonon combination of the band Ω_1 . On the other hand, assuming the two-magnon nature of the band Ω_3 , one need explain unusually weak pressure dependence of this band, weaker even than the dependence of the Raman band Ω_1 (see slopes in Fig. 3a), which is quite untypical for magnetic scattering [20,21]. Such kind of behavior of the two-magnon scattering band, which spectral position is proportional to the AFM exchange integral J , could be related to initially strong overlap of the atomic Fe^{3+} and O^{2-} wavefunctions, so that further compression does not lead to substantial increase in superexchange interaction. Really, simple estimations of J for a cubic G-type AFM ordering in LaFeO_3 give large value of $J \sim 33$ meV (≈ 270 cm^{-1}) [15] as compare to classical antiferromagnetic compounds like K_2MnF_4 or K_2NiF_4 with $J \sim 6$ – 77 cm^{-1} [12]. However, these arguments are rather qualitative. A more complete understanding of the superexchange interaction nature in orthoferrites and its quantitative description requires appropriate theoretical analysis and model calculations. Also, to establish the dependence of the superexchange constant J on the distance d between the transition metal and anion (Fe–O bond length) in the distorted FeO_6 octahedron additional thorough X-ray diffraction measurements are necessary also, similar to ones made in Ref. [23]. Such studies could clarify another interesting and intriguing feature of spectra at high-pressure, namely a broadening of the high energy band Ω_3 with pressure until $P \sim 15$ GPa while at higher pressures $P > 15$ GPa it gets narrow again (Figs. 2 and 3). Contrary, the full width at half amplitude (FWHA) of the Raman band Ω_1 (~ 80 cm^{-1} at ambient conditions) changes insignificantly in the whole pressure range (Fig. 3b). One may suggest that observed change in broadening of the high energy band Ω_3 , identified in present research with the two-magnon scattering band, is related to some kind of magnetic transition in substituted strontium orthoferrite $\text{La}_{0.5}\text{Sr}_{0.5}\text{FeO}_{3-\delta}$, like the first-order phase transition in LaFeO_3 from the high-spin to the low-spin state of Fe^{3+} ions at $P \sim 38$ GPa [23].

5. Conclusions

In this research we show that additionally to conventional approaches to study of antiferromagnetic materials by varying temperature below and above the Néel point [28] one can effectively use the high pressure technique for clarifying the nature of the high-energy bands in Raman spectra of antiferromagnetic orthoferrites. Performed Raman studies of polycrystalline sample of substituted orthoferrite $\text{La}_{0.5}\text{Sr}_{0.5}\text{FeO}_{3-\delta}$ at high pressure (up to $P = 18$ GPa) revealed difference in pressure behavior of the high-energy band at ~ 1400 cm^{-1} from the expected doubled combination of the Raman band at ~ 700 cm^{-1} , thus indicating the two-magnon nature of this high-energy band. Strong drop of intensity of this high-energy band upon approaching the Néel temperature of this compound directly confirms such an interpretation.

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CRediT authorship contribution statement

S.V. Zaitsev: Conceptualization, Data curation, Formal analysis, Funding acquisition, Project administration, Supervision, Writing – original draft, Writing – review & editing. **V.D. Sedykh:** Data curation, Methodology, Resources, Software, Validation, Writing – review &

editing. **K.P. Meletov**: Conceptualization, Funding acquisition, Investigation, Methodology, Resources, Software, Visualization, Writing – review & editing.

Declaration of competing interest

The authors of this work declare that they have no conflicts of interest.

Data availability

No data was used for the research described in the article.

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