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# Lattice and magnetic dynamics of a quasi-one-dimensional chain antiferromagnet $\text{PbFeBO}_4$

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## Abstract

A group of recently synthesized orthorhombic  $Pnma$  crystals  $\text{PbMBO}_4$  ( $M = \text{Cr, Mn, Fe}$ ) demonstrates a number of unusual structural and magnetic properties. We report on polarized Raman scattering study of the lattice and magnetic dynamics in single crystals of an antiferromagnet  $\text{PbFeBO}_4$  below and above  $T_N = 114$  K. Polarization properties of the observed magnetic excitations below  $T_N$  as well as intense quasi-elastic scattering support the quasi-one-dimensional character of the magnetic structure of  $\text{PbFeBO}_4$ . Frequency overlapping of magnetic excitations and low-frequency phonons in the range of  $90\text{--}200\text{ cm}^{-1}$  leads to pronounced asymmetric anomalies thus confirming intrinsic coupling of magnetic and lattice subsystems. This conclusion is also supported by observation of anomalous temperature behaviour of higher frequency phonons in the vicinity of  $T_N$ . Experimental investigations are supported by relevant magnetic symmetry analysis which allows us to explain previously observed anomalous results.

Keywords: Raman scattering, spin and phonon excitations, spin-phonon interaction, antiferromagnetism, magnetic symmetry analysis, two-magnon scattering

(Some figures may appear in colour only in the online journal)

## 1. Introduction

There is a large family of mullite-type boron compounds which contains the chains of edge-sharing  $\text{MO}_6$  octahedra where  $M$  is an octahedrally coordinated cation in the chains [1]. A new group of materials with the general formula  $\text{PbMBO}_4$  ( $M = \text{Cr, Mn, Fe}$ ) crystallizing in a previously unknown type of chains of edge-sharing  $\text{MO}_6$  octahedra similar to those in mullites was discovered recently [2]. Structure determination and analysis based on both the x-ray and neutron powder diffraction data led to the orthorhombic  $Pnma$  space group,  $Z = 4$ , with the edge-sharing  $\text{MO}_6$  octahedra running along the  $b$  axis [2].

In this new group,  $\text{PbFeBO}_4$  and  $\text{PbCrBO}_4$  both are antiferromagnets with  $T_N = 114$  K and 9 K, respectively [2, 3]. A big surprise in these investigations was the observation that

$\text{PbMnBO}_4$  is *ferromagnetic* with  $T_C = 31$  K because ferromagnetism is a very rare phenomenon among the  $3d$  insulators. We may suppose that this phenomenon is due to the Jahn–Teller  $\text{Mn}^{3+}$  ( $3d^4$ ) ion which strongly distorts the local environment and thus favoring ferromagnetic interaction. Magnetic susceptibility measurements of single crystals of  $\text{PbFeBO}_4$  showed that the spins of  $\text{Fe}^{3+}$  ions ( $3d^5$ ,  $S = 5/2$ ) are antiferromagnetically ordered along the  $c$  axis [3]. Magnetic and dielectric studies of  $\text{PbFeBO}_4$  and  $\text{PbMnBO}_4$  showed a strong anisotropy of both these properties [4, 5]. Density-functional analysis (DFT) of exchange interactions, magnetic properties and electronic structure for the large group of magnetic  $\text{PbMBO}_4$  compounds was reported in [6, 7]. X-ray, neutron diffraction, Raman spectroscopy and DFT calculations were applied for the detailed studies of  $\text{PbFeBO}_4$  polycrystalline samples where anisotropic lattice expansion was observed [8].

However, up to now several physical properties of PbFeBO<sub>4</sub> remain unstudied and unexplained. For example, the presence of the forbidden neutron diffraction peaks for the suggested magnetic structure [2]; a well pronounced kink on the susceptibility curves, as well as a strong anisotropy of susceptibility at  $T \rightarrow 0$  in absence of uncompensated magnetic moment [3]. A question remains about a short-range-order magnetic phase transition at  $T \approx 280$  K [2] which was not confirmed in more recent studies [3].

In this work we report comprehensive symmetry analysis based on both magnetic space group and representation theory which allowed us to explain earlier mentioned inconsistencies by proposing symmetry breaking involving two magnetic representations. Polarized Raman scattering study is employed for investigating lattice and magnetic excitations in PbFeBO<sub>4</sub> ( $T_N = 114$  K) in a broad temperature range from 10 to 600 K which covers both the antiferromagnetic and paramagnetic regions. Most symmetry-allowed phonons are found and their polarization properties and temperature dependencies are investigated. Polarization properties of the observed magnetic excitations as well as quasi-elastic scattering above  $T_N$  support the quasi-one-dimensional character of the magnetic structure of PbFeBO<sub>4</sub>. Frequency overlapping of magnetic excitations and phonons, spin-phonon interaction and pronounced anomalies for several phonons around  $T_N$  confirm intrinsic coupling between magnetic and lattice subsystems.

## 2. Theoretical analysis

### 2.1. Crystal structure and lattice excitations

Crystal structure of PbFeBO<sub>4</sub> is shown in figure 1. It belongs to the orthorhombic point group  $mmm$ , the space group  $Pnma$  (#62,  $Z = 4$ ) [2]. It can be seen that the crystal structure is built of single chains of strongly distorted edge-sharing FeO<sub>6</sub> octahedra elongated along the  $b$  axis which provide a strongly anisotropic one-dimensional (1D) character of the whole structure, see figure 1 obtained with the use of the VESTA [9]. The chains are linked by both the BO<sub>3</sub> groups and the Pb<sup>2+</sup> ions with 6s<sup>2</sup> lone electron pair in the fourfold coordination sites. We note that links between the magnetic ions via BO<sub>3</sub> and/or BO<sub>4</sub> groups are typical for many other oxyborates [10–12]. The presence of the BO<sub>3</sub> groups and the Pb<sup>2+</sup> ions between the FeO<sub>6</sub> magnetic chains weakens the exchange interaction between the chains due to (i) increase of the distance between iron ions and (ii) increased path of the Fe–O–O–Fe link instead of Fe–O–Fe one. Another characteristic mark of the chains is absence of the inversion center between magnetic ions, which can lead to the Dzyaloshinskii–Moriya (DM) interaction. It is supposed that the rigid BO<sub>3</sub> groups are responsible for the distortions of the FeO<sub>6</sub> chains, see figure 1(b), and the anisotropic lattice expansion [8]. Moreover, these groups are assumed to be responsible for inability to synthesize PbMBO<sub>4</sub> compounds with larger ions  $M = \text{Sc, Y, and In}$  [2]. Virtual compounds PbMBO<sub>4</sub> where  $M = \text{Ti, V, and Co}$  were recently analyzed using the DFT approach in [7] though no report on synthesis of such compounds is known.

The group-theory analysis leads to a following set of phonon modes in the center of the Brillouin zone at the  $\Gamma = 0$  point:

$$\Gamma = 11A_g + 7B_{1g} + 11B_{2g} + 7B_{3g} + 10A_u + 14B_{1u} + 10B_{2u} + 14B_{3u} \quad (1)$$

In this equation there are three acoustic modes  $B_{1u}$ ,  $B_{2u}$ , and  $B_{3u}$ ; thirty six Raman-active even  $g$ -modes; and thirty eight infrared (IR) polar modes active in reflection and absorption. Ten  $A_u$  modes are silent. Raman tensors have the following forms:

$$A_g = \begin{pmatrix} a & 0 & 0 \\ 0 & b & 0 \\ 0 & 0 & c \end{pmatrix}, B_{1g} = \begin{pmatrix} 0 & d & 0 \\ d & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix},$$

$$B_{2g} = \begin{pmatrix} 0 & 0 & e \\ 0 & 0 & 0 \\ e & 0 & 0 \end{pmatrix}, B_{3g} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & f \\ 0 & f & 0 \end{pmatrix} \quad (2)$$

These tensors show that the complete characterization of the Raman-active even modes requires measurements of three diagonal and three off-diagonal spectra. However, the shape and the size of available samples did not allow us to measure the spectra in pure ( $ab$ ) and ( $ac$ ) polarizations. The small size of the available samples did not allow us to study the IR spectra.

### 2.2. Magnetic symmetry analysis

According to recent magnetic measurements, PbFeBO<sub>4</sub> is an antiferromagnet below  $T_N = 114$  K [2–4]. Neutron diffraction study shows that magnetic wave vector is  $k = (0, 0, 0)$  and spins of the Fe<sup>3+</sup> ions ( $3d^5$ ,  $S = 5/2$ ) are oriented along the  $c$  axis [2], in agreement with magnetic susceptibility data [3]. These studies showed that behaviour of the magnetic susceptibilities at and below  $T_N$  is characteristic for the weak ferromagnets; however, no magnetic moment was found.

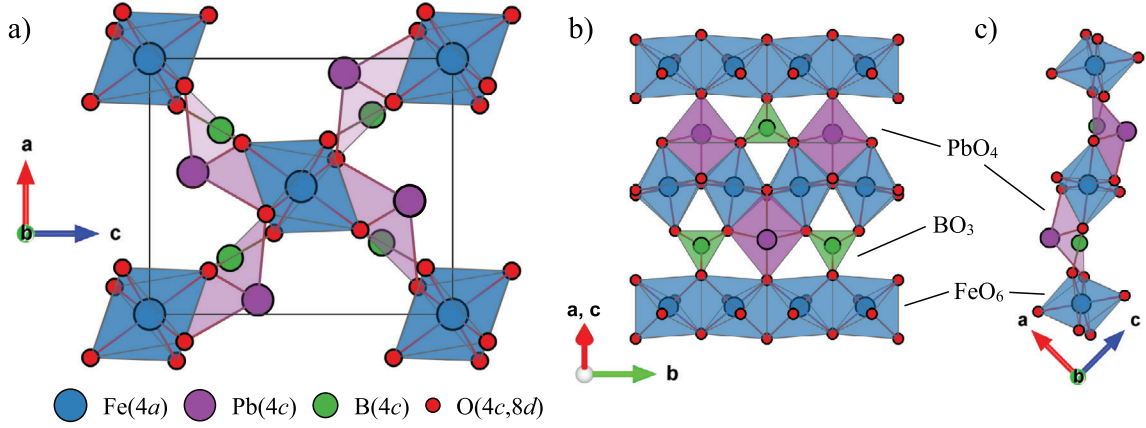
Up to now, no systematic symmetry analysis of admissible magnetic structures and specific effects in PbMBO<sub>4</sub> compounds was performed which could confirm or disregard particular magnetic effects such as ferromagnetism, weak ferromagnetism, piezomagnetism, magnetoelectric effect, etc [13]. For analyzing the magnetic structures either magnetic space group (MSG) analysis [14] or irreducible representations (*irreps*) method [15] can be used. However, the use of both of these methods can reveal some additional restrictions on possible magnetic structures. We performed such analysis by using both MAXMAGN program [16] and ISODISTORT code [17]. In both cases, the analysis begins from the paramagnetic gray space group  $Pnma1'$ . Group-subgroup graph obtained by the MSG analysis is shown in figure 2.

The four magnetic Fe<sup>3+</sup> ions in the unit cell of PbFeBO<sub>4</sub> occupy the following  $4a$  ( $\bar{1}$ ) positions:

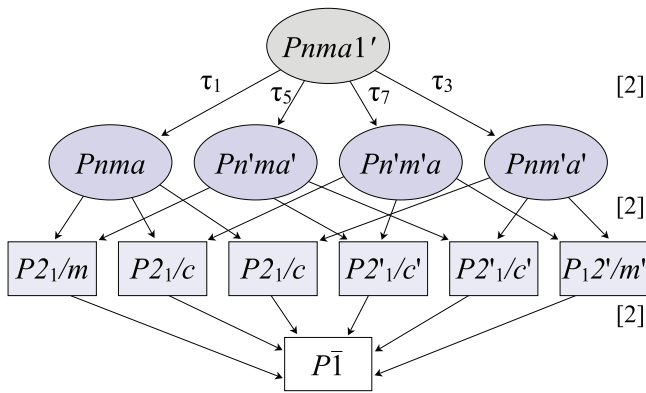
$$\text{Fe}_1(0, 0, 0); \text{Fe}_2(1/2, 1/2, 1/2); \text{Fe}_3(0, 1/2, 0); \text{Fe}_4(1/2, 0, 1/2) \quad (3)$$

The irreducible representations for these ions can be expanded in the following way:

$$\Gamma_{\text{Fe}(4a)} = 3\tau_1 + 0\tau_2 + 3\tau_3 + 0\tau_4 + 3\tau_5 + 0\tau_6 + 3\tau_7 + 0\tau_8 \quad (4)$$



**Figure 1.** (a) The (010) projection of crystal structure of  $\text{PbFeBO}_4$ . (b) Inter-connection of the  $\text{FeO}_6$  groups in the (10-1) projection. (c) Inter-connection of the  $\text{FeO}_6$  groups in the (010) projection. It is clear that there is no inversion center between neighbouring magnetic ions.



**Figure 2.** Possible magnetic symmetries for  $k = (0, 0, 0)$  for the paramagnetic phase with the space group  $Pnma1'$ . The  $k$ -maximal groups are highlighted with elliptical frames. Indices for group/subgroup pair are shown in square brackets.

The relevant basis spin functions are given in table 1. All representations are one-dimensional and therefore both methods mentioned above are equivalent. The first group in table 1 does not include operations with the time reversal but all the three others do. The basis functions of these three groups allow for a ferromagnetic component along  $x$ ,  $y$ , and  $z$  axis, respectively. From the point of view of the global symmetry, all vector/basis functions are equivalent and the resulting magnetic structure will be defined by the anisotropy. In this case, the main basis vector can induce small relativistic perturbations of the two other basis functions within *irrep* which will be responsible for the appearance of the weak ferromagnetism/antiferromagnetism.

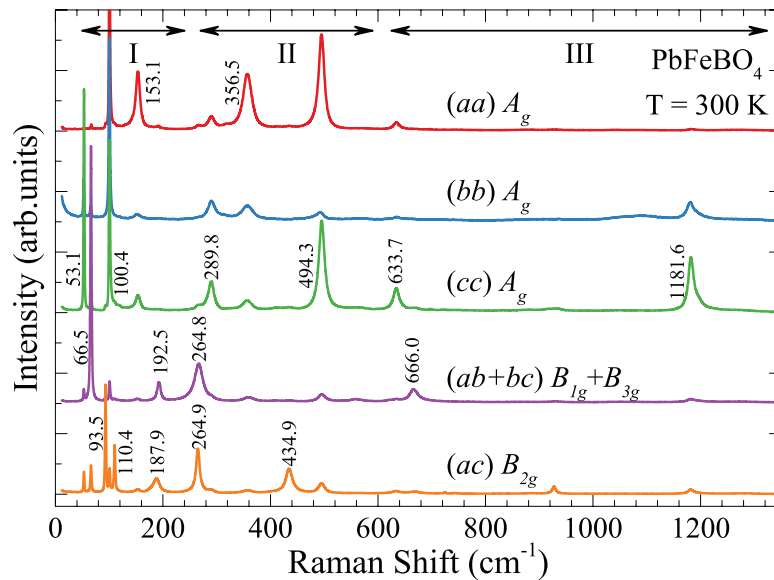
In order to find out which of the discussed above magnetic groups is realized in  $\text{PbFeBO}_4$  let us analyze the available experimental data on powder neutron diffraction experiments [2] and magnetic measurements [3]. A magnetic structure corresponding to the *irrep*  $\pi_1$  with the main basis vector  $\Psi_z$  was proposed in [2]. However, several magnetic "extra" peaks, namely (211), (222), (004) were observed which are forbidden for the basis functions of the  $Pnma$  group [16]. On the other hand, the magnetic susceptibility along the  $c$  axis is lower than the

**Table 1.** Basis function for irreducible representations for  $4a$  sites of Fe ions in  $\text{PbFeBO}_4$ .

<i>irrep</i>	Basis function	Spin components	MSG
$\pi_1$	$\Psi_x$	$S_1 + S_2 - S_3 - S_4$	$Pnma$
	$\Psi_y$	$S_1 - S_2 + S_3 - S_4$	
	$\Psi_z$	$S_1 - S_2 - S_3 + S_4$	
$\tau_3$	$\Psi_x$	$S_1 + S_2 + S_3 + S_4$	$Pnm'a'$
	$\Psi_y$	$S_1 - S_2 - S_3 + S_4$	
	$\Psi_z$	$S_1 - S_2 + S_3 - S_4$	
$\tau_5$	$\Psi_x$	$S_1 - S_2 - S_3 + S_4$	$Pn'ma'$
	$\Psi_y$	$S_1 + S_2 + S_3 + S_4$	
	$\Psi_z$	$S_1 + S_2 - S_3 - S_4$	
$\tau_7$	$\Psi_x$	$S_1 - S_2 + S_3 - S_4$	$Pn'm'a$
	$\Psi_y$	$S_1 + S_2 - S_3 - S_4$	
	$\Psi_z$	$S_1 + S_2 + S_3 + S_4$	

two others when temperature  $T \rightarrow 0$  [3] which proves that the spins are aligned antiferromagnetically along this axis. Other important experimental results are (i) nonvanishing magnetic susceptibility along all three orthorhombic axes (compensated antiferromagnetism) and (ii) a peak of susceptibility for  $H \parallel b$  at  $T_N = 114$  K [3] which is an intrinsic property of the weak ferromagnetism [18]. However, no magnetic moment is allowed for the proposed  $Pnma$  magnetic space group.

This inconsistency obliges us to assume that the magnetic symmetry of  $\text{PbFeBO}_4$  cannot be described by the  $k$ -maximal group and therefore a group  $P2_1/m$  of the lower symmetry should be applied. In this case, a magnetic phase transition should involve two magnetic representations  $\pi_1 \oplus \tau_5$ ; an alternative scenario is the structural distortions which may also take place. However no structural transition was experimentally observed. It should be noted, that phase transition between the point groups  $mmm$  and  $2/m$  is ferroelastic. The ratio of the group orders is equal to four which allows the existence of the two types of nontrivial magnetic domains with oppositely oriented weak ferromagnetic moments. Thus, the absence of the magnetic moment in magnetostatic measurements can be explained by these domains. Since no



**Figure 3.** Single-crystal polarized Raman scattering spectra at  $T = 300$  K for different diagonal and off-diagonal polarizations. Frequencies of the most intense phonons are marked. See text for details.

spin-flip or spin-flop transitions were observed in magnetic field up to the 28 T [3] strong anisotropy can be expected in  $\text{PbFeBO}_4$ . This kind of the analysis is also valid for other isostructural magnetics of the  $Pnma1'$  group. Finally, we add that the decisive determination of the magnetic structure of  $\text{PbFeBO}_4$  without any doubt requires single-crystal neutron-diffraction experiments.

### 3. Experimental

Single-crystal samples of  $\text{PbFeBO}_4$  were grown by spontaneous crystallization from a solution in a melt, for details see [3]. Samples were oriented with the use of the x-ray diffractometry. Only small millimeter-size crystals were available and this did not allow us to study all required polarizations for complete characterization of the lattice and magnetic excitations. Thin platelets of single crystals were of a green color similar to other well-known iron-boron compounds  $\text{FeBO}_3$  (dark green) [19] and  $\text{GdFe}_3(\text{BO}_3)_4$  (light green) [20]. The green color of iron borates stems from a transparency window around 2.3 eV in the optical absorption spectra [20]. Interestingly, another iron borate  $\text{Fe}_3\text{BO}_6$  is opaque because the window disappears due to the red shift of the fundamental band gap [21].

Raman scattering spectra were measured in the range of 10–2000  $\text{cm}^{-1}$  with the use of a Jobin-Yvon T64000 spectrometer equipped with a nitrogen-cooled CCD camera. The 532 nm (2.33 eV) Nd:YAG-laser line which falls in the transparency window was used as an excitation source. All measurements were done in the backscattering geometry for the diagonal ( $aa$ ), ( $bb$ ), ( $cc$ ), off-diagonal ( $ac$ ) and mixed ( $ab + bc$ ) polarization settings. A 50 $\times$  objective was employed both to focus the incident beam and to collect the scattered light. Temperature dependencies of the spectra were recorded in the range of 10–600 K using a helium closed-cycle cryostat (Cryo Industries, Inc.) and a nitrogen cryostat (Linkam).

### 4. Results and discussion

Figure 3 shows phonon Raman spectra measured in five different polarizations at the room temperature. Phonons of different types are summarized in table 2 and their frequencies are compared with previously observed in polycrystalline samples and obtained by the DFT calculations [8]. Observed phonons can be distributed over three characteristic spectral regions, marked in figure 3. In the low frequency range I from 50 to 250  $\text{cm}^{-1}$ , phonons are related to heavy  $\text{Pb}^{2+}$  ions (see [8] for more details). In the middle spectral range II from 250 to 600  $\text{cm}^{-1}$ , phonons are related to  $\text{FeO}_6$  octahedral groups. Phonons related to the rigid  $\text{BO}_3$  groups dominate in the high-frequency range III from 600 to 1300  $\text{cm}^{-1}$ . These high-frequency phonons (645, 926, 1207  $\text{cm}^{-1}$ ) are also observed in other magnetic oxyborates, for example in  $\text{FeBO}_3$  [22],  $\text{CuB}_2\text{O}_4$  [11],  $\text{Ni}_3(\text{BO}_3)_2$  [12], etc. Since there are four  $\text{BO}_3$  groups in the unit cell one might expect the presence of the Davydov splitting of the relevant phonons. However, no splitting was observed assuming it be hidden in line width. Some phonons are weak at room temperature but are readily detected at low temperature.

Raman spectra of  $\text{PbFeBO}_4$  were measured in the temperature range of 10–600 K that allowed us to observe several new features related to the lattice and magnetic dynamics. Along with conventional hardening of phonon frequencies and narrowing of phonon line width at low temperature related to the change of the lattice volume and anharmonic effects [23], some phonons demonstrated anomalous behaviour. For example, the 495  $\text{cm}^{-1}$  phonon of the  $A_g$  type shows anomalous hardening by 2  $\text{cm}^{-1}$  below  $T_N$ , see figure 4. According to [8] this phonon corresponds to symmetric O–Pb–O vibration. It is involved in the coupling within and between the  $\text{FeO}_6$  chains, as can be seen in figure 1, and therefore it is responsible for the spin-phonon interaction.

Temperature dependence of the specific phonon frequency can be used as a probe for investigating the spin-spin

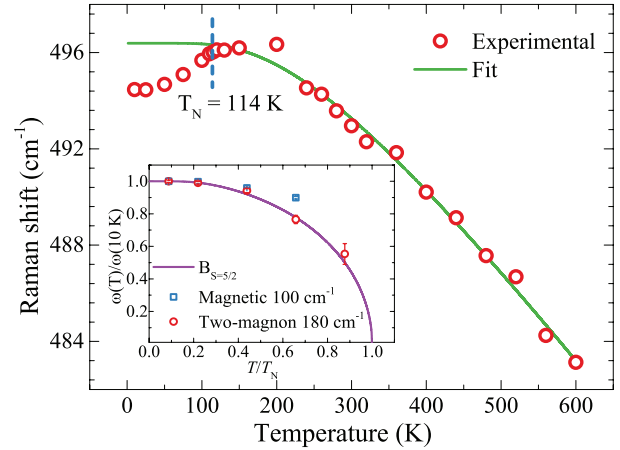
**Table 2.** Phonon frequencies of PbFeBO<sub>4</sub> (in cm<sup>-1</sup>) observed in single crystals (this work) in comparison with DFT calculations [8] and Raman scattering in polycrystalline samples [8].

This work	DFT [8]	Experimental [8]	Mode symmetry	Intensity
53.1	56.8	54.63	A <sub>g</sub>	S
66.5	67.6	67.9	B <sub>1g</sub>	S
67.1	70.5	66.9	B <sub>3g</sub>	W
93.5	95.9	92.5	B <sub>2g</sub>	S
100.4	97.4	100.7	A <sub>g</sub>	S
110.4	112.8	—	B <sub>2g</sub>	M
153.1	162.4	—	A <sub>g</sub>	M
177.3	194.9	191.1	B <sub>2g</sub>	VW
187.9	202.9	193.4	B <sub>3g</sub>	W
192.5	203.7	—	B <sub>1g</sub>	W
264.8	269.7	261.8	B <sub>1g</sub>	M
264.9	270.3	269	B <sub>2g</sub>	M
266.7	274.5	—	B <sub>3g</sub>	W
289.8	298.5	287.9	A <sub>g</sub>	M
318.2	325.4	—	A <sub>g</sub>	W
—	330.1	—	B <sub>3g</sub>	—
356.5	350.2	—	A <sub>g</sub>	M
361.0	367.2	—	B <sub>2g</sub>	W
368	373.8	359.9	B <sub>1g</sub>	VW
434.9	433.7	432.3	B <sub>2g</sub>	W
483.8	505	491.7	B <sub>3g</sub>	VW
494.3	507.9	505	A <sub>g</sub>	S
—	538.9	—	B <sub>2g</sub>	—
558.2	574.4	556.5	B <sub>1g</sub>	VW
—	625.1	634	B <sub>1g</sub>	—
—	628.4	—	B <sub>2g</sub>	—
633.7	636.1	—	A <sub>g</sub>	M
666.0	682.8	665.1	B <sub>3g</sub>	W
697.1	695.6	676	A <sub>g</sub>	VW
724.9	725.8	687	B <sub>2g</sub>	VW
927.7	942.1	925.5	B <sub>2g</sub>	W
932.7	957.1	—	A <sub>g</sub>	VW
1181.6	1221	1176	A <sub>g</sub>	M
1201	1238.4	1184.3	B <sub>3g</sub>	M
1241	1240.2	1195.7	B <sub>1g</sub>	M
1278	1319.9	—	B <sub>2g</sub>	M

Note: Intensity of the lines are given in the following notation: S–Strong, M–Medium, W–Weak, VW–Very Weak.

correlations via spin-phonon coupling [24, 25]. We must note that no anomaly was observed in our studies for any phonon around 280 K where a short-range ordering was supposed to take place on the basis of magnetic susceptibility measurements of polycrystalline samples [2]. Recent investigations showed that those anomalies were most probably due to impurities of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> while no anomalies are found in this temperature range in single crystals [3, 4].

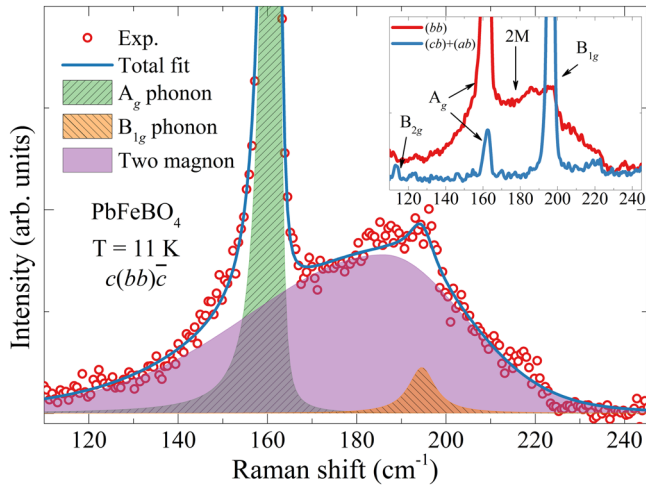
Another interesting manifestation of magnetic dynamics in PbFeBO<sub>4</sub> was observed below  $T_N$  in a form of a (*bb*)-polarized asymmetric broad band in the region of 125–250 cm<sup>-1</sup> as shown in figure 5. Temperature increase leads to the frequency softening and the band-width broadening when approaching  $T_N$  from below. Close to  $T_N$ , the band becomes indistinguishable.



**Figure 4.** Temperature dependence of the Pb–O–Pb phonon frequency and fitting curve according to [23]. Noticeable hardening slightly above and below  $T_N$  is due to the spin-phonon interaction. Inset: Normalized frequency of the magnetic excitations and Brillouin function  $B_{5/2}$  versus normalized temperature.

Such temperature behaviour of this band with the maximum at  $\approx 180$  cm<sup>-1</sup> allows us to assign it to a two-magnon (2M) scattering process when a two-magnon state with opposite wave vectors of single magnons within the Brillouin zone is created. Its position and the shape are defined by energy of magnons in the vicinity of the Brillouin-zone border and the interaction between them. We can estimate high-frequency cutoff of the two-magnon spectrum neglecting the magnetic anisotropy and the DM interaction as  $\omega_{\max} = 2ZSJ$ , where  $Z = 2$  is the number of nearest-neighbour ions in the chain,  $S = 5/2$  is the spin of the Fe<sup>3+</sup> ion and  $J = -26$  K  $\approx 18$  cm<sup>-1</sup> is intrachain exchange according to [2]. This estimate gives the frequency of 180 cm<sup>-1</sup> in good agreement with our observation.

Remarkably, the two-magnon band in PbFeBO<sub>4</sub> exerts overlapping with two A<sub>g</sub> phonons at 100 and 160 cm<sup>-1</sup> and the asymmetric Fano-like broadening of the band can be treated as a direct prove of the modulation of the exchange interaction by the relevant phonon [26, 27] between FeO<sub>6</sub> octahedra within the chains, and also between the chains. The fitting [28] of the two-magnon band and the two superimposed phonon modes to the total scattering intensity in PbFeBO<sub>4</sub> is shown in figure 5. In fact, Fe<sup>3+</sup> ions occupy 4*a* positions within inversion center, so these ions are inactive in the Raman scattering process, however the A<sub>g</sub> phonon at 160 cm<sup>-1</sup> is attributed to the Pb–O–Pb scissor mode [8] which results in the modulation of the exchange interaction by changing the angles of the Fe–O–Fe link within the FeO<sub>6</sub> chains, see figure 1(b). Though a two-magnon scattering process is a well-known phenomenon in magnetically-ordered materials [29, 30], overlapping of the two-magnon band with phonons demonstrating the clear signs of interaction between them is a rare phenomenon. As an example, we may note another iron borate FeBO<sub>3</sub> where a similar phenomenon in the region of the two-magnon band at 600–700 cm<sup>-1</sup> was observed [22]. However, FeBO<sub>3</sub> possesses a very different three-dimensional crystal structure and the modulation of the exchange interaction took place due to an

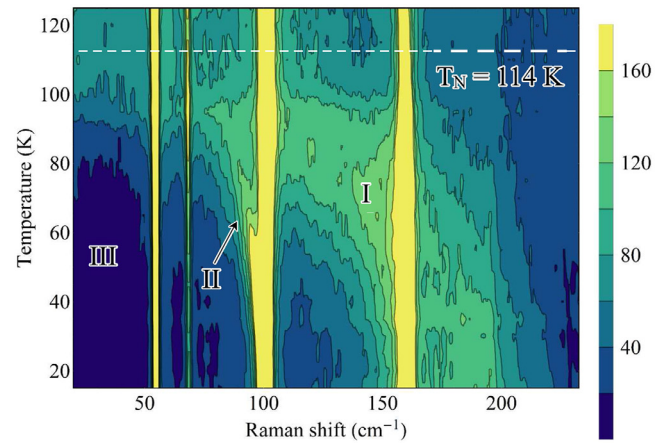


**Figure 5.** Raman scattering spectrum (symbols) for the  $(bb)$  polarization at  $T = 11$  K and the fitting of the asymmetric 2M band taking into account the allowed  $A_g$  phonon and a leakage of the  $B_{1g}$  phonon. Note the highly asymmetric Fano-like shape of the  $160\text{ cm}^{-1}$  phonon line. Inset shows Raman spectrum at  $T = 11$  K for  $c(bb)c$  and  $c(ab)c + a(cb)a$  polarizations.

internal mode of the  $\text{BO}_3$  group at  $660\text{--}680\text{ cm}^{-1}$ . The overlapping of the  $660\text{--}680\text{ cm}^{-1}$  phonon with the two-magnon band in  $\text{FeBO}_3$  was achieved by applying to the sample the hydrostatic pressure which increased the exchange interaction and moved the two-magnon band to higher frequencies. As noted above, in  $\text{PbFeBO}_4$  the exchange interaction between magnetic ions within and between the chain is weakened which results in a lower frequency position of the 2M band where it overlaps with the low-frequency Pb–O–Pb scissor mode.

One more interesting magnetic feature was observed as an appearance of a weak and narrow line in the low-temperature Raman spectra in the close vicinity to the  $100\text{ cm}^{-1}$  phonon line, see inset in figure 5. This feature sinks in the background at about  $T = (2/3)T_N$ , as shown in figure 6. Temperature dependence of its frequency and rather high energy ( $12.4\text{ meV}$ ) is not typical for a one-magnon excitation, and in order to clarify its origin further studies are required, for example measurements of its behaviour in an applied magnetic field. Important to note that this feature and the two-magnon band discussed above are both observed only in the  $(bb)$  polarization, i.e. in the case when both incident and scattered polarizations of the light are oriented along the magnetic  $\text{FeO}_6$  chains thus proving the dominant role of the exchange interaction within the chains [30]. Temperature dependencies of these excitation frequencies versus Brillouin functions for  $S = 5/2$  are shown in inset in figure 4.

Another observation in the Raman scattering deserves to be mentioned. It is an intense quasi-elastic  $(bb)$  polarized scattering which is observed even at room temperature, see the low energy part of figure 3. Since the  $(bb)$  polarization corresponds to the direction of the magnetic  $\text{FeO}_6$  chains it should reflect the fluctuations of the energy density of the spin system [31, 32]. The Lorentzian shape of the quasi-elastic scattering supports this mechanism. Below  $T_N$  when the long-range order is established this scattering vanishes.



**Figure 6.** Temperature dependence of the scattering spectra in  $(bb)$  polarization in the low-frequency region. Zones of particular interest are marked: (I) asymmetric resonance of the overlapping 2M band and  $A_g$  phonon line; (II) magnetic excitation (see text for details); (III) vanishing of the quasi-elastic scattering below  $T_N$ .

## 5. Conclusions

In conclusion, we have studied the lattice and magnetic dynamics of a quasi-one-dimensional antiferromagnetic insulator  $\text{PbFeBO}_4$  ( $T_N = 114\text{ K}$ ) using single crystal samples and the polarized Raman light-scattering spectroscopy. Experiments were done in a broad temperature range from 10 to 600 K. Most of the predicted phonons were detected. Some of them showed anomalous behaviour in the vicinity and below  $T_N$  thus confirming pronounced spin-phonon interaction. Several manifestations of magnetic excitations and their close couplings with particular features of the crystal structure and particular phonons were observed. A broad band centered at  $\approx 180\text{ cm}^{-1}$  was assigned to a two-magnon scattering process. Within the range of overlapping of this band and phonons, an asymmetric Fano-like resonance was observed which confirms intrinsic coupling of magnetic and lattice subsystems via the modulation of exchange interaction by particular phonons. The origin of another line near  $100\text{ cm}^{-1}$  which was observed at low temperature only below  $T_N$  still remains unclear and requires further studies, for example in an applied magnetic field. Besides these two magnetic features, a quasi-elastic scattering of magnetic origin was observed. Remarkably, all magnetic features in the light scattering were observed in the  $(bb)$  polarization which corresponds to the direction of the chains of  $\text{FeO}_6$  octahedra elongated in the direction of the crystallographic  $b$  axis. All these manifestations of the magnetic scattering support the quasi-one-dimensional character of the magnetic interactions and structure of  $\text{PbFeBO}_4$ . Magnetic symmetry analysis was performed which allowed us to explain previously observed anomalous peaks in neutron scattering by proposing the symmetry breaking at  $T_N$  involving two magnetic representations.

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