

Phonon spectrum of $\text{Pr}_2\text{Zr}_2\text{O}_7$ and $\text{Pr}_2\text{Ir}_2\text{O}_7$ as an evidence of coupling of the lattice with electronic and magnetic degrees of freedom

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Magnetic materials with pyrochlore crystal structure form exotic magnetic states due to the high lattice frustration. In this work we follow the effects of coupling of the lattice and electronic and magnetic degrees of freedom in two praseodymium-based pyrochlores $\text{Pr}_2\text{Zr}_2\text{O}_7$ and $\text{Pr}_2\text{Ir}_2\text{O}_7$. In either of these materials, the presence of magnetic interactions does not lead to magnetically ordered low temperature states, however their electronic properties are different. A comparison of Raman phonon spectra of $\text{Pr}_2\text{Zr}_2\text{O}_7$ and $\text{Pr}_2\text{Ir}_2\text{O}_7$ allows us to identify magneto-elastic coupling in $\text{Pr}_2\text{Zr}_2\text{O}_7$ that elucidates its magnetic properties at intermediate temperatures, and allows us to characterize phonon-electron scattering in the semimetallic $\text{Pr}_2\text{Ir}_2\text{O}_7$. We also show that the effects of random disorder on the Raman phonon spectra is small.

I. INTRODUCTION

Frustrated magnetism and the search for spin liquid materials is one of the main topics of condensed matter physics in recent years. The pyrochlores crystal structure provides a geometrically frustrated lattice suitable for hosting classical and quantum spin-ice and spin liquid states [1–3].

In this work we present a phonon Raman scattering study of praseodymium-based pyrochlores $\text{Pr}_2\text{Zr}_2\text{O}_7$ and $\text{Pr}_2\text{Ir}_2\text{O}_7$. In both materials Pr^{3+} is in the magnetic $J = 4$ state, and in $\text{Pr}_2\text{Ir}_2\text{O}_7$ the Ir^{4+} is also magnetic with $J_{\text{eff}} = 1/2$. Despite the presence of magnetic interactions, the highest quality samples do not order magnetically down to the lowest measured temperatures for either of these compounds. These two materials are rarely discussed together due to the drastically different electronic properties. $\text{Pr}_2\text{Zr}_2\text{O}_7$ is a band insulator and a quantum spin ice candidate [4]. $\text{Pr}_2\text{Ir}_2\text{O}_7$ shows metallic resistivity which flattens below 50 K due to a Kondo effect [5]. This material is suggested to be a Luttinger semimetal, that is to host a quadratic band touching at the Γ point of the Brillouin zone (BZ) [6]. Early on it was suggested to be a chiral metallic spin liquid [5, 7–9]. We found that a comparative study of their phonon spectra can reveal information of the coupling of the lattice to magnetic and electronic degrees of freedom which is difficult to identify otherwise.

While these two compounds are relatively well studied, the origin of their low temperature states is still under discussion. In both of these materials, structural disorder was claimed to influence the low temperature state [4, 10–12], but other subtle effects related to the magneto-elastic interactions and phonon-electron scattering for metallic $\text{Pr}_2\text{Ir}_2\text{O}_7$ can be important.

In this study we use phonon Raman spectroscopy to study $\text{Pr}_2\text{Zr}_2\text{O}_7$ and $\text{Pr}_2\text{Ir}_2\text{O}_7$. Raman scattering has shown its high sensitivity to magneto-elastic coupling, small lattice distortions, and structural disorder[13]. Somewhat unexpectedly, we do not find any significant effects of random disorder on the Raman spectra of these materials. For both materials, the only phonons that show broadening and splitting are E_g phonons, which can be associated with the tilting of octahedra as discussed in Ref. [14]. A very similar phonon spectrum originated from the similar crystal structures but different electronic properties allow us to identify phonon-electron scattering in $\text{Pr}_2\text{Ir}_2\text{O}_7$, and effects of magneto-elastic coupling in $\text{Pr}_2\text{Zr}_2\text{O}_7$.

II. EXPERIMENTAL

Polarized Raman scattering spectra were measured from (111) surface of the $\text{Pr}_2\text{Zr}_2\text{O}_7$ and $\text{Pr}_2\text{Ir}_2\text{O}_7$ single crystals grown by the floating zone method and the flux method respectively [15, 16]. Raman scattering was excited with 514.5 nm line of Ar^+ - Kr^+ mixed gas laser. Raman spectra were measured using the Jobin-Yvon T64000 triple monochromator spectrometer with a liquid nitrogen cooled CCD detector in the temperature range from 300 down to 14 K, and in frequency range from 800 down to about 30 cm^{-1} .

The pyrochlore lattice has $Fd\bar{3}m$ (No. 227) space group corresponding to O_h point group. The polarization-resolved spectra were measured in (x,x) and (x,y) geometries, where x denotes an arbitrary direction in the (111) plane and y is perpendicular to x . In Tab. I we present what symmetries of scattering channels are observed in the two measured geometries.

TABLE I. Components of Raman tensor for (x, x) and (x, y) polarizations.

Geometry	A_{1g}	E_g	T_{2g}
(x, x)	a^2	b^2	c^2
(x, y)	0	b^2	$\frac{2}{3}c^2$

TABLE II. Wyckoff positions and Γ point representations for $\text{Pr}_2\text{Zr}_2\text{O}_7$ ($\text{Pr}_2\text{Ir}_2\text{O}_7$).

Element	Wyckoff position	Γ representation
Pr	16c	Inactive
Zr (Ir)	16d	Inactive
O	48f	$A_{1g} + E_g + 3T_{2g}$
O'	8a	T_{2g}

III. RESULTS

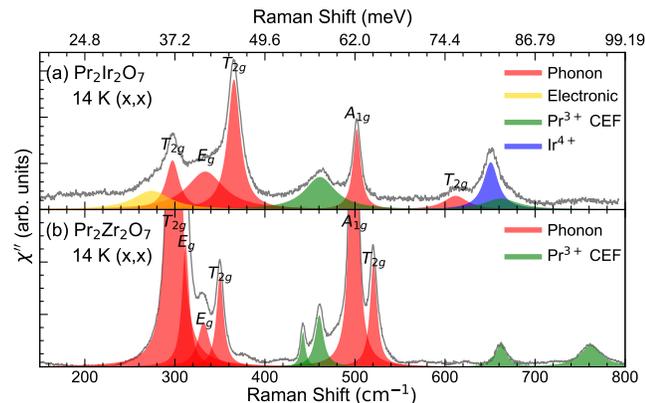


FIG. 1. Raman scattering spectra of (a) $\text{Pr}_2\text{Ir}_2\text{O}_7$ and (b) $\text{Pr}_2\text{Zr}_2\text{O}_7$ at 14 K in parallel polarization configuration.

Raman scattering spectra of the single crystals of $\text{Pr}_2\text{Zr}_2\text{O}_7$ and $\text{Pr}_2\text{Ir}_2\text{O}_7$ in the spectral range between 150 and 800 cm^{-1} in (x, x) scattering channel at $T = 14$ K are presented in Fig. 1. The low temperature data allows to resolve not only phonon excitations, but also crystal electric field (CEF) which can be observed only at low temperatures [17]. This spectral range covers all Raman-active phonons and excitations except the lowest excited state at about 80 cm^{-1} discussed in Ref. [17]. Due to the similarities of the crystal structure, many of the observed excitations show similar energies in these two compounds, however the Raman response of $\text{Pr}_2\text{Ir}_2\text{O}_7$ is approximately two orders of magnitude weaker than that of $\text{Pr}_2\text{Zr}_2\text{O}_7$, due to the fact that the first material is metallic. The screening present in the metallic state also affects the relative intensity of the phonons and CEF excitations. For the latter, in $\text{Pr}_2\text{Ir}_2\text{O}_7$ spectra we observe only the CEF excitation at around 460 cm^{-1} , which is coupled to phonons by a vibronic coupling process [17].

Raman-active phonons (marked red in Fig. 1) are discussed in this work. CEF excitations of Pr^{3+} (marked green) were assigned based on the neutron scattering results for these two materials [18–20] and are discussed in Ref. [17]. Additionally, in the spectra of $\text{Pr}_2\text{Ir}_2\text{O}_7$ we observe electronic excitations at around 250 cm^{-1} (marked yellow) and excitations typical for iridates at around 650 cm^{-1} (marked blue) [21].

TABLE III. Phonon modes assignment based on DFT calculation and experimental observation.

Mode	Frequency (cm^{-1})			
	$\text{Pr}_2\text{Ir}_2\text{O}_7$ DFT	$\text{Pr}_2\text{Ir}_2\text{O}_7$ Exp	$\text{Pr}_2\text{Zr}_2\text{O}_7$ DFT	$\text{Pr}_2\text{Zr}_2\text{O}_7$ Exp
$T_{2g}^{(1)}$	306	297 (18.0)	289	299 (6.7)
E_g	318	334 (50.0)	305	312 (9.8) 332 (17.1)
$T_{2g}^{(2)}$	388	366 (17.1)	391	350 (9.7)
A_{1g}	487	502 (10.5)	466	499 (7.2)
$T_{2g}^{(3)}$	555	-	512	521 (9.4)
$T_{2g}^{(4)}$	633	612 (32.6)	719	-

According to the symmetry analysis following the $Fd\bar{3}m$ symmetry of the unit cell, in the Raman spectra of $\text{Pr}_2\text{Zr}_2\text{O}_7$ and $\text{Pr}_2\text{Ir}_2\text{O}_7$ there are six Raman-active phonons (see Table II). Note that Pr and Zr (Ir) are Raman inactive. Experimentally observed frequencies of the phonons are in a good agreement with DFT calculations (see Table III). In the Raman spectra of both materials, A_{1g} and T_{2g} phonon bands appear as sharp peaks, while E_g phonons show more complicated spectra. The phonon lines of $\text{Pr}_2\text{Ir}_2\text{O}_7$ are broadened compared to $\text{Pr}_2\text{Zr}_2\text{O}_7$ spectra. For $\text{Pr}_2\text{Ir}_2\text{O}_7$, our experimental and calculated phonon spectra are in agreement with Ref. [22].

According to the calculations, E_g phonon frequency in $\text{Pr}_2\text{Zr}_2\text{O}_7$ spectra is expected at about 305 cm^{-1} . Instead, we observe two bands at 312 and 332 cm^{-1} , which are well resolved at low temperatures. Intensity of both bands follows polarization dependence of an E_g phonon in pyrochlores [22, 23] (see also Fig.S1 in Supplemental Material (SM) [24]), but the phonon band at 332 cm^{-1} shows a weaker polarization dependence (see Fig.S1 in SM [24]). The band of E_g vibration in $\text{Pr}_2\text{Ir}_2\text{O}_7$ spectra is found at about 334 cm^{-1} . It shows the largest width of all the Γ phonons of about 55 cm^{-1} and very weak temperature dependence. While we cannot identify multiple components of this band as in $\text{Pr}_2\text{Zr}_2\text{O}_7$ spectra even at low temperatures, the large line width suggest an additional broadening or splitting into multiple partially overlapping components.

We follow the temperature dependence of A_{1g} and T_{2g} phonons of $\text{Pr}_2\text{Zr}_2\text{O}_7$ and $\text{Pr}_2\text{Ir}_2\text{O}_7$. Fig. 5 compares the temperature behavior of the widths and frequencies of the four lower frequency Raman-active phonons, which show the stronger temperature dependence. On a decrease of the sample temperature from 300 K, the phonons show

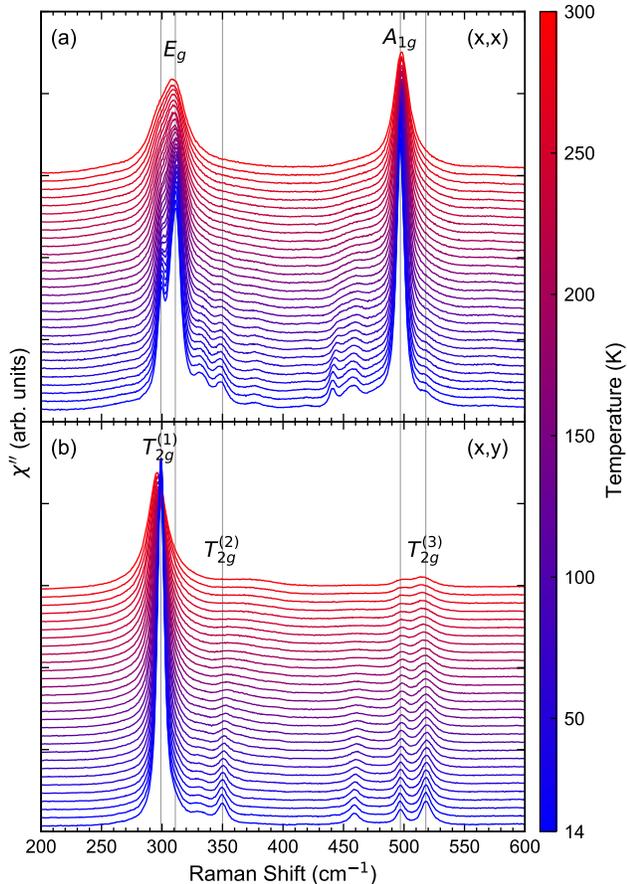


FIG. 2. Temperature dependence of the Raman scattering spectra of $\text{Pr}_2\text{Zr}_2\text{O}_7$ in (a) (x, x) channel and (b) (x, y) channel.

hardening due to thermal contraction (see Fig. 2), except for $T_{2g}^{(2)}$ mode, which is discussed below. All phonons in $\text{Pr}_2\text{Zr}_2\text{O}_7$ show a conventional decrease of the line width due to phonon-phonon scattering [25], following the general formula

$$\Gamma_{\text{ph-ph}}(T) = \Gamma_0 + A(1 + 2n_B(\omega/2, T)), \quad (1)$$

with Γ_0 of $5 - 7 \text{ cm}^{-1}$, depending on the phonon. The subtle effects of phonon-electron scattering in $\text{Pr}_2\text{Ir}_2\text{O}_7$ become apparent when compared to the behavior of the $\text{Pr}_2\text{Zr}_2\text{O}_7$ phonons, see Fig. 5. At the lowest temperature all of the $\text{Pr}_2\text{Ir}_2\text{O}_7$ phonons show larger width, while the temperature dependence of the width is less steep, and is described better by the scattering of phonons on inter-band transitions, as observed in semimetals [26],

$$\Gamma_{\text{ph-el}}(T) = \Gamma_0 + F(n_F(\hbar\omega_a, T) - n_F(\hbar\omega_a + \hbar\omega_{\text{ph}}, T)). \quad (2)$$

The $T_{2g}^{(2)}$ phonon in the spectra of $\text{Pr}_2\text{Zr}_2\text{O}_7$ shows unconventional behavior different from the discussed above. In the spectral range of approximately $330 - 430 \text{ cm}^{-1}$, the changes of the spectra on cooling reveal the $T_{2g}^{(2)}$

phonon as a sharp band only below 100 K (see Fig. 4a). The frequency of 380 cm^{-1} corresponds to a CEF transition from the first excited A_{1g} state at 77 cm^{-1} to the second excited state at about 440 cm^{-1} (see Fig. 4d). In the first approximation, the total Raman intensity should be a superposition of CEF and phonon response, where CEF response will be changing as the population of the first excited A_{1g} level at $E_1 = 77 \text{ cm}^{-1}$, and the second excited at $E_2 = 440 \text{ cm}^{-1}$. The spectral weight in this range can be calculated as $I(T) = \int_{430 \text{ cm}^{-1}}^{330 \text{ cm}^{-1}} \chi''(\omega) d\omega$ and is decreasing on cooling, indeed following a dependence of $I(T) = A + B(e^{-E_1/k_B T} - e^{-E_2/k_B T})$ (see Fig. 4c). While the picture of a superposition of intensities works as a good approximation for the temperature dependence of the spectral weight, it does not explain the shape of the $T_{2g}^{(2)}$ phonon. In fact, the phonon appears as a weak antiresonance at the frequency of 371 cm^{-1} at room temperature, and gains the shape of a peak as the spectral weight of the CEF decreases. The position of the $T_{2g}^{(2)}$ phonon defined as a position of an antiresonance or a maximum, depending on temperature, softens from 371 cm^{-1} down to 350 cm^{-1} on cooling from 300 K down to 14 K. The $A_{1g} \rightarrow E_g$ excitation is absent in $\text{Pr}_2\text{Ir}_2\text{O}_7$ spectra, however, the T_{2g} phonon shows moderate softening from the frequency from 375 cm^{-1} at room temperature down to 364 cm^{-1} at 14 K.

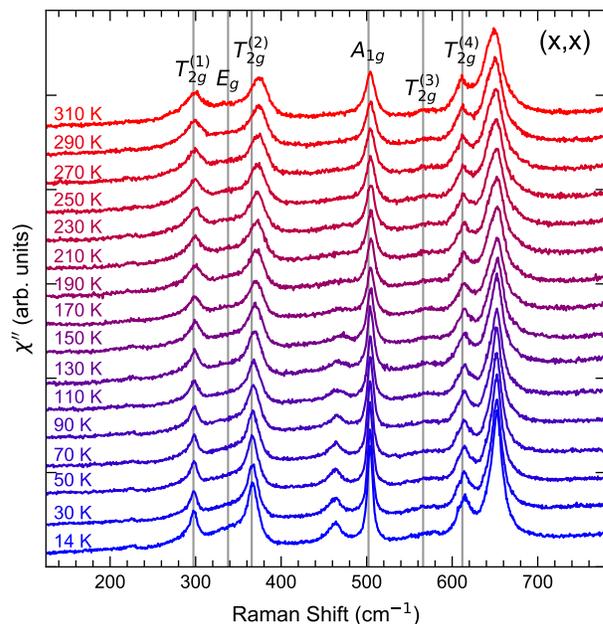


FIG. 3. Temperature dependence of the Raman scattering spectra of $\text{Pr}_2\text{Ir}_2\text{O}_7$.

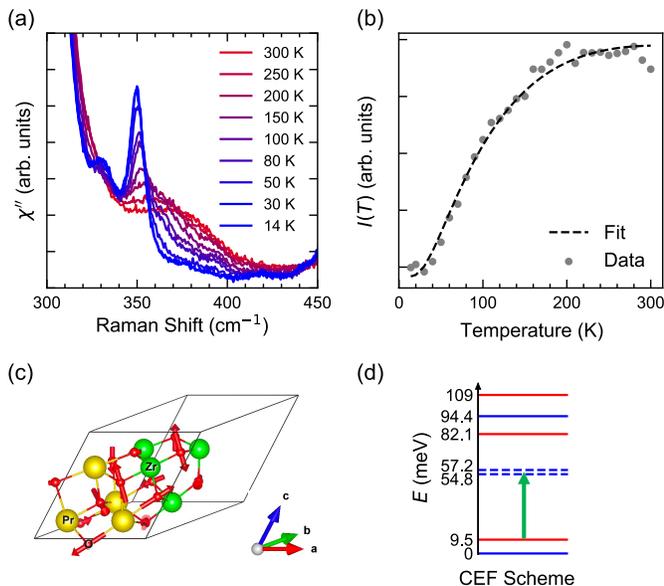


FIG. 4. (a) Temperature dependence of Raman scattering spectra of Pr₂Zr₂O₇ in the region of $A_{1g} \rightarrow E_g$ crystal electric field transitions in (x, y) channel. (b) Temperature dependence of spectral weight $I(T) = \int_{430}^{330} \chi''(\omega) d\omega$. (c) Atomic displacement of $T_{2g}^{(2)}$ phonon mode. (d) Crystal field scheme of Pr³⁺ ions in Pr₂Zr₂O₇ crystal environment.

IV. DISCUSSION

A. Phonon-electron scattering

The energies of the phonon modes are very similar between Pr₂Ir₂O₇ and Pr₂Zr₂O₇, as expected for materials with similar crystal structures, which differ only by a substitution of B position in the $A_2B_2O_7$ of pyrochlore structure. However, the difference both in low-temperature width of the phonons, and in their temperature dependence is considerable. At low temperatures, all the phonon bands of Pr₂Ir₂O₇ show larger line width than that of Pr₂Zr₂O₇. We assign this difference not to the larger random disorder in Pr₂Ir₂O₇, but to the effects of phonon-electron coupling. It was shown [26, 27] that in semimetals, phonon can scatter on the direct ($q = 0$) interband transitions, producing a temperature dependence of width very different from the Klemens' model. This can explain the temperature behavior of the phonons in Pr₂Ir₂O₇ (Fig. 5). The fact that two phonons of different symmetries, T_{2g} and A_{1g} , which are not coupled to magnetic degrees of freedom, show the evidence of phonon-electron scattering, suggests that the scattering occurs on the interband transitions away from the highest symmetry points of the BZ, and is not restricted by symmetry. The high probability of such scattering could be explained based on the calculated Pr₂Ir₂O₇ band structure, which suggests a band touching at the Γ point of BZ, and a narrow gap between nearly parallel

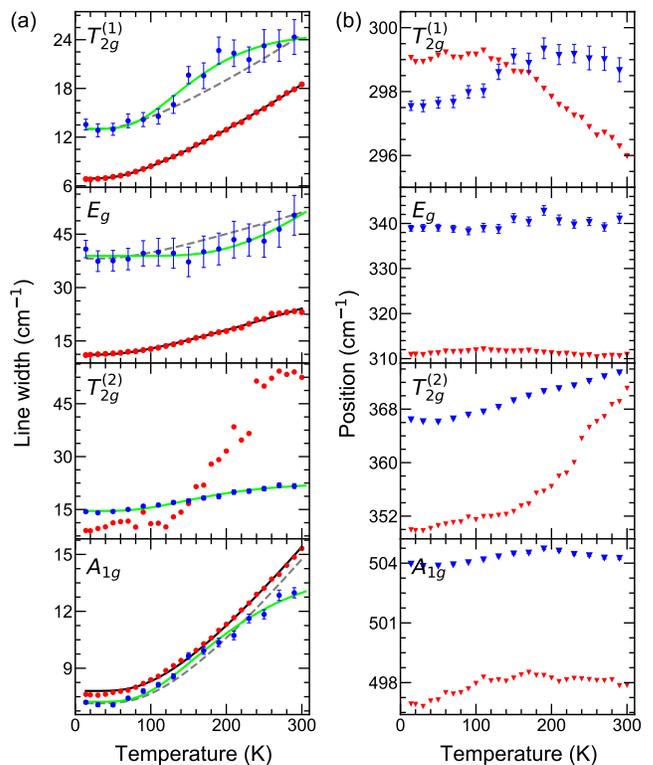


FIG. 5. Temperature dependence of (a) line widths and (b) positions for Pr₂Zr₂O₇ (blue) and Pr₂Ir₂O₇ (red). Black lines are fits of line width of Pr₂Zr₂O₇ phonons with extended Klemens model. Dashed lines show the same temperature dependence with Γ_0 increased for Pr₂Ir₂O₇. Green lines are the fits of line width of Pr₂Ir₂O₇ phonons by the phonon-electron scattering model. Note that the temperature dependence for Pr₂Ir₂O₇ phonons is best fit by phonon-electron scattering. Green lines were fit by the phonon-electron scattering model for Pr₂Ir₂O₇.

bands between Γ and L points [28, 29], while the calculations Ref. [30] suggest these parallel bands below the Fermi energy. The gap in the range of 300 – 500 cm⁻¹ (37 – 65 meV) between these bands would provide a suitable phase space for phonon-electron scattering on interband transitions. Moreover, the presence of this scattering testifies for the existence of such a band gap. An interesting proposal of an increase of conductivity via electron-phonon scattering on acoustic modes [26] could be also relevant to Pr₂Ir₂O₇.

B. Control of the super-exchange values through structure

The information about the phonons and their temperature dependence supply us the knowledge of the subtle effects of magneto-elastic interactions, and the importance of the structure for magnetic behavior. Here we will focus on the behavior of the $T_{2g}^{(2)}$ phonon found at

about 350 cm^{-1} which involves the change of Pr-O-Pr angle, which determines the size of the super-exchange interactions between Pr atoms. In the spectra of both materials, the $T_{2g}^{(2)}$ phonon is softening on cooling (see Fig. 5). However, the DFT calculations do not find any significant magneto-elastic coupling for this phonon.

We suggest that the phonon behavior reflects the changes of the lattice on thermal contraction. This effect is much larger in $\text{Pr}_2\text{Zr}_2\text{O}_7$ (20 cm^{-1} shift) compared to $\text{Pr}_2\text{Ir}_2\text{O}_7$ (8 cm^{-1} shift), where magnetic interactions are more complex due to the magnetism of Ir. Softening of the phonon can evidence the change of Pr-O-Pr angle that in turn leads to the decrease of the super-exchange values. Indeed, a decrease of super-exchange below 100 K in $\text{Pr}_2\text{Zr}_2\text{O}_7$ was suggested as an interpretation of the temperature dependence of magnetic susceptibility [20]. A similar but weaker tendency is observed for $\text{Pr}_2\text{Ir}_2\text{O}_7$ [5].

In the spectra of $\text{Pr}_2\text{Zr}_2\text{O}_7$, the behavior of the T_{2g} phonon is more involved than a pure softening. At temperatures above about 100 K, this phonon shows very strong changes associated with the decrease of CEF $A_{1g} \rightarrow E_g$ intensity due to the depopulation of the A_{1g} level. Moreover, at room temperature the phonon appears as an antiresonance in the broad band of CEF $A_{1g} \rightarrow E_g$ transition, which is an evidence of an interaction of the phonon with this transition [31]. The observed spectroscopic effect is very different from vibronic effects on mixing of CEF and phonons, discussed in [17, 32].

C. E_g phonons

Anomalous behavior was also detected from E_g phonons, which show a double band in the spectra of $\text{Pr}_2\text{Zr}_2\text{O}_7$, and an increased width in the spectra of $\text{Pr}_2\text{Ir}_2\text{O}_7$.

E_g degree of freedom is sensitive to magneto-elastic coupling in pyrochlore materials as revealed on magnetic phase transitions [22]. However, both compounds are known not to order magnetically, and the properties of the E_g phonons do not show any pronounced temperature dependence. A possible interpretation of a splitting of a doubly degenerate band observed in the whole temperature range is a local symmetry breaking. For the highest quality crystals of $\text{Pr}_2\text{Zr}_2\text{O}_7$ free from oxygen vacancies and site mixing [33], a shift of Pr ion from a central position [12, 15], and a local tilting of octahedra [14], which reduces local symmetry from $Fd\bar{3}m$ (point group O_h) to $P4_32_12$ (point group D_4) is discussed. With this symmetry reduction, E_g phonons split into two in-plane modes of B_1 symmetry (see Table. IV). T_{2g} phonons split into B_2 and E modes, where the E modes will be observed in xz and yz channels which can be only detected in out-of-plane scattering, and thus will not appear in the spectra in (x, y) and $(x^2 - y^2)$ channels. This symmetry considerations can explain why T_{2g} phonons do not show

any anomalous behavior of their width.

TABLE IV. Correlations between O_h and D_4 groups and symmetries.

	O_h		D_4
A_{1g}	$(x^2 + y^2 + z^2)$		$A_1 (x^2 + y^2, z^2)$
E_g	$(x^2 - y^2)$ $2z^2 - x^2 - y^2$	\longrightarrow	$A_1 + B_1 \longrightarrow B_1 (x^2 - y^2)$
T_{2g}	(xy, xz, yz)	\longrightarrow	$E + B_2$ $B_2 (xy)$ $E (xz, yz)$

The large width of E_g phonons in $\text{Pr}_2\text{Ir}_2\text{O}_7$ spectra, which appear to be about twice the width of the other phonons, suggest that a splitting of this band is also present in $\text{Pr}_2\text{Ir}_2\text{O}_7$, but cannot be resolved due to the large band width, and can have a similar origin.

V. CONCLUSIONS

In this work we compare the Raman phonon spectra of $\text{Pr}_2\text{Zr}_2\text{O}_7$ and $\text{Pr}_2\text{Ir}_2\text{O}_7$, which have a very similar crystal structure, but drastically different electronic properties. Raman phonons observed at similar frequencies demonstrate different behavior with temperature, determined by phonon-phonon scattering in the case of the insulating $\text{Pr}_2\text{Zr}_2\text{O}_7$, and phonon-electron scattering in the case of $\text{Pr}_2\text{Ir}_2\text{O}_7$. A softening of the phonon changing Pr-O-Pr angle on cooling explains the decrease of magnetic interactions J deduced previously from magnetic susceptibility measurements. The broadening of the E_g phonons demonstrates the presence of the disordered tilting of tetrahedra suggested for pyrochlore materials. As a whole, our study elucidates many subtle questions about electronic and magnetic properties of these materials through the behavior of the underlying lattice.

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