Phonon excitations in Eu$_2$Ir$_2$O$_7$ probed by inelastic X-ray scattering

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Abstract.

The study of phonon dynamics and its interplay with magnetic ordering is crucial for understanding the unique quantum phases in the pyrochlore iridates. Here, through inelastic X-ray scattering on a single crystal sample of the pyrochlore iridate Eu$_2$Ir$_2$O$_7$, we map out the phonon excitation spectra in Eu$_2$Ir$_2$O$_7$ and compare them with the theoretical phonon spectra calculated using the density functional theory. Possible phonon renormalization across the magnetic long-range order transition is revealed from the temperature dependence of the phonon spectra.

Keywords: spin-orbit coupling (SOC), phonon excitations, inelastic X-ray scattering (IXS), density functional theory

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1. Introduction

The explorations of the 4d and 5d heavy transitional metal electronic systems represent a cutting-edge research domain in condensed matter physics. These systems harbor a plethora of unconventional correlated states, including quantum spin liquids [1, 2, 3], metal-insulator transitions [4, 5], Weyl semimetals (WSM) [6], topological insulators [7, 8], non-Fermi liquids [9], magnetic monopole-like phase [10], etc. The intriguing manifestations of these states arise from a unique amalgamation of factors, including extended 5d/4d orbitals [11], strong spin-orbit coupling (SOC), and geometrically frustrated lattices [12], thus offering a rich platform to search for exotic correlated states.

Among the heavy transitional metal electron systems, the pyrochlore iridates, $R_2Ir_2O_7$ ($R = Y$ and rare earth ions) [13, 14, 15, 16, 17], stand out as a fertile ground to realize novel quantum states. The structure of the pyrochlore iridates is presented in Fig. 1(a), where the Ir$^{4+}$ ions form a pyrochlore lattice with corner-sharing tetrahedra. The Ir$^{4+}$ ions of the low-spin configuration form an effective doublet of $J = 1/2$, where $J$ is the total angular momentum [18].

For compounds with a relatively large $R^{3+}$ ion radius, a metal-insulator transition (MIT) has been observed, where the transition temperature, $T_N$, can be tuned by various external parameters including chemical composition [19, 20, 21], pressure [22, 23, 24], and magnetic field [25, 26, 27, 28]. In the insulating phase, the magnetic moments of the Ir$^{4+}$ ions form an ‘all-in/all-out’ (AIAO) magnetic long range-order, which can be viewed as a solidified phase of magnetic monopoles [29]. For compounds with a relatively small $R^{3+}$ ion radius, the paramagnetic phase at temperatures above the ordering transition become insulating, indicating a strong correlation between the chemical pressure and electronic bands [30].

The lattice degree of freedom of the pyrochlore iridates also contains rich information about the spin correlations because the lattice is directly connected to the orbitals and, consequently, indirectly influences the spins through SOC [31]. Recent Raman scattering experiments on Eu$_2$Ir$_2$O$_7$ revealed significant renormalization of the phonon frequencies across $T_N \sim 115$ K [32]. Furthermore, the noncollinear character of the AIAO structure allows a linear coupling between the magnons and phonons, meaning that hybridized spin-lattice excitations may emerge if the exchange couplings between the Ir$^{4+}$ spins depend on their distances [32, 33].

In this work, we performed non-resonant inelastic X-ray scattering (IXS) experiments to map out the phonon dispersion in Eu$_2$Ir$_2$O$_7$ and compare it to the theoretical spectra calculated by the first-principle density functional theory (DFT). Possible phonon renormalization across $T_N$ is observed at selected wave vector transfers near the Brillouin zone center, although hybrid magnon-phonon excitations are not resolved in our experiments possibly due to their relatively low scattering cross sections.

2. Methods

Our IXS experiments were performed on the RIKEN Quantum NanoDynamics Beamline, BL43LXU [34], at the SPring-8 synchrotron light source in Japan. This beamline provides world-leading intensity for IXS experiments using $3 \times 5$ m insertion devices [35, 36] in a small, 50 µm diameter beam spot. A piece of KF-flux grown Eu$_2$Ir$_2$O$_7$ single crystal [37], with a dimension of $0.4\times0.4\times0.1$ mm$^3$, was used for the experiments. The reflection scattering geometry was employed due to the relatively short attenuation length of $\sim 20$ µm at an incoming x-ray energy of 20 keV. The (111) surface of the crystal was polished and vertically attached to the sample holder, which was then aligned with the (HHL) plane horizontally. The 24 analyzer array allows parallel measurements over a large area of momentum transfers. The Si (11,11,11) setup with a

Figure 1. (a) Crystal structure of the pyrochlore iridates. The large blue sphere is the Eu site. The large green sphere with polyhedra is Ir. The small grey one is O. (b) Brillouin zone and high symmetry points for the face-centered cubic (FCC) lattice. (c) DFT calculations of the phonon dispersion along the high-symmetry directions Γ-W-X-Γ-L.
resolution of $>1.3$ meV (depending on analyzer) was employed. A closed cycle cryostat was mounted in the Eulerian cradle to access temperatures down to $\sim 50$ K. The IXS energy scale is expected to be accurate to 0.5 % based on calibration against a standard [38].

Theoretical phonon spectra for Eu$_2$Ir$_2$O$_7$ at zero temperature were calculated using the first-principles density functional theory (DFT) as implemented in the Vienna ab initio simulation package (VASP). The projector augmented wave (PAW) method with the generalized gradient approximation (GGA) and the Perdew-Burke-Ernzerhof (PBE) exchange potentials were employed [39, 40, 41, 42]. The Debye Waller factor was not considered in our calculations. The plane-wave cutoff energy was set as 600 eV and the $k$-point mesh was set as $6 \times 6 \times 6$ for the conventional cell of the cubic $Fd\bar{3}m$ phase (No. 227) of Eu$_2$Ir$_2$O$_7$. For the structural optimization in the paramagnetic phase, the lattice constant was fixed at the experimental value of $a = 10.167$ Å, and the atomic positions were fully relaxed until the Hellman-Feynman force on each atom was smaller than 0.001 eV/Å. Force constants were calculated by density functional perturbation theory [43, 44] as implemented in VASP. Phonon dispersion relations were obtained using the PHONONPY software in a primitive unit cell [45, 46].

3. Results and Discussions

Figure 1 presents an overview of the calculated phonon dispersion along the high symmetry lines in reciprocal space. The absence of imaginary frequencies corroborates the accuracy of our structural optimization. Altogether 66 phonon bands are observed in our calculations, which is consistent with the number of phonon modes for 22 atoms per primary unit cell. At the Brillouin zone center, i.e. the $\Gamma$ point, there are 6 Raman-active phonon bands according to group-theoretical analysis [32]:

$$\Gamma^{op} = A_{1g} + E_g + 4T_{2g}. \quad (1)$$

These Raman active modes are indicated in Fig. 1(c). As compared in Tables 1 and 2 for the Raman- and infrared-active modes, respectively, our calculated frequencies are in good agreement with the previous DFT calculations and the experimental observations at $T = 300$ K [32]. For the $E_g$ mode that is the focus of our present study, the calculated and experimental energies are 47.2 and 41.8 meV, respectively. This slightly overestimated energy may arise from the coupling between phonons and low-energy excitations of the valence electrons [32], which is not included in DFT calculations.

Figure 2 compares the experimental and calculated IXS cross sections along the (66L) and (HH8) directions. The black dots in panels (a) and (c) indicate the positions where IXS spectra were collected.

Figure 3. Experimental (black dots) and calculated (red line) phonon spectra at momentum transfer $Q = (6, 6, 8)$ measured at $T = 50$ K. The calculated IXS cross section is convoluted by a pseudo-Voigt instrumental resolution function. The phonon modes corresponding to each peak are indicated, with their calculated energy shown by vertical bars at the bottom. The height of the vertical bars corresponds to the calculated IXS cross sections.
modes at the Brillouin zone center can be identified as $E_a$ pseudo-Voigt peak at $\gamma$.

Comparison between the experimental and calculated cross sections at $(668)$ up to $\sim 40$ meV is shown in Fig. 3, where the red line is the calculated cross section plus a pseudo-Voigt peak at $E = 0$. The observed phonon modes at the Brillouin zone center can be identified as the $T_{2g}(8.64)$, $E_u(12.08)$, $T_{1u}(13.94)$, $T_{1u}(18.12)$, $T_{2u}(20.10)$, $E_u(25.40)$, $T_{1u}(26.64)$, $A_{2u}(27.13)$, $T_{1g}(32.34)$, $A_{2u}(35.16)$, and $T_{2g}(39.95)$ modes, where the calculated energies in units of meV are shown in brackets following each mode. The dispersion of the phonon excitations, together with their IXS cross sections, are well described by our DFT calculations.

As the detector bank of the IXS spectrometer at the BL43LXU beamline is composed of 24 detectors that are arranged in a 4-by-6 array, a series of IXS spectra can be collected simultaneously at $Q$ positions around the target wavevector transfer. For a target wavevector transfer of $Q = (6.114, 6.088, 8.123)$ r.l.u., the simultaneously detected $Q$ positions are plotted in Fig. 4, where the target wavevector position is marked by an asterisk.

Figure 5 presents the IXS spectra collected at 12 representative $Q$ positions around $(668)$ measured at $T = 50$ K, below $T_N \sim 115$ K. The $Q$ position for each panel is indicated in Fig. 4 as red dots. The red lines in Fig. 5 represent the calculated cross-sections plus a pseudo-Voigt peak with a FWHM of 1.3 meV at $E = 0$. The experimental data shown in Fig. 5 reveals that in the magnetically ordered phase, the strongest IXS cross section is observed in an energy transfer range of $E \sim [10, 30]$ meV, above which the scattering intensity decreases by an order of magnitude up to $E = 50$ meV. The calculated spectra reproduce the main features of the experimental data, although deviations of $\sim 2$ meV are observed for the strong modes at 25 and 33 meV. These deviations appear in all detector banks and can be ascribed to the difference in lattice constants employed in our DFT calculations. A second type of deviation is observed at higher energy transfers. For example, at $Q = (6.114, 6.088, 8.123)$ r.l.u. that is close to the Brillouin zone center as shown in Fig. 5(c), a weak peak is observed at $\sim 38$ meV that

Table 1. Comparison between the experimentally determined and calculated energies of the Raman-active phonon modes for Eu$_2$Ir$_2$O$_7$ at room temperature. Energies are measured in units of meV.

<table>
<thead>
<tr>
<th></th>
<th>$T_{2g}(1)$</th>
<th>$E_g$</th>
<th>$T_{2g}(2)$</th>
<th>$A_{1g}$</th>
<th>$T_{2g}(3)$</th>
<th>$T_{2g}(4)$</th>
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</thead>
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<tr>
<td>experimental [32]</td>
<td>37.5</td>
<td>41.8</td>
<td>47.1</td>
<td>63.0</td>
<td>67.3</td>
<td>84.3</td>
</tr>
<tr>
<td>previous cal. [32]</td>
<td>39.3</td>
<td>46.0</td>
<td>51.7</td>
<td>65.7</td>
<td>72.9</td>
<td>83.9</td>
</tr>
<tr>
<td>our DFT cal.</td>
<td>39.9</td>
<td>47.2</td>
<td>48.4</td>
<td>66.1</td>
<td>72.9</td>
<td>87.2</td>
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</table>

Table 2. Comparison between the experimentally determined and calculated energies of the infrared-active $T_{1u}$ phonon modes Eu$_2$Ir$_2$O$_7$ at room temperature. Energies are measured in units of meV.

<table>
<thead>
<tr>
<th></th>
<th>$T_{2u}(1)$</th>
<th>$E_u$</th>
<th>$T_{2u}(2)$</th>
<th>$A_{2u}$</th>
<th>$T_{1u}(3)$</th>
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<tr>
<td>experimental [32]</td>
<td>14.2</td>
<td>18.5</td>
<td>25.6</td>
<td>42.1</td>
<td>53.8</td>
<td>60.5</td>
</tr>
<tr>
<td>previous cal. [32]</td>
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<td>18.6</td>
<td>27.3</td>
<td>45.4</td>
<td>57.2</td>
<td>61.6</td>
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<tr>
<td>our DFT cal.</td>
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<td>26.6</td>
<td>41.9</td>
<td>54.8</td>
<td>64.2</td>
</tr>
</tbody>
</table>

Figure 4. The simultaneously detected 24 $Q$ points in reciprocal space with the targeting detector fixed at $Q = (6.114, 6.088, 8.123)$ r.l.u. as indicated by the asterisk. Red dots correspond to the selected 12 positions that are presented in Fig. 5 and Fig. 6.
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Figure 5. Representative IXS spectra of Eu$_2$Ir$_2$O$_7$ measured at $T = 50$ K with the target detector fixed at $Q = (6.114, 6.088, 8.123)$ r.l.u. Solid red lines represent the calculated phonon cross section convoluted by a pseudo-Voigt instrumental resolution function.

Figure 6. Temperature-dependence of the IXS spectra for Eu$_2$Ir$_2$O$_7$ measured at $T = 50$ K, 100 K, and 150 K.
Int (a.u.)

non-resonant inelastic x-ray scattering technique.

Fig. 6 compares the IXS spectra for the same 12 Q positions at T = 50, 100, and 150 K. Focusing at Q = (6.114, 6.088, 8.123) r.l.u., for which the high energy data at T = 50 and 150 K is reproduced in Fig. 7, the weak peak observed at E = 38.8 meV at T = 50 K gradually shifts to E = 42.8 meV at T = 150 K, which may correspond to the renormalized $E_g$ mode as reported in the previous Raman scattering experiments [32]. Considering the rather weak intensity of the $E_g$ mode, further IXS experiments with better statistics will be required to resolve the dispersion of the $E_g$ mode as a function of momentum transfer and temperature. Besides the mode softening, we also searched for emergent hybridized spin-lattice excitations that were previously observed in Raman scattering experiments [16]. However, the energy of the expected hybridized spin-lattice excitation, which is ~26 meV at the Brillouin zone center, overlaps with the strong conventional phonon modes, making it difficult to confirm its existence using our current IXS data. It is also possible that the emergent mode observed at ~26 meV in Raman scattering is one of the strong phonon modes that are visible in IXS, which becomes Raman active in the LRO ordered phase.

4. Conclusion

In conclusion, the phonon excitations of the pyrochlore iridate Eu$_2$Ir$_2$O$_7$ have been investigated using the non-resonant inelastic x-ray scattering technique. Comparisons to the DFT calculations reveal that the cross sections are dominated by Raman-inactive modes in an energy transfer range of [10, 30] meV. Analysis of the IXS spectra measured at temperatures below and above $T_N$ reveals possible phonon renormalizations across the long-range-order transition as reported in the previous Raman scattering experiments.

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