Isospin-phonon coupling and Fano-interference in spin-orbit Mott insulator Sr$_2$IrO$_4$

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The isospin-phonon coupling in Sr$_2$IrO$_4$ is investigated by temperature dependent phonon Raman scattering. Anomalous behavior in the frequency of all studied optical phonons is observed below the magnetic transition temperature $T_N \sim 240$ K. The strongest effect is detected for the $A_{1g}$ mode at 272 cm$^{-1}$ associated with the modulation of the Ir-O-Ir bond angle. Additionally, the $A_{1g}$ mode at 560 cm$^{-1}$ shows a Fano asymmetric lineshape sensitive to $T_N$, supporting the existence of low-energy ($\sim 70$ meV) electronic excitations that are renormalized by the magnetic order. These results reveal new aspects of the interaction between the crystal lattice and electronic degrees of freedom in this spin-orbit entangled Mott insulator.

Materials with unique combination of spin-orbit coupling (SOC) and electron correlations offer opportunities for the discovery of novel quantum states of matter. The Rud elsden-Popper series of layered perovskite strontium iridates (Sr$_{n+1}$Ir$_n$O$_{3n+1}$, $n = 1, 2$) are the key materials in this class. Mutual cooperation of strong SOC ($\sim 0.5$ eV) and moderate electron correlation ($U \sim 1.5 - 2$ eV) energies give rise to the emergence of the spin-orbit entangled insulating state in Sr$_2$IrO$_4$. The SOC creates a half filled band of isospins ($J_{eff} = 1/2$), which is further split by the on-site Coulomb interaction and opens up a Mott-like insulating gap. The parent Sr$_2$IrO$_4$ crystallizes in a tetragonal phase with space group $I4_1/acd$, showing a rotation of the IrO$_6$ octahedra by 11° along the c-axis. The presence of a significant Dzyaloshinskii-Moriya-type (DM) exchange interaction leads to a canted magnetic structure for the isospins with a weak ferromagnetic moment of 0.06-0.14 $\mu_B$/Ir below $T_N \sim 240$ K.

The effect of cross-coupling between collective spin and orbital ordering with the lattice degrees of freedom has an important role on the fundamental properties of correlated materials. Particularly, the spin-lattice coupling strongly depends on spin-orbit interaction, and it is important to stabilize the uncommon magnetic behavior of Sr$_2$IrO$_4$. The external influences like temperature, application of pressure, and chemical doping can change the bond length and/or bond angle, which leads to a change in magnetic ordering and consequently to the spin-lattice coupling. In Sr$_2$IrO$_4$, the strong SOC plays a crucial role in the realization of the magnetic behavior, and its presence is expected to bring a strong coupling between the $J_{eff} = 1/2$ pseudospins and the lattice degrees of freedom. For instance, the $J_{eff} = 1/2$ isospin directions are nearly locked to the rotation of IrO$_6$ octahedra along the c-axis.

In general, the coupling of magnetism to the ionic displacements in second order leads to a spin-phonon coupling in magnetic materials, which may provide useful information on the microscopic exchange coupling mechanism. In this letter, we investigate the temperature-dependent phonon Raman scattering of Sr$_2$IrO$_4$ single crystal. Our results reveal the existence of an isospin-phonon coupling effect below the magnetic ordering temperature. We have also observed an asymmetric phonon lineshape of apical O stretching $A_{1g}$ mode, which is ascribed to the coupling of this phonon with a low-energy continuum of electronic excitations.

The Sr$_2$IrO$_4$ single crystal was grown by the flux method. The base materials SrCO$_3$, IrO$_2$, and SrCl$_2$ (flux) were mixed in molar ratio 2:1:7, respectively; melted at 1280°C in a platinum crucible, and then cooled down to 880°C at the rate of 6°C/hour. Finally, the crystals were free cooled to room temperature in a programmable furnace. The crystals were in sub-mm size (0.5-0.8 mm) with shiny surfaces. Raman scattering experiments were performed in a quasi-backscattering geometry using the 488.0 nm line of Ar$^+$ laser with focus spot size $\sim 50$ µm. A Jobin-Yvon T64000 triple-mate spectrometer with 1800 mm$^{-1}$ gratings was employed. An LN$_2$-cooled multichannel CCD was used to collect and process the scattered data. The sample was mounted on a cold finger of closed-cycle He cryostat with base temperature 25K. The dc-magnetization measurements as a function of temperature were performed with a Superconducting Quantum Interference Device (SQUID) magnetometer. The measurements were carried out under warming after field cooling (FCW, $H = 0.5$ T).

Unpolarized Raman spectra of Sr$_2$IrO$_4$ single crystal at 25K are shown in Fig. 1. Six Raman-active optical modes have been detected and labeled as $M_1$ to $M_6$ at 183, 272, 399, 559, 715, and 742 cm$^{-1}$, respectively. These modes were identified in previous works. The most intense modes $M_2$ and $M_4$ at 25 K correspond to the $A_{1g}$ symmetry, where $M_2$ is a rotational mode of IrO$_6$ octahedra around the tetragonal c-axis, and $M_4$ is a stretching of apical oxygen atoms along the c-axis. The $M_3$ vibration with $B_{2g}$ symmetry is a bending mode of oxygen squares in the ab-plane. Peak $M_1$ is a superposition of $A_{1g}$ and $B_{2g}$ phonons with closely spaced frequencies. The $A_{1g}$ mode corresponds to a rotation of IrO$_6$ octahedra combined with an in-phase Sr displacement along c-axis; while $B_{2g}$ is associated with the out-of-phase Sr vibrations. The broad $M_5$ mode at $\sim 715$ cm$^{-1}$ originates most likely from the two-phonon scattering, while $M_6$ at $\sim 742$ cm$^{-1}$ is a breathing mode of in-plane oxygen atoms with $B_{1g}$ symmetry. The observed modes are in good agreement with the previous symmetry-resolved single crystal Raman study and our ab-initio lattice
FIG. 1: (Color online) Unpolarized Raman spectra of Sr$_2$IrO$_4$ single crystal at 25K. The phonon modes associated with M$_1$-M$_6$ are explained in the text.

dynamics calculations and powder measurements\cite{14}. The broad shoulder type peak (\sim 334 cm$^{-1}$) at the high energy tail of M$_2$ was assigned as an A$_{1g}$ mode\cite{18}, however we do not observe any change in frequency or intensity of this peak with temperature. The same type feature at \sim 335 cm$^{-1}$ was also observed in Sr$_2$IrO$_4$ single crystal Raman scattering measurements\cite{20}. Temperature dependent Raman scattering of Sr$_2$IrO$_4$ is shown in Fig. 2. All the phonon modes are shifted towards lower frequency with increasing temperature. M$_4$ (A$_{1g}$) shows an asymmetric lineshape throughout the temperature range under study, and the asymmetry decreases with increasing temperature. In addition to these phonon modes (M$_1$ to M$_6$), we have detected a shoulder-type peak (*) at \sim 510 cm$^{-1}$, which gradually decreases its intensity and disappear at \sim 240 K; interestingly, the frequency of this peak does not change with temperature.

FIG. 2: (Color online) Temperature dependent Raman spectra of Sr$_2$IrO$_4$ single crystal. All the phonon modes are softening with increasing temperature.

FIG. 3: (Color online) (a)-(d) Solid circles represent the experimental phonon frequency change with temperature; solid lines represent the conventional anharmonic behavior estimated from two-phonon decay process. We have also observed a fluctuation of phonon mode frequencies at \sim 100 K. Figures 4(a-d) represent

dementia of three or more phonon decay are expected to
add only minor corrections in both frequency and damping constant with respect to the two-phonon decay in the temperature interval under study. For $M_1$ and $M_2$, an increased broadening is observed above $T_N \sim 240$ K, indicating that isospin disorder contribute to the damping of these modes. Remarkably, $M_4$ shows an asymmetric lineshape in the whole temperature range (25-310K); Fig. 5(a) illustrates the phonon profile of $M_4$ at 25K and 240K at selected temperatures. The solid lines represent the fitting of asymmetric phonon profile using Fano line-shape $I(\omega) = I_0(q + \epsilon)/(1 + \epsilon)^2$, where $I_0$ is the intensity, $q$ is the asymmetry parameter, and $\epsilon \equiv (\omega - \omega_0)/\Gamma$, with $\omega_0$ and $\Gamma$ being the phonon frequency and linewidth, respectively. The inverse of asymmetry parameter $(1/q)$ is a measure of the electronic continuum-phonon coupling strength. It is interesting to note that the $(1/q)$ decreases slowly with increasing temperature up to $T_N$, and decrease steeply afterward (Fig. 5(b)). The anomalous phonon frequency change ($\Delta\omega$) of modes $M_1$-$M_4$, obtained after subtraction of the expected anharmonic contribution, is shown in Fig. 5(c). The mode $M_2$ shows the maximum anomalous change ($\sim 5$ cm$^{-1}$) at 25 K; whereas, all other modes this value is $\sim 2$-3 cm$^{-1}$. The temperature-dependent bulk magnetization of Sr$_2$IrO$_4$ is shown in Fig. 5(d). It is well known that the phonon frequencies may be sensitive to spin correlations in magnetic materials. Anomalous phonon behavior below the magnetic ordering temperature is often interpreted as a manifestation of spin-phonon coupling. This coupling occurs when the magnetic exchange energy is sensitive to a phonon normal coordinate, leading to the magnetic contribution to the harmonic energy of the lattice. In $J_{eff} = 1/2$ systems the magnetic Hamiltonian is written in terms of isospins rather than pure spins and therefore the observed phonon anomalies may be ascribed to an isospin-phonon coupling. Earlier, Gretarsson et al. identified the pseudospin-lattice coupling in Sr$_2$IrO$_4$ by analyzing the asymmetric lineshape of the lowest energy phonon mode ($\sim 187$ cm$^{-1}$) above $T_N$, however, it was not possible to identify in their data anomalies in phonon frequency at $T_N$, that characterizes the spin-phonon coupling mechanism. An experimental signature of the spin-phonon coupling in antiferromagnetic materials in general is a scaling of the anomalous phonon frequency changes to the square of the sublattice magnetization below $T_N$, which in turn is proportional to the antiferromagnetic Bragg peak intensities obtained in magnetic diffraction measurements. In the present case, a complication arises from the non-collinear canted magnetic structure so that the dominant antiferromagnetic and the ferromagnetic sublattices may show different order parameters. In fact, a resonant x-ray scattering study shows that the temperature-dependence of the intensities of the antiferromagnetic Bragg peaks scales linearly rather than quadratically to the weak ferromagnetic moment obtained by bulk measurement indicating a temperature-dependent spin canting angle. Thus, the anomalous phonon frequency changes due to the isospin-phonon coupling in Sr$_2$IrO$_4$ may be also expected to scale linearly to the bulk magnetic moment. Indeed, Figs. 5(a) and 5(b) shows that $(\Delta\omega)_{spin-ph}$ scales better to the linear bulk magnetization M than to M$^2$. This analysis provide strong evidence that the anomalous phonon shifts reported here are due to an isospin-phonon coupling mechanism.
modes (see Figs. 3 and 5) may be due to a reorientation or change of the stacking pattern of the magnetic moments at this temperature. A careful account of which normal modes of vibration show spin-phonon couplings may provide valuable microscopic information on the magnetic coupling mechanisms. In our case, all studied modes $M_1-M_4$ show anomalous hardenings characteristic of spin-phonon coupling. Modes $M_1-M_3$ are assigned to vibrations involving modulation of the Ir-O-Ir angle, therefore isospin-phonon anomalies are not too surprising to be observed for such modes. On the other hand, mode $M_4$ corresponds to a stretching of the apical oxygen against the Ir ions along the $c$-direction and this mode might not be expected at first sight to modulate the magnetic coupling energy within the IrO$_6$ octahedra; this phonon mode shows an asymmetric lineshape throughout the investigated temperature range. Such asymmetry is a signature of the coupling of the phonon with the underlying electronic charge and/or spin continuum excitation. Earlier reports showed no indication of Fano-interference for the $M_4$ ($\sim 560 \text{ cm}^{-1}$) in either Sr$_2$IrO$_4$ or La-doped Sr$_2$IrO$_4$ single crystals. On the other hand, an asymmetric phonon lineshape of $M_1$ ($\sim 185 \text{ cm}^{-1}$) mode was detected in Sr$_2$IrO$_4$ single crystal above $T_N$ ($\sim 240 \text{ K}$) and in La-doped Sr$_2$IrO$_4$ single crystal above $50 \text{ K}$ which is not observed in our single crystal. In short, these results indicate low energy electronic excitations that are strongly sample dependent, and may be sensitive to the magnetic ordering temperature [see Fig. 5(b)]. Such effects are likely associated with the possible presence of charge carriers induced by intrinsic impurities in these samples. The macroscopic electrical properties of Sr$_2$IrO$_4$, including the non-ohmic I-V response, is the subject of great interest in this field and is most likely dominated by low energy electronic excitations such as those revealed by our spectroscopic data. Further theoretical and more systematic experimental studies are necessary to clarify this possible connection.

In summary, temperature dependent Raman scattering of Sr$_2$IrO$_4$ single crystals was investigated, revealing new aspects of the interaction between the crystal lattice and electronic degrees of freedom. The anomalous phonon hardening observed below the magnetic transition temperature is a signature of isospin-phonon coupling in this antiferromagnetic square lattice. The strongest effect is detected for the $A_{1g}$ ($\sim 272 \text{ cm}^{-1}$) mode associated with the modulation of in-plane Ir-O-Ir bond angle. The asymmetric lineshape of $M_4$ mode at $560 \text{ cm}^{-1}$ ($\sim 70 \text{ meV}$) originates from the coupling of this phonon with the underlying electronic continuum excitation, and this excitation is sensitive to the magnetic ordering temperature.

We thank Jean Souza for experimental support. This work was financially supported by FAPESP Grants No. 2016/00756-6 and No. 2017/10581-1, Brazil.

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