Spiral magnetic phase in Li-doped Na_2IrO_3 K. Rolfs,^{1,*} S. Toth,^{2,3} E. Pomjakushina,¹ D. Sheptyakov,² J. Taylor,^{4,5} and K. Conder¹¹Laboratory for Developments and Methods, Paul Scherrer Institut, CH-5232 Villigen, Switzerland²Laboratory for Neutron Scattering and Imaging, Paul Scherrer Institut, CH-5232 Villigen, Switzerland³Laboratory for Quantum Magnetism, ICMP, Ecole Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland⁴ISIS Facility, Science and Technology Facilities Council, Rutherford Appleton Laboratory, OX110QX Chilton, United Kingdom⁵European Spallation Source, Universitetsparken 1, DK-2100 Copenhagen, Denmark

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The doping of the honeycomb lattice compound Na_2IrO_3 with cations having smaller ionic radius such as lithium was supposed to drive the system into a Kitaev spin liquid phase. Even at the smallest doping level the long range magnetic order, present in the parent compound, got suppressed as evidenced by susceptibility and heat capacity measurements. At low doping levels, the long range ordered magnetic phase is accompanied by the formation of a glassy state with a transition temperature of $T_F \sim 5$ K as determined by dc and ac magnetic susceptibility. The magnetic excitation spectrum, measured by inelastic neutron scattering, shows a significant change with doping. Our inelastic neutron scattering data can be well described by linear spin wave theory, revealing the formation of a spiral magnetic phase.

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Within recent years a promising new direction for finding new compounds with spin-liquid ground state has been opened by focusing on Mott insulators approaching the metal insulator transition [1]. It has been suggested, that such compounds with spin-liquid ground states can create new phases, such as high- T_c superconductivity in cuprates [2]. Several iridates, such as Na_2IrO_3 , have been discovered to be quantum frustrated Mott insulators [3]. In these compounds, the strong spin-orbit coupling is the compelling property, which stabilizes the insulating state even though the on-site Coulomb interactions are relatively weak. Another interesting attribute of Na_2IrO_3 , as well as of Li_2IrO_3 , is their honeycomb structure [4,5], enabling the realization of the exactly solvable spin model with spin-liquid ground state as proposed by Kitaev [6]. It was suggested that these materials contain the necessary anisotropic exchange interactions (J_K) and that the spin-liquid ground state resists the small but always present isotropic exchange (J) [7]. However, Na_2IrO_3 and Li_2IrO_3 order magnetically at 15 K, even though this transition temperature is low compared to the characteristic exchange energy [8].

The ordering temperature of Na_2IrO_3 is relatively low when compared to the Curie-Weiss temperature T_{CW} . This gives a large $f = 8$ frustration ratio that cannot be explained within the J - J_K model. Reuther [9] suggested a spiral order in the honeycomb iridate Li_2IrO_3 based on an extended Heisenberg-Kitaev model with next-nearest Heisenberg and Kitaev couplings. For Na_2IrO_3 a zigzag structure was measured in the ordered phase [10]. Using mean-field theory, this phase can be realized only if further neighbor interactions are taken into account. Therefore the Heisenberg model has to assume further next-nearest and next-next-nearest neighbor interactions (J_2 and J_3) [11]. To access the spin-liquid phase, the reduction of these isotropic exchange terms or the increase of the anisotropic interactions are necessary. Reuther *et al.* [12] suggested that the reduction of the chemical pressure along the c axis can increase J_K and therefore induce spin-liquid

behavior. This can be achieved either by exerting pressure in the ab plane or substituting Na by smaller Li ions. Another possible chemical modification of Na_2IrO_3 is hole doping, which is predicted to lead to topological superconductivity and Fermi-liquid behavior in the vicinity of the Kitaev spin-liquid phase [5,13]. Manni *et al.* showed that $\text{Na}_{2-x}\text{Li}_x\text{IrO}_3$ with $0 < x < 1.2$ shows magnetic ordering, which gets gradually suppressed above $x = 0.5$ due to a phase separation into $\text{Na}_3\text{Ir}_2\text{LiO}_6$ and Li_2IrO_3 with a high degree of site disorder in the latter phase causing the suppression [14].

To determine the influence of Li substitution on the magnetic order of Na_2IrO_3 , polycrystalline samples of $\text{Na}_{2-x}\text{Li}_x\text{IrO}_3$ with $x = 0, 0.05, 0.1$, and 0.15 were synthesized and studied, making sure to stay below the doping level, where phase separation takes place. The samples were obtained by a solid state reaction at 1000°C using IrO_2 , Na_2CO_3 , and Li_2CO_3 as starting materials in the appropriate ratios. For all doping levels, we obtained a single crystallographic phase, determined by neutron powder diffraction (see Fig. 1). The measurements were performed at the high-resolution powder diffractometer (HRPT) at Paul Scherrer Institut (PSI) at 1.8 K [15]. Further data was collected at 50 K showing no evidence of structural phase transition or long-range magnetic order. Based on our good fits of the diffraction data using Rietveld refinements (the goodness of the fit of the 1.8 K data is $R_{\text{Bragg}} = 5.40$ and $\chi^2 = 3.06$) with a single structural phase, a phase separation could be excluded at all our doping levels. The crystal symmetry of $\text{Na}_{2-x}\text{Li}_x\text{IrO}_3$ for all doping levels could be fitted with the $C2/m$ space group, same as the parent compound, and therefore it is in good agreement with the results of Manni *et al.* [14]. However, our refinement did not show that additional lithium preferred the sodium site within the honeycomb layer [Na(1) site], contrary to their results. The best fit suggests lithium substitution on all sodium sites (see Table I).

Both samples with the doping levels $x = 0.1$ and 0.15 were also measured at the cold neutron diffractometer DMC at PSI in a momentum transfer range of 0 – $2.5 \text{ \AA}^{-1}$ at 50 and 1.5 K, in order to search for possible magnetic ordering; however, no

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FIG. 1. (Color online) Neutron powder diffraction patterns of $\text{Na}_{1.85}\text{Li}_{0.15}\text{IrO}_3$ measured at (a) 50 K and (b) 1.8 K on HRPT. Red circles denote the measured data, black lines show the result of the Rietveld refinement, and blue lines give the difference of the two.

magnetic Bragg peaks were found. By simulating the possible magnetic structures, we determined the minimum detectable ordered moment would be $0.3\mu_B$. Thus if there is any magnetic long-range order at 1.8 K, the ordered moment of iridium has to be smaller than this threshold.

The magnetic susceptibilities of the doped compounds show a deviation from the parent compound and the susceptibilities measured on single crystals by Manni *et al.* [14]. In all three samples, the transition around 15 K is suppressed and only visible as a weak kink (see Fig. 2). The two higher doped samples ($x = 0.1$ and 0.15) indicate a spin-glass-like behavior below 5 K in the dc susceptibility [here exemplarily shown for the $x = 0.15$ doped sample in Fig. 2(b)]. The Curie-Weiss temperatures (T_{CW}) of these two samples were fitted to be -126 K for the $x = 0.1$ doped sample and -125 K for the $x = 0.15$ doped sample, which are close to the T_{CW} of the parent compound. Also the ac susceptibility measurements (not shown for clarity) of the two compounds confirm the spin-glass-like behavior.

In order to better understand the magnetic correlation in the doped compounds, we measured inelastic neutron scattering (INS) of $\text{Na}_{1.85}\text{Li}_{0.15}\text{IrO}_3$ below the phase transition T_N . The experiment was performed at the time-of-flight spectrometer (TOF) MARI at ISIS with the incident neutron energy of

TABLE I. Atomic positions and occupancies of $\text{Na}_{1.85}\text{Li}_{0.15}\text{IrO}_3$ in space group $C2/m$, refined from neutron diffraction data at 1.8 K. The lattice parameters are $a = 5.3764(6)$ Å, $b = 9.3106(10)$ Å, $c = 5.5749(3)$ Å, and $\beta = 108.683(7)^\circ$.

Site	x	y	z	Occ.
Ir	1/2	0.1660(6)	0	1.00
Na(1)/Li(1)	0	0	0	0.92(1)/0.08
Na(2)/Li(2)	1/2	0	1/2	0.96(1)/0.04
Na(3)/Li(3)	1/2	0.3398(18)	1/2	0.91(1)/0.09
O(1)	0.7303(31)	0	0.2077(12)	1.00
O(2)	0.7609(25)	0.1619(7)	0.7981(8)	1.00

FIG. 2. (Color online) Magnetic susceptibilities of (a) $\text{Na}_{1.95}\text{Li}_{0.05}\text{IrO}_3$ and (b) $\text{Na}_{1.85}\text{Li}_{0.15}\text{IrO}_3$ in 0.1 T. T_N indicates magnetic phase transition; T_F pinpoints the freezing temperature, where the sample undergoes a spin-glass-like transition.

18 meV. The measured magnetic spectrum as a function of momentum transfer Q and energy transfer are shown in Fig. 3(a).

On the measured magnetic spectrum, at low Q , two spin wave branches centered around 0.85 Å^{-1} could be observed. One branch progresses towards lower Q , with an increased intensity at 0.8 Å^{-1} and an energy of 3 meV, which is fading around $Q \leq 0.6 \text{ Å}^{-1}$. The second branch shows a sinusoidal behavior towards higher Q with a maximum below 4 meV. The momentum integrated cut of the data in Fig. 3(e) shows clearly a peak around 0.8 Å^{-1} at 5 K. By measuring the sample above the magnetic phase transition at 30 K, the signal disappears [see Fig. 3(b)], verifying the magnetic origin of the observed intensities measured at 5 K. The increased background is due to phonons of the sample and the aluminum sample holder. The cut of the high temperature data show only a flat signal in the observed Q range [see Fig. 3(f)].

The low temperature measurement shows a clear deviation from the INS data measured on the parent compound Na_2IrO_3 by Choi *et al.* [10]. The observed excitations are shifted from 0.67 Å^{-1} in the zigzag phase to 0.85 Å^{-1} . Furthermore there is the development of low energy excitation between 0.9 and

FIG. 3. (Color online) INS data of $\text{Na}_{1.85}\text{Li}_{0.15}\text{IrO}_3$ at (a) 5 K and (b) 30 K measured at the TOF spectrometer MARI. Simulation of the (c) spiral 1 phase with parameters $J_2/J_1 = 0.6$ and $J_3/J_1 = 0.4$ and (d) the zigzag phase with parameters $J_2/J_1 = 0.78$ and $J_3/J_1 = 0.9$. Both simulated powder spectra are based on the Heisenberg model including first to third neighbor interactions and the magnetic form factor of Ir^{4+} . Intensity cuts integrated in energy between 2 and 3.2 meV of the TOF data are shown in (e) and (f) for 5 and 30 K, respectively. Blue and red lines denote the same cut of the spin wave simulation in the spiral 1 and zigzag phases, respectively.

$1.4 \text{ \AA}^{-1}$, which is not present in the zigzag phase [see simulated pattern of the zigzag phase in Fig. 3(d)].

In order to model the observed magnetic spectrum, we calculated the mean-field magnetic phase diagram and the spin wave dispersions using SPINW [16]. Based on previous spin wave results on Na_2IrO_3 [10], we extended the calculation for the spiral magnetic phases and assuming Heisenberg interactions up to the third neighbor in the honeycomb plane and neglecting interplanar couplings (see Supplemental Material [17]). Thus the magnetic Hamiltonian is the following:

$$H = \sum_{\langle i,j \rangle} J_1 S_i S_j + \sum_{\langle\langle i,j \rangle\rangle} J_2 S_i S_j + \sum_{\langle\langle\langle i,j \rangle\rangle\rangle} J_3 S_i S_j. \quad (1)$$

Even though a spin-glass phase was observed below T_F for doping levels $x > 0.05$, we expect that linear spin wave theory can be used to determine the exchange parameters. Since the glass state is the result of a weak structural disorder as evidenced by neutron powder diffraction we expect that a small random perturbation of the exchange interactions is causing the glassy ground state. This weak perturbation causes

FIG. 4. (Color online) Spiral 1 magnetic structure calculated based on the Heisenberg model including first to third neighbor interactions with values $J_2/J_1 = 0.6$ and $J_3/J_1 = 0.4$.

shortening of the magnetic correlation length and time scales. However, due to the relatively low momentum and energy resolution of the measured data (not better than 2%–4% of the incident energy and momentum) we expect that the glassy state cannot be distinguished from the long-range-ordered state of the unperturbed ideal Hamiltonian.

The magnetic phase diagram (see Supplemental Material), was calculated for next-nearest-neighbor (NN) coupling J_2 and next-next-nearest-neighbor (NNN) coupling J_3 ranging between $J_2/J_1 \in [0, 1]$ and $J_3/J_1 \in [-1, 2]$, respectively. Furthermore, the magnetic form factor of Ir^{4+} was taken into account [18]. The overall energy scale of the interactions was fixed to the Curie-Weiss temperature of -125 K using the following mean-field formula:

$$T_{CW} = -S(S+1)(J_1 + 2J_2 + J_3)/k_B. \quad (2)$$

The calculated magnetic phase diagram conforms with Fouet's calculation [19], revealing three commensurate and three incommensurate spiral phases. Comparing the simulation with the measured spin wave dispersion, it is clearly visible that the spin wave spectrum of the zigzag phase does not coincide with the spectrum measured for $\text{Na}_{1.85}\text{Li}_{0.15}\text{IrO}_3$ [see Figs. 3(a) and 3(d)]. The spin wave calculation fitting significantly better to the data shows a coupling of $J_3/J_1 = 0.4$, which is placed well below the phase boundary of the zigzag and the spiral 1 phase with an ordering wave vector of $k = (\phi/\pi, 0, 0)$ (see Fig. 4). To our best knowledge, the best fitting NN coupling is $J_2/J_1 = 0.6$ [see Fig. 3(c)] resulting in $k = (0.42, 0, 0)$ with $\phi = 75.5^\circ$. The corresponding exchange constants are $J_1 = 5.52 \text{ meV}$, $J_2 = 3.31 \text{ meV}$, and $J_3 = 2.21 \text{ meV}$. However, the change of J_2/J_1 between 0.5 and 0.8 does not result in a significant change of the dispersion and can also be considered as suitable solutions (see Supplemental Material). Nevertheless, all possible solutions are very well positioned in the parameter space of the spiral 1 phase.

Introducing the Kitaev coupling J_K and keeping the isotropic exchange parameter within the spiral 1 phase shows that the phase with $k = (\phi/\pi, 0, 0)$ is only stable up to a small value of J_K . Increasing the Kitaev coupling above

$J_K/J_1 > 0.05$ leads to the instability of the phase and a more complex magnetic structure, which is not comparable with the measured data.

Remarkably, low lithium doping of Na_2IrO_3 leads to significant changes of its magnetism. Although $\text{Na}_{2-x}\text{Li}_x\text{IrO}_3$ has a similar magnetic ordering temperature for all doping levels, the light doping with $x = 0.15$ (7.5 at. % of Li) results in a significant change of the low temperature magnetic phase. Comparing the excitation spectrum of the doped and parent compound suggests a change of the exchange parameters. The change of the NN and NNN coupling has to be caused by the introduction of the smaller Li cations as a perturbation. This can induce a slight distortion of the honeycomb lattice and results in the observed change of the coupling strength. With this modified exchange coupling also the magnetic structure changes. As a result the lightly doped system shows a spiral magnetic phase in the ordered state.

The introduction of ferromagnetic Kitaev coupling to the system was only possible for a small contribution of less than 5% of J_1 . Larger anisotropic interactions lead to the instability of the spiral 1 phase with the given wave vector and the formation of a more complex magnetic structure, which has to be determined in more detail. Clearly this structure is not present in this system, since the possible spin wave spectra do not conform with the measured dispersions. As discussed in [20], the noncubic crystal field symmetry of the Li-doped Na_2IrO_3 leads to a reduced anisotropic exchange, which is in agreement with our observations.

The overall suppression of the magnetic ordering is accompanied by the emergence of a spin-glass phase above $x = 0.05$ Li doping, which could be explained by a higher level of disorder generally present in powder samples than in single crystals. However, the exact nature and origin of this spin-glass phase is not understood yet. Na_2IrO_3 already has a significant amount of site disorder, higher than the here examined doping levels, without suppressing the magnetic long-range order. The phase separation observed at higher lithium content by Manni *et al.* can be excluded here due to the low doping level. Since the Li distributes approximately evenly on the sodium sites, the strength of the interactions between the honeycomb layers, could increase at these specific positions and result in a weak perturbation of the planar magnetic structure. Due to the low doping level, this would not be visible on the inelastic data, but may show its influence in the susceptibility data by the development of a glassy state.

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