12-31-2013

Evolution of Magnetism in the Single-Crystal Honeycomb Iridates \((\text{Na}_{1-x}\text{Li}_x)\text{IrO}_3\)

Gang Cao  
*University of Kentucky, gang.cao@uky.edu*

Tongfei Qi  
*University of Kentucky, tongfei.qi@uky.edu*

L. Li  
*University of Kentucky*

Jasminka Terzic  
*University of Kentucky, jasminka.terzic@uky.edu*

Vincent Shian Cao  
*University of Kentucky, vincent.cao@uky.edu*

*See next page for additional authors*

Click here to let us know how access to this document benefits you.

Follow this and additional works at: [https://uknowledge.uky.edu/physastron_facpub](https://uknowledge.uky.edu/physastron_facpub)

Part of the [Condensed Matter Physics Commons](https://uknowledge.uky.edu/physastron_facpub)

Repository Citation

Cao, Gang; Qi, Tongfei; Li, L.; Terzic, Jasminka; Cao, Vincent Shian; Yuan, Shujuan; Tovar, M.; Murthy, Ganpathy; and Kaul, Ribhu K., "Evolution of Magnetism in the Single-Crystal Honeycomb Iridates \((\text{Na}_{1-x}\text{Li}_x)\text{IrO}_3\)" (2013). Physics and Astronomy Faculty Publications. 447.  
[https://uknowledge.uky.edu/physastron_facpub/447](https://uknowledge.uky.edu/physastron_facpub/447)

This Article is brought to you for free and open access by the Physics and Astronomy at UKnowledge. It has been accepted for inclusion in Physics and Astronomy Faculty Publications by an authorized administrator of UKnowledge. For more information, please contact UKnowledge@lsv.uky.edu.
Authors
Gang Cao, Tongfei Qi, L. Li, Jasmina Terzic, Vincent Shian Cao, Shujuan Yuan, M. Tovar, Ganpathy Murthy, and Ribhu K. Kaul

Evolution of Magnetism in the Single-Crystal Honeycomb Iridates (Na$_{1-x}$Li$_x$)$_2$IrO$_3$

Notes/Citation Information

©2013 American Physical Society

The copyright holder has granted permission for posting the article here.

Digital Object Identifier (DOI)
https://doi.org/10.1103/PhysRevB.88.220414
Evolution of magnetism in the single-crystal honeycomb iridates (Na$_{1-x}$Li$_x$)$_2$IrO$_3$


1Department of Physics & Astronomy, University of Kentucky, Lexington, Kentucky 40506-0055, USA
2Paul Laurence Dunbar High School, Lexington, Kentucky 40513, USA
3Department of Physics, Shanghai University, Shanghai, China

(Received 8 July 2013; revised manuscript received 16 September 2013; published 31 December 2013)

We report the successful synthesis of single crystals of the layered iridate (Na$_{1-x}$Li$_x$)$_2$IrO$_3$, 0 ≤ x ≤ 0.9, and a thorough study of its structural, magnetic, thermal, and transport properties. This compound allows a controlled interpolation between Na$_2$IrO$_3$ and Li$_2$IrO$_3$, while maintaining the quantum magnetism of the honeycomb Ir$^{4+}$ planes. The measured phase diagram demonstrates a suppression of the Néel temperature $T_N$ at an intermediate $x$, indicating that the magnetic orders in Na$_2$IrO$_3$ and Li$_2$IrO$_3$ are distinct. X-ray data show that for $x = 0.7$, when $T_N$ is suppressed the most, the honeycomb structure is least distorted, leading to the speculation that at this intermediate doping of the material is closest to the spin liquid that has been sought after in Na$_2$IrO$_3$ and Li$_2$IrO$_3$. By analyzing our magnetic data with a single-ion theoretical model we also show that the trigonal splitting on the Ir$^{4+}$ ions changes sign from Na$_2$IrO$_3$ to Li$_2$IrO$_3$.

DOI: 10.1103/PhysRevB.88.220414

PACS number(s): 75.40.Cx, 75.10.Jm, 75.40.Gb, 75.50.Lk

Introduction. The iridates have been recognized recently as a unique arena for the study of new phases of matter that arise from simultaneously strong electron-electron and spin-orbit interactions. Thus far, the most novel manifestation of a theoretical analysis [6] showed that the oxygen mediated superexchange processes between the Ir$^{4+}$ moments in the honeycomb iridates Na$_2$IrO$_3$ and Li$_2$IrO$_3$ result in the celebrated Kitaev model (KM) for the $J_{eff} = 1/2$ degrees of freedom, $H_K = K \sum_{i,j} \sigma_i^x \sigma_j^y$, where $\sigma_x$, $\sigma_y$, $\sigma_z$ denotes a different Pauli matrix for each direction of bond on the honeycomb lattice and $\sigma_i^x$ acts on the $J_{eff} = 1/2$ states on site $i$. The KM can be solved exactly, and its ground state is an exotic magnetically disordered quantum “spin liquid.” [7]; However, it is experimentally established that both honeycomb iridate compounds order magnetically: Na$_2$IrO$_3$ orders at $T_N = 18$ K [8], and Li$_2$IrO$_3$ orders at $T_N = 15$ K [9,10]. There are many theoretical proposals for interactions that are supplementary to the Kitaev model that would cause magnetic ordering, including additional exchange processes [10–16], strong trigonal fields [17], or weak coupling instabilities [18]; currently there is no consensus on which of these is correct.

On the experimental side, there are now fairly thorough studies of Na$_2$IrO$_3$ using both momentum resolved resonant inelastic x-ray and neutron scattering techniques that establish the pattern of magnetic ordering to be of an unusual zigzag type [12,19–21]. This has been possible in part due to the availability of large single crystals of Na$_2$IrO$_3$. Because of various difficulties in chemical synthesis, no such single crystals are available for Li$_2$IrO$_3$ and the detailed magnetic ordering pattern of this compound is still unknown. It is noted that an early study on polycrystal Li$_2$IrO$_3$ exhibited no magnetic order above 5 K [22], but more recent measurements show a magnetic transition at $T_N = 15$ K [10]. The conspicuous absence of single crystals of Li$_2$IrO$_3$ is clearly a major roadblock in a complete characterization of this material.

In this Rapid Communication we fill the gap in our understanding by the successful synthesis and study of single crystals of (Na$_{1-x}$Li$_x$)$_2$IrO$_3$ [23]. The central findings of our work are as follows: As $x$ is tuned, we find from x-ray data that the lattice parameters evolve monotonically from Na to Li, retaining the basic Mott insulating honeycomb structure of the Ir$^{4+}$ planes for all $x$. Even so, there is a nonmonotonic dramatic change in Néel temperature $T_N$ with $x$, in which $T_N$ initially decreases from 18 K at $x = 0$ to 1.2 K at $x = 0.70$ before it rises to 7 K at $x = 0.90$, indicating that the magnetic ground states at $x = 0$ and 1 are not related linearly, as had been previously suggested [10]. X-ray structure data show that the Ir$^{4+}$ honeycomb lattice is least distorted at $x \approx 0.7$. Interestingly, we find the lowest $T_N$ and highest frustration parameter also at $x \approx 0.7$. In addition, the high-temperature anisotropy in the magnetic susceptibility is simultaneously reversed and enhanced upon Li doping, and as a result, the in-plane magnetic susceptibility $\chi_{//}(T)$ becomes significantly greater than the perpendicular-to-plane susceptibility $\chi_{\perp}(T)$ or $\chi_{//}(T) > \chi_{\perp}(T)$ for $x = 0.90$, which sharply contrasts with the weaker magnetic anisotropy for $x = 0$ where $\chi_{//}(T) < \chi_{\perp}(T)$. Using a single-ion theoretical model, we show that the anisotropy arises from a trigonal crystal field $\Delta$ oriented perpendicular to the honeycomb layers, and the anisotropy change is the result of a sign change in the local trigonal field between the Na and Li compounds. We thus conclude that the magnetic ground states of the pure Na and Li compounds are distinct and are separated by a quantum phase transition that is driven by the evolution of the crystal structure as $x$ is varied.

Measurements. The methods by which our single crystals are grown and the measurements are carried out are described in the Supplemental Material (SM) [24]. Li doping retains the space group of C2/m that Na$_2$IrO$_3$ adopts but induces a systematic decrease in the lattice parameters since the ionic radius of the Li ion is approximately 25% smaller than that of the Na ion. The lattice parameters are shown in Fig. 1(a). An
and the basal plane $\beta = 6.5\%$, respectively. The corresponding angle between the susceptibility for $x$ in inset of Fig. 2(b), we find consistent values for $x$ peaks in a evolution of distortion of the honeycomb lattice of Ir$_4$C.

Inset: An illustration of the crystal structure of Na$_2$IrO$_3$. (b) The evolution of distortion of the honeycomb lattice of Ir$^{4+}$ ions from $L_2 > L_1$ for $x = 0$ to $L_1 > L_2$ for $x = 1$. At $x \approx 0.7$, the system is a near perfect honeycomb.

Important feature of this change is that the lattice parameter $c$ is more severely compressed than $a$ and $b$. For example, for $x = 0.90$, the decrease in $a$, $b$, and $c$ is 2.5%, 2.7%, and 6.5%, respectively. The corresponding angle between the $c$ axis and the basal plane $\beta$ increases to 109.58° for $x = 0.90$ from 108.67° for $x = 0$. In Fig. 1(b), we show how the distortion of the $a$-$b$ honeycomb lattice on which the Ir$^{4+}$ moments reside evolves with $x$. The ratio $L_2/L_1$ (defined in the inset) clearly shows the lattice anisotropy reversal from Na to Li.

We extract $T_N$ by locating the low-temperature peak in the specific heat $C(T)$, shown in Fig. 2(a), as well as the in-plane susceptibility $\chi_{\parallel}(T)$, shown in Fig. 2(b). The pronounced peaks in $C(T)/T$ unambiguously signal a continuous magnetic phase transition for all $x$. As shown in the main panel and inset of Fig. 2(b), we find consistent values for $T_N$ extracted from $\chi_{\parallel}(T)$. Interestingly, $T_N(x)$ is not a smooth interpolation between the already known $x = 0$ and 1 limits. It is initially suppressed from 18 K for $x = 0$ to 5 K for $x = 0.28$ and then to 1.2 K for $x = 0.70$ before it rises to 1.4 K for $x = 0.80$ and finally 7 K for $x = 0.90$. We note that the trend of $T_N$ increasing again in our single crystal, $x = 0.9$, is consistent with previous measurements on polycrystalline samples of Li$_2$IrO$_3$ [10]. A phase diagram that summarizes $T_N$ and the Curie-Weiss scale $\theta_{CW}$ as a function of $x$ is shown in Figs. 3(a) and 3(b). A natural conclusion based on the strongly suppressed value of $T_N$ is that it goes to zero for some $x$ and one encounters at least one quantum phase transition in the evolution from Na$_2$IrO$_3$ to Li$_2$IrO$_3$ at $x \approx 0.7$, implying that the magnetic ground states of Na$_2$IrO$_3$ and Li$_2$IrO$_3$ are not adiabatically connected. It is interesting to note that at $x \approx 0.7$, when $T_N$ is suppressed the most, the honeycomb plane is closest to ideal [i.e., $L_2/L_1 \approx 1$ in Fig. 1(b)]. Finally, we note that the dominant role of Li doping is to tune the chemical pressure, which in turn causes an evolution of the lattice structure. This can be verified by noting that if we dope in K instead of Li, $T_N$ increases, as shown in Fig. 3(a). This is consistent with K doping achieving a negative chemical pressure because the ionic radius of K is larger than Na.

**Anisotropy in $\chi_{\parallel}\chi_{\perp}$.** There are a number of striking features observed in our measurements of the direction dependent susceptibility in our single-crystal samples; the data for $x = 0$ and 0.9 are shown in Fig. 4. First, there are large anisotropies in the susceptibility even when $T \gg T_N$; indeed, the Curie constant $A$ itself depends on the direction of the applied field. We define the Curie constant by the usual definition, $\lim_{T \to \infty} \chi_{\parallel,\perp} = \frac{A}{T}$. It is natural to attribute such anisotropies to the spin-orbit coupling (we study this in detail below). Second, the anisotropy between $\chi_{\parallel}(T)$ and
\[ H = -\lambda \vec{s} - \Delta (\vec{n} \cdot \vec{s}) - \vec{n} \cdot (2\vec{s} - \vec{t}), \]

where \( \vec{t} \) are the usual spin-1 matrices and \( \vec{s} \) are the usual spin-1/2 matrices, satisfying \( [l_x, l_y] = il_z \) and \( [s_x, s_y] = is_z \). We have made use of the well-known \( l = 1 \) description of the \( f_{2g} \) states [25]. The trigonal distortion vector \( \vec{n} \) must point along a body diagonal of a cube that circumscribes the oxygen octahedra. In the material [see the inset of Fig. 1(a)] the direction perpendicular to the honeycomb planes indeed is the natural direction to associate with \( \vec{n} \) (we will verify this assumption from an analysis of the magnetic data below; structural data included in the SM [24] also verify this assertion). We calculate \( A_{\parallel} < A_{\perp} \), which in our theoretical calculation (see Supplemental Material [24] for details) only depends on \( \Delta/\lambda \), and these are plotted in Fig. 5(a). We make the following observations from our model calculations: Because of the rotational symmetry, \( A \) is the same for all directions perpendicular to \( \vec{n} \); when \( \Delta = 0 \) the response is rotationally invariant (i.e., \( A_{\parallel} = A_{\perp} \)) even when \( \lambda \neq 0 \); the anisotropy between \( A_{\parallel} \) and \( A_{\perp} \) is reversed as the sign of \( \Delta \) changes; and, as expected for \( \Delta/\lambda \to +\infty \), the system becomes rotationally invariant again.

At high temperatures (\( T > \theta_{\text{CW}} \)), the Ir ions contribute independently to the susceptibility and one can hence use the high-\( T \) experimental data to extract the Curie constants \( A \). First of all, we find that the experimentally measured \( A \) is the same within our errors of analysis for different directions in the honeycomb plane, but it is clearly different for the direction perpendicular to the honeycomb layers [shown for \( x = 0 \) by the rotation experiments in Fig. 4(b)]; this fact substantiates our claim that the \( \vec{n} \) vector is along the direction perpendicular to the honeycomb layers. Next, as noted above, the anisotropy in the susceptibility requires a finite \( \Delta \), indicating that this parameter cannot be neglected in models of these materials. From Fig. 5, it is clear that the change in anisotropy between...
An extrapolation of the experimental $\chi(T)/\chi_0(T)$ in the high-temperature limit. At $T = \infty$ this ratio should be simply $A_\parallel/A_\perp$. Note that Na$_2$IrO$_3$ has $A_\perp/A_\parallel > 1$ and hence $\Delta < 0$, and based on the shown extrapolation for $x = 0.9$, Li$_2$IrO$_3$ will extrapolate to $A_\perp/A_\parallel < 1$ with $\Delta > 0$. In both cases, clearly $\lambda \gg |\Delta|$.

$x = 0$ and 0.9 indicates that the sign of $\Delta$ changes between Na$_2$IrO$_3$ and Li$_2$IrO$_3$. Quantitatively, we extract the ratio $A_\perp/A_\parallel$ by extrapolating $\chi_\perp/\chi_\parallel$ as a function of $1/T$, as shown in Fig. 5(b). For Na$_2$IrO$_3$ we can do this reliably. We estimate $\Delta/\lambda = -0.05$ for Na$_2$IrO$_3$, which we note is smaller than previous estimates [18,21]. Based on our data, we conclude that for Li$_2$IrO$_3$ the sign of $\Delta$ changes and its magnitude is somewhat larger: Our best estimate gives $\Delta/\lambda \approx 0.1$.

In summary, we present evidence that Na$_2$IrO$_3$ and Li$_2$IrO$_3$ have distinct magnetic orders, by studying the evolution of structural, thermodynamic, and magnetic properties of (Na$_{1-x}$Li$_x$)$_2$IrO$_3$ with $x$ across a phase transition at $x \approx 0.7$. Two possible tuning parameters for the phase transition that we have identified are the crystal field splitting $\Delta$ and the anisotropy of the distortion of the honeycomb layers, both of which change sign from the Na to Li compounds. It is likely that a competition between the two is required to explain the magnetic ordering. Exploring these issues is an exciting direction for future theoretical research.

The authors are thankful to Natasha Perkins and Feng Ye for useful discussions. This work was supported by the National Science Foundation under Grants No. DMR-0856234, No. EPS-0814194, No. DMR-1265162, and No. DMR-1056536 (R.K.K. and M.T.). G.C. also acknowledges the hospitality of the China High Magnetic Field Laboratory of the Chinese Academy of Sciences.

[23] For comparison only, we also present some results on (Na$_{1-x}$K$_x$)$_2$IrO$_3$ (with $x < 0.02$); the pure compound K$_2$IrO$_3$ has not yet been synthesized.