Antiferromagnetic resonance in the cubic iridium hexahalides 
(NH$_4$)$_2$IrCl$_6$ and K$_2$IrCl$_6$


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Transition-metal compounds with partly filled 4d and 5d orbitals have recently attracted enormous attention as promising candidates for realizing novel magnetic phenomena, emerging from the interplay between crystal-field effects and spin-orbit interactions [1–3]. In particular, honeycomb structures distinct from the honeycomb geometry [12–17] remain focused on honeycomb materials as the most promising platform for the Kitaev interaction [9–11], there is also a significant interest in detecting anisotropic exchange terms (including the Kitaev interaction) in Ir4+ compounds with structures distinct from the honeycomb geometry [12–17]. However, most of the nonhoneycomb iridates studied over the last decade still evade detailed spectroscopic characterization with an unambiguous experimental determination of their interaction parameters. In particular, the absence of large single crystals as well as the notoriously strong neutron absorption by Ir atoms (which is of crucial importance for inelastic neutron scattering studies) and the insufficient energy resolution (in case of resonant inelastic x-ray scattering, RIXS) have often hindered the experimental access to relevant magnetic excitations.

Here we focus on two compounds from the family of Ir4+ antifluorites [18–21], (NH4)2IrCl6 and K2IrCl6, that have been recently revisited by crystallographic and thermodynamic studies [22–24]. These compounds feature Ir4+ ions arranged on a face-centered cubic (fcc) lattice with four sublattices [Fig. 1(a)] and distinct long-range superexchange pathways mediated by the covalently bonded halogen ions [Fig. 1(b)]. The presence of possible frustration in fcc lattices is interesting in its own right as it shows an intricate competition of magnetic ground states, even in the absence of Kitaev or any other exchange anisotropy [25–27]. In contrast to many other iridates, these compounds are available as relatively large single crystals amenable to laboratory spectroscopic probes, featuring a cubic symmetry of the molecule that not only ensures the spin-orbit-coupled j eff = 1/2 state of the Ir4+ ions, but also restricts the number of relevant interaction parameters.

In the following we present electron spin resonance (ESR) studies of (NH4)2IrCl6 and K2IrCl6, revealing the presence of two gapped magnon modes in each of the compounds. Employing linear spin-wave-theory calculations, we estimate the spin-Hamiltonian parameters and, consequently, establish the main interaction terms.

Single crystals of (NH4)2IrCl6 and K2IrCl6 were grown from solutions prepared by dissolving commercially available powders (Alfa Aesar) in deionized water and keeping the solutions at 60 °C for several days. The resulting crystals had well-defined hexagonal (111) faces and sizes of ~2–3 mm3. Magnetization measurements revealed magnetic ordering transitions at 2.15 K for (NH4)2IrCl6 and 3.1 K for K2IrCl6, in agreement with previous studies [20,22,23,28].
High-field electron spin resonance (ESR) measurements were performed employing a transmission-type ESR spectrometer (similar to that described in Ref. [29]), in magnetic fields up to 16 T. Measurements were done in the frequency range of 60–400 GHz, using a set of VDI microwave-chain radiation sources (product of Virginia Diodes, Inc., USA). An InSb hot-electron bolometer (QMC Instruments Ltd., UK) was used to record the spectra. We measured single crystals in the Faraday configuration with magnetic field $H \parallel [111]$ and in the Voigt configuration with $H \perp [111]$. For the powder samples we confined the specimens by a binding agent such as high vacuum grease. The powders were obtained by crushing single crystals to ensure consistency between single-crystal and powder measurements. The stable free-radical molecule DPPH (2,2-diphenyl-1-picrylhydrazyl) was used as a frequency-field marker.

ESR is traditionally recognized as a powerful tool to probe crystal-field effects in solids. A very sensitive test of the presence of noncubic distortions in covalently bound complexes is provided by a $g$-factor anisotropy [18]. In Fig. 2 we show powder and single-crystal spectra obtained for (NH$_4$)$_2$IrCl$_6$ (a) and K$_2$IrCl$_6$ (b) at a temperature of 50 K. Both powder spectra were fit using a Lorentzian function with $g = 1.79(1)$, and linewidths of 0.93 and 1.23 T for (NH$_4$)$_2$IrCl$_6$ and K$_2$IrCl$_6$, respectively. These parameters perfectly agree with the simulation results for the single crystals along both $H \parallel [111]$ and $H \perp [111]$, revealing isotropic paramagnetic $g$ factors, and thus evidencing the cubic symmetry for both compounds. The reduction of the $g$ factor from the free-spin value ($g = 2$) is attributed to the covalent nature of the Ir and Cl bonds [30,31]. Large covalency of the Ir$^{4+}$ halides was indeed confirmed by recent RIXS studies [24], detecting also minor deviations from the free state [23], despite the absence of any macroscopic symmetry lowering [22].

Upon cooling, the ESR spectra for $H \parallel [111]$ exhibit significant broadening, evidencing enhancement of magnetic correlations, with the maximum in the vicinity of $T_N$ (Figs. 3 and 4). On further decreasing the temperature, the ESR linewidth rapidly decreases, revealing the onset of long-range ordering below $T_N$. This transition into the ordered state also results in a pronounced low-temperature shift of the ESR field positions.

Two antiferromagnetic resonance (AFMR) modes $A_1$ and $A_2$ were observed in the magnetically ordered state (Figs. 5 and 7). Selected AFMR spectra measured at 1.5 K with magnetic field applied along the [111] direction are shown in Fig. 6 for (NH$_4$)$_2$IrCl$_6$, and in the inset of Fig. 7 for K$_2$IrCl$_6$.

The frequency-field dependencies of the modes $A_1$ and $A_2$ can be described using the equation

$$\nu = \frac{\Delta \pm g_{\text{eff}} \mu_B B}{\hbar},$$

where $\hbar$ is the Planck constant, $\nu$ represents the excitation frequency, $g_{\text{eff}}$ is the effective $g$ factor, and $\mu_B$ is the Bohr magneton. From this linear fit we obtain the zero-field magnon gaps $\Delta = 235 \pm 10$ and $295 \pm 10$ GHz (which correspond to 11.3 and 14.2 K; $g_{\text{eff}} = 0.8$) for (NH$_4$)$_2$IrCl$_6$ and K$_2$IrCl$_6$, respectively. For both materials, mode $A_1$ shows a linear increase in the resonance-field position, while some deviation from the linear dependence was observed for mode $A_2$ in high
fields. Noticeably, the mode $A_2$ disappears above $\sim 6$ T. This field corresponds to a field-induced transition reported for $K_2\text{IrCl}_6$ [32], whereas in $(\text{NH}_4)_2\text{IrCl}_6$ the changes in applied field appear to be limited to a domain repopulation wherein the number of domains with magnetic moments oriented perpendicular to the applied field increases [33].

A general form of spin-spin interactions in magnetic systems with an fcc crystal structure was discussed by several authors [13,22,34,35]. Apart from the Heisenberg exchange, it includes symmetry-allowed anisotropic terms typical for materials with strong spin-orbit coupling. According to an ab initio calculation [22] two strongest spin-spin interactions in $(\text{NH}_4)_2\text{IrCl}_6$ and $K_2\text{IrCl}_6$ are the Heisenberg exchange $J_1 > 0$ and the Kitaev interaction $K > 0$ for the nearest-neighbor (nn) pairs of Ir ions. In addition, a weak next-nearest-neighbor (nnn) exchange $J_2 > 0$ is necessary to explain the experimentally observed type-III antiferromagnetic order [36]. Accordingly, we consider the following Hamiltonian for effective $S = 1/2$ moments of iridium ions:

$$\hat{H} = \sum_{\langle ij \rangle} (J_1 \mathbf{S}_i \cdot \mathbf{S}_j + K \mathbf{S}_i^\gamma \mathbf{S}_j^\gamma) + J_2 \sum_{\langle ij \rangle} \mathbf{S}_i \cdot \mathbf{S}_j,$$

where $\mathbf{S}_i$ and $\mathbf{S}_j$ are spin-1/2 operators at site $i$ and $j$, respectively. In the anisotropic Kitaev term, $\gamma$ is one of the cubic axes ($x, y, z$) that is orthogonal to a given bond.

The Heisenberg fcc antiferromagnet with only the nearest-neighbor interactions has highly degenerate classical ground states [37]. A small positive next-nearest-neighbor exchange $J_2$ lifts this degeneracy in favor of the type-III magnetic structure described by the propagation vector $\mathbf{Q} = (2\pi/a, \pi/a, 0)$ [38] [note that $\mathbf{Q}' = (0, \pi/a, 2\pi/a) = -\mathbf{Q} + \mathbf{G}$, where $\mathbf{G}$ is a reciprocal lattice vector]. In addition, the anisotropy $K > 0$ locks magnetic moments in the $(0,1,0)$ direction:

$$\mathbf{S}_i = \sqrt{2} S \mathbf{y} \cos(\mathbf{Q} \cdot \mathbf{r}_i \pm \pi/4).$$

Together with two other equivalent $\mathbf{Q}$, obtained by permutation of $\mathbf{Q}_{x,y,z}$, there are in total six domains for the type-III collinear structure.

Following a recent theoretical study of the excitation spectra in fcc antiferromagnets [26], we have performed linear spin-wave calculations for the Hamiltonian (2) with $J_2, K > 0$. The ESR response corresponds to long wavelength excitations with $k \to 0$. Accordingly, the ESR spectrum is formed by two degenerate pairs of gapped magnons with the zero-field excitation energies:

$$\Delta_1 = 2\sqrt{K J_2}, \quad \Delta_u = 2\sqrt{4K J_1 + 2K^2 + K J_2}. \quad (4)$$

Note that the size of the low-energy gap $\Delta_1$ is determined by both $K$ and $J_2$, while the upper gap $\Delta_u$ depends mainly on the strength of the Kitaev interaction. Moreover, in the absence of $K$ both gaps vanish, while at $J_2 \to 0$ they have substantially different magnitudes.
The next-nearest-neighbor isotropic exchange coupling was recently estimated from the ab initio calculation as $J_2/k_B \approx 0.2$ K for both (NH$_4$)$_2$IrCl$_6$ and K$_2$IrCl$_6$ [22,23]. In addition, we use the expression for the Curie-Weiss temperature [39]

$$\theta_{CW} = 3J_1 + K + \frac{3}{2}J_2.$$  

Experimental values for $\theta_{CW}/k_B$ are 32 K for (NH$_4$)$_2$IrCl$_6$ [33] and 42.6 K for K$_2$IrCl$_6$ [22]. They are obtained by fits to the magnetic-susceptibility data in the 100–400 K and 150–400 K range, respectively. The corresponding effective moment of 1.73 $\mu_B$ confirms that mostly the ground-state doublet is occupied in this temperature range. Using Eqs. (4) and (5) we estimate $J_1/k_B = 10.3$ K and $K/k_B = 0.7$ K for (NH$_4$)$_2$IrCl$_6$, and $J_1/k_B = 13.8$ K and $K/k_B = 0.9$ K for K$_2$IrCl$_6$ ($K/J_1 \approx 6\%–7\%$). The exchange coupling $J_1$ is stronger for K$_2$IrCl$_6$ compared to (NH$_4$)$_2$IrCl$_6$, due to

the lattice parameter difference ($a = 9.77$ vs $9.87$ Å [22,23], respectively), with the respective negative pressure reducing magnetic interactions in (NH$_4$)$_2$IrCl$_6$. It is worth noting that our experimental value of $K$ is much smaller than the 5 K reported in Ref. [22]. This discrepancy may indicate the importance of Hund’s coupling on the Cl ligand, an effect that has been neglected in the superexchange theory used in Ref. [22] and generally leads to a ferromagnetic contribution, which counteracts antiferromagnetic superexchange. Similar effects were previously reported in Cu$^{2+}$ halides [40].

Using the parameters, as obtained above, the size of low-energy gaps was also estimated, yielding $\Delta_1/k_B \approx 1$ K. Our thorough search did not reveal the low-energy AFMR modes (note also that our ESR probe has a cut-off frequency limit of 60–70 GHz that is higher than the expected size of $\Delta_1$). The absence of the low-energy ESR modes, which directly depends on $J_2$, may indicate, on the other hand, that the next-nearest-neighbor exchange in these compounds is very small. In such a case the quantum order-by-disorder effect can play a significant role in the Kitaev fcc antiferromagnets [41].

Summarizing, we presented systematic ESR studies of the two iridium hexahalide compounds (NH$_4$)$_2$IrCl$_6$ and K$_2$IrCl$_6$. In the paramagnetic state, our measurements reveal isotropic g factors $g \approx 1.79(1)$ for Ir$^{3+}$ ions, confirming their cubic symmetries. By measuring the ESR spectra in the ordered state, we were able to determine the nearest-neighbor Heisenberg exchange $J_1$ and the Kitaev interaction $K$ for both materials, revealing $K \ll J_1$. The intriguing possibility of the realization of the quantum order-by-disorder effect as well as details of the high-field behavior of magnetic excitations in these frustrated compounds deserves further experimental and theoretical studies.

FIG. 7. Frequency-field diagram of ESR excitations in K$_2$IrCl$_6$ measured at 1.5 K with magnetic field applied parallel to the [111] direction. The dashed lines represent linear fits using Eq. (1). In the inset, examples of normalized ESR spectra for K$_2$IrCl$_6$ at different frequencies and $T = 1.5$ K with $H \parallel [111]$ are shown. The spectra are offset for clarity.

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