Spin-orbit entangled $j = \frac{1}{2}$ moments in Ba$_2$CeIrO$_6$: A frustrated fcc quantum magnet

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We establish the double perovskite Ba$_2$CeIrO$_6$ as a nearly ideal model system for $j = \frac{1}{2}$ moments, with resonant inelastic x-ray scattering indicating that the ideal $j = \frac{1}{2}$ state contributes by more than 99% to the ground-state wave function. The local $j = \frac{1}{2}$ moments form an fcc lattice and are found to order antiferromagnetically at $T_N = 14$ K, more than an order of magnitude below the Curie-Weiss temperature. Model calculations show that the geometric frustration of the fcc Heisenberg antiferromagnet is further enhanced by a next-nearest neighbor exchange, and a significant size of the latter is indicated by ab initio theory. Our theoretical analysis shows that magnetic order is driven by a bond-directional Kitaev exchange and by local distortions via a strong magnetoelastic effect. Both, the suppression of frustration by Kitaev exchange and the strong magnetoelastic effect are typically not expected for $j = \frac{1}{2}$ compounds making Ba$_2$CeIrO$_6$ a riveting example for the rich physics of spin-orbit entangled Mott insulators.

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I. INTRODUCTION

Spin-orbit entangled Mott insulators stand out in the growing family of quantum materials with strong spin-orbit coupling for their correlation-driven phenomena [1]. Of particular interest are materials with partially filled 4$d$ and 5$d$ orbitals, such as the iridates, in which the formation of local $j = \frac{1}{2}$ moments is an iridescence source of rich physics [2]. The spin-orbit entangled wave function of these Kramers doublets gives rise to fundamentally different types of exchange interactions depending on the geometric arrangement of the elementary octahedral IrO$_6$ building blocks [3–5]. Corner-sharing octahedra yield isotropic Heisenberg exchange, which has been explored as a potential source of spin-orbit assisted superconductivity [6–10] in the context of Sr$_2$IrO$_4$ [11,12], an isostructural analog of the high-$T_c$ parent compound La$_2$CuO$_4$. Edge-sharing octahedra, in contrast, give rise to Kitaev-type bond-directional exchange, which has initiated an intense search for spin-orbit driven frustrated quantum magnetism in so-called Kitaev materials [13] such as the honeycomb iridates Na$_2$IrO$_3$, $\alpha$-Li$_2$IrO$_3$, and H$_2$LiIr$_2$O$_6$ [14–16] and the related $\alpha$-RuCl$_3$ [17]. Possibly the most spectacular experimental result in this realm is the recent claim of a quantized thermal Hall effect in $\alpha$-RuCl$_3$ [18], a direct signature of the long sought-after Kitaev spin liquid [19].

In this paper, we first demonstrate experimentally that the double perovskite Ba$_2$CeIrO$_6$ is a nearly ideal realization of a $j = \frac{1}{2}$ Mott insulator, forming a model system for frustrated quantum magnetism on the fcc lattice. Our x-ray diffraction results show a global cubic $Fm\bar{3}m$ structure, while resonant inelastic x-ray scattering (RIXS) reveals a small noncubic distortion resulting in a ground-state wave function which overlaps by more than 99% with the ideal cubic $j = \frac{1}{2}$ state. The magnetic susceptibility shows an antiferromagnetic ordering temperature $T_N = 14$ K which is suppressed by more than an order of magnitude compared to the Curie-Weiss temperature $|\Theta_{CW}|$, resulting in a large frustration parameter $f = |\Theta_{CW}|/T_N \gtrsim 13$. Employing a combination of density functional theory and microscopic model simulations, we address the minimal model for Ba$_2$CeIrO$_6$ and its phase diagram. The system shows a particularly high degree of frustration, since the geometric frustration of antiferromagnetic nearest-neighbor Heisenberg exchange on the fcc lattice is augmented by next-nearest-neighbor Heisenberg coupling, yielding a wide window of a quantum spin liquid ground state. However, an antiferromagnetic Kitaev-type bond-directional exchange is found to counteract this geometric frustration and turns out to be instrumental in stabilizing long-range magnetic order—in contrast to the common wisdom that Kitaev...
interactions in $j = 1/2$ compounds enhance frustration and induce spin liquid physics.

It is also common wisdom that the $j = 1/2$ wave function does not show orbital degeneracy and hence is not Jahn-Teller active. Commonly, this is interpreted as a protection to the center of 12 nearest neighbors [orange and black lines in (c)] and to six next-nearest neighbors [along the edges of the cube in (c)], enhancing the frustration. Our RIXS data reveal local distortions from cubic symmetry. Assuming that the distortion is tetragonal, as schematically illustrated in (b), we find a massive bond-dependent variation of the nearest-neighbor exchange constants between Ir moments as depicted in (c), where couplings indicated in orange and black have different strength, reducing the frustration.

II. SYNTHESIS AND STRUCTURE

Single crystals of $\text{Ba}_2\text{CeIrO}_6$ of about 1 mm$^3$ size were grown by melt solution growth (see Appendix A). X-ray diffraction shows a well ordered double perovskite with Ce-Ir order as illustrated in Fig. 1(a). The cation order can be explained by the notably different bond lengths of 2.20 Å for Ce-O and 2.04 Å for Ir-O. For $5d^5$ Ir$^{4+}$, the formation of ideal $j = 1/2$ moments requires a cubic crystal field. Thus far, deviations from cubic symmetry were reported for all $5d$ iridate compounds [2,13], as discussed in more detail in the section on RIXS below.

For $\text{Ba}_2\text{CeIrO}_6$, our powder diffraction peaks—measured using a Stoe Stadi MP 198 powder diffractometer—are very well described in the cubic space group $Fm\bar{3}m$ with a lattice constant of 8.47 Å at 300 K. However, we find a clear broadening of Bragg peaks in particular for large diffraction angles $2\theta > 80^\circ$. Such broadened Bragg peaks may explain a previous claim of tiny ($<0.2\%$) monoclinic distortions of the metric in polycrystalline $\text{Ba}_2\text{CeIrO}_6$ [20]. Note that the issue of cubic or noncubic symmetry is often discussed controversially in double perovskites, for instance for the closely related $\text{Ba}_2\text{PrIrO}_6$ [20,21].

To resolve this issue, we collected single-crystal x-ray diffraction data. Our results strongly support a cubic structure of $\text{Ba}_2\text{CeIrO}_6$. We employed a Bruker X8 Apex diffractometer, a sample with octahedral shape (1111) faces, and a distance to the center of 12.5 μm. At room temperature (100 K) 32921 (13274) Bragg reflection intensities were recorded, yielding 198 (205) independent reflections in space group $Fm\bar{3}m$. The single-crystal data do not yield any evidence for significant superstructure reflections with respect to $Fm\bar{3}m$, neither at room temperature nor at 100 K (see Appendix A). From this and the description of the powder diffraction pattern with the cubic lattice we must conclude that the average structure of $\text{Ba}_2\text{CeIrO}_6$ is cubic.

However, the atomic displacement parameters shown in Table I provide evidence for local distortions since they are (i) larger than expected for a purely dynamical displacement, (ii) very similar at 300 K and 100 K, and (iii) similar for the heavy Ba ions and the lighter O ions. The large values observed for O perpendicular to its bond at room temperature reflect the general instability of a perovskite against tilting. But the small difference in the room-temperature and 100 K displacement values in general indicates some local distortions. Moreover, a normal dynamical effect cannot explain the fact that the atomic displacement parameter of the heavy Ba is of the same magnitude (a root mean square displacement of the order of 0.1 Å) as the one of the much lighter O. Fits of the data in space groups with the same translation lattice but reduced symmetry do not yield significant improvement. However, a split model in which the Ba ions are statistically distributed over sites slightly displaced by δBa against the cubic (0.25,0.25,0.25) position results in $\delta_{\text{Ba}} = 0.13(1) \text{ Å}$ and 0.14(2) Å at 300 K and 100 K, respectively. The statistical character may be related to the existence of about 5% of vacancies on the Ir sites.

One example for structural distortions that were first sensed by enlarged atomic displacement parameters is $\text{KH}_2\text{PO}_4$, a prototype ferroelectric material that exhibits highly enlarged atomic displacement parameters above its ferroelectric transition of order-disorder character [22]. Another example is $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$, in which enhanced atomic displacement
factors are observed in samples which do not show long-range tilt order [23]. In Ba$_2$CeIrO$_6$, the presence of local distortions from cubic symmetry is supported by our RIXS data, see below. This can be reconciled with the observation of a global cubic structure in x-ray diffraction by assuming a negligible correlation length of the distortions. We conclude that Ba$_2$CeIrO$_6$ is cubic on average but exhibits small local distortions.

This result is in contrast to an earlier report on a monoclinic structure of Ba$_2$CeIrO$_6$ in Ref. [20] which was based on powder data and a tiny monoclinic distortion of the metric ($a/b = 1.0016$ [20]) that can result from the broadening of Bragg peaks. Combining the typical rotation of octahedra in the GdFeO$_3$ structure type of a perovskite $ABO_3$ with the doubling of the unit cell in the double perovskite results in a monoclinic distortion, $P2_1/c$. One may examine the possible instability of Ba$_2$CeIrO$_6$ by calculating the Goldschmidt tolerance factor for perovskites

$$t_p = \frac{r_A + r_O}{\sqrt{2(r_A + r_O)}}$$

where $r_A$ and $r_O$ are the ionic radii. For an ideal cubic perovskite, $t_p = 1$. For the hypothetic perovskites BaIrO$_3$ and BaCeO$_3$ this yields $t_p = 1.06$ and 0.94 not indicating sizable bond-length mismatch. The same analysis for distorted Sr$_2$CeIrO$_6$ yields $t_p = 0.90$ and 0.80. Alternatively, one may consider the tolerance factor $t_{dp}$ for an ordered double perovskite $AB'_2B'O_6$ with $r_B$ in Eq. (1) to be replaced by $(r_B + r_{B'})/2$. A monoclinic structure is favored for $t_{dp} \leq 0.96$ while values close to 1 point towards a cubic structure [24]. For Ba$_2$CeIrO$_6$, one finds $t_{dp} = 0.991$, supporting a cubic structure.

III. MAGNETIC SUSCEPTIBILITY

To explore the magnetism of the local moments in Ba$_2$CeIrO$_6$ we measured the magnetization and the magnetic susceptibility $\chi(T)$. We used an assembly of 20 single small crystals in order to enhance the magnetic signal. The crystals were not aligned because an isotropic magnetic susceptibility is expected in the paramagnetic phase of the (global) cubic structure. As shown in the lower inset of Fig. 2, we observe a field-linear magnetization. The main panel of Fig. 2 shows $\chi(T)$. Its high-temperature behavior essentially follows a Curie-Weiss behavior from 300 K down to about $T_N = 14$ K, where a distinct drop in $\chi(T)$ signals antiferromagnetic ordering. For the quantitative analysis we use

$$\chi(T) = N_A \frac{\mu_{\text{eff}}^2}{3k_B(T - \Theta_{\text{CW}})} + \chi_0,$$

where $N_A$ and $k_B$ denote Avogadro’s and Boltzmann’s constant, respectively, $\Theta_{\text{CW}}$ is the Curie-Weiss temperature, and the constant $\chi_0 = \chi_{\text{dia}} + \chi_{\text{v}}$ represents core diamagnetism $\chi_{\text{dia}} \approx -1.7 \times 10^{-4}$ emu/mol and valence paramagnetism $\chi_{\text{v}} > 0$, which are expected to be of the same order of magnitude [25]. A fit based on Eq. (2) describes the data above $T_N$ very well, see red line in Fig. 2, and yields the parameters $\chi_0 = 1.2 \times 10^{-4}$ emu/mol, $\mu_{\text{eff}} = 1.41 \mu_B$, and $\Theta_{\text{CW}} = -184$ K. Very similar values, $\mu_{\text{eff}} = 1.3 \mu_B$ and $\Theta_{\text{CW}} = -177$ K, were reported in a previous study on polycrystalline Ba$_2$CeIrO$_6$ [20]. To estimate the reliability of our result, we compare with a fit assuming $\chi_0 = 0$, which shows Curie-Weiss behavior above about 120 K (blue line in Fig. 2), $\mu_{\text{eff}} = 1.69 \mu_B$ and $\Theta_{\text{CW}} = -263$ K, i.e., an even larger value of $|\Theta_{\text{CW}}|$. Thus, both fits result in an effective magnetic moment that is moderately reduced from $\mu_{\text{eff}} = 1.73 \mu_B$ expected for $j = 1/2$ moments in an ideal cubic crystal field [26] and indicate substantial frustration with a frustration parameter $f = |\Theta_{\text{CW}}|/T_N > 13$.

IV. RIXS

Ba$_2$CeIrO$_6$ indeed realizes nearly ideal local $j = 1/2$ moments, which can be inferred from our RIXS results. In cubic symmetry, a single $5d^5$ Ir$^{3+}$ site with a $t_{2g}^5$ configuration is expected to show a local $j = 1/2$ ground state and a $j = 3/2$ excited state, the so-called spin-orbit exciton, at $1.5 \lambda$ with $\lambda = 0.4$–0.5 eV. The effect of a noncubic crystal field is described by the single-site Hamiltonian

$$H_{\text{single}} = \lambda \hat{S} \cdot \hat{L} + \Delta_{\text{CF}} \hat{L}_z^2,$$

which shows a crystal-field splitting of the $j = 1/2$ quartet and a mixing of $j = 1/2$ and $3/2$ wave functions in the ground state, $|0\rangle = \alpha |\frac{1}{2}, \frac{1}{2}\rangle + \beta |\frac{3}{2}, 0\rangle$ in the $|j, j_z\rangle$ basis. With $\alpha = (\sin \theta + \sqrt{2} \cos \theta)/\sqrt{3}$ and $\tan 2\theta = \sqrt{8}/(1 - 2\Delta_{\text{CF}}/\lambda)$ [5] we can readily infer the ground state wave function by measuring $\Delta_{\text{CF}}$.

To do so, we performed RIXS measurements at the Ir $L_3$ edge, the most sensitive probe for the corresponding intra-$t_{2g}$ excitations. For $\Delta_{\text{CF}}/\lambda \ll 1$, the experimentally observed peak splitting amounts to $\Delta_{\text{exp}} \approx \frac{1}{2} \Delta_{\text{CF}}$. Thus far, all experimental results on the spin-orbit exciton in iridates show a finite noncubic crystal-field splitting [2,13,27–31]. The smallest values $\Delta_{\text{exp}} = 0.11$–0.14 eV were reported for Rb$_2$IrF$_6$, Na$_2$IrO$_3$, and Sr$_2$IrO$_4$ [27–29]. In Rb$_2$IrF$_6$, F-Ir-F bond angles...
narrow RIXS peaks on a negligible background, see Fig. 3. a textbook example of the spin-orbit exciton by showing two
were reported for Rb2IrF6 \cite{29} and Ba3Ti2 
Similar RIXS spectra with a slightly larger peak splitting
/0.71 eV correspond to excitations to
compounds with well separated Ir4
0.71 eV , both at 10 K and at 300 K. The observation of
show more complex RIXS features \cite{27,28} with, e.g., further
bond angles of 157
octahedra with Ir-O bond lengths of 1.98–2.06 Å and Ir-O-Ir
vary from 87
 to 93° \cite{29}, while Sr2IrO4 shows distorted IrO6
tetrahedra with Ir-O bond lengths of 1.98–2.06 Å and Ir-O-Ir
bond angles of 157° \cite{32}. Despite the substantial distortions,
these compounds are widely accepted as realizations of the
j = 1/2 scenario. In contrast, strong deviations from the
j = 1/2 model are reported for Sr3CuIrO6 and CaIrO3 with
\Delta_{\text{exp}} = 0.23 eV and 0.6 eV, respectively \cite{30,31}.

For Ba2CeIrO6, we measured RIXS data on a polished (0 0 1) surface at the ID20 beamline at ESRF using an incident
energy of 11.215 keV with an overall resolution of 25 meV \cite{33,34}. The incident photons were \pi polarized. Our data offer
a textbook example of the spin-orbit exciton by showing two
narrow RIXS peaks on a negligible background, see Fig. 3. Similar RIXS spectra with a slightly larger peak splitting
were reported for Rb2IrF6 \cite{29} and Ba2Ti2.7IrO3 \cite{35}, two compounds with well separated Ir3+ ions. In comparison, 5d5
iridates with stronger hopping such as Na2IrO3 and Sr2IrO4 show more complex RIXS features \cite{27,28} with, e.g., further
peaks, broader linewidths, and/or a continuum contribution.

In Ba2CeIrO6, the peaks are located at about 0.61 eV and
0.71 eV, both at 10 K and at 300 K. The observation of two
peaks signals noncubic local distortions in agreement with our
analysis of the x-ray diffraction data. A fit using two peaks with the Pearson VII line shape \cite{36} that mimics a convolution
of an intrinsic Lorentzian line shape and a Gaussian profile
with the experimental resolution yields a splitting
\Delta_{\text{exp}} = (100 \pm 4) meV, the smallest splitting reported thus far in L
edge RIXS for the spin-orbit exciton in iridates \cite{27–31,35}. The peak values of 0.61 eV and 0.71 eV allow for two different
solutions of Eq. (3) with \lambda = 0.43 eV and \Delta_{\text{CF}} = 0.17 eV or
−0.15 eV, which correspond to elongation or compression,
respectively. This results in a ground-state wave function
\langle 0 | = 0.991 \begin{pmatrix} 1 \\ 2 \\ 2 \end{pmatrix} - 0.130 \begin{pmatrix} 3 \\ 2 \\ 2 \end{pmatrix} \rangle
in the |j, j\rangle basis for elongation, while for compression the coefficients are 0.995 and 0.100, respectively. Note that both
solutions deviate by less than 1% from the ideal j = 1/2 case.

To probe the intersite hopping interactions, we have measured
the dispersion via RIXS for q along different high-symmetry directions. Data along \Gamma−K and \Gamma−L paths reveal a finite dispersion of up to 15–20 meV, while peak energies
are nearly independent of q along \Gamma−X, see the lower panels of Fig. 3. The corresponding delocalization of the j = 3/2
excited state is a clear signature of microscopic hopping pro-
cesses and intersite interactions that are closely related to the
magnetic exchange interactions between localized j = 1/2
moments \cite{28,37}. Roughly, this common microscopic origin
is reflected in the common energy scale of 15–20 meV of the
spin-orbit exciton dispersion and the Curie-Weiss temperature,
which also is a measure of the size of magnetic exchange
interactions.

V. MICROSCOPIC MODEL

A. fcc lattice with cubic site symmetry

A symmetry analysis \cite{38–40} of exchange interactions on
the undistorted fcc lattice shows that the most general nearest-
neighbor spin Hamiltonian allows for Heisenberg coupling J1,
Kitaev coupling K, and symmetric off-diagonal exchange \Gamma.
We estimate the coupling constants using density functional
theory (GGA+U+SOC) for different magnetic configurations
and J/U perturbation theory for an effective tight-binding model (see Appendix B). Both approaches consistently yield
an antiferromagnetic J1 ≈ 5–7 meV and two subdominant cou-
plings \( K \approx J_2 \approx 0.2 J_1 \), where \( J_2 \) denotes a next-nearest neighbor
Heisenberg coupling. We find that \( \Gamma/J \lesssim 0.05 \) is neg-
ligible. The corresponding Curie-Weiss temperature \( \Theta_{\text{CW}} =
\frac{-3 J_1 + K + 3 J_2}{2} \approx -200 K \) agrees with the experimental \( \chi(T); \) see Fig. 2. Note that we find an antifer-
romagnetic Kitaev coupling, in contrast to the ferromagnetic ones inferred for the honeycomb-based iridates and \alpha-RuCl3
\cite{41}. The ferromagnetic Kitaev coupling of the latter arises from Hund’s coupling in the virtually excited intermediate
state with two holes on the same site, favoring parallel hole
spins. For the honeycomb materials with a 90° Ir-O-Ir exchange
path, this translates into a ferromagnetic coupling of
j = 1/2 pseudospins. In Ba2CeIrO6, exchange proceeds via
an Ir-O-O-Ir path with a different combination of orbitals in
the virtual state. Again, Hund’s coupling favors parallel spins of the two holes, but for the relevant orbitals this translates to antiferromagnetic coupling of
j = 1/2 pseudospins (see Appendix C).
To study the competition of geometric and exchange frustration, we explore the minimal microscopic model

$$\mathcal{H} = J_1 \sum_{\langle i, j \rangle} \vec{S}_i \cdot \vec{S}_j + K \sum_{\langle i, j \rangle} S_i^z S_j^z + J_2 \sum_{\langle i, j \rangle} S_i \cdot \vec{S}_j,$$

(5)

where \(\langle i, j \rangle\) denotes nearest-neighbor pairs in the plane perpendicular to axis \(y = x, y, z\), \(\langle i, j \rangle\) runs over next-nearest-neighbor pairs, and the spin operators \(\vec{S}\) refer to \(j = 1/2\) moments. We have calculated its rich phase diagram using a pseudofermion functional renormalization group (pf-FRG) approach [42]. This numerical scheme combines elements from 1/N expansion [43] and 1/N expansion [44,45], allowing it to capture both magnetic order and spin-liquid ground states. There are four magnetically ordered phases, one of them showing incommensurate spiral order, see Fig. 4(a). These phases can be readily understood in the classical limit of model (5) via a Luttinger-Tisza approach [46,47], with the classical phase boundaries also indicated in Fig. 4(a). The quantum model additionally exhibits a spin-liquid phase with no magnetic order. Its origin is revealed by two points of special interest in the classical model, see white and black circles in Fig. 4(a): (i) \(J_2 = K = 0\), the fcc nearest-neighbor Heisenberg antiferromagnet. It exhibits a degenerate manifold of coplanar spin spiral ground states [48]. The corresponding set of \(q\) vectors is shown in Fig. 4(b). (ii) \(J_2 = J_1/2\), \(K = 0\), where three ordered phases meet in the classical model. This feature appears an even larger set of degenerate coplanar spin-spiral ground states, depicted by the surface of \(q\) vectors in Fig. 4(c). The presence of a considerable (but still subextensive) manifold of (nearly) degenerate low-energy states appears to give rise to an extended spin liquid regime in the quantum model, centered around the classical high-degeneracy point [49].

To further investigate the interplay of geometric and exchange frustration, we calculate [50] the dimensionless frustration parameter \(f = |\Theta_{CW}|/T_N\), see Fig. 4(d), using estimates of \(\Theta_{CW}\) and \(T_N\) obtained from fits of the magnetic susceptibility numerically obtained by FRG calculations. The frustration parameter diverges in the spin liquid regime due to the absence of finite-temperature order. Furthermore, \(f\) is particularly large along the phase boundary between the \((1\bar{1}0)\) and \((\bar{1}11)\) phases, where both \(J_2\) and \(K\) are substantial and antiferromagnetic. This boosts \(|\Theta_{CW}|\) while \(T_N\) is small close to the phase boundary. Close to the spin-liquid regime for the parameter set estimated for Ba$_2$CeIrO$_6$ [cf. star in Fig. 4(d)], we also find large values of \(f\). However, moving away from the spin-liquid regime the frustration is quickly reduced with increasing strength of the Kitaev coupling. This is consistent with a previous classical Monte Carlo study [38,39], although such a classical analysis by itself is not reliable in the deep quantum limit of \(j = 1/2\). Our results show that the Kitaev coupling, in competition with the geometric frustration of the Heisenberg exchange, indeed induces magnetic order for the system at hand – in striking contrast to a number of \(j = 1/2\) materials where the Kitaev coupling is primarily considered a source of frustration [2,13].

**B. Distortions**

The strong frustration in Ba$_2$CeIrO$_6$ boosts the importance of magnetoelastic coupling. We find theoretically that even small local distortions severely affect the exchange couplings, although the ground state wave function remains closest to the \(j = 1/2\) limit, see Eq. (4). The precise character of the local distortions cannot be determined from our x-ray diffraction results, which show global cubic symmetry. A putative tetragonal distortion of strength \(\Delta_C\) gives rise to a strong spatial anisotropy, which can be rationalized as follows. Focusing, e.g., on the dominant contribution to exchange within the \(xy\) plane, we find \(J_{10}^{xy}\) to depend quadratically on the occupation probability of the \(xy\) orbital. Comparing cubic \(\Delta_C = 0\) with the distorted case \(\Delta_C = 0.4\) derived above, the \(xy\) occupation is strongly enhanced from 0.46 to 0.46 and as a result the nearest-neighbor Heisenberg exchange \(J_{10}^{xy}\) increases by about a factor of two, which corresponds to a dramatic magnetoelastic effect. In particular, \(\Delta_C > 0\) strengthens (weakens) \(J_1, J_2,\) and \(K\) in the \(xy\) plane (\(yz\) and \(xz\) planes), while \(\Delta_C < 0\) has the reverse effect. This strong spatial anisotropy of the couplings is sketched in Fig. 1(c). Note that a change of the \(xy\) occupation \(\sin^2 \theta\) has a much more pronounced effect on the exchange, \(J_1 \propto \sin^4 \theta\), than
on the coefficient $\alpha = \sqrt{17/3} \sin \theta + \sqrt{2/3} \sqrt{1 - \sin^2 \theta}$ of the $|\frac{1}{2}, \frac{1}{2}\rangle$ contribution to the ground state wave function. The comparably small change of $\alpha$ indicates a small deviation from a cubic charge distribution and a concomitant small energy cost for lattice distortions, while the larger change of $J_1$ and, analogously, for $J_2$ to the parameter set indicated by a star in Fig. 4(d), i.e., the enhanced $J_{xy}$ and, analogously, for $J_{yz}$ as $J_{xz}$ and in particular its spatial anisotropy yield a significant gain on the coefficient $\theta_{\text{CF}}$ shown in Fig. 1(c). Specifically, we have modeled the dependence of the coupling parameters on the distortion $\Delta_{\text{CF}}$ as

$$J_j \rightarrow \begin{cases} J_1 + \delta J(\Delta_{\text{CF}}), & \text{xy plane,} \\ J_1 - \delta J(\Delta_{\text{CF}}), & \text{yz, xz planes,} \end{cases}$$

(6)

and, analogously, for $J_2$ and $K$. For $\Delta_{\text{CF}} = 0$ this corresponds to the parameter set indicated by a star in Fig. 4(d), i.e., $J_2 = K = 0.2 J_1$, while for $\Delta_{\text{CF}} = \Delta_{\text{CF}}^{\text{max}} = 160$ meV we have the enhanced $J_{xy}$ couplings $J_{xy}^{\text{max}} = 2J_1$, $J_{yz} = 1.2J_2$, and $K_{yz} = 1.2K$ for simultaneously reduced parameters $J_1^{\text{max}} = 0.6J_1$, $J_2^{\text{max}} = 0.7J_2$, and $K_{xz}^{\text{max}} = 0.8K$ in the $xz$ and $yz$ plane. The function $\delta J(\Delta_{\text{CF}})$ is well approximated as a linear interpolation

$$\delta J(\Delta_{\text{CF}}) = \frac{\Delta_{\text{CF}}}{\Delta_{\text{CF}}^{\text{max}}} \left( J(\Delta_{\text{CF}}^{\text{max}}) - J(\Delta_{\text{CF}} = 0) \right).$$

(7)

Results for pf-FRG calculations are summarized in Fig. 5 showing the frustration parameter $f = |\theta_{\text{CF}}|/K_{\text{th}}$ as a function of the distortion $\Delta_{\text{CF}}$. As clearly visible, the frustration is strongly suppressed by the distortions, it quickly approaches a nonfrustrated regime $f \lesssim 5$ for distortions of the order of $|\Delta_{\text{CF}}| \approx 40$ meV, independent of the sign of the distortion. Additionally, the data indicate a potential change of magnetic order, for instance to (100) order, depending on the sign and the strength of $\Delta_{\text{CF}}$. These results agree with the small $f \lesssim 2$ reported for the globally distorted monoclinic 5$d^2$ double perovskites La$_2$ZnIrO$_6$ and La$_2$MgIrO$_6$ [39]. However, this result for a global distortion is significantly smaller than the value of $f > 13$ measured in Ba$_2$CeIrO$_6$. This suggests that the statistical distribution of local distortions along different tetragonal axes, in contrast to a global distortion, is important in order to recover the experimentally observed large frustration.

The existence of a weak (but unavoidable) magnetoelastic effect was recently discussed for Sr$_2$IrO$_4$ [51]. The strong effect of the magnetoelastic coupling in Ba$_2$CeIrO$_6$, however, is due to an additional mechanism arising from an interplay of distortions and magnetic frustration, which is not present in Sr$_2$IrO$_4$, but will be relevant, e.g., in tetragonal bilayer Sr$_3$Ir$_2$O$_7$ and in the 3D honeycomb iridates.

**VI. CONCLUSIONS**

The spin-orbit entangled $j = 1/2$ wave function has proved to be a versatile source for novel states of quantum matter. Its experimental realization in the double perovskite Ba$_2$CeIrO$_6$ deviates less than 1% from the ideal theoretical scenario for a cubic system and is one of the most pristine $j = 1/2$ incarnations reported so far in the literature. Combining structural analysis, magnetic susceptibility measurements, andRIXS with *ab initio* and functional renormalization group calculations for the obtained microscopic model Hamiltonian we find that the collective magnetism of this fcc compound is governed by a competition of geometrical frustration, Kitaev-type bond-directional exchange, and magnetoelastic coupling. In striking contrast to the honeycomb-based Kitaev materials, the Kitaev exchange is antiferromagnetic and in fact stabilizes long-range magnetic order in proximity to a spin liquid phase. Importantly, the exchange couplings turn out to be highly sensitive to small deviations from cubic symmetry, giving rise to a dramatic magnetoelastic coupling. This should be contrasted with the common notion that $j = 1/2$ moments are not Jahn-Teller active, as the orbital degeneracy is lifted by spin-orbit coupling. The strong magnetoelastic coupling resurrects the prominent role of lattice distortions on the low-energy properties of $j = 1/2$ compounds.

*Note added.* Recently, Aczel et al. reported similar experimental results on polycrystalline samples of Ba$_2$CeIrO$_6$ [52]. They find (100) magnetic order, in agreement with our calculations for negative $\Delta_{\text{CF}}$. Furthermore, Khan et al. [53] reported on the realization of cubic site symmetry in K$_2$IrCl$_6$ based on x-ray diffraction data; a spectroscopic proof of this claim is still missing.

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In the lattice parameters on the ionic radius of the lanthanide ions of BaCl₂ from the melt solution. Within three weeks single crystals were separated from the flux by dissolving the flux. The crucible was sealed with a lid to prevent evaporation.

In Ba₂CeIrO₆, the Ir⁴⁺ valence state is proven and characterized by the very low value of the optical conductivity in the mid-infrared range, σ₁(ω) ≈ 1 (Ω cm)⁻¹, see Fig. 7. Using a Bruker IFS 66/s Fourier-transform infrared spectrometer, we measured the transmittance on a single crystal with a thickness of (30 ± 5) μm. On the low-frequency side, the accessible frequency range is cut off by strong phonon absorption suppressing the transmittance. The steep edge in σ₁(ω) at about 0.1 eV corresponds to the upper limit for single phonon absorption, while the weak features up to about 0.2 eV can be attributed to multiphonon absorption. On the high-frequency side, the transmittance is suppressed by electron-hole excitations across the gap, giving rise to the increase of σ₁(ω) above 0.2 eV.

APPENDIX A: SINGLE-CRYSTAL GROWTH AND CHARACTERIZATION

We have grown single crystals of Ba₂CeIrO₆ by melt solution growth using BaCl₂ as melt solvent and BaCO₃ (Merck, p.a.), IrO₂ (Chempur, 99.9%), and CeO₂ (Auer Remy, 99.9%) as educts for the crystals. Due to the moderate solubility of metal oxides in halide melts [57], a ratio flux/crystal of 15:1 was used to achieve sufficient dissolution of the oxides. The crucible was sealed with a lid to prevent evaporation of BaCl₂ from the melt solution. Within three weeks single crystals of about 1mm³ size were obtained. The black single crystals were separated from the flux by dissolving the flux in deionized water and analyzed by energy-dispersive x-ray scattering.

Our single-crystal x-ray diffraction data strongly support a cubic structure of Ba₂CeIrO₆, as explained in the main text. Figure 6 shows the distribution of the observed peak intensities I divided by their error bars σ(I) for all reflections that are not allowed in space group Fm̅3m. The width of the distributions is approximately 1, which is an indication for meaningful statistical errors of the intensities. Both at room temperature and at 100 K, we find a Gaussian profile peaking at a value of I/σ(I) close to zero or much smaller than 1, i.e., the intensities of forbidden peaks are negligible within the experimental error bars.

The excellent agreement of the RIXS spectra shown in Fig. 3 with the expectations for the spin-orbit excitation provides an unambiguous fingerprint of the Ir⁴⁺ valence state. RIXS spectra for 5d⁴ Ir⁴⁺ are distinctly different, as reported for, e.g., the double perovskites Sr₂YIrO₆ and Ba₂YIrO₆ [58,59]. In Ba₂CeIrO₆, the Ir⁴⁺ valence means that also the Ce ions are tetravalent, as claimed before [20] based on the dependence of the lattice parameters on the ionic radius of the lanthanide ions Ln in Ba₂LnIrO₆.

The Mott-insulating character of Ba₂CeIrO₆ is demonstrated by the very low value of the optical conductivity in the mid-infrared range, σ₁(ω) ≈ 1 (Ω cm)⁻¹, see Fig. 7. Using a Bruker IFS 66/s Fourier-transform infrared spectrometer, we measured the transmittance on a single crystal with a thickness of (30 ± 5) μm. On the low-frequency side, the accessible frequency range is cut off by strong phonon absorption suppressing the transmittance. The steep edge in σ₁(ω) at about 0.1 eV corresponds to the upper limit for single phonon absorption, while the weak features up to about 0.2 eV can be attributed to multiphonon absorption. On the high-frequency side, the transmittance is suppressed by electron-hole excitations across the gap, giving rise to the increase of σ₁(ω) above 0.2 eV.

APPENDIX B: DERIVATION OF MICROSCOPIC MODEL

Ab initio calculations.—In order to calculate Heisenberg-type and Kitaev-type exchange constants, we used the projector augmented-wave (PAW) method [60] as realized in the pseudopotential VASP code [61]. The exchange-correlation potential was chosen in the form proposed by Perdew, Burke, and Ernzerhof [62]. Electronic correlations and spin-orbit coupling were considered in the framework of the GGA+U+SOC formalism [63] with U − J₉ = 2.0 eV [11], where U and J₉ denote the on-site Coulomb repulsion and intra-atomic Hund’s exchange, respectively. The integration was performed on a 7 × 7 × 7 mesh of the Brillouin zone. We calculated total energies of three magnetic configurations (FM, AFM type I and type II) to extract nearest and next-nearest neighbor exchange constants J₁ and J₂. The Kitaev coupling K was computed via the difference of the total energies of two AFM type I configurations with spins pointing along a and c, respectively.

Perturbative approach. For the perturbative calculation of exchange couplings, we use one-hole and two-hole eigenstates and energies obtained by numerical diagonalization of the single-site Hamiltonian

\[ H_{\text{site}} = -i \frac{\lambda}{2} \sum_{\ell mn} \varepsilon_{\ell mn} d_{\ell \sigma}^\dagger d_{\ell \sigma} \sigma_{\ell \ell}^\alpha \beta + \frac{U}{2} \sum_{\ell \neq \ell'} n_{\ell \uparrow} n_{\ell \downarrow} - 2 J_H \sum_{\ell \neq \ell'} \mathbf{S}_\ell \cdot \mathbf{S}_{\ell'} + J_H \sum_{\ell \neq \ell'} d_{\ell \uparrow}^\dagger d_{\ell \downarrow}^\dagger d_{\ell' \downarrow}^\dagger d_{\ell' \uparrow}, \]  

(B1)

with \( \lambda = 0.43 \) eV deduced from our RIXS data, Hund’s coupling \( J_H = 0.25 \) eV [58] and \( U = 2.25 \) eV as a typical estimate for the Hubbard repulsion (which leads to \( U - J_H = 2.0 \) eV as in the ab initio calculations). For the inter-site Hamiltonian, we use \( H_{\text{hop}} = \sum_{\ell} \sum_{ij} d_{\ell \sigma}^\dagger T_{ij} \cdot \mathbf{d}_{\ell' \sigma}, \) with \( \mathbf{d}_{\ell \sigma}^\dagger \) representing the creation operators for the three \( t_{2g} \) orbitals, \( (d_{\ell \uparrow}, d_{\ell \downarrow}, d_{\ell \sigma}) \). For
the hopping amplitudes $t_{\alpha-\beta}$ between a pair of orbitals ($\alpha$, $\beta$) on nearest-neighbor sites ($i$, $i + \hat{x} + \hat{y}$), we retain only the by far dominant one $t_{xy} \approx -150$ meV, which is an order of magnitude larger than $t_{xz}$, which again is larger than $t_{xz} \approx 30$ meV, while others vanish by symmetry. For second-neighbor pairs ($i$, $i + 2\hat{x}$), we employ $t_{xy} \approx -150$ meV, while other hopping amplitudes vanish by symmetry. For the cubic fcc lattice, the corresponding hopping amplitudes between all other nearest-neighbor or next-nearest-neighbor pairs are determined by symmetry. To extract the two-site exchange Hamiltonian, we carry out second-order degenerate perturbation theory in $t/U$, evaluating matrix elements numerically using exact single-site eigenfunctions and energies. The resulting exchange Hamiltonian has dominant nearest-neighbor Heisenberg exchange interaction $J_1$ with subdominant Kitaev and second-neighbor Heisenberg terms as listed in the main text and a negligible $\Gamma \lesssim 0.05 J_1$ exchange term.

**APPENDIX C: ANTFERROMAGNETIC CHARACTER OF KITAEV COUPLING**

The $j = 1/2$ wave function is given by

$$\begin{aligned}
\frac{1}{\sqrt{3}} |yz, \downarrow\rangle &+ i |xz, \downarrow\rangle + |xy, \uparrow\rangle.
\end{aligned}$$

We address superexchange interactions between two sites A and B in the $xy$ plane. For comparison, we first consider edge-sharing geometry with Ir-O-Ir bonds [5] as approximately realized in the honeycomb iridates. In this case, the hopping $t_{xy} \approx 30$ meV, while others vanish by symmetry. For the cubic fcc lattice, the corresponding hopping amplitudes between all other nearest-neighbor or next-nearest-neighbor pairs are determined by symmetry. To extract the two-site exchange Hamiltonian, we carry out second-order degenerate perturbation theory in $t/U$, evaluating matrix elements numerically using exact single-site eigenfunctions and energies. The resulting exchange Hamiltonian has dominant nearest-neighbor Heisenberg exchange interaction $J_1$ with subdominant Kitaev and second-neighbor Heisenberg terms as listed in the main text and a negligible $\Gamma \lesssim 0.05 J_1$ exchange term.

### References


\( \chi_{\alpha \alpha} \approx -1.7 \times 10^{-6} \) emu/mol results from the tabulated values [54] for the ions in Ba2CeIrO6.


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[49] A similar scenario has recently been discussed in the context of the $J_1 - J_2$ Heisenberg model on the diamond lattice [55, 56].


