Frustration enhanced by Kitaev exchange in a $j_{\text{eff}} = \frac{1}{2}$ triangular antiferromagnet

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Triangular Heisenberg antiferromagnets are prototypes of geometric frustration, even if for nearest-neighbor interactions quantum fluctuations are not usually strong enough to destroy magnetic ordering: stronger frustration is required to stabilize a spin-liquid phase. On the basis of static magnetization and electron spin resonance measurements, we demonstrate the emergence of $j_{\text{eff}} = \frac{1}{2}$ moments in the triangular-lattice magnet Na$_2$Co(PO$_4$)$_2$. These moments are subject to an extra source of frustration that causes magnetic correlations to set in far above both the magnetic ordering and Weiss temperatures. Corroborating the $j_{\text{eff}} = \frac{1}{2}$ ground state, theory identifies ferromagnetic Kitaev exchange anisotropy as an additional frustrating agent, altogether putting forward Na$_2$BaCo(PO$_4$)$_2$ as a promising Kitaev spin-liquid material.

I. INTRODUCTION

Quantum spin liquids are of topical interest as a promising host for fractionalized quasiparticles [1–5]. The quest for a spin-liquid ground state goes back to Anderson’s conjecture on resonating valence bonds in the geometrically frustrated two-dimensional triangular lattice [6]. It is now firmly established, however, that the pure spin 1/2 triangular-lattice Heisenberg model has an ordered ground state [7]. This seemingly frustrating result is a blessing in disguise, though, as subsequent studies of modified triangular-lattice models found that long-range ordering can be suppressed by three disparate alterations: additional second-neighbor exchange [8–13], spatial anisotropy [14, 15], and exchange anisotropy [16, 17]. These findings opened new perspectives for realizing a spin-liquid state in the triangular lattice geometry, and boosted the search for candidate materials.

A recent breakthrough in triangular-lattice magnets pertains to the discovery of two material classes [18]. The first group of candidate materials are $4f$ magnets with Yb$^{3+}$: YbMgGaO$_4$ [19, 20] and NaYbX$_2$ (with $X=O,S,Se$) [21]. The key element of their physics is the crystal-field (CF) splitting of Yb$^{3+}$, giving rise to the ground-state doublet and hence the effective spin 1/2 behavior at low temperatures, and, in the former material, the significant effects of chemical disorder between the magnetic layers [22]. A similar scenario, with the lowest-lying doublet dominating the low-temperature physics, is realized in the other promising group of materials – Co$^{2+}$ cobaltates. Here, the ground-state doublet is stabilized by the spin-orbit (SO) coupling as long as the low-symmetry crystal field distortions remain small (Fig. 1, a). Despite the overall tendency towards ferromagnetic exchange, several cobaltates with antiferromagnetic (AFM) interactions are known. The most studied material of this handful, Ba$_3$CoSb$_2$O$_9$, shows intriguing high-field behavior [23–25], but evades the spin-liquid regime by developing a long-range order at 3.7 K [23]. Interestingly, in the related layered honeycomb magnet BaCo$_2$(AsO$_4$)$_2$ the magnetic order can be suppressed by a low magnetic field yielding a nonmagnetic material [26].

The recently synthesized cobaltate Na$_3$BaCo(PO$_4$)$_2$ (Fig. 1, b) is a promising candidate for realization of a spin-liquid state on a triangular lattice. The first experimental study reported a sizable antiferromagnetic exchange and no long-range ordering down to 50 mK [27]. Very recently, ultralow-temperature specific heat measurements revealed a magnetic ordering transition at $T_N = 148$ mK [28], i.e.,~20 times smaller than the Weiss temperature $\theta = 2.5$ K obtained from the static magnetic susceptibility $\chi(T)$ [28]. Another interesting observation is the linear dependence of the residual thermal conductivity [29], compatible with the spinon Fermi surface scenario advocated for critical spin liquids. However, the microscopic model for Na$_2$BaCo(PO$_4$)$_2$ remains hitherto unexplored.

In this Letter, we fill this gap and demonstrate that exchange anisotropy stabilizes the spin-liquid behavior in Na$_2$BaCo(PO$_4$)$_2$ over a temperature range spanning two orders of magnitude. Our Co$^{2+}$ electron spin resonance (ESR) measurements firmly establish the effective spin 1/2 state of the Co$^{2+}$ ions [30] by determining the $g$ factor tensor and evaluating the excitation energy of the first excited state with effective spin 3/2. Further, the ESR data indicate the onset of magnetic correlations at the surprisingly high temperature of $\sim 20 K$, which is two orders of magnitude larger than $T_N$. Hence, magnetic correlations in this material build up far above the phenomenological energy scale set by the moderate Weiss temperature and the low saturation field of the magnetization. To reconcile these seemingly conflicting observations, we perform a microscopic analysis based...
II. EXPERIMENTAL RESULTS

Magnetization and ESR experiments were conducted on both powder and single-crystal samples of Na2BaCo(PO4)2 with a substantial ferromagnetic Kitaev exchange K1. The competition of antiferromagnetic J1 and ferromagnetic K1 lowers the saturation field and the Weiss temperature, but promotes the buildup of magnetic correlations to higher temperatures.

A representative fit for the powder sample is shown in the main panel of Fig. 2(a). It yields AFM J = 1.37 K and a g factor gM = 4.38. For the single crystal, the g factors were found to be gM = 4.81 and gM = 4.22. The slight g factor anisotropy is likely related to a small trigonal distortion of the CoO6 octahedra [33].

The inverse susceptibility χ−1(T) per Co2+ ion at μ0H = 20 mT is shown in Fig. 2(b) together with the result of a population model. The latter is derived from the diagonalization of a single-ion Hamiltonian including the spin-orbit coupling and the Zeeman interactions, $H = \lambda S \cdot L - \mu_0 H (g_S S_z + g_L L_z)$ with $g_S = 2$, $g_L = -3/2$ and thermal average $\langle M \rangle = Z^{-1} \sum \langle E_i \rangle e^{-E_i/k_B T} |\mu_2 | E_i \rangle$, Z being the partition sum. $\chi^{-1}(T)$ does not obey a simple Curie-Weiss law $\propto T$, but rather possesses a remarkable inflection point around $T \sim 150$ K which is reasonable to attribute to the thermally assisted population of the excited $j_2 = 3/2$ multiplet (Fig. 1). The modeling reproduces the experimental data with the energy splitting $\Delta E_{j_1,j_2} = E_{j_2} - E_{j_1} = 419$ K.

The main results of the ESR measurements for both the powder- and single-crystalline samples at the X-band frequency of $\nu = 9.6$ GHz conducted with a commercial ESR spectrometer from Bruker are summarized in Figs. 3(a) and (b). A rather broad Lorentzian-shaped signal was observed [Fig. 3(a)]. The Lorentzian fitting yielded the width $\Delta H$ and the resonance field $H_{res}$ from which the effective g factor can be calculated according to resonance condition $hf = g \mu_B H_{res}$. The angular dependence measurements revealed an anisotropy of the g factor which follows the conventional angular dependence $g(\alpha) = \sqrt{g_{ab}^2 \cos^2(\alpha) + g_c^2 \sin^2(\alpha)}$ with $\alpha$ being the angle which the applied field makes with the $c$ axis [Fig. 3(a), inset]. The fit yielded the val-
Absorption derivative of the microwave absorption at ν = 9.6 GHz for the H || c axis at selected temperatures. Inset: Angular dependence of the g factor at ν = 9.6 GHz and at T = 4 K (data points). The solid line is a fit to the dependence g(α) = [g_α^2 cos^2(α) + g_β^2 sin^2(α)]^{1/2}. (b) T dependence of the ESR linewidth of the single- and polycrystalline samples at ν = 9.6 GHz (data points). Solid lines are the calculated dependences according to the population model (see the text). (c) Left scale: ν vs. field position of the peak of the powder HF-ESR spectrum at T = 3 K (dots). The solid line is the fit to the dependence ν = gμBH; Right scale: Powder HF-ESR spectra at selected frequencies ν at T = 3 K and at selected temperatures at ν = 708 GHz.

ues g_c ≈ 4.83 and g_ab ≈ 4.42 for the out-of-plane and in-plane orientation of the field, respectively, consistent with the static magnetization data.

More accurate estimates of the g_ab value were provided by multi-frequency high-field ESR (HF-ESR) measurements on the powder sample which were carried out with a homemade setup [34]. Selected HF-ESR spectra at T = 3 K and different excitation frequencies are shown in Fig. 3(c). The signal is a single Lorentzian-shaped line at lower frequencies and develops a shoulder at ν ≥ 150 GHz. Such a structure typical of the ESR response of a powder sample with an anisotropic g factor [35] can be most clearly resolved at the highest frequency of 708 GHz. In the case of the uniaxial g anisotropy the resonance field of the peak is determined by the g factor component perpendicular to the symmetry axis, i.e., by g_ab in our case [35]. The field position of the peak plotted versus ν exhibits a linear dependence according to the relation ν = g_abμBH and gives g_ab^{HF} = 4.24 [Fig. 3(c)]. Note that this linear dependence features a negligible intercept with the frequency axis evidencing the absence of any gap in the uniform spin excitation spectrum larger than 9.6 GHz (0.04 meV). Thus, taken together the X-band and HF-ESR results yield the g tensor [g_c, g_ab] = [4.83, 4.24] consistent with the estimate [g_c^{MF}, g_ab^{MF}] = [4.81, 4.22] from the magnetization data. Interestingly, with increasing the temperature close to 100 K the peak of the HF-ESR spectrum at ν = 708 GHz shifts by an amount of μ_BδH_0 ≈ 0.35 T towards higher fields, suggesting a reduction of the g factor [Fig. 3(c)]. At T = 100 K, a linear ν versus H g factor fit of this peak yields g_c(100 K) = 4.11. Such a reduction indicates the involvement of the thermally-populated excited 3j_2 = 3/2 multiplet which is characterized by a smaller g factor [33].

Both X-band and HF-ESR spectra broaden significantly with increasing the temperature [Figs. 3(a) and (c)]. Analysis of the origin of this broadening provides important insights into the spin dynamics and temperature effects in Na_2BaCo(PO_4)_2. On the quantitative level, the ΔH(T) dependence can be more accurately evaluated from the X-band data because strong fields applied in an HF-ESR experiment may cause additional inhomogeneous broadening, and instrumental distortions of the lineshape are possible in the HF-ESR apparatus.

In Fig. 3(b), the temperature dependence of the linewidth, as obtained from the Lorentzian fits, is shown for the powder- and single-crystalline samples. While lowering the temperature the width decreases down to approximately 50 K, then remains constant until approximately 20 K, where it starts to rise again. The high-temperature behavior is likely due to the above discussed population effect of the excited 3j_2 = 3/2 multiplet [Fig. 1(a)]. This leads to a broadening of the linewidth, while at lower temperatures, only the 3j_1 = 1/2 multiplet is populated. This behavior can be reproduced by a population model with Boltzmann weights for the energy levels of the Co^{2+} ions in an octahedral oxygen environment, as described in Ref. [36]. From this model, one obtains the energy splitting ΔE^{pow}_{j_1=3/2} = 510 K for the powder sample, which is somewhat larger than the estimate from the modeling of the static susceptibility. For the single crystal, one has, similarly, ΔE^{cr}_{j_2=1/2} = 495 K. For the in-plane direction of the field, the linewidth could not be modeled well due to the uncertainty of the Lorentzian fits.

The upturn of ΔH(T) below 20 K is remarkable. It cannot be described by the single-ion population model, suggesting that magnetic correlations between the Co
spins begin to develop gradually. Usually this signifies proximity to a magnetic phase transition where the spin dynamics experiences a critical slowing down [37]. However, such a phase transition in Na$_2$BaCo(PO$_4$)$_2$ takes place at two orders of magnitude lower temperature of $T_N = 148$ mK [28] which evidences an extended low-temperature regime of the spin-liquid like, slow spin fluctuations in the electron spin system.

III. THEORY AND DISCUSSION

To understand why magnetic correlations set on at such a high temperature, we performed a microscopic numerical analysis based on DFT band-structure as well as multiplet calculations. For the former, we do full-relativistic nonmagnetic DFT calculations within the generalized gradient approximation (GGA) [38], as implemented in the full-potential local-orbital code fplo [39].

As an input, we use the experimental crystal structure described within the space group $P3m1$ [27]. The unit cell contains one Co atom with the local trigonal symmetry (point group $3m$). The GGA band structure features a ten-band manifold crossing the Fermi level, as expected for a unit cell containing one Co atom featuring five $d$ orbitals and two spin flavors. In the absence of spin polarization, each band is doubly degenerate in accord with the Kramers theorem. As a result, the band structure features only five distinct band dispersions (Fig. 4, left). The strong octahedral crystal field splits these bands into two manifolds that are well separated from the rest of the valence band and are formed almost exclusively by Co $d$ states (Fig. 4, right) [40]. For further analysis, we single out these states by resorting to Co-centered Wannier functions (WFs). Following the procedure described in Ref. [41], we obtain excellent agreement between the Fourier-transformed WF and the respective GGA bands (Fig. 4, a).

In the WF basis, the Hamiltonian is a sum of local and nonlocal terms. The former describes the one-particle spectrum of an isolated trigonally distorted CoO$_6$ octahedron, and key parameters of the local Hamiltonian can be extracted directly from WF [42]. By inspecting different contributions, we find a well-defined hierarchy of energy scales: the strong cubic CF, followed by the SO interactions, the trigonal CF splitting, and finally, the Zeeman term. The separation of energy scales allows us to disentangle the underlying processes and arrive at an intuitive physical picture, which we show in Fig 1(a). First, the cubic CF splits the $^4T_1$ multiplet of the free Co$^{2+}$ ion into three multiplets where the lower one, $^4T_{1g}$, contains predominantly only one-electron $t_{2g}$ holes. Next, the $^4T_{1g}$ multiplet is further split by the SO interaction. An isolated $^4T_{1g}$ multiplet can be solved analytically [33], resulting in effective $j$ values, from lowest to highest energy $j_1 = \frac{1}{2}$, $j_2 = \frac{3}{2}$ and $j_3 = \frac{5}{2}$ [43]; the respective $g$ factors amount to $g_1 = \frac{13}{8}$, $g_2 = \frac{16}{15}$ and $g_3 = \frac{3}{5}$, and the two splittings amount to $\frac{3}{2} \lambda$ and $\frac{5}{2} \lambda$, where $\lambda = 33$ meV is the effective SO interaction parameter [44]. The trigonal CF further splits the second and third multiplets, giving rise to the experimentally observed $g$ factor anisotropy. Finally, the Zeeman interaction lifts the remaining degeneracy.

The GGA calculations (Fig. 4) imply a one-electron picture in an effective mean-field potential and cannot display the multiplet structure directly. To account for the ensuing electronic correlations, we perform multiplet calculations using the parameters extracted from the WF, and obtain a complete numerical solution of the local many-body problem. Skipping methodological aspects of this procedure that will be published elsewhere, we go straight to the most important result: the splitting between the $j_1 = \frac{1}{2}$ ground state and the lowest-lying $j_2 = \frac{3}{2}$ component amounts to $\Delta E_{j_1,j_2} = 472$ K, in a fair agreement with our experimental estimates [45]. The splitting exceeds by far the magnetic energy scale. Therefore, the magnetism of Na$_2$BaCo(PO$_4$)$_2$ can be safely described in an effective $j_{\text{eff}} = \frac{1}{2}$ model. Another important observable is the $g$ tensor anisotropy, i.e. the difference between $g_c$ and $g_{ab}$.

Our calculations lead to an anisotropy of $g_c = 4.33$ and $g_{ab} = 4.55$ being slightly smaller than the experimental one and of opposite sign. The reason for this discrepancy is the extreme sensitivity of the $g$ factor anisotropy to the small (10 meV) trigonal CF parameter: a small readjustment of the CF parameter reproduces the experimental values ($g_{c\text{eff}} = 4.80$ and $g_{ab\text{eff}} = 4.31$). And since the trigonal CF is in turn governed by the oxygen positions in the crystal structure, additional structural refinements, especially at lower temperatures, are needed for a conclusive analysis.

Having solved the local problem, we turn to hopping processes that underlie the magnetic exchange. By analyzing the respective WF, we find that Na$_2$BaCo(PO$_4$)$_2$ is an excellent model system: further longer-range in-
plane as well as interplane hoppings are orders of magnitude weaker than the leading nearest-neighbor terms. As we are dealing with a multi-orbital problem, a direct determination of the magnetic exchange integrals from the hopping terms is very challenging. Therefore, we start with a qualitative analysis. By inspecting the hoppings between different orbitals, we find that for every pair of neighboring Co atoms, the leading contribution pertains to a single matrix element: virtual electron transfer between two $t_{2g}$ orbitals lying in the same plane [e.g., the plane in Fig. 1(b)]. Although this hopping implicitly includes transfer to and between the ligand orbitals, it is effectively equivalent to the direct hopping denoted as $t'$ in Refs. [31, 32]. We note that this hopping is underlain by the perfect mutual alignment of neighboring CoO$_6$ octahedra and may be strongly suppressed if the octahedra are tilted.

Next, we estimate the exchange integral $J_1$ quantitatively. To this end, we perform full-relativistic magnetic DFT+$U$ calculations [45]. We find that large orbital moments, a prerequisite for the correct description of $j_{\text{eff}} = \frac{1}{2}$ physics, are stable only if the quantization axis coincides with the threefold rotation crystal axis. We construct three supercells and perform total-energy calculations for different collinear magnetic arrangements. By mapping the total energies onto a classical Heisenberg model with effective spins $\hat{j}_{\text{eff}} = \frac{1}{2}$, we estimate the nearest-neighbor exchange to be $11.6 \pm 2.0$ K, where the error bars pertain to the uncertainty in choosing the $U$ value ($U = 5 \pm 1$ eV).

Why is the DFT+$U$ estimate for $J_1$ so large? To find the root cause, we first recollect that the magnetic exchange in Na$_2$BaCo(PO$_4$)$_2$ is anisotropic. As the orientation of magnetic moments in DFT+$U$ is fixed, such calculations provide only one component of the magnetic exchange, $J_1^{zz}$. To estimate the anisotropic terms we go a step back and apply the recently developed perturbative expressions, [31, 32] parametrized by our WF. Using just the dominant hopping term $t' = 82$ meV [45] we arrive at $J_1^{zz} = J_1 + K_1/3 = 2.3$ K, which is smaller than the DFT+$U$ estimate. Surprisingly, we find, besides the leading antiferromagnetic term $J_1 = (16/81)(t')^2/U = 3.1$ K, also a sizable ferromagnetic Kitaev term $K_1 = (-4/27)(t')^2/U = -2.3$ K. Other anisotropic terms are smaller, and hence nearest-neighbor exchange and Kitaev terms dominate the magnetic interactions. These results agree with our mean-field estimate of $J$ from the magnetization $M(H)$ dependence [Fig. 2(a)].

We are now in a position to combine our results into a coherent physical picture. Na$_2$BaCo(PO$_4$)$_2$ is a nearest-neighbor $j_{\text{eff}} = \frac{1}{2}$ triangular magnet with a strongly anisotropic exchange: Its magnetism is driven by the competition of the dominant antiferromagnetic contribution with a sizable ferromagnetic Kitaev term. The latter lowers the saturation field, which otherwise would be of the order of $J_1$. But the energy scale of magnetic correlations is set by the absolute values of magnetic exchanges, and hence it is enhanced by $K_1$. Therefore, the onset of the spin-spin correlations already at $T \sim 20$ K $\gg T_N$, manifested in the observed broadening of the ESR linewidth, is a combined effect of $J_1$ and $K_1$.

IV. CONCLUSIONS

Our static magnetization and ESR results on the spin-liquid candidate material Na$_2$BaCo(PO$_4$)$_2$ enable us to classify it as an anisotropic triangular magnet in the effective spin $j_{\text{eff}} = \frac{1}{2}$ ground state well isolated from the higher energy effective spin-$\frac{3}{2}$ state. Furthermore, the ESR data provide strong indications of the magnetic correlations setting in far above the magnetic ordering temperature $T_N$ and the Weiss temperature $\theta$. We established the anisotropic $j_{\text{eff}} = \frac{1}{2}$ ground state on the theory level as well and reveal, besides the antiferromagnetic isotropic nearest-neighbor exchange interaction $J_1$, a significant ferromagnetic Kitaev interaction term $K$, which is beneficial for the realization of a spin liquid in this compound. The competition between $J_1$ and $K$ reduces the temperature scale $\theta$ but does not affect magnetic correlations the energy scale of $\sim 20$ K $\gg T_N$ of which is probed by ESR. Altogether our findings put forward Na$_2$BaCo(PO$_4$)$_2$ as a promising Kitaev-exchange-assisted spin-liquid material and call for further extensive exploration of the exciting physics of this class of compounds.

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require that the cobalt in the compound must be present as Co$^{2+}$, as in all phosphates. Its charge and the electropositive nature of Na and Ba are used for cobaltates: $\zeta$ (for the one-electron picture), $\lambda$ (for the many-body picture) and $\tilde{\lambda}$ (effective parameter for the orbital angular momentum equal to unity). For $d^7$ Co$^{2+}$, $\zeta \equiv -\lambda \equiv \tilde{\lambda}$.

See Supplemental Material for the matrix elements of the hopping term, details of application of perturbation-theory expressions for magnetic exchange integrals, the dependence of the DFT+$U$ theory expressions for magnetic exchange integrals, the local Wannier Hamiltonian and of the nearest-neighbor hopping terms, in the temperature and energy range of consideration. Note that three definitions of the SO coupling constant are used for cobaltates: $\zeta$ (for the one-electron picture), $\lambda$ (for the many-body picture) and $\tilde{\lambda}$ (effective parameter for the orbital angular momentum equal to unity). For $d^7$ Co$^{2+}$, $\zeta \equiv -\lambda \equiv \tilde{\lambda}$.
Supplemental Material for

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WANNIER FUNCTIONS: LOCAL TERMS

We analyse the full-relativistic non spin-polarized GGA band structure of Na$_2$BaCo(PO$_4$)$_2$ (Fig. 4 in the manuscript) by constructing Wannier functions (WF) describing the Co 3$d$ states. To this end, we resort to the trigonal basis:

$$
\begin{align*}
|x| &= \sqrt{\frac{1}{3}} |x^2 - y^2| - \sqrt{\frac{1}{3}} |xz| \\
|y| &= -\sqrt{\frac{1}{3}} |xy| - \sqrt{\frac{1}{3}} |yz| \\
|z| &= |z^2| \\
|v| &= \sqrt{\frac{1}{3}} |x^2 - y^2| + \sqrt{\frac{1}{3}} |xz| \\
|w| &= -\sqrt{\frac{1}{3}} |xy| + \sqrt{\frac{3}{4}} |yz|,
\end{align*}
$$

(1)

In this basis, the local terms of the resulting Hamiltonian are given by the following Hermitian matrix:

$$
H_0 = \begin{pmatrix}
-793.8 & 0.0 & 32.9i & 0.0 & 0.0 & -33.8 & 10.7 & 33.5i & 47.4i & 33.5i \\
-793.8 & 0.0 & -32.9i & 33.8 & 0.0 & -33.5 & 10.7 & 33.5i & 47.4i & -33.5 \\
-793.8 & 0.0 & 33.8i & 0.0 & 33.8i & -47.4i & 33.5i & 10.7 & -33.5 \\
-793.8 & 33.8i & 0.0 & 33.5i & 47.4i & 33.5 & 10.7 \\
-804.4 & 0.0 & 0.0 & -47.5 & 0.0 & 47.5i & 0.0 \\
-804.4 & 47.5 & 0.0 & 47.5i & 0.0 \\
88.5 & 0.0 & 0.0 \\
88.5 & 0.0 \\
88.5 & 88.5
\end{pmatrix},
$$

(2)

where we show only the upper triangular part. All values are in meV.

WANNIER FUNCTIONS: NEAREST-NEIGHBOR HOPPING

To describe the nearest-neighbor hopping $t_1$, it is reasonable to resort to the standard $d$ basis ($|xy|$, $|yz|$, $|3z^2 - r^2|$, $|xz|$, and $|x^2 - y^2|$):

$$
t_1 = \begin{pmatrix}
-2.0 & -17.3 & 7.1 & 1.3 & 1.8 \\
-2.0 & -2.0 & 1.3 & 7.0 & \\
33.8 & -8.0 & -31.2 & \\
-82.8 & -13.8 & \\
-2.2
\end{pmatrix}.
$$

(3)

Note that the matrix elements in Eq. (3) are given for the pair of Co atoms separated by the lattice translation vector $a$, i.e. along the crystallographic direction [100]. We now use these hopping parameters for a rough estimate of anisotropic exchange couplings. For that purpose we apply the perturbative formulas which were recently developed [1, 2] for edge shared CoO$_6$ octahedra appearing for instance in Na$_2$Co$_2$SbO$_6$ where the Co$^{2+}$ ions build a honeycomb lattice. These formulas can be applied in our case of Na$_2$BaCo(PO$_4$)$_2$ with the only difference that the octahedra edges do not touch directly but are just close together such that the shortest Co-O-Co exchange path is replaced by Co-O-Co-Co. That makes, however, no difference in the perturbative formulas which are formulated for hopping parameters between effective $d$-like orbitals. As it was shown in [1, 2] the most relevant hoppings are those between $t_{2g}$ orbitals. From (3) one can read out a very important hopping $t' = -82.8$ meV between neighbouring $|xz|$ orbitals.
FIG. 5. The magnetic exchanges as a function of the onsite Coulomb repulsion $U$; the shaded area demarcates the range of plausible values. The relevant exchange pathways are schematically depicted in the inset.

and a much smaller hopping $t = −17.3$ meV between $|xy⟩$ and $|yz⟩$, where we used already the notation of [1, 2]. Taking only $t'$ and neglecting $t$ completely we can read out from the last line of Eq. (7) in [1] the isotropic exchange $J_1 = (16/81)(t')^2/U = 3.1$ K and the Kitaev term $K_1 = -(4/27)(t')^2/U = −2.3$ K. Here, we also neglected the influence of the trigonal splitting $Δ$ (in the notation of [2]) on the exchange terms.

EXCHANGE INTEGRALS FROM DFT+$U$ CALCULATIONS

We estimate the magnetic exchanges by solving a redundant system of linear equations parameterized by spin-polarized GGA+$U$ total energies. Full-relativistic SGGA+$U$ calculations are done using the fully-localized-limit double-counting correction with the onsite Coulomb repulsion of 3.5...6.5 eV and the onsite Hund’s exchange of 1 eV. Figure 5 shows how the DFT+$U$-evaluated magnetic exchanges depend on the Coulomb interaction $U$.

MULTIPLET CALCULATIONS BY EXACT DIAGONALIZATION

To calculate the multiplet spectrum of a single Co$^{2+}$ center we treat a local Hamiltonian for the configuration $3d^7$, containing Coulomb, ligand field, and spin-orbit (SO) interactions, leading to a 120$^*120$ matrix problem. The influence of the surrounding octahedra of O ligands with a slight trigonal distortion (point group D$_{3d}$) is taken into account by three ligand field (LF) parameters. The local single-ion Hamiltonian can be written as

$$H = H_{\text{Coul}} + H_{\text{LF}} + H_{\text{SO}},$$

and it is diagonalized exactly using the computer code ELISA (electrons localized in single atoms) which was used before to calculate the X-ray absorption spectra (XAS) of Mn-TCNB (Mn-tetracyanobenzene) [3]. The Coulomb and spin-orbit interactions are treated as in rotationally invariant atoms. Its matrix elements are well known, and their parameters are fitted to the spectra for a free Co$^{2+}$ ion [4] subject to a slight reduction in the periodic crystal. A reduction to 80 per cent of the free ion value gives the Coulomb Slater parameter $F^{(2)} = 7.54$ eV and $F^{(4)} = 5.11$ eV, but those parameters are not very critical for the low energy spectra. The free ion spectra are well fitted by a spin orbit coupling of $ζ = 66$ meV (given for the one-electron basis) which coincides accidentally with the WF parameter.

The multiplet spectrum depends crucially on the ligand field part, which can be expressed in terms of Steven’s operators. The cubic symmetry is broken due to the elongation of the octahedron along the $c$-axis and the ligand-field (or crystal-field) Hamiltonian is split into cubic and trigonal parts:

$$H_{\text{LF}} = H_{\text{cub}} + H_{\text{trig}} = -\frac{2}{3}B_4^0(O_4^0 - 20\sqrt{2}O_4^1) + B_2^0O_2^0 + B_4^0O_4^0,$$
We remark a clear order of interactions as concerns the spin-orbit coupling and the ligand field parameter: \( \zeta \). For the sake of clarity we neglect the spin-orbit coupling \( \zeta \) and the small trigonal LF parameters \( v \) and \( v' \).

where the explicit expression of the Steven’s operators is given in the book of Abragam and Bleaney [5], for example. There exist several notations for the three ligand field parameters for \( d \)-electrons in the trigonal case. Here we use the parameters \( \Delta \), \( v \) and \( v' \) like Koidl [6] and MacFarlane [7] (see also Ref. 8):

\[
B_4^0 = -\frac{\Delta}{120} - \frac{1}{360} \left( v + \frac{3\sqrt{2}}{2} v' \right), \quad B_4' = -\frac{1}{140} \left( v + \frac{3\sqrt{2}}{2} v' \right), \quad B_2'' = \frac{v - 2\sqrt{2}v'}{21}.
\] (6)

The LF and SO parameters are determined by a fit to the on-site Wannier expansion (2). Expressing (5) in terms of the trigonal basis (1) one finds the diagonal matrix elements

\[
\langle x|H_0|x \rangle = \langle y|H_0|y \rangle = \frac{2}{5} \Delta + \frac{v}{3}, \quad \langle z|H_0|z \rangle = \frac{2}{5} \Delta - \frac{2}{3} v, \quad \langle v|H_0|v \rangle = \langle w|H_0|w \rangle = -\frac{3}{5} \Delta ,
\] (7)

and the two off-diagonal elements (where we correct the misprinted sign of the \( v' \) term in [8])

\[
\langle x|H_0|v \rangle = \langle y|H_0|w \rangle = -v'.
\] (8)

The other off-diagonal elements of (2) including the imaginary parts correspond to the SO coupling. So, we can simply read out the LF and SO parameters from the matrix (2) and find:

\[
\Delta = -885.9 \text{ meV}, \quad v = 10.6 \text{ meV}, \quad v' = -10.7 \text{ meV}, \quad \zeta = 67.0 \text{ meV}.
\]

We remark a clear order of interactions as concerns the spin-orbit coupling and the ligand field parameter: \( |\Delta| \ll \zeta \gg v, v' \). Also, the Wannier fit leads to practically the same spin-orbit coupling \( \zeta = 67 \text{ meV} \) as that one obtained by fitting the optical spectra of a free Co\(^{2+}\) ion. That is surprising as we expect a reduction of the SO coupling in a crystal with respect to the free ion and can be explained by a slight overestimation of SO coupling in the GGA functional.

Taking into account the established order of interactions, we analyze first the multiplet spectrum neglecting the small trigonal distortion and the spin-orbit coupling (see Table I). The level scheme follows the general rules for a \( d^7 \) configuration in octahedral environment as treated in detail in the book of Abragam and Bleaney [5]. The lowest \( ^4F \) multiplet of the free ion is split into \( ^4T_{1g}, ^4T_{2g} \) and \( ^4A_{2g} \), where \( ^4T_{1g} \) is the lowest one for \( \Delta < 0 \) (octahedral environment). As can be seen in Tab. I, the \( ^4A_{2g} \) multiplet is higher than the lowest state with spin 1/2 (\( ^2E_g \)) in the given case.

Introducing the spin-orbit coupling of \( \zeta = 66 \text{ meV} \) leads to a splitting of the \( ^4T_{1g} \) multiplet. In pure cubic symmetry the \( ^4T_{1g} \) multiplet can be described by an effective orbital moment \( \ell_{eff} = 1 \). Correspondingly, the spin-orbit splitting leads to an effective \( \hat{j}_1 = 1/2 \) lowest doublet, followed by a \( \hat{j}_2 = 3/2 \) quartet and a high-lying \( \hat{j}_3 = 5/2 \) multiplet. In the ideal cubic case and neglecting any interaction to higher lying multiplets, the lowest doublet (effective spin 1/2) has an isotropic \( g \)-factor of \( g = 4.33 \). The trigonal distortion, i.e., the parameters \( v \) and \( v' \), lead to anisotropic \( g \)-factors as presented in Table II. The WF parameter values \( v = 10 \text{ meV} \) and \( v' = -10 \text{ meV} \) lead to an opposite anisotropy \( \Delta g = g_c - g_ab = -0.22 \) with respect to the experimental results. But a slight correction recovers the correct order. That correction is not unique since \( v \) and \( v' \) influence the \( g \)-factor anisotropy in the form \( \Delta g = (50v + 73v')/eV \) when all the other parameters are fixed and we present in Table II two parameter sets which lead to \( \Delta g \) being in reasonable agreement with experiment. We give in Table II also the trigonal splitting parameter \( \Delta_{\text{Lines}} \) which was introduced.

| Term | Degeneracy | Energy (eV) |
|------|------------|-------------|
| \(^4T_{1g}\) | 12 | 0.00 |
| \(^4T_{2g}\) | 12 | 0.77 |
| \(^2E_g\) | 4 | 1.03 |
| \(^4A_{2g}\) | 4 | 1.66 |
| \(^2T_{1g}\) | 6 | 1.72 |
| \(^2T_{2g}\) | 6 | 1.76 |
| \(^4T_{1g}\) | 12 | 2.09 |

Table I. Predicted multiplet energies of Co\(^{2+}\) in Na\(_2\)BaCo(PO\(_4\))\(_2\). The Coulomb parameters \( F^{(2)} = 7.54 \text{ eV} \) and \( F^{(4)} = 5.11 \text{ eV} \) are chosen to have 80 per cent of their free ion value and the cubic crystal field splitting \( \Delta = -0.8856 \text{ eV} \) of the Wannier fit is used. For the sake of clarity we neglect the spin-orbit coupling \( \zeta \) and the small trigonal LF parameters \( v \) and \( v' \).
by Lines [9] and used recently [2] to analyze Na$_3$Co$_2$SbO$_6$. It is defined as the trigonal splitting in the $^4T_{1g}$ multiplet when spin-orbit coupling is switched off.

The SO coupling parameter $\zeta$ for one $d$ electron is related to $\lambda = -\zeta/3$ being the SO coupling between $S = 3/2$ and $L = 3$ in the $^4F$ multiplet of a free ion. The effective SO coupling constant $\tilde{\lambda} = -3\lambda/2$ is defined as the coupling between $S = 3/2$ and $L_{\text{eff}} = 1$ in cubic symmetry. The theoretical SO coupling $\zeta = 66$ meV leads to the low-energy scheme which is shown in Table III with an energy difference $\Delta E_{\tilde{j}_1\tilde{j}_2} = 40.7$ meV (or 472 K) between the lowest $\tilde{j} = 1/2$ doublet and first excited quartet $\tilde{j} = 3/2$. As already noted in the main text, this theoretical energy difference lies in between the energy splittings deduced from the susceptibility data (419 K) and that one from the broadening of the ESR line width (510 K for the powder sample). The susceptibility data correspond to a SO coupling of $\zeta = 48.1$ meV (deduced from $\Delta E_{\tilde{j}_1\tilde{j}_2} = 3\lambda/2 = 3\zeta/4$) and we show in Table III also the low-energy spectrum for this SO coupling parameter.

$\begin{array}{|l|l|l|l|l|}
\hline
v \text{ (meV)} & v' \text{ (meV)} & g_c & g_{a/b} & \Delta g \\
\hline
0 & 0 & 4.48 & 4.48 & 0.0 \\
10 & -10 & 4.33 & 4.55 & -0.22 \\
10 & 0 & 4.81 & 4.31 & 0.50 \\
4 & 4 & 4.80 & 4.31 & 0.49 \\
\hline
\end{array}$

TABLE II. $g$-factors for $\zeta = 66$ meV and varying trigonal distortion.

$\begin{array}{|l|l|l|}
\hline
\zeta & \tilde{j} = 1/2 & \tilde{j} = 3/2 \\
\hline
66.0 \text{ meV} & 0.0 \text{ meV} & 40.7 \text{ meV} \\
48.1 \text{ meV} & 45.6 \text{ meV} & 84.0 \text{ meV} \\
\hline
\end{array}$

TABLE III. Comparison of energy splitting in the lowest multiplet $^4T_{1g}$ and of the $g$-factors for two different spin-orbit coupling parameters $\zeta$. The trigonal LF parameters were chosen to be $v = v' = 4$ meV.

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