Low-temperature enhancement of ferromagnetic Kitaev correlations in α-RuCl₃

Andreas Koitzsch,[1] Eric Müller,[1] Martin Knupfer,[1] Bernd Büchner,[1,2] Domenic Nowak,[3] Anna Isaeva,[3]
Thomas Doert [3] Markus Grüninger,[4] Satoshi Nishimoto,[1,2] and Jeroen van den Brink[1,2,*]

[1]*IFW Dresden, Helmholtzstraße 20, 01069 Dresden, Germany*
[2]*Institut für Theoretische Physik and Würzburg-Dresden Cluster of Excellence ct.qmat,
Technische Universität Dresden, 01062 Dresden, Germany*
[3]*Department of Chemistry and Food Chemistry, TU Dresden, 01069 Dresden, Germany*
[4]*II Physikalisches Institut, Universität zu Köln, Zülpicher Strasse 77, D-50937 Köln, Germany*

Kitaev-type interactions between neighboring magnetic moments emerge in the honeycomb material α-RuCl₃. It is debated, however, whether these Kitaev interactions are ferromagnetic or antiferromagnetic. With electron energy loss spectroscopy (EELS) we study the lowest excitation across the Mott-Hubbard gap, which involves a d^4 triplet in the final state and therefore is sensitive to nearest-neighbor spin-spin correlations. At low temperatures the spectral weight of these triplets is strongly enhanced, in accordance with optical data. We show that the magnetic correlation function that determines this EELS spectral weight is directly related to a Kitaev-type spin-spin correlator and that the temperature dependence agrees very well with the results of a microscopic magnetic Hamiltonian for α-RuCl₃ with *ferromagnetic* Kitaev coupling.

I. INTRODUCTION

The celebrated Kitaev model describes bond-dependent spin-1/2 interactions on the honeycomb lattice [1]. It has attracted enormous attention because it is conceptually simple but harbors rich physics and is still exactly solvable. Among its solutions are quantum spin liquids, which show a number of peculiar properties, such as the absence of magnetic long-range order at $T = 0$ despite the presence of sizable moments, and exotic fractionalized excitations like Majorana fermions with potential applications for quantum information processing.

After the identification of iridates as possible solid-state realizations of the Kitaev model [2] much work has been devoted to Ir^{4+} systems, with its $5d^5$ electron configuration and the effective $J_{eff} = 1/2$ description in order to uncover signatures of the quantum spin liquid [3,4]. However, research on the iridates is hampered by, e.g., the difficult crystal growth and lattice distortions. Recently, α-RuCl₃ has been established as a promising $4d$ analog to the iridates [5,6]. Neutron and Raman scattering studies gave evidence of fractionalized excitations typical for the Kitaev quantum spin liquid [6–10] and both recent theoretical [11] and recent experimental [9,12–21] investigations indicate in this material the presence of a transition into a quantum spin liquid state in an external magnetic field.

Thus the quantification of the bond-dependent Kitaev interaction term K is a key issue for α-RuCl₃. For a deeper understanding and correct theoretical description of the material properties knowledge of K is crucial, much like knowledge of the Heisenberg exchange parameter J for ordinary magnets. In spite of extensive and detailed investigations of its electronic and magnetic structure [8–10,22–43] even the sign of K is under debate for α-RuCl₃. Whereas Banerjee *et al.* [6,8] introduce a positive K, that is, antiferromagnetic coupling, to fit spin-wave spectra measured by inelastic neutron scattering, quantum chemistry studies favor a negative (ferromagnetic) K [11]. Other neutron scattering experiments indeed claim a better agreement with a ferromagnetic K [9,39].

Here we shed light on this controversy by measuring the temperature-dependent loss function by electron energy loss spectroscopy (EELS) and comparing the results to the spectral weight derived from a microscopic Hamiltonian. We conclude from this that as the temperature goes down the nearest-neighbor Kitaev spin-spin correlations become more ferromagnetic, pointing unequivocally to a ferromagnetic K in the Hamiltonian for α-RuCl₃.

II. CONCEPTUAL BACKGROUND

In α-RuCl₃ the basic structural building blocks, $(RuCl_6)$ octahedra, are connected via edges into layers propagating in the *ab* plane [see Fig. 1(a)]. The d^5 configuration of Ru^{3+} has a single hole in the t_{2g} shell, where the wave functions of the three t_{2g} orbitals d_{xy}, d_{yz}, and d_{zx} are indicated in Fig. 1. The strong spin-orbit coupling splits the t_{2g} states into a $j = 3/2$ quartet and $j = 1/2$ Kramers doublet, the latter forming the ground state. It is important to note that for edge-sharing octahedra the hopping between the t_{2g} orbitals via the ligands has a very specific symmetry [2]: the largest hopping t is between the d_{yz} and the d_{zx} orbitals at neigboring sites, as indicated in Figs. 1(b) and 1(c). Additional hopping amplitudes are symmetry allowed but tend to be much weaker; an example
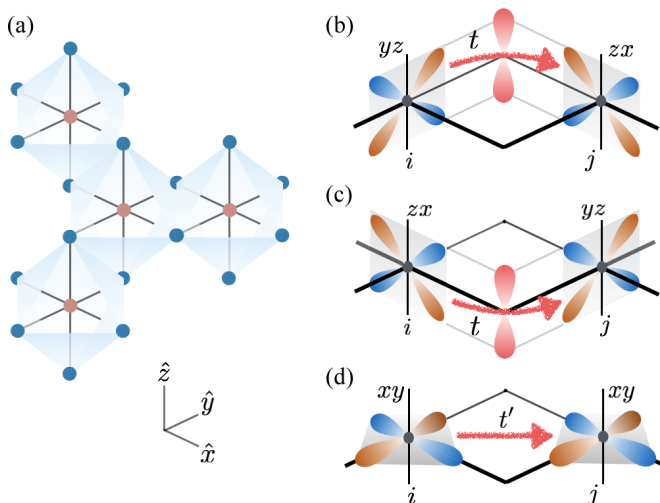
*j.van.den.brink@ifw-dresden.de

FIG. 1. (a) Illustration of edge-sharing (RuCl$_6$) octahedra comprising a single honeycomb layer of α-RuCl$_3$ and representation of the hopping integrals between Ru t_{2g} orbitals of d_{yz}, d_{zx}, and d_{xy} symmetry. Note that along the two different paths with amplitude t from i to j indicated in (b) and (c), different orbitals are involved. (d) Direct hopping t' between d_{xy} states.

FIG. 2. Temperature-dependent low-energy loss function measured at $\mathbf{q} = 0.1$ Å^{-1}. Inset: Peak A background corrected and normalized.

is the direct hopping t' between d_{xy} orbitals at neighboring sites [see Fig. 1(d)].

Orbital-dependent superexchange interactions [44,45] of these spin-orbit-coupled Ru^{3+} magnetic moments are generated by intersite hopping processes of the type d^5-$d^5 \rightarrow d^4$-$d^6 \rightarrow d^5$-d^5. It turns out that at leading order (t^2/U, with hopping t and Hubbard U) the exchange interactions vanish, but at next-to-leading order ($t^2 J_H/U^2$, with Hund's rule coupling J_H) the interactions are precisely of the bond-directional type as they appear in the Kitaev Hamiltonian [2,46]. The essential ingredient that causes the Kitaev coupling K to become finite is the fact that J_H splits up the d^4 intermediate states, for which there are two holes at the same site, into a local manifold of triplets ($^3T_1$; nine states) and singlets ($^1T_2$, ^1E, ^1A; six states). As J_H is ferromagnetic, the $^3T_1$ multiplet is well below the singlet states in energy.

These hopping amplitudes not only determine the form and magnitude of the exchange interactions, but also determine the spectral weight of intersite d^5-$d^5 \rightarrow d^4$-d^6 excitations [45–50], i.e., excitations across the Mott-Hubbard gap as measured in, for instance, EELS and optical spectroscopy. For the lowest d^4-d^6 excited states, it is sufficient to consider a single d^6 (t_{2g}^6) multiplet and the lowest d^4 multiplets. Accordingly, the intersite excitations in RuCl$_3$ are also split into the d^4 triplet and singlet multiplets, i.e., they are directly related to the intermediate states of the superexchange interaction, and their spectral weight is linked, in particular, to magnetic correlations of the Kitaev type, as we quantify in the following.

III. ELECTRON ENERGY LOSS MEASUREMENTS

Our EELS experiments on RuCl$_3$ were performed on plateletlike single crystals up to several millimeters in diameter, grown by c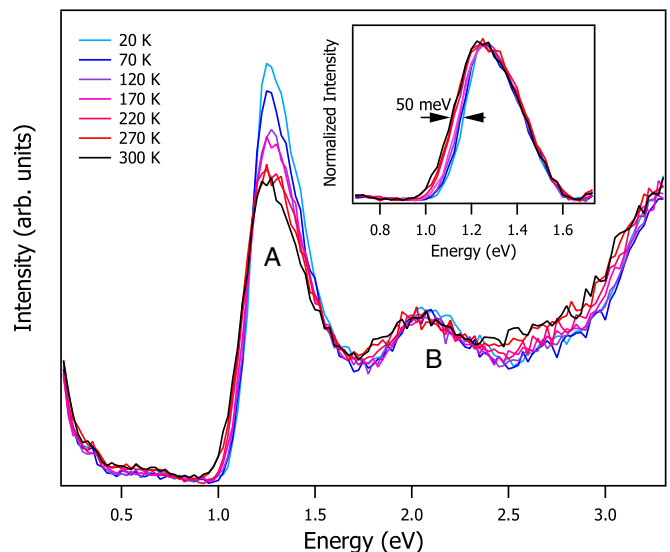hemical vapor transport reactions, exhibiting a single magnetic transition; see Ref. [28] for details of crystal growth and characterization. The EELS measurements were carried out using a purpose-built transmission electron energy-loss spectrometer [51,52] with a primary electron energy of 172 keV and energy and momentum resolutions of $\Delta E = 85$ meV and $\Delta \mathbf{q} = 0.035$ Å^{-1}, respectively. The films ($d \approx 100$ nm) were exfoliated by scotch tape. Subsequently, the films were mounted onto standard electron microscopy grids and transferred into the EELS spectrometer.

Figure 2 shows the low-energy loss function measured between $T = 20$ K and $T = 300$ K in the quasioptical limit of low momentum transfer ($\mathbf{q} = 0.1$ Å^{-1}). The spectra are normalized at a higher energy ($E = 4$ eV). The lowest EELS features can be assigned to optical excitations of the d^5-$d^5 \rightarrow d^4$-d^6 type across the Mott-Hubbard gap of 1.1 eV. We observe peaks at $E_A = 1.2$ eV and $E_B = 2.1$ eV, consistent with our previous studies [28] and with optical conductivity data [37]. As indicated in Fig. 3(a) the EELS d^4-d^6 final state may contain a d^4 spin singlet ($S = 0$) or triplet ($S = 1$) state, which significantly differ in energy due to Hund's rule, i.e., interorbital exchange interaction J_H. The triplet is expected at a much lower energy, $2J_H \approx 0.8$ eV, thus the lowest-energy feature, peak A, is associated with the d^4 triplet multiplet, in agreement with previous reports [28,38,53]. Peak B has been assigned either to the d^4 singlet multiplet [38] or to a crystal-field excitation to empty e_g states [28]. Our analysis is focused on peak A because a quantitative correlation between the spectral weight and the nearest-neighbor spin-spin correlations requires a clear separation between different multiplets, which typically is only realized for the lowest excitation across the gap. This is supported by the temperature dependence. The spectral weight of peak A decreases significantly with increasing temperature [see Fig. 3(b)], in agreement with recent optical conductivity data [38] [see Fig. 4(a)]. In contrast, peak B does not show such a clear temperature dependence.
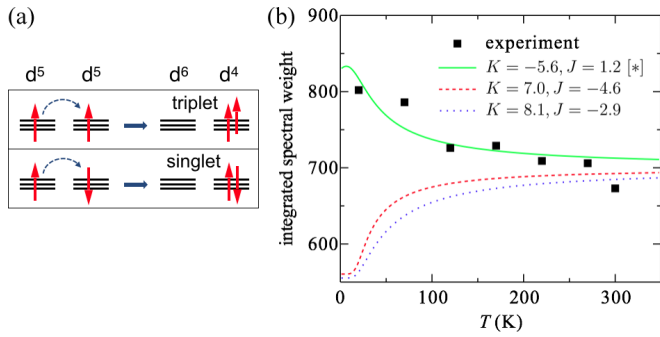
(a)

(b)

FIG. 3. (a) Schematics of the Mott excitation involving the t_{2g} shells of two neighboring Ru^{3+} sites. Red arrows refer to holes. (b) Integrated spectral weight I of peak A in Fig. 2 after background subtraction as a function of the temperature compared to the results of exact diagonalization calculations for different parametrizations of the magnetic interactions; [*] refers to the exchange parameters determined in Ref. [11] (see also the text).

A. Qualitative interpretation

It is well known that nearest-neighbor spin-spin correlations in Mott-Hubbard insulators may cause large spectral weight changes across magnetic phase transitions at T_N even when $k_B T_N$ is much smaller than the energy gap [47,48,50,54].

This simply reflects the spin selection rule for optical excitations. As quantified below, excitations to d^4 triplets acquire a finite spectral weight *only* if the initial alignment of the magnetic moments on two neighboring Ru sites is parallel, as is the case for a dominating ferromagnetic Kitaev exchange. The increase in spectral weight at lower temperatures implies that the nearest-neighbor Kitaev spin-spin correlation becomes more ferromagnetic. This directly points to the Kitaev term in the Hamiltonian being ferromagnetic, in line with quantum chemistry calculations [11]. If one assumes, on the other hand, the scenario of dominant antiferromagnetic nearest-neighbor Kitaev exchange, the spectral weight of peak A should be suppressed at low temperatures, which is at odds with the experimental data.

According to the arguments above, with increasing temperature the ferromagnetic Kitaev correlations should be reduced, giving rise to an increase in the spectral weight of the spin singlet states at higher energies. Indeed, Fig. 2 does show spectral weight transfer from peak A to a broad region between $E \approx 1.5$ eV and $E \approx 3.5$ eV.

The inset in Fig. 2 presents peak A in a normalized and background-subtracted fashion in order to monitor the temperature dependence of the line shape and peak position. The line shape is slightly asymmetric but remains almost constant with the temperature except for a modest broadening. The broadening and gap change are of the order of 50 meV and
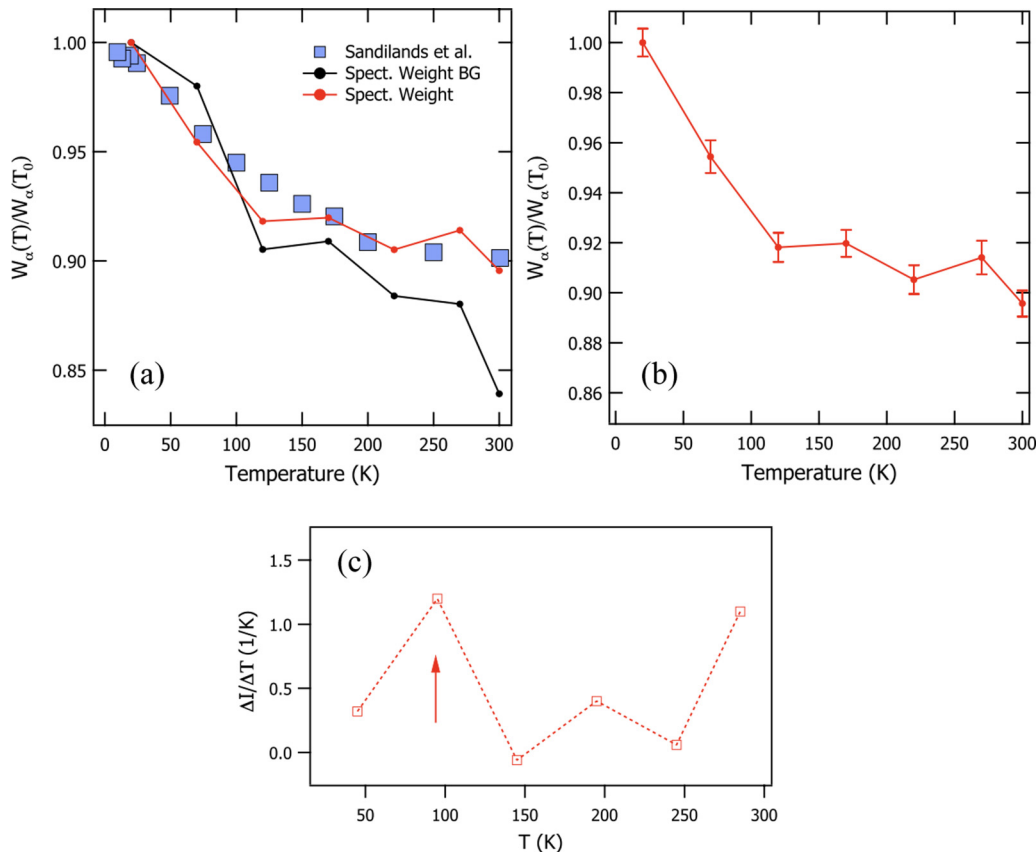

FIG. 4. (a) Spectral weight evolution of the optical conductivity data reproduced from Sandilands *et al.* [38] and our data, with and without background subtraction. The data are normalized to the lowest available temperature. (b) Measured temperature-dependent intensity of peak A with explicit error bars. (c) Differential quotient of the temperature evolution of the intensity of peak A in Fig. 2. The red arrow highlights the temperature of largest change relevant for the Kitaev energy scale.

can be explained by conventional thermal effects. Figure 2 clearly shows that the temperature-induced change in spectral weight is not caused by a change in the line shape of peak A. Therefore we may rule out an excitonic effect as the origin of the spectral weight change, confirming our interpretation in terms of spin-spin correlations.

IV. QUANTITATIVE RELATION BETWEEN TRIPLET WEIGHT AND MAGNETIC CORRELATIONS

We now wish to determine microscopically and quantitatively how the spectral weight of the lowest-energy triplet excitations depends on the relative orientation of neighboring $j = 1/2$ moments. Following Ref. [2], we define creation operators for a hole in the d_{xy}, d_{yz}, and d_{zx} orbitals at site j as $x_{j\sigma}^\dagger$, $y_{j\sigma}^\dagger$, and $z_{j\sigma}^\dagger$ with spin $\sigma = \uparrow$ or $\downarrow$. The creation operator $a_{\bar\sigma}^\dagger$ for a $j = 1/2$ doublet state with pseudospin $\bar\sigma = \bar\uparrow$ or $\bar\downarrow$ is

$$a_{\bar\uparrow}^\dagger = x_\uparrow^\dagger \sin\theta + \cos\theta(iz_\downarrow^\dagger + y_\downarrow^\dagger)/\sqrt{2},$$

$$a_{\bar\downarrow}^\dagger = x_\downarrow^\dagger \sin\theta + \cos\theta(iz_\uparrow^\dagger - y_\uparrow^\dagger)/\sqrt{2}. \tag{1}$$

The strong spin-orbit coupling puts the $j = 3/2$ quartet at a much higher energy. Note that $\tan\theta = 1/\sqrt{2}$ for the high-symmetry "cubic" $j = 1/2$ states which have equal contributions from the three t_{2g} orbitals. The corresponding hopping Hamiltonian on a z bond is

$$H_{\langle ij\rangle}^0 = \sum_\sigma [(ty_{j\sigma}^\dagger z_{i\sigma} + tz_{j\sigma}^\dagger y_{i\sigma} + t'x_{j\sigma}^\dagger x_{i\sigma}) + \text{H.c.}]. \tag{2}$$

The optical/EELS spectral function is generated by the response of the system to the current operator H', which is obtained from Eq. (2) by substituting $(t, t') \to (it, it')$. The matrix elements that we wish to evaluate are of the type $\langle \psi_T | H' | \bar\sigma_i \bar\sigma_j' \rangle$, where ψ_T are the spin-triplet d^4 states. It is easy to show that the part of H' that is governed by t', the direct d_{xy}-d_{xy} channel, only causes singlet d^4 excitations and is therefore irrelevant for triplet spectral weight. A detailed calculation provides, along a z bond, $\sum_T |\langle \psi_T | H'/t | \bar\downarrow\bar\downarrow\rangle|^2 = \sum_T |\langle \psi_T | H'/t | \bar\uparrow\bar\uparrow\rangle|^2 = \cos^4\theta + \frac{1}{2}\sin^2\theta\cos^2\theta$ and $\sum_T |\langle \psi_T | H'/t | \bar\uparrow\bar\downarrow\rangle|^2 = \sum_T |\langle \psi_T | H'/t | \bar\downarrow\bar\uparrow\rangle|^2 = \sin^2\theta\cos^2\theta$. Collecting terms, the total intensity I_T of the triplets is, apart from a constant term,

$$I_T = \sum_{T,\langle ij\rangle} |\langle \psi_T | H' | \bar\sigma_i \bar\sigma_j\rangle|^2 = \frac{2t^2}{3} \sum_{\langle ij\rangle} \left(S_i^z S_j^z + 1/4\right) \tag{3}$$

for "cubic" $j = 1/2$ states ($\tan^2\theta = 1/2$ and $\cos^2\theta = 2/3$), where $S_i^z S_j^z$ is the Kitaev term on the z bond; the other bonds follow by replacing S^z with S^y/S^x, respectively. From this expression it is clear that the triplet spectral weight is maximum when the pseudospins are oriented ferromagnetically and, vice versa, smallest when the neighboring $j = 1/2$ moments are oriented antiparallel. This is in line with the general expectation that two parallel neighboring moments are more likely to be excited into a triplet state than a pair of antiparallel moments.
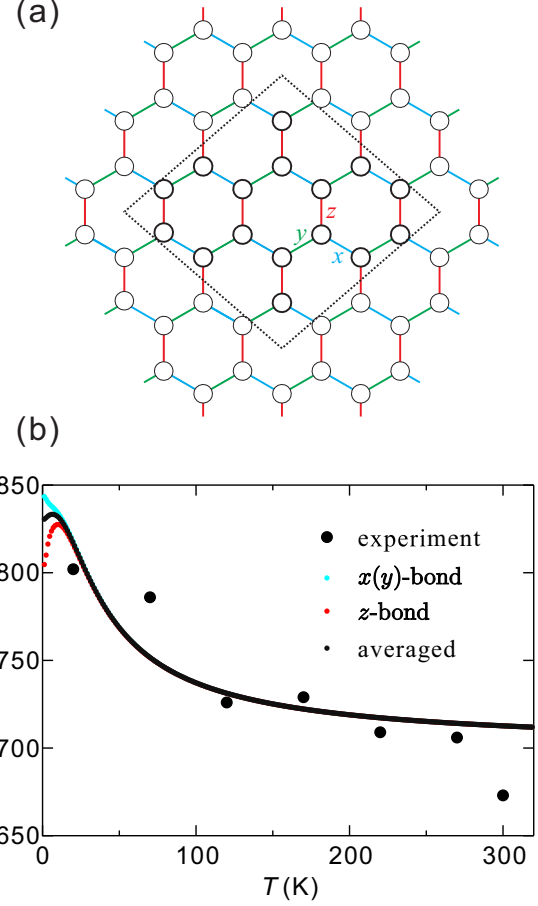

(a)

(b)

FIG. 5. (a) Sixteen-site cluster with periodic boundary conditions used in the full exact diagonalization calculations. (b) Effect of the bond-dependent correlator, with the anisotropic 16-site cluster, on the integrated spectral weight I. The experimental data are also plotted.

A. Evaluation of magnetic correlations

To compare with the experimental data, we evaluated the temperature-dependent correlator in Eq. (3) numerically for the extended Heisenberg-Kitaev Hamiltonian for RuCl$_3$ with all symmetry-allowed nearest-neighbor couplings, which on the z bonds takes the form

$$H_{\langle ij\rangle}^M = J\mathbf{S}_i \cdot \mathbf{S}_j + KS_i^z S_j^z + \sum_{\alpha\neq\beta} \Gamma_{\alpha\beta}\left(S_i^\alpha S_j^\beta + S_i^\beta S_j^\alpha\right),$$

with appropriate permutations for the x and y bonds on the honeycomb lattice. We use the magnetic couplings derived from quantum chemistry calculations: $J = 1.2$ meV, $K = -5.6$ meV, $\Gamma_{xy} = -1.2$ meV, $\Gamma_{zx} = -\Gamma_{xy} = -0.7$ meV, and further neighbor exchange $J_2 = J_3 = 0.26$ meV [11]. Note that $|K/J| = 4.6$ and K is ferromagnetic. Full exact diagonalization calculations with a 16-site periodic cluster [see Fig. 5(a)] were performed. Due to the dominant Kitaev term, finite-size effects are small. At zero temperature the nearest-neighbor spin-spin correlation in our model is 0.1087 and it is close to 0.1323 in the ferromagnetic Kitaev limit (for Heisenberg $J = 0$), where the finite-size effect disappears (also see Ref. [11]). We calculated the expectation value of the correlator in the canonical ensemble; here, only excitations

with momentum transfer $\mathbf{q} = \mathbf{0}$ that are relevant for EELS are summed up. The expectation value of the nearest-neighbor spin-spin correlation is obtained as an averaged one of the three bonds, i.e., $\langle S_i^x S_j^x \rangle$ for the x bond, $\langle S_i^y S_j^y \rangle$ for the y bond, and $\langle S_i^z S_j^z \rangle$ for the z bond. Since this cluster is spatially anisotropic, one may concern an artificial enhancement of anisotropy in the correlations by finite-size effect. In Fig. 5(b) we plot the integrated spectral weight I with the correlator for each bond denoted in Fig. 5(a). A small bond dependence is seen at very low temperatures; nevertheless, it seems not to affect the region where the numerical data are compared to the experiment. The averaged values are used in Fig. 3(b).

B. Parameter dependence of the correlator

To further confirm the importance of dominant ferromagnetic Kitaev coupling in α-RuCl$_3$, we have investigated the parameter dependence of the correlator corresponding to the integrated spectral weight I in the EELS experiment. To see the effect of each parameter clearly, we calculated the correlator by changing one of our parameters ($J = 1.2$ meV, $K = -5.6$ meV, $\Gamma_{xy} = -1.2$ meV, $\Gamma_{zx} = -\Gamma_{yz} = -0.7$ meV, and $J_2 = J_3 = 0.26$ meV) and fixing the others. In Fig. 6 we show the dependence of the correlator on J, J_2 (J_3), and Γ_{xy}.

1. J dependence

The Heisenberg J term is a nearest-neighbor interaction so that it directly affects the correlator. As long as J is sufficiently smaller than $|K|$, the fit works fine. However, when J becomes comparable to $|K|$, the behavior suddenly changes and fitting is impossible. Thus, we can confirm that the dominant character of a ferromagnetic Kitaev coupling is necessary to obtain a good description of the EELS data.

2. J₂, J₃ dependence

The correlator is hardly affected by the longer-range Heisenberg terms J_2 and J_3 if they are in a realistic range. This means that the determination of K from the fitting of the integrated spectral weight is not much affected by the values of J_2 and J_3.

3. Γ_xy dependence

The effect of anisotropic coupling Γ_{xy} on the correlator is also small. A change of Γ_{xy} affects only the low-temperature behavior. Since the fitting of the integrated spectral weight is performed for a wide range of temperatures, the estimated K value is not strongly dependent on Γ_{xy}.

V. DISCUSSION

A direct comparison of the numerically evaluated spin-spin correlator in Eq. (3) with the temperature dependence of the EELS spectral weight of peak A is provided in Fig. 3(b). We obtain a good agreement using magnetic interactions in the Hamiltonian previously derived on the basis of quantum chemistry calculations, in particular, a ferromagnetic Kitaev exchange, $K = -5.6$ meV (see Ref. [11]). The same calculations done with antiferromagnetic Kitaev exchange, using, in particular, the values of K and J suggested from neutron
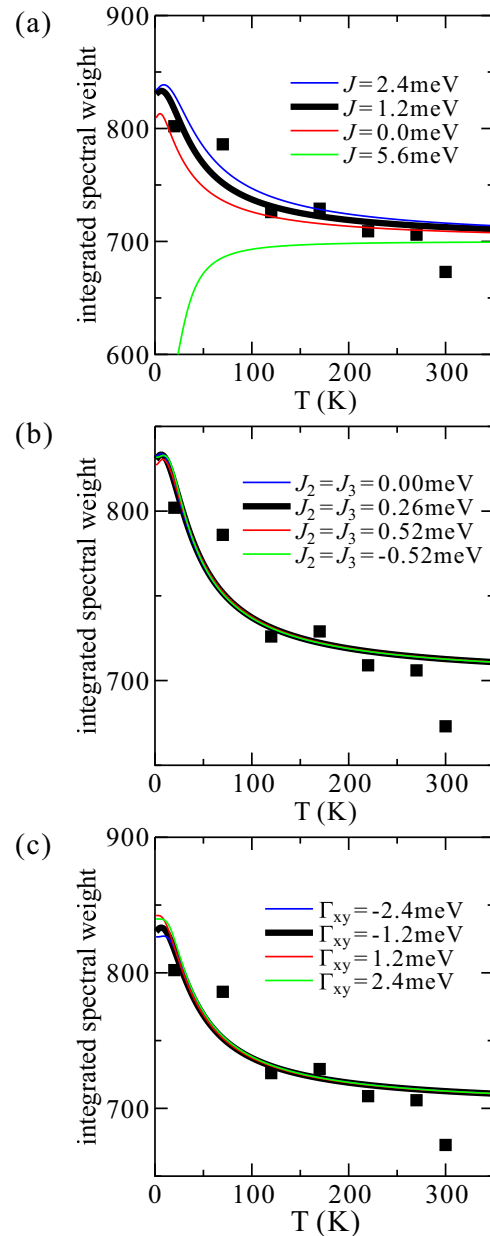
FIG. 6. Parameter dependence of the correlator calculated with the anisotropic 16-site cluster. The dependences on (a) J, (b) J_2, J_3, and (c) Γ_{xy} are shown. The experimental data are also plotted with filled squares.

scattering in Ref. [6], provide temperature trends that clearly do not agree with the EELS data, as shown in Fig. 3(b). The gradual decrease in the spectral weight up to temperatures far above T_N is typical for magnetic systems with enhanced quantum fluctuations such as two-dimensional systems [55] and thus expected for the strongly frustrated Kitaev model. Based on solely the experimental data one can also obtain an estimate for $|K|$. Figure 4(a) shows how the spectral weight of peak A, which is associated with the formation of spin triplets, decreases with increasing temperature. The temperature scale that governs the reduction of the spectral weight should roughly correspond to the energy scale of $|K|$. Based on the differential quotient of the temperature evolution of peak A

one obtains $|K| \approx 90$ K or 7.7 meV [see Fig. 4(c)], which indeed is qualitatively in agreement with the detailed theory.

VI. CONCLUSIONS

The importance of the Kitaev exchange in α-RuCl$_3$ has been established on the basis of various of its magnetic properties: the fractionalized excitations seen in inelastic neutron scattering [6] and Raman spectroscopy [56], consequences for the static magnetic order [25,31,34], and magnetic-field-induced transitions into a quantum liquid state [10–17]. These approaches have so far not resolved the question whether the Kitaev exchange in α-RuCl$_3$ is actually ferromagnetic or antiferromagnetic. Here we follow a different ansatz by analyzing how the spin-spin correlations affect the *electronic* excitation spectrum. We show that the magnetic correlation function that determines the EELS and optical spectral weights is directly related to a Kitaev-type spin-spin correlator. The experimental observation of the triplet spectral weight's increasing at low temperatures implies *ferromagnetic* Kitaev-type correlations becoming stronger. The measured temperature dependence of the EELS spectral weight agrees with calculations for a microscopic magnetic Hamiltonian for α-RuCl$_3$ with ferromagnetic Kitaev coupling. Calculations for systems with antiferromagnetic Kitaev coupling exhibit a temperature dependence that is opposite to the one experimentally observed. Thus we obtain from EELS measurements at temperatures above the magnetic ordering temperature a zero-temperature property: the sign of the dominant magnetic Kitaev exchange interaction.

[1] A. Kitaev, Ann. Phys. **321**, 2 (2006).

[2] G. Jackeli and G. Khaliullin, Phys. Rev. Lett. **102**, 017205 (2009).

[3] B. J. Kim, H. Jin, S. J. Moon, J.-Y. Kim, B.-G. Park, C. S. Leem, J. Yu, T. W. Noh, C. Kim, S.-J. Oh, J.-H. Park, V. Durairaj, G. Cao, and E. Rotenberg, Phys. Rev. Lett. **101**, 076402 (2008).

[4] J. G. Rau, E. K.-H. Lee, and H.-Y. Kee, Phys. Rev. Lett. **112**, 077204 (2014).

[5] K. W. Plumb, J. P. Clancy, L. J. Sandilands, V. V. Shankar, Y. F. Hu, K. S. Burch, H.-Y. Kee, and Y.-J. Kim, Phys. Rev. B **90**, 041112(R) (2014).

[6] A. Banerjee, C. A. Bridges, J. Q. Yan, A. A. Aczel, L. Li, M. B. Stone, G. E. Granroth, M. D. Lumsden, Y. Yiu, J. Knolle, S. Bhattacharjee, D. L. Kovrizhin, R. Moessner, D. A. Tennant, D. G. Mandrus, and S. E. Nagler, Nat. Mater. **15**, 733 (2016).

[7] L. J. Sandilands, Y. Tian, K. W. Plumb, Y.-J. Kim, and K. S. Burch, Phys. Rev. Lett. **114**, 147201 (2015).

[8] A. Banerjee, J. Yan, J. Knolle, C. A. Bridges, M. B. Stone, M. D. Lumsden, D. G. Mandrus, D. A. Tennant, R. Moessner, and S. E. Nagler, Science **356**, 1055 (2017).

[9] A. Banerjee, P. Lampen-Kelley, J. Knolle, C. Balz, A. A. Aczel, B. Winn, Y. Liu, D. Pajerowski, J. Yan, C. A. Bridges, A. T. Savici, B. C. Chakoumakos, M. D. Lumsden, D. A. Tennant, R. Moessner, D. G. Mandrus, and S. E. Nagler, npj Quantum Mater. **3**, 8 (2018).

[10] J. Nasu, J. Yoshitake, and Y. Motome, Phys. Rev. Lett. **119**, 127204 (2017).

[11] R. Yadav, N. A. Bogdanov, V. M. Katukuri, S. Nishimoto, J. van den Brink, and L. Hozoi, Sci. Rep. **6**, 37925 (2016).

[12] S.-H. Baek, S.-H. Do, K.-Y. Choi, Y. S. Kwon, A. U. B. Wolter, S. Nishimoto, J. van den Brink, and B. Büchner, Phys. Rev. Lett. **119**, 037201 (2017).

[13] A. U. B. Wolter, L. T. Corredor, L. Janssen, K. Nenkov, S. Schönecker, S.-H. Do, K.-Y. Choi, R. Albrecht, J. Hunger, T. Doert, M. Vojta, and B. Büchner, Phys. Rev. B **96**, 041405(R) (2017).

[14] R. Hentrich, A. U. B. Wolter, X. Zotos, W. Brenig, D. Nowak, A. Isaeva, T. Doert, A. Banerjee, P. Lampen-Kelley, D. G. Mandrus, S. E. Nagler, J. Sears, Y.-J. Kim, B. Büchner, and C. Hess, Phys. Rev. Lett. **120**, 117204 (2018).

[15] J. Zheng, K. Ran, T. Li, J. Wang, P. Wang, B. Liu, Z.-X. Liu, B. Normand, J. Wen, and W. Yu, Phys. Rev. Lett. **119**, 227208 (2017).

[16] I. A. Leahy, C. A. Pocs, P. E. Siegfried, D. Graf, S.-H. Do, K.-Y. Choi, B. Normand, and M. Lee, Phys. Rev. Lett. **118**, 187203 (2017).

[17] A. Sahasrabudhe, D. A. S. Kaib, S. Reschke, R. German, T. C. Koethe, J. Buhot, D. Kamenskyi, C. Hickey, P. Becker, V. Tsurkan, A. Loidl, S. H. Do, K. Y. Choi, M. Grüninger, S. M. Winter, Z. Wang, R. Valentí, and P. H. M. van Loosdrecht, Phys. Rev. B **101**, 140410(R) (2020).

[18] Z. Wang, J. Guo, F. F. Tafti, A. Hegg, S. Sen, V. A. Sidorov, L. Wang, S. Cai, W. Yi, Y. Zhou, H. Wang, S. Zhang, K. Yang, A. Li, X. Li, Y. Li, J. Liu, Y. Shi, W. Ku, Q. Wu, R. J. Cava, and L. Sun, Phys. Rev. B **97**, 245149 (2018).

[19] N. Janša, A. Zorko, M. Gomilšek, M. Pregelj, K. W. Krämer, D. Biner, A. Biffin, C. Rüegg, and M. Klanjšek, Nat. Phys. **14**, 786 (2018).

[20] A. N. Ponomaryov, E. Schulze, J. Wosnitza, P. Lampen-Kelley, A. Banerjee, J.-Q. Yan, C. A. Bridges, D. G. Mandrus, S. E. Nagler, A. K. Kolezhuk, and S. A. Zvyagin, Phys. Rev. B **96**, 241107(R) (2017).

[21] Y. Kasahara, T. Ohnishi, Y. Mizukami, O. Tanaka, S. Ma, K. Sugii, N. Kurita, H. Tanaka, J. Nasu, Y. Motome, T. Shibauchi, and Y. Matsuda, Nature **559**, 227 (2018).

[22] Y. Kubota, H. Tanaka, T. Ono, Y. Narumi, and K. Kindo, Phys. Rev. B **91**, 094422 (2015).

[23] M. Majumder, M. Schmidt, H. Rosner, A. A. Tsirlin, H. Yasuoka, and M. Baenitz, Phys. Rev. B **91**, 180401(R) (2015).

[24] J. A. Sears, M. Songvilay, K. W. Plumb, J. P. Clancy, Y. Qiu, Y. Zhao, D. Parshall, and Y.-J. Kim, Phys. Rev. B **91**, 144420 (2015).

[25] H.-S. Kim, V. Shankar V., A. Catuneanu, and H.-Y. Kee, Phys. Rev. B **91**, 241110(R) (2015).

[26] I. Rousochatzakis, J. Reuther, R. Thomale, S. Rachel, and N. B. Perkins, Phys. Rev. X **5**, 041035 (2015).

[27] X. Zhou, H. Li, J. A. Waugh, S. Parham, H.-S. Kim, J. A. Sears, A. Gomes, H.-Y. Kee, Y.-J. Kim, and D. S. Dessau, Phys. Rev. B **94**, 161106(R) (2016).

[28] A. Koitzsch, C. Habenicht, E. Müller, M. Knupfer, B. Büchner, H. C. Kandpal, J. van den Brink, D. Nowak, A. Isaeva, and T. Doert, Phys. Rev. Lett. **117**, 126403 (2016).

[29] H.-S. Kim and H.-Y. Kee, Phys. Rev. B **93**, 155143 (2016).

[30] H. B. Cao, A. Banerjee, J.-Q. Yan, C. A. Bridges, M. D. Lumsden, D. G. Mandrus, D. A. Tennant, B. C. Chakoumakos, and S. E. Nagler, Phys. Rev. B **93**, 134423 (2016).

[31] S. M. Winter, Y. Li, H. O. Jeschke, and R. Valentí, Phys. Rev. B **93**, 214431 (2016).

[32] F. Lang, P. J. Baker, A. A. Haghighirad, Y. Li, D. Prabhakaran, R. Valentí, and S. J. Blundell, Phys. Rev. B **94**, 020407(R) (2016).

[33] L. Janssen, E. C. Andrade, and M. Vojta, Phys. Rev. Lett. **117**, 277202 (2016).

[34] Y. Sizyuk, P. Wölfle, and N. B. Perkins, Phys. Rev. B **94**, 085109 (2016).

[35] M. Ziatdinov, A. Banerjee, A. Maksov, T. Berlijn, W. Zhou, H. B. Cao, J.-Q. Yan, C. A. Bridges, D. G. Mandrus, S. E. Nagler, A. P. Baddorf, and S. V. Kalinin, Nat. Commun. **7**, 13774 (2016).

[36] S. Sinn, C. H. Kim, B. H. Kim, K. D. Lee, C. J. Won, J. S. Oh, M. Han, Y. J. Chang, N. Hur, H. Sato, B.-G. Park, C. Kim, H.-D. Kim, and T. W. Noh, Sci. Rep. **6**, 39544 (2016).

[37] L. J. Sandilands, Y. Tian, A. A. Reijnders, H.-S. Kim, K. W. Plumb, Y.-J. Kim, H.-Y. Kee, and K. S. Burch, Phys. Rev. B **93**, 075144 (2016).

[38] L. J. Sandilands, C. H. Sohn, H. J. Park, S. Y. Kim, K. W. Kim, J. A. Sears, Y.-J. Kim, and T. W. Noh, Phys. Rev. B **94**, 195156 (2016).

[39] K. Ran, J. Wang, W. Wang, Z.-Y. Dong, X. Ren, S. Bao, S. Li, Z. Ma, Y. Gan, Y. Zhang, J. T. Park, G. Deng, S. Danilkin, S.-L. Yu, J.-X. Li, and J. Wen, Phys. Rev. Lett. **118**, 107203 (2017).

[40] S. Agrestini, C.-Y. Kuo, K.-T. Ko, Z. Hu, D. Kasinathan, H. B. Vasili, J. Herrero-Martin, S. M. Valvidares, E. Pellegrin, L.-Y.

Jang, A. Henschel, M. Schmidt, A. Tanaka, and L. H. Tjeng, Phys. Rev. B **96**, 161107(R) (2017).

[41] Y. S. Hou, H. J. Xiang, and X. G. Gong, Phys. Rev. B **96**, 054410 (2017).

[42] S. M. Winter, A. A. Tsirlin, M. Daghofer, J. van den Brink, Y. Singh, P. Gegenwart, and R. Valentí, J. Phys.: Condens. Matter **29**, 493002 (2017).

[43] W. Wang, Z.-Y. Dong, S.-L. Yu, and J.-X. Li, Phys. Rev. B **96**, 115103 (2017).

[44] K. I. Kugel' and D. I. Khomskii, Sov. Phys. Usp. **25**, 231 (1984).

[45] G. Khaliullin, Prog. Theor. Phys. Suppl. **160**, 155 (2005).

[46] J. Chaloupka, G. Jackeli, and G. Khaliullin, Phys. Rev. Lett. **105**, 027204 (2010).

[47] N. N. Kovaleva, A. V. Boris, C. Bernhard, A. Kulakov, A. Pimenov, A. M. Balbashov, G. Khaliullin, and B. Keimer, Phys. Rev. Lett. **93**, 147204 (2004).

[48] J. S. Lee, M. W. Kim, and T. W. Noh, New J. Phys. **7**, 147 (2005).

[49] A. Gössling, R. Schmitz, H. Roth, M. W. Haverkort, T. Lorenz, J. A. Mydosh, E. Müller-Hartmann, and M. Grüninger, Phys. Rev. B **78**, 075122 (2008).

[50] J. Reul, A. A. Nugroho, T. T. M. Palstra, and M. Grüninger, Phys. Rev. B **86**, 125128 (2012).

[51] J. Fink, Adv. Electron. Electron Phys. **75**, 121 (1989).

[52] F. Roth, A. König, J. Fink, B. Büchner, and M. Knupfer, J. Electron Spectrosc. Relat. Phenom. **195**, 85 (2014).

[53] A. Koitzsch, C. Habenicht, E. Müller, M. Knupfer, B. Büchner, S. Kretschmer, M. Richter, J. van den Brink, F. Börrnert, D. Nowak, A. Isaeva, and T. Doert, Phys. Rev. Mater. **1**, 052001 (2017).

[54] C. M. Naon, M. J. Salvay, and M. L. Trobo, Phys. Rev. B **70**, 195109 (2004).

[55] A. Gössling, M. W. Haverkort, M. Benomar, H. Wu, D. Senff, T. Möller, M. Braden, J. A. Mydosh, and M. Grüninger, Phys. Rev. B **77**, 035109 (2008).

[56] J. Nasu, J. Knolle, D. L. Kovrizhin, Y. Motome, and R. Moessner, Nat. Phys. **12**, 912 (2016).