Static magnetic and ESR spectroscopic properties of the dimer-chain antiferromagnet BiCoPO$_5$

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We report a comprehensive study of the static susceptibility, high-field magnetization and high-frequency/high-magnetic field electron spin resonance (HF-ESR) spectroscopy of polycrystalline samples of the bismuth cobalt oxy-phosphate BiCoPO$_5$. This compound features a peculiar spin system that can be considered as antiferromagnetic (AFM) chains built of pairs of ferromagnetically coupled Co spins and interconnected in all three spatial directions. It was previously shown that BiCoPO$_5$ orders antiferromagnetically at $T_N \approx 10$ K and this order can be continuously suppressed by magnetic field towards the critical value $\mu_B H_c \approx 15$ T. In our experiments we find strongly enhanced magnetic moments and spectroscopic $g$ factors as compared to the expected spin-only values, suggesting a strong contribution of orbital magnetism for the Co$^{2+}$ ions. This is quantitatively confirmed by $ab$ initio quantum chemical calculations. Within the AFM ordered phase, we observe a distinct field-induced magnetic phase transition. Its critical field rises to $\sim 6$ T at $T \ll T_N$. The HF-ESR spectra recorded at $T \ll T_N$ are very rich comprising up to six resonance modes possibly of the multimagnonic nature that soften towards the critical region around 6 T. Interestingly, we find that the Co moments are not yet fully polarized at $H_c$ which supports a theoretical proposal identifying $H_c$ as the quantum critical point for the transition of the spin system in BiCoPO$_5$ to the quantum disordered state at stronger fields.

I. INTRODUCTION

In the field of condensed matter quantum magnetism there is a recent rapidly growing interest in Co-containing compounds, which promise a rich material base for the realization of unconventional magnetic ground states. The expected interesting physics is related to a sufficiently strong spin-orbit coupling of the Co$^{2+}$ (3$d^7$) ion that entangles the spin $S = 3/2$ and the effective orbital momentum $I = 1$. In crystalline lattices of certain symmetries this gives rise to strongly anisotropic and frustrated exchange paths with resulting exotic spin orders or Kitaev spin liquid behaviors [1, 2]. The most studied materials in this respect are Na$_3$Co$_2$SbO$_6$ [3–5] and Na$_2$Co$_2$TeO$_6$ [6–12], with honeycomb spin lattices, and Ba$_3$CoSb$_2$O$_9$ [13–15] and Na$_2$BaCo(PO$_4$)$_2$ [16–19] with triangular spin lattice.

The magnetism of the title compound, the dimer-chain antiferromagnet BiCoPO$_5$, has received so far lesser attention though, in general, materials containing spin dimer units interconnected in spin networks of different topology often demonstrate exotic quantum magnetic behaviors. To name a few examples, these are, e.g., a field-induced quantum phase transition into the transverse Néel ordered state in the double-chain compound TICl$_3$$_2$ [20], or the Haldane spin-gap state and the field-induced Bose-Einstein condensation of magnons in the one-dimensional (1D) two-leg ladder spin-1/2 compounds IPA-CuCl$_3$$_2$ [21, 22] and CuBr$_4$(C$_3$H$_2$N)$_2$ [23, 24] (for a comprehensive review see Ref. [25]).

The crystal crystal structure of BiCoPO$_5$ was extensively studied in Refs. [26–28] and is shown in Fig. 1(a). The compound crystallizes in a monoclinic structure, space group $P2_1/n$ (no. 14). The main building units are CoO$_6$ octahedra sharing one edge and forming structural dimers. The dimers are connected via PO$_4$ tetrahedra and form chains along the $c$ axis which are interconnected by PO$_4$ tetrahedra along the $a$ and $b$ axes. The Co spins in the structural dimer are exchange coupled into a ferromagnetic dimer and form antiferromagnetic chains along the $c$ axis that exhibit a noncollinear Néel order below $T_N \approx 10$ K due to weaker interchain couplings [28] [Fig. 1(b)].

The basic magnetic properties of BiCoPO$_5$ were originally reported in Refs. [26, 28] and re-investigated in Ref. [29]. In the latter work also the magnetic specific heat $C_{mag}(T)$ was measured in its dependence on the applied field. The $C_{mag}(T, H)$ data evidenced a continuous reduction of $T_N$ in an increasing magnetic field with the critical field for the suppression of the antiferromagnetic (AFM) order of $\mu_B H_c \approx 15$ T. Based on this finding Cai et al. [30] developed a theoretical model proposing BiCoPO$_5$ as a candidate material to show a quantum phase transition at $H_c$ from the AFM ordered to a quantum disordered, spin-liquid like phase.

Exploration of the interesting physics that can be hosted by BiCoPO$_5$ requires first of all thorough characterization of its magnetic properties in the $T-H$ parameter space. With this aim we carried out detailed measurements of the magnetic susceptibility in static fields.
Polycrystalline samples of BiCoPO$_5$ were prepared by a conventional solid state reaction technique described before in Ref. [29]. Powder x-ray diffraction measurements confirmed the phase purity of the synthesized samples which were found to crystallize in a monoclinic structure with space group $P2_1/n$ with the lattice parameters $a \approx 7.2441$ Å, $b \approx 11.2828$ Å, $c \approx 5.2258$ Å, and $\beta \approx 107.84^\circ$.

Static magnetic susceptibility $\chi(T, H)$ measurements were carried out with a Quantum Design MPMS-XL superconducting quantum interference device (SQUID) magnetometer in a temperature range 2 – 750 K and in magnetic fields up to 7 T. The magnetization $M(H)$ curves were recorded in the Dresden High Magnetic Field Laboratory with a pulsed magnet generating fields up to 60 T. Magnetization of the sample was obtained by integration of the voltage induced in a compensated pick-up coil system surrounding the sample and calibrated by measuring the $M(H)$ curve of the sample up to 7 T with the SQUID magnetometer (for further technical details see Ref. [31]).

HF-ESR experiments in a frequency range 75 – 500 GHz were performed with a home-made multifrequency spectrometer which employed a vector network analyzer (PNA-X from Keysight Technologies) for measurements at frequencies up to 330 GHz, and a modular Amplifier/Multiplier Chain (AMC from Virginia Diodes, Inc.) in a combination with a hot electron InSb bolometer (QMC Instruments) for measurements at higher frequencies. The sample was placed into a probe head operational in the transmission mode. The probe was mounted into a $^4$He variable temperature inset of a superconducting magnet system (Oxford Instruments) generating fields up to 16 T (see also Ref. [32]).

For insights into the Co 3d-level electronic structure, quantum chemical computational methods and an embedded-cluster material model were employed. The quantum mechanical cluster itself, a [CoO$_5$P$_4$O$_{12}$]$^{14-}$ fragment, is immersed within an array of point charges at lattice positions (see Fig. 2). With lattice parameters as derived from neutron powder diffraction by Mentre et al. [28], the point charge field was optimized using the Ewald program [33, 34]. For the initial charge optimization, formal oxidation numbers of +3, +2, +5 and –2 were assumed for Bi, Co, P, and O, respectively. A much more flexible description was adopted however for O species having to do with PO$_4$ tetrahedra — those were explicitly included in the quantum mechanical cluster. This ensures an accurate representation of the electronic charge distribution around the reference Co$^{2+}$ ion up to the third atomic coordination shell. Between the quantum cluster and the point charges, a boundary region consisting of capped effective core potentials (cECPs)
was devised, using the pseudopotentials of Küchle [35] for Bi$^{3+}$ and of Dolg [36] for Co$^{2+}$. By introducing this additional region, artificial polarization of outer cluster orbitals toward adjacent positive point charges is prevented. DKH-def2-TZVPP basis sets [37] were adopted for the central CoO$_6$ part of the quantum mechanical cluster, while smaller DKH-def2-SVP basis sets [37] for the neighboring PO$_4$ fragments were used. Excited state energies were estimated through ab initio complete active space self-consistent field (CASSCF) theory [38] by including the five 3$d$ atomic orbitals of Co$^{2+}$ into the active space and averaging over all possible multiplets (10 quartets and 40 doublets). Scalar relativistic properties were accounted for by enabling the second-order Douglas-Kroll-Hess (DKH) algorithm [39, 40]. Secondly, dynamical correlation was treated by N-electron valence second-order perturbation (NEVPT2) theory and multiplicity equation of motion (MR-EOM-T) theory. For NEVPT2, all internal orbitals were correlated, while for MR-EOM-T localized internal orbitals comprising 18 2$p$ atomic orbitals of the nearest-neighbor oxygens and 3$s$ plus 3$p$ atomic orbitals of the Co ion were considered. All calculations were performed with the program package Orca v5.0 [41].

III. EXPERIMENTAL RESULTS

A. Susceptibility and magnetization

The static susceptibility $\chi(T)$ of BiCoPO$_5$ as a function of temperature measured up to $T = 750$ K at $\mu_B H = 0.1$ T is shown in Fig. 3. The plot of $1/\chi(T)$ on the same Figure reveals a linear dependence down to $T \sim 100$ K. It can be well fitted to the Curie-Weiss (CW) law $\chi(T) =$ $\chi_0 + C/(T + T_{CW})$ yielding a small temperature independent contribution $\chi_0 \sim -2.14 \cdot 10^{-4}$ cm$^3$/molCo, the Curie constant $C \sim 3.79$ cm$^3$/K/molCo and the CW temperature $T_{CW} \sim 21$ K. At lower temperatures the data deviate from the CW law [Fig. 3(inset)] and the $\chi(T)$ dependence exhibits a peak at $T_m = 11.8$ K signaling a transition to the AFM ordered state. These results are in a reasonable agreement with the previous $\chi(T)$ measurements by Mathews et al. [29].

With increasing the field strength the peak of $\chi(T)$ broadens and shifts to lower temperatures and is not observed anymore above $\mu_B H = 6$ T [Fig. 4(a)]. The peak temperature $T_m$ can be accurately determined by plotting the derivative $d\chi(T)/dT$ where the maximum of $\chi(T)$ corresponds to $d\chi(T)/dT = 0$ and the inflection point $T_{inf}$ of $\chi(T)$ at $T < T_m$ corresponds to $d\chi(T)/dT = \text{max}$ [Fig. 4(b)]. The results are shown in the inset to Fig. 4(b) together with the field dependence of the critical Néel temperature of an AFM phase transition $T_N^{CP}(H)$ obtained from the specific heat measurements by Mathews et al. [29]. There, the position of the $dM/dH$ peak at different temperatures shown in Fig. 5 is presented as well. A comparison of these characteristic temperatures reveals that at small magnetic fields the inflection point of the $\chi(T)$ curve $T_{inf}$ corresponds well with the critical Néel temperature $T_N^{CP}(H)$ whereas the peak of the $\chi(T)$ dependence occurs at a slightly higher temperature $T_m$.

The field dependence of the magnetization $M(H)$ of BiCoPO$_5$ at $T = 2$ K is shown in the main panel of Fig. 5. After an initial shallow increase the $M(H)$ rises up above the inflection point $H_{inf} \sim 6.3$ T and gradually reaches the saturation value $M_{sat} \simeq 3.2 \mu_B$/Co by approaching a field of 60 T. The differential magnetization $dM(H)/dH$ at selected temperatures in the field range around the
to the depopulation of the excited multiplet states of the Co$^{2+}$ ion [19]. Exemplary spectra recorded at the excitation frequency $\nu = 329$ GHz are shown in Fig. 6(a) and the temperature dependence of their width $\Delta H(T)$ is plotted in Fig. 6(b). To obtain the spectroscopic $g$ factor in the paramagnetic state HF-ESR spectra at $T = 28 \, \text{K} > T_N$ and at various frequencies were collected. The relation between the position of the absorption peak and $\nu$ is plotted in Fig. 7. The data can be fitted to the paramagnetic resonance condition $\nu = h^{-1} g_{\text{pow}} \mu_B \mu_B H$ yielding the powder-averaged $g$ factor $g_{\text{pow}} \simeq 3.59$. Further, the HF-ESR signals were modeled with the powder-averaged Lorentzian line profiles with an anisotropic $g$ tensor. Assuming for simplicity the uniaxial $g$ factor anisotropy the modeling curves matched well with the experimental lineshapes at different frequencies with the $g$ tensor $g_\parallel = 4.94$ and $g_\perp = 2.91$ [Fig. 7(inset)]. Its average, $\sqrt{(g_\parallel^2 + 2g_\perp^2)}/3 = 3.71$ is consistent with the $g_{\text{pow}}$ value obtained from the fit in Fig. 7.

By lowering the temperature below $T_N$ the HF-ESR signal gradually transforms into a complex spectrum of multiple excitations. Its evolution at $T = 3 \, \text{K}$ with changing the frequency is shown in Fig. 8(a). The spectrum converges to an almost single resonance line at the minimum frequency $\nu = 75$ GHz. The resonance fields of the observed excitations are summarized in the $\nu$ versus $H$ diagram in Fig. 8(b). They can be classified into six resonance branches as indicated there. It appears that the critical field region around 6 T identified in the analysis of the magnetization data [Fig. 4(inset)] also plays

B. ESR spectroscopy

A very broad HF-ESR spectrum of BiCoPO$_5$ can be first observed at $T \sim 100 \, \text{K}$. It narrows significantly by lowering the temperature $T \sim 60 \, \text{K} \gg T_N$ possibly due

FIG. 4. (a) Temperature dependence of the static susceptibility $\chi(T)$ at different applied fields (symbols connected with lines). (b) Derivatives of the respective $\chi(T)$ curves. The inset shows the field dependence of the temperature $T_m$ of the maximum $\chi(T)$ corresponding to $d\chi/dT = 0$ (closed circles) and of the temperature $T_{\text{inf}}$ of the inflection point of $\chi(T)$ corresponding to $d\chi/dT = \text{max}$ (open circles). Star symbols correspond to the position of the $dM/dH$ peak in Fig. 5. Open squares are the ordering temperature $T^0_{\text{up}}$ determined from the specific heat data in Ref. [29]. The solid line depicts the fit to the phenomenological relation $T_N(H) = T_N(H = 0)[1 - (H/H_c)^3]$ with $T_N(H = 0) = 9.8 \, \text{K}$ and $H_c = 15.3 \, \text{T}$ [29].

inflection point of the $M(H)$ curve is shown in the inset. The position of the peak of $dM(H)/dH$ corresponds to $H_{\text{inf}}$ at a given temperature. With decreasing the temperature the peak develops hysteresis. The average peak position between the up- and down-field sweeps is plotted in the inset to Fig. 4.
a special role for the HF-ESR excitations in the AFM ordered state of BiCoPO$_3$.

**IV. DISCUSSION**

**A. Paramagnetic state**

1. Experimental phenomenology

In the phenomenological description of the static susceptibility $\chi(T)$ of BiCoPO$_3$ with the Curie-Weiss law the Curie constant $C$ is defined as $C = N_{Co}N_A K_B M_{eff}^2 / 3k_B$. Here, $N_{Co}$, $N_A$ and $K_B$ are the number of Co ions in the formula unit, the Avogadro number and the Boltzmann constant, respectively. $M_{eff}$ is the effective magnetic moment $M_{eff} = g(j(j+1))^{1/2} \mu_B$ in the units of Bohr magneton and $g$ and $j$ are the $g$ factor and the effective spin.

With $C = 3.79$ cm$^3$/mol Co from the CW fit (Fig. 3) one obtains $M_{eff} = 5.51 \mu_B$/Co. One the other hand, $M_{eff}$ is related to the saturation magnetization $M_{sat} = g jj \mu_B$ as $M_{eff}^2 = M_{sat}^2 + g M_{sat}$. According to this relation with $M_{sat} = 3.2 \mu_B$/Co obtained from the $M(H)$ dependence (Fig. 5) the $g$ factor should amount to $g = 6.29$ in a strong disagreement with the experimental value $g_{pow} = 3.59$ (Fig. 7) and with the predictions of the canonical ligand theory [42]. In its framework the $g$ factor in the ground state of an isolated Co$^{2+}$ ion in a regular octahedral coordination should be isotropic and amount to $g_{cub} = 10/3 + k$ where $k$ is the orbital reduction factor $k < 1$ due to the covalency effect. For the ionic bond $k$ equals to 1. The $g$ factor much larger than the spin-only value $g = 2$ results from the combined action of a strong ligand cubic field and the spin-orbit coupling. Distortion of the ligand octahedron causes anisotropy of the $g$ factor while the mean $g$ factor remains close to $g_{cub}$ [43, 44]. In the case of BiCoPO$_3$ the $g_{pow}$ is smaller than the pure ionic value of 4.33 which may indicate a substantial covalency of the Co–O bonds. Similar reduced mean $g$ factors were found, e.g., for some covalently bonded Co(II) inorganic complexes [44, 45].

A consistency between the static magnetic data and the $g$ factor obtained in the HF-ESR measurements can be restored assuming that the ferromagnetic coupling between the spins in the Co$_2$O$_{10}$ structural dimers in the AFM ordered spin structure of BiCoPO$_3$ (see Sect. IV B) is so strong that the ferromagnetic (FM) dimers are present also in the paramagnetic state. In this scenario, deviation of the experimental $1/\chi(T)$ dependence from the CW law at $T > 500$ K (Fig. 3) might indicate the breakdown of the FM dimers. Recalculating the Curie constant per mole of the Co–Co FM dimers $C_{Co_2} = 2C = 7.58$ cm$^3$/mol Co$_2$ yields the effective moment of the dimer $M_{Co_2}^eff = 7.79 \mu_B$/Co$_2$. Considering the above relation between $M_{eff}$ and the saturation magnetization $M_{sat}$, with $g_{pow} = 3.59$ one obtains $M_{Co_2}^sat = 6.2 \mu_B$/Co$_2$ which corresponds to $3.1 \mu_B$ per one Co site, in a close agreement with the experiment.

![FIG. 6. Temperature dependence of the ESR spectrum at $\nu = 329$ GHz (a) and of the width $\Delta H(T)$ at half-height of the ESR line in the paramagnetic state (b).](image_url)

![FIG. 7. Position of the ESR peak at different frequencies at $T = 28$ K. The solid line depicts the linear dependence $\nu = h^{-1}g_{pow}\mu_B H$ with the powder-averaged $g$ factor $g_{pow} = 3.59$. Insets show exemplary ESR signals (black) together with the powder-averaged model curves (blue). (see the text for details)](image_url)
FIG. 8. HF-ESR spectra at $T = 3$ K and at different frequencies (a). Summary of the peak positions of the spectral lines which are grouped in branches labeled from 1 to 6 (b). Lines connecting the data points in (b) are the guides for the eye.

2. Ab initio multiplet structure

The multiplet structure of the $[\text{CoO}_6\text{P}_4\text{O}_{12}]^{14-}$ cluster for the minimal CAS(7e,5o) space (i.e., all possible configurations related to distributing seven electrons within the five Co $3d$ orbitals) is illustrated in Table I. Due to the strong distortion of the CoO$_6$ octahedron, the ground state $^4T_{1g}$ term [46] is split into three non-degenerate states. The magnitude of these splittings is significant, up to 90 meV. Even richer structure is obtained after including spin-orbit couplings (SOCs) in the computations. The emerging picture is that of six Kramers doublets (KDs) grouped into two sets of states — two KDs defining a low-energy scale of 25 meV for the on-site excitations and another four KDs implying excitation energies of 90–170 meV. Similar $t^2_2g^2$ multiplet structures were found in Co$^{2+}$ complexes of interest in the field of single molecule magnets [47–50].

Correcting the CASSCF approach by NEVPT2 and MR-EOM-T$^{1}$-h-v schemes yields only minor corrections within the group of states related to the $t^2_2g^2$ electron configuration. The corrections are however important for higher-lying multiplets. In particular, the $t^2_2g^2$ states are stabilized with respect to the $t^4_2g^4$ states (correlation effects involving O-to-Co charge transfer are more important for the former since there is less charge in the $\sigma$-type Co $e_g$ orbitals). There are additionally “differential” effects within the group of $t^2_2g^2$ states, e.g., modification of the sequence of the $^4A_{2g}$ and $^2E_g$ terms.

For direct connection with experiment, using the tools available with the Orca package [41] and on the basis of the multiplet spectrum summarized in Table I, we computed magnetization and magnetic susceptibility curves (see Fig. 9). Focusing first on the magnetization curve, no considerable difference is observed between the different applied computational methods. Compared to the experimental $M(H)$ dependence shown in Fig. 5, the magnetization curve calculated for $T = 2$ K initially goes steeper for low applied fields, since inter-octahedral magnetic interactions yielding long-range AFM order (Sect. IV B) are not captured with a single-octahedron cluster model. However, the experimentally determined saturation value $M_{sat}^{exp} = 3.2 \mu_B/Co$ corresponding to practically full alignment of the Co moments by approaching a field of 60 T is reasonably well reproduced in theory ($M_{sat}^{theor} = 3.09 \mu_B$ for NEVPT2). The calculated inverse magnetic susceptibility $1/\chi$ is shown in the inset of Fig. 9. The experimental and computational data coincide over a wide temperature range from about 100 to 400 K.

FIG. 9. Field dependence of the magnetization $M$ calculated at $T = 2$ K for the $[\text{CoO}_6\text{P}_4\text{O}_{12}]^{14-}$ cluster. Inset: Computed temperature dependence of the inverse magnetic susceptibility $1/\chi(T)$ in an applied field of 0.1 T (CASSCF(7e,5o): red, NEVPT2: blue, MR-EOM-T$^{1}$-h-v: green, experimental CW fit: black).

Subsequently, the average $g_{avg}$ factor was determined by mapping the SO eigenvalues onto a $\hat{S}=1/2$ effective Hamiltonian [51]. A value of $g_{avg}=4.30$ was found by
TABLE I. Co$^{2+}$ $3d^7$ multiplet structure as computed for a [CoO$_6$P$_4$O$_{12}$]$^{14-}$ cluster (CAS(7e,5o)/DKH-def2-TZVPP). Notations corresponding to octahedral $O_h$ point-group symmetry are used, although the actual symmetry is much lower.

| $d^7$ term | CASSCF [meV] | CASSCF+SOC [meV] | NEVPT2+SOC [meV] | MR-EOMT$|T^{1-h-v}+$SOC [meV] |
|------------|--------------|------------------|------------------|-----------------------------|
| $^4T_{1g}$ | 0            | 0, 25            | 0, 24            | 0, 25                      |
|            | 63           | 86, 128          | 93, 132          | 95, 135                    |
| $^4T_{2g}$ | 91           | 147, 160         | 158, 170         | 160, 173                   |
|            | 606          | 652, 662         | 811, 820         | 758, 768                   |
|            | 657          | 701, 708         | 893, 899         | 825, 833                   |
|            | 739          | 784, 799         | 989, 1002        | 911, 925                   |
| $^4A_{2g}$ | 1389         | 144, 145         | 1819, 1820       | 1675, 1676                 |
| $^2E$      | 1909         | 1952             | 1421             | 1716                       |
|            | 2149         | 2190             | 1757             | 2035                       |
| $^2T_{1g}$ | 2414         | 2451             | 2168             | 2083                       |

NEVPT2 ($g_{av}=4.37$ by CASSCF(7e,5o)). The NEVPT2 and CASSCF values are quite similar, in agreement with the magnetization and magnetic susceptibility curves shown in Fig. 9. However, the $g_{av}$ factor deviates somewhat from the value determined by HF-ESR. Test CASSCF computations on a larger, two-octahedra cluster [Co$_2$O$_{10}$P$_8$O$_{24}$]$^{24-}$ confirm the localized nature of the Co valence orbitals found in the single-octahedron calculations and the presence of ferromagnetic exchange between the two edge-sharing octahedra. More involved post-CASSCF computations for quantitative analysis of the inter-site magnetic couplings are left for future work.

B. Magnetically ordered state

The magnetic structure of BiCoPO$_5$ was solved by powder neutron diffraction experiments by Mentre et al. [28]. In this work also the topological analysis of the relative strength and sign of different Co-Co exchange paths was performed. The strongest FM coupling was found in the Co$_2$O$_{10}$ structural dimer which thus can be considered as a magnetic unit with the magnetic moment with the size twice of that of the Co$^{2+}$ ion. The dimer moments build up AFM chains along the $c$ axis which are interconnected by weaker interchain exchange interactions [Fig. 1(b)].

The dimer moments in the neighboring $ac$ planes of the chain are tilted by an angle of 47.6$^\circ$ (132.4$^\circ$) with respect to each other. These moments can be grouped in four sublattices [black, red, green and blue in Fig. 1(b)] which together form a four-sublattice noncollinear and nonorthogonal AFM ordered structure referred to as a compensated AFM ordered phase (c-AFM) with zero net magnetization in the limit $(H, T) \rightarrow 0$ (Fig. 10). The ordered moment of the Co$^{2+}$ ion was found to be 3.5$\mu_B$ in a reasonable agreement with the saturation magnetization in 58 T where the almost full polarization of the Co moments in BiCoPO$_5$ can be achieved (Fig. 5).

Application of the external magnetic field tilts the sublattices which causes a shift of the peak in $\chi(T)$ at $T_m$ and of the inflection point $T_{inf}$ below the peak to lower temperatures and broadens the peak (Fig. 4). The sharp peak of the differential magnetization at $T_{dM/dH}$ [Fig. 5(inset)] shows a similar $T$ versus $H$ behavior as $T_{in}(H)$ and $T_{inf}(H)$ which altogether may indicate a field induced magnetic phase transition in the spin system of BiCoPO$_5$. This is a transition from the c-AFM state...
to a stronger magnetized uncompensated AFM state (u-AFM) within the AFM ordered phase below the $T_N(H)$ phase line determined in the specific heat measurements in Ref. [29] (Fig. 10). Usually a strong field induced increase of the magnetization $M(H)$ is ascribed to the spin-flop transition if $H$ is applied parallel to the magnetic easy axis (direction of spins) of a collinear antiferromagnet. The hysteresis character of this transition [Fig. 5(inset)] suggests that it is of first order, which is typical for a spin-flop transition [52]. However, in the noncollinear magnetic structure of BiCoPO$_5$ there are at least two easy axes and the sublattices cannot be flopped at a unique critical field value even in a single crystal. Powder averaging should further broaden the transition region as indeed observed for the dimer-chain antiferromagnet BiMnVO$_5$ possessing the crystal structure similar to BiCoPO$_5$ [53]. The sharpness of the $dM/dH$ peak at $T = 2.7\,K$ is thus somewhat surprising and may indicate a more complex nature of the field induced magnetic transition in BiCoPO$_5$.

We notice here an interesting similarity of the $H - T$ phase diagram of BiCoPO$_5$ sketched in Fig. 10 with that of the Kitaev-like honeycomb magnet Na$_2$Co$_2$TeO$_6$ [6]. There, a sharp first-order field-induced spin reorientation transition to a stronger magnetized state was observed at $\mu_0H \sim 6\,T$ which evolves into a tentative quantum paramagnetic state at still higher fields, qualitatively similar to the scenario proposed for BiCoPO$_5$ in Ref. [30] (see Fig. 10).

The complexity of the ground state of BiCoPO$_5$ manifests also in the HF-ESR excitation spectrum at $T = 3\,K < T_N$ comprising multiple lines that disperse differently in the magnetic field (Fig. 8). Line 3 in the HF-ESR spectrum in Fig. 8(a) and the position of the corresponding branch 3 in Fig. 8(b) do not depend on frequency. The occurrence of line 3 is most likely due to a nonresonant change of the microwave absorption by the sample due to the change of its magnetization. Indeed, its position coincides with the peak of the differential magnetization [Fig. 5(inset)] and thus branch 3 delimits the excitations in the two magnetic phases of BiCoPO$_5$ at this low temperature. Branches $1-2$ on the low field side and branches $4-6$ on the high-field side of the $\nu(H)$ diagram soften towards the critical field region around $\sim 6\,T$. It should be noted that in the more conventional three-dimensional (3D) antiferromagnet BaCo$_2$(SeO$_3$)$_3$-3H$_2$O containing structural Co-dimer chains only two ESR modes softening towards the critical field of the spin-flop transition were observed, that correspond to the expected single-magnon excitations of a two-sublattice collinear antiferromagnet [54].

It would be tempting to attribute the steep resonance branches in Fig. 8 to complex multiparticle excitations in BiCoPO$_5$. For example, branch 1 could be well approximated by the softening two-magnon excitation $\nu_1 = \Delta_1(H = 0) - h^{-1}\text{ln} \mu_0 H \Delta S_z$ with the double spin flip $\Delta S_z = 2$ and the zero-field excitation gap $\Delta_1(H = 0) = 565\,\text{GHz}$. The multiple modes in BiCoPO$_5$ bear some similarities with the ESR excitation spectrum of α-RuCl$_3$, a prominent Heisenberg-Kitaev spin liquid candidate, where the resonance lines strongly dispersing in the magnetic field and softening towards the critical field for the transition from an AFM ordered phase to a partially polarized disordered phase were attributed to multimagnonic excitations [55–59]. Such excitations were reproduced in numerical calculations based on the Heisenberg-Kitaev Hamiltonian with sizable off-diagonal anisotropic exchange $\Gamma$-terms [60]. It has been recently discussed that the signatures of the Kitaev physics could be found not only in anisotropic quasi-two-dimensional honeycomb and triangular spin lattices but also, e.g., in the 1D spin chains [61–63], or in the 3D cobalt spinels and pyrochlores [64]. Given a significant spin-orbit entanglement found for Co$^{2+}$ ions in BiCoPO$_5$ such H–K–$\Gamma$ Hamiltonian might possibly be relevant for this material as well. However, the exact assignment of the ESR branches would require complex calculations of the magnon modes in a four-sublattice noncollinear antiferromagnet which is beyond the scope of the present work.

Finally, it is not possible to draw a definite conclusion on the existence of the theoretically predicted new resonance mode emerging out of the tentative quantum critical point $\mu_0H_c \sim 15\,T$ where the bulk AFM order in BiCoPO$_5$ is suppressed [30]. Considering that the low temperature magnetization is still far from being saturated at $H_c$ (Fig. 5), one can conjecture that this field might indeed be a special critical point for the transition of the spin system in BiCoPO$_5$ to a partially polarized, disordered state (Fig. 10). According to Cai al. [30] the predicted excitation mode should have zero energy (zero frequency) at $H_c$ and acquire a linear in field energy gap at $H > H_c$. Unfortunately with the current experimental HF-ESR setup limited to fields $\mu_0H \leq 16\,T$ and frequencies $\nu \geq 75\,\text{GHz}$ this mode might lie outside the available $\nu - H$ observation window and remain undetected.

V. CONCLUSIONS

In summary, we discussed the results of detailed measurements of the static susceptibility, magnetization and high-frequency ESR in the paramagnetic and AFM ordered state of the dimer-chain antiferromagnet BiCoPO$_5$. The Co$^{2+}$ 3$d^7$ multiplet structure was calculated with many-body, ab initio quantum chemical methods. The experimentally observed large magnetic moment and a large and anisotropic spectroscopic $g$ factor of the Co$^{2+}$ ion are consistently reproduced in the calculations and explained as being a consequence of the combined action of sizable spin-orbit coupling and strong low-symmetry ligand fields. In the phenomenological analysis of the static magnetic data indications of the existence of ferromagnetic Co-dimers in the paramagnetic state up to high temperatures were found. However, the quantum chemical computations do not provide evidence for the formation of quasi-molecular orbitals, as found in vari-
ous 4d and 5d compounds [65–67]. This should be related with the more compact nature of 3d orbitals and with the presence of stronger correlations in 3d systems [66].

Low temperature magnetization and HF-ESR data give evidence for a rather sharp field-induced magnetic phase transition within the AFM ordered phase of BiCoPO$_5$ taking place at a field of $\sim 6$ T at the lowest temperature. HF-ESR spectra at $T = 3 K < T_N$ feature multiple resonance modes tentatively ascribed to multi-magnonic excitations that soften towards this critical 6 T field region. The magnetization is not yet saturated at a critical field for the suppression of the AFM order $\mu_0 H_c = 15$ T [29] favoring a theoretical proposal in Ref. [30] on the occurrence of a quantum disordered state in BiCoPO$_5$ above $\mu_0 H_c$ (Fig. 10). However, the new resonance mode emergent in this theory at $\mu_0 H_c$ was not detected, possibly due to the technical limitations of the used HF-ESR setup.

The properties of the field-induced u-AFM phase at $6 - 7 < \mu_0 H < 15$ T (Fig. 10) are not captured in the theory in Ref. [30] and require further clarification. At present it is not clear whether this phase is long-range or only short-range ordered, possibly due to the enhanced quantum fluctuations in proximity to the conjectured quantum critical point at $\mu_0 H_c \sim 15$ T, and whether the c-AFM\!→\!u-AFM transition is of a classical or quantum nature. Altogether our results call for further exploration of the interesting magnetic phase diagram of BiCoPO$_5$ with local spin probes and development of theoretical models of exchange interactions and magnetic excitations which could pinpoint the envisaged field-induced quantum criticality in BiCoPO$_5$.

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