

Crystal fields and the properties of the Kitaev candidate $\text{Na}_3\text{Co}_2\text{SbO}_6$ probed with x-ray absorption spectroscopy

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We directly probe the local electronic structure and magnetic properties of $\text{Na}_3\text{Co}_2\text{SbO}_6$ using x-ray absorption linear dichroism (XLD) and x-ray magnetic circular dichroism, complemented by full-multiplet cluster calculations. The Co $L_{2,3}$ -edge XLD spectra reveal significantly distorted CoO_6 octahedra, which are quantitatively described by a low-symmetry cluster model incorporating Co-O covalency and orbital mixing. We identify a dominant trigonal crystal-field splitting of approximately -42.5 meV, which drives the system away from the ideal $J_{\text{eff}} = 1/2$ limit. We also demonstrate that a purely trigonal description is insufficient: small additional splittings of the e_g^π and e_g^σ orbitals are essential to consistently reproduce the full set of experimental data, including the observed macroscopic in-plane magnetization anisotropy. Our results further establish $\text{Na}_3\text{Co}_2\text{SbO}_6$ as a honeycomb cobaltate relevant to Kitaev quantum spin liquid physics, featuring a doubly degenerate ground state.

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I. INTRODUCTION

The search for materials capable of realizing a Kitaev quantum spin liquid (QSL) has recently expanded to $3d$ -electron systems [1]. In contrast to the more widely studied $4d$ - and $5d$ -electron compounds, $3d$ materials possess comparatively weaker spin-orbit coupling (SOC). Nevertheless, anisotropic hopping processes can generate sizable bond-dependent interactions, making these systems promising platforms for Kitaev physics.

Among these candidates, $\text{Na}_3\text{Co}_2\text{SbO}_6$ has emerged as a promising platform for Kitaev physics [2]. It crystallizes in a monoclinic $C2/m$ structure [3–8], consisting of layers of edge-sharing CoO_6 octahedra arranged on a honeycomb lattice, with Sb ions occupying the centers of the hexagons and Na layers separating the Co-Sb-O planes (Fig. 1). A recent theoretical study inferred that coexisting e_g and t_{2g} exchange channels suppress Heisenberg interactions and enhance the Kitaev term [2]. It was therefore suggested that tuning the trigonal distortion of the CoO_6 octahedra by ~ 20 meV could provide a possible route to a QSL state. Experimentally, $\text{Na}_3\text{Co}_2\text{SbO}_6$ develops zigzag magnetic order below

$T_N \sim 5\text{--}8$ K [3,4,6], while inelastic neutron scattering has revealed signatures consistent with proximity to a Kitaev QSL regime [7,9–11].

Despite extensive interest, the microscopic magnetic Hamiltonian of $\text{Na}_3\text{Co}_2\text{SbO}_6$ remains under debate, with no consensus regarding either the magnitude or the sign of the Kitaev interaction [7–9,11–18]. A key issue is the role of the local crystal-field environment at the Co^{2+} site. Early theoretical descriptions mainly considered anisotropic exchange interactions under the assumption of an ideal trigonal distortion, whereas more recent studies have highlighted the importance of in-plane anisotropy. Consequently, the corresponding details in the local structural distortions do matter, also for attempts to tune the system toward a Kitaev QSL state [19–23].

A direct experimental determination of the local electronic structure of Co^{2+} is therefore important. X-ray linear dichroism (XLD) and x-ray magnetic circular dichroism (XMCD) at the Co $L_{2,3}$ edges, combined with full-multiplet configuration-interaction cluster calculations, provide powerful and highly sensitive probes of the ground-state quantum numbers and low-energy excitations [24–30]. Previous x-ray absorption spectroscopy (XAS) studies on $\text{Na}_3\text{Co}_2\text{SbO}_6$ have provided valuable insights, but have also yielded conflicting conclusions, for example, about the sign of the trigonal crystal-field distortion [31,32]. Moreover, Ref. [31] concluded that the in-plane component of the Co $3d$ charge distribution is isotropic, based on the absence of in-plane linear dichroism. Such a result is difficult to reconcile with macroscopic magnetization

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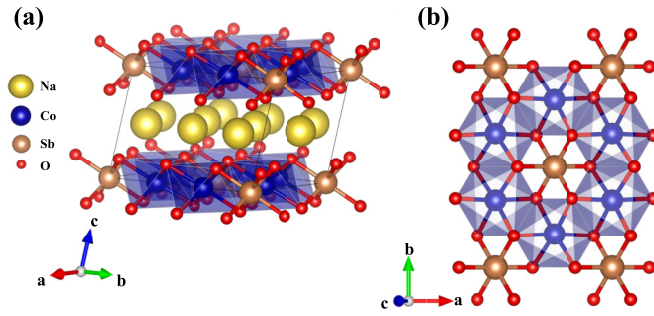


FIG. 1. (a) Unit cell of $\text{Na}_3\text{Co}_2\text{SbO}_6$, displaying the layered structure. (b) Honeycomb arrangement of edge-sharing CoO_6 octahedra within a single layer. Structure obtained from our single-crystal XRD refinement (see Appendix).

measurements showing strong in-plane anisotropy [8,20], as well as with structural reports consistently describing a monoclinic $C2/m$ environment, in which the Co site symmetry is substantially lower than D_{3d} [3–8]. In addition, earlier XAS experiments employed conventional detection modes, such as total electron yield and total fluorescence yield, which can suffer from surface sensitivity, charging effects and self-absorption, thereby affecting the line shape and, consequently, their quantitative reliability. Temperature-dependent XAS, which can further test the energy-level scheme through thermal population of low-lying excited states, has also remained unexplored.

These considerations motivate the use of bulk-sensitive XAS methods capable of measuring insulating samples without ad hoc corrections. In the present work, we employ inverse partial fluorescence yield (iPFY) XAS [33,34], a technique well suited for measurement of insulating cobalt-oxide-based materials [35,36]. This method allows us to carry out accurate polarization-dependent and temperature-dependent measurements on $\text{Na}_3\text{Co}_2\text{SbO}_6$ and to compare the spectra in great detail with the results of full-multiplet cluster calculations. We succeeded to simultaneously reproduce the XAS spectra, the XMCD response, and the observed macroscopic in-plane magnetization anisotropy, thereby establishing a robust microscopic description of the electronic and magnetic ground state and low-lying states of $\text{Na}_3\text{Co}_2\text{SbO}_6$.

II. METHODS

$\text{Na}_3\text{Co}_2\text{SbO}_6$ single crystals were grown from as-sintered $\text{Na}_3\text{Co}_2\text{SbO}_6$ powder using a $\text{Na}_2\text{O-Sb}_2\text{O}_3$ flux and a high-temperature slow-cooling procedure, following Ref. [8].

The temperature- and polarization-dependent XAS measurements were performed at beamline TPS-45A1 of the National Synchrotron Radiation Research Center in Taiwan [37], while the XMCD measurements were carried out at the BL29 Boreas beamline of the ALBA synchrotron radiation facility [38].

For the out-of-plane linear dichroism XAS measurements, a dark-purple single crystal of $\text{Na}_3\text{Co}_2\text{SbO}_6$ was mounted on an aluminum sample holder such that the Poynting vector and the linear vertical polarization of the incident x-ray beam lay in the ab plane, as shown in Figs. 2(a) and 2(b). For each XAS

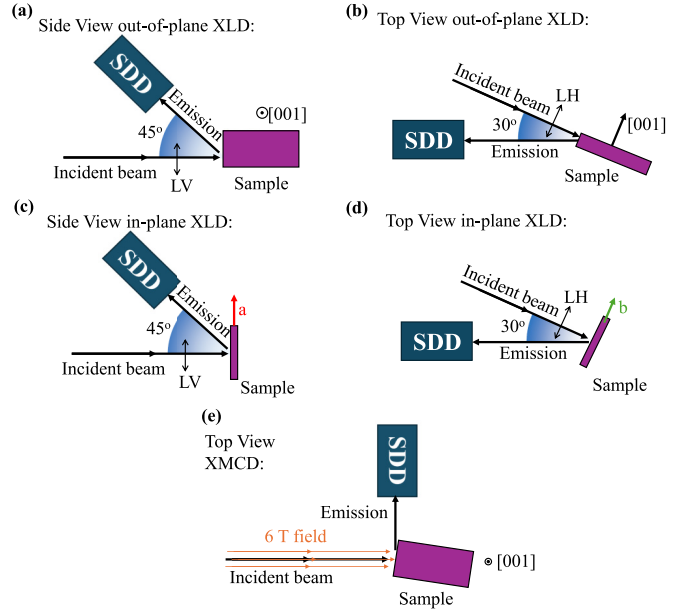


FIG. 2. Schematic of the experimental geometry for the XLD and XMCD measurements, illustrating the orientation of the incident x-ray beam, linear polarization directions, the silicon drift detector (SDD), and the externally applied magnetic field relative to the sample. Panels (a) and (b) show the out-of-plane XLD geometry, while panels (c) and (d) show the in-plane XLD geometry. Panel (e) shows the XMCD geometry.

scan, the beam polarization was set to either linear horizontal (LH) or linear vertical (LV) to probe the dichroism between the in-plane and out-of-plane directions. Measurements were performed at 300, 200, 100, and 20 K.

For the in-plane linear dichroism XAS measurements, another crystal was mounted such that LH was parallel to b and LV was parallel to a , thereby probing the dichroism within the ab plane, as shown in Figs. 2(c) and 2(d).

For the XMCD measurements, a crystal was mounted such that the Poynting vector of the incident beam lay within the ab plane as shown in Fig. 2(e). The beam helicity was alternated between left- and right-circular polarization for each energy scan. A magnetic field of 6 T was applied along the direction of the incident x-ray beam. XMCD spectra were collected at 20 K.

All samples were cleaved *in situ* in ultrahigh vacuum to obtain clean surfaces before the actual XAS and XMCD measurements were carried out.

For spectral acquisition, we employed the iPFY method developed by Hawthorn and co-workers [33,34].

Calculations of the XAS and XMCD spectra, as well as the magnetization, were performed using the QUANTY code [39–42]. Crystal-field parameters were treated as fitting parameters and adjusted to best reproduce the experimental data across all measurements. Parameters for the multipole part of the Coulomb interaction and SOC were taken from Hartree-Fock values [43]. The monopole part of the Coulomb interaction and the O $2p$ to Co $3d$ charge-transfer energies were estimated from photoemission experiments on Co^{2+} compounds [44]. The SOC value of 66 meV used here for the Co $3d^7$ configuration has been shown to reproduce well

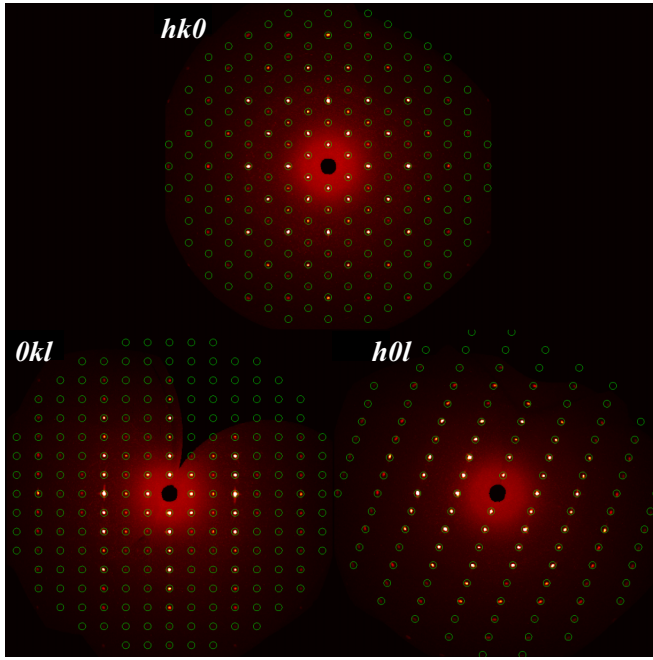


FIG. 3. Precession maps of x-ray intensities in the $hk0$, $0kl$, and $h0l$ planes of reciprocal space. Green circles indicate the expected peak positions.

the XAS spectra and ground-state properties of other Co^{2+} oxides [26,28,35,36,45].

Hybridization parameters and the crystal field acting on the oxygen ligands were derived from a tight-binding model based on the *ab initio* Wannierized Local-Density Approximation (LDA) band structure, using the structure obtained from our single-crystal x-ray diffraction (XRD) refinement. Density functional theory (DFT) calculations and Wannierization were performed using FPLO [46,47] and the FPLORE package [48]. To achieve better agreement with experiment, the hybridization parameters were further tuned by scaling them to 90% of their DFT values.

Field-dependent magnetization measurements were performed using a commercial magnetometer (MPMS3, Quantum Design), with the magnetic field applied along the crystallographic a and b axes.

Single-crystal x-ray diffraction measurements were performed using $\text{Mo } K\alpha$ radiation on a Bruker D8 VENTURE diffractometer equipped with a bent graphite monochromator, providing an approximately threefold intensity enhancement, and a Photon III complementary metal-oxide semiconductor large-area detector. These measurements were used to determine the crystal structure of a $\text{Na}_3\text{Co}_2\text{SbO}_6$ sample approximately $(20 \mu\text{m})^3$ in size.

The x-ray diffraction intensities in different planes of reciprocal space are shown in Fig. 3. These maps indicate the high crystal quality of the small sample prepared from a larger piece. The crystal structure of $\text{Na}_3\text{Co}_2\text{SbO}_6$ can be described by the space group $C2/m$, with three twin domains rotated by 120° with respect to one another around the c^* axis. The dominant twin domain accounts for approximately 82% of the crystal. The refinement results are listed in the Appendix, Tables I and II, and the resulting crystal structure is shown

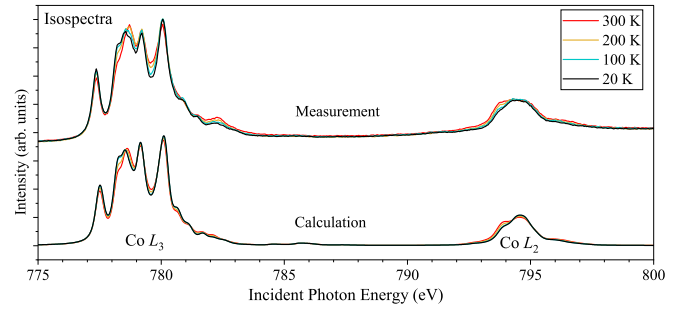


FIG. 4. Temperature-dependent isotropic $\text{Co } L_{2,3}$ -edge spectra of $\text{Na}_3\text{Co}_2\text{SbO}_6$. Experimental data are compared with simulated spectra obtained from the cluster model [49].

in Fig. 1. The refinement indicates about 6(1)% Co occupancy on the Sb site and about 1.3(6)% Sb occupancy on the Co site.

III. X-RAY ABSORPTION SPECTROSCOPY

Figure 4 shows the isotropic $\text{Co } L_{2,3}$ -edge spectra of $\text{Na}_3\text{Co}_2\text{SbO}_6$ as a function of temperature, constructed as $I_{\text{iso}} = 2I_{\parallel} + I_{\perp}$, where $I_{\parallel}$ and $I_{\perp}$ correspond to spectra measured with polarization parallel and perpendicular to the ab plane, respectively. The calculated temperature-dependent isotropic spectra were analogously constructed from the calculated out-of-plane and in-plane spectra.

The temperature dependence of the isotropic spectra arises from the thermal population of low-lying excited states, while the overall multiplet line shape is characteristic of high-spin Co^{2+} compounds [28]. As shown below, these spectra are well reproduced by CoO_6 cluster calculations that include crystal-field effects, spin-orbit coupling, Coulomb interactions, and Co-O covalency. The parameters used in the calculations are listed in Ref. [49] and were determined to also reproduce the XLD and XMCD spectra. The temperature dependence adds hereby another constraint since the energy positions of the excited states must also be described correctly by the model parameters.

To investigate the effect of distortions of the CoO_6 octahedra, we performed polarization-dependent $\text{Co } L_{2,3}$ -edge XAS measurements. Specifically, we probed the linear dichroism both between the in-plane and the out-of-plane directions and within the ab plane. As shown in Figs. 5 and 6, both measurements exhibit polarization-dependent spectra, indicating that the local symmetry of the Co^{2+} ions is significantly lower than O_h . The dichroism is much more pronounced between the in-plane and out-of-plane directions than between the two in-plane directions. This indicates that the dominant crystal-field anisotropy distinguishes the crystal $[001]$ direction from the ab plane. In the local CoO_6 environment, this anisotropy is captured primarily by the trigonal component of the crystal field. We therefore first focus on the dominant dichroism between the out-of-plane and in-plane directions, shown in Fig. 5. The smaller but finite in-plane dichroism, shown in Fig. 6, requires additional lower-symmetry crystal-field terms and is addressed subsequently.

The origin of the dominant dichroism can be understood as follows. For high-spin Co^{2+} with a $3d^7$ configuration in

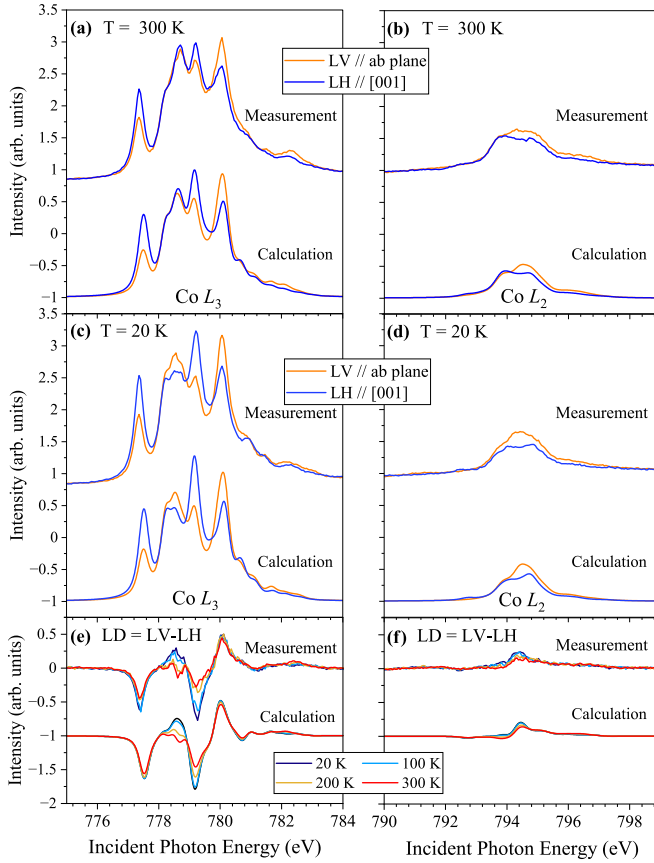


FIG. 5. Polarization-dependent Co $L_{2,3}$ -edge spectra at the highest temperature, 300 K (a) and (b), and at the lowest temperature, 20 K (c) and (d), compared with theoretical spectra obtained from the cluster model. The temperature-dependent differences between the in-plane and out-of-plane experimental and calculated spectra are plotted in (e) and (f).

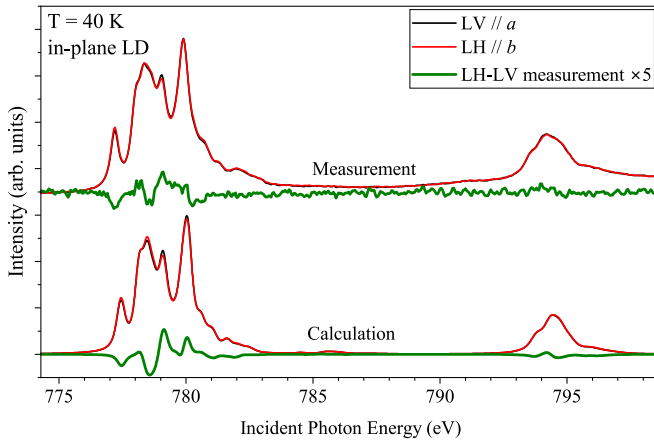


FIG. 6. Experimental and simulated linear dichroism for spectra measured and calculated with the incident beam polarization along the crystallographic a (black curves) and b (red curves) directions. The difference between the two in-plane spectra (green curves) is multiplied by a factor of 5 for clearer visualization.

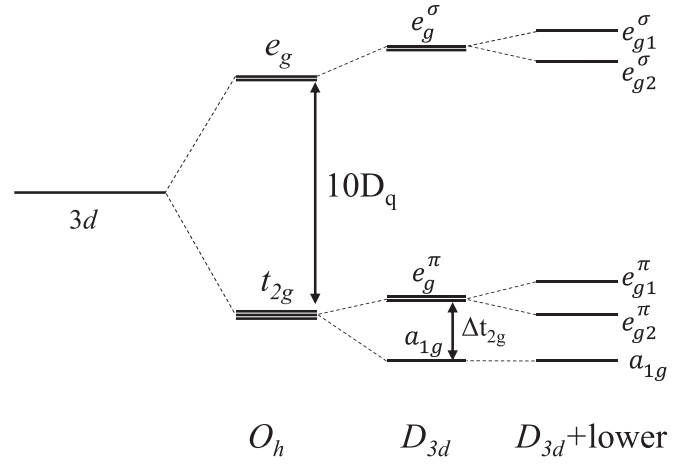


FIG. 7. Schematic one-electron crystal-field level diagram for the Co 3d states. In octahedral symmetry O_h , the levels split into t_{2g} and e_g manifolds separated by $10D_q$. A trigonal distortion along [111] lowers the symmetry to D_{3d} , splitting t_{2g} into a_{1g} and e_g^π , with an energy separation Δt_{2g} . Further lowering of the symmetry considered here removes the remaining doublet degeneracies, splitting the e_g^π and e_g^σ levels into nondegenerate states.

an ideal octahedral crystal field, the single-particle 3d levels split into the t_{2g} and e_g manifolds, yielding the high-spin $t_{2g}^5 e_g^2$ configuration. A trigonal distortion along the octahedral [111] direction further lowers the symmetry and modifies the crystal-field levels. In the resulting trigonal crystal field, the t_{2g} manifold splits into an a_{1g} singlet and an e_g^π doublet, while the cubic e_g doublet transforms as e_g^σ , as shown in Fig. 7. The trigonal distortion is parametrized here by two quantities, Δt_{2g} and V_{mix} . The parameter Δt_{2g} is defined as the difference between the on-site energies of the e_g^π and a_{1g} states:

$$\Delta t_{2g} \equiv E(e_g^\pi) - E(a_{1g}). \quad (1)$$

Considering only a local CoO_6 cluster and in the absence of the orbital mixing term, $\Delta t_{2g} > 0$ corresponds to trigonal compression, which raises the e_g^π level relative to a_{1g} , while $\Delta t_{2g} < 0$ corresponds to trigonal elongation, which raises the a_{1g} level relative to e_g^π . It should be noted that longer-range electrostatic interactions contribute and could even reverse the energy levels [2,30,36]. The orbital-mixing term between the e_g^π and e_g^σ states is defined as $V_{\text{mix}} = \langle e_g^\sigma | H | e_g^\pi \rangle$. Such mixing is allowed because the e_g^σ and e_g^π orbitals transform according to the same irreducible representation [29,30,50]. In the cluster-model calculation, we use the following basis functions:

$$e_{g1}^\sigma = \sqrt{\frac{2}{3}} d_{xz} - \frac{1}{\sqrt{3}} d_{xy}, \quad (2)$$

$$e_{g2}^\sigma = -\frac{1}{\sqrt{3}} d_{x^2-y^2} + \sqrt{\frac{2}{3}} d_{yz}, \quad (3)$$

$$e_{g1}^\pi = -\frac{1}{\sqrt{3}} d_{xz} - \sqrt{\frac{2}{3}} d_{xy}, \quad (4)$$

$$e_{g2}^\pi = -\sqrt{\frac{2}{3}} d_{x^2-y^2} - \frac{1}{\sqrt{3}} d_{yz}, \quad (5)$$

$$a_{1g} = d_{3z^2-r^2}. \quad (6)$$

Although these parameters capture the dominant trigonal distortion, additional lower-symmetry crystal-field terms are required to describe the observed in-plane dichroism. Earlier XAS studies on this compound modeled the CoO_6 cluster using purely ionic calculations constrained to D_{3d} symmetry in Ref. [31] and C_{3v} symmetry in Ref. [32]. While these trigonal approaches qualitatively reproduce the dichroism between the [001] direction and the ab plane, their trigonal symmetry enforces an isotropic in-plane charge distribution and therefore cannot account for the finite in-plane dichroism observed in the present work, as shown in Fig. 6. Specifically, we observe a small but finite dichroism between the a and b directions. This in-plane dichroism was further confirmed by repeating the measurement at several different beam positions on the sample surface, which consistently yielded the same dichroic signal.

To capture this in-plane dichroism, it is necessary to consider a symmetry lower than trigonal symmetry. To this end, we introduce perturbative splittings of the e_g^π and e_g^σ doublets, with the corresponding orbital splittings defined as $\delta(e_g^\sigma) = E(e_{g1}^\sigma) - E(e_{g2}^\sigma)$ and $\delta(e_g^\pi) = E(e_{g1}^\pi) - E(e_{g2}^\pi)$. In addition, we lift the degeneracy of the orbital-mixing terms by allowing the two matrix elements $M_{eg1} = \langle e_{g1}^\sigma | H | e_{g1}^\pi \rangle$ and $M_{eg2} = \langle e_{g2}^\sigma | H | e_{g2}^\pi \rangle$ to become inequivalent. Figure 7 presents a schematic crystal-field level diagram illustrating the progressive lowering of the symmetry of the Co^{2+} ion within a one-electron picture.

By accounting for this lowered symmetry, we consistently reproduce all measured spectra: the isotropic spectra (Fig. 4), the linear dichroism between the in-plane and out-of-plane directions, and the linear dichroism between the two in-plane directions, as shown in Figs. 5 and 6 respectively. This agreement highlights both the sensitivity of the technique and the important role of local distortions.

IV. X-RAY MAGNETIC CIRCULAR DICHROISM

To determine the quantum numbers characterizing the magnetism of $\text{Na}_3\text{Co}_2\text{SbO}_6$, we performed XMCD measurements. Figure 8 shows a comparison between the experimental and calculated circular right- (σ^+ blue line) and left- (σ^- magenta line) polarization, as well as XMCD = $\sigma^- - \sigma^+$ (green line) at 20 K. The experimental line shapes are well reproduced by the lower-symmetry model including the applied magnetic field, further supporting the validity of the cluster model.

From our cluster-model calculation in a 6 T magnetic field, we obtain spin and orbital quantum numbers of $2\langle S_x \rangle = -1.868$ and $\langle L_x \rangle = -0.779$ along the a direction, and $2\langle S_y \rangle = -2.007$ and $\langle L_y \rangle = -0.887$ along the b direction. These values correspond to total magnetic moments of $M_a = 2.647\mu_B/\text{CoO}_6$ and $M_b = 2.894\mu_B/\text{CoO}_6$.

V. DISCUSSION: CRYSTAL FIELDS

We now will discuss the types and magnitudes of the crystal fields that determine the properties of $\text{Na}_3\text{Co}_2\text{SbO}_6$. To this end we will use our cluster model with the parameters that describes accurately the entire set of XAS, XMCD, and magnetization data. To extract the effective crystal fields, i.e.,

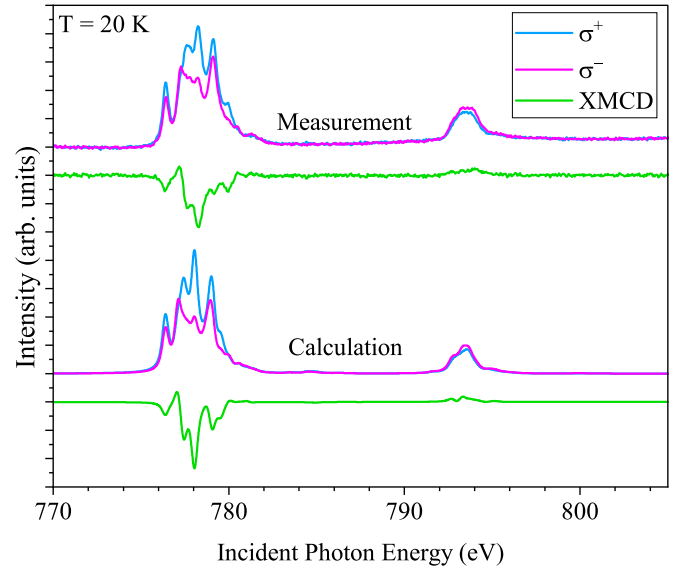


FIG. 8. Comparison between measured and calculated circular right- (σ^+) and left- (σ^-) polarization spectra as well as XMCD = $\sigma^- - \sigma^+$ of $\text{Na}_3\text{Co}_2\text{SbO}_6$. Spectra were collected at 20 K with the beam Poynting vector aligned within the ab plane under an applied magnetic field of 6 T parallel to the beam direction.

the crystal field due to both the electrostatic (ionic) crystal fields and the effect of the hybridization with the ligands, we perform total energy calculations of the cluster model with the SOC parameter set to zero. To determine the effective octahedral crystal field $10Dq_{\text{eff}}$, we remove all lower-than-octahedral crystal-field terms, i.e., we set the orbital-mixing term and the t_{2g} , e_g^π , and e_g^σ splittings to zero. The effective cubic splitting is then given as the energy of the first excited ${}^4T_{2g}$ term minus that of the ${}^4T_{1g}$ ground-state term,

$$10Dq_{\text{eff}} = E({}^4T_{2g}) - E({}^4T_{1g}).$$

The energy positions of these two terms in cubic symmetry are shown in the left part of Fig. 9. We obtain a value of $10Dq_{\text{eff}} = 0.68$ eV. The ${}^4T_{1g}$ and ${}^4T_{2g}$ terms can be associated predominantly with the high-spin $t_{2g}^5 e_g^2$ and $t_{2g}^4 e_g^3$ configurations, respectively.

Next, to extract the effective t_{2g} splitting, we set the e_g^π and e_g^σ splittings to zero while keeping the trigonal crystal-field parameter, $\Delta_{t_{2g}}$, fixed at its best-fit value. The orbital-mixing term was set to the average of the two lower-symmetry mixing matrix elements. This procedure gives an effective splitting of $\Delta_{t_{2g}}^{\text{eff}} = -42.5$ meV. To keep the sign convention consistent with the one-electron definition in Eq. (1), this effective splitting is defined as

$$\Delta_{t_{2g}}^{\text{eff}} = E({}^4A_{2g}) - E({}^4E_g).$$

It therefore corresponds to the energy difference between the ${}^4A_{2g}$ and 4E_g terms derived from the trigonal splitting of the ${}^4T_{1g}$ term, as shown in the left part of Fig. 9. With this convention, the negative value indicates that the 4A_2 term lies below the 4E_g term, corresponding to a ground state with the hole predominantly in the a_{1g} orbital. Thus, although XRD indicates compressed octahedra, our calculation yields an effective negative trigonal distortion.

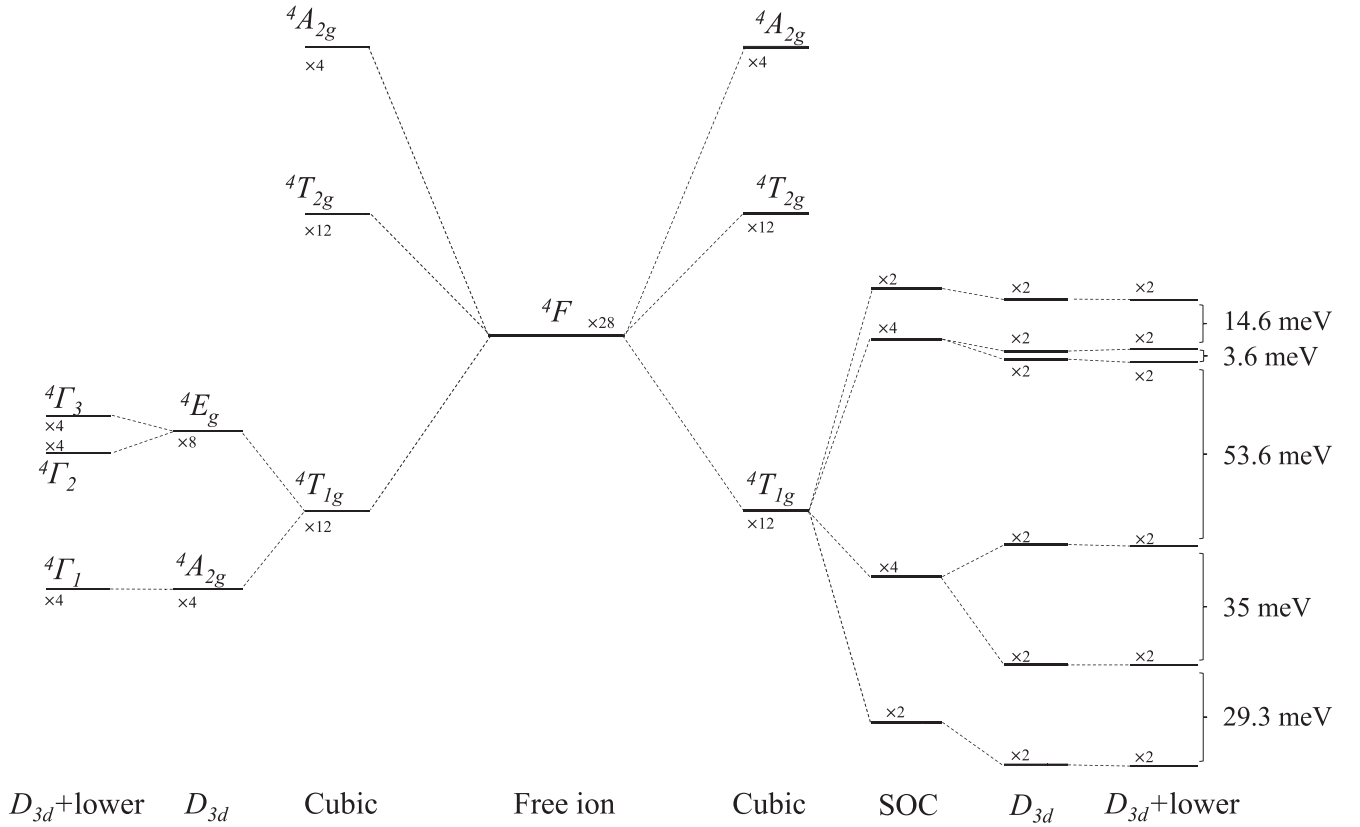


FIG. 9. Stepwise splitting of the $\text{Co}^{2+} 3d^7$ manifold obtained from the cluster-model calculation. Left: splitting by the cubic crystal field, trigonal distortion, and additional lower-symmetry crystal-field terms in the absence of spin-orbit coupling. Right: corresponding splitting including spin-orbit coupling, showing the resulting total energy-level scheme determined for $\text{Na}_3\text{Co}_2\text{SbO}_6$.

Such an inversion relative to the structural distortion agrees with previous experimental reports [9,31] and has been attributed to the influence of neighboring Sb^{5+} ions [2]. This reversal of the trigonal crystal-field splitting relative to the local octahedral distortion therefore originates from longer-range electrostatic interactions and has also been observed in other systems, such as BaCoO_3 [30] and $\text{Na}_2\text{BaCo}(\text{PO}_4)_2$ [36]. The obtained effective trigonal distortion, $\Delta_{t_{2g}}^{\text{eff}} = -42.5$ meV, lies within the -35 to -60 meV range reported in previous XAS work when expressed in the present sign convention [31]. It is also comparable to the trigonal-field scale inferred from susceptibility analysis, $\Delta \simeq -38$ meV [2], and larger in magnitude than the $\Delta \simeq -12$ meV value obtained from modeling spin-orbit excitons [9].

We would like to note that an XAS study on $\text{Na}_3\text{Co}_2\text{SbO}_6$ in thin-film form reported a trigonal crystal field with the opposite sign: $\Delta_{t_{2g}} \simeq +25.1$ meV [32]. The finding is thus that the t_{2g} hole is not in the a_{1g} orbital but rather in the e_g^π orbital. This claim was based on the O K -edge data. However, looking at their Co $L_{2,3}$ XAS data, we notice that the linear-polarization dependence is very similar to ours and to that of Ref. [31]. In particular, the linear dichroic spectra have the same sign. We can double-check the hole occupation by applying the so-called orbital occupation sum rule [26], which makes use of the integrated intensities of the linearly polarized spectra over the entire $L_{2,3}$ region. From panels (e)

and (f) of Fig. 5, we can observe that the integral of the dichroic spectra is negative, i.e., the integrated intensity of the spectra taken with the electric-field vector parallel to the [001] direction is larger than that of the spectra measured with the electric-field vector in the ab plane. From this, it follows immediately that the t_{2g} hole has more a_{1g} orbital character than e_g^π character. In terms of orbital occupations, the cluster calculations find 1.423 electrons in the a_{1g} , 1.722 in the e_g^π , 1.746 in the e_{g1}^π , 1.109 in the e_{g2}^π , and 1.110 in the e_{g1}^σ . The effective trigonal crystal-field value must therefore be negative, as we indeed found from the detailed analysis using cluster-model calculations. Consequently, the interpretation of the O K -edge data also requires consideration of, for example, non-Co contributions.

To obtain the effective e_g^π splitting, we set the e_g^σ splitting to zero, while keeping the e_g^π splitting and the remaining crystal-field parameters fixed at their best-fit values. Using the convention $\delta(e_g^\pi) = E(e_{g1}^\pi) - E(e_{g2}^\pi)$, we infer $\delta_{\text{eff}}(e_g^\pi)$ from the total-energy difference between the two states obtained by interchanging the hole between e_{g1}^π and e_{g2}^π . This gives $\delta_{\text{eff}}(e_g^\pi) = -6$ meV. Applying the same procedure to the e_g^σ orbitals gives an effective e_g^σ splitting of 13 meV.

A previous *ab initio* study [19] reported a splitting of about 15 meV between the e_g^σ -like orbitals and splittings of 6 and 12 meV within the t_{2g} manifold. A DFT + DMFT study found a much smaller Jahn-Teller-like splitting within the e_g^π orbitals, of about 1 meV at zero strain [22]. Because the

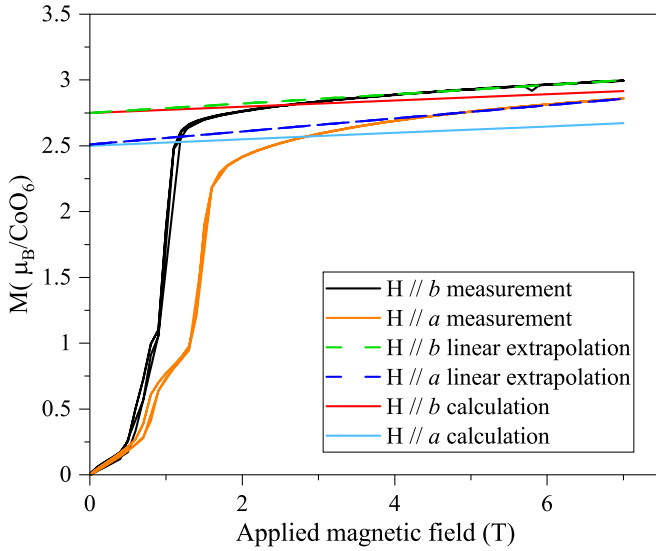


FIG. 10. Field-dependent magnetization of $\text{Na}_3\text{Co}_2\text{SbO}_6$ measured at 2 K for magnetic fields applied along the a and b axes, together with the corresponding cluster-model calculations. The pronounced directional dependence highlights the in-plane magnetic anisotropy of the system. Dashed lines indicate linear fits to the high-field regimes of the experimental magnetization curves. The extrapolated zero-field value gives an estimate for the saturated moments. See text.

sign of these splittings depends on the choice of orbital basis and labeling convention, we compare only their magnitudes. Our effective splittings are therefore in reasonable agreement with previous theoretical estimates. Interestingly, an earlier single-crystal study already pointed to the need to consider covalency and anisotropy in this compound [6].

Switching on again the SOC, we find with our cluster model that the first excited state is at 29.3 meV above the ground-state doublet, as shown in right part of Fig. 9. This energy scale is consistent with previous reports of ~ 27.1 meV from inelastic neutron scattering [7], 28 to 29 meV from another inelastic neutron-scattering study [9], and ~ 28 meV from a theoretical study [19]. It is also broadly comparable to an estimate of 247 K (~ 21 meV) obtained from a magnetic susceptibility study [8]. Raman spectroscopy has suggested a smaller splitting of 15 meV [51].

VI. DISCUSSION: MAGNETIC PROPERTIES

To further test our model, we compare the calculated magnetization with the in-plane magnetization measurements shown in Fig. 10. Consistent with the experimentally observed in-plane linear dichroism, the magnetization also depends on the orientation of the applied magnetic field within the ab plane. The cluster model reproduces this in-plane anisotropy, as shown in Fig. 10. Moreover, the magnetization data confirm that, at the 6 T magnetic field used during the XMCD experiment, the moments are largely field aligned. Notably, a pure D_{3d} or C_{3v} model does not yield the observed in-plane anisotropy in the magnetization, demonstrating that the lower-symmetry orbital splitting, although small, plays a significant role in determining the macroscopic magnetic response.

These results are consistent with the magnetization data shown in Fig. 10. From the experimental magnetization curves, the saturated moments were estimated from the zero-field intercepts of the high-field linear regime, yielding $M_a^{\text{expt}} = 2.51\mu_B$ and $M_b^{\text{expt}} = 2.75\mu_B$. The measured magnetization is also consistent with previous reports of the in-plane magnetization anisotropy [8,20]. Both the experimental and the calculated magnetization exhibit a gradual, nearly linear increase with increasing applied field, characteristic of a van Vleck contribution arising from field-induced mixing with low-lying excited states [52]. However, the calculated and experimental magnetization curves do not coincide at higher fields. This discrepancy may arise because the cluster model does not account for field-dependent intersite correlations or diamagnetic contributions from the nonmagnetic ions in the compound. Therefore, to compare the saturated moments directly, the high-field regime of the calculated magnetization curves was used for an extrapolation to zero field, as shown in Fig. 10. This procedure gives $M_a^{\text{calc}} = 2.50\mu_B$ and $M_b^{\text{calc}} = 2.75\mu_B$, in excellent agreement with the experiment. We have also calculated the corresponding g factors. Using the relation $M = gM_{\text{eff}}$, with $M_{\text{eff}} = 1/2$, we obtain $g_a = 5.0$, $g_b = 5.5$, and $g_{[001]} = 2.86$. These values are in good agreement with the previously reported values $g_{ab} = 4.6$ and $g_c = 3.0$ in Ref. [2], and to a lesser extent with $g_a = 6.2$, $g_b = 6.4$, and $g_{[001]} = 3.6$ reported in Ref. [8].

VII. DISCUSSION: GROUND-STATE DEGENERACY

Using our cluster model, we find that the ground state is doubly degenerate and has an effective total angular momentum of $J_{\text{eff}} = 0.93$. To assess the deviation from the ideal $J_{\text{eff}} = 1/2$ limit due to crystal-field effects, we first consider an idealized cubic scenario by setting the trigonal distortion, the orbital-mixing terms, and both the e_g^π and e_g^σ splittings to zero. In this cubic limit, the ground state remains doubly degenerate and yields $J_{\text{eff}} = 0.83$.

The deviation from the ideal $J_{\text{eff}} = 1/2$ value reflects the way J_{eff} is evaluated, namely, using an effective orbital operator L_{eff} constructed within the t_{2g} -derived manifold after projecting out the e_g states. Because the finite cubic crystal-field splitting is not large enough to fully project out the e_g states, the full multiplet wave function retains residual admixture beyond a pure t_{2g} -only description, leading to a calculated J_{eff} value larger than the ideal $1/2$. Nevertheless, since the cubic-limit ground state remains a Kramers doublet derived from the spin-orbit-split $^4T_{1g}$ manifold, it can still be regarded as an effective $J_{\text{eff}} = 1/2$ -like pseudospin doublet.

By contrast, the larger value $J_{\text{eff}} = 0.93$ obtained for the realistic crystal-field environment indicates a stronger departure from the ideal cubic $J_{\text{eff}} = 1/2$ limit. To identify the origin of this additional deviation, we repeated the calculation retaining only the cubic crystal field and the small e_g^π and e_g^σ splittings, while removing the trigonal distortion. This again gives $J_{\text{eff}} = 0.83$, showing that the increase from 0.83 to 0.93 is primarily caused by the trigonal distortion.

Since the trigonal distortion is identified as the dominant source of the deviation from the ideal cubic $J_{\text{eff}} = 1/2$ -like limit, external tuning of the local crystal-field environment may provide a route to bring the system closer to this regime,

provided the high-spin Co^{2+} state is preserved. Possible approaches include uniaxial pressure along the [001] direction or in-plane strain. A recent quasihydrostatic pressure study on $\text{Na}_3\text{Co}_2\text{SbO}_6$ showed that the trigonal distortion is reduced under applied pressure, accompanied by anisotropic lattice compression, but higher pressures drive a high-spin to low-spin crossover that destroys the orbital magnetism required for the $J_{\text{eff}} = 1/2$ -like state [53]. A subsequent theoretical analysis of $\text{Co } K_\beta$ x-ray emission attributed the broad pressure range of this crossover to spin-orbit-induced mixing between high- and low-spin states [54]. Uniaxial pressure may therefore provide an alternative route for tuning the system toward a Kitaev QSL state.

A recent theoretical study [22] also proposed that tensile strain in $\text{Na}_3\text{Co}_2\text{SbO}_6$ may suppress or reverse the trigonal crystal-field splitting, moving the system closer to a Kitaev QSL regime, although their results for the unstrained compound show a nearly occupied a_{1g} orbital, in contrast to our findings. Furthermore, Ref. [55] theoretically demonstrated that magnetic interactions can be manipulated via strain to realize a QSL state in other hexagonal systems. Strain engineering has also been shown to tune crystal-field splittings in CoO [26]. In addition, Ref. [32] reported that in-plane strain in $\text{Cu}_3\text{Co}_2\text{SbO}_6$ thin films suppresses the Néel temperature, T_N .

Regarding in-plane anisotropy, recent studies have shown that direction-dependent in-plane magnetic fields strongly tune the magnetic response and field-induced phases of $\text{Na}_3\text{Co}_2\text{SbO}_6$ [8,15,21,23,56]. Furthermore, doping studies have shown that long-range antiferromagnetic order in $\text{Na}_3\text{Co}_2\text{SbO}_6$ can be suppressed, highlighting chemical substitution as another route for modifying the balance of competing interactions and tuning the magnetic ground state [57,58].

Taken together, these studies highlight the importance of our results, which clarify how the local crystal-field environment affects the J_{eff} ground state and provide a microscopic framework for evaluating external tuning strategies aimed at realizing Kitaev physics in $\text{Na}_3\text{Co}_2\text{SbO}_6$. The agreement between experiment and calculation supports the role of local distortions as key control parameters of the electronic and magnetic ground states, providing a quantitative foundation for future studies of Kitaev physics in this system.

VIII. CONCLUSION

To conclude, our results demonstrate the power of XAS for directly determining local crystal-field effects in $\text{Na}_3\text{Co}_2\text{SbO}_6$. In particular, our findings support an effective negative trigonal crystal-field splitting of $\Delta_{t_{2g}}^{\text{eff}} = -42.5$ meV, as well as effective e_g^π and e_g^σ orbital splittings of -6 meV and 13 meV, respectively. Our model is not only successful in reproducing the XAS/XMCD spectra but also the macroscopic anisotropic magnetization data, highlighting the important role of local distortions for the properties of the material. These results suggest in turn that tuning the local crystal-field environment, for example through strain or uniaxial pressure, may provide a route toward the conditions required for realizing a Kitaev QSL, while potentially suppressing conventional long-range magnetic order.

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DATA AVAILABILITY

The data that support the findings of this article are openly available [59].

APPENDIX: SINGLE-CRYSTAL X-RAY DIFFRACTION

The results of the single-crystal x-ray diffraction measurements (see main text) are shown in Tables I and II.

TABLE I. Crystallographic and structural refinement data of a single-crystal x-ray diffraction measurement of $\text{Na}_3\text{Co}_2\text{SbO}_6$. The crystallographic software JANA was used for the structural refinement [60]. The size of the dominant twin domain amounts to 81.6(7.6)%. The other two twin domains were present in amounts of 9.4(5.3)% and 9.1(5.5)%, respectively.

Crystal	$\text{Na}_3\text{Co}_2\text{SbO}_6$
Density	5.0277 g/cm ³
Temperature	Room temperature
Wavelength	Mo $K\alpha$
Crystal system	Monoclinic
Space group	$C2/m$ (12)
Unit cell dimensions	$a = 5.3649(3)$ Å $b = 9.2735(5)$ Å $c = 5.6475(3)$ Å $\beta = 108.548(2)^\circ$
Volume	266.376(39) Å ³
Z	2
$F(000)$	371
Crystal size	~ 20 μm
$\Theta_{\text{max}}/\Theta_{\text{full}}$	37.94°/36.95°
Index range	h : $-9 \rightarrow 9$ k : $-15 \rightarrow 15$ l : $-9 \rightarrow 8$
Reflections in total/independent	6052/800
Observed reflections/independent	5670/779
R_σ (obs/all)	4.93%/5.03%
R_{int} (obs/all)	3.52%/3.52%
Redundancy	7.565
Completeness up to $\Theta_{\text{max}}/\Theta_{\text{full}}$	93%/98%
Absorption correction	Multiscan
Min./max. transmission	0.7650/1
Refinement method	Least squares on F^2
Goodness of fit	1.09
R/R_w [$I > 3\sigma(I)$]	1.72%/3.85%
R/R_w (all)	1.84%/3.90%

TABLE II. Refinement results of single-crystal x-ray diffraction measurements of $\text{Na}_3\text{Co}_2\text{SbO}_6$. $U_{i,j}$ are in units of $\text{\AA}^2$.

Atom	Occ.	x	y	z	U_{iso}	
Sb1	0.942(11)	0.5	0.5	0	0.00679(7)	
Co1	0.987(6)	0	0.66603(15)	0	0.00802(12)	
Na1	1	0.5	0.6743(5)	0.5	0.0125(4)	
Na2	1	0.5	0	0.5	0.0130(5)	
O2	1	0.2544(5)	0.5	0.2036(4)	0.0095(5)	
O3	1	0.7250(4)	0.65743(11)	0.2055(3)	0.0093(4)	
Co2	0.058(11)	0.5	0.5	0	0.00679(7)	
Sb2	0.013(6)	0	0.66603(15)	0	0.00802(12)	
Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sb1	0.00602(10)	0.00561(10)	0.00860(9)	0	0.00214(15)	0
Co1	0.0069(2)	0.00734(16)	0.00976(16)	0	0.00256(17)	0
Na1	0.0124(7)	0.0138(6)	0.0116(5)	0	0.0041(5)	0
Na2	0.0120(9)	0.0120(8)	0.0124(8)	0	0.0002(6)	0
O2	0.0091(7)	0.0101(7)	0.0098(7)	0	0.0036(6)	0
O3	0.0084(7)	0.0085(5)	0.0107(5)	−0.0012(3)	0.0025(5)	−0.0010(4)
Co2	0.00602(10)	0.00561(10)	0.00860(9)	0	0.00214(15)	0
Sb2	0.0069(2)	0.00734(16)	0.00976(16)	0	0.00256(17)	0

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