Noncollinear antiferromagnetic order in the buckled honeycomb lattice of magnetoelectric $\text{Co}_4\text{Ta}_2\text{O}_9$ determined by single-crystal neutron diffraction

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$\text{Co}_4\text{Ta}_2\text{O}_9$ exhibits a three-dimensional magnetic lattice based on the buckled honeycomb motif. It shows unusual magnetoelectric effects, including, in particular, the sign change and nonlinearity. These effects cannot be understood without the detailed knowledge of the magnetic structure. Herein, we report neutron diffraction and direction-dependent magnetic susceptibility measurements on $\text{Co}_4\text{Ta}_2\text{O}_9$ single crystals. Below 20.3 K, we find a long-range antiferromagnetic order in the alternating buckled and flat honeycomb layers of $\text{Co}^{2+}$ ions stacked along the $c$-axis. Within experimental accuracy, the magnetic moments lie in the $ab$-plane. They form a noncollinear antiferromagnetic structure with a tilt angle of $\sim 14^\circ$ at 15 K in the buckled layers, while the magnetic moments in each flat layer are collinear. This is directly supported by a finite $(0, 0, 3)$ magnetic Bragg peak intensity, which would be absent in the collinear magnetic order. The magnetic space group is $C2'/c$, which is different from the one previously found in powder neutron diffraction, as well as in the isostructural $\text{Co}_4\text{Nb}_2\text{O}_9$. The revised magnetic structure successfully explains the major features of the magnetoelectric tensor within the framework of the spin-flop model.

I. INTRODUCTION

Controlling magnetism with an electric field, and the polarization with a magnetic field, is of both technological and fundamental significance. Energy-efficient devices of new types could be developed, for example, using the cross-coupling between the electric and magnetic orders in magnetoelectric (ME) and multiferroic compounds. The research of the ME effects was initiated by a theoretical proposal that allows terms for couplings between the electric and magnetic fields in the free energy are allowed in compounds possessing certain structural and magnetic symmetries. The first compound exhibiting the ME effect, $\text{Cr}_2\text{O}_3$, was discovered shortly thereafter. Since then, significant efforts were devoted to the search of new ME compounds, especially of those with a strong ME coupling as relevant to technological applications. This search is hindered by the rather restrictive symmetry requirements for the candidate materials. However, even when such requirements are met, a physical mechanism producing a strong ME coupling must be present in the system. As a result, the number of compounds showing the strong ME effect is still quite limited.

$\text{Cr}_2\text{O}_3$ displays a rather strong and linear ME effect, which are both desirable properties. Compounds possessing similar structures, combined with the increased spin-lattice coupling, may therefore be considered promising ME candidates. The $\text{A}_4\text{B}_2\text{O}_9$ ($\text{A} = \text{Mn}, \text{Fe}, \text{Co}$, and $\text{B} = \text{Nb}, \text{Ta}$) compounds are based on this corundum structure, and contains magnetic ions such as $\text{Co}^{2+}$ and $\text{Fe}^{3+}$ expecting to have significant orbital magnetic moments conducive to increased spin-lattice coupling. In addition, they contain heavy nonmagnetic elements (Nb, Ta) with strong intrinsic spin-orbit interaction, which may facilitate the ME coupling indirectly. Recently, several members of this family have indeed been shown to exhibit complicated ME and multiferroic properties.

The structure of the $\text{A}_4\text{B}_2\text{O}_9$ compounds is derived from the well-known corundum crystal structure of $\text{Cr}_2\text{O}_3$ in which four Cr sites are occupied by the magnetic $\text{A}^{2+}$ ions, and another two sites by the nonmagnetic $\text{B}^{5+}$. This structure is illustrated in Fig. 1 using $\text{Co}_4\text{Ta}_2\text{O}_9$ as the example. The space group is trigonal $P \bar{3}c1$ (No. 165) consistent with a recent report. There are two crystallographically distinct sites occupied by the $\text{Co}^{2+}$ ions. One of them (Co1) forms the buckled honeycomb network shown in Fig. 1(b) [denoted as buckled], while the other (Co2) makes a rather flat honeycomb layer shown in Fig. 1(c) [denoted as flat]. These layers are stacked along the $c$-axis, forming a three-dimensional structure.

The ME properties of $\text{Co}_4\text{Nb}_2\text{O}_9$ have been studied most extensively so far. It shows a significant linear ME effect in the magnetically ordered state, arguably influenced by the unquenched orbital moment of $\text{Co}^{2+}$. The direction of the induced electric polarization could be switched by rotating the magnetic field in the honeycomb
FIG. 1. (color online) (a) Crystal structure of Co$_4$Ta$_2$O$_9$. Black solid lines defines the unit cell. Crystallographically-different Co1 and Co2 sites are shown in dark and light blue, respectively. CoO$_6$ octahedra are highlighted. The buckled honeycomb (0.1 ≤ z ≤ 0.4), and the flat honeycomb (0.4 ≤ z ≤ 0.5) layer fragments are shown in (b) and (c), respectively.

Magnetic order is key for understanding the ME effect. However, the magnetic structure of Co$_4$Nb$_2$O$_9$ has been a subject of certain controversy. In specific, it is not agreed whether the spins are collinear within the buckled honeycomb planes, as well as whether any c-axis spin component is present or absent. The strongest components of the ME tensor in Co$_4$Nb$_2$O$_9$ have been accounted for by the spin-flop model in Ref. 5. However, this model does not explain all the tensor components observed experimentally. Also, a more recent neutron diffraction study in an applied magnetic field did not find the spin flop. Instead, the field-dependent magnetic domain populations, at least in moderately applied fields, is proposed to explain the ME effects. Thus, it is clear that detailed knowledge of the magnetic structure, the understanding of the magnetic domain population factors, and their effects are needed to explain the complex magnetoelectricity of Co$_4$Nb$_2$O$_9$.

Recently, the complex ME response of Co$_4$Ta$_2$O$_9$ has been reported in the magnetically ordered state. In contrast to the isostructural Co$_4$Nb$_2$O$_9$, this response is strongly non-linear. Also, for some directions of the applied magnetic field, the induced electric polarization changes its sign with the increasing field. This is somewhat puzzling because the only major difference between Co$_4$Ta$_2$O$_9$ and Co$_4$Nb$_2$O$_9$ is in the non-magnetic ions, Ta$^{5+}$ and Nb$^{5+}$, respectively. The origin of the distinct ME effects in these two compounds, therefore, deserves a detailed investigation. The magnetic structure of Co$_4$Ta$_2$O$_9$ has been recently determined by neutron powder diffraction. It proposed a noncollinear magnetic structure in the $ab$-plane, similar to the one determined for Co$_4$Nb$_2$O$_9$ in the same magnetic space group, C2/c'.

Given the current controversial results on the magnetic structure of Co$_4$Nb$_2$O$_9$, the key role of the magnetic order in the ME effect, and the apparent failure of the current models to explain these effects in Co$_4$Nb$_2$O$_9$, it is essential to determine the magnetic structure of Co$_4$Ta$_2$O$_9$ accurately. We also note that conflicting reports exist for the magnetic structure of the isostructural Fe$_3$Nb$_2$O$_9$ which further reflect a general difficulty in determining the magnetic structure of the A$_4$B$_2$O$_9$ compound series. Single-crystal neutron diffraction studies, supported by other relevant measurements, are essential to address this problem.

In this paper, we determine the magnetic structure of Co$_4$Ta$_2$O$_9$ using single-crystal neutron diffraction complemented by direction-dependent magnetic susceptibility measurements. A few characteristic features of the magnetic structure of Co$_4$Ta$_2$O$_9$ in our study, including the $ab$-plane spins and the tilted (collinear) antiferromagnetic order in the buckled (flat) honeycomb planes, are similar to the previous work on Co$_4$Ta$_2$O$_9$ and the isostructural Co$_4$Nb$_2$O$_9$. However, we find a distinct magnetic space group, C2'/c, as opposed to C2/c' reported in these references. The major difference is the direction of the magnetic moments. Symmetry analysis of the newly-determined magnetic order of Co$_4$Ta$_2$O$_9$ accounts for the observed ME tensor in the framework of the spin-flop model giving a better agreement with the experimental data than the previously-reported magnetic symmetry. While the neutron diffraction results do favor the C2'/c group over the C2/c', the difference in the quality of the fit is small. Importantly, we found that direction-dependent magnetic susceptibility data were crucial for the confirmation of the C2'/c magnetic space group in Co$_4$Ta$_2$O$_9$. Thus, our results emphasize the importance of the careful choice of the complementary measurements set for the determination of the correct magnetic structure of the A$_4$B$_2$O$_9$ compounds.

This paper is organized as follows. Section II describes the experiments. Magnetic susceptibility and neutron diffraction results are given in Section III and Section IV, respectively. Implications of those results are discussed in Section V and conclusions are summarized in Section VI. Appendix A and Appendix B provide details of the analysis of the magnetic susceptibility and neutron diffraction data, respectively. The symmetries of the C2'/c and the C2/c' magnetic space groups and the corresponding magnetic structures are discussed in Appendix C and the magnetic structure factors of key magnetic Bragg peaks, (0, 0, L), are given in Appendix D.

II. EXPERIMENTAL DETAILS

Two sets of Co$_4$Ta$_2$O$_9$ single crystals were used in this work. One set was grown using the flux method, as described in Ref. 7. We refer to them as the flux crystals.
FIG. 2. (color online) ZFC and FC magnetic susceptibilities along (a) the [1 1 0] and (b) [0 0 1] trigonal directions for the flux (blue empty circles) and TSFZ (red empty squares) crystals. The FC data for the TSFZ crystal is omitted for clarity in (b). The corresponding temperature derivatives using the ZFC data are shown in (c) and (d). Cyan solid lines indicate the fits used to determine a magnetic transition temperature at 20.3 K and a complex magnetic phase at 6.65 K: they are depicted by the vertical dashed lines.

The other set was produced using the traveling solvent floating zone method, the TSFZ crystals. The polycrystalline powder of Co$_4$Ta$_2$O$_9$ was obtained by a solid-state reaction technique from the stoichiometric mixture of Co$_3$O$_4$ (99.99%) and Ta$_2$O$_5$ (99.99%) powders sintered at 1200 °C for 10 hours in the air. It was used to make the feed and seed rods in the TSFZ growth.

Magnetic susceptibility measurements were done with SQUID magnetometry, using either a normal DC accessory or a reciprocating sample measurement system to increase a signal to noise ratio. Susceptibility measurements between 30 K and the base temperature (typically 2 or 3 K) were done in 0.1 T applied magnetic field. Measurements at higher temperatures were also taken. Zero-field-cooled (ZFC) and field-cooled (FC) measurements were done when necessary. Crystallographic axes were pre-determined by Laue x-ray diffraction, cross-checked by a fixed-wavelength single-crystal x-ray diffraction (a Mo source).

Neutron diffraction experiments were performed at the Single Crystal Diffractometer (SXD) beamline at ISIS, where the time-of-flight Laue technique is used to access large 3-D volumes of reciprocal space in a single measurement. Single crystals were screened by magnetic susceptibility, x-ray diffraction, and followed by further quality checks with neutron Laue diffraction at room-temperature on SXD. One crystal from each growth method was chosen for the neutron diffraction measurements. The 22-mg flux crystal was of a spherical shape, about 2 mm in diameter. The data were collected at three identical rotation angles, in the paramagnetic state at 25 K for 18 hrs, and in the magnetically ordered state at 15 K for 42 hrs. The 1.28 g TSFZ crystal was of a cylindrical shape, 6 mm in diameter, cut from a bigger rod. For this crystal, the data were collected at six identical rotation angles at 25 and 15 K for 41.2 and 68.7 hrs, respectively.

FIG. 3. (color online) ZFC magnetic susceptibility for various directions of the magnetic fields in the ab-plane. The data were taken using the flux-grown crystal depicted in the inset (a different crystal from those used in Fig. 2). The inset shows the color code for the directions of the magnetic field with respect to the trigonal crystallographic axes, and lists several directions equivalent by the symmetry. The data were averaged as discussed in the text. Vertical dashed lines indicate two characteristic temperatures, which are the same as those extracted from Fig. 2(c).

### III. MAGNETIC SUSCEPTIBILITY

We performed direction-dependent magnetic susceptibility measurements on Co$_4$Ta$_2$O$_9$ using both the flux and TSFZ crystals. The major features are shown in Fig. 2. The in-plane susceptibility with the magnetic field along the [1 1 0] direction is depicted in Fig. 2(a), while the c-axis susceptibility (field parallel to [0 0 1]) is shown in Fig. 2(b). Figs. 2(c, d) show the corresponding derivatives using the ZFC data with respect to temperature. The transition temperature for the antiferromagnetic order T$_N$, defined as an onset temperature with a sharp cusp of $\chi(T)$ in the in-plane data, is 20.3 K in the both samples. The anomaly at the T$_N$ is much less pronounced...
FIG. 4. (color online) Neutron diffraction data analysis showing the calculated structure factor $F_{\text{calc}}$ versus the observed structure factor $F_{\text{obs}}$. Panels (a) and (d) are for the paramagnetic state at 25 K, the remaining panels show the data for the ordered state at 15 K with chosen Bragg peaks whose wave vectors are $Q \leq 6.28 \text{ Å}$. In panels (a), (b), (d), and (e) only the nuclear structure is plotted, which was refined using the whole data at 25 K (not shown). Magnetic refinement results (with a fixed nuclear structure) are shown in (c) and (f) for the in-plane noncollinear magnetic model in $C2'/c$ marked with the dagger ($\dagger$) symbols in Table I (see the text for the details). The top (a-c) and the bottom (d-f) panels are for the flux and the TSFZ crystals, respectively.

in the $c$-axis data. This means that magnetic moments are dominantly confined in the $ab$-plane.

There is an additional anomaly at a lower temperature, at which a bifurcation between the FC and ZFC data is observed. As determined by the minimum in the temperature derivative, it occurs at 6.65 K in the flux crystal. While less pronounced, this anomaly is also present in the TSFZ crystal at a slightly higher temperature. The observed temperature hysteresis and the sample dependence indicate a more complex magnetic phase at such lower temperatures. In this work, as Co$_4$Ta$_2$O$_9$ magnetic structure was determined at 15 K well above 6.65 K, our analysis is free from this magnetic complexity. Detailed studies on the magnetism below 6 K will be highly desirable, but is beyond the scope of this paper.

To characterise the in-plane magnetic anisotropy, we made magnetic susceptibility measurements for a large number of representative high-symmetry directions in the trigonal $ab$-plane. A flux crystal of a hexagonal shape with well-defined facets was used (after the crystallographic axes were confirmed by x-ray Laue measurements). Fig. 3 shows the data for five such directions, averaged for several repetitive measurements as discussed in detail in Appendix A. Below $T_N$, the largest and the lowest susceptibilities are found for the magnetic field along the [1 -1 0] and the [1 1 0] trigonal directions, respectively. For the other directions, the data interpolated between these values. These measurements clearly demonstrate that the magnetic moments point predominantly along the [1 1 0] direction, assuming a (nearly) collinear antiferromagnetic structure and a dominant single magnetic domain state (to be discussed in detail later). By convention, this means that the magnetic easy axis is [1 1 0], while the hard axis is [1 -1 0]. These results will play an important role in the analysis of the neutron diffraction data discussed in the next Section.
TABLE I. Magnetic structure refinement results for various models, for the flux and the TSFZ samples. The data were collected at \( T = 15 \) K. The observed peaks with intensities \( I > 3.0 \times \sigma(I) \) and \( Q \leq 6.28 \) Å were used in the fits. Single-domain model was used for the flux sample, while the model with three equally populated magnetic domains was utilized for the TSFZ crystal. Asterisk (*) symbols mark the refinements with unrealistically large moments along the \( c \)-axis compared to moments in the \( ab \)-plane. Dagger (†) symbols indicate the final models. \( |M| \) is the size of magnetic moments. Terms of collinear and noncollinear mean arrangements of antiferromagnetic moments in the \( ab \)-plane. \( \text{R}_{\text{obs}} \) is given in the unit of %.

| Magnetic model | \( C2'c' \) (No. 15.88) | \( C2'/c \) (No. 15.87) |
|---------------|----------------|----------------|
| \text{R}_{\text{obs}} | | |
| Collinear, \( M_c=0 \) | 5.94% | 6.15% |
| Collinear, \( M_c\neq0 \) | 5.97% | 6.15% |
| Noncollinear, \( M_c=0 \) | 6.31% | 5.92% |
| Noncollinear, \( M_c\neq0 \) | 6.06% | 5.91% |
| \text{Flux} | | |
| Collinear, \( M_c=0 \) | 10.43% | 10.71% |
| Collinear, \( M_c\neq0 \) | 10.31% | 10.26% |
| Noncollinear, \( M_c=0 \) | 10.53% | 10.34% |
| Noncollinear, \( M_c\neq0 \) | 10.27% | 10.03% |
| \text{TSFZ} | | |

IV. NEUTRON DIFFRACTION

To determine the magnetic structure of Co\(_4\)Ta\(_2\)O\(_9\), neutron diffraction measurements were performed using the both types of single crystals. We used the same single crystals previously characterized in the magnetic susceptibility [see Fig. 2]; the susceptibility was done on a piece of the same TSFZ crystal used for neutron diffraction. In this paper, we determine the magnetic structure at \( T = 15 \) K, above the magnetic transition to the complex magnetic phase at 6.65 K. The results of the neutron diffraction data analysis are shown in Fig. 4. Panels (a-c) and (d-f) present the calculated versus the observed structure factors for the flux and the TSFZ crystal, respectively.

The nuclear structure in the paramagnetic state was refined first, using the whole data collected at 25 K [see Figs. 3(a, d)]. The nearly identical crystal structure compared to that determined at room temperature by x-rays was found in the same \( P3\overline{1}c1 \) trigonal space group. When this fixed nuclear structure is used for the data taken in the magnetically ordered state at 15 K, additional unaccounted diffraction signal is clearly observed for a set of experimental Bragg peaks. That is, \( F_{\text{obs}} \) is larger than \( F_{\text{calc}} \) for these peaks. They are evidently seen below the linear \( F_{\text{obs}} = F_{\text{calc}} \) line in Figs. 4(b, e).

Importantly, this additional intensity is only observed in the reflections with lower wave vectors \( Q \) located near the coordinate origins in Fig. 4. This indicates the magnetic origin of the extra intensity for these peaks. In the data of Fig. 4, the identical Bragg peaks are used at both temperatures. Also, a small number of new Bragg peaks were found in the magnetically ordered phase (to be discussed later). They were all indexed using the integer positions in the parent crystal structure. This shows that the magnetic and the nuclear structures have the same unit cell, and that the magnetic ordering wave vector is \( q = (0, 0, 0) \). The set of the observed peaks with \( Q \leq 6.28 \) Å, as appropriate for the magnetic structure determination, was used in the refinements discussed below. The most reliable results are shown in Figs. 4(c, f) [also corresponding results with dagger (†) symbols in Table 1]. The addition of the magnetic structure to the refinements resulted in the obviously better fits. This is reflected by the reduction of the reliability factor \( \text{R}_{\text{obs}} \) by 2.56% and 5.18% for the flux and the TSFZ samples, respectively. The details of the refinement procedure can be found in Appendix 2.

To find the magnetic space group candidates, group symmetry analysis was applied to the parent nuclear space group \( P3\overline{1}c1 \) (No. 165) with \( q=(0, 0, 0) \). All the trigonal subgroups were inconsistent with the magnetic susceptibility data because they disallowed magnetic moments in the \( ab \)-plane. The next available highest-symmetry choice is monoclinic. We found two candidates that were compatible with the predominantly in-plane magnetic moments, and that resulted in good fits to the neutron diffraction data collected at 15 K. These were \( C2/c' \) (No. 15.88) and \( C2'/c \) (No. 15.87). One of them, \( C2'/c' \), was previously proposed for both the Co\(_4\)Nb\(_2\)O\(_9\) and Co\(_4\)Ta\(_2\)O\(_9\). Both these groups allow collinear and noncollinear antiferromagnetic order in the \( ab \)-plane, as well as an antiferromagnetic \( c \)-axis component. We have carried out refinements of the magnetic structure, starting with the simplest possible model, the collinear in-plane antiferromagnetic structure with no \( c \)-axis components. More complex models, allowing noncollinear in-plane structures, as well as the out-of-plane moment, were then considered. When the symmetry is lowered from the trigonal to monoclinic at the magnetic transition, three types of in-plane magnetic domains are possible, distinguished by the three possible directions of the unique \( b_m \) axis in the monoclinic cell. The full de-
fits are characterized by the standard quality fit factor of the flux crystal is better than that of the TSFZ crystal. The indexing is with the trigonal setting. A clear magnetic Bragg peak at 15 K and a tiny signal at 25 K (possibly due to multiple diffraction) are seen. The data is from the TSFZ crystal.

FIG. 5. (color online) Neutron diffraction patterns in the vicinity of the (0, 0, 3) position in the antiferromagnetic phase at (a) T = 15 K, and in the paramagnetic state at (b) T = 25 K. Panel (c) shows cuts through the peak position in the directions indicated by white arrows in (a, b).

The intensity of these peaks is practically zero both in the plane magnetic order in $C2'/c$ and $C2'/c$ (with or without the $c$-axis component). They acquire intensity as the spins start tilting in the $ab$-plane, away from the collinear antiferromagnetic alignment. Thus, the tilting angle can be determined from the refinement including these (0, 0, odd) peaks. We emphasize that the same constraint for noncollinear magnetic moments apply in both the buckled and flat honeycomb, and their noncollinear moments in the buckled (within the layer) and the flat (between layers) honeycomb can contribute the (0, 0, odd) magnetic Bragg peak intensity [see the details in Appendix D for a derivation and discussion of the magnetic structure factor of the (0, 0, L) peaks].

Secondly, most of the models involving nonzero out-of-plane moment produced unrealistically large values of $M_\parallel$, which is incompatible with the magnetic susceptibility results. They are marked with asterisk symbols in Table I. The only noncollinear in-plane structure that converged well with reasonable out-of-plane spin components is the $C2'/c$ model for the flux crystal: it gives a $M_\parallel \sim 0.2 \mu_B$ component, corresponding to a 6° out-of-plane tilt, only for the moments in the flat honeycomb layers. However, it does not result in the improvement of the $R_{obs}$ over the fully in-plane structure. We therefore conclude that within the error of our experimental method (as outlined above), the magnetic moments of $\text{Co}_2\text{Ta}_2\text{O}_9$ are confined to the $ab$-plane. We note that this conclusion matches the results reported in Ref. [12] for $\text{Co}_4\text{Ta}_2\text{O}_9$, and in Refs. [14] and [15] for the isostructural $\text{Co}_4\text{Nb}_2\text{O}_9$.

Among the noncollinear structures with the $ab$-plane magnetic moments, our fits slightly favor the $C2'/c$ space group that now has a meaningfully smaller $R_{obs}=5.92$ (10.34) % than the $R_{obs}=6.31$ (10.53) % for the $C2'/c$ space group in the flux (TSFZ) crystal. However, given the reports of the $C2'/c$ structure for both $\text{Co}_2\text{Ta}_2\text{O}_9$ and $\text{Co}_2\text{Nb}_2\text{O}_9$, a stronger evidence is desirable to determine the minimal magnetic structure confidently.

Such evidence comes from the direction-dependent magnetic susceptibility data. To interpret these data, one must understand the key difference between two magnetic space groups. In the collinear in-plane order, for both the CoI and Co2 sites, magnetic moment (M) components are constrained by $M_a = 2 M_b$ for $C2'/c$ while $M_c = 0$ in $C2'/c$. On the one hand, in the $C2'/c$ space group, this condition means that the magnetic moments essentially point along the [0 1 0] trigonal direction: by symmetry, the $[1 0 0]$ and $[1 1 0]$ are equivalent to $[0 1 0]$. Note that [-1 -1 -1] is indistinguishable with $[1 1 0]$ when ignoring the anti-phase relation. Therefore, three types of the in-plane magnetic domains, with the magnetic moments pointing along either the $[1 0 0]$, $[0 1 0]$, or $[1 1 0]$ can form. On the other hand, in the $C2'/c$ space group, the magnetic moment directions are perpendicular to the ones listed above; one such direction (out of three) is $[1$
The refined noncollinear magnetic order in the ab-plane of Co$_4$Ta$_2$O$_9$ at $T = 15$ K. The magnetic symmetry group is $C2'/c$. (b) and (c) show the buckled and the flat honeycomb layers, respectively. The magnetic arrangement is noncollinear (tilted) in the former, and collinear in the latter. The high-temperature trigonal crystallographic axes, as well as the corresponding unit cells, are shown. This structure corresponds to the [0 1 0] easy axis magnetic domain. Magnetic moments, $M(Col) = (-0.73, 2.3, 0)$ $\mu_B$ and $M(Co2) = (0.73, 2.3, 0)$ $\mu_B$ were visualized obtained from a refinement with the dagger (i) symbol in Table II. Magnetic moments are given for #1 sites in Table II and Fig. 9(c) in Appendix.

FIG. 6. (color online) (a) The refined magnetic structure of Co$_4$Ta$_2$O$_9$ at $T = 15$ K. The magnetic symmetry group is $C2'/c$. (b) and (c) show the buckled and the flat honeycomb layers, respectively. The magnetic arrangement is noncollinear (tilted) in the former, and collinear in the latter. The high-temperature trigonal crystallographic axes, as well as the corresponding unit cells, are shown. This structure corresponds to the [0 1 0] easy axis magnetic domain. Magnetic moments, $M(Col) = (-0.73, 2.3, 0)$ $\mu_B$ and $M(Co2) = (0.73, 2.3, 0)$ $\mu_B$ were visualized obtained from a refinement with the dagger (i) symbol in Table II. Magnetic moments are given for #1 sites in Table II and Fig. 9(c) in Appendix.

V. DISCUSSION

In this paper, we report the refined magnetic order of Co$_4$Ta$_2$O$_9$ in $C2'/c$, with the easy-axis along the trigonal [1 1 0] (or equivalent) direction. This finding could only be reached by combined single-crystal neutron diffraction and direction-dependent magnetic susceptibility measurements. A different magnetic symmetry group, $C2'/c'$, with the easy axis along [1 -1 0] was reported for the isostructural Co$_4$Nb$_2$O$_9$ compound. This difference is intriguing because it highlights a possible significance of the nonmagnetic ions (Ta$^{5+}$ or Nb$^{5+}$) in the anisotropy of the magnetic Co$^{2+}$ lattice. It might be related to the fact that both Ta and Nb are heavy elements with sizeable on-site spin-orbit coupling. Co$^{2+}$ is among a small number of 3d ions, showing a significant orbital component of the magnetic moment. In combination, these properties may result in a complex coupling between the lattice and magnetic moments. They could therefore play a key role in the observed complex magnetoelectric effects. Systematic first principles studies are highly required to establish the origin of the magnetic anisotropy and the nature of the ME coupling in this family of compounds. Experimentally, it is important to determine the microscopic magnetic interactions, as they stabilize the long-range magnetic order, and may help understand the observed ME effect. This is best done using inelastic neutron scattering. Co$_4$Nb$_2$O$_9$ has been studied using this technique, but higher energy resolution is needed to determine the interactions responsible for the proposed noncollinear structure. Such interactions typically depend on the spin-orbit coupling, and therefore are expected to play an important influence on the ME effect. A well-known example is the Dzyaloshinskii-Moriya
FIG. 7. (color online) The induced electric polarization $P$ in an applied magnetic field $H$, as predicted by the spin-flop model described in the text. Dark red arrows represent the magnetic moments. Panels (a) and (b) show the spin-flop model that is applicable to both $\text{Co}_4\text{Ta}_2\text{O}_9$ and $\text{Co}_4\text{Nb}_2\text{O}_9$. Panel (c) illustrates the collinear $C2'/c$ structure, approximating the refined noncollinear magnetic order of $\text{Co}_4\text{Ta}_2\text{O}_9$. The domain with the [1 1 0] magnetic easy axis is chosen in an applied magnetic field $H$. The induced electric polarization vector ($P$) is pointing in the magnetic field vector ($H$) direction with a canting parallel to $P$ connecting the induced electric polarization vector ($P$) to the magnetic field vector ($H$), have been measured. Then, the experimental observations of the polarization for $H \geq 1 \text{T}$ were attempted to be explained in the framework of the spin-flop model. In detail, for $H // [1 1 0]$, the spins flop in the perpendicular [1 -1 0] direction with a small canting parallel to $H$ [see Fig. 7(a)]. Similarly, for $H // [1 -1 0]$, the spins flop in the perpendicular [1 1 0] direction with a canting parallel to $H$ [see Fig. 7(b)]. For both phases, the symmetry analysis only allows the electric polarization parallel to [1 1 0]. However, for $H // [0 0 1]$, there is no a spin flop transition because the spins are already perpendicular to $[0 0 1]$. Thus, the symmetry analysis of the $C2'/c'$ structure proposed for $\text{Co}_4\text{Nb}_2\text{O}_9$ leads to the prediction that the $P$ components parallel to [-1 1 0] and [0 0 1] are allowed for $H // [0 0 1]$, but, importantly, no $P // [1 1 0]$ allowed. Experimentally, the major electric polarization component induced in both $H // [1 1 0]$ and $H // [1 -1 0]$ is indeed along [1 1 0] in $\text{Co}_4\text{Nb}_2\text{O}_9$, in agreement with this spin-flop model. However, a very significant, but unpredicted component of $P$ is also observed along [1 -1 0]: this inconsistency was suggested by the presence of multi-domains of the magnetic state. Thus, the situation is less satisfactory for $H // [0 0 1]$ as equal $P$ components along the allowed [1 -1 0] and the forbidden [1 1 0] directions are observed experimentally. This is more challenging to explain by the domain effects. An alternative scenario was proposed in a more recent single-crystal neutron diffraction study in an applied magnetic field, reporting no spin flop for $H < 10 \text{Tesla}$, and the zero-field symmetry is retained. The induced electric polarization was proposed to be related to the field-induced redistribution of the magnetic domain populations, at least in the moderate fields. Therefore, even the major features of the ME effect in $\text{Co}_4\text{Nb}_2\text{O}_9$ are far from being understood clearly.

Interestingly, the spin-flop model applicable to the magnetoelectric effect in $\text{Co}_4\text{Ta}_2\text{O}_9$ is much more satisfactory. The ME effect of $\text{Co}_4\text{Ta}_2\text{O}_9$ is qualitatively different from that of $\text{Co}_4\text{Nb}_2\text{O}_9$. In specific, at low temperatures (below 10 K), $P$ is strongly nonlinear, with switchings of $P$ directions in applied magnetic field. However, the induced $P$ is more trivial at around $T = 15 \text{K}$. This complexity requires extensive experimental and theoretical work to be understood in future.

Our goal in this paper is to establish the relation between the refined magnetic structure and components of $\text{Co}_4\text{Ta}_2\text{O}_9$ ME tensor (i.e., the allowed and forbidden ones), using the magnetic symmetry, similar to what has been tried for $\text{Co}_4\text{Nb}_2\text{O}_9$. Firstly, we note that a clearer spin-flop transition has been observed in $\text{Co}_4\text{Ta}_2\text{O}_9$ at $H \sim 0.3 \text{T}$ in both the magnetic susceptibility and polarization measurements. Thus, the spin-flop model developed for $\text{Co}_4\text{Nb}_2\text{O}_9$ can be applied to $\text{Co}_4\text{Ta}_2\text{O}_9$ with no modification: the spin-flop state is identical in the both compounds in fact. For both the [1 1 0] and [1 -1 0] in-plane magnetic fields, the induced electric polarization along the [1 1 0] direction is expected [see Figs. 7(a, b)]. This is indeed dominantly observed experimentally. A significantly smaller $P$ along [1 -1 0] is also present in $\text{Co}_4\text{Ta}_2\text{O}_9$, as in $\text{Co}_4\text{Nb}_2\text{O}_9$. The spin-flop model therefore provides a more satisfactory match to the data in $\text{Co}_4\text{Ta}_2\text{O}_9$, at least for one of the in-plane directions.

On the other hand, the applied magnetic field along the [0 0 1] direction is qualitatively different in the spin-flop model for $\text{Co}_4\text{Ta}_2\text{O}_9$ [see Fig. 7(c)] and $\text{Co}_4\text{Nb}_2\text{O}_9$ [see Fig. 4(l) in Ref. 5]. We emphasize that the field does not induce the spin flop in this case as the initial spins are already normal to the c-axis in zero field, but the spins slightly rotate towards the c-axis instead. In this situation, the zero-field magnetic symmetry plays the decisive role in predicting the ME effect, and their expected $P$ directions are different for the $C2'/c$ and the $C2'/c'$ structures.

We begin with the collinear models, to characterize the major contributions to the magnetoelectric effect. Using the spin-flop model, we find that the allowed $P$ is perpendicular to the [1 1 0] for the $C2'/c'$ group, as reported for $\text{Co}_4\text{Nb}_2\text{O}_9$. In contrast, the symmetries of the $C2'/c'$ space group established for $\text{Co}_4\text{Ta}_2\text{O}_9$ in this paper are only compatible with $P$ parallel to [1 1 0]. The collinear magnetic structure, magnetic field vector, and the induced polarization for the latter case are schematically shown in Fig. 7(c). Intriguingly, the predictions for the two magnetic space groups are mutually exclusive (owing to the exclusive application of the time-reversal symmetry). Experimentally, the induced polar-
ization in Co₄Ta₂O₉ is essentially along the [1 1 0], with only a small and additional [1 -1 0] component. Given the always existing possibility of the presence of minority magnetic domains, this is a very satisfactory match to the prediction based on the C'2'/c magnetic symmetry. Based on these results, in turn, one can also argue that the results of the ME measurements of Ref. [7] provide an additional independent confirmation of the C'2'/c magnetic space group in Co₄Ta₂O₉. We note that the symmetry-operational similarity approach [23] might also explain the selection rules of P in this buckled honeycomb lattice.

As discussed, the simplified collinear magnetic order in C'2'/c explains the major nonzero terms of the ME tensor of Co₄Ta₂O₉. The small spin tilting of the refined noncollinear magnetic order will modify this symmetry analysis results, and will allow additional ME terms, but should not modify the big picture. The larger effect is, probably, the presence of minority magnetic domains in the samples, as proposed in the Co₄Nb₂O₉ [21,22] and Co₄Ta₂O₉ [23] literature. The unexplained polarization along the [1 -1 0] with the in-plane magnetic field, for example, could be mimicked by minority [0 1 0]-type domains (as defined by the direction of the monoclinic bₘ axis) with the correctly predicted polarization, coexisting with the majority [1 1 0]-type domain. Therefore, single-domain samples are crucial for the reliable characterization of the ME effects in the A₄B₂O₉ compounds. One of the important properties of Co₄Ta₂O₉ is thus its tendency to form the dominant single-domain state in the flux-grown samples. Without this property, it would be practically impossible to establish the correct magnetic symmetry group, and to measure the ME tensor properly. It would be essential to check the anisotropic magnetic and magnetoelectric properties in single-domain samples of Co₄Nb₂O₉, and determine whether the existing description of this compound, including its magnetic symmetry, require any modification.

To explain the complex ME properties of Co₄Ta₂O₉ at the lowest temperatures, including the nonlinearity and sign reversal of the polarization, further experimental and theoretical work is called for. Characterization of the magnetic order below the anomaly at T = 6.5 K is an important task for the future work. Improvements in the consistent preparation of single-domain samples would be crucial for this work. Interestingly, a similar low-temperature anomaly was found in polycrystalline Mn₄Ta₂O₉ [15] indicating a potential role of Ta ions in this transition.

The peculiar magnetic and structural symmetries with the buckled honeycomb lattice in the A₄B₂O₉ compounds are also expected to give rise to further unusual phenomena, such as quadrupolar excitations and directional dichroism [21,23]. Thus, studies of these phenomena could result from the interplay of the subpolarizations related to the two inequivalent Co sites [2,23]. In overall, the A₄B₂O₉ compounds holds a significant promise for many future works.

VI. CONCLUSIONS

In summary, we report the magnetic order in the magnetoelectric Co₄Ta₂O₉ compound. It consists of collinear and noncollinear antiferromagnetic subsystems for the flat and buckled layers, which are alternating along the c-axis by forming the three-dimensional magnet. The direct evidence for the noncollinear magnetic order in the ab-plane is the finite intensity of (0, 0, 3) Bragg peak in the magnetically ordered phase, which is chemically-forbidden. The new magnetic space group, C'2'/c, is different from the one reported previously for the polycrystalline compound, as well as for the isostructural Co₄Nb₂O₉. This conclusion was possibly made, by combining single-crystal neutron diffraction and direction-dependent magnetic susceptibility measurements using a single crystal close to a single magnetic domain. The revised magnetic structure successfully explains the major features of the complex magnetoelectric effect in Co₄Ta₂O₉ based on the spin-flop model.

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TABLE II. Symmetry relations in the two magnetic space group candidates for Co₄Ta₂O₉. To help visualize the magnetic structure, all the magnetic moments are expressed with the trigonal lattice of the parent structure. The Symmetry column shows how magnetic moments are generated from the general atomic position, \((x, y, z)\), using the Seitz notation. The atomic numbering is illustrated in Fig. 9. At room temperature \(z=0.19186\) and 0.98604 for the Co ions in the buckled and flat layers, respectively. The ions are in the special positions with \(x\) and \(y\) taking the values of 1/3 and 2/3 [see the text for the detail]. The chosen magnetic domain has the easy axis along with \([0 1 0]\). This corresponds to the characteristic monoclinic \(b_m\) axis associated with the two-fold and mirror symmetries.

| Models | No. | Coordinates | Moments | Symmetry |
|--------|-----|-------------|---------|----------|
| \(C2'/c'\) | #1 | \((x, y, z)\) | \((M_a, M_b, M_c)\) | \{1|0\} |
| (No. 15.88) | #2 | \((1,0,0)+(-x, -x+y, -z+1/2)\) | \((-M_a, -M_a+M_b, -M_c)\) | \{2|0\|0 0 1/2\} |
| #3 | \((0,1,0)+(-x, -y, -z)\) | \((-M_a, -M_b, -M_c)\) | \{-1\|0\} |
| #4 | \((1,1,1)+(-x, -y, -z)\) | \((-M_a, -M_b, -M_c)\) | \{-1\|0\} |
| \(C2'/c\) | #1 | \((x, y, z)\) | \((M_a, M_b, M_c)\) | \{1|0\} |
| (No. 15.87) | #2 | \((1,0,0)+(-x, -x+y, -z+1/2)\) | \((M_a, M_a-M_b, M_c)\) | \{2|0\|0 0 1/2\} |
| #3 | \((0,1,0)+(-x, -y, -z)\) | \((-M_a, -M_a+M_b, -M_c)\) | \{m|0\|0 0 1/2\} |
| #4 | \((1,1,1)+(-x, -y, -z)\) | \((-M_a, -M_b, -M_c)\) | \{-1\|0\} |

This fixed crystal structure was utilized in magnetic refinements. To attain the most reliable magnetic structure determination, the refinements in the ordered state at 15 K were done using only the lower wave vector peaks with \(Q \leq 6.28 \text{ Å}^{-1}\). This is a standard scheme in magnetic structure refinements because the magnetic form factor of \(
C^{2+}\) goes essentially to zero for the higher \(Q\) (beyond \(7 \text{ Å}^{-1}\)) (assuming only the spin angular momentum). We find this common magnetic form factor works well with our data.

For the systematic analysis, we used the common set of reflections in the refinements at two temperatures. Also, all other parameters with the fixed crystal structure including the extinction parameters, the scaling factors and so on, which were obtained from the whole 25 K reflection, were fixed, too in the magnetic refinements. In this approach, we assume that the change in intensities of Bragg peaks below \(T_N\) could be ignorable as they are expected to be much smaller than the change in intensities of Bragg peaks owing to the onset of the magnetic order. This could be justified with a weak and isotropic magnetodielectric coupling observed in \(\text{Co}_2\text{Nb}_2\text{O}_9\) below \(T_N\) without an external magnetic field.

As a result, 397 (1006) reflections were used in the magnetic refinements for the flux (TSFZ) sample. These are the reflections shown in Fig. 4 in the main text. The values of the \(\text{Co}^{2+}\) magnetic moments shown in Table I are systematically smaller for the flux crystal in comparison to those of the TSFZ sample. This discrepancy is slightly reduced if multi-domain refinements are done for the flux crystal. Since the quality of the fit was not improved significantly in such trials, and because our magnetic susceptibility measurements consistently identify the flux crystal, being close to the dominant single-domain, these refinements were not pursued further. We note that the observed variation of the magnetic moment values lies well within the limits of the discrepancy of the

\(q=(0, 0, 0)\) was done in Bilbao Crystallographic Server[13]. The observed reflections with the intensities \(I > 3.0\sigma(I)\) were used in the refinements.

The nuclear structure at 25 K (the paramagnetic state) was refined first, using the entire set of the collected Bragg peaks (by also including peaks for \(Q > 6.28 \text{ Å}\)).

![FIG. 8. (color online) ZFC magnetic susceptibilities for various directions of the ab-plane magnetic fields, as classified in an inset. The trigonal notation is adopted. The data for the opposite magnetic field directions, such as \([1 1 0]\) and \([-1 -1 0]\) are shown with the line and the symbol of the same color. Vertical dashed lines mark the transition for the long-range magnetic order at 20.3 K and a complex magnetic state at 6.65 K.](image-url)
Appendix C: Magnetic symmetry relations

In this work, the magnetic refinements were carried out using two candidates, monoclinic magnetic space groups, $C2/c'$ and $C2'/c$. As the magnetic order in the $A_2B_2O_9$ compounds can be visualized better using the unit cell and crystallographic axes of the parent trigonal space group $P3c1$, we consistently adopted the trigonal setting in this paper. This Appendix provides the relevant symmetry relations for those magnetic space groups. The parent trigonal $Co_4Ta_2O_9$ structure have two crystallographically different $Co$ sites, denoted as $Co1$ and $Co2$. These distinct sites form the buckled and the flat $Co$ layers, respectively. They occupy the 4d Wyckoff position, generating four equivalent sites: $(1/3, 2/3, z)$, $(2/3, 1/3, -z+1/2)$, $(2/3, 1/3, -z)$, and $(1/3, 2/3, z+1/2)$. For the buckled layer, $z \sim 0.192$, while for the flat later $z \sim 0.986$ (room temperature values). The symmetry operators connecting the magnetic moments are given using the Seitz notation in Table 11. This notation gives the rotational transformation on the left, and the following translational transformation on the right. The atoms connected by these transformations are marked with white arrows in Fig. 9(a). The relations between the crystallographic axes of the trigonal and monoclinic unit cells are shown in Fig. 9(a). There unit cells are transformed by $a_m = 2a + b$, $b_m = b$, $c_m = c$, where the subscript $m$ refers to the monoclinic axes. Table 11 provides the magnetic moments in the trigonal notation, and therefore it can be used directly to generate the magnetic structures in the extended parent unit cell. As an example, two magnetic structures generated using these rules for the $C2/c'$ and the $C2'/c$ groups are shown in Figs. 9(b, c). In Figs. 9(b, c), we again confirm that the total magnetic moments is zero within the unit cell by illustrating clearly how moments are canceled out even with a general noncollinear in-plane magnetic order of the buckled layer. Note that these magnetic structures are one of the most general types, unrelated to the actual structure of $Co_4Ta_2O_9$.

Regarding $Co_4Ta_2O_9$, the important realizations of these symmetry rules are the collinear structures with zero $e$-axis moments. For such structures, Table 11 gives $M_a = 2M_b$ for $C2/c'$, and $M_a = 0$ for $C2'/c$. The corresponding magnetic structures are illustrated in Fig. 10. Note that the magnetic moments in one of these structures (and therefore the corresponding magnetic easy axis) are perpendicular to the moments in the other. The origin of the three in-plane magnetic domains can be best understood using the structure shown in Figs. 10(e, f) and the crystallographic axes in Fig. 9(a). In both figures, the moments are along the coinciding trigonal $b$ and monoclinic $b_m$ axes. We note that the other two magnetic domains are generated when the $b_m$ axis points along the equivalent $[1 0 0]$ and $[-1 -1 0]$ trigonal directions. The latter domain, with the easy axis along the $[1 1 0]$ (ignoring the anti-phase), and the hard axis along $[1 -1 0]$ is usually used in the literature describing the

reported moments for $Co_4Nb_2O_9$ and is therefore attributable to the general accuracy of the method.

For completeness, we provide fitted magnetic moments of noncollinear magnetic structures with nonzero $M_e$ components at $15$ K in $C2'/c$. $M(\text{Co1}) = (-0.61, 1.64, 0) \mu_B$ and $M(\text{Co2}) = (0.61, 1.64, -0.2) \mu_B$ from the flux data, and $M(\text{Co1}) = (-0.58, 2.29, 0.23) \mu_B$ and $M(\text{Co2}) = (0.58, 2.29, 1.58) \mu_B$ from the TSFZ data. Note that both flux and TSFZ data is fitted well with reversed signs of $M_e$, meaning its insensitivity to determine the sign of $M_e$ in our analysis.
FIG. 10. (color online) Collinear antiferromagnetic order in the plane, assuming $M_c = 0$, by (a-c) the $C_2'/c$ space group, and by (d-f) the $C_2/c'$ space group. Trigonal unit cells were used. These magnetic orders are refined using the TSFZ crystal data analysis given in Table I in the main text. $M(Co1) = (3.26, 1.63, 0) \mu_B$, $M(Co2) = (2.13, 1.06, 0) \mu_B$ for (a-c) and $M(Co1) = (0, 2.2, 0) \mu_B$, $M(Co2) = (0, 2.2, 0) \mu_B$ for (d-f): magnetic moments for #1 sites in Table II are given with respect to trigonal notations.

magnetoelectric effects in this family of compounds.

Appendix D: Magnetic structure factor of (0, 0, L) peaks

Herein, the analytical expression for the magnetic structure factor of the (0, 0, L) peaks is given for the $C_2'/c$ and the $C_2/c'$ magnetic space groups. The magnetic structure factor is defined as

$$F_{hkl} = \sum_{i=1}^{N} M_i e^{i \mathbf{k} \cdot \mathbf{R}_i}, \quad (D1)$$

where $M_i$ is the magnetic moment vector at the $i$-th ionic site, $\mathbf{R}_i$ is the fractional coordinate of the $i$-th ion in the unit cell. $N$ runs from 1 to 4 as there are four equivalent atomic sites in these magnetic space groups. The magnetic structure factors of (0, 0, L) can be calculated using the atomic coordinates and the magnetic moments in Table II. For each Co1 and Co2 ions, one obtains

$$F_{(0,0,L)} = -2i \sin(2\pi z_1)(M_a - 2M_b)\hat{b} \quad (D2)$$

for $C_2'/c$ (No. 15.88) and

$$F_{(0,0,L)} = 2i \sin(2\pi z_1)(2M_a\hat{a} + M_b\hat{b} + 2M_c\hat{c}) \quad (D3)$$

for $C_2'/c$ (No. 15.87). Here $\mathbf{M} = (M_a, M_b, M_c)$ is the magnetic moment of the #1 site in the trigonal notation, $z$ is its fractional coordinate of the #1 site for either Co1 or Co2, and $\hat{a}$, $\hat{b}$, $\hat{c}$ are the trigonal crystallographic unit vectors. Equations (D2) and (D3) are identical for both the Co1 and Co2 positions. The net magnetic structure factor is the sum of the contributions from both Co sites in the unit cell, and the magnetic Bragg peak intensity is proportional to $|F_{(0,0,L)}|^2$.

We point out that the (0, 0, odd) nuclear Bragg peaks are forbidden in the parent trigonal structure, and also in the monoclinic space group of No. 15. The condition of magnetic moments, $M_a = 2 M_b$ in $C_2'/c'$, and $\mathbf{M} = M_b \hat{b}$ in $C_2'/c$ (as discussed in a previous section), Eqs. (D2) and (D3) give zero intensities for all (0, 0, odd) peaks. However, when the above conditions are violated, finite (0, 0, odd) peaks are measured.

In Eq. (D3), a finite $M_c$ in the $C_2'/c$ group gives a finite $F_{(0,0,L)}$. However, the only perpendicular component of magnetic moments to the scattering vector can be measured in neutrons. As $M_c$ is parallel to the wave vector (0, 0, odd), the experimentally observed neutron intensity of the (0, 0, odd) peak cannot contain the contribution from $M_c$. Note that, in the $C_2'/c'$ group, $M_c$ does not contribute $F_{(0,0,L)}$, as shown in Eq. (D2).

Our experimental observation of the (0, 0, 3) peak in Co$_4$Ta$_2$O$_9$ at 15 K [see Fig. 5] thus directly proves the existence of the $M_a$ component in the $C_2'/c$ magnetic structure. Our refined magnetic order [see Fig. 6] showed finite $M_a$ values for both the buckled and flat honeycomb, indicating contributions from both types of layers.
note that the finite $M_a$ of Co2 ions (the flat honeycomb) also contribute the $(0, 0, 3)$ peak intensity, according to Eq. (D3), although their moments are collinear within one flat honeycomb layer due to the $-1'$ symmetry between moments of #1 and #4, and those of #2 and #3 in Table II. This might be rather counterintuitive at a first glance, however, the contribution in fact comes from the noncollinear relation between moments lying in the different flat layer in the unit cell [see Fig. 6(a)].