Zeeman effect in centrosymmetric antiferromagnets controlled by electric field

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Centrosymmetric antiferromagnets, although abundant in nature, seem less promising than ferromagnets or ferroelectrics for practical applications in semiconductor spintronics. As a matter of fact, the lack of spontaneous polarization and magnetization hinders the efficient utilization of electronic spin in these materials. Here, we propose a paradigm to harness electronic spin in centrosymmetric antiferromagnets via Zeeman spin splittings of electronic energy levels – termed as spin Zeeman effect – which is controlled by an electric field. By symmetry analysis, we identify twenty-one centrosymmetric antiferromagnetic point groups that accommodate such a spin Zeeman effect. We further predicted by first-principles that near-room temperature antiferromagnetic SrFe$_2$S$_2$O is an excellent candidate showcasing a Zeeman splitting as large as $\sim$75 meV, induced by an electric field of 0.15 V/Å. Moreover, the electronic spin magnetization associated to the split energy levels is switchable when reversing the electric field. Our work thus sheds light on the electric-field control of electronic spin in antiferromagnets, which broadens the scope of application of centrosymmetric antiferromagnets.

Introduction

The spontaneous magnetization in ferromagnets breaks the time-reversal symmetry, causing spin Zeeman effect, the spin splittings of electronic energy levels \([1, 2]\). Similarly, ferroelectrics lose their inversion center because of their spontaneous polarization \([3, 4]\). Consequently, the spin-orbit interaction may also lift the degeneracy of electronic spin energy levels, known as Rashba-Dresselhaus effect \([3, 6]\). The Zeeman and Rashba-Dresselhaus effects result in a sequence of intriguing phenomena such as spin interference and spin Hall effect \([2, 7, 8]\). More promisingly, Zeeman and Rashba-Dresselhaus effects in ferromagnets and ferroelectrics are easily controllable by magnetic or electric field via the modification of magnetization or polarization, which is important for the design of novel semiconductor spintronic devices (e.g., spin transistor) \([24]\).

In sharp contrast to ferromagnets and ferroelectrics, centrosymmetric antiferromagnets are provided with no polarization and a magnetization that is either null or tiny. The centrosymmetric antiferromagnets – in spite of their abundance in nature – thus seem not that exciting for practical applications in semiconductor spintronics \([9, 13]\). In the absence of polarization and magnetization, it is challenging to control the antiferromagnetic structures in centrosymmetric antiferromagnets \([9, 14]\), and, consequently, electric and magnetic fields seem to be unlikely to control electronic spin efficiently in these materials. Interestingly, two recent works, focusing on nonlinear photocurrent in MnBi$_2$Te$_4$ \([15]\) and magneto-optic Kerr effect in MnPSe$_3$ \([16]\), hint a possibility towards the field-induced spin splittings in antiferromagnets. Lately, efforts were also made to explore the possible spin splittings hosted by antiferromagnets, with the discoveries of several previously-overlooked patterns (see, e.g., Refs. \([13, 17–23]\)). Yet, the general conditions and underlying mechanisms to the control of spin splittings by magnetic or electric field in centrosymmetric antiferromagnets still remain elusive.

Here, we combine symmetry analysis and first-principles simulations to explore the possible spin splittings – controllable by electric field – that are hosted by centrosymmetric antiferromagnets. We discover that there are twenty-one centrosymmetric antiferromagnetic point groups that accommodate electrically controllable Zeeman spin splitting. We further predict that the near-room temperature antiferromagnetic SrFe$_2$S$_2$O is a promising real material, in which a large Zeeman spin splitting of $\sim$75 meV can be created by electric field of 0.15 V/Å. The electronic spin magnetization associated to the split spin energy levels is confirmed to be switchable by reversing the electric field.

Results

Couplings between polarization and spin. – Let us start with eleven type-II Shubnikov magnetic point groups \([24]\), namely, $1'$, $2/m1'$, $mmm1'$, $4/m1'$, $4/mmm1'$, $31'$, $3m1'$, $6/m1'$, $6/mmm1'$, $m31'$, and $m3m1'$, that contain both inversion \(i\) and time-reversal
θ symmetry operations. Any of these magnetic point groups (e.g., $G'$) can be uniformly written as $G' = G \cup \theta G$, where $G = G_0 \cup \theta G_0$ is the crystallographic point group and $G_0$ is the subgroup of $G$ containing only proper rotations $[24][20]$. We aim at finding the minimal couplings involving electric polarization and spin with respect to $G'$ group. To this end, we examine the transformation behaviors of spin angular momentum operator $S_{\alpha}$ and electric polarization $P_{\beta}$ under $\theta$ and $\bar{\theta}$, where $\alpha, \beta = x, y, z$ denote the Cartesian components (see Fig. 1). Normally, the coupling $P_{\beta}S_{\alpha}$ (if existing) implies the electronic spin splittings induced by polarization $P_{\beta}$, recalling that spin splitting is characterized by $\sigma_{\alpha}$ where $S_{\alpha} = \frac{h}{2} \sigma_{\alpha}$ in $S_z$-representation. Figures $\text{I}^\prime$–$\text{III}$ indicate the following transformation rules, namely, $\bar{\theta} : S_{\alpha} \rightarrow -S_{\alpha}, \sigma_{\alpha} \rightarrow -\sigma_{\alpha}, P_{\beta} \rightarrow -P_{\beta}$ and $\theta : S_{\alpha} \rightarrow S_{\alpha}, \sigma_{\alpha} \rightarrow \sigma_{\alpha}, P_{\beta} \rightarrow P_{\beta}$. Hence, the bilinear coupling between polarization and spin does not exist in the presence of either inversion or time-reversal, because $\bar{\theta} : P_{\beta}\sigma_{\alpha} \rightarrow -P_{\beta}\sigma_{\alpha}$; $\theta : P_{\beta}\sigma_{\alpha} \rightarrow -P_{\beta}\sigma_{\alpha}$.

We move on to explore the trilinear coupling $XP_{\beta}\sigma_{\alpha}$ is allowed by symmetry or not. First, to fulfill the inversion and time-reversal symmetries, $X$ should be a quantity such that under $\theta : X \rightarrow -X$ and $\bar{\theta} : X \rightarrow -X$. Figures $\text{I}^\prime$–$\text{III}$ showcase such a possible $X$ extracted from an antiferromagnetic structure. For demonstrating purpose, we simply assume that the $X$ quantity, namely, magnetic order parameter, is formed by two atoms labelled by $X'$ and $X''$, where $X'$ and $X''$ are of the same atomic species, but carry magnetic moments along opposite directions (see Fig. $\text{I}^\prime$). Under inversion $\bar{\theta}$, the $X'$ and $X''$ atoms swap their positions, while their carried magnetic moments remain unchanged (see Fig. $\text{I}^\prime$); Under time-reversal $\theta$, the $X'$ and $X''$ atoms remain in place with the magnetic moments being flipped (see Fig. $\text{I}^\prime$). This leads to $\bar{\theta} : X \rightarrow -X$ and $\theta : X \rightarrow X'$. Consequently, $XP_{\beta}\sigma_{\alpha}$ is compatible with inversion and time-reversal symmetries. Next, $XP_{\beta}\sigma_{\alpha}$ should be allowed by the proper rotation operations in $G_0$, subgroup of $G'$. The $11'$ magnetic point group is the simplest case to tackle, because its corresponding $G_0$ group only contains identity symmetry operation $\bar{\theta}$. Consequently, nine different couplings $XP_{\beta}\sigma_{\alpha}$ with $\alpha, \beta = x, y, z$ are permitted by symmetry operations of $11'$ group. Unfortunately, the situation for the remaining ten Shubnikov magnetic point groups is quite complicated, since $G_0$ group contains more symmetry operations than identity, leading to additional symmetry constraint to $XP_{\beta}\sigma_{\alpha}$. For instance, $z_{\alpha}$, rotation of $\pi$ along $z$ direction, transforms $P_x, P_z$, and $\sigma_z$ as $z_{\alpha} : P_x \rightarrow P_z, P_z \rightarrow -P_x, \sigma_z \rightarrow -\sigma_z$. As a result, $z_{\alpha}$ transforms $XP_z\sigma_z$ and $XP_z\sigma_z$, via $z_{\alpha} : XP_z\sigma_z \rightarrow XP_z\sigma_z, XP_z\sigma_z \rightarrow -XP_z\sigma_z$, assuming that $X$ is invariant under $z_{\alpha}$. In this case, $XP_z\sigma_z$ is allowed by $z_{\alpha}$ rotation, while $XP_z\sigma_z$ is not. Apparently, the symmetry analysis regarding these ten Shubnikov magnetic point

| Group | $P_x$ | $P_y$ | $P_z$ |
|-------|-------|-------|-------|
| $\sigma_x$ | $\sigma_y$ | $\sigma_z$ |
| $1'$ | $\lambda_{\alpha,\beta}P_{\beta}\sigma_{\alpha}$ | $\lambda_{\alpha,\beta}P_{\beta}\sigma_{\alpha}$ | $\lambda_{\alpha,\beta}P_{\beta}\sigma_{\alpha}$ |
| $2/m'$ | $\lambda_{\alpha,\beta}P_{\beta}\sigma_{\alpha}$ | $\lambda_{\alpha,\beta}P_{\beta}\sigma_{\alpha}$ | $\lambda_{\alpha,\beta}P_{\beta}\sigma_{\alpha}$ |
| $2/m$ | $\lambda_{\alpha,\beta}P_{\beta}\sigma_{\alpha}$ | $\lambda_{\alpha,\beta}P_{\beta}\sigma_{\alpha}$ | $\lambda_{\alpha,\beta}P_{\beta}\sigma_{\alpha}$ |
| $m'm'm'$ | $\lambda_{\alpha,\beta}P_{\beta}\sigma_{\alpha}$ | $\lambda_{\alpha,\beta}P_{\beta}\sigma_{\alpha}$ | $\lambda_{\alpha,\beta}P_{\beta}\sigma_{\alpha}$ |
| $mmm$ | $\lambda_{\alpha,\beta}P_{\beta}\sigma_{\alpha}$ | $\lambda_{\alpha,\beta}P_{\beta}\sigma_{\alpha}$ | $\lambda_{\alpha,\beta}P_{\beta}\sigma_{\alpha}$ |
| $4/m'$ | $\lambda_{\alpha,\beta}P_{\beta}\sigma_{\alpha}$ | $\lambda_{\alpha,\beta}P_{\beta}\sigma_{\alpha}$ | $\lambda_{\alpha,\beta}P_{\beta}\sigma_{\alpha}$ |
| $4'/m'$ | $\lambda_{\alpha,\beta}P_{\beta}\sigma_{\alpha}$ | $\lambda_{\alpha,\beta}P_{\beta}\sigma_{\alpha}$ | $\lambda_{\alpha,\beta}P_{\beta}\sigma_{\alpha}$ |
| $4'/m'm'$ | $\lambda_{\alpha,\beta}P_{\beta}\sigma_{\alpha}$ | $\lambda_{\alpha,\beta}P_{\beta}\sigma_{\alpha}$ | $\lambda_{\alpha,\beta}P_{\beta}\sigma_{\alpha}$ |
| $6/m'$ | $\lambda_{\alpha,\beta}P_{\beta}\sigma_{\alpha}$ | $\lambda_{\alpha,\beta}P_{\beta}\sigma_{\alpha}$ | $\lambda_{\alpha,\beta}P_{\beta}\sigma_{\alpha}$ |
| $6/m'm'$ | $\lambda_{\alpha,\beta}P_{\beta}\sigma_{\alpha}$ | $\lambda_{\alpha,\beta}P_{\beta}\sigma_{\alpha}$ | $\lambda_{\alpha,\beta}P_{\beta}\sigma_{\alpha}$ |
| $m'3$ | $\lambda_{\alpha,\beta}P_{\beta}\sigma_{\alpha}$ | $\lambda_{\alpha,\beta}P_{\beta}\sigma_{\alpha}$ | $\lambda_{\alpha,\beta}P_{\beta}\sigma_{\alpha}$ |
| $m'3'$ | $\lambda_{\alpha,\beta}P_{\beta}\sigma_{\alpha}$ | $\lambda_{\alpha,\beta}P_{\beta}\sigma_{\alpha}$ | $\lambda_{\alpha,\beta}P_{\beta}\sigma_{\alpha}$ |
FIG. 2. Panel a shows the crystal structure of SrFe$_2$S$_2$O. Panel b displays the magnetic configuration. Panels c and d give the resulting magnetic structures after transforming panel b by time-reversal $\theta$ and inversion $\bar{1}$, respectively. The black sphere in panels b–d marks the inversion center.

groups is rather tedious and is thus omitted here. Interested readers may find the details in our Supplementary Material (SM).

Now we interpret the physical meaning of the symmetry-allowed coupling $XP_{\beta}\sigma_\alpha$, which is derived with respect to type-II Shubnikov $G'$ magnetic point groups. Let us recall that the existence of order parameter $X$ breaks inversion $\bar{1}$, time-reversal $\theta$, and/or some other symmetry operations of $G'$ group. Such symmetry breaking lowers the symmetry of the system from $G'$ group to its subgroup $g'$ which contains the operations that are not broken by $X$. In such sense, $X$ is invariant under all the symmetry operations of $g'$. With respect to $g'$ group, the effective Hamiltonian term $\lambda'_{\beta,\alpha}XP_{\beta}\sigma_\alpha$ can be re-written as $\lambda'_{\beta,\alpha}P_{\beta}\sigma_\alpha$, noting that the invariant quantity $X$ is absorbed by the coefficient $\lambda'_{\beta,\alpha}$. Therefore, to find a real material hosting $X$ order parameter and $\lambda'_{\beta,\alpha}P_{\beta}\sigma_\alpha$ coupling, effort should be made to search for materials with magnetic point group $g'$. Following this logic, we have found twenty-one type-III Shubnikov magnetic point groups that accommodate the $\lambda'_{\beta,\alpha}P_{\beta}\sigma_\alpha$ couplings, summarized in Table I (see SM for our detailed derivations). These magnetic point groups do not have inversion $\bar{1}$ or time-reversal $\theta$, but rather exhibit parity-time symmetry ($i\theta$). In essence, these twenty-one type-III Shubnikov magnetic point groups are centrosymmetric in the four-dimensional spacetime, since the $i\theta$ symmetry operation transform the spatial-temporal coordinate $(x,y,z,t)$ to $(-x,-y,-z,-t)$. Hence, none of these twenty-one magnetic point groups host spontaneous ferromagnetism or electric polarization. According to the $\lambda'_{\beta,\alpha}P_{\beta}\sigma_\alpha$ coupling, the $i\theta$ symmetry operation is broken in the presence of polarization, yielding Zeeman-type spin splittings. This coincides with the previous symmetry analysis which indicates that the generation of spin splitting requires the breakdown of parity-time symmetry (see e.g., Refs. [13, 15–18, 27–29]).

Let us take $m'm'm'$ magnetic point group as our testing bed. Table I indicates the $\lambda_{x,x}, \lambda_{y,y}$, and $\lambda_{z,z}$ couplings for $m'm'm'$ magnetic point groups. We thus arrive at the effective Hamiltonian for $m'm'm'$ as

$$H(m'm') = \lambda_{z,z}P_{z}\sigma_z + \lambda_{x,x}P_{x}\sigma_x + \lambda_{y,y}P_{y}\sigma_y = \kappa_{z,z}E_z\sigma_z + \kappa_{x,x}E_x\sigma_x + \kappa_{y,y}E_y\sigma_y,$$  \hspace{1cm} (1)

where $E_\alpha$ is the electric field along $\alpha$ direction. Here, the second line comes from the fact that $E_\alpha$ polarizes centrosymmetric materials by creating $P_\alpha$. Strikingly, the $\kappa_{\alpha,\alpha}E_\alpha\sigma_\alpha$ term in Eq. (1) is mathematically similar to the conventional Zeeman energy $\mu_BB_\alpha\sigma_\alpha$ ($\mu_B$ being Bohr magneton) [2, 31]. This means that, in $m'm'm'$ magnetic point group, electric field $E_\alpha$ plays a similar role as “magnetic field” to create Zeeman-type effect and control electronic spin. Another example is the effective Hamiltonian for $3'm'$, given by

$$H(3'm') = \lambda_{x,x}(E_x\sigma_x + E_y\sigma_y) + \lambda_{z,z}E_z\sigma_z,$$  \hspace{1cm} (2)

which indicates that applying electric field $E_z$ to $3'm'$ creates Zeeman spin splittings. Such splittings were claimed to be critical for the nonlinear photocurrent effect in topological material MnBi$_2$Te$_4$ [15].
Controlling Zeeman effect by electric field. – Based on Table I it is readily to search from the magnetic database (e.g., MAGNDATA [32]) for possible materials which permit such a Zeeman effect controllable by electric field. Promisingly, we have found an antiferromagnetic material SrFe$_2$S$_2$O with a Néel temperature of 216 K [33], near room temperature. The associated magnetic order parameter of SrFe$_2$S$_2$O breaks inversion and time-reversal (see Fig. 2), giving rise to $Pm'\bar{n}'o'$ magnetic space group ($m'n'm'$ point group). Specifically, SrFe$_2$S$_2$O carries a magnetic structure whose predominant magnetic moments for Fe$_1$ and Fe$_3$ (respectively, Fe$_2$ and Fe$_4$) are along $y$ (respectively, $-y$) direction. Employing this magnetic structure, we use first-principles to compute the band structures of SrFe$_2$S$_2$O (see Figs. S2 and Section III.1 in the SM). In particular, we consider four typical cases, namely, SrFe$_2$S$_2$O having no electric polarization, or with polarization created by electric field $E_x$, $E_y$, or $E_z$ with a magnitude of 0.15 V/Å. The valence band maximum (VBM) for these cases are all located at the $\Gamma$ point, and the spin levels are (i) degenerate for non-polarized, (ii) nearly degenerate for $E_x$-polarized, (iii) slightly split for $E_z$-polarized, and (iv) obviously split for $E_y$-polarized SrFe$_2$S$_2$O material. Promisingly, the $E_y$ electric field of 0.15 V/Å generates a large Zeeman spin splitting of $\sim$75 meV, comparable to the Zeeman splitting value in typical diluted magnetic semiconductors (e.g., $\sim$75 meV driven by magnetic field of $\sim$ 3 T in Zn$_{0.95}$Mn$_{0.05}$Te [34]).

Our numerical simulations further indicate that the magnitudes of Zeeman spin splitting are in perfect linear relationship with $E_x$ (see Fig. 3), confirming Eq. [1]. We notice that the electric field $E_x$ of 0.15 V/Å causes nearly null Zeeman spin splitting. This implies the smallness of the coupling coefficient $\kappa_{x,x}$ in Eq. [1]. Interestingly, the spin splittings induced by $E_y$ and $E_z$ in SrFe$_2$S$_2$O exhibit highly distinct characteristics. That is, the Zeeman spin splitting induced by $E_y$ is far larger than that generated by $E_z$ of the same magnitude as $E_y$. To interpret such features, we analyze the spin magnetization ($S_x$, $S_y$, $S_z$) associated with the two top most energy sublevels at the $\Gamma$ point. When polarizing SrFe$_2$S$_2$O by $E_\alpha$ ($\alpha = x, y, z$) electric field, an effective magnetic field $B_{\alpha}^{\text{eff}} \propto E_\alpha$ is created in the material. The effective magnetic field $B_{\alpha}^{\text{eff}}$ couples with $S_\alpha$ spin magnetization, causing a Zeeman energy proportional to $\pm B_{\alpha}^{\text{eff}} S_\alpha$, where the $\pm$ sign characterizes the sublevels whose $\alpha$ spin magnetization component are positive or negative. Polarizing SrFe$_2$S$_2$O by $E_y$=0.15 V/Å and $E_z$=0.15 V/Å leads to the spin magnetization of $S_y \approx \pm 0.7$ and $S_z \approx \pm 0.07$, respectively. The predominant $S_y$ component implies that the Zeeman spin splitting created by $E_y$ is the most prominent. The detailed analysis can be found in Section III.2 of the SM.

We now address whether the spin magnetization for SrFe$_2$S$_2$O at the VBM is switchable by electric field. We focus on the top valence band structures along the Z-$\Gamma$-X-$\Gamma$-Y line. The band structures for SrFe$_2$S$_2$O polarized by $E_y$ = +0.15 V/Å and $E_y$ = −0.15 V/Å are shown in Figs. 4a and 4b, respectively. When switching the electric field from $E_y$ = +0.15 V/Å to $E_y$ = −0.15 V/Å, the spin magnetization at the VBM changes from $S_y$ = 0.75 to $S_y$ = −0.75. Also, the $S_z$ component can also be switched by $E_z$ (see Fig. S3 of the SM). However, the $S_z$ spin magnetization at the VBM is quite small, for instance, 0.07 in the presence of $E_z$ = +0.15 V/Å, as indicated above. Moreover, the spin splittings induced by $E_y$ = +0.15 V/Å and $E_z$ = −0.15 V/Å are too tiny to detect. For interpretation, we further analyze the orbital-projected spin magnetization at the $\Gamma$ point for SrFe$_2$S$_2$O material, shown in Sections III.2 and III.3 of the SM.
Discussion

We have shown that electric field induces polarization distortion in materials belonging to one of the twenty-one magnetic point groups (Table I), yielding an effective magnetic field which causes Zeeman spin splitting. Let us recall that such an effective magnetic field might also drive net magnetization in these antiferromagnets. As shown in Ref. [35], the tabulated magnetoelectric tensors for these twenty-one groups are similar to our derived Zeeman coupling coefficients (Table I). In such sense, our proposed twenty-one magnetic point groups also host the magnetoelectric effect. We then examine the net magnetization of the antiferromagnetic SrFe$_2$S$_2$O in the presence of $E_\parallel$=0.15 V/Å, $E_\perp$=0.15 V/Å, and $E_\perp$=0.15 V/Å. The electric-field-driven net magnetization is found to be too tiny to detect (i.e., $< 0.003 \mu_B/\text{f.u.}$). This demonstrates somewhat why centrosymmetric antiferromagnets are not so promising for spintronic applications, as commonly believed. On the other hand, our work clearly indicates that for spintronic applications, as commonly believed.

On the kinetic cutoff energy of 550 eV and a $k$-point mesh of 10×4×6 for the unit cell of SrFe$_2$S$_2$O given by Pmma space group [see Fig. 2(a) of the Main Text]. Our structural relaxations are carried out by using conjugate gradient algorithm (e.g., IBRION = 2 in the INCAR) with the force convergence criteria of 5 meV/Å. We mimic the effect of electric field on crystal structure of SrFe$_2$S$_2$O using a first-principles-based approach (see, e.g., Ref. [30]). Various databases, toolkits and packages are also widely used in this work, including Mathematica [43], Materials project [40, 47], VESTA [48], VASPKit [49, 50], Matplotlib [51], SeeK-path [52–54], Findsym [55, 56], and Bilbao Crystallographic Server [57, 58] (the POINT [59] and MAGNDA T [32] modules). In particular, our band structures are analyzed and visualized thanks to the PyProcar code [60, 61].

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Competing interests

The authors declare no competing financial interests.

Methods

In the present work, we use the VASP code [40, 41] – based on projector augmented wave potentials [42] together with LDA (Ceperley-Alder) functional [43] – to perform the first-principles simulations. We employ the LDA functional because such a functional improves the numerical convergence when doing the non-collinear magnetism calculations for SrFe$_2$S$_2$O compound. For the same reason, we use a relatively low Hubbard $U$ value (i.e., 2.0 eV, by the “Dudarev” approach [44]) to treat the strong correlation effect of Fe’s 3$d$ electrons. We solve 10 electrons for Sr (4$s^2p^6$s), 16 for Fe (3$s^2p^6$d$^8$), 6 for S (3$s^3$p), and 6 for O (2$s^2$p), respectively, with the kinetic cutoff energy of 550 eV and a $k$-point mesh of $10 \times 4 \times 6$ for the unit cell of SrFe$_2$S$_2$O given by Pmma space group [see Fig. 2(a) of the Main Text]. Our structural relaxations are carried out by using conjugate gradient algorithm (e.g., IBRION = 2 in the INCAR) with the force convergence criteria of 5 meV/Å. We mimic the effect of electric field on crystal structure of SrFe$_2$S$_2$O using a first-principles-based approach (see, e.g., Ref. [30]). Various databases, toolkits and packages are also widely used in this work, including Mathematica [43], Materials project [40, 47], VESTA [48], VASPKit [49, 50], Matplotlib [51], SeeK-path [52–54], Findsym [55, 56], and Bilbao Crystallographic Server [57, 58] (the POINT [59] and MAGNDA T [32] modules). In particular, our band structures are analyzed and visualized thanks to the PyProcar code [60, 61].

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