

Article

Symmetry Classification of Antiferromagnets with Four Types of Multipoles

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Abstract: A plethora of antiferromagnetic structures have been so far found in condensed matter physics, where the antiferromagnetic phase transition is characterized by symmetry lowering under the magnetic point group. Depending on the types of symmetry lowering, various cross-correlation phenomena, such as the anomalous Hall effect, magneto-electric effect, and magneto-piezoelectric effect, emerge below the critical temperature. We revisit a close relationship between the symmetry of the antiferromagnetic structures and cross-correlations based on the augmented multipoles consisting of electric, magnetic, magnetic toroidal, and electric toroidal multipoles with different spatial inversion and time-reversal parities. The symmetry classification will be useful for further exploration of functional antiferromagnetic materials.

Keywords: antiferromagnets; multipole; magnetic toroidal multipole; cross-correlation; magnetic point group; group theory

1. Introduction

Magnetic ordering is one of the most fundamental electronic orderings in solids, where the spin degree of freedom in electrons is ordered through the electron correlation. Owing to the breaking of time-reversal symmetry, various physical phenomena emerge below the magnetic phase transition temperature; ferromagnetic ordering gives rise to the anomalous Hall effect [1–7] and antiferromagnetic ordering breaking the spatial inversion symmetry gives rise to the linear magnetoelectric effect [8–14]. Meanwhile, recent studies have revealed that the same physical phenomena are often caused under totally different magnetic structures when the symmetry of the magnetic structures is the same. For example, the anomalous Hall effect is induced by various types of antiferromagnetic structures including collinear [15–22], noncollinear [23–27], and noncoplanar ones [28–31] when the symmetry of the antiferromagnetic state is the same as that of the ferromagnetic state. This example suggests that antiferromagnetic ordering has the potential to exhibit further intriguing physical phenomena, which would be important for the realization of functional antiferromagnetic materials applied to spintronic devices.

The concept of augmented multipoles has been introduced to smoothly make the antiferromagnetic structures correspond to physical phenomena [32,33]. There are four types of multipoles with different spatial inversion and time-reversal parities: electric multipole with $(\mathcal{P}, \mathcal{T}) = [(-1)^l, +1]$, magnetic multipole with $(\mathcal{P}, \mathcal{T}) = [(-1)^{l+1}, -1]$, magnetic toroidal multipole with $(\mathcal{P}, \mathcal{T}) = [(-1)^l, -1]$, and electric toroidal multipole with $(\mathcal{P}, \mathcal{T}) = [(-1)^{l+1}, +1]$, where \mathcal{P} and \mathcal{T} stand for the spatial inversion and time-reversal parities, respectively, and l is the rank of the multipole. Since the four types of multipoles constitute a complete basis set in physical Hilbert space, any antiferromagnetic structures can be described by a ferroic alignment of any multipoles [34,35]. Figure 1 represents the examples of symmetry lowering by magnetic phase transitions under the tetragonal symmetry $4/mmm1'$; the antiferromagnetic structures are characterized by the magnetic monopole M_0 and the magnetic toroidal dipole T_z with $(\mathcal{P}, \mathcal{T}) = (-1, -1)$. Furthermore,



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the systematic classification of antiferromagnetic structures has been performed under the 122 magnetic point groups based on magnetic representation analysis [36].

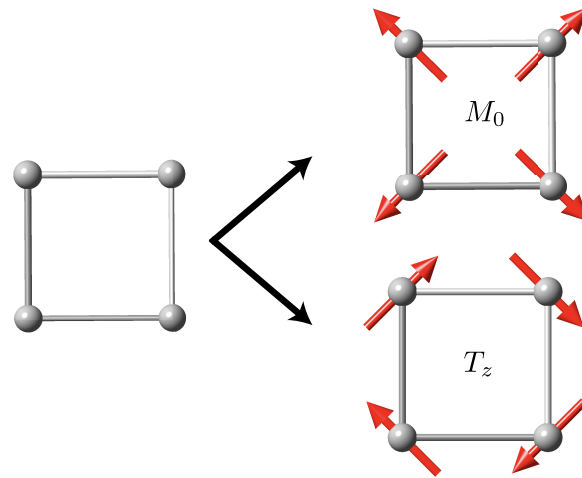


Figure 1. Examples of symmetry lowerings under magnetic phase transitions. The magnetic monopole (M_0) and the magnetic toroidal dipole (T_z) are induced when the A_{1u}^- and A_{2u}^- representations belong to the totally symmetric irreducible representation, where the superscript “ $-$ ” of irrep indicates parity with respect to the antiunitary time-reversal operation.

In the present study, we revisit such a correspondence between antiferromagnetic structures and multipoles under 122 magnetic point groups in order to demonstrate which magnetic materials exhibit functional properties. By classifying the 122 magnetic point groups in terms of the four types of multipoles, we show that almost all of the magnetic point groups accompany the multipole moments up to rank 3, and hence, we expect rich cross-correlation phenomena in antiferromagnetic materials. In order to stimulate the experimental observation, we list candidate materials and expected cross-correlations in each multipole. The present results provide useful information not only in exploring functional antiferromagnetic materials but also in reexamining the well-known materials from the multipole viewpoint.

The rest of this paper is organized as follows: In Section 2, we first introduce the four types of multipoles. Then, we show the correspondence between antiferromagnetic structures and multipoles by taking an example in the tetragonal system in Section 3. In Section 4, we discuss the expected cross-correlations when the multipole is induced. We conclude the present results in Section 5.

2. Four Types of Multipoles

First, we briefly review the four types of multipoles, consisting of electric multipole Q_{lm} , magnetic multipole M_{lm} , magnetic toroidal multipole T_{lm} , and electric toroidal multipole G_{lm} , where the subscripts l and m represent the orbital angular momentum (rank of multipole) and its z component, respectively; $m = -l, -l + 1, \dots, l$. The operator expressions of the four multipoles in spinless space are given by [37,38]

$$Q_{lm} = O_{lm}, \quad (1)$$

$$M_{lm} = \frac{1}{2} [(\nabla O_{lm}) \cdot \hat{\mathbf{m}}_l + \hat{\mathbf{m}}_l \cdot (\nabla O_{lm})], \quad (2)$$

$$T_{lm} = \frac{1}{2} [(\nabla O_{lm}) \cdot \hat{\mathbf{t}} - \hat{\mathbf{t}} \cdot (\nabla O_{lm})], \quad (3)$$

$$G_{lm} = \frac{1}{2} [(\nabla_\alpha \nabla_\beta O_{lm}) \hat{g}_l^{\alpha\beta} - (\hat{g}_l^{\alpha\beta})^\dagger (\nabla_\alpha \nabla_\beta O_{lm})], \quad (4)$$

where $O_{lm}(\mathbf{r})$ is proportional to the spherical harmonics as follows:

$$O_{lm}(\mathbf{r}) = \sqrt{\frac{4\pi}{2l+1}} r^l Y_{lm}(\hat{\mathbf{r}}), \tag{5}$$

with $\hat{\mathbf{r}} = \mathbf{r}/r$. $\hat{\mathbf{m}}_l$, $\hat{\mathbf{t}}_l$, and $\hat{g}_l^{\alpha\beta}$ are represented by

$$\hat{\mathbf{m}}_l = \frac{2\hat{\mathbf{l}}}{l+1}, \tag{6}$$

$$\hat{\mathbf{t}}_l = \frac{2}{(l+1)(l+2)} (\mathbf{r} \times \hat{\mathbf{l}}), \tag{7}$$

$$\hat{g}_l^{\alpha\beta} = \hat{t}_l^\alpha \hat{m}_l^\beta, \tag{8}$$

$$\hat{\mathbf{l}} = -i(\mathbf{r} \times \nabla). \tag{9}$$

The expression of multipoles in spinful space is obtained by the addition rule of the above multipole operator and Pauli matrix in spin space [38].

We denote the monopole as X_0 , dipole as $X_{1m} = (X_x, X_y, X_z)$, quadrupole as $X_{2m} = (X_u, X_v, X_{yz}, X_{zx}, X_{xy})$, and octupole as $X_{3m} = (X_{xyz}, X_x^\alpha, X_y^\alpha, X_z^\alpha, X_x^\beta, X_y^\beta, X_z^\beta)$ for $X = Q, M, T, G$. The specific expressions of O_{lm} up to rank 3 are given by

$$O_0 = 1, \tag{10}$$

$$(O_x, O_y, O_z) = (x, y, z), \tag{11}$$

$$O_u = \frac{1}{2}(3z^2 - r^2), \tag{12}$$

$$O_v = \frac{\sqrt{3}}{2}(x^2 - y^2), \tag{13}$$

$$(O_{yz}, O_{zx}, O_{xy}) = \sqrt{3}(yz, zx, xy), \tag{14}$$

$$O_{xyz} = \sqrt{15}xyz, \tag{15}$$

$$(O_x^\alpha, O_y^\alpha, O_z^\alpha) = \frac{1}{2}(x(5x^2 - 3r^2), y(5y^2 - 3r^2), z(5z^2 - 3r^2)), \tag{16}$$

$$(O_x^\beta, O_y^\beta, O_z^\beta) = \frac{\sqrt{15}}{2}(x(y^2 - z^2), y(z^2 - x^2), z(x^2 - y^2)). \tag{17}$$

The spatial inversion and time-reversal parities in each multipole are summarized in Table 1.

The four types of multipoles also describe the spin-split band structures and band deformations in momentum space. By reading \mathbf{r} with the wave vector \mathbf{k} in $O_{lm}(\mathbf{r})$, the momentum-space description of multipoles is given by [39]

$$Q_{lm}(\mathbf{k}) \equiv \begin{cases} \sigma_0 O_{lm}(\mathbf{k}) & (l = 0, 2, 4, 6, \dots) \\ (\mathbf{k} \times \boldsymbol{\sigma}) \cdot \nabla_{\mathbf{k}} O_{lm}(\mathbf{k}) & (l = 1, 3, 5, \dots) \end{cases} \tag{18}$$

$$M_{lm}(\mathbf{k}) \equiv \begin{cases} 0 & (l = 0, 2, 4, 6, \dots) \\ \boldsymbol{\sigma} \cdot \nabla_{\mathbf{k}} O_{lm}(\mathbf{k}) & (l = 1, 3, 5, \dots) \end{cases} \tag{19}$$

$$T_{lm}(\mathbf{k}) \equiv \begin{cases} 0 & (l = 0) \\ (\mathbf{k} \times \boldsymbol{\sigma}) \cdot \nabla_{\mathbf{k}} O_{lm}(\mathbf{k}) & (l = 2, 4, 6, \dots) \\ \sigma_0 O_{lm}(\mathbf{k}) & (l = 1, 3, 5, \dots) \end{cases} \tag{20}$$

$$G_{lm}(\mathbf{k}) \equiv \begin{cases} \mathbf{k} \cdot \boldsymbol{\sigma} & (l = 0) \\ \boldsymbol{\sigma} \cdot \nabla_{\mathbf{k}} O_{lm}(\mathbf{k}) & (l = 2, 4, 6, \dots) \\ 0 & (l = 1, 3, 5, \dots) \end{cases} \tag{21}$$

where σ_0 and σ denote the identity and Pauli matrices in spin space, respectively. Thus, the even-rank (odd-rank) electric (magnetic toroidal) multipoles describe the symmetric (antisymmetric) band deformation without spin dependence. Meanwhile, the odd-rank (even-rank) electric (magnetic toroidal) multipoles and the even-rank (odd-rank) electric toroidal (magnetic) multipoles describe the antisymmetric (symmetric) spin splitting in the band structure.

Table 1. Four types of multipoles (MPs) up to rank 3. “#” in the sixth column represents the number of magnetic point groups to possess multipoles in the totally symmetric irreducible representation. The seventh column represents the band dispersion in the presence of multipoles. The eighth, ninth, and tenth columns denote the induced multipoles under the electric field E , magnetic field H , and electric current J .

MP	Rank	Notation	\mathcal{P}	\mathcal{T}	#	Band Dispersion	E	H	J
E	0	Q_0	+1	+1	122	1	Q_{1m}	M_{1m}	T_{1m}
E	1	Q_{1m}	−1	+1	31	$\mathbf{k} \times \boldsymbol{\sigma}$	Q_0, G_{1m}, Q_{2m}	M_0, T_{1m}, M_{2m}	T_0, M_{1m}, T_{2m}
E	2	Q_{2m}	+1	+1	106	$O_{lm}(\mathbf{k})$	Q_{1m}, G_{2m}, Q_{3m}	M_{1m}, T_{2m}, M_{3m}	T_{1m}, M_{2m}, T_{3m}
E	3	Q_{3m}	−1	+1	58	$(\mathbf{k} \times \boldsymbol{\sigma}) \cdot \nabla_{\mathbf{k}} O_{lm}(\mathbf{k})$	Q_{2m}, G_{3m}, Q_{4m}	M_{2m}, T_{3m}, M_{4m}	T_{2m}, M_{3m}, T_{4m}
M	0	M_0	−1	−1	32	−	M_{1m}	Q_{1m}	G_{1m}
M	1	M_{1m}	+1	−1	31	$\boldsymbol{\sigma}$	M_0, T_{1m}, M_{2m}	Q_0, G_{1m}, Q_{2m}	G_0, Q_{1m}, G_{2m}
M	2	M_{2m}	−1	−1	42	−	M_{1m}, T_{2m}, M_{3m}	Q_{1m}, G_{2m}, Q_{3m}	G_{1m}, Q_{2m}, G_{3m}
M	3	M_{3m}	+1	−1	58	$\boldsymbol{\sigma} \cdot \nabla_{\mathbf{k}} O_{lm}(\mathbf{k})$	M_{2m}, T_{3m}, M_{4m}	Q_{2m}, G_{3m}, Q_{4m}	G_{2m}, Q_{3m}, G_{4m}
MT	0	T_0	+1	−1	32	−	T_{1m}	G_{1m}	Q_{1m}
MT	1	T_{1m}	−1	−1	31	\mathbf{k}	T_0, M_{1m}, T_{2m}	G_0, Q_{1m}, G_{2m}	Q_0, G_{1m}, Q_{2m}
MT	2	T_{2m}	+1	−1	42	$(\mathbf{k} \times \boldsymbol{\sigma}) \cdot \nabla_{\mathbf{k}} O_{lm}(\mathbf{k})$	T_{1m}, M_{2m}, T_{3m}	G_{1m}, Q_{2m}, G_{3m}	Q_{1m}, G_{2m}, Q_{3m}
MT	3	T_{3m}	−1	−1	58	$O_{lm}(\mathbf{k})$	T_{2m}, M_{3m}, T_{4m}	G_{2m}, Q_{3m}, G_{4m}	Q_{2m}, G_{3m}, Q_{4m}
ET	0	G_0	−1	+1	32	$\mathbf{k} \cdot \boldsymbol{\sigma}$	G_{1m}	T_{1m}	M_{1m}
ET	1	G_{1m}	+1	+1	43	−	G_0, Q_{1m}, G_{2m}	T_0, M_{1m}, T_{2m}	M_0, T_{1m}, M_{2m}
ET	2	G_{2m}	−1	+1	42	$\boldsymbol{\sigma} \cdot \nabla_{\mathbf{k}} O_{lm}(\mathbf{k})$	G_{1m}, Q_{2m}, G_{3m}	T_{1m}, M_{2m}, T_{3m}	M_{1m}, T_{2m}, M_{3m}
ET	3	G_{3m}	+1	+1	71	−	G_{2m}, Q_{3m}, G_{4m}	T_{2m}, M_{3m}, T_{4m}	M_{2m}, T_{3m}, M_{4m}

The multipole description is also useful for understanding the cross-correlation phenomena when the external field or current is applied [39,40]. When the applied field/current is a rank-1 quantity, the rank of the induced multipoles is characterized by $l - 1$, l , and $l + 1$ for the rank- l multipole in antiferromagnets. For example, when the electric field E , which corresponds to Q_{1m} , is applied to the antiferromagnet with the magnetic toroidal dipole T_{1m} , any of the magnetic toroidal monopole T_0 , magnetic dipole M_{1m} , or magnetic toroidal quadrupole T_{2m} are induced depending on the field direction owing to the tensor product $Q_{1m} \otimes T_{1m} \rightarrow T_0 \oplus M_{1m} \oplus T_{2m}$. Thus, the linear magneto-electric effect as a consequence of the cross-coupling between M_{1m} and Q_{1m} is expected under the T_{1m} order. In addition, one finds that cross-correlations between Q_{1m} and T_0 (T_{2m}) occur, which means that T_0 (T_{2m}) is induced by the electric field in antiferromagnets with T_{1m} . Similar cross-correlation phenomena are straightforwardly investigated for different fields/currents, such as the magnetic field H corresponding to M_{1m} and the electric current J corresponding to T_{1m} . We summarize the correspondence among the multipoles, band dispersions, and couplings to E , H , and J in Table 1.

3. Multipoles in Antiferromagnets

By using the four types of multipoles, we describe any complicated magnetic structures by the ferroic alignment of the multipoles. In order to exemplify this, we consider the magnetic point group $4/mmm1'$. As shown in Table 2, all the irreducible representations without the time-reversal symmetry are characterized by either magnetic or magnetic toroidal multipoles [36]. For example, when the magnetic structure is characterized by the irreducible representation B_{1g}^- , the magnetic toroidal quadrupole T_v and magnetic octupole

M_{xyz} are induced. In such a situation, one expects the appearance of the symmetric spin-split band structure and electric-field-induced magnetic quadrupole from Table 1.

The correspondence between the irreducible representations and magnetic patterns is investigated for the space group $P4/mmm$. We show the possible multipole orderings when the ions with the magnetic moments are located at the $1a$, $2f$, $4l$, and $8p$ sites in Table 2 [35]. For the $1a$ site, the possible magnetic structure is a ferromagnetic one, which indicates that only the irreducible representations corresponding to the magnetic dipole (M_x, M_y, M_z) are possible. When the site symmetry is lowered, other multipoles belonging to different irreducible representations are induced; the magnetic toroidal quadrupole T_{xy} belonging to the irreducible representation B_{2g}^- is possible for the $2f$ site and odd-parity multipoles like M_0 and T_z are possible for the $4l$ site. Furthermore, in the case of the $8p$ site, all the irreducible representations are possible. The real-space spin configurations belonging to the different irreducible representations in the $8p$ site are shown in Figure 2. One finds that unconventional multipole orderings, such as the magnetic toroidal monopole T_0 belonging to A_{1g}^- and magnetic toroidal quadrupole T_v belonging to B_{1g}^- , are constructed various collinear and noncollinear spin configurations.

Table 2. Irreducible representations (irreps) of four types of multipoles under the magnetic point group (MPG) $4/mmm1'$ [36]. The superscript “−” of irrep indicates the parity with respect to the antiunitary time-reversal operation. MP in the second column represents the multipole, which corresponds to the order parameter under magnetic orderings. From the fourth to seventh columns, possible $q = 0$ magnetic orderings for the Wyckoff positions under the space group $P4/mmm$ are shown [35].

Irrep	MP	Subgroup	1a (0 0 0)	2f (0 1/2 0)	4l (x 0 0)	8p (x y 0)
A_{1g}^-	T_0, T_u	$4/mmm$	−	−	−	✓
A_{2g}^-	M_z, M_z^α	$4/mm'm'$	✓	✓	✓	✓
B_{1g}^-	T_v, M_{xyz}	$4'/mmm'$	−	−	−	✓
B_{2g}^-	T_{xy}, M_z^β	$4'/mm'm$	−	✓	✓	✓
E_g^-	$T_{yz}, M_x, M_x^\alpha, M_x^\beta$	$mm'm'$	✓	✓	✓	✓
	$T_{zx}, M_y, M_y^\alpha, M_y^\beta$	$m'mm'$	✓	✓	✓	✓
A_{1u}^-	M_0, M_u	$4/m'm'm'$	−	−	✓	✓
A_{2u}^-	T_z, T_z^α	$4/m'mm$	−	−	✓	✓
B_{1u}^-	T_{xyz}, M_v	$4'/m'm'm$	−	−	✓	✓
B_{2u}^-	T_z^β, M_{xy}	$4'/m'mm'$	−	−	✓	✓
E_u^-	$T_x, T_x^\alpha, T_x^\beta, M_{yz}$	$m'mm$	−	−	✓	✓
	$T_y, T_y^\alpha, T_y^\beta, M_{zx}$	$mm'm$	−	−	✓	✓

The above example indicates that various multipoles are activated in the antiferromagnetic structures according to their magnetic point groups. Indeed, 32, 31, 42, and 58 out of 122 magnetic point groups possess M_0, M_{1m}, M_{2m} , and M_{3m} , respectively. Similarly, 122, 31, 106, and 58 magnetic point groups possess Q_0, Q_{1m}, Q_{2m} , and Q_{3m} , respectively, 32, 31, 42, and 58 magnetic point groups possess T_0, T_{1m}, T_{2m} , and T_{3m} , respectively, and 32, 43, 42, and 71 magnetic point groups possess G_0, G_{1m}, G_{2m} , and G_{3m} , respectively. In order to show the active multipoles under 122 magnetic point groups, we classify them in each magnetic point group, as shown in Table 3. It is noted that magnetic structures without the breaking of the time-reversal symmetry are possible when the $q \neq 0$ state is considered. The typical magnetic materials from MAGNDATA [41] are also listed. This table is useful for seeing which types of multipoles are present in magnetic materials.

Table 3. Classification of four types of multipoles up to rank 3 under the 122 magnetic point groups. The number in the column for the multipoles X_{lm} ($X = Q, M, T, G$) represents the number of active multipoles belonging to the totally symmetric irreducible representation. The materials taken from MAGNDATA [41] are also listed in the rightmost column.

	MPG	$(\mathcal{P}, \mathcal{T}) = (+1, +1)$				$(-1, +1)$				$(+1, -1)$				$(-1, -1)$				Material	
		Q_0	Q_{2m}	G_{1m}	G_{3m}	G_0	G_{2m}	Q_{1m}	Q_{3m}	T_0	T_{2m}	M_{1m}	M_{3m}	M_0	M_{2m}	T_{1m}	T_{3m}		
#1	1	1	5	3	7	1	5	3	7	1	5	3	7	1	5	3	7	Mn ₂ ScSbO ₆ [42]	
#2	11'	1	5	3	7	1	5	3	7									LiFeAs ₂ O ₇ [43]	
#3	$\bar{1}$	1	5	3	7					1	5	3	7					RbMnF ₄ [44]	
#4	$\bar{1}1'$	1	5	3	7													CuMnO ₂ [45]	
#5	$\bar{1}'$	1	5	3	7									1	5	3	7	MnPSe ₃ [46]	
#6	2	1	3	1	3	1	3	1	3	1	3	1	3	1	3	1	3	LiFeP ₂ O ₇ [47]	
#7	21'	1	3	1	3	1	3	1	3									Yb ₂ CoMnO ₆ [48]	
#8	2'	1	3	1	3	1	3	1	3		2	4		2	2	4		BaDy ₂ O ₄ [49]	
#9	<i>m</i>	1	3	1	3		2	2	4	1	3	1	3		2	2	4		Mn ₄ Nb ₂ O ₉ [50]
#10	<i>m</i> 1'	1	3	1	3		2	2	4										DyFeWO ₆ [51]
#11	<i>m</i> '	1	3	1	3		2	2	4		2	4		1	3	1	3		ScFeO ₃ [52]
#12	2/ <i>m</i>	1	3	1	3					1	3	1	3						Cu ₂ OSO ₄ [53]
#13	2/ <i>m</i> 1'	1	3	1	3														CuSe ₂ O ₅ [54]
#14	2'/ <i>m</i>	1	3	1	3										2	2	4		YbCl ₃ [55]
#15	2/ <i>m</i> '	1	3	1	3									1	3	1	3		Co ₂ V ₂ O ₇ [56]
#16	2'/ <i>m</i> '	1	3	1	3						2	4							Mn ₃ Ti ₂ Te ₆ [57]
#17	222	1	2		1	1	2		1	1	2	1		1	2		1		FePO ₄ [58]
#18	2221'	1	2		1	1	2		1			1							AgNiO ₂ [59]
#19	2'2'2	1	2		1	1	2		1		1	2			1	1	2		VNb ₃ S ₆ [60]
#20	<i>mm</i> 2	1	2		1		1	1	2	1	2		1		1	1	2		FeSb ₂ O ₄ [61]
#21	<i>mm</i> 21'	1	2		1		1	1	2										EuNiO ₃ [62]
#22	<i>m</i> ' <i>m</i> 2'	1	2		1		1	1	2		1	2		1	1	2			CaBaCo ₄ O ₇ [63]
#23	<i>m</i> ' <i>m</i> '2	1	2		1		1	1	2		1	2		1	2		1		α -Cu ₂ V ₂ O ₇ [64]
#24	<i>mmm</i>	1	2		1					1	2		1						α -Mn ₂ O ₃ [65]
#25	<i>mmm</i> 1'	1	2		1														BaFe ₂ As ₂ [66]
#26	<i>mmm</i> '	1	2		1										1	1	2		U ₃ Ru ₄ Al ₁₂ [67]
#27	<i>m</i> ' <i>m</i> ' <i>m</i>	1	2		1						1	2							NiF ₂ [68]
#28	<i>m</i> ' <i>m</i> ' <i>m</i> '	1	2		1														TbB ₄ [69]
#29	4	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1		Ce ₅ TeO ₈ [70]
#30	41'	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1		CeAuAl ₃ [71]

Table 3. Cont.

MPG	$(\mathcal{P}, \mathcal{T}) = (+1, +1)$				$(-1, +1)$				$(+1, -1)$				$(-1, -1)$				Material
	Q_0	Q_{2m}	G_{1m}	G_{3m}	G_0	G_{2m}	Q_{1m}	Q_{3m}	T_0	T_{2m}	M_{1m}	M_{3m}	M_0	M_{2m}	T_{1m}	T_{3m}	
#31	4'	1	1	1	1	1	1	1	1	2		2		2		2	
#32	$\bar{4}$	1	1	1	1			2	2	1	1	1	1		2		2
#33	$\bar{4}1'$	1	1	1	1			2	2								
#34	$\bar{4}'$	1	1	1	1			2	2				1	1	1	1	
#35	4/m	1	1	1	1					1	1	1	1				
#36	4/m1'	1	1	1	1												
#37	4'/m	1	1	1	1					2		2					
#38	4/m'	1	1	1	1								1	1	1	1	
#39	4'/m'	1	1	1	1									2		2	
#40	422	1	1			1	1			1	1		1	1			
#41	4221'	1	1			1	1										
#42	4'22'	1	1			1	1			1		1		1		1	
#43	42'2'	1	1			1	1					1	1		1	1	
#44	4mm	1	1					1	1	1	1				1	1	
#45	4mm1'	1	1					1	1								
#46	4'mm'	1	1					1	1		1	1		1		1	
#47	4m'm'	1	1					1	1		1	1	1	1			
#48	$\bar{4}2m$	1	1				1		1	1	1			1		1	
#49	$\bar{4}2m1'$	1	1				1		1								
#50	$\bar{4}'m2'$	1	1				1		1		1	1			1	1	
#51	$\bar{4}'2m'$	1	1				1		1		1	1	1	1			
#52	$\bar{4}2'm'$	1	1				1		1		1	1		1		1	
#53	4/mmm	1	1							1	1						
#54	4/mmm1'	1	1														
#55	4'/m'mm	1	1												1	1	
#56	4'/m'mm'	1	1							1		1					
#57	4'/m'm'm	1	1											1		1	
#58	4'/m'm'm'	1	1								1	1					
#59	4'/m'm'm'm'	1	1										1	1			
#60	3	1	1	1	3	1	1	1	3	1	1	1	3	1	1	1	3
#61	31'	1	1	1	3	1	1	1	3								
#62	$\bar{3}$	1	1	1	3					1	1	1	3				
#63	$\bar{3}1'$	1	1	1	3												
#64	$\bar{3}'$	1	1	1	3								1	1	1	3	
#65	32	1	1			1	1		1	1		1	1	1	1	1	

La_{0.33}Sr_{0.67}FeO₃ [99]

Table 3. Cont.

MPG	$(\mathcal{P}, \mathcal{T}) = (+1, +1)$				$(-1, +1)$				$(+1, -1)$				$(-1, -1)$				Material
	Q_0	Q_{2m}	G_{1m}	G_{3m}	G_0	G_{2m}	Q_{1m}	Q_{3m}	T_0	T_{2m}	M_{1m}	M_{3m}	M_0	M_{2m}	T_{1m}	T_{3m}	
#66	321'	1	1		1	1		1									DyFe ₃ (BO ₃) ₄ [100]
#67	32'	1	1		1	1		1			1	1			1	1	BaCu ₃ V ₂ O ₈ (OD) ₂ [101]
#68	3m	1	1		1			1	1	1		1			1	1	PbNiO ₃ [102]
#69	3m1'	1	1		1			1	1								Ba ₃ Nb ₂ NiO ₉ [103]
#70	3m'	1	1		1			1	1		1	1	1	1			CrSe [104]
#71	$\bar{3}m$	1	1		1				1	1		1					Li ₂ MnTeO ₆ [105]
#72	$\bar{3}m1'$	1	1		1												SrRu ₂ O ₆ [106]
#73	$\bar{3}'m$	1	1		1										1	2	Ca ₂ YZr ₂ Fe ₃ O ₁₂ [107]
#74	$\bar{3}'m'$	1	1		1								1	1		1	Na ₂ MnTeO ₆ [108]
#75	$\bar{3}m'$	1	1		1						1	2					Co ₃ Sn ₂ S ₂ [109]
#76	6	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	BaCoSiO ₄ [110]
#77	61'	1	1	1	1	1	1	1	1								
#78	6'	1	1	1	1	1	1	1				1					YMnO ₃ [111]
#79	$\bar{6}$	1	1	1	1				1	1	1	1					
#80	$\bar{6}1'$	1	1	1	1												ErAuIn [112]
#81	$\bar{6}'$	1	1	1	1							1	1	1	1	1	Tb ₁₄ Ag ₅₁ [113]
#82	6/m	1	1	1	1				1	1	1	1					FeF ₃ [114]
#83	6/m1'	1	1	1	1												
#84	6'/m	1	1	1	1											2	K ₂ Mn ₃ (VO ₄) ₂ CO ₃ [115]
#85	6'/m'	1	1	1	1								1	1	1	1	U ₁₄ Au ₅₁ [116]
#86	6'/m'	1	1	1	1						2						
#87	622	1	1			1	1		1	1			1	1			
#88	6221'	1	1			1	1										ScMn ₆ Ge ₆ [117]
#89	6'22'	1	1			1	1				1					1	
#90	62'2'	1	1			1	1				1	1			1	1	EuIn ₂ As ₂ [118]
#91	6mm	1	1					1	1	1					1	1	HoMnO ₃ [119]
#92	6mm1'	1	1					1	1								
#93	6'mm'	1	1					1	1		1					1	Co ₂ Mo ₃ O ₈ [120]
#94	6m'm'	1	1					1	1		1	1	1	1			LuFeO ₃ [121]
#95	$\bar{6}m2$	1	1						1	1						1	Ba ₃ CoSb ₂ O ₉ [122]
#96	$\bar{6}m21'$	1	1														CsCr _{0.94} Fe _{0.06} F ₄ [123]
#97	$\bar{6}'m'2$	1	1									1	1				UNiGa [124]
#98	$\bar{6}'m2'$	1	1									1			1	1	CsFeCl ₃ [125]
#99	$\bar{6}m'2'$	1	1								1	1				1	HoPdIn [126]
#100	6/mmm	1	1						1	1							

Table 3. Cont.

MPG	$(\mathcal{P}, \mathcal{T}) = (+1, +1)$				$(-1, +1)$				$(+1, -1)$				$(-1, -1)$				Material
	Q_0	Q_{2m}	G_{1m}	G_{3m}	G_0	G_{2m}	Q_{1m}	Q_{3m}	T_0	T_{2m}	M_{1m}	M_{3m}	M_0	M_{2m}	T_{1m}	T_{3m}	
#101	6/mmm1'	1	1														FeGe [127]
#102	6/m'mm	1	1												1	1	
#103	6'/mmm'	1	1													1	
#104	6'/m'mm'	1	1								1						CsCoCl ₃ [128]
#105	6/mm'm'	1	1								1	1					Fe _{2.71} GeTe ₂ [129]
#106	6/m'm'm'	1	1										1	1			
#107	23	1		1	1		1	1	1		1		1			1	Mn ₃ IrSi [130]
#108	231'	1		1	1		1	1									MnGe [131]
#109	m $\bar{3}$	1		1					1		1						MnTe ₂ [132]
#110	m $\bar{3}1'$	1		1													Au ₇₂ Al ₁₄ Tb ₁₄ [133]
#111	m' $\bar{3}$ '	1		1									1			1	
#112	432	1			1				1				1				SrCuTe ₂ O ₆ [134]
#113	4321'	1			1												
#114	4'32'	1			1						1						BaCuTe ₂ O ₆ [135]
#115	$\bar{4}3m$	1					1	1	1							1	
#116	$\bar{4}3m1'$	1					1										Gd ₂ Ti ₂ O ₇ [136]
#117	$\bar{4}'3m'$	1					1				1		1				
#118	m $\bar{3}m$	1							1								
#119	m $\bar{3}m1'$	1															NdZn [137]
#120	m' $\bar{3}$ 'm	1														1	
#121	m $\bar{3}m'$	1									1						Tb ₃ Ga ₅ O ₁₂ [138]
#122	m' $\bar{3}$ 'm'	1											1				

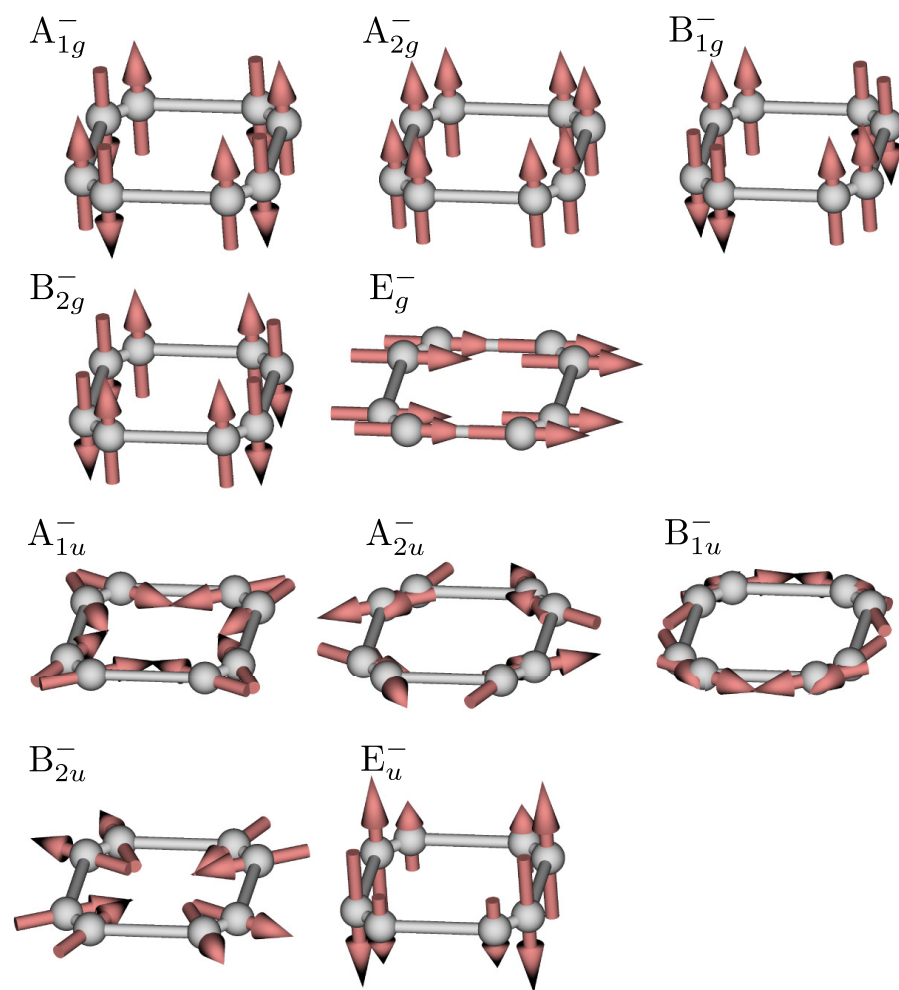


Figure 2. Magnetic structures belonging to different irreducible representations for the $8p$ site under the space group $P4/mmm$. The arrows represent the direction of magnetic moments.

4. Cross-Correlations in Antiferromagnets with Multipoles

In this section, we briefly show the expected cross-correlations and transports in magnetic materials with multipoles: the electric dipole Q_{1m} in Section 4.1, the electric quadrupole Q_{2m} in Section 4.2, the electric octupole Q_{3m} in Section 4.3, the magnetic monopole M_0 in Section 4.4, the magnetic dipole M_{1m} in Section 4.5, the magnetic quadrupole M_{2m} in Section 4.6, the magnetic octupole M_{3m} in Section 4.7, the magnetic toroidal monopole T_0 in Section 4.8, the magnetic toroidal dipole T_{1m} in Section 4.9, the magnetic toroidal quadrupole T_{2m} in Section 4.10, the magnetic toroidal octupole T_{3m} in Section 4.11, the electric toroidal monopole G_0 in Section 4.12, the electric toroidal dipole G_{1m} in Section 4.13, the electric toroidal quadrupole G_{2m} in Section 4.14, and the electric toroidal octupole G_{3m} in Section 4.15.

4.1. Electric Dipole

There are 31 magnetic point groups accompanying the electric dipole Q_{1m} , as shown in Table 4. We classify 31 magnetic point groups in terms of the presence and absence of M_{1m} and T_{1m} . Since M_{1m} and T_{1m} are coupled to the magnetic field and electric current, respectively, they can be used to control the domain of the antiferromagnetic state with Q_{1m} .

Table 4. Classification of magnetic point groups (MPGs) with the electric dipole Q_{1m} according to the presence and absence of the magnetic dipole M_{1m} and the magnetic toroidal dipole T_{1m} .

MPG	M_{1m}	T_{1m}
1, 2, 2', m, m', m'm2', 4, 3, 6	✓	✓
m'm'2, 4m'm', 3m', 6m'm'	✓	
mm2, 4mm, 3m, 6mm		✓
11', 21', m1', mm21', 41', 4', 4mm1'		
4'mm', 31', 3m1', 61', 6', 6mm1', 6'mm'		

The magnetic materials with Q_{1m} exhibit the antisymmetric spin polarization in the band structure, which corresponds to the Rashba-type spin–orbit coupling in the form of $\mathbf{k} \times \boldsymbol{\sigma}$. Accordingly, the transverse Edelstein effect, where the magnetization is induced by the electric current in a perpendicular way, occurs. The materials with Q_{1m} also show the nonlinear Hall effect based on the Berry curvature dipole mechanism [139]. Moreover, the system with Q_{1m} shows the magnetic toroidal moment in the external magnetic field. One of the candidate materials is CrSe, where the symmetry reduces from $P6_3/mmc$ to $P31m'$ (magnetic point group $3m'$) by the magnetic phase transition [104]. In this material, the above physical phenomena are induced only below the critical temperature. In addition, the single domain can be obtained by performing magnetic field cooling.

4.2. Electric Quadrupole

There are 106 magnetic point groups accompanying the electric quadrupole Q_{2m} . We classify them in terms of the presence and absence of Q_{1m} , M_{1m} , and T_{1m} , as shown in Table 5, where the presence of Q_{1m} means that the single-domain formation can be controlled by applying the electric field when Q_{1m} is simultaneously induced below the critical temperature. The nematic ordering belongs to this category.

Table 5. Classification of magnetic point groups (MPGs) with the electric quadrupole Q_{2m} according to the presence and absence of the electric dipole Q_{1m} , the magnetic dipole M_{1m} , and the magnetic toroidal dipole T_{1m} .

MPG	Q_{1m}	M_{1m}	T_{1m}
1, 2, 2', m, m', m'm2', 4, 3, 6	✓	✓	✓
m'm'2, 4m'm', 3m', 6m'm'	✓	✓	
mm2, 4mm, 3m, 6mm	✓		✓
2'2'2, 42'2', 32', 62'2'		✓	✓
11', 21', m1', mm21', 41', 4', 4mm1'	✓		
4'mm', 31', 3m1', 61', 6', 6mm1', 6'mm'	✓		
$\bar{1}$, 2/m, 2'/m', m'm'm, $\bar{4}$, 4/m, $\bar{4}2'm'$		✓	
4/mmm', $\bar{3}$, $\bar{3}m'$, $\bar{6}$, 6/m, $\bar{6}m'2'$, 6/mmm'm'		✓	
$\bar{1}'$, 2'/m, 2/m', mmm', $\bar{4}'$, 4/m', $\bar{4}'m2'$			✓
4/m'mm, $\bar{3}'$, $\bar{3}'m$, $\bar{6}'$, 6/m', $\bar{6}'m2'$, 6/m'mm			✓
$\bar{1}1'$, 2/m1', 222, 2221', mmm, mmm1', m'm'm'			
$\bar{4}1'$, 4/m1', 4'/m, 4'/m', 422, 4221', 4'22', $\bar{4}2m$			
$\bar{4}2m1'$, $\bar{4}'2m'$, 4/mmm, 4/mmm1', 4'/mmm'			
4'/m'm'm, 4'/m'm'm', $\bar{3}1'$, 32, 321', $\bar{3}m$			
$\bar{3}m1'$, $\bar{3}'m'$, $\bar{6}1'$, 6/m1', 6'/m, 6'/m', 622			
6221', 6'22', $\bar{6}m2$, $\bar{6}m21'$, $\bar{6}'m'2$, 6/mmm			
6/mmm1', 6'/mmm', 6'/m'mm', 6'/m'm'm'			

Although Q_{2m} has the same spatial inversion and time-reversal properties as the electric monopole Q_0 , it exhibits intriguing electromagnetic responses according to its spatial anisotropy. In addition to the conjugate physical quantities, additional higher-rank multipoles are induced under external fields and currents. In other words, the responses

against the fields and currents are different from the case with Q_0 . For example, the electric toroidal quadrupole G_{2m} , the magnetic toroidal quadrupole T_{2m} , and the magnetic quadrupole M_{2m} are induced by the electric field, magnetic field, and electric current, respectively. In particular, the momentum-dependent spin splitting, which arises from T_{2m} , in addition to Zeeman-type uniform spin splitting, occurs in the magnetic field.

4.3. Electric Octupole

The electric octupole Q_{3m} is included in 58 magnetic point groups, where 27 magnetic point groups do not possess Q_{1m} , as shown in Table 6. Similarly to Q_{1m} , the magnetic materials with Q_{3m} also exhibit the antisymmetric spin-split band structure including the Dresselhaus-type one in the form of $k_x(k_y^2 - k_z^2)\sigma_x + k_y(k_z^2 - k_x^2)\sigma_y + k_z(k_x^2 - k_y^2)\sigma_z$. Meanwhile, the magnetic octupole instead of the magnetic dipole (magnetization) is induced by the electric current in contrast to Q_{1m} . The candidate material is VNB_3S_6 , where the symmetry reduction occurs from $P6_322$ to $C2'2'2_1$ (magnetic point group $2'2'2$) [60]. Since M_{1m} and T_{1m} are simultaneously induced under $2'2'2$, either the magnetic field or electric current cooling can lead to the single domain of Q_{3m} .

Table 6. Classification of magnetic point groups (MPGs) with the electric octupole Q_{3m} according to the presence and absence of the electric dipole Q_{1m} , the magnetic dipole M_{1m} , and the magnetic toroidal dipole T_{1m} . The upper (lower) columns represent the magnetic point groups with (without) Q_{1m} .

MPG	Q_{1m}	M_{1m}	T_{1m}
1, 2, 2', m, m', m'm2', 4, 3, 6 m'm'2, 4m'm', 3m', 6m'm'	✓	✓	✓
mm2, 4mm, 3m, 6mm	✓		✓
11', 21', m1', mm21', 41', 4', 4mm1' 4'mm', 31', 3m1', 61', 6', 6mm1', 6'mm'	✓		
2'2'2, 32'		✓	✓
$\bar{4}$, $\bar{4}2'm'$, $\bar{6}$, $\bar{6}m'2'$ $\bar{4}'$, $\bar{4}'m2'$, $\bar{6}'$, $\bar{6}'m2'$		✓	✓
222, 2221', $\bar{4}1'$, $\bar{4}2m$, $\bar{4}2m1'$, $\bar{4}'2m'$ 32, 321', $\bar{6}1'$, $\bar{6}m2$, $\bar{6}m21'$, $\bar{6}'m'2$ 23, 231', $\bar{4}3m$, $\bar{4}3m1'$, $\bar{4}'3m'$			

4.4. Magnetic Monopole

Among 122 magnetic point groups, 32 magnetic point groups include the magnetic monopole M_0 , as shown in Table 7. This becomes the origin of the linear longitudinal magneto-electric effect, where the magnetization M_{1m} (electric polarization Q_{1m}) is induced in the electric-field (magnetic-field) direction [140–143]. TbB_4 (magnetic point group $m'm'm'$) [69,144,145] and FePO_4 (magnetic point group 222) [58] are typical examples to exhibit physical phenomena related to magnetic monopoles.

Table 7. Classification of magnetic point groups (MPGs) with the magnetic monopole M_0 according to the presence and absence of the electric dipole Q_{1m} , the magnetic dipole M_{1m} , and the magnetic toroidal dipole T_{1m} .

MPG	Q_{1m}	M_{1m}	T_{1m}
1, 2, m', 4, 3, 6 m'm'2, 4m'm', 3m', 6m'm'	✓	✓	✓
$\bar{1}'$, 2/m', $\bar{4}'$, 4/m', $\bar{3}'$, $\bar{6}'$, 6/m'	✓	✓	✓
222, m'm'm', 422, $\bar{4}'2m'$, 4/m'm'm', 32, $\bar{3}'m'$ 622, $\bar{6}'m'2$, 6/m'm'm', 23, m' $\bar{3}'$, 432, $\bar{4}'3m'$, m' $\bar{3}'m'$			

4.5. Magnetic Dipole

The magnetic dipole M_{1m} is included in 31 magnetic point groups, as shown in Table 8 [146–148]. Since M_{1m} corresponds to the ferroic alignment of spin, i.e., the ferromagnetic state, the Berry curvature occurs in the band structure, which becomes the origin of the physical phenomena under magnetization or magnetic field occur, such as the Hall effect, Nernst effect, and magneto-optical Kerr effect [149,150]. Meanwhile, the magnetic point groups with M_{1m} are also realized in the antiferromagnetic structure even without (or with a negligibly small) net magnetization, as found in the noncollinear antiferromagnets like Mn_3Sn [25,26,151–153] and collinear antiferromagnets [19,154] like LaMO_3 ($M = \text{Cr, Mn, and Fe}$) [15], the bilayer MnPSe_3 [16], κ -type organic conductors [18], and so on. Recently, different types of magnetic dipole have been introduced such as the “anisotropic magnetic dipole” M'_{1m} , which consists of the product of the electric quadrupole Q_{2m} and conventional magnetic dipole (spin) M_{1m} , and they are regarded as a microscopic indicator of the presence of the anomalous Hall effect in antiferromagnets [21,155]. Since the symmetry conditions for M_{1m} and M'_{1m} are the same as each other, the magnetic materials belonging to 31 magnetic point groups in Table 8 result in “ferromagnetic” physical phenomena irrespective of the ferromagnetic and antiferromagnetic structures.

Table 8. Classification of magnetic point groups (MPGs) with the magnetic dipole M_{1m} according to the presence and absence of the electric dipole Q_{1m} and the magnetic toroidal dipole T_{1m} .

MPG	Q_{1m}	T_{1m}
1, 2, 2', m , m' , $m'm'2'$, 4, 3, 6	✓	✓
$m'm'2$, $4m'm'$, $3m'$, $6m'm'$	✓	
$2'2'2$, $42'2'$, $32'$, $62'2'$		✓
$\bar{1}$, $2/m$, $2'/m'$, $m'm'm$, $\bar{4}$, $4/m$, $\bar{4}2'm'$		
$4/mmm'm'$, $\bar{3}$, $\bar{3}m'$, $\bar{6}$, $6/m$, $\bar{6}m'2'$, $6/mmm'm'$		

In addition, the materials with M_{1m} exhibit further cross-correlations. One of the examples is the switching response between the magnetic dipole and magnetic toroidal dipole (T_{1m}) of circularly polarized light. Another example is the electric-current-induced chirality (electric toroidal monopole G_0).

4.6. Magnetic Quadrupole

A total of 42 out of 122 magnetic point groups possess the magnetic quadrupole M_{2m} , as shown in Table 9; of these, 27 magnetic point groups accompany M_0 , while the remaining 15 magnetic point groups do not have M_0 . Since the physical properties of M_{2m} are similar to those of M_0 owing to the same spatial inversion and time-reversal parities, it is desired to focus on the materials listed in the lower columns when the pure nature of the magnetic quadrupole is investigated. Similarly to the materials with M_0 , the materials with M_{2m} show the linear magneto-electric effect [156–158], as found in Cr_2O_3 [159–163]. In addition, M_{2m} becomes the microscopic origin of the magneto-piezoelectric effect found in EuMnBi [164,165], which arises from the spin-orbital-momentum locking in the band structure [166], and the intrinsic nonlinear Hall effect [167–169]. KOsO_4 (magnetic point group $4'/m'$) [76,170] and $\text{Er}_2\text{Ge}_2\text{O}_7$ (magnetic point group $4'22'$) [79] are other candidate materials with M_{2m} but without Q_{1m} , M_{1m} , or T_{1m} .

Table 9. Classification of magnetic point groups (MPGs) with the magnetic quadrupole M_{2m} according to the presence and absence of the electric dipole Q_{1m} , the magnetic dipole M_{1m} , the magnetic toroidal dipole T_{1m} , and the magnetic monopole M_0 . The upper (lower) columns represent the magnetic point groups with (without) M_0 .

MPG	Q_{1m}	M_{1m}	T_{1m}	M_0
1, 2, m' , 4, 3, 6	✓	✓	✓	✓
$m'm'2$, $4m'm'$, $3m'$, $6m'm'$	✓	✓		✓
$\bar{1}'$, $2/m'$, $\bar{4}'$, $4/m'$, $\bar{3}'$, $\bar{6}'$, $6/m'$			✓	✓
222, $m'm'm'$, 422, $\bar{4}'2m'$, $4/m'm'm'$				✓
32, $\bar{3}'m'$, 622, $\bar{6}'m'2$, $6/m'm'm'$				✓
$2'$, m , $m'm2'$	✓	✓	✓	
$mm2$	✓		✓	
$2'2'2$		✓	✓	
$4'$, $4'mm'$	✓			
$\bar{4}$, $\bar{4}2'm'$		✓		
$2'/m$, mmm'			✓	
$4'/m'$, $4'22'$, $\bar{4}2m$, $4'/m'm'm$				

4.7. Magnetic Octupole

There are 58 magnetic point groups to possess the magnetic octupole M_{3m} , as shown in Table 10. Among them, 27 magnetic point groups are characterized by the magnetic point groups without M_{1m} ; the pure effect of M_{3m} is expected. The materials with magnetic octupole M_{3m} induce rank-2, rank-3, and rank-4 multipoles when external fields and currents are applied. Since T_{3m} (Q_{2m}) are induced for the applied electric field (magnetic field), the band structure is modulated in an antisymmetric (symmetric) way. In addition, M_{3m} becomes the microscopic origin of the magnetic-field-induced striction, i.e., magnetostriction [171]. $\text{Er}_2\text{Ge}_2\text{O}_7$ (magnetic point group $4'22'$) [79] is one of the candidates to have M_{3m} .

Table 10. Classification of magnetic point groups (MPGs) with the magnetic octupole M_{3m} according to the presence and absence of the electric dipole Q_{1m} , the magnetic dipole M_{1m} , and the magnetic toroidal dipole T_{1m} . The upper (lower) columns represent the magnetic point groups with (without) M_{1m} .

MPG	Q_{1m}	M_{1m}	T_{1m}
1, 2, $2'$, m , m' , $m'm2'$, 4, 3, 6	✓	✓	✓
$m'm'2$, $4m'm'$, $3m'$, $6m'm'$	✓	✓	
$2'2'2$, $42'2'$, $32'$, $62'2'$		✓	✓
$\bar{1}$, $2/m$, $2'/m'$, $m'm'm$, $\bar{4}$, $4/m$, $\bar{4}2'm'$		✓	
$4/mm'm'$, $\bar{3}$, $3m'$, $\bar{6}$, $6/m$, $\bar{6}m'2'$, $6/mm'm'$		✓	
$mm2$, $3m$	✓		✓
$4'$, $4'mm'$, $6'$, $6'mm'$	✓		
$\bar{4}'$, $\bar{4}'m2'$, $\bar{6}'$, $\bar{6}'m2'$			✓
222, mmm , $4'/m$, $4'22'$, $\bar{4}'2m'$, $4'/mmm'$			
32, $\bar{3}m$, $6'/m'$, $6'22'$, $\bar{6}'m'2$, $6'/m'mm'$			
23, $m\bar{3}$, $4'32'$, $\bar{4}'3m'$, $m\bar{3}m'$			

4.8. Magnetic Toroidal Monopole

Magnetic toroidal monopole T_0 is included in the 32 magnetic point groups, as shown in Table 11. Since T_0 corresponds to a time-reversal-odd scalar quantity, it leads to the time-reversal switching responses, such as the electric-field-induced magnetic toroidal dipole T_{1m} and the magnetic-field-induced electric toroidal dipole G_{1m} [172,173]. Such

cross-correlations have recently been observed in Co_2SiO_4 [174]. Another candidate is $\text{Ho}_2\text{Ge}_2\text{O}_7$ under magnetic point group 422 [77], for example.

Table 11. Classification of magnetic point groups (MPGs) with the magnetic toroidal monopole T_0 according to the presence and absence of the electric dipole Q_{1m} , the magnetic dipole M_{1m} , and the magnetic toroidal dipole T_{1m} .

MPG	Q_{1m}	M_{1m}	T_{1m}
1, 2, m , 4, 3, 6	✓	✓	✓
$mm2$, $4mm$, $3m$, $6mm$	✓		✓
$\bar{1}$, $2/m$, $\bar{4}$, $4/m$, $\bar{3}$, $\bar{6}$, $6/m$		✓	
222, mmm , 422, $\bar{4}2m$, $4/mmm$, 32, $\bar{3}m$, 622			
$\bar{6}m2$, $6/mmm$, 23, $m\bar{3}$, 432, $\bar{4}3m$, $m\bar{3}m$			

4.9. Magnetic Toroidal Dipole

Magnetic toroidal dipole T_{1m} is allowed for 31 magnetic point groups, as shown in Table 12 [175]. It is the most typical multipole degree of freedom to exhibit the cross-correlation phenomena in magnetic materials. The representative phenomenon is the linear transverse magneto-electric effect in magnetic insulators [176–180], although a similar phenomenon has been observed in magnetic metals like UNi_4B [181–185]. In addition, as T_{1m} corresponds to the time-reversal-odd polar vector, it gives rise to asymmetric band deformation without the spin dependence. Accordingly, T_{1m} induces further cross-correlations and transports, such as nonreciprocal transport [186–190], asymmetric magnon excitations [191–193], and nonlinear spin Hall/Nernst effect [194,195].

Table 12. Classification of magnetic point groups (MPGs) with the magnetic toroidal dipole T_{1m} according to the presence and absence of the electric dipole Q_{1m} and the magnetic dipole M_{1m} .

MPG	Q_{1m}	M_{1m}
1, 2, $2'$, m , m' , $m'm2'$, 4, 3, 6	✓	✓
$mm2$, $4mm$, $3m$, $6mm$	✓	
$2'2'2$, $42'2'$, $32'$, $62'2'$		✓
$\bar{1}'$, $2'/m$, $2/m'$, mmm' , $\bar{4}'$, $4/m'$, $\bar{4}'m2'$		
$4/m'mm$, $\bar{3}'$, $\bar{3}'m$, $\bar{6}'$, $6/m'$, $\bar{6}'m2'$, $6/m'mm$		

4.10. Magnetic Toroidal Quadrupole

There are 42 magnetic point groups to possess the magnetic toroidal quadrupole T_{2m} , as shown in Table 13; 27 out of 42 magnetic point groups possess T_0 , whereas 15 magnetic point groups do not. The materials with T_{2m} show the momentum-dependent symmetric spin-split band structure, which results in the directional-dependent spin current generation [196,197]. Moreover, in the materials with T_{2m} , the ferroaxial nature is induced when the magnetic field is applied. One of the candidate materials is CoF_2 under magnetic point group $4'/mmm'$ [90], although the domain control might be difficult in this material owing to no simple conjugate fields to T_{2m} . In this context, $\text{Mn}_3\text{Ti}_2\text{Te}_6$ under magnetic point group $2'/m'$ [57] is another candidate material, where the magnetic field cooling enables us to select a single domain.

Table 13. Classification of magnetic point groups (MPGs) with the magnetic toroidal quadrupole T_{2m} according to the presence and absence of the electric dipole Q_{1m} , the magnetic dipole M_{1m} , the magnetic toroidal dipole T_{1m} , and the magnetic toroidal monopole T_0 . The upper (lower) columns represent the magnetic point groups with (without) T_0 .

MPG	Q_{1m}	M_{1m}	T_{1m}	T_0
1, 2, m , 4, 3, 6	✓	✓	✓	✓
$mm2$, $4mm$, $3m$, $6mm$	✓		✓	✓
$\bar{1}$, $2/m$, $\bar{4}$, $4/m$, $\bar{3}$, $\bar{6}$, $6/m$		✓		✓
222, mmm , 422, $\bar{4}2m$, $4/mmm$, 32				✓
$\bar{3}m$, 622, $\bar{6}m2$, $6/mmm$				✓
$2'$, m' , $m'm2'$	✓	✓	✓	
$m'm'2$	✓	✓		
$2'2'2$		✓	✓	
$4'$, $4'mm'$	✓			
$2'/m'$, $m'm'm$		✓		
$\bar{4}'$, $\bar{4}'m2'$			✓	
$4'/m$, $4'22'$, $\bar{4}'2m'$, $4'/mmm'$				

4.11. Magnetic Toroidal Octupole

A total of 58 magnetic point groups possess the magnetic toroidal octupole T_{3m} , where 31 magnetic point groups also possess T_{1m} , as shown in Table 14. Since T_{3m} induces asymmetric band modulation similar to T_{1m} , the materials with T_{3m} show nonreciprocal transport against the electric field and thermal gradient [198–200]. One of the potential candidates is CrSe under the magnetic point group $3m'$ [104], where physical phenomena related to the MT octupole can be controlled by both electric and magnetic fields.

Table 14. Classification of magnetic point groups (MPGs) with the magnetic toroidal octupole T_{3m} according to the presence and absence of the electric dipole Q_{1m} , the magnetic dipole M_{1m} , and the magnetic toroidal dipole T_{1m} . The upper (lower) columns represent the magnetic point groups with (without) T_{1m} .

MPG	Q_{1m}	M_{1m}	T_{1m}
1, 2, $2'$, m , m' , $m'm2'$, 4, 3, 6	✓	✓	✓
$mm2$, $4mm$, $3m$, $6mm$	✓		✓
$2'2'2$, $42'2'$, $32'$, $62'2'$		✓	✓
$\bar{1}'$, $2'/m$, $2'/m'$, mmm' , $\bar{4}'$, $4'/m'$, $\bar{4}'m2'$			✓
$4'/m'mm$, $\bar{3}'$, $\bar{3}'m$, $\bar{6}'$, $6'/m'$, $\bar{6}'m2'$, $6'/m'mm$			✓
$m'm'2$, $3m'$	✓	✓	
$4'$, $4'mm'$, $6'$, $6'mm'$	✓		
$\bar{4}$, $\bar{4}2'm'$, $\bar{6}$, $\bar{6}m'2'$		✓	
222, $m'm'm'$, $4'/m'$, $4'22'$, $\bar{4}2m$, $4'/m'm'm$			
32, $\bar{3}'m'$, $6'/m$, $6'22'$, $\bar{6}m2$			
$6'/mmm'$, 23, $m'\bar{3}'$, $4'32'$, $\bar{4}3m$, $m'\bar{3}'m$			

4.12. Electric Toroidal Monopole

A total of 32 magnetic point groups possess the electric toroidal monopole G_0 , as shown in Table 15. As G_0 is characterized as the time-reversal-even pseudoscalar quantity, it corresponds to the chirality [201–203], which becomes the microscopic origin of the hedgehog-type antisymmetric spin–orbit coupling $k \cdot \sigma$, the longitudinal Edelstein effect [204–206], and the electrical magnetochiral effect [207]. Although such a chirality is usually accompanied by lattice structures without the mirror and spatial inversion symmetries, it can be generated by the magnetic phase transition when G_0 additionally belongs to the totally symmetric irreducible representation below the critical temperature. For

example, FePO_4 under magnetic point group 222 [58], ScMn_6Ge_6 under magnetic point group 6221' [117], and $\text{La}_{0.33}\text{Sr}_{0.67}\text{FeO}_3$ under magnetic point group 32 [99] belong to the materials showing the G_0 property driven by the magnetic phase transition.

Table 15. Classification of magnetic point groups (MPGs) with the electric toroidal monopole G_0 according to the presence and absence of the electric dipole Q_{1m} , the magnetic dipole M_{1m} , and the magnetic toroidal dipole T_{1m} .

MPG	Q_{1m}	M_{1m}	T_{1m}
1, 2, 2', 4, 3, 6	✓	✓	✓
2'2'2, 42'2', 32', 62'2'		✓	✓
11', 21', 41', 4', 31', 61', 6'	✓		
222, 2221', 422, 4221', 4'22', 32, 321', 622			
6221', 6'22', 23, 231', 432, 4321', 4'32'			

4.13. Electric Toroidal Dipole

The electric toroidal dipole G_{1m} is included in 43 magnetic point groups, as shown in Table 16. The electric toroidal dipole has recently been attracted since it brings about an unconventional electronic state, invariant under both spatial inversion and time-reversal operations; its ordering is referred to as ferro-rotational order or ferro-axial order [208–212], which have been observed in $\text{RbFe}(\text{MoO}_4)_2$ [210,213] and NiTiO_3 [213–216]. The materials with G_{1m} exhibit transverse responses of the conjugate physical quantities, such as antisymmetric thermopolarization [217], longitudinal spin current generation [218,219], nonlinear transverse magnetization [220], and second-order nonlinear magnetostriction [221]. Such physical properties driven by G_{1m} can be induced by the magnetic phase transition. FeF_3 , which undergoes the phase transition from $P6/mmm$ to $P6_3/m$ (magnetic point group $6/m$), is one of the candidate materials to exhibit the property of G_{1m} by magnetic phase transition [114]. Another candidate is a magnetic vortex accompanying both magnetic monopole and magnetic toroidal dipole [222]. In magnetic materials, G_{1m} contributes to the magnetic anisotropy to tilt the spin moments from the crystal axis by combining the relativistic spin–orbit coupling [223].

Table 16. Classification of magnetic point groups (MPGs) with the electric toroidal dipole G_{1m} according to the presence and absence of the electric dipole Q_{1m} , the magnetic dipole M_{1m} , and the magnetic toroidal dipole T_{1m} .

MPG	Q_{1m}	M_{1m}	T_{1m}
1, 2, 2', m , m' , 4, 3, 6	✓	✓	✓
11', 21', $m1'$, 41', 4', 31', 61', 6'	✓		
$\bar{1}$, 2/ m , 2'/ m' , $\bar{4}$, 4/ m , $\bar{3}$, $\bar{6}$, 6/ m		✓	
$\bar{1}'$, 2'/ m , 2/ m' , $\bar{4}'$, 4/ m' , $\bar{3}'$, $\bar{6}'$, 6/ m'			✓
$\bar{1}1'$, 2/ $m1'$, $\bar{4}1'$, 4/ $m1'$, 4'/ m , 4'/ m'			
$\bar{3}1'$, $\bar{6}1'$, 6/ $m1'$, 6'/ m , 6'/ m'			

4.14. Electric Toroidal Quadrupole

The electric toroidal quadrupole G_{2m} can be found in 42 magnetic point groups, as shown in Table 17. Among them, 27 magnetic point groups also possess G_0 . The materials with G_{2m} show parity-violating physical phenomena, such as the nonlinear Hall effect based on the Berry curvature dipole mechanism [139] and Edelstein effect [224–226]. GeCu_2O_4 under the magnetic point group $\bar{4}2m1'$ is one of the candidate materials to exhibit the physical phenomena of G_{2m} below the critical temperature [84].

Table 17. Classification of magnetic point groups (MPGs) with the electric toroidal quadrupole G_{2m} according to the presence and absence of the electric dipole Q_{1m} , the magnetic dipole M_{1m} , the magnetic toroidal dipole T_{1m} , and the electric toroidal monopole G_0 . The upper (lower) columns represent the magnetic point groups with (without) G_0 .

MPG	Q_{1m}	M_{1m}	T_{1m}	G_0
1, 2, 2', 4, 3, 6	✓	✓	✓	✓
2'2'2, 42'2', 32', 62'2'		✓	✓	✓
11', 21', 41', 4', 31', 61', 6'	✓			✓
222, 2221', 422, 4221', 4'22'				✓
32, 321', 622, 6221', 6'22'				✓
$m, m', m'm2'$	✓	✓	✓	
$m'm'2$	✓	✓		
$mm2$	✓		✓	
$m1', mm21'$	✓			
$\bar{4}, \bar{4}2'm'$		✓		
$\bar{4}', \bar{4}'m2'$			✓	
$\bar{4}1', \bar{4}2m, \bar{4}2m1', \bar{4}'2m'$				

4.15. Electric Toroidal Octupole

There are 71 magnetic point groups that include the electric toroidal octupole G_{3m} , as shown in Table 18. Of these, 28 out of the 71 do not possess G_{1m} . Although the physical phenomena of G_{3m} have not been investigated compared to other multipoles, the materials with G_{3m} show similar physical phenomena to G_{1m} owing to the same spatial inversion and time-reversal parities. For example, the longitudinal spin current generation is possible in materials with G_{3m} [219]. FePO_4 (magnetic point group 222) [58] is one of the candidates to exhibit physical phenomena by G_{3m} through the magnetic phase transition.

Table 18. Classification of magnetic point groups (MPGs) with the electric toroidal octupole G_{3m} according to the presence and absence of the electric dipole Q_{1m} , the magnetic dipole M_{1m} , the magnetic toroidal dipole T_{1m} , and the electric toroidal dipole G_{1m} . The upper (lower) columns represent the magnetic point groups with (without) G_{1m} .

MPG	Q_{1m}	M_{1m}	T_{1m}	G_{1m}
1, 2, 2', $m, m', 4, 3, 6$	✓	✓	✓	✓
11', 21', $m1', 41', 4', 31', 61', 6'$	✓			✓
$\bar{1}, 2/m, 2'/m', 4, 4/m, \bar{3}, \bar{6}, 6/m$		✓		✓
$\bar{1}', 2'/m, 2/m', 4', 4/m', \bar{3}', \bar{6}', 6/m'$			✓	✓
$\bar{1}1', 2/m1', 41', 4/m1', 4'/m, 4'/m'$				✓
$31', 61', 6/m1', 6'/m, 6'/m'$				✓
$m'm2'$	✓	✓	✓	
$m'm'2, 3m'$	✓	✓		
$mm2, 3m$	✓		✓	
2'2'2, 32'		✓	✓	
$mm21', 3m1'$	✓			
$m'm'm, \bar{3}m'$		✓		
$mmm', \bar{3}'m$			✓	
222, 2221', $mmm, mmm1', m'm'm', 32, 321'$				
$\bar{3}m, \bar{3}m1', \bar{3}'m', 23, 231', m\bar{3}, m\bar{3}1', m'\bar{3}'$				

5. Conclusions

To summarize, we have revisited the multipole classification under 122 magnetic point groups, with an emphasis on magnetic materials. We have shown that four types of multipoles (electric, magnetic, magnetic toroidal, and electric toroidal multipoles) emerge

in magnetic materials irrespective of their rank. Since each multipole gives rise to different cross-correlations and transports, the systematic correspondence between multipoles and magnetic point groups enables us to design and engineer functional magnetic materials, including topological spin textures like magnetic skyrmions [227–229], which will be useful for future spintronic applications.

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