Impact of electric toroidal order in stacked honeycomb layers

1. **Electric toroidal invariance generates distinct transverse electromagnetic responses**
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2. **Raman optical activity induced by ferroaxial order in $NiTiO_3$**
   Authors: G. Kusuno, T. Hayashida, T. Nagai, H. Watanabe, R. Oiwa, T. Kimura, and T. Satoh
   arXiv:2505.22488

Recommended with a Commentary by Atsushi Fujimori, *National Tsing Hua University*

In 1959, Dzyaloshinskii [1] predicted by symmetry consideration that the corumdum-type Cr_2O_3 (space group $R\bar{3}c$; point group D_{3d}) should exhibit linear magneto-electric (ME) effect in the antiferromagnetic (AFM) phase. The corumdum structure consists of buckled Cr honeycomb layers stacked along the c direction, as shown in Fig. 1(a). In the paramagnetic (PM) state, the crystal is invariant by C_3 rotation around the c axis as well as by mirror reflection σ_d with respect to planes including the c axis and by spatial inversion I. The Cr ions are shifted from the centers of the CrO_6 octahedra in the $\pm c$ direction alternately so that the upper and lower oxygen triangle faces of the octahedra are expanded or contracted alternately. Upon AFM ordering, both the inversion symmetry and the mirror symmetry are broken but, if time reversal T is applied simultaneously, namely, under IT and under $\sigma_d T$, the system remains invariant. It then follows that the free energy contains non-vanishing $E_i H_i$ terms that lead to the linear ME effect.

The ilmenite-type $MTiO_3$ has a crystal structure similar to the corumdum-type Cr_2O_3 but consists of an alternating stack of buckled metal M honeycomb and Ti honeycomb layers, as shown in Fig. 1(b). Neighboring edge-sharing MO_6 or TiO_6 octahedra are twisted oppositely [Fig. 1(b)], breaking the mirror symmetry of the corumdum structure and leaving C_3's and I the only symmetry operations (space group $R\bar{3}$; point group $C_{3i} \equiv C_3 \otimes C_i$). As a result, all the expanded (contracted) triangles are rotated clockwise (counter-clockwise) throughout the entire crystal domain, forming a "ferro-rotational" or "ferro-axial" domain and leading to a finite electric toroidal moment $\mathbf{A} \equiv \sum_i \mathbf{r}_i \times \mathbf{p}_i$ ($\mathbf{p}_i$: displacement-induced

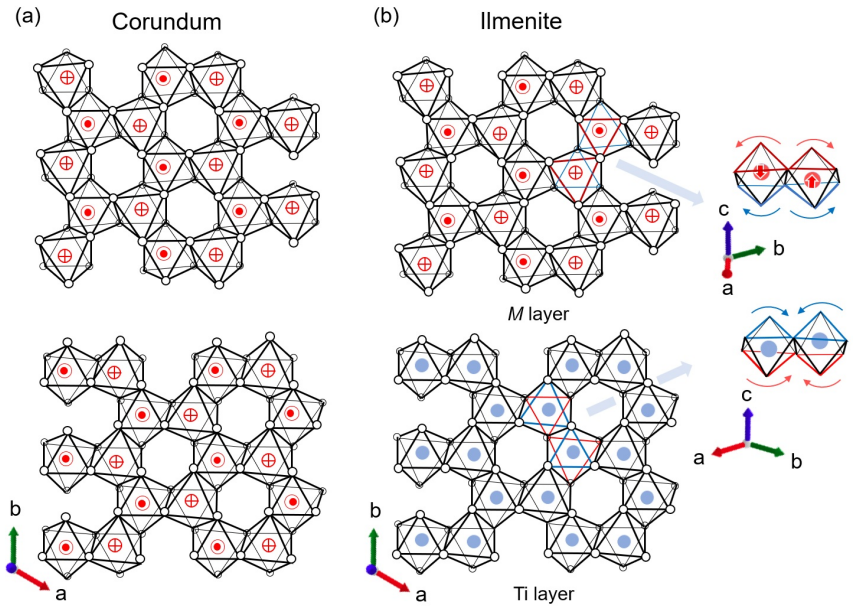

Figure 1: Crystal structures in terms of stacked honeycomb layers for (a) the corundum-type Cr_2O_3 and (b) the ilmenite-type MTiO$_3$. In MTiO$_6$, neighboring MO$_6$ octahedra and the neighboring TiO$_6$ octahedra, respectively, from the M and Ti layers are oppositely twisted. The c lattice parameter of the conventional (hexagonal, not primitive) unit cell is equal to the thickness of six honeycomb layers. The collinear AFM spin moments along the c axis of the Cr and M ions are indicated by red $\oplus$, $\bullet$, and arrows.

electric dipole of ion i at position $\mathbf{r}_i$) pointing towards the $+c$ or $-c$ direction in each ferro-rotational domain.

The opposite twists of neighboring MO$_6$ or TiO$_6$ octahedra in an M or Ti layer mean opposite *local* chiralities, leading to vanishing *global* chirality of the crystal. Because the two neighboring M ions have opposite magnetization in the AFM state [Fig. 1(b)], the product of the local magnetization and the local chirality, which can be termed the local magnetic toroidal moment, has the same sign, leading to finite magnetochiral dichroism (MChD)* in optical absorption, as reported for MnTiO$_3$ [2] and NiTiO$_3$ [3]. The MChD changes sign not only between different ferro-rotational domains but also between different Néel domains because the sign of the E_cH_c term in the free energy is proportional to the c-parallel component of the Néel vector $\mathbf{L}$.

The electric toroidal moment $\mathbf{A}$ defined above is invariant under both spatial inversion I and time reversal T. This is contrasted with the magnetic toroidal moment $\mathbf{T} \equiv \sum_i \mathbf{r}_i \times \mathbf{m}_i$ ($\mathbf{m}_i$: magnetic moment of ion i at position $\mathbf{r}_i$), which changes sign both under I and under T and leads to *transverse linear* responses such as anomalous Hall effect and Faraday rotation [4]. Therefore, one might think that no remarkable magnetic and electronic responses are induced when the order parameter $\mathbf{A}$ becomes finite, i.e., when a ferro-rotational order occurs. However, in the first recommended paper, Du *et al.* report the observation of *trans-*

*MChD is directional dichroism between photon helicities parallel and antiparallel to the applied magnetic field or the magnetization, and is typically observed for globally chiral materials.

verse magnetization along the c direction under external magnetic fields applied applied in the a-b plane using atomic force microscopy. Because of the off-stoichiometry of their samples ($Fe_{1.23}Ti_{0.77}O_3$), the system is ferrimagnetic and the AFM order is irrelevant. It is shown group-theoretically that, under the C_{3i} symmetry, the lowest-order transverse magnetic susceptibility is of the *fifth order*. Du *et al.* also observed that, at boundaries between domains of opposite **A** directions, the magnetization is reduced.

In the second recommended paper, Kusuno *et al.* report a new type of natural CD of phonon Raman scattering, that is, natural Raman optical activity, in the PM phase of $NiTiO_3$. Since the ilmenite structure has spatial inversion symmetry and hence no chirality, there cannot exist chiral phonons that can be viewed as a combined object of rotating atomic vibration within the a-b plane (with finite angular momentum L_c) and its propagation along the c direction (with finite linear momentum q_c): chirality being $\propto L_c q_c$. Nevertheless, the 2D rotating motion of atoms within the a-b plane (finite L_c without q_c dispersion), so-called *planer chiral* or ferro-rotational phonons, can occur.

Selection rules for the Raman scattering of circularly polarized light in the PM $NiTiO_3$ having the electric toroidal order are determined by the symmetries of the phonon modes and those of the incident and scattered light within the C_{3i} point group, where I and T symmetries are preserved but mirror symmetry σ_d is broken. The C_{3i} group has one-dimensional irreducible representations A_g and A_u and two-dimensional representations E_g and E_u. Among these phonon modes, A_g and E_g symmetries are Raman-active. The E_g representation consists of two irreducible representations ${}^1E_g$ or ${}^2E_g$ which are degenerate and related to each other via T operation. As a result, their Stokes-line intensities of Raman scattering depend on the circular polarization of the incident and scattered light defined by the polarizer and the analyzer of the measurement system (R: right-handed; L: left-handed) with respect to the toroidal moment **A** of the crystal domain: R $\rightarrow$ L scattering and L $\rightarrow$ R scattering for one of the E_g phonon modes in $NiTiO_3$ showed different intensities, corresponding to the excitation of ${}^1E_g$ and ${}^2E_g$ modes.

Finally, it is interesting to remark on the ilmenite-derived chiral material Ni_3TeO_6, in which Ni atoms are located at three distinct crystallographic sites Ni_I, Ni_{II}, and Ni_{III}, as shown in Fig. 2. The two metal sites in each honeycomb layer are, therefore, occupied by two inequivalent atoms. The $Ni_{III}O_6$ and TeO_6 octahedra from the

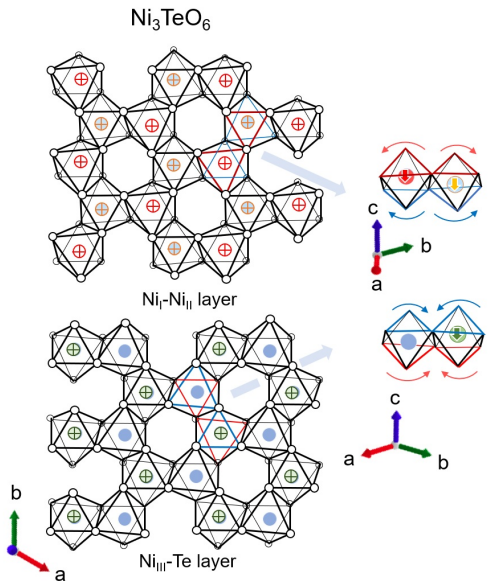

Figure 2: Crystal structure of the ilumenite-derived Ni_3TeO_6. Note that the Ni_I, Ni_{II}, and Ni_{III} atoms are located at crystallographically different sites. All the spins shown in the figure are aligned in the same (-c) direction while those in the neighboring two layers (above and below the indicated two layers) are aligned in the opposite (+c) direction. The c lattice parameters of the structural and magnetic unit cells contain six and twelve honeycomb layers, respectively.

Ni_{III}-Te layers are oppositely twisted. Likewise, the Ni_IO_6 and $Ni_{II}O_6$ octahedra from the Ni_I-Ni_{II} layers are oppositely twisted, too. This breaks the spatial inversion I symmetry of the ilmenites and the crystal symmetry is lowered to space group $R3$ and point group C_3. Now, the oppositely twisted neighboring octahedra in each honeycomb layer have different "strengths" of local chirality, and hence no cancellation occurs in the global chirality. In the absence of inversion symmetry, the electric toroidal moment **A** loses its meaning, while chirality is now well-defined. In fact, instead of the ferro-rotational phonons in the ilumenites as described by Kusuno *et al.* and Huang *et al.* [5], chiral phonons have been predicted and were observed in Ni_3TeO_6 [6].

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