Dichroism as a probe for parity-breaking phases of spin-orbit coupled metals

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(Dated: March 10, 2015)

Recently, a general formalism has been presented for gyrotropic, ferroelectric, and multipolar order in spin-orbit coupled metals induced by spin-spin interactions. Here, I point out that the resulting order parameters are equivalent to expectation values of operators that determine natural circular dichroic signals in optical and x-ray absorption, and list several examples in this connection.

The particular case of the tensor order in the pyrochlore superconductor Cd$_2$Re$_2$O$_7$ is discussed in more detail.

PACS numbers: 78.70.Dm, 75.25.Dk, 75.70.Tj

In an interesting paper, Fu has pointed out that spin-spin interactions in the presence of spin-orbit coupling not only lead to magnetism, but other types of order due to momentum-spin locking [1]. This gives rise to the free-energy

$$E_{ss} = \sum_{k,k'} F_0 s(k) \cdot s(k') + F_1 (k \cdot s(k)) (k' \cdot s(k')) + F_2 (k \times s(k)) (k' \times s(k')) + F_3 Q_{ij}(k) Q_{ij}(k')$$

(1)

where the quadrupolar term is

$$Q_{ij}(k) = \frac{1}{2} (k_i s_j(k) + k_j s_i(k)) - \frac{1}{3} (k \cdot s(k)) \delta_{ij}$$

(2)

with $k$ the momentum and $s$ the spin. For each term, one can specify a particular order - ferromagnetism for $F_0$, isotropic gyrotropic order for $F_1$, ferroelectricity for $F_2$, and pseudo-deviator $F_3$ order for $F_3$ - the last has been suggested for the pyrochlore superconductor Cd$_2$Re$_2$O$_7$ [1]. Moreover, as also discussed in Ref. [1], each term leads to a unique splitting of the Fermi surface due to inversion symmetry breaking (for some illustrations of this splitting, see Ref. [1]).

Here, I wish to point out that the resulting operators listed above $(k \cdot s(k), \text{etc.})$ are equivalent to operators that have been suggested to determine optical and x-ray dichroism [1, 2] if a mapping is made between $k$ and $t$, where $t$ is the polar toroidal moment [7, 8]. $k$ and $t$ have the same transformation properties under inversion and time reversal (both being odd), [8], and thus for the argumentation made in Refs. [1] and [2], they are equivalent. This can also be appreciated from the analogy between the spin-orbit interaction, $(k \times \nabla V) \cdot s$, and the toroidal contribution to the free energy, $-t \cdot (P \times M)$, where $V$ is the crystal potential, $P$ the polarization, and $M$ the magnetization. Polar toroidal ordering has been seen in a number of multiferroics [10, 11], and is also the basis for a novel theory of the pseudogap phase of cuprates by Varma and collaborators [12], following earlier theoretical suggestions of Gorbatsevich et al. [13].

To understand the consequences of this, we discuss each order parameter in turn, denoting each as $X_i$, where $i$ is the index of $F_i$ in Eq. 1 (that is, $X_0 = \sum_k s(k)$, $X_1 = \sum_k k \cdot s(k)$, etc.). $X_0$ is ferromagnetism, and can be determined by XMCD (x-ray magnetic circular dichroism) [11]. The rest, though, are associated with natural (as opposed to non-reciprocal) optical activity, and correspond to HHE (piezo-electric) terms in the free energy, where $H$ and $E$ are the magnetic and electric fields [5]. $X_1$ is a pseudo-scalar (also known as an axial toroidal monopole [15]). It can be seen in natural optical dichroism, due to an interference between electric dipole (E1) and magnetic dipole (M1) terms, and the condition for its observation for various point groups has been tabulated by Jerphagnon and Chemla [16], with a few relevant examples shown in Table 1. Recently, natural dichroism has also been seen in connection with spin wave excitations in a field induced chiral magnet, where it is due to dynamic terms in the diagonal part of the magnetoelectric susceptibility tensor [17]. In general, one expects natural dichroism to be present for chiral magnets since $S \times S \equiv iS$, leading to a $k \cdot S$ term in scattering [18]. In the x-ray regime, it is difficult to observe since the M1 matrix element for excitations out of core orbitals is typically very small.

TABLE I: Examples of several non-centrosymmetric materials and the types of natural optical activity that can occur [19], where PS stands for pseudo-scalar, PV for polar vector, and PD for pseudo-deviator (with 1 denoting allowed). Just because it is allowed does not necessarily mean dichroism can occur. For instance, for Cd$_2$Re$_2$O$_7$ (I4m2 space group) and Bi$_2$2212, XNCD is zero for x-rays propagating along the c axis.

| Material | Space Group | PS | PV | PD |
|----------|-------------|----|----|----|
| HgTe     | F43m        | 0  | 0  | 0  |
| TaAs     | I41md       | 0  | 1  | 0  |
| Cd$_2$Re$_2$O$_7$ | I4$_1$22 | 1  | 0  | 1  |
| LiOsO$_3$ | R3c        | 0  | 1  | 0  |
| CdS, ZnO | P6$_3$mc    | 0  | 1  | 0  |
| Te       | P3$_1$21    | 1  | 0  | 1  |
| Bi$_2$Sr$_2$CaCu$_2$O$_{8+x}$ | Bb2b | 0  | 1  | 1  |
As commented in Ref. 1, \( X_3 \) is equivalent to ferroelectric order. The dichroism associated with this is the vector part of the natural optical activity, commonly known as Voigt-Fedorov dichroism. It is due to a longitudinal component of the electric polarization \( \mathbf{P} \), a specific property of pyroelectric materials \( \mathbf{P} \), and has been seen optically in CdS where it induces polarization rotation in the reflected beam \( \mathbf{P} \). Recently, it has also been seen by resonant x-ray scattering in ZnO as an x-ray circular intensity differential \( \mathbf{P} \). Since the latter measurements were done at the Zn K edge, the resulting operator actually involves the orbital and orbital toroidal moments rather than their spin counterparts \( \mathbf{P} \). The non-centrosymmetric point groups associated with this order may or may not have a pseudo-scalar component as well \( \mathbf{P} \) (Table 1). Note that for toroidal order, the application of an electric field perpendicular to the toroidal moment induces a magnetic field perpendicular to both, and vice versa \( \mathbf{P} \). A similar ‘inverse Rashba effect’ has been discussed in Ref. 4 for Rashba spin-orbit coupled metals (with \( k \times S \) along \( z \)), where current applied along \( y \) leads to a magnetic field along \( x \) and vice versa \( \mathbf{P} \). For Dresselhaus coupling, one finds a longitudinal response instead \( \mathbf{P} \). Ref. 1 also mentions the recently claimed ferroelectric metal LiOsO\(_3\) \( \mathbf{P} \). At the structural transition, the space group converts from the centrosymmetric \( \mathbf{P} \) to the non-centrosymmetric \( \mathbf{P} \). According to Ref. 1, the latter space group should give rise to vector optical activity, but no pseudo-scalar or pseudo-deviator, and in that sense is similar to CdS and ZnO, as well as the Weyl semimetal TaAs \( \mathbf{P} \) (Table 1).

Most interesting is \( X_3 \), which is known in the dichroic literature as a pseudo-deviator \( \mathbf{P} \), and again may or may not be observed depending on the space group. This operator defines x-ray natural circular dichroism (XNCD) \( \mathbf{P} \), and is due to electric dipole \( \mathbf{P} \) - electric quadrupole \( \mathbf{P} \) interference resulting from inversion breaking (circular dichroism being the difference in absorption between left and right circularly polarized light). At the transition metal K edge, it again involves orbital as opposed to spin operators. There are five possible terms (since \( Q \) is a traceless symmetric matrix), and depending on the crystal symmetry, they can form one-dimensional, two-dimensional or three-dimensional representations. As discussed in Ref. 1, a double-dimensional representation has been proposed for the tetrahedral pyrochlore \( \mathbf{P} \) with the associated Goldstone mode seen by Raman scattering \( \mathbf{P} \). Though no optical activity has been reported, second harmonic generation has been seen \( \mathbf{P} \).

When considering such tensor order in \( \mathbf{P} \), note that the double-dimensional representation has as a basis the two space groups, \( \mathbf{P} \) and \( \mathbf{P} \). Below the structural ordering temperature, this degeneracy is broken, and the latter crystal structure has been claimed from x-ray measurements \( \mathbf{P} \). On the other hand, it has been proposed that the former is realized below a second lower structural transition temperature \( \mathbf{P} \). This can be determined by XNCD. Assuming \( \mathbf{P} \) propagating along the \( c \) axis of the tetragonally distorted crystal (advantageous as well, since it eliminates any contamination from linear dichroism), the XNCD signal is zero for the latter crystal structure due to the presence of a mirror plane. But it does exist for the former, and explicit calculations at the O K edge using the FDMNES program \( \mathbf{P} \) find a sizable dichroism of order \( 10^{-3} \) of the absorption peaks \( \mathbf{P} \). The dichroism, though, is present without spin-orbit, but the energy dependence of the signal differs from that which includes spin-orbit. This difference could be used to test whether the dichroism has a structural or electronic origin. The absorption at the O K edge for \( \mathbf{P} \) has been reported by two groups (qualitatively consistent with these calculations), but no dichroism has been reported up to now \( \mathbf{P} \). Certainly, if dichroism was looked for, it could be used to tell which space group is realized below the upper and lower structural phase transitions.

It may seem puzzling that natural optical activity is being described by products of operators that each break time reversal. As commented on by Di Matteo et al. \( \mathbf{P} \), although XNCD is often claimed to be due to the rank-2 tensor product of the orbital angular momentum and orbital toroidal moment \( \mathbf{P} \), a more natural explanation is due to a quadrupolar arrangement of electric dipoles, known as an axial toroidal quadrupole. Such is easily demonstrated to be present in \( \mathbf{P} \), for instance, due to movements of the oxygen atoms off their high symmetry locations to form counter propagating dipole moments on the hexagonal planes above and below the vanadium sites \( \mathbf{P} \).

Finally, more detailed information can often be obtained from x-ray scattering, since one can obtain information as a function of incoming and outgoing polarization, as well as azimuthal angle. An additional advantage is that local inversion-breaking effects can also be seen in centrosymmetric space groups due to the differing phase factor on each atom that arises from Bragg vectors not at the origin \( \mathbf{P} \).

In summary, natural circular dichroism is a sensitive probe that can be used to identify the inversion-symmetry breaking order parameters suggested in Ref. 1. In addition, if time-reversal is broken, other novel types of dichroism can occur as well, including magneto-chiral and non-reciprocal linear dichroism \( \mathbf{P} \), along with their x-ray scattering analogues \( \mathbf{P} \).

The author thanks Liang Fu and Sergio Di Matteo for several helpful discussions. This work was supported by the Materials Sciences and Engineering Division, Basic Energy Sciences, Office of Science, US DOE.
A pseudo-deviator is a rank-2 tensor that is odd under inversion.

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