Physics Letters A 378 (2014) 2461–2465

Contents lists available at ScienceDirect

Physics Letters A

www.elsevier.com/locate/pla

Molecular theory of linear magnetoelectricity

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ARTICLE INFO

Article history:
Received 5 May 2014
Received in revised form 18 June 2014
Accepted 18 June 2014
Available online 23 June 2014
Communicated by P.R. Holland

Keywords:
Magnetoelectric tensors
Molecular polarizability
Property tensors
Origin dependence
Crystal point groups
Post constraint

ABSTRACT

We present a theory of molecular contributions to magnetoelectric tensors for anisotropic linear media, due to induced moments at electric quadrupole–magnetic dipole order. This includes a constraint-breaking pseudoscalar (axion) X, evaluated relative to crystallographic axes. In general, the crystal point groups are classified according to the structures they permit for these tensors, including whether non-zero X (and hence violation of the Post constraint) is allowed. The calculated macroscopic observable X is origin independent (dependent) if the time-odd electric dipole–electric dipole polarizability density $\bar{\alpha}'_{ij} = 0 (\neq 0)$; a feature that prompts an analogy with the Buckingham effect.

1. Introduction

In a previous paper [1] we presented a molecular theory of the magnetoelectric tensors for Cr_2O_3 – work that was motivated by the discovery [2–4] of a pseudoscalar (axion) contribution in antiferromagnetic Cr_2O_3 (cf. the quantity X in (2) and (3)). The analysis in [1] applies to a crystal having the uniaxial point group $\underline{\bar{3}m}$ of Cr_2O_3. This paper is a sequel to [1] in which we extend the theory at electric quadrupole–magnetic dipole order to cover all crystal point-group symmetry classes.

The pseudoscalar X is a macroscopic observable of considerable significance in its own right [2–5]; here we are interested in a theory of X with a view to clarifying a long-standing debate over the role of the so-called Post constraint (5) in the electromagnetic constitutive tensor for linear anisotropic media. The theory (Section 3) also enables us to discuss the question of origin independence/dependence of the molecular contribution to X (and the other magnetoelectric observables V_{ij} and W_{ij} in (2) and (3)), and to make an analogy in this regard with the Buckingham effect (Section 4).

In Section 5 we consider the theory in relation to the various crystal point groups. This leads to a classification of point groups according to which of V_{ij}, W_{ij}, and X they permit. The classification is valid to any multipole order, and also for other contributions to the magnetoelectric response.

2. Magnetoelectric relations

We consider linear magnetoelectric relations that are expressed in 3-dimensional Cartesian form and connect the macroscopic response fields **D, H** with the electromagnetic fields **E, B**:

$$D_i = T_{ij} B_j, \qquad H_i = U_{ij} E_j, \tag{1}$$

where the magnetoelectric tensors T_{ij} and U_{ij} are axial and time odd. Also, a repeated subscript implies summation from 1 to 3. In the molecular theory of Section 3 we obtain the general forms (our notation is that of [1])

$$T_{ij} = -iV_{ij} + W_{ij} + X\delta_{ij}, \tag{2}$$

$$U_{ij} = -iV_{ji} - W_{ji} - X\delta_{ij}, \tag{3}$$

where W_{ij} is traceless:

$$W_{ii} = 0. \tag{4}$$

V_{ij} is time even; W_{ij} and X are time odd. Each term in (2) and (3) is an axial tensor – thus, X is an axial scalar (pseudoscalar). (By "general" we mean that (2) and (3) should apply to all crystal symmetries, and not just the point group $\underline{\bar{3}m}$ of Cr_2O_3 that was considered in [1]. It turns out that (2) and (3) are general also in other ways – see Section 5.)

There has been an extensive debate (see [2–6] for discussion and references) concerning the validity of the Post constraint [7]

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http://dx.doi.org/10.1016/j.physleta.2014.06.030

$$T_{ii} = U_{ii} \tag{5}$$

requiring equality of the traces of the magnetoelectric tensors [8, Chap. 4]. According to (2)–(4),

$$X = \frac{1}{6}(T_{ii} - U_{ii}) \tag{6}$$

is the parameter (also known as the Tellegen constitutive parameter [5]) that indicates whether (5) is satisfied. The finding of a non-zero value of X in antiferromagnetic Cr_2O_3 (see [2–4], where X is denoted by $\tilde{\alpha}$) demonstrates that (5) is not a universal condition (see also Section 6). We are interested here in a molecular theory of the observables in (2) and (3) that applies to all point-group symmetry classes, and its significance for the status of the Post constraint in linear electrodynamics.

3. Molecular theory of the magnetoelectric tensors

We wish to determine the leading contributions to the dynamic magnetoelectric tensors due to induced molecular multipole moments in semi-classical electrodynamics. This means working to electric quadrupole–magnetic dipole order [8], and therefore (as explained in [1]) we are concerned, in general, with 6 molecular polarizability tensors. These are obtained from quantum-mechanical perturbation theory for molecules interacting with harmonic, plane electromagnetic waves **E** and **B** [8,9].

Of importance in the theory are the space and time properties of the dynamic polarizabilities: namely, whether they are polar or axial; time even or time odd; and origin dependent or independent (with respect to the choice of molecular coordinate origin relative to which they are evaluated). These properties of the molecular tensors are contained in their quantum-mechanical formulae [8, Chap. 3], and they carry over to the corresponding polarizability densities, such as those defined for crystals in (9).

Two of the 6 polarizabilities are of electric dipole order: the time-even electric dipole–electric dipole polarizability α_{ij} and its time-odd counterpart α'_{ij} (both are polar and origin independent). The other four are of electric quadrupole–magnetic dipole order: the time-even electric dipole–magnetic dipole polarizability G'_{ij} and its counterpart G_{ij} (both are axial, origin dependent); and the time-even electric dipole–electric quadrupole polarizability a_{ijk} and its counterpart a'_{ijk} (both are polar, origin dependent) [8,9].

The polarizabilities contribute separately to the induced molecular moments, and therefore also to the associated response fields **D** and **H** [1,10,11]. Thus, some results can be transcribed from [1] where the contributions of α_{ij}, G_{ij}, and a'_{ijk} are derived relative to crystallographic axes (these are the only relevant polarizabilities for Cr_2O_3). In particular [1, Eqs. (26), (27)],

$$W_{ij} = \bar{G}_{ij} - \frac{1}{3}\bar{G}_{kk}\delta_{ij} - \frac{1}{6}\omega\varepsilon_{jk\ell}\bar{a}'_{k\ell i}, \tag{7}$$

$$X = \frac{1}{3}\bar{G}_{kk}, \tag{8}$$

where ω is the angular frequency of the fields and $\varepsilon_{jk\ell}$ is the Levi-Civita tensor. Here, and in what follows, a bar denotes a polarizability density

$$\bar{t}_{ij\ldots} \equiv \sum_{\gamma} \mathcal{N}^{(\gamma)} t^{(\gamma)}_{ij\ldots}. \tag{9}$$

The sum in (9) is over all molecules (ions/charge distributions) in a unit cell, each having polarizability $t^{(\gamma)}_{ij\ldots}$ (evaluated relative to crystallographic axes) and number density $\mathcal{N}^{(\gamma)}$. An ensemble average [12] is implicit in (9).

We mention that a'_{ijk} also contributes to the permittivity of the medium, as do α_{ij} and α'_{ij} (in the combination $\alpha_{ij} - i\alpha'_{ij}$ [8, Eq. (2.110)]). Then, from (24) of [1], we find that the permittivity in $D_i = A_{ij}E_j$ is

$$A_{ij} = \varepsilon_0\delta_{ij} + \bar{\alpha}_{ij} - i\bar{\alpha}'_{ij} + k_k S_{ijk}, \tag{10}$$

where **k** is the wave vector of the fields, and

$$S_{ijk} = \frac{1}{3}\left(\bar{a}'_{ijk} + \bar{a}'_{jki} + \bar{a}'_{kij}\right). \tag{11}$$

This leaves the contributions of G'_{ij} and a_{ijk} to the magnetoelectric tensors (2) and (3). We give an outline of the calculation because it illustrates further the direct method used in [1]. We continue to work relative to crystallographic axes. Our starting point is the contribution of these polarizabilities to the macroscopic induced bound source densities, namely

$$\rho_b = \frac{1}{\omega}\varepsilon_{ik\ell}V_{j\ell}\nabla_i\nabla_j E_k, \tag{12}$$

$$J_{bi} = i(\varepsilon_{ij\ell}V_{k\ell} + \varepsilon_{jk\ell}V_{i\ell})\nabla_j E_k, \tag{13}$$

where

$$V_{ij} = \bar{G}'_{ij} - \frac{1}{2}\omega\varepsilon_{jmn}\bar{a}_{mni}. \tag{14}$$

(Eq. (12) can be obtained from (31) of [10] by including an ensemble average [12] and taking account of the unit cell structure. Similarly for $\mathbf{J}_b$ in (13) – cf. (35) of [10].) The arguments of the fields and sources in (12), (13), and what follows are $(\mathbf{r}, t)$.

The contributions of the property tensors [13] $\bar{G}'_{ij}$ and $\bar{a}_{ijk}$ to **D** and **H** are obtained by using (12) and (13) in the inhomogeneous macroscopic Maxwell equations for **E** and **B** [8],

$$\varepsilon_0\nabla_i E_i = \rho_f + \rho_b, \tag{15}$$

$$\mu_0^{-1}\varepsilon_{ik\ell}\nabla_k B_\ell = J_{fi} + J_{bi} + \varepsilon_0\dot{E}_i, \tag{16}$$

where ρ_f and $\mathbf{J}_f$ are free source densities. The calculations employ two tensor identities, namely

$$\varepsilon_{ik\ell}V_{j\ell}\nabla_i\nabla_j E_k = -V_{ij}\nabla_i\dot{B}_j \tag{17}$$

and

$$(\varepsilon_{ij\ell}V_{k\ell} + \varepsilon_{jk\ell}V_{i\ell})\nabla_j E_k = \varepsilon_{ik\ell}V_{j\ell}\nabla_k E_j - V_{ij}\dot{B}_j, \tag{18}$$

that are based on Faraday's law, $\varepsilon_{ik\ell}\nabla_i E_k = -\dot{B}_\ell$. According to (12) and (17) with $\dot{B}_j = -i\omega B_j$, (15) can be written $\nabla \cdot \mathbf{D} = \rho_f$ where

$$D_i = \varepsilon_0\delta_{ij}E_j - iV_{ij}B_j. \tag{19}$$

And, according to (13) and (18) we can write (16) as $\nabla \times \mathbf{H} = \mathbf{J}_f + \dot{\mathbf{D}}$, where **D** is given again by (19) and

$$H_i = \mu_0^{-1}\delta_{ij}B_j - iV_{ji}E_j. \tag{20}$$

Thus, (19) and (20) show that the tensor V_{ij} in (2) and (3) is expressed, to electric quadrupole–magnetic dipole order, by the linear combination (14).

To summarize, the 6 molecular polarizabilities up to electric quadrupole–magnetic dipole order provide 6 polarizability densities that are property tensors [13] for the induced bound source densities, and contribute to the macroscopic observables of the constitutive tensor as follows: At electric dipole order, $\bar{\alpha}_{ij} - i\bar{\alpha}'_{ij}$ is the leading multipole term in the permittivity (10). At the next order, the two time-even densities ($\bar{G}'_{ij}$ and $\bar{a}_{ijk}$) provide the leading contributions to V_{ij} in the magnetoelectric tensors (2) and (3). And their time-odd counterparts ($\bar{G}_{ij}$ and $\bar{a}'_{ijk}$) provide 3 contributions – to W_{ij} and X in (2) and (3), and a second-order contribution $k_k S_{ijk}$ to the permittivity (10). It is apparent that (2) and (3)