Third-rank piezoelectricity in isotropic chiral solids

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The highest symmetry in which piezoelectricity was thought to occur is cubic. Here it is shown that third rank piezoelectricity can occur in isotropic chiral solids. Polarization is coupled via an isotropic third rank tensor to the antisymmetric part of the stress. Asymmetric stress can occur if balanced by moments distributed over area or volume. Such moments occur in heterogeneous solids in which there exists a characteristic length associated with the microstructure: the Cosserat or micropolar solids. Effects associated with nonzero structure size are predicted, including radial polarization in response to torsion. These effects do not occur in gradient type flexoelectric materials; they are governed by a different tensorial rank and symmetry.

Piezoelectric materials produce an electric polarization when stressed mechanically, and they deform in response to an electric field. They are widely used in transducers, sensors and actuators. The quest for enhanced properties has been the subject of much research. Piezoelectric single crystals and polycrystalline aggregates always have chiral asymmetry. The strain ϵ_{ij} depends on stress σ_{kl} via the elastic compliance J_{ijkl}, and on electric field $\mathcal{E}_k$ via the piezoelectric modulus tensor [1] d_{kij}. Strain also varies with temperature change ΔT via the thermal expansion α_{ij}. The electric displacement vector $\mathcal{D}_i$ depends on electric field via the dielectric permittivity tensor k_{ij}. In pyroelectric materials $\mathcal{D}_i$ depends on temperature change ΔT via the pyroelectric coefficient p_i. Aside from the requirement of chirality, the allowable symmetry conditions have been thought to be immutable and not to provide freedom for material development.

$$\epsilon_{ij} = J_{ijkl}\sigma_{kl} + d_{kij}\mathcal{E}_k + \alpha_{ij}\Delta T \qquad (1a)$$
$$\mathcal{D}_i = d_{ijk}\sigma_{jk} + k_{ij}\mathcal{E}_j + p_i\Delta T \qquad (1b)$$

Triclinic asymmetry can result in a fully populated piezoelectric sensitivity tensor, while a cubic material has three shear coefficients such as d_{123}, all of equal magnitude [1]. There are currently no known isotropic piezoelectric materials. In this Letter we show that third rank piezoelectricity is in fact possible in isotropic chiral materials that have a characteristic length scale.

The relation between chirality and third rank properties such as piezoelectricity is generalized to include isotropy. For the sensitivity d_{ijk} to have at least one nonzero component, there must be chiral asymmetry. There are no known isotropic piezoelectric materials and no obvious reason to seek them; such effects are not expected in classically elastic solids in view of the direction independence of isotropic solids. For example, coupling of a uniform electric field vector to uniform shear strain is not expected in isotropic materials because shear has directional aspects. In the following, it is demonstrated that third rank piezoelectricity can occur in isotropic chiral materials; the directional aspect is provided via rotation gradient.

There is one isotropic third rank tensor, the permutation symbol e_{ijk}. This suggests the possibility of third rank piezoelectricity in isotropic solids. However, $e_{ijk} = -e_{ikj}$ so isotropic piezoelectric effects entail antisymmetric stress via Eq. 1b or antisymmetric displacement gradient. The stress is symmetric in classical elastic solids. Also, only the symmetric part of the displacement gradient, the strain, enters the classical constitutive equation 1a.

These effects may be understood in the context of Cosserat [2] elasticity, also called micropolar [3] elasticity. Cosserat elasticity [4] is a *continuum* theory that incorporates a rotation of points as well as the translation assumed in classical elasticity. The stress σ_{jk} (force per unit area) can be asymmetric. The couple stress m_{jk} (a torque per unit area) balances the moment from the asymmetric stress. The antisymmetric part of the stress is related to rotations as $\sigma_{jk}^{antisym} = \kappa e_{jkm}(r_m - \phi_m)$ in which κ is an elastic constant, ϕ_m is the rotation of points, and $r_k = \frac{1}{2}e_{klm}u_{m,l}$ is rotation based on the antisymmetric part of gradient of displacement u_i. The constitutive equations [3] for isotropic Cosserat elasticity are as follows.

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$$\sigma_{kl} = \lambda\epsilon_{rr}\delta_{kl} + 2G\epsilon_{kl} + \kappa e_{klm}(r_m - \phi_m) \quad (2a)$$

$$m_{kl} = \alpha\phi_{r,r}\delta_{kl} + \beta\phi_{k,l} + \gamma\phi_{l,k} \quad (2b)$$

An isotropic non-chiral Cosserat solid is describable by six independent elastic constants. The elastic constants λ and G have the same meaning as in classical elasticity with G the shear modulus; α, β, γ represent sensitivity to gradients of local rotation in different directions, allowing a nonlocal interaction. κ quantifies the coupling between the rotation field and deformation field. Characteristic lengths are defined based on ratios of tensorial constants. The characteristic length for torsion is $\ell_t = \sqrt{\frac{\beta+\gamma}{2G}}$. The characteristic length for bending is $\ell_b = \sqrt{\frac{\gamma}{4G}}$. A dimensionless coupling number $N = \sqrt{\frac{\kappa}{2G+\kappa}}$ quantifies the degree of coupling between rotation and displacement fields; it is between zero and one. A dimensionless polar ratio $\Psi = \frac{\beta+\gamma}{\alpha+\beta+\gamma}$ relates effects of rotation gradients in different directions; it is between zero and 1.5. These elastic constants have been determined in several cellular materials from size effect experiments [5, 6]. In these foams, the characteristic length is on the order of the cell size; 0.3-1 mm. Moreover, asymmetry of the stress in cellular solids has been demonstrated via holographic interferometry [7, 8]. Waves associated with rotational freedom have been observed [9] in granular materials.

Piezoelectricity in isotropic chiral solids at constant temperature is envisaged with a direct effect sensitivity $d_{ijk}^{iso} = e_{ijk}d$. So $d_{ijk}^{iso}\sigma_{jk}^{antisym}$ contributes to the electric displacement $\mathcal{D}_i$ in Eq. 1b via the last term in Eq. 2a, with k as the dielectric permittivity:

$$\mathcal{D}_i = d_{ijk}\kappa e_{jkm}(r_m - \phi_m) + k\delta_{ij}\mathcal{E}_j. \quad (3)$$

As for the converse isotropic piezoelectric effect via displacement gradients, the strain ϵ_{ij} is symmetric by definition. The antisymmetric part of the displacement gradient $r_k = \frac{1}{2}e_{kji}u_{i,j}$ is related to rotation $r_{ij} = \frac{1}{2}(u_{i,j} - u_{j,i})$, so in a converse effect, electric field is related to rotation difference rather than strain. The rotation difference gives rise to an asymmetric stress via Eq. 2a. The antisymmetric converse effect for isotropic materials is expressed

$$\frac{\kappa}{G}e_{ijm}(r_m - \phi_m) = d_{kij}^{iso}\mathcal{E}_k. \quad (4)$$

The symmetric part is the usual elasticity relation $\epsilon_{ij} = \frac{\sigma_{ij}}{2G} - \frac{\nu\sigma_{nn}\delta_{ij}}{2G(1+\nu)}$. Both asymmetric stress and asymmetric displacement gradient are related to observable deformation fields in this class of materials.
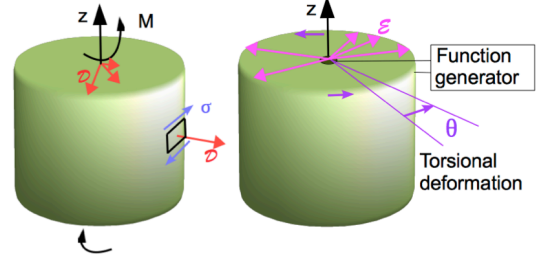

FIG. 1. Left, diagram of torsion moment M causing asymmetric stress $\sigma_{z\theta} - \sigma_{\theta z}$ as driver for electric displacement $\mathcal{D}$. Right, diagram of torsional deformation in response to an applied radial electric field $\mathcal{E}$.

This is in contrast to nonlocal integral approaches [10] that are approximated as gradient effects.

All materials have at least one structural length scale, that of the spacing of atoms; composites and cellular solids also have much larger structural length scales. Piezoelectric solids also have a characteristic distance of charge separation, typically on the order of the unit cell size. Piezoelectric solids, when characterized in a quasi-static experiment, are typically subjected to a uniform stress or a uniform electric field. The response is also considered to be uniform. The chirality that gives rise to piezoelectric response is on the atomic or molecular scale, too small to observably perturb the elastic field unless the experiment probes the nano-scale.

As for predicted phenomena in chiral, directionally isotropic solids with a length scale, asymmetric stress associated with twist in an elastically isotropic Cosserat solid is shown in Figure 1, left. A rod of radius R and shear modulus G is subjected to a torsional moment M. The asymmetric stress [11] is balanced by a moment per area and is given by

$$\sigma_{z\theta} - \sigma_{\theta z} = 2\kappa C_9 I_1(pr). \quad (5)$$

This stress is coupled to electric displacement via Eq. 3 in the piezoelectric isotropic solid. Here I_1 is the modified Bessel function of order 1 and $p^2 = \frac{2\kappa}{\alpha+\beta+\gamma}$. This can be expressed in terms of the characteristic length ℓ_t, defined above, as $p = \frac{1}{\ell_t}\sqrt{\frac{\kappa}{G}}\sqrt{\Psi}$. $C_9 = \frac{M}{2\pi R^2}[[\frac{R^2}{4\ell_t^2} + \frac{3}{2}](\alpha + \beta + \gamma)pI_0(pR) - [\frac{R^2}{4\ell_t^2} + 2]\frac{\beta+\gamma}{R}I_1(pR)]]^{-1}$. It is expedient for the purpose of visualization to consider a limiting case $pR << 1$. For that case, which corresponds to $N << 1$ or weak coupling, $C_9 \approx \frac{M}{G\pi R^4}\ell_t\sqrt{\frac{G}{\kappa}}\frac{\sqrt{\Psi}}{1-\Psi/2}$. So in this case, the asymmetric stress, hence the electric displacement, increases radially as $\kappa\frac{M}{G\pi R^4}\frac{\sqrt{\Psi}}{1-\Psi/2}r$.

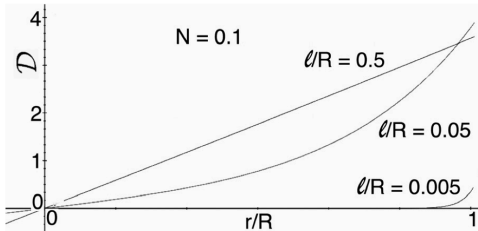To observe the piezoelectric effect by this method,

FIG. 2. Electric displacement $\mathcal{D}$ depends on radial distance r as a function of characteristic length ℓ_t at constant coupling number N via Eq. 5.
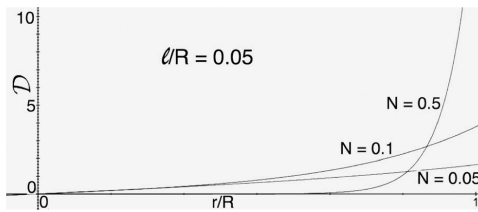

FIG. 3. Electric displacement $\mathcal{D}$ (arbitrary units) depends on radial distance r as a function of coupling number N at constant characteristic length ℓ_t via Eq. 5.

a rod of material is subjected to torsion, and polarization is measured between electrodes at the rod central axis and on the curved surface. This is a direct effect. As is the case with the usual measurements of piezoelectric polarization $\mathcal{P}$, a charge amplifier fixes the electric field to zero by feedback. Electric displacement is then equivalent to polarization via $\mathcal{D} = \epsilon_0 \mathcal{E} + \mathcal{P}$. The microstructure size cannot be negligible in comparison with experimental length scales or $\ell_t \to 0$ and the effect vanishes. Observation of a radial signal suffices to demonstrate the effect. To quantitatively determine the sensitivity d via Eq. 5 and 3, it is necessary to determine the Cosserat elastic constants, e. g. by measuring the size effect of rigidity in torsion. For foams studied previously, ℓ_t is 0.3 to 1 mm, on the order of the cell size, and N is from 0.1 to 0.2.

The radial electric displacement in response to torsion also depends on radial distance r and on characteristic length ℓ_t based on the exact solution Eq. 5 as shown in Figure 2. Dependence on coupling number N at constant ℓ_t is shown in Figure 3. The magnitude of the effect tends to increase with ℓ_t and with N. The r dependence is a function of elastic constants associated with the microstructure; electrodes within the material can be used to determine this dependence.

A suggested experimental modality to detect twisting deformation in response to a radial elec-

tric field is shown in Figure 1, right. In both direct and converse methods, electrodes (which can be flexible if needed for a foam material) are applied to the curved surface and along the z axis. To demonstrate effects in three orthogonal directions, a cubical specimen could be used; this entails use of a more complicated analytical solution or of approximations for interpretation. Heterogeneous materials are unlikely to be perfectly isotropic; nevertheless, detection of radial effects will suffice to demonstrate the concept.

Isotropic chiral materials include gels made from randomly oriented molecules of the protein collagen. Not surprisingly, such gels do not exhibit piezoelectricity when measured using the usual methods [12], however piezoelectricity occurs if anisotropy is induced via a strong DC electric field. Collagen is piezoelectric in its oriented form. Chirality may occur in self assembled materials [13], but piezoelectricity in them has not been explored. Piezoelectricity in these chiral materials differs from the effects predicted here in that uniform fields or stresses were applied. Piezoelectric effects in chiral isotropic elastic solids may have escaped notice thus far because (i) the chiral characteristic lengths in typical piezoelectric material are likely to be on the order of the unit cell size (atomic scale), much smaller than dimensions of typical experimental samples; (ii) the role of elastic chirality has not been appreciated and the requisite experiments have not been done. Chirality is known in two dimensional lattices [14] with nodes that rotate under strain. Variants with nodes that rotate in opposite directions [15] are not expected to exhibit elastic chirality.

These effects are distinct from gradient effects that are known [10, 16–18] in piezoelectric materials:

$$\mathcal{D}_i = d_{ijkl} \frac{\partial \sigma_{jk}}{\partial x_l}. \tag{6}$$

Such effects involve a fourth rank coupling tensor in contrast to a tensor of third rank considered above. Recently, gradient effects have been explored further and named flexo-electric; these are of interest in the context of the potential for large effects [19]. Moreover, while gradients occur in bending, bending is not essential to produce a gradient in stress or strain. For example, compression of a cone gives rise to a gradient coupled via d_{3333}; such cones have been considered in the context of piezoelectric composites [20]. Such gradient effects do not require chirality in the material. Gradient effects can occur in materials of various symmetry [21] including isotropic materials. Observe that the fourth rank d_{ijkl} can be an isotropic tensor, $A\delta_{ij}\,\delta_{kl} + B\delta_{ik}\,\delta_{jl} + C\delta_{il}\,\delta_{jk}$. For torsion in which σ_{23} varying along the 1 direction gives rise to $\mathcal{D}_1$, there can be no effect due to gradient piezoelectricity in an isotropic material because

$d_{1231} = 0$. By contrast an effect is predicted via the coupling considered here. So the effects can be readily distinguished. Too, flexo-electric effects are ordinarily so weak that signals from them are not detectable on a macroscopic scale.

If chirality occurs on a sufficiently large length scale in comparison with experimental dimensions, effects may be observable in elastic deformation. For such solids, consider the chiral Cosserat constitutive equations [22] as follows. $\sigma_{kl} = \lambda\epsilon_{rr}\delta_{kl} + 2G\epsilon_{kl} + \kappa e_{klm}(r_m - \phi_m) + C_1\phi_{r,r}\delta_{kl} + C_2\phi_{k,l} + C_3\phi_{l,k}$, $m_{kl} = \alpha\phi_{r,r}\delta_{kl} + \beta\phi_{k,l} + \gamma\phi_{l,k} + C_1\epsilon_{rr}\delta_{kl} + (C_2 + C_3)\epsilon_{kl} + (C_3 - C_2)e_{klm}(r_m - \phi_m)$. The elastic constants C_1, C_2 and C_3 represent the effect of chirality. There are nine elastic constants compared with six for isotropic non-chiral Cosserat elasticity, and two for classical elasticity. As with the non-chiral case, characteristic lengths are defined based on ratios of tensorial constants. In chiral Cosserat elasticity [22] there is coupling between stretch and twist. Such stretch-twist coupling has been analyzed for cholesteric elastomers [23] and for helical nano - structures pertinent to DNA [24]. Stretch-twist coupling is a function of all nine elastic constants [22].

As for experiment, chiral gels or rubbers may be considered for small scale experiments. Polymer foams with cells 0.1 to 1 mm in size may be permanently twisted to obtain chirality on a macroscopic scale. The experimental size scale must not exceed the material characteristic length by too large a factor. This is not onerous; it is done in study of flexo-electric effects and in generalized continuum elasticity, e.g. Cosserat, nonlocal. Such materials exhibit non-affine deformation that appears as noise.

Effects associated with micro-structure are predicted, including radial polarization in response to torsion. These effects are in contrast to prior analyses in which piezoelectric composite materials with particulate, fibrous, and platelet microstructure have been studied. These effects also differ in kind from flexo-electric effects. Continuum models for them have been classical in nature, neglecting size effects associated with the microstructure [25, 26]. Such piezoelectric composites have advantages over homogeneous materials [25, 27]. None of these composite designs makes explicit use of microstructure size in the analysis or design. By contrast, the degrees of freedom considered in the present analysis provide further latitude for design.

To conclude, piezoelectric effects are predicted in isotropic chiral solids. The effects are interpreted in the context of Cosserat elasticity in which there is a non-negligible characteristic length scale associated with the microstructure (in comparison with experimental length scales). The effects differ in kind and symmetry from those associated with gradient piezoelectric / flexo - electricity.

[1] J. F. Nye, *Physical Properties of Crystals*, Oxford, Clarendon, (1976).

[2] E. Cosserat and F. Cosserat, Theorie des Corps Deformables, Hermann et Fils, Paris, (1909).

[3] A. C. Eringen, Theory of micropolar elasticity. In Fracture, **1**, 621, Academic, NY (1968).

[4] R. D. Mindlin, Int. J. Solids Structures, **1**. 265-271 (1965).

[5] R. S. Lakes, Int. J. Solids and Struct., **22** 55 (1986).

[6] W. B. Anderson and R. S. Lakes, J. Materials Science, **29**, 6413, (1994).

[7] R. S. Lakes, D. Gorman, and W. Bonfield, J. Materials Science, **20** 2882 (1985).

[8] W. B. Anderson, R. S. Lakes, and M. C. Smith, Cellular Polymers, **14**, 1, (1995).

[9] A. Merkel, V. Tournat, and V. Gusev, Phys. Rev. Lett. **107**, 225502 (2011).

[10] E. V. Bursian and N. N. Trunov, Sov. Phys. Solid State **16**, 760 (1974).

[11] R. D. Gauthier and W. E. Jahsman. J. Applied Mechanics, **42**, 369, (1975).

[12] R. L. Zimmerman, Biophys. J. **16**, 1341, (1976).

[13] G. T. Pickett, M. Gross, and H. Okuyama, Phys. Rev. Lett. **85**, 3652, (2000).

[14] D. Prall, R. Lakes, Int. J. Mech. Sci., **39**, 305-314 (1996)

[15] Y. J. Chen and F. Scarpa and Y. J. Liu and J. S. Leng, Int. J. of Solids Struct., **50**, 996 -1004 (2013).

[16] E. V. Bursian, O. I. Zaikovskii, Sov. Phys. Solid State, **10**, 1121, (1968).

[17] R. D. Mindlin, Int. J. Solids Structures, **4**. 637-642 (1968).

[18] N. N. Trunov, Sov. Phys. Solid State, **17**, 1860, (1975).

[19] I. Naumov, A. M. Bratkovsky, and V. Ranjan, Phys. Rev. Lett. **102**, 217601 (2009).

[20] J. Fousek, L. E. Cross, D. B. Litvin, Materials Letters **39**, 287, (1999).

[21] H. L. Quang and Q. C. He, Proceedings of the Royal Society A: rspa20100521 (2011).

[22] R. S. Lakes and R. L. Benedict, Int. J. Engng Sci., **29**, 1161 (1982).

[23] M. Warner, E. M. Terentjev, R. B. Meyer, and Y. Mao, Phys. Rev. Lett. **85**, 2320, (2000).

[24] J. S. Wang, Y. H. Cui, T. Shimada, H. P. Wu, and T. Kitamura, Appl. Phys. Lett. **105**, 043702 (2014).

[25] E. Newnham, D. P. Skinner, and L. E. Cross, Mater. Res. Bull., **13**, 525 (1978).

[26] K. Schulgasser, J. Mech. Phys. Solids **40** 473 (1992).

[27] W.A. Smith, IEEE ultrasonics symp. 755 (1989).