Nat. Phys. 20, 358–359 (2024)

Metal poles around the bend

Gustau Catalan

ICREA-Institucio Catalana de Recerca i Estudis Avançats, Barcelona, Catalonia.

ICN2-Institut Catala de Nanociencia i Nanotecnologia, Barcelona Institute of Science and Technology (BIST), Campus Universitat Autonoma de Barcelona, Catalonia.

Electric dipoles are common in insulators, but extremely rare in metals. This situation may be about to change, thanks to flexoelectricity.

Electric polarization can be induced by an external field, or appear spontaneously in ferroelectric materials. In insulators, electric fields can propagate easily, and the resulting long-range interactions facilitate the polarization of the lattice. In contrast, as we know since the times of Faraday, metals are impermeable to electric fields, due to them having charges that can screen them. As a consequence, polar metals [1] are among the scarcest types of functional materials [2-4].

Writing in *Nature* Physics, Wei Peng and colleagues [5] report that the scarcity of polar metals can be circumvented by taking a non-polar metal (SrRuO3) and polarizing it. Since an electric field cannot be used for this purpose in a metal, they used instead a mechanical field; specifically, a strain gradient. Unlike electric fields, mechanical deformations can penetrate any material, including metals — as the dictum goes, “strain cannot be screened”. And inhomogeneous strains can induce electric dipoles in any material, thanks to flexoelectricity.

Flexoelectricity is defined as the coupling between electric polarization and strain gradients [6]. The latter (caused, for example, by inhomogeneous deformations, such as kinks or bends) are inherently asymmetric: the strain difference along the gradient direction breaks the equivalence between the two sides. And, once the lattice has asymmetrically deformed, an asymmetric charge distribution – that is, polarization – can occur. Since the lattice asymmetry is caused by the deformation itself, flexoelectric polarization can happen in *any* material, irrespective of its crystal structure. The growing range of materials for which flexoelectricity has been reported includes examples as diverse as ceramics, polymers, semiconductors, bones, ear-hairs, electrets, and even frozen water [7]. Basically, anything that can be bent can be polarized.

In principle, metals can also be flexoelectric [8]. However, measuring a metal’s flexoelectricity is not easy, because the gradient-induced polarization can be compensated by a redistribution of the metal’s free charges, and therefore bending a metal does not generate any external voltage (Figure 1). Peng and co-workers resolved this difficulty by using high-resolution transmission electron microscopy to determine the actual atomic positions inside a metal; by working with bright-field imaging, they can determine the positions of the oxygen ions (which are negatively charged) and the Sr and Ru ions (which are positively charged), showing how the centres of mass of (nominal) positive and negative charge are separated in each unit cell, and thus mapping the polarization. In addition, they observed second harmonic generation (SHG), an optical property of polar materials that allows them to absorb two photons of the same wavelength and re-emit them as a single photon of half the wavelength. Since this property does not feature in centrosymmetric materials, its detection in

SrRuO3is an indication of its polarization. Together with complementary structural characterizations and first-principles calculations, the evidence indicates that thin films of $SrRuO_3$, a non-polar metal, can become polar due to strain gradients.

The strain gradients in the $SrRuO_3$ films studied by Peng and colleagues were generated by ferroelastic domain walls: boundaries between regions of different crystallographic orientation that help relax the substrate-induced strain. In a way, ferroelastic domain walls can be viewed as atomic-scale wrinkles of a crystal's structure. As such, ferroelastic domain walls concentrate very large strain gradients and hence flexoelectricity. But ferroelastic twinning is not the only way to generate strain gradients. They can also be engineered by compositional grading or, in free-standing films, by actual wrinkles or spontaneous curling deformations. Strain-gradient engineering is a rising area of research in oxide ferroelectrics, and the present results suggest that oxide metals can also offer rich pickings in that context.

Are flexoelectric metals useful? While applications should *not* be the primary concern when exploring new physics, finding functionalities is both fun and fundable. Peng and colleagues have already demonstrated one: the conversion of reflected light from one wavelength to another by SHG. It has also been proposed that polar metals with low carrier concentrations may display bulk photovoltaic effects [9]. More generally, any polarization-dependent functionality that can be envisaged for a ferroelectric metal, should also exist in a flexoelectric one. Spintronics is a particularly promising area of functionality, via flexomagnetism. For example, the Rashba-Edelstein effect posits that electrons moving through a polar lattice perceive the moving polarization (with respect to the electron framework) as an effective magnetic field, and can thus become spin-polarized [10]. Since the symmetry argument is independent of whether the polarization is spontaneous (as in a ferroelectric metal) or induced (as in a bent metal), the door is open for a "flexo-Rashba" effect in curved metals.

The discovery of flexoelectric polarization in $SrRuO_3$ is important precisely because there is nothing special about this material from a flexoelectric point of view; if this particular metal can be polarized by strain gradients, surely others will be too. Thus, while ferroelectric metals may remain rare, flexoelectrically-polarized ones may soon become quite common.

The author declares no conflict of interest.

REFERENCES

1. P. W. Anderson and E. I. Blount, "Symmetry Considerations on Martensitic Transformations: "Ferroelectric" Metals?". Phys. Rev. Lett. 14, 217 (1965).
2. T. Kolodiazhnyi, M. Tachibana, H. Kawaji, J. Hwang, and E. Takayama-Muromachi, "Persistence of Ferroelectricity in $BaTiO_3$ through the Insulator-Metal Transition". Phys. Rev. Lett. 104, 147602 (2010).
3. Y. Shi et al., "A ferroelectric-like structural transition in a metal". Nature Materials 12, 1024–1027 (2013).
4. Z. Fei, W. Zhao, T. A. Palomaki, B. Sun, M. K. Miller, Z. Zhao, J. Yan, X. Xu, D. H. Cobden, Ferroelectric switching of a two-dimensional metal. Nature 560, 336–339 (2018).
5. W. Peng *et al*, Flexoelectric polarizing and control of a ferromagnetic metal. Nature Physics XX.

6. P. Zubko, G. Catalan, A.K. Tagantsev, "Flexoelectric Effect in Solids". Ann. Rev. of Mat. Res. 43, 387 (2013).
7. X. Wen, Q. Ma, S. Shen, G. Catalan, "Flexoelectricity and surface phase transition in natural ice" arXiv:2212.00323 (2022).
8. A. Zabalo, M. Stengel, "Switching a Polar Metal via Strain Gradients". Physical Review Letters 126, 127601 (2021).
9. A. Filippetti, V. Fiorentini, F. Ricci, P. Delugas & J. Íñiguez, "Prediction of a native ferroelectric metal" Nature Communications 7, Article number: 11211 (2016).
10. V. M. Edelstein, "Magnetoelectric Effect in Polar Superconductors" Phys. Rev. Lett. 75, 2004 (1995).

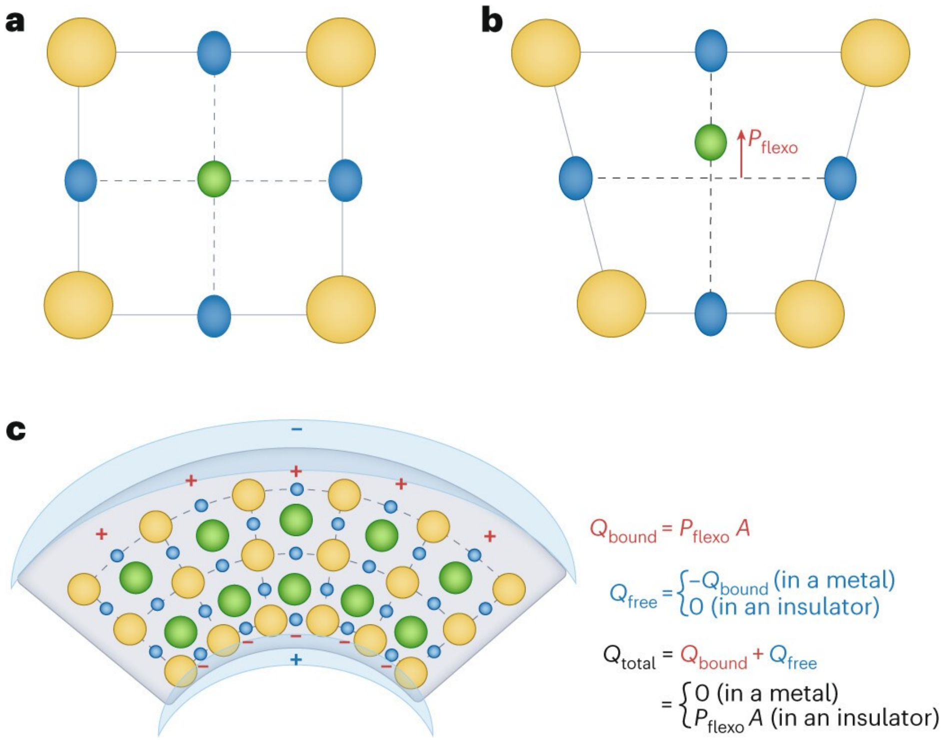

Figure 1: Flexoelectric polarization in a centrosymmetric crystal, and carrier redistribution in a polarized metal vs. a polarized insulator. **(a)** An idealized perovskite unit cell viewed from the side. This is similar to the unit cell of $SrRuO_3$, although for simplicity we show a cubic structure rather than the real orthorhombic one of this material. The blue spheres represent the oxygen ions, which are negatively charged; all other ions are positively charged. Since the centres of positive and negative charge coincide, the unit cell is non-polar. **(b)** In the presence of a vertical strain gradient (in-plane compression at the bottom, in-plane extension at the top), the vertical inversion symmetry is lost and thus the unit cell becomes polar. **(c)** A bent crystal becomes compressed at the bottom and stretched at the top, thereby becoming polar. In an insulator, the flexoelectric polarization (Pflexo) generates a measurable voltage $V = Q_{bound}/C$, where C is the capacitance between the top and bottom surfaces of the crystal and Qbound is the bound charge ($Q_{bound} = P_{flexo}A$, where A is the surface area). In a metal, however, free charges (Q_{free}) can internally compensate the bound charges, such that there is no net charge at the surfaces and therefore no externally measurable voltage. Determining the polarization in this case requires alternative strategies, such as directly visualizing atomic positions using high-resolution electron microscopy, or using second harmonic generation to show the presence of polarization.