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I. B. Bersuker

Citation: [Applied Physics Letters](#) **106**, 022903 (2015); doi: 10.1063/1.4905679

View online: <http://dx.doi.org/10.1063/1.4905679>

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Pseudo Jahn–Teller effect in the origin of enhanced flexoelectricity

I. B. Bersuker

Institute for Theoretical Chemistry, University of Texas at Austin, Austin, Texas 78712, USA

(Received 9 December 2014; accepted 27 December 2014; published online 12 January 2015)

The controversy between the theory and experiment in explaining the origin of enhanced flexoelectricity is removed by taking into account the pseudo Jahn-Teller effect (PJTE) which, under certain conditions, creates local dipolar distortions of dynamic nature, resonating between two or more equivalent orientations. The latter become nonequivalent under a strain gradient thus producing enhanced flexoelectricity: it is much easier to orient ready-made dipoles than to polarize an ionic solid. For BaTiO₃, the obtained earlier numerical data for the adiabatic potential energy surface in the space of dipolar displacements in the Ti centers were used to estimate the flexoelectric coefficient f in the paraelectric phase in a one-dimensional model with the strain gradient along the [111] direction: $f = -0.43 \times 10^{-6} \text{Cm}^{-1}$. This eliminates the huge contradiction between the experimental data of $f \sim \mu \text{Cm}^{-1}$ for this case and the theoretical predictions (without the PJTE) of 3–4 orders-of-magnitude smaller values. Enhanced flexoelectricity is thus expected in solids with a sufficient density of centers that have PJTE induced dipolar instabilities. It explains also the origin of enhanced flexoelectricity observed in other solids, noticeable containing Nb perovskite centers which are known to have a PJTE instability, similar to that of Ti centers. The SrTiO₃ crystal as a virtual ferroelectric in which the strain gradient eases the condition of PJTE polar instability is also discussed. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4905679>]

Flexoelectricity, polarization of centrosymmetric dielectric solids under a strain gradient, first suggested long ago,¹ gained attention just recently, when it was shown that it affects significantly the properties of dielectrics, and it may have interesting applications (see Refs. 2–25 including reviews of Refs. 2–7 and references therein). The physical origin of flexoelectricity is, in general, quite transparent: a strain gradient removes the inversion symmetry of the lattice in at least one direction, thus inducing a polar distortion of the charge distribution. All the theories show that the coefficient of flexoelectric polarization is rather small, of the order of nCm^{-1} . In a recent paper,⁸ it is concluded that this is approximately the upper limit of the flexoelectricity strength that can be achieved in ionic crystals.

Meanwhile, the experimental measurements of the flexoelectricity effect in ferroelectric systems show that it can be much larger than the theoretical predictions by 3–4 orders of magnitude.^{6,7,9–11} The largest effect is obtained in the paraelectric phase of BaTiO₃, but it is much smaller in the similar SrTiO₃ crystal, while it approximately follows the theoretical predictions in the majority of other nonferroelectric crystals. For BaTiO₃, the flexoelectric coefficient f (the component of the tensor coefficient of proportionality between the polarization and strain gradient in the one-dimensional model) decreases significantly when moving from the paraelectric phase to its ferroelectric phases of consequent lower symmetry and becomes “normal” (of the order of magnitude predicted by the theory) in the rhombohedral phase. In *ab initio* calculations, for the latter, $f \approx -0.37 \pm 0.03 \text{ nCm}^{-1}$; for SrTiO₃, $f \approx -1.38 \pm 0.65 \text{ nCm}^{-1}$.¹²

Some of the above-cited authors state that the origin of this big discrepancy between the theory and experiment is at present not understood; others relate it to crystal imperfections assuming that in the paraelectric BaTiO₃, there are

polar islands that are reoriented by the strain gradient. An expert conclusion⁸ states that “The magnitude of upper bonds obtained suggest that the anomalously high flexoelectricity coupling documented for perovskites ceramics can hardly be attributed to a manifestation of the static bulk effect.” But in a more recent paper,¹³ using a variety of experimental procedures including pyroelectric current, it is shown that the effect is intrinsic (bulk), and it is due to some polar formations in dielectric solids that exist beyond (and independent of) the external strain. The authors¹³ suggest also some hypothetical causes of this built-in dipolar behavior referring to procedures of the crystal (ceramic) synthesis.

The explanation of the origin of flexoelectricity is thus full of significant controversies, and we would summarize them by formulating a question which seems to be illustrative: “Why the flexoelectric coefficients of two very similar perovskites crystals, paraelectric BaTiO₃, and SrTiO₃, prepared under the same conditions, differ by several orders of magnitude?” Of course, there may be some differences between the paraelectric barium titanate and the very similar in atomic and electronic structure strontium titanate due to the difference in the sizes of the two ions, Ba²⁺ and Sr²⁺, but in the usual theoretical description, this cannot amount to the observed several orders of magnitude difference in the flexoelectric coefficient. No one of the papers, cited above, gives a reasonable explanation of this controversy beyond the unproved assumption of different crystal imperfections.

In the present paper, we show that the essential controversies in the origin of flexoelectricity disappear, at least on a qualitative level, when the pseudo Jahn-Teller effect (PJTE) is taken into account. In treating the lattice-strain interaction, the papers above do not take into account the details of the local electronic structure and *vibronic coupling* that under certain conditions produce a local dipolar instability and dipolar

distortions, which in the free system are of dynamic nature, but become oriented by the gradient of strain. The specific vibronic coupling effect that leads to dipolar instability in the dielectric systems under consideration is the PJTE^{26,27} (regrettably, so far, this effect remains unknown to many solid state researchers).

The PJTE emerges from first principles as an extension of the Jahn-Teller effect (JTE)²⁶ in which, instead of the degenerate state, there are two or more close in energy (pseudodegenerate) states. Similar to the JTE, the latter become mixed by the perturbation of vibronic coupling, resulting (under certain conditions) in spontaneous symmetry breaking (SSB). In the simplest one-dimensional case, if the energy gap 2Δ between two states $|1\rangle$ and $|2\rangle$ is sufficiently small, the ground state becomes unstable with respect to low-symmetry displacements Q of the nuclear framework, for which the vibronic coupling constant (H is the Hamiltonian)

$$F = \langle 1 | (\partial H / \partial Q)_0 | 2 \rangle \quad (1)$$

is nonzero. The two branches of the adiabatic potential energy surface (APES) are^{26,27}

$$\varepsilon_{1,2} = (1/2)K_0Q^2 \pm [\Delta^2 + F^2Q^2]^{1/2}, \quad (2)$$

where K_0 is the primary force constant characterizing the stiffness of the system without the vibronic coupling. The lower branch, under the condition

$$\Delta < F^2/K_0, \quad (3)$$

has two equivalent minima at $\pm Q_0 = [(F/K_0)^2 - (\Delta/F)^2]^{1/2}$, in which the system is distorted in the Q direction. If the polyatomic system is centrosymmetric and the two pseudodegenerate states have opposite parity, the Q distortion leads to the formation of a dipole moment in the minima.

Not very much attention was paid to this PJTE (it was considered as a particular case of the JTE) before it was shown that within the condition of instability (3) the energy gap 2Δ may be very large (in some cases instability occurs at $2\Delta \sim 10\text{--}15\text{ eV}$ (Ref. 28)), and it was proved that *the PJTE is the only source of SSB in polyatomic systems in nondegenerate states* (see Refs. 26–29 and references therein). Together with the well-known JTE as the source of instability of systems in degenerate states, this leads to the *two-state paradigm*: at least, two electronic states must be involved in SSB in polyatomic systems.²⁷

To demonstrate how the PJTE affects the flexoelectricity, we note first that—similar to the simplest case of two equivalent minima noted above—in any SSB, there are two or more equivalent directions of distortions with possible dynamics of the system resonating between them. In crystals, if the PJTE-produced broken-symmetry configurations at its centers are dipolar, their sufficiently strong interaction may result in ferroelectric phases at lower temperatures, or remain weakly-interacting centers with resonating, dynamically disordered dipoles. In all these cases, a strain gradient restores their static orientation, in the same direction for all the centers, thus polarizing the centrosymmetric system.

Consider the most studied flexoelectric crystal, BaTiO_3 . For better demonstrative purposes, we employ here the

terminology of the simpler description in the cluster approximation considering the Ti centers in the octahedral environment of the six oxygens as the active units,^{30–32} qualitatively similar results were obtained recently in a more sophisticated Green's functions approach³³ in which the Ti center interacts with the *whole crystal* via its electronic and vibrational band structure, and we use below these later results.

For the electronic structure of the octahedral fragment $[\text{TiO}_6]^{8-}$, the molecular orbital (MO) presentation as linear combinations of atomic orbitals is shown in Fig. 1.³⁴ The highest occupied MOs (HOMOs) are formed by the atomic $2p_\pi$ orbitals of the six oxygen atoms. They belong to the representations T_{1u} , T_{2u} , and T_{1g} of the octahedral symmetry group and are denoted in Fig. 1 by t_{1u} , t_{2u} , and t_{1g} , respectively. The lowest unoccupied MOs (LUMOs) are t_{2g} ($3d$) orbitals of the transition metal: $|yz(\text{Ti})\rangle$, $|xz(\text{Ti})\rangle$, and $|xy(\text{Ti})\rangle$. In the regular cubic configuration, these HOMO-LUMO orbitals are orthogonal and do not participate in the Ti–O bonding (the bonding is realized via the inner σ orbitals and ionic interactions). Obviously, any off-center displacement of the Ti ion lowers the cubic symmetry and makes their overlap nonzero, meaning additional covalence in the Ti–O bonding, thus explaining the origin of the spontaneous symmetry breaking via the PJTE as due to added covalence. The latter is the driving force in the spontaneous symmetry breaking via the PJTE, triggering the local dipolar instability that produces the ferroelectric polarization of the crystal.²⁷

With the fully occupied HOMO, the ground state is A_{1g} . Since the three polar normal coordinates of the Ti center, Q_x , Q_y , and Q_z , transform as t_{1u} , the general PJTE vibronic coupling problem is $(A_{1g} + T_{1u}) \otimes t_{1u}$, where T_{1u} is the excited electronic state formed by the one-electron excitation HOMO \rightarrow LUMO ($t_{1u} \rightarrow t_{2g}$). There may be many such excitations, so the problem is better formulated as the vibronic coupling of the six HOMOs t_{1u} and t_{2u} to the three LUMOs t_{2g} via the dipolar displacements Q_x , Q_y , and Q_z .

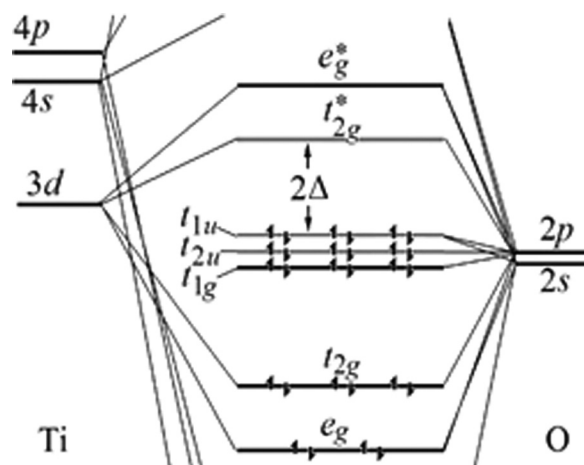


FIG. 1. Schematic presentation of the MO energy level scheme for the TiO_6^{8-} cluster in BaTiO_3 type crystals with indication of the orbital occupancy. Their HOMO-LUMO PJT mixing under the off-center displacements of the titanium atom results in a specific APES with eight minima and two types of saddle points which explain the origin of the ferroelectric phases and their partial disorder. From I. B. Bersuker, *The Jahn-Teller Effect*. Copyright 2006 by Cambridge University Press. Reprinted by permission of Cambridge University Press.

With the linear vibronic coupling included, the secular equation of the PJTE yields the following APES^{30–33} ($Q^2 = Q_x^2 + Q_y^2 + Q_z^2$):

$$U(Q) = \frac{1}{2}K_0Q^2 - 2 \left[\sqrt{\Delta^2 + 2F^2(Q^2 - Q_x^2)} + \sqrt{\Delta^2 + 2F^2(Q^2 - Q_y^2)} + \sqrt{\Delta^2 + 2F^2(Q^2 - Q_z^2)} \right], \quad (4)$$

where F —the vibronic coupling constant (cf. Eq. (1)),

$$F = \left\langle 2p_z(O) \left| \left(\frac{\partial H}{\partial Q_x} \right)_0 \right| 3d_{xy}(\text{Ti}) \right\rangle, \quad (5)$$

and Δ and K_0 are defined above.

This three-dimensional APES has a specific form. Under the condition similar to (3),

$$\Delta < 8F^2/K_0, \quad (6)$$

the surface (4) has a maximum (meaning instability) when the Ti ion is in the center of the octahedron, eight equivalent minima placed along the four trigonal axes in which the Ti ion is displaced toward three oxygen ions (away from the other three); higher-in-energy 12 equivalent saddle points along the six C_{2v} axes at which the Ti ion is displaced toward two oxygen ions (at the top of the lowest barrier between two near-neighbor minima); and next six higher-in-energy equivalent saddle points at which the Ti ion is displaced to one of the oxygen ions along the fourfold axes.^{30–33} For BaTiO₃, the vibronic coupling parameters were estimated using the Green's function description³³ and two experimentally determined structural constants: the energy gap $2\Delta = 2.8$ eV and the vibrational frequency at the bottom of the trigonal minimum $\hbar\omega_E = 193$ cm⁻¹. With these data, all the other essential parameters were estimated, including K_0 , F , the positions of the minima $Q_x = Q_y = Q_z = Q_0$ and first saddle points $Q_x = Q_y = q_0$, $Q_z = 0$, their PJTE stabilization energies, and the barrier between them δ shown in Table I.

The origin of the specific properties of BaTiO₃ ferroelectrics accumulated in years find reasonable explanations in the PJTE theory briefly outlined above. Of particular interest here is the *prediction of disorder in two ferroelectric phases and in the cubic paraelectric phase*^{30,31} (see a more updated version in Ref. 35). The picture of phase transitions in the crystal with the APES (4) is as follows.^{30,31,35} At low temperatures, the Ti ion is positioned in the lowest trigonal minima of the APES, the ordered dipole moments producing the rhombohedral ferroelectric phase polarized along [111] type directions. By increasing the temperature, the lowest saddle points between the near-neighbor ([111] and [-111] type) minima are overcome, resulting in a macroscopically averaged orthorhombic phase with polarization along [011].

The averaging means that the local distortions will not be fully ordered as in the rhombohedral phase, but disordered in one direction. At higher temperatures, the next saddle point is overcome and the crystal is macroscopically polarized along [100], featuring the averaged (over four near-neighbor minima) tetragonal ferroelectric phase with the lattice ordered in one direction and disordered in the two other ones. Finally, at sufficiently high temperatures, all the eight minima come into play in the averaging, producing the fully disordered cubic paraelectric phase.

This result was completely strange and hardly acceptable at the time,³⁰ as it was in controversy with the paradigm of displacive phase transitions in crystals like BaTiO₃. The predictions of the theory were fully confirmed later together with a variety of other empirical facts that have no explanation in displacive theories (see Refs. 26, 31, and 33). Of special interest here are the experimental conclusions that in all the phases, the Ti ion is *instantly* displaced in the trigonal direction in disagreement with displacive theories in which the metal off-center displacement occurs as a result of the phase transition to the ferroelectric phases. This basic conclusion was confirmed directly by a variety of experimental methods, noticeable EXAFS,^{36–38} EPR experiments with probing ions,^{39–41} NMR,^{42,43} neutron scattering,⁴⁴ etc. Not only is the Ti ion displaced along the [111] type direction in the paraelectric phase where the averaged symmetry is cubic, but it is as well displaced in this trigonal direction in the tetragonal phase where the crystal symmetry and the macroscopic polarization are tetragonal.⁴⁴ The theory was extended recently to formulate the necessary condition of coexisting magnetic and ferroelectric (multiferroicity) properties in ABO₃ crystals with B as a transition metal ion in a d^n configuration, $n = 1, 2, \dots, 10$,⁴⁵ that found already confirmation in experimental measurements^{46,47} and *ab initio* calculations.

This briefly outlined above picture of ferroelectric properties of perovskites crystals is directly related to their flexoelectricity and explains the origin of the big differences between the observed magnitudes of this effect in at-face similar systems. To begin with, the criterion of PJTE polar instability (6) holds well for the Ti center in BaTiO₃ (Table I),³³ and it does not hold for the same ion in SrTiO₃. The reason of this is straightforward: The size of the Sr²⁺ ion that controls the unit cell dimensions is smaller, and hence, the interatomic Ti–O distance is smaller in the latter case, and this, in turn, leads to larger stiffness K_0 and smaller F value, both deteriorating the condition of instability (6). For the same reason, SrTiO₃ becomes ferroelectric under negative pressure that increases the Ti–O distance, Ba_xSr_{1-x}TiO₃ becomes ferroelectric when $x > 0.45$, and the nonferroelectric CaMnO₃ becomes ferroelectric when Ca is substituted by Ba⁴⁸ (according to the PJTE theory Mn⁴⁺ is a ferroelectric ion⁴⁵).

TABLE I. Numerical values of the PJTE vibronic coupling and APES parameters of the Ti active centers in the BaTiO₃ crystal.³³

K_0	Δ	F	$\hbar\omega_E$	Q_0	q_0	$E_{JT}[111]$	$E_{JT}[110]$	δ
55 eV/Å ²	1.4 eV	3.42 eV/Å	193 cm ⁻¹	0.14 Å	0.16 Å	-1250 cm ⁻¹	-1130 cm ⁻¹	120 cm ⁻¹

In the paraelectric BaTiO₃, the Ti ions are dipolar displaced in the trigonal minima, but in the macroscopic picture, the crystal is cubic and centrosymmetric because of their noted above averaged position due to the tunneling between the equivalent minima. In this situation, any small perturbation in the form of strain gradient makes the PJTE minima nonequivalent, thus violating the conditions of tunneling between them and restoring some of the local dipole moments; the strain gradient acts as a “stop-flow” terminating a part of the tunnelings. Since the strain gradient has the same direction for all the unit cells, this leads to the polarization of the crystal. The data in Table I allow for an approximate estimation of the energy level splitting by tunneling between two adjacent minima $\delta_0 \cong 35 \text{ cm}^{-1}$.³³ For a further estimate of the flexoelectric coefficient, we assume that the tunneling is violated when the splitting Δ_s of the twofold degenerate energy level in the minima of the APES by the strain gradient $g = dS/dx$ reaches a reasonably significant value, as compared with the tunneling splitting δ_0 . Because of the exponential nature of the latter, we assume that the restoration of the dipole moment of the unit cell d by the gradient g along the [111] direction follows approximately the relation $d = d_0[1 - \exp(-p)]$, where d_0 is the dipole moment of the unit cell with the Ti ion at the minimum position and $p = \Delta_s/(\delta_0 - \Delta_s)$, so that at $\Delta_s = 10^{-1}\delta_0$, the almost full polarization $d = 0.9d_0$ is restored (the order of magnitude of the results is not strongly affected by this choice). Introducing the coupling constant between strain-gradient and energy $e = dE/dg$, we get the strain-gradient-induced splitting as $\Delta_s = 2ge$. On the other hand, the strain energy E can be estimated from the data obtained above. In polar normal displacements along [111], Q is the normalized difference between the Ti and three O ion displacements, so the strain is equal to $\Delta S = Q/a$, where a is the lattice constant, and the derivative $g \cong \Delta S/dx = Q/a^2$. The gradient-strain induced energy is $E = (1/2)K_0Q^2 = (1/2)K_0a^4g^2$, wherefrom we get the strain-energy coupling constant e and the energy level splitting $\Delta_s = 2ge$. Then, from the equations $\Delta_s = 10^{-1}\delta_0$ and $P = fg$, we obtain the final formula for estimating the approximate value of f

$$f = (d_0/a)(20K_0/\delta_0)^{1/2}, \quad (7)$$

where we used the expression for the polarization $P = d_0/a^3$. The dipolar minimum position from Table I is $x_0 = \sqrt{3}Q_0$, and the effective (Born) charge of the Ti ion is $Z^* = 8.7e$,³³ hence $d_0 = -\sqrt{3}Z^*eQ_0$. With these numerical values of the parameters and K_0 from Table I, we get the following estimate: $f = -0.43 \times 10^{-6} \text{ Cm}^{-1}$.

Thus, instead of (and in addition to) producing a polar charge redistribution in a rigid cubic crystal of the order of $n\text{Cm}^{-1}$, the strain gradient in the paraelectric phase of a PJTE ferroelectric just recovers the virtual local dipole moments (suppresses their dynamical averaging), inducing the ferroelectric polarization of the order of μCm^{-1} . This removes the main controversy in the theory of flexoelectricity explaining the origin of the 3–4 orders of magnitude larger flexoelectric coefficient f in paraelectric BaTiO₃ as compared with nonferroelectric crystals. Note that under an electric field gradient, the mechanism of polarization of

paraelectric BaTiO₃ is quite similar to that described above under strain gradient explaining the proportionality between the flexoelectric coefficient and permittivity.

As the PJTE is of local origin, the enhanced flexoelectric effect takes place everywhere the PJTE produces local dipolar distortions, and the density of such PJTE centers is high enough for experimental observation. Very similar to BaTiO₃ are the ferroelectric properties of the KNbO₃ perovskite crystal (BaTiO₃ and KNbO₃ were the first two crystals in which the order-disorder nature of the phase transitions predicted in Ref. 30 was observed by X-ray diffuse scattering⁴⁹); the NbO₆ centers have a qualitatively similar to the TiO₆ PJTE polar instability producing local dipole moments. This explains the origin of the enhanced flexoelectricity in perovskite systems that contain a significant amount of NbO₆ centers, e.g., Pb(Mg_{1/3}Nb_{2/3})O₃¹⁴ and (Bi_{1.5}Zn_{0.5})(Zn_{0.5}Nb_{1.5})O₇/Ag.¹⁵ As mentioned above, the SrTiO₃ crystal is not ferroelectric, but it is a virtual ferroelectric becoming one under negative pressure or with Ba impurities. This means that the PJTE in its Ti centers is not strong enough to obey the inequality (6) and produce dipolar instability, but its values Δ and $8F^2/K_0$ are close, so the criterion of the PJTE instability $\Delta < 8F^2/K_0$ may be induced by the strain gradient. Indeed, the latter is softening the crystal in at least one direction thus lowering the K_0 value, hence allowing dipolar distortion (polarization) in this direction. This explains (qualitatively) the order of magnitude larger flexoelectric coefficient in this crystal¹² as compared with expected in the theory without the PJTE. The assumptions in some publications cited above (see, e.g., Refs. 13 and 14) about possible polar formations in the bulk crystal that are responsible for the enhanced flexoelectricity in a way resonate (are compatible) with the results of this paper. Obviously, many other crystals with dipolar centers of PJTE origin including organic and biological systems may have similar enhanced flexoelectric properties.

In conclusion, the PJTE under certain conditions produces local dipolar distortions of dynamic nature that in the average do not remove the inversion symmetry of the solid, but a strain gradient suppresses this dynamics restoring the static dipole moment, thus leading to polarization and enhanced flexoelectricity. Estimates for paraelectric BaTiO₃ show that this effect explains the origin of 3–4 orders of magnitude higher flexoelectricity in solids with PJTE centers and eliminates the controversy between the theoretical predictions without taking into account the PJTE and experimental measurements of this property. Enhanced flexoelectricity is expected in any centrosymmetric solid with a sufficient number of dipolar unstable PJTE centers.

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