

Flexocoupling-induced phonons and ferrons in van der Waals ferroelectrics

Anna N. Morozovska^{1,*}, Eugene A. Eliseev², Oleksiy V. Bereznykov¹, Mykola Ye. Yeliseiev³, Guo-Dong Zhao⁴, Yujie Zhu⁵, Venkatraman Gopalan^{4,†}, Long-Qing Chen^{4,‡}, Jia-Mian Hu^{5,§} and Yulian M. Vysochanskii^{6,||}

¹*Institute of Physics, National Academy of Sciences of Ukraine, 46, pr. Nauky, 03028 Kyiv, Ukraine*

²*Frantsevich Institute for Problems in Materials Science, National Academy of Sciences of Ukraine, Omeliana Pritsaka str., 3, Kyiv 03142, Ukraine*

³*Institute of Semiconductor Physics, National Academy of Sciences of Ukraine, 45, pr. Nauky, 03028 Kyiv, Ukraine*

⁴*Department of Materials Science and Engineering, Pennsylvania State University, University Park, Pennsylvania 16802, USA*

⁵*Department of Materials Science and Engineering, University of Wisconsin-Madison, Madison, Wisconsin 53706, USA*

⁶*Institute of Solid-State Physics and Chemistry, Uzhhorod University, 88000 Uzhhorod, Ukraine*



(Received 15 March 2025; revised 31 May 2025; accepted 27 June 2025; published 21 July 2025)

The contribution of flexoelectric coupling to the long-range order parameter fluctuations in ferroics can be critically important to the ferron dispersion and related polar, pyroelectric, and electrocaloric (EC) properties. Here, we calculate analytically the dispersion relations of soft optic and acoustic flexocoupling-induced phonons and ferrons by incorporating the flexoelectric coupling, damping, and higher elastic gradients in the Landau-Ginzburg-Devonshire free-energy functional using the van der Waals uniaxial ferroelectric CuInP_2S_6 as an example. We analyze the changes in the flexocoupling-induced phonon and ferron spectra arising from the appearance of spatially modulated phases induced by the flexoelectric coupling. We show that the free-energy landscape of CuInP_2S_6 determines the specific features of its phonon spectra and ferron dispersion. We also discuss the contributions of optic and acoustic flexocoupling-induced ferrons to the pyroelectric and EC responses of CuInP_2S_6 at low temperatures.

DOI: [10.1103/mr9v-khtj](https://doi.org/10.1103/mr9v-khtj)

I. INTRODUCTION

The static flexoelectric effect is a measure of the amount of electric polarization induced by a strain gradient and vice versa in solids [1]. There is ample evidence that the flexoelectric effect can make significant contributions to the electromechanics of mesoscale and especially nanoscale objects [2,3], for which the strong strain gradients are inevitably present at the surfaces, interfaces, and around point and topological defects [4–6]. The flexoelectric coupling (shortly *flexocoupling*) can play a decisive role in the emergence of unusual polar and conductive domain walls [7,8] and spatially modulated phases [9] in ferroics and multiferroics, such as incipient and/or proper ferroelectrics, with or without anti-ferrodistortive long-range ordered phases. In fact, for several physical problems, such as the influence of the static [10] and dynamic [11] flexocouplings on the long-range order parameter fluctuations in the ordered phase of ferroics [12], the

impact of flexocoupling can be critical. Existing experimental and theoretical results (see, e.g., Refs. [13–15]) have been mostly focused on material-specific flexocoupling impacts on scattering spectra. Importantly, experimental determination of phonon dispersion can be very informative to study the influence of flexocoupling on the spatially modulated long-range-ordered phases in ferroelectrics. The basic experimental methods to obtain information about the fluctuations include dynamic dielectric measurements and neutron and Brillouin scattering [16–18].

The impact of flexocoupling on the generalized susceptibility as well as soft optical and acoustic phonon dispersions in the long-range-ordered phases of ferroelectrics were previously studied within the framework of the Landau-Ginzburg-Devonshire (LGD) approach in Ref. [19]. It was shown that flexocoupling essentially broadens the momentum (k) spectrum of generalized susceptibility and leads to the additional separation of the soft optical and acoustic mode phonon branches. Degeneration of the transverse optic and acoustic phonon modes disappears in the ferroelectric phase in comparison with the paraelectric phase due to the joint action of flexoelectric coupling and ferroelectric nonlinearity. It appeared that the dispersion of the soft optical phonons was less sensitive to flexocoupling than that of acoustic phonons. The frequency of acoustic phonons tends to zero and becomes purely imaginary when the flexocoupling constant exceeds a critical value, which depends on the electrostriction and elastic constants, temperature, and gradient coefficients in the LGD free-energy functional [20,21]. When the frequency

*Contact author: anna.n.morozovska@gmail.com

†Contact author: vxg8@psu.edu

‡Contact author: lqc3@psu.edu

§Contact author: jhu238@wisc.edu

||Contact author: vysochanskii@gmail.com

of the acoustic phonons goes to zero, a spatially modulated incommensurate phase may appear in commensurate ferroelectrics [21].

The concept of a *ferron* quasiparticle was introduced by Bauer *et al.* [22,23] and Tang *et al.* [24], who identified the bosonic excitations in displacive ferroelectrics that carry electric dipoles from the phenomenological LGD approach and introduced the quasiparticles emerging from the joint action of anharmonicity and broken inversion symmetry in these materials. A ferron represents a collective amplitude mode of the long-range-order parameter (spontaneous polarization) fluctuations in displacive ferroelectrics [22], including both volume-type [25] and surface-type ferron excitation modes, which carry electric dipoles [26,27]. Compared with the ferroelectric soft optical phonons (soft mode), which are quanta of a coherent polarization wave with well-defined phase and frequency [28,29], ferrons are typically not associated with a coherent wave, and therefore, they are incoherent. While the quanta of a coherent polarization wave are also referred to as coherent ferrons (as in Ref. [25]), the ferrons mentioned hereafter in this paper are all incoherent.

Using the calculated ferron spectrum in k space, Tang *et al.* [24] predicted the significant contribution of ferrons to the temperature-dependent pyroelectric and electrocaloric (EC) properties at low temperatures, electric-field-tunable heat and polarization transport, and ferron-photon hybridization. Bauer *et al.* [25] argued that the introduction of dipole-carrying elementary incoherent excitations of the ferroelectric long-range order, i.e., ferrons, allows for the modeling of many observables and potentially leads to applications in thermal, information, and communication technologies. Subsequently, Wooten *et al.* [30] showed experimentally that an external electric field changes the velocity of the longitudinal acoustic ferrons, which carry heat and polarization, leading to the changes of thermal conductivity in a bulk ferroelectric. The revealed effect appeared four times larger than previously reported and was ascribed to the field-dependent scattering of phonons.

Recently, the concept of ferron was extended by Yang and Chen [31] to the vector fluctuations of the long-range-ordered spontaneous polarization, considering zero-point oscillations and thermal fluctuations. It was found that the finite temperature free energy of the long-range-ordered polarization with bare parameters of the ground state (which can be found by first-principles calculations) is renormalized by zero-point fluctuations at $T = 0$ K and by thermal fluctuations at finite temperatures. The thermal excitations of the collective vector mode reduce the ferroelectric polarization to zero with heating and lead to the transition into nonpolar paraelectric phase at temperatures above T_C . Obviously, this occurs when fluctuations of polarization exceed the magnitude of the order parameter, namely, the spontaneous polarization. Considering ferrons as vector fluctuations of the long-range-ordered spontaneous polarization, the dimension of the vector space was taken equal to 3 for the case of displacive ferroelectrics like PbTiO_3 [31,32]. For this case, Zhao *et al.* [32] have shown that the energy of ferrons is gapped in the long-wavelength limit at temperatures well below the ferroelectric-paraelectric phase transition temperature T_C , and the gap softens to minimal or

gapless values as T_C is approached, leading to a significant contribution to thermal properties.

A negative frequency of the unstable phonon mode, which exists in the incipient ferroelectrics (like SrTiO_3 and KTaO_3) according to first-principles calculations, is renormalized to a positive frequency by zero-point fluctuations in the ground state. The frequency of the long-wave ferrons, which are bosonic thermal excitations, increases proportionally to the thermally averaged polarization fluctuations $\langle \delta P^2(T) \rangle$. Based on this, the temperature dependence of the second power of the inverse dielectric permittivity $\varepsilon^{-2}(T)$ is dominated by quantum fluctuations in the low-temperature range. The temperature dependence of its first power $\varepsilon^{-1}(T)$ is dominated by thermal fluctuations with heating [31]. The temperature dependence $\varepsilon^{-1}(T)$ of the quantum paraelectric SrTiO_3 shows an upturn below several kelvins instead of a plateau (at $T \leq T_s$) with cooling in the low-temperature limit ($T \rightarrow 0$ K). This peculiarity can be explained by the electrostriction coupling of gapless acoustic phonons with polarization field [33]. The saturation temperature T_s is related to the energy E_0 of zero-point fluctuations and crossover temperature T_q as $k_B T_s = \frac{\hbar \omega_0}{4}$ and $T_s = \frac{T_q}{2}$ [34]. Note that the saturation temperature is well defined in the displacive limit involving one Einstein oscillator, while the crossover from a classical behavior to a saturated behavior becomes smeared (or even continuous) when several high-frequency phonon modes (which individually saturate at relatively high temperatures) are coupled to the phase transition order parameter [34]. In this case, the order parameter saturation appears at higher temperatures.

The main objective in this work is to extend the concept of the ferron to van der Waals (vdW) ferroelectrics [35]. For this purpose, we consider the layered [in fact two-dimensional (2D)] vdW ferroelectric CuInP_2S_6 as an example because of its negative electrostriction [36] and the multiwell potential energy landscape [37–40] leading to a range of interesting phenomena, including the unusual dynamics of polarization in CuInP_2S_6 thin films and nanoparticles [41,42], the temperature and strain tunability of the multiple energy-degenerate metastable polar states in CuInP_2S_6 [43,44], as well as the emergence of controllable negative capacitance states [45,46]. However, the contribution of ferrons to the phonon spectra and thermodynamic properties of CuInP_2S_6 has not been studied.

CuInP_2S_6 is a representative of a large family of phosphorous chalcogenides of metals, including three-dimensional (3D)-ferroelectric $\text{Sn}_2\text{P}_2\text{S}_6$ and quantum paraelectric $\text{Pb}_2\text{P}_2\text{S}_6$ crystals [47]. The ferroelectric phase transition temperature T_C tends to 0 K in the $(\text{Pb}_y\text{Sn}_{1-y})_2\text{P}_2\text{S}_6$ compound at $y \rightarrow 0.61$. The crossover from quantum paraelectric behavior at low temperatures [$\varepsilon^{-1}(T) \sim T^2$] to classical Curie-Weiss behavior above the saturation temperature T_s [$\varepsilon^{-1}(T) \sim T$] is observed in quantum paraelectric $\text{Pb}_2\text{P}_2\text{S}_6$ with $\omega_0 = 47 \text{ cm}^{-1}$ and $E_0 = 0.003 \text{ eV}$ (72 K). For $\text{Sn}_2\text{P}_2\text{S}_6$, $\omega_0 = 60 \text{ cm}^{-1}$ and $E_0 = 0.004 \text{ eV}$ (86 K). According to dielectric measurements [47], the crossover temperature T_q is estimated as 190 K, proving the presence of several Einstein oscillators. It is worth noting that the energy E_0 correlates with Debye temperature T_D , which is ~ 85 K for $\text{Pb}_2\text{P}_2\text{S}_6$ and ~ 83 K for $\text{Sn}_2\text{P}_2\text{S}_6$ [48]. For the CuInP_2S_6 crystal, $T_D \approx 129$ K [49], and thus, the ferroelectric phase transition at $T_C \approx 312$ K falls to the

region of classic thermal fluctuations. The ferrielectric spontaneous polarization of CuInP_2S_6 contains the anticollinear contributions from Cu^+ and In^{3+} cations moving out of the middle of the structural layers [50]. The Cu^+ cations obey ordering in the multiwell potential determined by the second-order Jahn-Teller effect [51] in surrounding octahedron of sulfur atoms. The In^{3+} cations demonstrate the displacement/ordering dynamics in a three-well local potential inside the sulfur octahedron [52]. Also, the sound velocity softening was observed by Brillouin scattering and ultrasonic measurements of CuInP_2S_6 crystals above T_C [53,54], which can be related to the presence of the long-range interactions among polar clusters and requires consideration of the flexoelectric coupling. Authors of recent studies have revealed that a very strong or giant flexoelectric effect determines domain engineering [55,56] and mechanical and optoelectronic properties [57,58] of CuInP_2S_6 .

To the best of our knowledge, theoretical studies of the dispersion of ferrons under flexocoupling (abbreviated as *flexo-ferrons* for brevity) and related polar, pyroelectric, and thermal properties are currently missing. Here, we calculate analytically the dispersion law $\omega(\mathbf{k})$ of soft optical and acoustic phonons, which refer to the ferroelectric soft mode and acoustic phonons under flexocoupling, respectively, abbreviated as *flexo-phonons* for brevity, and flexo-ferrons of the vdW ferrielectric CuInP_2S_6 . In addition to the flexocoupling, the effects of damping and higher elastic gradients are incorporated in these analytical calculations. The spectral density of flexo-ferrons $\delta p(\mathbf{k})$ is also calculated. Our focus is on the changes in the flexo-phonon and flexo-ferron spectra related to the increase in the flexocoupling strength. We also analyze the contribution of optic and acoustic flexo-ferrons to the pyroelectric and EC responses of CuInP_2S_6 at low temperatures.

II. PROBLEM STATEMENT

Let us begin by deriving the dispersion relations of the soft optical phonon $\omega_O(\mathbf{k})$ (namely, the ferroelectric soft mode) and the acoustic phonon $\omega_A(\mathbf{k})$ (associated with the strain) by incorporating flexocoupling. In what follows, we name them the soft optical and acoustic flexo-phonons, respectively. According to the symmetry principle, the LGD free-energy density F should be invariant with respect to the symmetry transformations of the paraelectric phase. Using LGD theory in the considered case of $2/m$ point group symmetry (space group $C2/c$) of CuInP_2S_6 in the paraelectric phase, the Lagrange function $L = \int dt \int_{-\infty}^{\infty} d\mathbf{x} (F - K)$ consists of the kinetic energy K and potential energy F . Following Refs. [19–21], the density of kinetic energy

$$K = \frac{\mu}{2} \left(\frac{\partial P_3}{\partial t} \right)^2 + M \frac{\partial P_3}{\partial t} \frac{\partial U_3}{\partial t} + \frac{\rho}{2} \left(\frac{\partial U_3}{\partial t} \right)^2 \quad (1)$$

includes the dynamic flexocoupling with the coupling coefficient M ; ρ is the mass density of a material; and the coefficient μ is the polarization inertia, which can be expressed via the vacuum dielectric constant ϵ_0 and the plasma frequency ω_p as $\mu = \frac{1}{\epsilon_0 \omega_p^2}$ [24]. Hereinafter, we regard CuInP_2S_6 as a uniaxial ferroelectric, whose polar axis is along the 3 direction, and

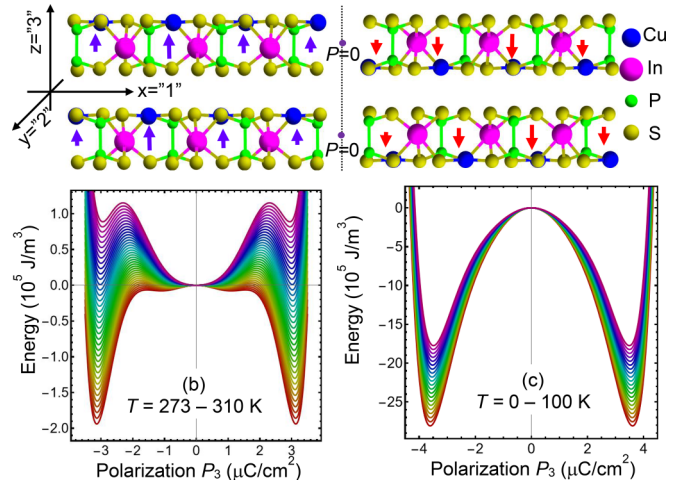


FIG. 1. (a) Schematic of CuInP_2S_6 layers with crystallographic coordinate system. The polar axis $z = 3$ is normal to the layers, and the axes $x = 1$ and $y = 2$ are in-plane of the layers. Blue and red arrows with varying lengths illustrate the transverse fluctuations of the ferrielectric polarization $\delta P_3(x)$, with a wave vector $\mathbf{k}$ along x . The vertical dotted line shows the break between the counterpolarized layers and corresponds to a virtual plane with zero polarization. (b) and (c) Schematic dependences of the CuInP_2S_6 free-energy density on the polarization P_3 calculated for zero stresses and electric field. The curve colors (from red to violet) correspond to different temperatures T (b) from 273 to 310 K with a step of 1 K and (c) from 0 to 100 K with a step of 5 K.

so consider the coupling among the polarization component P_3 , elastic displacement component U_3 , and corresponding strains u_{33} , u_{32} , and u_{31} [see Fig. 1(a)]. The y -axis 2 is the second-order symmetry axis in the CuInP_2S_6 parent phase, which is normal to the monoclinic plane m in the ferrielectric phase.

The bulk density F of CuInP_2S_6 free energy as a function of P_3 and u_{ij} and their gradients has the following form [43–46]:

$$F = F_{\text{LGD}} + F_{\text{el+flexo}}, \quad (2a)$$

$$F_{\text{LGD}} = \frac{\alpha}{2} P_3^2 + \frac{\beta}{4} P_3^4 + \frac{\gamma}{6} P_3^6 + \frac{\delta}{8} P_3^8 + \frac{g_{3ij}}{2} \frac{\partial P_3}{\partial x_i} \frac{\partial P_3}{\partial x_j} - P_3 E_3^{\text{ext}} - \frac{P_3 E_3^d}{2}, \quad (2b)$$

$$F_{\text{el+flexo}} = -q_{ij33} u_{ij} P_3^2 - z_{ij33} u_{ij} P_3^4 + f_{3ijk} u_{jk} \frac{\partial P_3}{\partial x_i} + \frac{c_{ijkl}}{2} u_{ij} u_{kl} + \frac{v_{ijk}}{2} \left(\frac{\partial u_{ij}}{\partial x_k} \right)^2 - N_3 U_3. \quad (2c)$$

According to Landau theory [59,60], the coefficient α depends linearly on the temperature T , $\alpha(T) = \alpha_T(T - T_C)$, which is valid for proper ferroelectrics well above quantum temperatures. The Barret-type expression $\alpha(T) = \alpha_T T_q (\coth \frac{T_q}{T} - \coth \frac{T_q}{T_C})$, where T_C is the Curie temperature and T_q is the quantum crossover temperature, is valid in a wider temperature range. All other coefficients in Eqs. (2a)–(2c) are assumed to be weakly dependent on temperature. The Landau coefficient $\delta \geq 0$ for the stability of the free

energy for all P_3 values. Note that the specific signs of Landau coefficients, namely, $\alpha < 0$, $\beta > 0$, $\gamma < 0$, and $\delta > 0$ in the Landau expansion $F_{\text{Landau}}(P_3) = \frac{\alpha}{2}P_3^2 + \frac{\beta}{4}P_3^4 + \frac{\gamma}{6}P_3^6 + \frac{\delta}{8}P_3^8$, make possible the appearance of the multiwell potential with lower and higher states of the spontaneous polarization in the definite temperature and/or strain range. For details, see Figs. 1(b) and 1(c) and Table SI in the Supplemental Material [61] for the values of Landau coefficients and their temperature dependences (collected from Refs. [41–46]).

Coefficients g_{ijkl} are the polarization energy gradient coefficients. Coefficients f_{ijkl} are the components of the static flexocoupling tensor. Coefficients c_{ijkl} are the components of the elastic stiffness tensor. Coefficients q_{ijkl} and z_{ijkl} are the second- and higher-order electrostriction coupling coefficients, respectively; v_{ijk} are the coefficients of strain gradient energy; N_3 is the third component of the external mechanical force bulk density; and E_3^{ext} is the third component of external electric field. Note that the longitudinal fluctuations of polarization (i.e., δP_3) are much smaller than transverse fluctuations due to the depolarization field E_3^d [62]. The field takes the form of $E_3^d = -\frac{\delta P_3}{\epsilon_0 \epsilon_h}$ in a thin CuInP_2S_6 membrane with an infinitely large xy plane and contributes to the free energy by the term $-\frac{P_3 E_3^d}{2}$.

Considering the Tani mechanism and Khalatnikov relaxation, the explicit form of the LGD-KT equations is

$$\Lambda \frac{\partial U_3}{\partial t} = -\frac{\delta L}{\delta U_3}, \quad \Gamma \frac{\partial P_3}{\partial t} = -\frac{\delta L}{\delta P_3}, \quad (3)$$

where Γ and Λ are phenomenological damping constants. Equation (3) linearized with respect to P_3 and U_3 allows calculating the generalized susceptibility of CuInP_2S_6 to the electric field and elastic force (see Eq. (S6) in the Supplemental Material [61]). The characteristic equation for the frequency dispersion $\omega(\mathbf{k})$ of the flexo-phonons can be derived from the singularity of the generalized susceptibility in the Fourier $\{\mathbf{k}, \omega\}$ space.

Next, we derive and analyze the frequency dispersion of the flexo-ferrons at low temperatures, following the approach of Tang *et al.* [24]. Generally, the electric dipole p_i ($i = 1, 2$, and 3) carried by ferrons can be computed as $p_i = -\frac{\hbar \partial \omega_i}{\partial E}$, where ω_i is the ferron frequency [25]. The frequency ω_i can be related to the frequencies $\omega_A(\mathbf{k})$ and $\omega_O(\mathbf{k})$ calculated using Eqs. (1)–(3) above. In this regard, the flexo-ferrons can be classified into acoustic and optical flexo-ferrons, respectively. Specifically, we consider the case when the mechanical force $\mathbf{N}$ and the electric field $\mathbf{E}$ in Eq. (3) are Langevin-type noise fields [24] which obey the fluctuation-dissipation theorem. Their correlators, averaged over the statistical ensemble in the quantum noise limit, have the following form in the Fourier $\{\mathbf{k}, \omega\}$ space [24]:

$$\langle \tilde{E}(\mathbf{k}, \omega) \tilde{E}^*(\mathbf{k}', \omega') \rangle = \frac{\Gamma}{(2\pi)^2} \hbar \omega \coth\left(\frac{\hbar \omega}{2k_B T}\right) \times \delta(\mathbf{k} - \mathbf{k}') \delta(\omega - \omega'), \quad (4a)$$

$$\langle \tilde{N}(\mathbf{k}, \omega) \tilde{N}^*(\mathbf{k}', \omega') \rangle = \frac{\Lambda}{(2\pi)^2} \hbar \omega \coth\left(\frac{\hbar \omega}{2k_B T}\right) \times \delta(\mathbf{k} - \mathbf{k}') \delta(\omega - \omega'). \quad (4b)$$

Here, the tilda-symbol corresponds to the Fourier image in the $\{\mathbf{k}, \omega\}$ space. As anticipated $\langle \tilde{E}(\mathbf{k}, \omega) \rangle = 0$ and $\langle \tilde{N}(\mathbf{k}, \omega) \rangle = 0$. Assuming that the damping constant is small (namely, $(\frac{\Gamma}{2\mu})^2 \ll \omega_p^2$) and using the perturbation theory, in Sec. S3 in the Supplemental Material [61], we derived the second-order correction for the polarization response to the Langevin-type electric noise

$$\langle p \rangle \approx \int_{-\infty}^{\infty} \frac{d^3 \mathbf{k}}{(2\pi)^3} \left\{ \coth\left[\frac{\hbar \omega_A(\mathbf{k})}{2k_B T}\right] \delta p_A(\mathbf{k}) + \coth\left[\frac{\hbar \omega_O(\mathbf{k})}{2k_B T}\right] \delta p_O(\mathbf{k}) \right\}, \quad (5)$$

where $\delta p_A(\mathbf{k})$ and $\delta p_O(\mathbf{k})$ are the spectral densities of acoustic and optical flexoferrons, $\omega_A(\mathbf{k})$ and $\omega_O(\mathbf{k})$ the eigenfrequencies of optical and acoustic flexophonons calculated without damping (i.e., for $\Gamma = 0$, $\Lambda = 0$), which should be positive for the convergency of the integral in Eq. (5).

Pyroelectric response is the polarization variation in response to the temperature change $P_3(T) = P_3(0) + \Delta P(T)$, where the contribution of the quantized fluctuations, represented by the flexo-ferrons, may become significant at temperatures much lower T_q [24]. Following the approach proposed in Ref. [24], we postulate that the pyroelectric variation of polarization $\Delta P(T)$ and the pyroelectric coefficient $\Pi(T) = -\frac{d}{dT} \Delta P(T)$ are given by

$$\Delta P(T) = \int_{-\infty}^{\infty} \frac{d^3 \mathbf{k}}{(2\pi)^3} \left[\frac{\delta p_O(\mathbf{k})}{\exp\left(\frac{\hbar \omega_O}{k_B T}\right) - 1} + \frac{\delta p_A(\mathbf{k})}{\exp\left(\frac{\hbar \omega_A}{k_B T}\right) - 1} \right], \quad (6a)$$

$$\Pi(T) = \int_{-\infty}^{\infty} \frac{d^3 \mathbf{k}}{(2\pi)^3} \left\{ \frac{\exp\left(\frac{\hbar \omega_O}{k_B T}\right) \frac{\hbar \omega_O}{k_B T^2}}{\left[\exp\left(\frac{\hbar \omega_O}{k_B T}\right) - 1\right]^2} \delta p_O(\mathbf{k}) + \frac{\exp\left(\frac{\hbar \omega_A}{k_B T}\right) \frac{\hbar \omega_A}{k_B T^2}}{\left[\exp\left(\frac{\hbar \omega_A}{k_B T}\right) - 1\right]^2} \delta p_A(\mathbf{k}) \right\}, \quad (6b)$$

where $\frac{1}{\exp\left(\frac{\hbar \omega}{k_B T}\right) - 1}$ is the Bose-Einstein distribution function.

According to Maxwell relations, the EC coefficient, defined as the isothermal entropy change with electric field E , is equal to the pyroelectric effect coefficient, i.e., $\Sigma = \left(\frac{\partial \Delta S}{\partial E}\right)_T = \left(\frac{\partial \Delta P}{\partial T}\right)_E$. The experimentally observed temperature dependence of the EC response deviates strongly from a Curie-Weiss power law. Using expressions for $\Pi(T, E)$, it is possible to estimate the EC response as [63]

$$\Delta T_{\text{EC}}(E) \cong T \int_0^E \frac{1}{\rho_P C_P} \Pi(T, E) dE, \quad (7a)$$

$$\Sigma(E) \cong \Pi(T, E). \quad (7b)$$

Here, ρ_P is the mass density, C_P is the heat capacity at constant pressure, and the field-dependent polarization $P(T, E)$ is substituted instead of the spontaneous polarization P_S . In Sec. S4 in the Supplemental Material [61], we calculate the contribution of the flexo-ferrons to pyroelectric and EC responses.

III. RESULTS AND DISCUSSION

A. Analytical solutions for the eigenfrequencies of the flexo-phonons and flexo-ferrons

In Sec. S2 in the Supplemental Material [61], we derive the characteristic equation for the frequency $\omega(\mathbf{k})$

$$(\mu\rho - M^2)\omega^4 + i(\Gamma\rho + \Lambda\mu)\omega^3 - C(\mathbf{k})\omega^2 - i\omega[\Gamma(\hat{\mathbf{v}}\mathbf{k}^4 + \hat{\mathbf{c}}\mathbf{k}^2) + \Lambda(\alpha_S + \hat{\mathbf{g}}\mathbf{k}^2)] + B(\mathbf{k}) = 0, \quad (8a)$$

where the functions $C(\mathbf{k})$ and $B(\mathbf{k})$ are

$$C(\mathbf{k}) = \alpha_S\rho + \Gamma\Lambda + (\hat{\mathbf{c}}\mathbf{k}^2\mu - 2\hat{\mathbf{f}}\mathbf{k}^2M + \hat{\mathbf{g}}\mathbf{k}^2\rho) + \mu\hat{\mathbf{v}}\mathbf{k}^4, \quad (8b)$$

$$B(\mathbf{k}) = \alpha_S\hat{\mathbf{c}}\mathbf{k}^2 - 4P_S^2(\hat{\mathbf{q}}\mathbf{k} + 2\hat{\mathbf{z}}\mathbf{k}P_S^2)^2 + \hat{\mathbf{c}}\mathbf{k}^2\hat{\mathbf{g}}\mathbf{k}^2 - (\hat{\mathbf{f}}\mathbf{k}^2)^2 + \alpha_S\hat{\mathbf{v}}\mathbf{k}^4 + \hat{\mathbf{g}}\mathbf{k}^2\hat{\mathbf{v}}\mathbf{k}^4. \quad (8c)$$

Hereinafter, a positive temperature-dependent function α_S is introduced as

$$\alpha_S = \alpha + 3\beta P_S^2 + 5\gamma P_S^4 + 7\delta P_S^6 - 2q_{33}u_S, \quad (9)$$

where P_S is the spontaneous polarization that corresponds to one of the stable potential wells (e.g., the deepest well) of the CuInP_2S_6 multiwell potential, and u_S is the corresponding spontaneous strain. Since the temperature and strain behavior of α_S determines the specific features of the phonon and ferron dispersion, the dispersion features are also conditioned by the multiwell free-energy landscape of CuInP_2S_6 .

The tensorial convolutions $\hat{\mathbf{c}}\mathbf{k}^2 = c_{3i3j}k_i k_j$, $\hat{\mathbf{v}}\mathbf{k}^4 = v_{3ij3lm}k_i k_j k_l k_m$, $\hat{\mathbf{f}}\mathbf{k}^2 = f_{3i3j}k_i k_j$, $\hat{\mathbf{g}}\mathbf{k}^2 = g_{3i3j}k_i k_j + \frac{k_3^2}{\epsilon_0\epsilon_b k^2}$, $\hat{\mathbf{q}}\mathbf{k} = g_{3i33}k_i$, and $\hat{\mathbf{z}}\mathbf{k} = z_{3i33}k_i$ are detailed in Sec. S2 in the Supplemental Material [61] for the case of $2/m$ symmetry. Notably, the last term in $\hat{\mathbf{g}}\mathbf{k}^2$, namely, $\frac{k_3^2}{\epsilon_0\epsilon_b k^2}$, is related to the depolarization field E_3^d .

Equations (8a)–(8c) can be utilized to calculate the dispersion relation of optic and acoustic phonon modes $\omega_O^D(\mathbf{k})$ and $\omega_A^D(\mathbf{k})$, respectively, where the superscript D is used to indicate that the damping factors Γ and/or Λ . The dispersion relation is the same for the coherent and incoherent ferrons, and thus, it is important to analyze the influence of the flexo-coupling and damping on the dispersions of $\omega_O^D(\mathbf{k})$ and $\omega_A^D(\mathbf{k})$. In what follows, we set $k_2 = k_3 = 0$ for the discussions of the results, while deferring the detailed analysis of the depolarization effect (i.e., the case $k_3 \neq 0$) in different directions in the $\mathbf{k}$ space to future studies. A general consideration should include the coupling between the ferrielectric polarization P_3 and all three components of displacement vector U_i , as required by the symmetry of the electrostrictive tensors q_{ijkl} and z_{ijkl} [see discussion after Eqs. (2a)–(2c)]. For the order-disorder-type ferroelectrics, Eqs. (8a)–(8c) allow us to calculate the inverse relaxation time.

Figures 2 and 3 show the dispersions of the real and imaginary parts of the optic and acoustic phonon modes frequencies $\omega_O^D(k_1)$ and $\omega_A^D(k_1)$ for $\Lambda = 0$, $k_2 = k_3 = 0$, and room ($T = 293$ K) and lower ($T = 10$ K) temperatures. The value of the damping constant Γ varies for different curves, and the flexoelectric constant f_{55} is fixed in Fig. 2. The flexoelectric coefficient f_{55} varies for different curves, and the damping coefficient Γ is fixed in Fig. 3. Note that ω_A^D and ω_O^D are even functions of k_1 .

The real part of ω_O^D decreases relatively weakly with increase in Γ [see Figs. 2(a) and 2(c)]. The difference between the curves calculated for $\Gamma = 0$ and $\Gamma > 0$ is noticeable for $k_1 = 0$, slightly increases with increase in k_1 , becomes maximal in the regions of optic and acoustic modes proximity (which is $0.25 < k_1 < 0.35 \text{ nm}^{-1}$ for $T = 293$ K and $0.55 < k_1 < 0.65 \text{ nm}^{-1}$ for $T = 10$ K), and then decreases with further increase in k_1 . The real part of ω_A^D is Γ independent for small k_1 . The dependence of $\text{Re}[\omega_A^D]$ on Γ appears in the regions of the modes proximity, then disappears in the cross-point of the $\text{Im}[\omega_A^D]$ curves (which is $k_1 \approx 0.3 \text{ nm}^{-1}$ for $T = 293$ K and $k_1 \approx 0.6 \text{ nm}^{-1}$ for $T = 10$ K), and appears again showing inverse tendency for further increase in k_1 . The increase in Γ leads to the so-called attraction of $\text{Re}[\omega_O^D]$ and $\text{Re}[\omega_A^D]$ dispersion curves, meaning that the distance between the curves becomes significantly smaller in the region of their proximity. The attraction is strongest at $k_1 \approx 0.3 \text{ nm}^{-1}$ for $T = 293$ K and $k_1 \approx 0.6 \text{ nm}^{-1}$ for $T = 10$ K. The imaginary parts of ω_O^D and ω_A^D are zero for $\Gamma = 0$ and increase strongly with increase in Γ [see Figs. 2(b) and 2(d)]. The increase in Γ leads to the significant difference between $\text{Im}[\omega_O^D]$ and $\text{Im}[\omega_A^D]$ curves, which is the strongest for the largest Γ (namely, for $\Gamma = 0.015 \text{ s m J/C}^2$). However, the dispersion curves for $\text{Im}[\omega_O^D]$ and $\text{Im}[\omega_A^D]$ intersect near the point of the optic and acoustic modes proximity.

The real and imaginary parts of ω_O^D and ω_A^D are almost independent of the flexoelectric coupling for small k_1 [see Figs. 3(a) and 3(c)]. When k_1 increases $> 0.2 \text{ nm}^{-1}$ for $T = 293$ K (or $> 0.4 \text{ nm}^{-1}$ for $T = 10$ K), $\text{Re}[\omega_O^D]$ begins to increase weakly and monotonically with increase in f_{55} . The difference between the dispersion curves of $\text{Re}[\omega_O^D]$ calculated for $f_{55} = 0$ and $f_{55} > 0$ becomes maximal in the region of the optic and acoustic modes proximity. For $k_1 > 0.3 \text{ nm}^{-1}$ and room temperature, $\text{Re}[\omega_A^D]$ decreases strongly with increase in f_{55} and disappears for $k_1 = k_{cr}$ since ω_A^D becomes purely imaginary $k_1 > k_{cr}$ (see red, orange, and yellow curves of $\text{Re}[\omega_A^D]$ in Fig. 3(a)). Note that the critical value k_{cr} exists only for $f_{55} > f_{cr}(T)$, where $f_{cr} \approx 5$ V at 293 K, and it decreases with increase in f_{55} (compare the ending of the red, orange, and yellow curves of $\text{Re}[\omega_A^D]$ in Fig. 3(a)). At much lower temperatures (e.g., at $T = 10$ K), $\text{Re}[\omega_A^D]$ decreases with increase in $k_1 > 0.5 \text{ nm}^{-1}$ and becomes zero for very high $k_1 > 5 \text{ nm}^{-1}$ and $f_{55} > f_{cr} > 12$ V, which are not shown in Fig. 3(c). The dispersion curves for $\text{Im}[\omega_O^D]$ and $\text{Im}[\omega_A^D]$ intersect near the proximity point of the optic and acoustic modes for all values of f_{55} , and their dependence on f_{55} becomes stronger with further increase in k_1 [see Figs. 3(b) and 3(d)].

It should be emphasized that the condition $\omega_A^D(\mathbf{k}, T) = 0$ at nonzero $\mathbf{k}$ may correspond to the commensurate-incommensurate transition induced by the flexoelectric coupling [20,21]. From Eqs. (8a)–(8c), the equation for the determination of $f_{cr}(\mathbf{k}, T)$ is $B(\mathbf{k}) = 0$. For CuInP_2S_6 with $2/m$ symmetry and $k_2 = k_3 = 0$, the explicit equation for $k_{cr}(f_{55}, T)$ is

$$g_{44}k_{cr}^4 v_{333} + (v_{333}\alpha_S - f_{55}^2 + c_{55}g_{44})k_{cr}^2 + c_{55}\alpha_S - 4P_S^2(q_{33} + 2P_S^2z_{33})^2 = 0. \quad (10a)$$

Here, we used Voigt notation. From Eq. (10a), the analytical expressions for k_{cr} and f_{cr} are

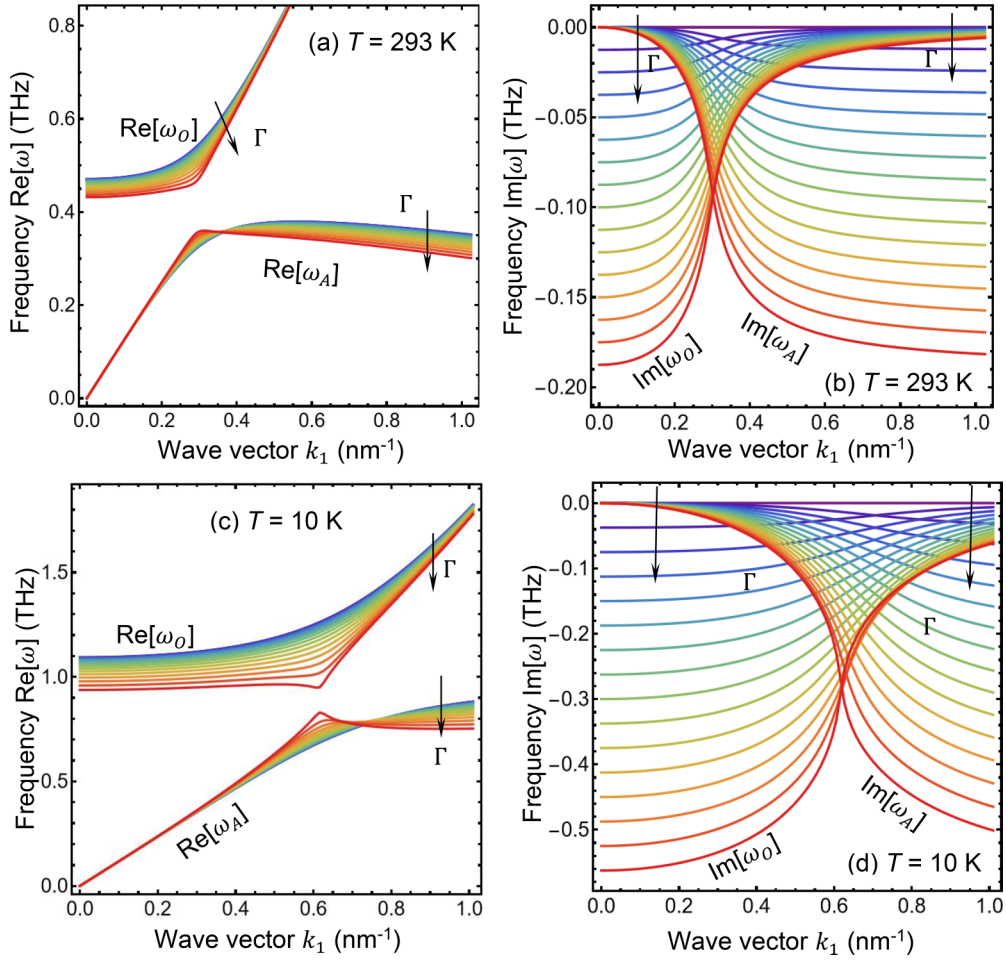


FIG. 2. Dispersion of the (a) and (c) real and (b) and (d) imaginary parts of the optical and acoustic phonon modes $\omega_O^D(k_1)$ and $\omega_A^D(k_1)$ calculated for $k_2 = k_3 = 0$, (a) and (b) $T = 293$ K and (c) and (d) $T = 10$ K. The value of damping constant Γ varies from 0 to 0.015 s m J/C^2 (with step size of 0.001 s m J/C^2) for different curves (from dark blue to red) in the plots in (a) and (b) and from 0 to 0.045 s m J/C^2 (with step size of 0.003 s m J/C^2) for different curves (from dark blue to red) in the plots in (c) and (d). The flexoelectric coefficient $f_{55} = 5 \text{ V}$ and $\Lambda = 0$ for all curves. The material parameters for CuInP_2S_6 are listed in Table SI in the Supplemental Material [61].

$$k_{cr}^2(f_{55}, T) = \frac{f_{55}^2 - v_{333}\alpha_S - c_{55}g_{44} \pm \sqrt{(v_{333}\alpha_S - f_{55}^2 + c_{55}g_{44})^2 - 4g_{44}v_{333}[c_{55}\alpha_S - 4P_s^2(q_{33} + 2P_s^2z_{33})^2]}}{2g_{44}v_{333}}, \quad (10b)$$

$$f_{cr}^2(T) = v_{333}\alpha_S + c_{55}g_{44} - 2\sqrt{g_{44}v_{333}[c_{55}\alpha_S - 4P_s^2(q_{33} + 2P_s^2z_{33})^2]}. \quad (10c)$$

Both signs $+$ and $-$ can have physical senses in Eq. (10b) when $f_{55}^2 - v_{333}\alpha_S - c_{55}g_{44} > 0$, meaning the gap of the finite region in the acoustic phonon spectra. We chose the $-$ sign before the radical in Eq. (10c) since v_{333} is very small. Note that the condition $v_{333} = 0$ leads to the expression $f_{cr}^2(T) = c_{55}g_{44}$, which agrees with the maximal values of the static flexoelectric effect coefficient (the upper thermodynamic limit) established by Yudin *et al.* [10]. The expressions in Eqs. (10b) and (10c) describe analytically the anomalous behavior of $\text{Re}[\omega_A^D(k_1, f_{55})]$ induced by the high flexoelectric coupling constant [Fig. 3(a)].

Without damping (i.e., at $\Gamma = 0$ and $\Lambda = 0$), the solution of Eq. (8a) can be represented in the form [19–21]

$$\omega_{O,A}^2(\mathbf{k}) = \frac{C(\mathbf{k}) \pm \sqrt{C^2(\mathbf{k}) - 4(\mu\rho - M^2)B(\mathbf{k})}}{2(\mu\rho - M^2)}. \quad (11)$$

The dispersion relation in Eq. (11) contains optical (O) and acoustic (A) phonon modes, corresponding to the signs $+$ and $-$ before the radical, respectively. The gap between these modes is proportional to the value $\frac{\sqrt{C^2(\mathbf{k}) - 4(\mu\rho - M^2)B(\mathbf{k})}}{2(\mu\rho - M^2)}$.

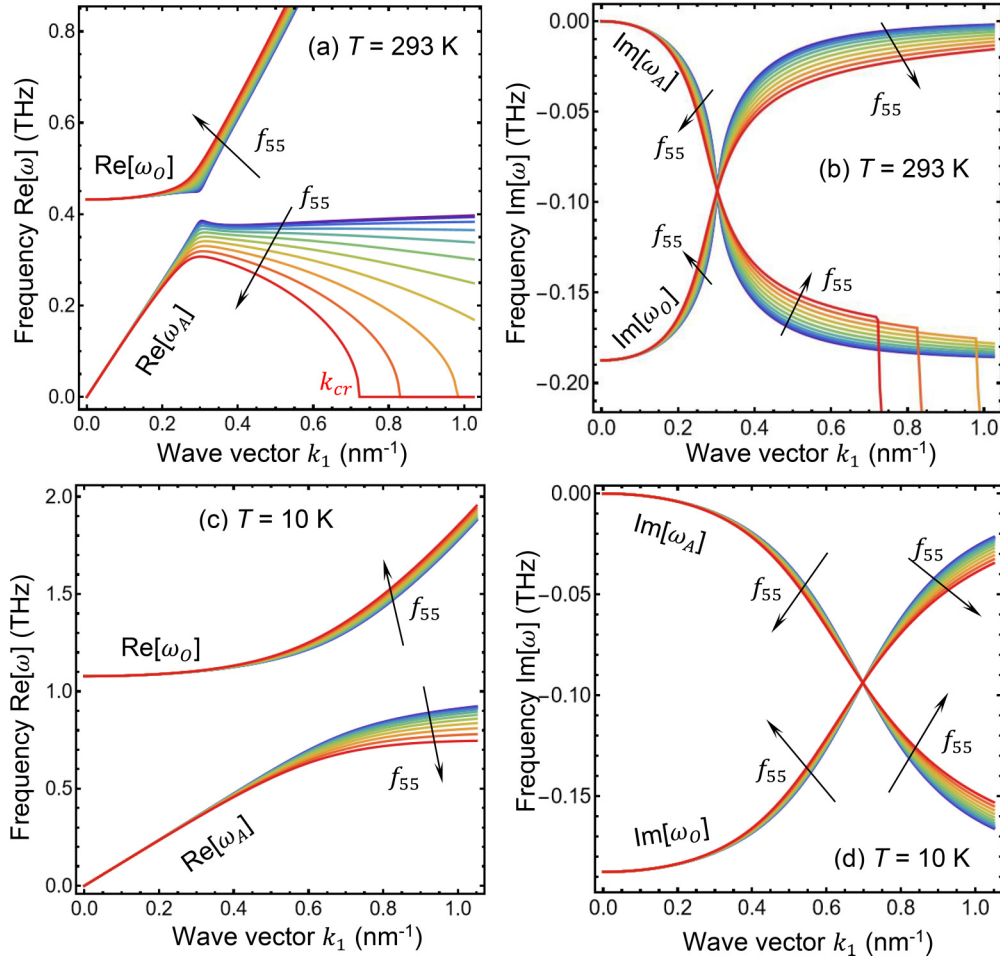


FIG. 3. Dispersion of the (a) and (c) real and (b) and (d) imaginary parts of the optical and acoustic phonon modes $\omega_O^D(k_1)$ and $\omega_A^D(k_1)$ calculated for $k_2 = k_3 = 0$, (a) and (b) $T = 293$ K and (c) and (d) $T = 10$ K. The flexoelectric coefficient f_{55} varies from 1 to 10 V (with step size of 1 V) for different curves (from dark blue to red), the damping coefficients $\Gamma = 0.015$ s m J/C² and $\Lambda = 0$ for all curves. The material parameters of CuInP₂S₆ are listed in Table SI in the Supplemental Material [61].

The frequency ω_O , given by Eq. (11), is a positive function that slightly increases with increase in $\mathbf{k}$ (see, e.g., violet curves in Figs. 2(a) and 2(c) corresponding to $\text{Re}[\omega_O]$ at $\Gamma = 0$). The dependence of ω_A on $\mathbf{k}$ becomes anomalous for high values of f_{55} , which is illustrated in Fig. 4.

Figures 4(a) and 4(b) show the color maps of real and imaginary parts of the acoustic phonon mode frequency ω_A as a function of the wave number k_1 and flexoelectric coefficient f_{55} , calculated for $T = 293$ and 10 K, respectively, and $k_2 = k_3 = 0$. The frequency ω_A is a monotonically increasing function of $\mathbf{k}$ for small f_{55} . Then it decreases with

further increase in f_{55} , becomes zero at $f_{55} = f_{cr}$ and purely imaginary for $f_{55} > f_{cr}$. The critical value of the flexoelectric coefficient f_{cr} depends on temperature T and wave vector $\mathbf{k}$. It is seen from Fig. 4 that f_{cr} increases strongly with increase in T . Also, f_{cr} depends nonmonotonically on k_1 : At first, it decreases strongly with increase in k_1 from 0 to several nm⁻¹, reaches minimum, and then increases very slightly with further increase in k_1 . Note that ω_A and ω_O are even functions of k_1 .

The analytical expression for the function $f_{cr}(k_1, T)$ can be easily obtained from Eq. (10a)

$$f_{cr}(k_1, T) = \pm \sqrt{\frac{1}{k_1^2} [g_{44}k_1^4 v_{333} + c_{55}\alpha_S - 4P_s^2(q_{33} + 2P_s^2 z_{33})^2] - v_{333}\alpha_S - c_{55}g_{44}}. \quad (12)$$

The expression in Eq. (12) describes analytically the boundary $\omega_A(k_1, f_{55}) = 0$ shown in Fig. 4. As argued in Refs. [20,21], the instability occurring at $f_{55} > f_{cr}(\mathbf{k}, T)$ may indicate a transition into the spatially modulated incommensurate phase. Note that the features of the commensurate-incommensurate

transition are observed in CuInP₂S₆ under high pressures [64]. However, the values of f_{cr} , corresponding to the possible transition, should be relatively high in accordance with our estimates (>6 – 12 V, see Fig. 4). At the same time, the values of $f_{55} > 4$ – 6 V are higher than the thermodynamic limit of

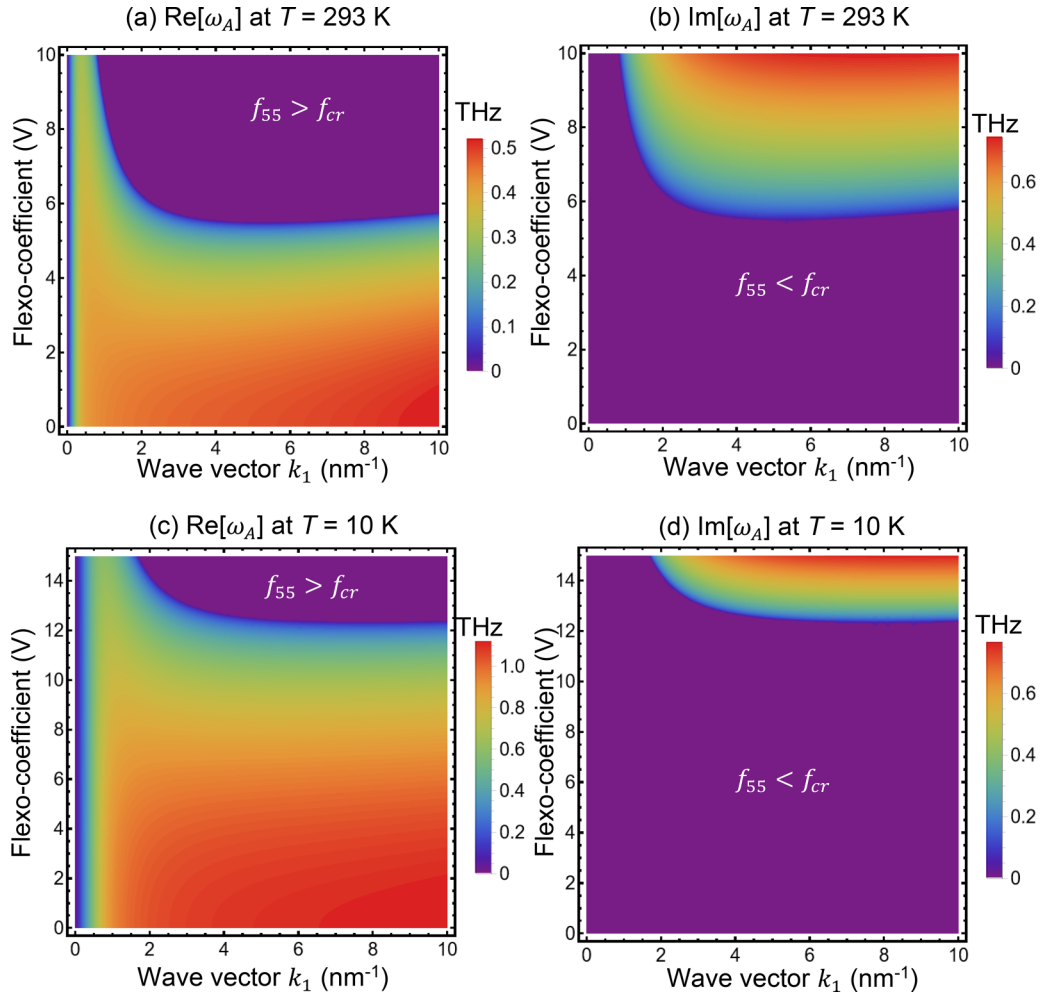


FIG. 4. Color maps of the (a) and (c) real and (b) and (d) imaginary parts of the acoustic phonon mode frequency ω_A as a function of the wave number k_1 and flexoelectric coefficient f_{55} calculated for $k_2 = k_3 = 0$, (a) and (b) $T = 293$ K and (c) and (d) $T = 10$ K. Damping is absent ($\Gamma = 0$, $\Lambda = 0$) for all plots. The material parameters of CuInP_2S_6 are listed in Table SI in the Supplemental Material [61].

flexocoupling estimated in Ref. [10]. The estimate of some f_{ij} obtained from current experiments [65] gives ~ 3 V, which is lower than the thermodynamic limit [10], but such moderate values unlikely can provide the giant flexoelectric effect observed by Chen *et al.* [55].

B. Analytical solution for the spectral density of flexo-ferrons

In Sec. S3 in the Supplemental Material [61], we derive approximate analytical expressions for the spectral densities of the acoustic and optic flexo-ferrons $\delta p_A(\mathbf{k})$ and $\delta p_O(\mathbf{k})$

$$\delta p_A(\mathbf{k}) \approx \frac{-\hbar}{2(\mu\rho - M^2)} \frac{3\beta^*P_S + 10\gamma^*P_S^3 + 21\delta P_S^5}{\alpha + 3\beta^*P_S^2 + 5\gamma^*P_S^4 + 7\delta P_S^6} \left| \frac{\hat{\mathbf{v}}\mathbf{k}^4 + \hat{c}\mathbf{k}^2 - \rho\omega_A^2(\mathbf{k})}{[\omega_O^2(\mathbf{k}) - \omega_A^2(\mathbf{k})]\omega_A(\mathbf{k})} \right|, \quad (13a)$$

$$\delta p_O(\mathbf{k}) \approx \frac{-\hbar}{2(\mu\rho - M^2)} \frac{3\beta^*P_S + 10\gamma^*P_S^3 + 21\delta P_S^5}{\alpha + 3\beta^*P_S^2 + 5\gamma^*P_S^4 + 7\delta P_S^6} \left| \frac{\hat{\mathbf{v}}\mathbf{k}^4 + \hat{c}\mathbf{k}^2 - \rho\omega_O^2(\mathbf{k})}{[\omega_A^2(\mathbf{k}) - \omega_O^2(\mathbf{k})]\omega_O(\mathbf{k})} \right|. \quad (13b)$$

Hereinafter, the effective Landau coefficients β^* and γ^* renormalized by the spontaneous strain are introduced, and expressions for $\omega_A(\mathbf{k})$ and $\omega_O(\mathbf{k})$ are given by Eq. (11).

The k dispersion of spectral densities $\delta p_A(k_1)$ and $\delta p_O(k_1)$ calculated from Eqs. (13a) and (13b) for $k_2 = k_3 = 0$, small damping (coefficient $\Gamma < 0.01$ s m/J/C²), different values of

the flexoelectric coefficient f_{55} , and temperatures 10 and 293 K are shown in Figs. 5(a) and 5(b), respectively. Note that δp_A and δp_O are even functions of k_1 .

The spectral density δp_O is a regular and monotonic function of k_1 and f_{55} . Its magnitude depends weakly on f_{55} and much more strongly on k_1 (see, e.g., different curves for δp_O in Figs. 5(a) and 5(b) as well as the color map

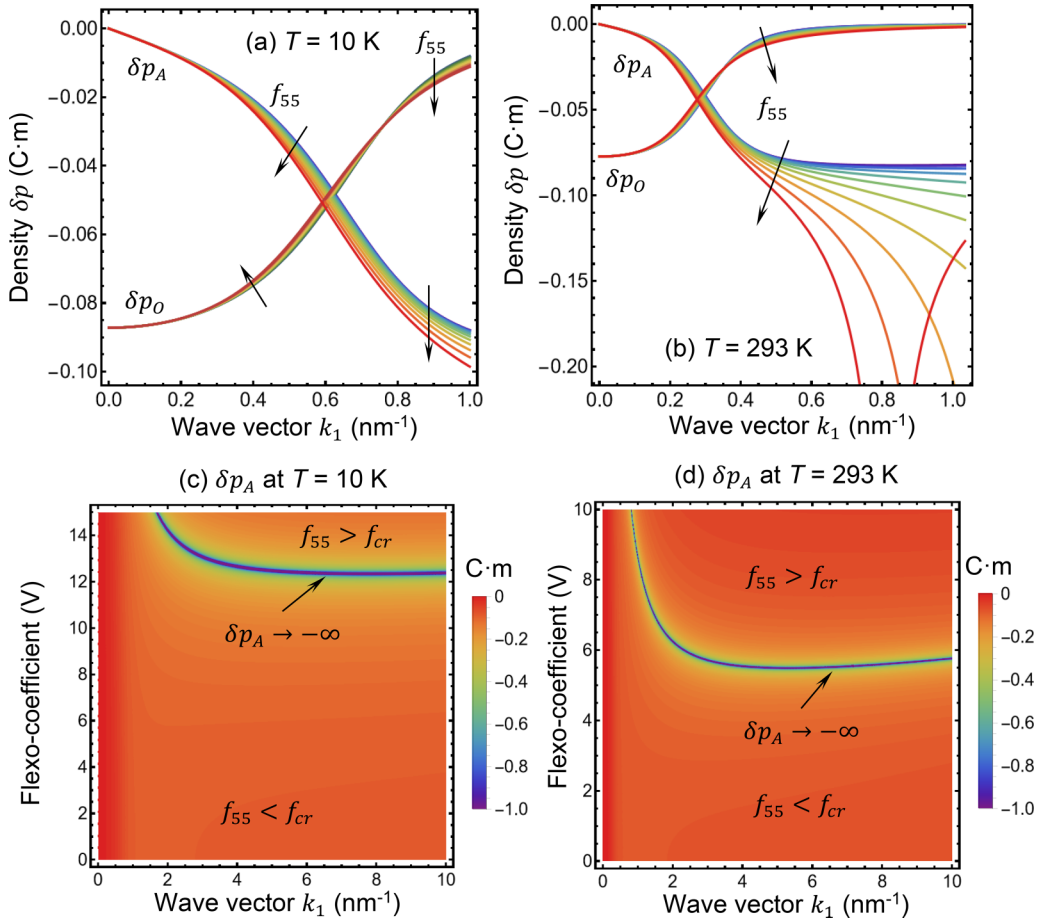


FIG. 5. k dispersion of flexo-ferron spectral densities $\delta p_A(k_1)$ and $\delta p_O(k_1)$ (in 10^{-30} C·m) calculated for $k_2 = k_3 = 0$, temperature (a) $T = 10$ K and (b) $T = 293$ K, and different values of the flexoelectric coefficient f_{55} varying from 0 to 10 V with step size of 1 V for different curves. The color maps of the $\delta p_A(k_1)$ as a function of the wave number k_1 and flexoelectric coefficient f_{55} calculated for $k_2 = k_3 = 0$, (c) $T = 10$ K and (d) $T = 293$ K. The material parameters of CuInP_2S_6 are listed in Table SI in the Supplemental Material [61].

in Fig. S2 in the Supplemental Material [61]). The spectral density δp_O is always negative. The absolute value $|\delta p_O|$ is maximal for $k_1 = 0$, and it monotonically decreases with increase in k_1 and tends to zero at $k_1 \rightarrow \infty$. Also, $|\delta p_O|$ increases weakly with decrease in temperature. The intersection of δp_O and δp_A curves happens very close to the k_1 point of the frequencies $\omega_O(k_1)$ and $\omega_A(k_1)$ maximal proximity.

The spectral density δp_A is a regular negative function of k_1 at $f_{55} < f_{cr}$. The function monotonically decreases with increase in k_1 and saturates for high k_1 [see, e.g., all δp_A curves in Fig. 5(a) and blue, green, and yellow δp_A curves in Fig. 5(b)]. For $f_{55} > f_{cr}$, δp_A curves become a strongly non-monotonic function of k_1 that diverged ($\delta p_A \rightarrow -\infty$) at $k_1 = k_{cr}(f_{55}, T)$. The position of the δp_A divergency is determined by the condition $\omega_A(k_1, T) = 0$ because $\delta p_A(k_1) \sim \frac{1}{\omega_A(k_1)}$ in accordance with Eq. (13a).

The color maps of δp_A as the function of the wave number k_1 and flexoelectric coefficient f_{55} are shown in Figs. 5(c) and 5(d) for $k_2 = k_3 = 0$ at $T = 10$ and 293 K, respectively. Since dynamic instability of acoustic mode occurs for $f_{55} \geq f_{cr}(k_1, T)$, the spectral density of acoustic flexo-ferron

diverges at $f_{55} = f_{cr}(k_1, T)$ [compare Figs. 5(c) and 5(d) with the behavior of $\omega_A(k_1, T)$ shown in Fig. 4]. It is seen from Figs. 5(c) and 5(d) that the width of the range where $|\delta p_A|$ reaches high values (e.g., $|\delta p_A| > 1$) decreases slightly with increase in T , and the position of the divergency curve ($\delta p_A \rightarrow -\infty$) shifts down with increase in T . The divergency curve nonmonotonically depends on k_1 : At first, it decreases strongly with increase in k_1 from 0 to several nm^{-1} , reaches minimum, and then increases very slightly with further increase in k_1 .

Since $\delta p_A(\mathbf{k})$ diverges at $\omega_A(\mathbf{k}) = 0$ and $f_{55} = f_{cr}$ as well as $\omega_A(k)$ becomes imaginary when $f_{55} > f_{cr}$, the acoustic contribution to the integral in the approximate expression in Eq. (5) also diverges, representing the fingerprint of a dynamic instability induced by the flexoelectric coupling (e.g., possible transition to a spatially modulated incommensurate phase). Thus, one should consider the case $f_{55} < f_{cr}$ for correct integration in Eq. (5). The case $f_{55} > f_{cr}$, when f_{55} is above the thermodynamic limit [10], requires other approaches for the correct analytical calculations of the flexo-phonon and flexo-ferron contributions to the polarization response.

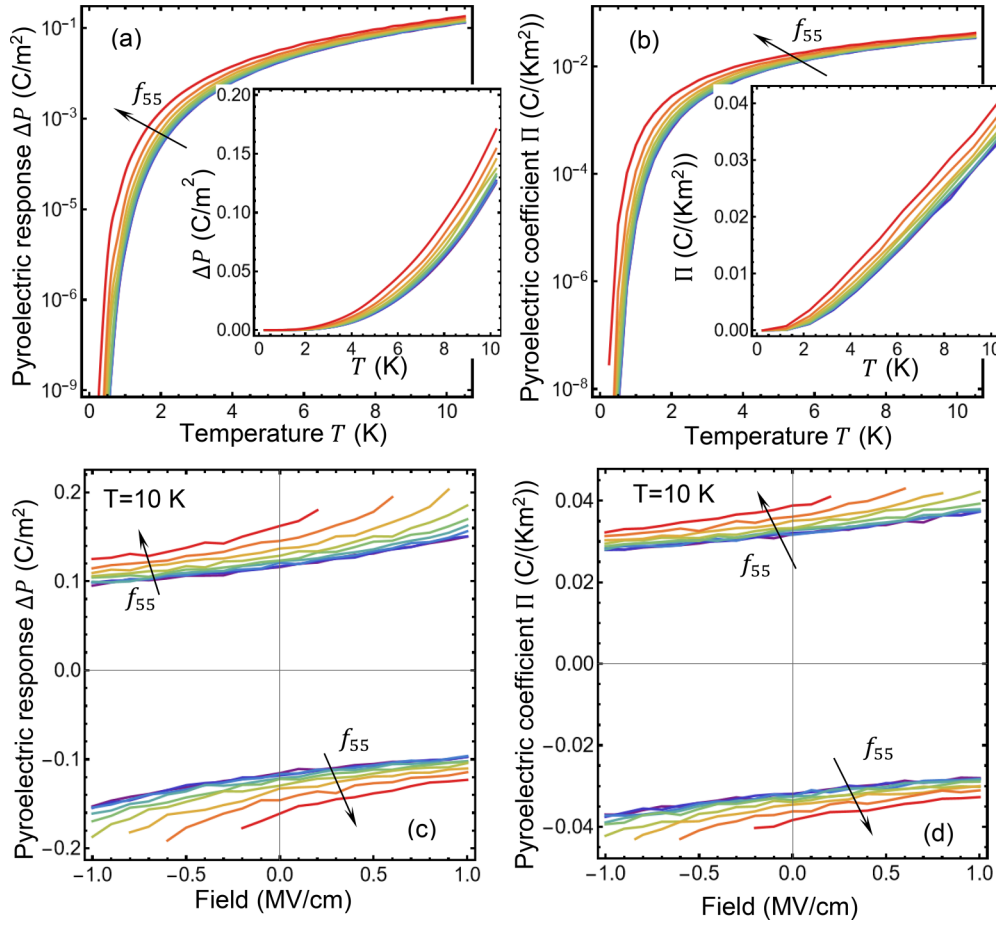


FIG. 6. (a) and (b) Temperature and (c) and (d) electric field dependences of the (a) and (c) polarization variation ΔP and (b) and (d) pyroelectric coefficient Π calculated from Eqs. (6a) and (6b) for different values of the flexoelectric coefficient f_{55} varying from 0 to 8 V with the step of 1 V (see different curves). Insets in plots (a) and (b) show the dependences $\Delta P(T)$ and $\Pi(T)$ in a linear scale. CuInP_2S_6 material parameters are listed in Table SI in the Supplemental Material [61], and damping is neglected ($\Gamma = \Lambda = 0$).

C. Contribution of flexo-ferrons to pyroelectric and EC responses

Temperature dependences of the polarization variation ΔP and pyroelectric coefficient Π calculated from Eqs. (6a) and (6b) for low temperatures, fixed damping coefficient Γ , and different values of the flexoelectric coefficient f_{55} are shown in Figs. 6(a) and 6(b), respectively. The temperature variation of polarization and pyroelectric coefficients increase weakly with increase in the flexoelectric coefficient; also, they increase with increase in temperature according to the power law. The saturation of the pyroelectric response with temperature may appear at the temperatures comparable with or higher than the crossover temperature $T_q \cong 50$ K. The saturation is almost independent of the value of f_{55} . Temperature dependences of the acoustic and optic flexo-ferron contributions to the pyroelectric coefficient Π calculated for different values of the flexoelectric coefficient f_{55} are shown in Fig. S3 in the Supplemental Material [61]. It is seen from the figure that the contribution of the optic ferrons becomes much lower (in 2–6 orders of magnitude) than the contribution of the acoustic ferrons for the temperatures above (0.5–1) K.

Electric field dependences of the polarization variation ΔP and pyroelectric coefficient Π calculated from Eqs. (6a) and (6b) for different values of the flexoelectric coefficient f_{55} and $T = 10$ K are shown in Figs. 6(c) and 6(d), respectively. These dependences reflect the contribution of the flexo-ferrons to the EC response. In this case, the contribution of the acoustic ferrons dominates over the contribution of the optic ferrons by 5–6 orders of magnitude. The terminations of the curves in Figs. 6(c) and 6(d) correspond to the critical value of the field for which the acoustic flexo-ferron frequency becomes zero. The critical field is much lower than the thermodynamic coercive field of CuInP_2S_6 at 10 K (~ 1.3 MV/cm). Notably, the critical value of the electric field exists at $f_{55} > f_{cr}$ and depends significantly on the flexoelectric coefficient f_{55} : It decreases strongly with increase in f_{55} . We would like to underline that the dependence of the ferron spectra on the applied electric field agrees with earlier results of Wooten *et al.* [30].

To explain numerical results, one should derive approximate analytical expressions for the pyroelectric response. In Sec. S4 in the Supplemental Material [61], we derive the approximate expression for the pyroelectric charge ΔQ using

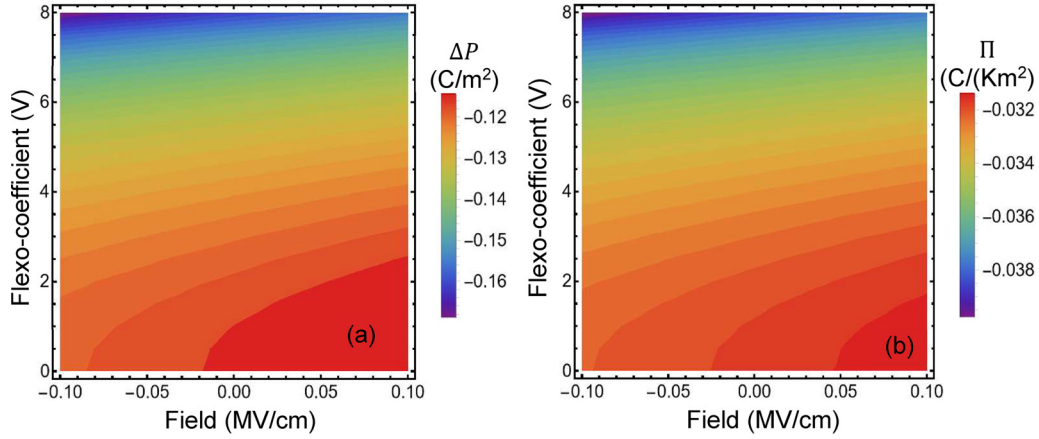


FIG. 7. Color maps of (a) polarization variation ΔP and (b) pyroelectric coefficient Π as a function of flexoelectric coefficient f_{55} and electric field E_3 . The maps are calculated using Eqs. (6a) and (6b) for CuInP_2S_6 material parameters (listed in Table SI in the Supplemental Material [61]), $T = 10$ K and without damping ($\Gamma = \Lambda = 0$).

the method of the steepest descent for the integration with exponential functions in Eqs. (6a) and (6b)

$\Delta Q(T)$

$$\approx \frac{-\hbar\rho}{2(\mu\rho - M^2)} \frac{3\beta^*P_S + 10\gamma^*P_S^3 + 21\delta P_S^5}{\alpha + 3\beta^*P_S^2 + 5\gamma^*P_S^4 + 7\delta P_S^6} \times \left[\frac{1}{\omega_O} \sqrt{\frac{2\pi k_B T}{\hbar\omega_O''}} \exp\left(-\frac{\hbar\omega_O}{k_B T}\right) + \frac{12}{\omega_O^2} v \left(\frac{\rho}{c}\right)^2 \left(\frac{k_B T}{\hbar}\right)^4 \right]. \quad (14)$$

Hereinafter, $\omega_O \equiv \omega_O(0)$ and $\omega_O'' = \frac{d^2}{dk^2}\omega_O(k)|_{k \rightarrow 0}$.

Disregarding the temperature dependence of the LGD coefficients at low temperatures, the temperature derivative of the pyroelectric charge $q(T) = \frac{Q(T)}{dT}$ can be estimated from Eq. (14) as

$$q(T) \approx \frac{\hbar\rho}{2(\mu\rho - M^2)} \frac{3\beta^*P_S + 10\gamma^*P_S^3 + 21\delta P_S^5}{\alpha + 3\beta^*P_S^2 + 5\gamma^*P_S^4 + 7\delta P_S^6} \times \left[\left(\frac{1}{\omega_O} \sqrt{\frac{\pi k_B}{2\hbar\omega_O'' T}} + \sqrt{\frac{2\hbar\pi}{k_B\omega_O'' T^3}} \right) \exp\left(-\frac{\hbar\omega_O}{k_B T}\right) + \frac{12}{\omega_O^2} v \left(\frac{k_B}{\hbar}\right)^4 \left(\frac{\rho}{c}\right)^2 T^3 \right]. \quad (15)$$

The expressions in Eqs. (14) and (15) are valid only at low temperatures and do not consider the role of the flexoelectric coupling correctly. However, they explain the dominant contribution of the acoustic ferrons to the pyroelectric and EC responses in comparison with the contribution of the optic ferrons which exponentially vanishes at low temperatures.

Polarization variation ΔP and pyroelectric coefficient Π as the function of flexoelectric coefficient f_{55} and electric field E_3 calculated for $T = 10$ K and without damping ($\Gamma = \Lambda = 0$) are shown in Figs. 7(a) and 7(b), respectively. It is seen that the increase of the flexocoupling constant f_{55} leads to a significant increase in ΔP and Π , at which these values become much less sensitive to the magnitude of the applied electric field due to the increase of the internal flexoelectric field, which is proportional to f_{55} . It is seen that the contour

lines of ΔP and Π have almost the same shape, which is corroborated by the analytical expressions in Eqs. (14) and (15). From these expressions, $\Pi \sim \Delta P/T$ at low temperatures.

IV. CONCLUSIONS

We analytically obtain the dispersion law of soft optical and acoustic flexo-phonons and flexo-ferrons by incorporating flexocoupling, damping, and higher elastic gradients in the LGD free-energy functional of the vdW uniaxial ferrielectric CuInP_2S_6 .

The increase of the flexocoupling constant f_{55} leads to dramatic changes in the flexo-phonon and flexo-ferron spectra related to possible appearance of spatially modulated phases induced by the flexoelectric coupling [20,21]. The acoustic flexo-phonon frequency $\omega_A^D(\mathbf{k}, T)$ becomes zero at $f_{55} = f_{cr}(k_1, T)$ and purely imaginary at $f_{55} > f_{cr}(k_1, T)$. The condition $\omega_A^D(\mathbf{k}, T) = 0$ at nonzero $\mathbf{k}$ corresponds to the dynamic instability induced by the increase in the flexoelectric coupling magnitude, which may indicate the commensurate-incommensurate transition. However, the observability of the transition is questionable because the magnitude of f_{cr} can be higher than the thermodynamic limit estimated in Ref. [10]. Since the dynamic instability occurs for $f_{55} > f_{cr}(k_1, T)$, the behavior of acoustic flexoferron responses to the transition at $f_{55} = f_{cr}(k_1, T)$, where the spectral density $\delta p_A(\mathbf{k})$ diverges.

The contribution of acoustic flexo-ferrons to the pyroelectric and EC responses of CuInP_2S_6 at low temperatures dominates over that of the optic flexo-ferrons by several orders of magnitude. The performed calculations of the EC response make physical sense for electric fields below the critical value. The critical field corresponds to the situation when the frequency of acoustic flexo-ferron becomes zero (which is possible only for the case $f_{55} > f_{cr}$). The critical value of the electric field decreases strongly with increase in the flexoelectric coefficient f_{55} . Notably, the dependence of the ferron spectra on applied electric field agrees with earlier results of Wooten *et al.* [30].

To verify theoretical predictions made in this work, inelastic neutron scattering measurements of phonon dispersion performed in a wide temperature range (e.g., at low and

room temperatures) in CuInP_2S_6 seem urgent. Analysis of the neutron scattering results together with available Raman spectroscopy [37,64] and ultrasound measurements [53,54] results will allow us to estimate the static and dynamic flexocoupling constants f_{55} and M as well as to determine the damping constants Γ and Λ . Next, low-temperature measurements of pyroelectric and EC responses of CuInP_2S_6 layers with various degrees of bending can be suggested to observe the flexo-ferro contribution.

ACKNOWLEDGMENTS

The authors are very grateful to the referees for fruitful discussions and valuable suggestions. The work of A.N.M., E.A.E., G.-D.Z., Y.Z., V.G., J.-M.H., and L.-Q.C. is supported by the U.S. Department of Energy (DOE) Software Project on “Computational Mesoscale Science and Open Software for Quantum Materials,” under Award No. DE-SC0020145 as part of the Computational Materials Sciences Program of DOE, Office of Science, Basic Energy Sciences. The work of O.V.B. is sponsored by the Target Program of the National Academy

of Sciences of Ukraine Project No. 5.8/25-II “Energy-saving and environmentally friendly nanoscale ferroics for the development of sensorics, nanoelectronics and spintronics” and B/222. Research of optical, polar and electrophysical properties of organic and inorganic hybrid nanostructures and nanomaterials of functional purpose. Y.M.V. and A.N.M. also acknowledge support from the Horizon Europe Framework Programme (HORIZON-TMA-MSCA-SE) Project No. 101131229, Piezoelectricity in 2D-materials: materials, modeling, and applications (PIEZO 2D).

A.N.M. generated the research idea, formulated the problem, performed most of the analytical calculations, and wrote the manuscript draft jointly with Y.M.V. E.A.E. with O.V.B. and M.Y.Y. wrote the codes and prepared figures. Y.Z., J.-M.H., G.-D.Z., V.G., L.-Q. C., and Y.M.V. worked on the analysis of results and manuscript improvement.

DATA AVAILABILITY

Results were visualized in Mathematica 14.0 [66], the data that support the findings of this article are openly available [67].

- [1] A. K. Tagantsev, Piezoelectricity and flexoelectricity in crystalline dielectrics, *Phys. Rev. B* **34**, 5883 (1986).
- [2] M. S. Majdoub, P. Sharma, and T. Cagin, Enhanced size-dependent piezoelectricity and elasticity in nanostructures due to the flexoelectric effect, *Phys. Rev. B* **77**, 125424 (2008).
- [3] S. Krichen and P. Sharma, Flexoelectricity: A perspective on an unusual electromechanical coupling, *J. Appl. Mech.* **83**, 030801 (2016).
- [4] D. Lee, A. Yoon, S. Y. Jang, J.-G. Yoon, J.-S. Chung, M. Kim, J. F. Scott, and T. W. Noh, Giant flexoelectric effect in ferroelectric epitaxial thin films, *Phys. Rev. Lett.* **107**, 057602 (2011).
- [5] P. V. Yudin and A. K. Tagantsev, Fundamentals of flexoelectricity in solids, *Nanotechnology* **24**, 432001 (2013).
- [6] P. Zubko, G. Catalan, and A. K. Tagantsev, Flexoelectric effect in solids, *Annu. Rev. Mater. Res.* **43**, 387. (2013).
- [7] A. N. Morozovska, E. A. Eliseev, M. D. Glinchuk, Long-Qing Chen, and Venkatraman Gopalan, Interfacial polarization and pyroelectricity in antiferrodistortive structures induced by a flexoelectric effect and rotostriction, *Phys. Rev. B* **85**, 094107 (2012).
- [8] E. A. Eliseev, A. N. Morozovska, Y. Gu, A. Y. Borisevich, L.-Q. Chen, V. Gopalan, and S. V. Kalinin, Conductivity of twin Walls–surface junctions in ferroelastics: Interplay of deformation potential, octahedral rotations, improper ferroelectricity and flexoelectric coupling, *Phys. Rev. B* **86**, 085416 (2012).
- [9] E. A. Eliseev, S. V. Kalinin, Y. Gu, M. D. Glinchuk, V. Khist, A. Borisevich, V. Gopalan, L.-Q. Chen, and A. N. Morozovska, Universal emergence of spatially-modulated structures induced by flexo-antiferrodistortive coupling in multiferroics, *Phys. Rev. B* **88**, 224105 (2013).
- [10] P. V. Yudin, R. Ahluwalia, and A. K. Tagantsev, Upper bounds for flexocoupling coefficients in ferroelectrics, *Appl. Phys. Lett.* **104**, 082913 (2014).
- [11] A. Kvasov and A. K. Tagantsev, Dynamic flexoelectric effect in perovskites from first-principles calculations, *Phys. Rev. B* **92**, 054104 (2015).
- [12] A. N. Morozovska and E. A. Eliseev, Surface and finite size effect on fluctuations dynamics in nanoparticles with long-range order, *J. Appl. Phys.* **107**, 044101 (2010).
- [13] G. Shirane, J. D. Axe, J. Harada, and J. P. Remeika, Soft ferroelectric modes in lead titanate, *Phys. Rev. B* **2**, 155 (1970).
- [14] G. Shirane, J. D. Axe, J. Harada, and A. Linz, Inelastic neutron scattering from single-domain BaTiO_3 , *Phys. Rev. B* **2**, 3651 (1970).
- [15] G. Shirane, B. C. Frazer, V. J. Minkiewicz, J. A. Leake, and A. Linz, Soft optic modes in barium titanate, *Phys. Rev. Lett.* **19**, 234 (1967).
- [16] W. Cochran, Dynamical, scattering and dielectric properties of ferroelectric crystals, *Adv. Phys.* **18**, 157 (1969).
- [17] J. Hlinka, I. Gregora, and V. Vorlicek, Complete spectrum of long-wavelength phonon modes in $\text{Sn}_2\text{P}_2\text{S}_6$ by Raman scattering, *Phys. Rev. B* **65**, 064308 (2002).
- [18] R. M. Yevych, Yu. M. Vysochanskii, M. M. Khoma, and S. I. Perechinskii, Lattice instability at phase transitions near the Lifshitz point in proper monoclinic ferroelectrics, *J. Phys.: Condens. Matter* **18**, 4047 (2006).
- [19] A. N. Morozovska, Y. M. Vysochanskii, O. V. Varenyk, M. V. Silibin, S. V. Kalinin, and E. A. Eliseev, Flexocoupling impact on the generalized susceptibility and soft phonon modes in the ordered phase of ferroics, *Phys. Rev. B* **92**, 094308 (2015).
- [20] A. N. Morozovska, E. A. Eliseev, C. M. Scherbakov, and Yu. M. Vysochanskii, The influence of elastic strain gradient on the upper limit of flexocoupling strength, spatially-modulated phases and soft phonon dispersion in ferroics, *Phys. Rev. B* **94**, 174112 (2016).
- [21] A. N. Morozovska, M. D. Glinchuk, E. A. Eliseev, and Yu. M. Vysochanskii, Flexocoupling-induced soft acoustic mode and

- the spatially modulated phases in ferroelectrics, *Phys. Rev. B* **96**, 094111 (2017).
- [22] G. E. W. Bauer, R. Iguchi, and K.-I. Uchida, Theory of transport in ferroelectric capacitors, *Phys. Rev. Lett.* **126**, 187603 (2021).
- [23] G. E. W. Bauer, P. Tanga, R. Iguchie, and K.-I. Uchida, Magnonics vs. ferronics, *J. Magn. Magn. Mater.* **541**, 168468 (2022).
- [24] P. Tang, R. Iguchi, K. Uchida, and G. E. W. Bauer, Excitations of the ferroelectric order, *Phys. Rev. B* **106**, L081105 (2022).
- [25] G. E. W. Bauer, P. Tang, R. Iguchi, J. Xiao, K. Shen, Z. Zhong, T. Yu, S. M. Rezende, J. P. Heremans, and K. Uchida, Polarization transport in ferroelectrics, *Phys. Rev. Appl.* **20**, 050501 (2023).
- [26] X. H. Zhou, C. Cai, P. Tang, R. L. Rodríguez-Suárez, S. M. Rezende, G. E. W. Bauer, and T. Yu, Surface ferron excitations in ferroelectrics and their directional routing, *Chin. Phys. Lett.* **40**, 087103 (2023).
- [27] R. L. Rodríguez-Suárez, X. H. Zhou, C. Y. Cai, P. Tang, T. Yu, G. E. W. Bauer, and S. M. Rezende, Surface and volume modes of polarization waves in ferroelectric films, *Phys. Rev. B* **109**, 134307 (2024).
- [28] S. H. Zhuang and J.-M. Hu, Role of polarization-photon coupling in ultrafast terahertz excitation of ferroelectrics, *Phys. Rev. B* **106**, L140302 (2022).
- [29] T. Chen, B. Wang, Y. Zhu, S. Zhuang, L.-Q. Chen, and J.-M. Hu, Analytical model and dynamical phase-field simulation of terahertz transmission across ferroelectrics, *Phys. Rev. B* **109**, 094305 (2024).
- [30] B. L. Wooten, R. Iguchi, P. Tang, J. S. Kang, K. Uchida, G. E. W. Bauer, and J. P. Heremans, Electric field-dependent phonon spectrum and heat conduction in ferroelectrics, *Sci. Adv.* **9**, eadd7194 (2023).
- [31] F. Yang and L. Q. Chen, Microscopic theory of displacive ferroelectricity: Applications to quantum criticality and classical phase transitions, *arXiv:2412.04308*.
- [32] G. D. Zhao, F. Yang, and L. Q. Chen, Thermal properties revisited in displacive ferroelectrics, *arXiv:2501.17833*.
- [33] S. Rowley, L. Spalek, R. Smith, M. Dean, M. Itoh, J. Scott, G. Lonzarich, and S. Saxena, Ferroelectric quantum criticality, *Nat. Phys.* **10**, 367 (2014).
- [34] E. K. H. Salje, B. Wruck, and H. Thomas, Order-parameter saturation and low-temperature extension of Landau theory, *Z. Phys. B* **82**, 399 (1991).
- [35] Ju. Banys, A. Dziaugys, K. E. Glukhov, A. N. Morozovska, N. V. Morozovsky, and Yu. M. Vysochanskii, *Van der Waals Ferroelectrics: Properties and Device Applications of Phosphorous Chalcogenides* (John Wiley & Sons, Weinheim, 2022).
- [36] S. M. Neumayer, E. A. Eliseev, M. A. Susner, B. J. Rodriguez, S. Jesse, S. V. Kalinin, M. A. McGuire, A. N. Morozovska, P. Maksymovych, and N. Balke, Giant negative electrostriction and dielectric tunability in a van der Waals layered ferroelectric, *Phys. Rev. Mater.* **3**, 024401 (2019).
- [37] Y. M. Vysochanskii, V. A. Stephanovich, A. A. Molnar, V. B. Cajipe, and X. Bourdon, Raman spectroscopy study of the ferrielectric-paraelectric transition in layered CuInP_2S_6 , *Phys. Rev. B* **58**, 9119 (1998).
- [38] N. Sivasdas, P. Doak, and P. Ganesh, Anharmonic stabilization of ferrielectricity in $\text{CuInP}_2\text{Se}_6$, *Phys. Rev. Res.* **4**, 013094 (2022).
- [39] J. A. Brehm, S. M. Neumayer, L. Tao, A. O'Hara, M. Chyashnavichus, M. A. Susner, M. A. McGuire, S. V. Kalinin, S. Jesse, P. Ganesh, and S. Pantelides, Tunable quadruple-well ferroelectric van der Waals crystals, *Nat. Mater.* **19**, 43 (2020).
- [40] A. N. Morozovska, E. A. Eliseev, S. V. Kalinin, Y. M. Vysochanskii, and P. Maksymovych, Stress-induced phase transitions in nanoscale CuInP_2S_6 , *Phys. Rev. B* **104**, 054102 (2021).
- [41] A. N. Morozovska, E. A. Eliseev, M. E. Yeliseiev, Y. M. Vysochanskii, and D. R. Evans, Stress-induced transformations of polarization switching in CuInP_2S_6 nanoparticles, *Phys. Rev. Appl.* **19**, 054083 (2023).
- [42] A. N. Morozovska, E. A. Eliseev, L. P. Yurchenko, V. V. Laguta, Y. Liu, S. V. Kalinin, A. L. Kholkin, and Y. M. Vysochanskii, The strain-induced transitions of the piezoelectric, pyroelectric and electrocaloric properties of the CuInP_2S_6 films, *AIP Advances* **13**, 125306 (2023).
- [43] A. N. Morozovska, E. A. Eliseev, A. Ghosh, M. E. Yeliseiev, Y. M. Vysochanskii, and S. V. Kalinin, Anomalous polarization reversal in strained thin films of CuInP_2S_6 , *Phys. Rev. B* **108**, 054107 (2023).
- [44] A. N. Morozovska, E. A. Eliseev, Y. Liu, K. P. Kelley, A. Ghosh, Y. Liu, J. Yao, N. V. Morozovsky, A. L. Kholkin, Y. M. Vysochanskii *et al.*, Bending-induced isostructural transitions in ultrathin layers of van der Waals ferrielectrics, *Acta Mater.* **263**, 119519 (2024).
- [45] A. N. Morozovska, S. V. Kalinin, E. A. Eliseev, S. Kopyl, Y. M. Vysochanskii, and D. R. Evans, Ferri-ionic coupling in CuInP_2S_6 nanoflakes: Polarization states and controllable negative capacitance, *Phys. Rev. Appl.* **22**, 034059 (2024).
- [46] A. N. Morozovska, E. A. Eliseev, Y. M. Vysochanskii, S. V. Kalinin, and M. V. Strikha, Size effect of negative capacitance state and subthreshold swing in van der Waals ferrielectric field-effect transistors, *Adv. Electron. Mater.* **11**, 2400495 (2024).
- [47] I. Zamaraitė, V. Liubachko, R. Yevych, A. Oleaga, A. Salazar, A. Dziaugys, J. Banys, and Yu. Vysochanskii, Quantum paraelectric state and critical behavior in $\text{Sn}(\text{Pb})_2\text{P}_2\text{S}(\text{Se})_6$ ferroelectrics, *J. Appl. Phys.* **128**, 234105 (2020).
- [48] K. Moriya, H. Kuniyoshi, K. Tashita, Y. Ozaki, S. Yano, and T. Matsuo, Ferroelectric phase transitions in $\text{Sn}_2\text{P}_2\text{S}_6$ and $\text{Sn}_2\text{P}_2\text{Se}_6$ crystals, *J. Phys. Soc. Jpn.* **67**, 3505 (1998).
- [49] V. Liubachko, A. Oleaga, A. Salazar, A. Kohutych, K. Glukhov, A. Pogodin, and Yu. Vysochanskii, Cation role in the thermal properties of layered materials $M^{1+}M^{3+}\text{P}_2(\text{S}, \text{Se})_6$ ($M^{1+} = \text{Cu}, \text{Ag}$; $M^{3+} = \text{In}, \text{Bi}$), *Phys. Rev. Mater.* **3**, 104415 (2019).
- [50] V. Maisonneuve, V. B. Cajipe, A. Simon, R. Von Der Muhll, and J. Ravez, Ferrielectric ordering in lamellar CuInP_2S_6 , *Phys. Rev. B* **56**, 10860 (1997).
- [51] Y. Fagot-Revurat, X. Bourdon, F. Bertran, V. B. Cajipe, and D. Malterre, Interplay between electronic and crystallographic instabilities in the low-dimensional ferroelectric CuInP_2S_6 , *J. Phys.: Condens. Matter* **15**, 595 (2003).
- [52] Y. Vysochanskii, V. Liubachko, K. Glukhov, R. Yevych, A. Kohutych, V. Hryts, A. Dziaugys, and J. Banys, Ordering/displacive ferrielectricity in 2D CuInP_2S_6 , *Ferroelectrics* **618**, 906 (2024).
- [53] V. Samulionis, J. Banys, A. Dziaugys, M. I. Gurzan, I. P. Pritz, and Y. Vysochanskii, Piezoelectric and ultrasonic Studies of new lamellar crystals of CuInP_2S_6 type, *Ferroelectrics* **419**, 97 (2011).

- [54] A. Kohutych, V. Liubachko, V. Hryts, Yu. Shiposh, M. Kundria, M. Medulych, K. Glukhov, R. Yevych, and Yu. Vysochanskii, Phonon spectra and phase transitions in van der Waals ferroics $\text{MM}'\text{P}_2\text{X}_6$, *Mol. Cryst. Liq. Cryst.* **747**, 14 (2022).
- [55] C. Chen, H. Liu, Q. Lai, X. Mao, J. Fu, Z. Fu, and H. Zeng, Large-scale domain engineering in two-dimensional ferroelectric CuInP_2S_6 via giant flexoelectric effect, *Nano Lett.* **22**, 3275 (2022).
- [56] W. Ming, B. Huang, S. Zheng, Y. Bai, J. Wang, J. Wang, and J. Li, Flexoelectric engineering of van der Waals ferroelectric CuInP_2S_6 , *Sci. Adv.* **8**, eabq1232 (2022).
- [57] L. Wang, D. Zhang, Z.-D. Luo, P. Sharma, and J. Seidel, Flexoelectric and electrostatic effects on mechanical properties of CuInP_2S_6 , *Appl. Mater. Today* **35**, 101981 (2023).
- [58] X. Wu, L. Qi, M. A. Iqbal, S. Dai, X. Weng, K. Wu, C. Kang, Z. Li, D. Zhao, W. Tang *et al.*, Revealing strong flexoelectricity and optoelectronic coupling in 2D ferroelectric CuInP_2S_6 via large strain gradient, *ACS Appl. Mater. Interfaces* **16**, 14038 (2024).
- [59] L. D. Landau and E. M. Lifshitz, *Theory of Elasticity. Theoretical Physics* (Butterworth-Heinemann, Oxford, 1998), Vol. 7.
- [60] G. A. Smolenskii, V. A. Bokov, V. A. Isupov, N. N. Krainik, R. E. Pasynkov, and A. I. Sokolov, *Ferroelectrics and Related Materials* (Gordon and Breach, New York, 1984).
- [61] See Supplemental Material at <http://link.aps.org/supplemental/10.1103/mr9v-khtj> for calculation details and material parameters.
- [62] B. A. Strukov and A. P. Levanyuk, *Ferroelectric Phenomena in Crystals: Physical Foundations* (Springer-Verlag, Berlin, 2012).
- [63] A. N. Morozovska, E. A. Eliseev, M. D. Glinchuk, H. V. Shevliakova, G. S. Svechnikov, M. V. Silibin, A. V. Sysa, A. D. Yaremkevich, N. V. Morozovsky, and V. V. Shvartsman, Analytical description of the size effect on pyroelectric and electrocaloric properties of ferroelectric nanoparticles, *Phys. Rev. Mater.* **3**, 104414 (2019).
- [64] R. Rao, B. S. Conner, J. Jiang, R. Pachter, and M. A. Susner, Raman spectroscopy study of pressure-induced phase transitions in single crystal CuInP_2S_6 , *J. Chem. Phys.* **159**, 224706 (2023).
- [65] X. Jiang, X. Wang, X. Wang, X. Zhang, R. Niu, J. Deng, S. Xu, Y. Lun, Y. Liu, T. Xia *et al.*, Manipulation of current rectification in van der Waals ferroionic CuInP_2S_6 , *Nat. Commun.* **13**, 574 (2022).
- [66] <https://www.wolfram.com/mathematica>.
- [67] <https://notebookarchive.org/2025-03-8a3v8ii>.