

Excitations of the ferroelectric order

Ping Tang¹, Ryo Iguchi², Ken-ichi Uchida^{2,3,4} and Gerrit E. W. Bauer^{1,3,4,5,6}¹WPI-AIMR, Tohoku University, 2-1-1 Katahira, Sendai 980-8577, Japan²National Institute for Materials Science, Tsukuba 305-0047, Japan³Institute for Materials Research, Tohoku University, 2-1-1 Katahira, Sendai 980-8577, Japan⁴Center for Spintronics Research Network, Tohoku University, Sendai 980-8577, Japan⁵Zernike Institute for Advanced Materials, University of Groningen, 9747 AG Groningen, Netherlands⁶Kavli Institute for Theoretical Sciences, University of the Chinese Academy of Sciences, Beijing 10090, China

(Received 13 March 2022; revised 17 May 2022; accepted 27 July 2022; published 8 August 2022)

We identify the bosonic excitations in ferroelectrics that carry electric dipoles from the phenomenological Landau-Ginzburg-Devonshire theory. The “ferron” quasiparticles emerge from the concerted action of anharmonicity and broken inversion symmetry. In contrast to magnons, the transverse excitations of the magnetic order, the ferrons in displacive ferroelectrics are longitudinal with respect to the ferroelectric order. Based on the ferron spectrum, we predict temperature-dependent pyroelectric and electrocaloric properties, electric-field-tunable heat and polarization transport, and ferron-photon hybridization.

DOI: [10.1103/PhysRevB.106.L081105](https://doi.org/10.1103/PhysRevB.106.L081105)

Introduction. The spontaneous emergence of order in condensed matter below a critical temperature breaks a symmetry, while the low-energy collective excitations of the order parameter tend to restore it. The latter can often be modeled by noninteracting quasiparticles that in extended systems are plane waves with a well-defined dispersion relation. Their lifetime is finite due to self-interactions or coupling with the environment. Wave packets of these quasiparticles transport energy, momentum, and the order parameter with the group velocity from the dispersion relations.

Lattice vibrations disturb the translational symmetry of homogeneous elastic media, and phonons are the associated quasiparticles. The excitations of a magnetic order are spin waves. The associated quanta, the magnons, carry magnetic moments that reduce the magnetization and can transport spin angular momentum and energy [1,2]. Gradients of the temperature and magnon chemical potential [3,4] induce magnon spin and heat currents, with associated spin Seebeck [5] and spin Peltier [6,7] effects.

Ferroelectric materials exhibit ordered electric dipoles with unique dielectric, pyroelectric, piezoelectric, and electrocaloric properties [8], with many analogies with ferromagnets [9]. However, to the best of our knowledge, the quasiparticles associated to the ferroelectric order have so far remained elusive. We previously addressed the elementary excitations of ferroelectrics or “ferrons” and the associated polarization and heat transport [10,11] by a phenomenological diffusion equation and a simple ball-spring model. The latter was inspired by magnons, which are transverse fluctuations that preserve the magnitude of the local magnetization. The assumption of local electric dipoles with fixed modulus should hold for order-disorder ferroelectrics such as NaNO_2 that are formed by stable molecular dipoles [12]. However, most ferroelectrics are “displacive,” i.e., formed by the condensation of a

particular soft phonon [13,14] with a flexible dipole moment (or are of mixed type [15–18]), and cannot be described by our previous model.

In this Letter, we formulate the quasiparticle excitations of displacive ferroelectrics in the framework of the Landau-Ginzburg-Devonshire (LGD) theory [19,20], which has been widely used to model ferroelectrics over a broad temperature range [21]. These ferrons are longitudinal rather than transverse fluctuations and carry electric polarization because of the nonparabolicity of the free energy around the local minima below the phase transition (see Fig. 1). The parameters of the LGD free energy are well known for many materials, which allows quantitative predictions of their thermodynamic and transport properties.

The LGD free energy $F(\mathbf{P})$ for a ferroelectric is a functional of the macroscopic polarization texture $\mathbf{P}(\mathbf{r})$ that obeys the crystal symmetry of the parent paraelectric phase [22]. For a uniaxial ferroelectric formed out of a centrosymmetric paraelectric phase the (Gibbs) free energy is an integral over the sample volume V [23],

$$F = \int d^3\mathbf{r} \left(\frac{g}{2} (\nabla P)^2 + \frac{\alpha}{2} P^2 + \frac{\beta}{4} P^4 + \frac{\lambda}{6} P^6 - \mathbf{E} \cdot \mathbf{P} \right), \quad (1)$$

where α , β , and $\lambda > 0$ are the Landau coefficients, $g > 0$ is the Ginzburg-type parameter that accounts for the energy cost of polarization textures, and \mathbf{E} an external electric field. A constant spontaneous polarization (\mathbf{P}_0) minimizes $F(\mathbf{P})$ of a uniform medium when

$$\alpha P_0 + \beta P_0^3 + \lambda P_0^5 = E, \quad (2)$$

where $P_0(E)$ is the modulus of the vectors $\mathbf{P}_0(\mathbf{E})$ and $\mathbf{E} \parallel \mathbf{P}_0$. Below a critical temperature T_c the system orders in a first

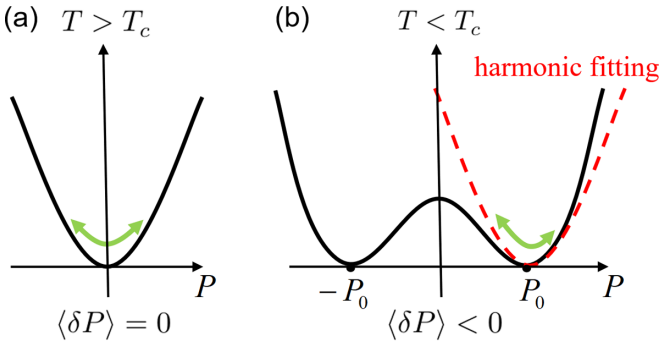


FIG. 1. Landau potential energy landscape for polarization fluctuations in ferroelectrics (green arrows). (a) Above the critical temperature T_c in the paraelectric phase the potential is symmetric for the fluctuations around the minimum $P_0 = 0$ and the average of the fluctuations $\langle \delta P \rangle = \langle P - P_0 \rangle = 0$ even in the presence of anharmonicity [see Eq. (8)]. (b) Below T_c the ferroelectric order breaks inversion symmetry and polarization fluctuates around finite $\pm P_0$ (e.g., the positive one in the figure) in an asymmetric potential, therefore carrying nonvanishing average electric dipoles, i.e., $\langle \delta P \rangle = \langle P - P_0 \rangle < 0$.

(second)-order phase transition for $\beta < 0$ ($\beta > 0$) with $P_0^2 = (-\beta + \sqrt{\beta^2 - 4\alpha\lambda})/2\lambda$ for $E = 0$.

In the presence of fluctuations, the longitudinal polarization dynamics ($\mathbf{P} \parallel \mathbf{P}_0$) obeys the Landau-Khalatnikov-Tani equation [24–27],

$$m_p \frac{\partial^2 P}{\partial t^2} + \gamma \frac{\partial P}{\partial t} = -\frac{\partial F}{\partial P} + E_{\text{th}}, \quad (3)$$

where $m_p = (\varepsilon_0 \omega_p^2)^{-1}$ is the polarization inertia, ε_0 the vacuum dielectric constant, and γ a phenomenological damping constant. The plasma frequency ω_p depends on the ionic masses M_i and charges Q_i in the unit cell of volume V_0 as $\omega_p^2 = (\varepsilon_0 V_0)^{-1} \sum_i Q_i^2 / M_i$ [26]. $E_{\text{th}}(\mathbf{r}, t)$ is a Langevin noise field that obeys a fluctuation-dissipation theorem [28],

$$\langle E_{\text{th}}(\mathbf{q}, \omega) E_{\text{th}}^*(\mathbf{q}', \omega') \rangle = \frac{(2\pi)^4 \gamma \hbar \omega \delta(\mathbf{q} - \mathbf{q}') \delta(\omega - \omega')}{\tanh(\hbar\omega/2k_B T)}$$

$$\xrightarrow{k_B T \gg \hbar\omega} (2\pi)^4 2\gamma k_B T \delta(\mathbf{q} - \mathbf{q}') \delta(\omega - \omega'), \quad (4)$$

where $\langle \dots \rangle$ is an ensemble average, $E_{\text{th}}(\mathbf{q}, \omega) = \int dt \int d^3 \mathbf{r} E_{\text{th}}(\mathbf{r}, t) e^{-i\mathbf{q} \cdot \mathbf{r} + i\omega t}$ the Fourier component of $E_{\text{th}}(\mathbf{r}, t)$, and the second line indicates the classical white noise limit. Substituting the small fluctuations $\delta P(\mathbf{r}, t) = P(\mathbf{r}, t) - P_0$ into Eq. (3),

$$\hat{G}^{-1} \delta P = E_{\text{th}} - (3\beta + 10\lambda P_0^2) P_0 \delta P^2 + O(\delta P^3), \quad (5)$$

where $\hat{G}^{-1} \equiv m_p \partial_t^2 + \gamma \partial_t - g \nabla^2 + (\alpha + 3\beta P_0^2 + 5\lambda P_0^4)$ is an inverse propagator. The nonlinear terms on the right-hand side of Eq. (5) are proportional to the anharmonicity parameters β and λ in Eq. (1). At temperatures sufficiently below the T_c the fluctuations E_{th} are small and we may solve Eq. (5) iteratively. To leading order,

$$\delta P = \delta P_{\text{h}} - (3\beta + 10\lambda P_0^2) P_0 \hat{G} \delta P_{\text{h}}^2 + O(E_{\text{th}}^3), \quad (6)$$

where $\delta P_{\text{h}} \equiv \hat{G} E_{\text{th}}$ are the harmonic thermal fluctuations that on average do not change the polarization since $\langle \delta P_{\text{h}} \rangle = 0$. In

Fourier space

$$\delta P_{\text{h}}(\mathbf{q}, \omega) = \frac{E_{\text{th}}(\mathbf{q}, \omega)}{m_p(\omega_{\mathbf{q}}^2 - \omega^2) - i\omega\gamma}, \quad (7)$$

where $\omega_{\mathbf{q}} = m_p^{-1/2}(\alpha + 3\beta P_0^2 + 5\lambda P_0^4 + g\mathbf{q}^2)^{1/2}$ is the dispersion relation. Assuming weak dissipation $\gamma \ll m_p \omega_{\mathbf{q}}$, Eqs. (4), (6), and (7) lead to fluctuations

$$\langle \delta P \rangle = -\frac{\hbar(3\beta + 10\lambda P_0^2) P_0}{2m_p(\alpha + 3\beta P_0^2 + 5\lambda P_0^4)} \int \frac{d^3 \mathbf{q}}{(2\pi)^3} \frac{1}{\omega_{\mathbf{q}}} \coth \frac{\hbar\omega_{\mathbf{q}}}{2k_B T} \quad (8)$$

that suppress the ground state polarization P_0 because of the anharmonicity (see Fig. 1). We may quantize the harmonic fluctuations as

$$\delta \hat{P}_{\text{h}} = \sqrt{\frac{\hbar}{2m_p V}} \sum_{\mathbf{q}} \hat{a}_{\mathbf{q}} \frac{e^{i\mathbf{q} \cdot \mathbf{r}}}{\sqrt{\omega_{\mathbf{q}}}} + \text{H.c.}, \quad (9)$$

where $\hat{a}_{\mathbf{q}}$ ($\hat{a}_{\mathbf{q}}^\dagger$) represents the bosonic annihilation (creation) operator of “ferrons” with wave vector \mathbf{q} and frequency $\omega_{\mathbf{q}}$. After subtracting the zero-point fluctuations, the elementary electric dipole carried by a single ferron is $\delta p_{\mathbf{q}} = \langle \mathbf{q} | \delta \hat{P} | \mathbf{q} \rangle - \langle 0 | \delta \hat{P} | 0 \rangle$, where $|\mathbf{q}\rangle = \hat{a}_{\mathbf{q}}^\dagger | 0 \rangle$ and $| 0 \rangle$ the vacuum. By substituting Eq. (9) into Eq. (6),

$$\delta p_{\mathbf{q}} = -\frac{\hbar(3\beta + 10\lambda P_0^2) P_0}{m_p(\alpha + 3\beta P_0^2 + 5\lambda P_0^4)} \frac{1}{\omega_{\mathbf{q}}}. \quad (10)$$

Using the nonlinear dielectric susceptibility $\chi = \partial P_0 / \partial E = (\alpha + 3\beta P_0^2 + 5\lambda P_0^4)^{-1}$ that follows from Eq. (2), Eq. (10) can be rewritten as

$$\delta p_{\mathbf{q}} = \frac{\hbar}{2m_p} \frac{\partial \ln \chi}{\partial P_0} \frac{1}{\omega_{\mathbf{q}}}. \quad (11)$$

Equations (10) and (11) agree with the intuitive relation

$$\delta p_{\mathbf{q}} = -\frac{\partial \hbar \omega_{\mathbf{q}}}{\partial E}, \quad (12)$$

which also holds for $E \neq 0$. According to Eq. (10) the ferron electric dipole reduces \mathbf{P}_0 (i.e., $\partial \ln \chi / \partial P_0 < 0$) and emerges from the anharmonicity of the free energy below the phase transition. As in order-disorder ferroelectrics [10,11] and in contrast to the magnetic dipole associated to magnons, the electric dipole of the longitudinal ferrons depends strongly and nonuniversally on the wave vector. In the paraelectric phase, the spontaneous polarization vanishes and hence $\delta p_{\mathbf{q}} = 0$, but a strong enough applied external field polarizes the paraelectric state and its elementary excitations as well.

The expansion to leading order in the amplitudes limits quantitative predictions to temperatures sufficiently below T_c . However, we may profit in the future from the large knowledge base on computing phononic nonlinearities in complex materials [29].

We assume dominance of a single-band soft mode that triggers the symmetry-breaking structural phase transitions to the ferroelectric state. In displacive ferroelectrics this is the lowest soft optical phonon that vibrates parallel to \mathbf{P}_0 . Hybridization with other, such as acoustic, phonon modes can become significant for some physical properties [30].

The free energy Eq. (1) does not introduce nonparabolicities to the transverse oscillations, which therefore do not carry

TABLE I. The material parameters introduced in the text for selected perovskite ferroelectrics at room temperature.

| | BaTiO ₃ [35] | PbTiO ₃ [31] | LiNbO ₃ [33] | Units |
|-------------|-------------------------|-------------------------|-------------------------|---------------------------------------|
| α | -5.544×10^{-2} | -0.3416 | -2.012 | 10^9 J m/C^2 |
| β | -2.590 | -0.29 | 3.608 | $10^9 \text{ J m}^5/\text{C}^4$ |
| λ | 4.802 | 0.1563 | 0 | $10^{10} \text{ J m}^9/\text{C}^6$ |
| g | 5.1 | 2 [47] | 5.39 [48] | $10^{-10} \text{ J m}^3/\text{C}^2$ |
| m_p | 1.35 | 1.59 [49] | 1.81 | $10^{-18} \text{ J m s}^2/\text{C}^2$ |
| τ [50] | 0.21 [51] | 0.15 [52] | 0.54 [53] | ps |
| V_0 | 66 | 63.18 | 317.73 | \AA^3 |

any dipolar moment. Order-disorder ferroelectrics can also be treated by Landau theory, but polarized fluctuations only emerge by introducing nonlinearities in the transverse amplitudes. At sufficiently low temperatures this can conveniently be achieved by the constraint $|\mathbf{P}| = P_0$, which to leading order gives rise to a finite dipole of the transverse ferrons, analogous to the magnetic moment of magnons [10,11]. Longitudinal and transverse ferrons may coexist in some multiaxial materials.

Since the LGD parameters are well documented for many ferroelectric materials [31–36], we are in an excellent position to quantitatively study ferron-related thermodynamic, optical, and transport properties. Table I summarizes the key information for selected displacive ferroelectrics with a perovskite crystal structure at room temperature.

Pyroelectricity and electrocalorics. Pyroelectricity (electrocalorics) is the change of polarization (entropy) under a temperature (electric field) change [37–41]. They are conventionally calculated directly by the LGD free energy with a linear temperature dependence of the Landau quadratic coefficient (α) [38,41]. However, this approach is valid only near the phase transition. At lower temperatures the fluctuations are well represented by the ferrons, and α becomes temperature independent. The total polarization is $P(T) = P(0) + \Delta P(T)$ with

$$\begin{aligned} \Delta P(T) &= \int \frac{d^3 \mathbf{q}}{(2\pi)^3} f_0(\xi_{\mathbf{q}}) \delta p_{\mathbf{q}} \\ &\rightarrow -\frac{\hbar(3\beta + 10\lambda P_0^2)P_0}{(2\pi g)^{3/2} m_p^{1/2}} \frac{1}{\xi_0^{3/2}} \exp(-\xi_0), \end{aligned} \quad (13)$$

where $f_0(\xi_{\mathbf{q}}) = [\exp(\xi_{\mathbf{q}}) - 1]^{-1}$ is the Planck distribution, $\xi_{\mathbf{q}} = \hbar\omega_{\mathbf{q}}/k_B T$, and in the second step we took the low-temperature limit $\xi_0 = \hbar\omega_0/k_B T \gg 1$ with $\omega_0 = m_p^{-1/2}(\alpha + 3\beta P_0^2 + 5\lambda P_0^4)^{1/2}$ the ferron gap (at $E = 0$). By disregarding the temperature dependence of material parameters, the low-temperature pyroelectric coefficient assumes the thermally activated form

$$\frac{\partial \Delta P}{\partial T} \rightarrow -\frac{(\hbar k_B)^{1/2} (3\beta + 10\lambda P_0^2) P_0}{(2\pi g)^{3/2} (m_p \omega_0)^{1/2}} \frac{1}{\sqrt{T}} \exp(-\xi_0). \quad (14)$$

The electrocaloric coefficient, i.e., the isothermal entropy change with electric field, is according to the Maxwell relation

$$\left(\frac{\partial \Delta S}{\partial E} \right)_T = \left(\frac{\partial \Delta P}{\partial T} \right)_E. \quad (15)$$

The temperature dependence deviates strongly from a Curie-Weiss power law. Glass and Lines [42] derived the scaling relation Eq. (14) in order to explain the low-temperature pyroelectricity of LiNbO₃ and LiTaO₃, thereby implicitly introducing the ferron concept for equilibrium properties a long time ago. Lang *et al.* [43] observed a negative pyroelectric coefficient in BaTiO₃ ceramic at low temperature, whose absolute value increases exponentially with temperature, in qualitative agreement with Eq. (14). However, the experimental $\partial \Delta P / \partial T = -5 \times 10^{-7} \text{ C}/(\text{m}^2 \text{ K})$ at 4.9 K is much larger than Eq. (14), which has been ascribed to a polarization of acoustic phonons coupled to the soft mode [44,45].

Polarization and heat transport by ferrons. We consider here diffuse and ballistic ferron transport in bulk ferroelectrics [10] and through constrictions [11], respectively. In the former case we focus on homogeneous single-domain ferroelectrics at local thermal equilibrium with an electric field generated by internal polarization and external charges. Electric field (∂E) and temperature (∂T) gradients set along the x direction induce polarization (j_p) and heat (j_q) current densities. The driving forces include nonequilibrium contributions from polarization and heat accumulations that should be computed self-consistently [10]. We can derive the polarization (σ) and thermal (κ) conductivities and the Seebeck (S_d) and Peltier (Π_d) coefficients in the linear response relations

$$\begin{pmatrix} -j_p \\ j_q \end{pmatrix} = \sigma \begin{pmatrix} 1 & S_d \\ \Pi_d & \kappa/\sigma \end{pmatrix} \begin{pmatrix} \partial E \\ -\partial T \end{pmatrix} \quad (16)$$

by the Landau theory introduced above. The linearized Boltzmann transport equation of the ferron gas in a constant relaxation time approximation [46] yields

$$\begin{aligned} \sigma &= \frac{\tau}{\hbar} \int (v_{\mathbf{q}}^x)^2 (\delta p_{\mathbf{q}})^2 \left(-\frac{\partial f_0}{\partial \omega_{\mathbf{q}}} \right) \frac{d^3 \mathbf{q}}{(2\pi)^3} \\ &= \frac{\tau \hbar}{8\pi^2 m_p^{3/2} g^{1/2}} \left[\frac{\partial \ln \chi}{\partial P_0} \right]^2 \begin{cases} \sqrt{\frac{\pi}{2}} \xi_0^{-3/2} e^{-\xi_0}, & \xi_0 \gg 1, \\ \frac{\pi}{16} \xi_0^{-1}, & \xi_0 \ll 1, \end{cases} \end{aligned} \quad (17)$$

$$\begin{aligned} S_d &= \frac{\tau}{\hbar(\sigma T)} \int (v_{\mathbf{q}}^x)^2 (-\delta p_{\mathbf{q}}) \hbar \omega_{\mathbf{q}} \left(-\frac{\partial f_0}{\partial \omega_{\mathbf{q}}} \right) \frac{d^3 \mathbf{q}}{(2\pi)^3} \\ &= \frac{\tau k_B^2 T}{12\pi^2 \hbar (m_p g)^{1/2} \sigma} \frac{\partial \ln \chi}{\partial P_0} \begin{cases} 3\sqrt{\frac{\pi}{2}} \xi_0^{1/2} e^{-\xi_0}, & \xi_0 \gg 1, \\ \frac{\pi^2}{3}, & \xi_0 \ll 1, \end{cases} \end{aligned} \quad (18)$$

$$\begin{aligned} \kappa &= \frac{\tau}{\hbar T} \int (v_{\mathbf{q}}^x)^2 (\hbar \omega_{\mathbf{q}})^2 \left(-\frac{\partial f_0}{\partial \omega_{\mathbf{q}}} \right) \frac{d^3 \mathbf{q}}{(2\pi)^3} \\ &= \frac{\tau k_B^4 T^3 m_p^{1/2}}{6\pi^2 \hbar^3 g^{1/2}} \begin{cases} 3\sqrt{\frac{\pi}{2}} \xi_0^{5/2} e^{-\xi_0}, & \xi_0 \gg 1, \\ \frac{4\pi^4}{15}, & \xi_0 \ll 1, \end{cases} \end{aligned} \quad (19)$$

and the Kelvin-Onsager relation $\Pi_d = T S_d$. Here, τ is the ferron relaxation time, and $v_{\mathbf{q}}^x = \partial \omega_{\mathbf{q}} / \partial q_x = g q_x / (m_p \omega_{\mathbf{q}})$ the group velocity in the transport (x) direction. We may define a Lorenz number

$$L_d \equiv \frac{\kappa}{\sigma T} = \frac{4m_p^2 k_B^4 T^2}{\hbar^4} \left[\frac{\partial \ln \chi}{\partial P_0} \right]^{-2} \begin{cases} \xi_0^4, & \xi_0 \gg 1, \\ \frac{64\pi^3}{45} \xi_0, & \xi_0 \ll 1, \end{cases}$$

that is material specific and, assuming that the other parameters are approximately constant, scales with T^{-2} (T) at low (high) temperatures.

Next, we consider a quasi-one-dimensional ballistic ferroelectric wire that connects to reservoirs. Within the linear

response regime, the effective field (ΔE) and temperature (ΔT) differences between the reservoirs generate the polarization (J_p) and heat (J_q) currents as [11]

$$\begin{pmatrix} -J_p \\ J_q \end{pmatrix} = G \begin{pmatrix} 1 & S_b \\ \Pi_b & K/G \end{pmatrix} \begin{pmatrix} \Delta E \\ -\Delta T \end{pmatrix}, \quad (20)$$

noting that the currents driven by an effective field difference are transient. The polarization (G) and thermal (K) conductances and the ballistic Seebeck (S_b) and Peltier ($\Pi_b = TS_b$) coefficients follow from the Landauer-Büttiker formalism [11],

$$G = \frac{1}{\hbar} \int (\delta p_k)^2 \left(-\frac{\partial f_0}{\partial \omega_k} \right) \frac{d\omega_k}{2\pi} \\ = \frac{\hbar \chi}{8\pi m_p} \left[\frac{\partial \ln \chi}{\partial P_0} \right]^2 \begin{cases} e^{-\xi_0}, & \xi_0 \gg 1, \\ \frac{1}{3} \xi_0^{-1}, & \xi_0 \ll 1, \end{cases} \quad (21)$$

$$S_b = \frac{1}{\hbar(GT)} \int (-\delta p_k) \hbar \omega_k \left(-\frac{\partial f_0}{\partial \omega_k} \right) \frac{d\omega_k}{2\pi} \\ = \frac{\hbar}{4\pi m_p(GT)} \frac{\partial \ln \chi}{\partial P_0} f_0(\xi_0), \quad (22)$$

$$K = \frac{1}{\hbar T} \int (\hbar \omega_k)^2 \left(-\frac{\partial f_0}{\partial \omega_k} \right) \frac{d\omega_k}{2\pi} \\ = K_0 \begin{cases} \frac{3}{\pi^2} \xi_0^2 e^{-\xi_0}, & \xi_0 \gg 1, \\ 1, & \xi_0 \ll 1, \end{cases} \quad (23)$$

where k is the wave vector of the ferrons propagating along the wire with the dispersion relation ω_k , $K_0 = \pi k_B^2 T / (6\hbar)$ the single-mode quantum thermal conductance, and the summation over transverse modes was restricted to the lowest subband. The Lorenz number turns out to be quite different,

$$L_b \equiv \frac{K}{GT} = \frac{4}{(T\chi)^2} \left[\frac{\partial \ln \chi}{\partial P_0} \right]^{-2} \begin{cases} 1, & \xi_0 \gg 1, \\ \pi^2 \xi_0^{-1}, & \xi_0 \ll 1. \end{cases} \quad (24)$$

All the above transport coefficients depend on an applied uniform electric field via the field dependence of P_0 [see Eq. (2)]. The integrand of the diffuse thermal conductivity Eq. (19) depends on the field only via the occupation numbers,

$$\kappa' \equiv \frac{\partial \kappa}{\partial E} = \frac{\tau}{T\hbar^2} \int (v_{\mathbf{q}}^x)^2 (\hbar \omega_{\mathbf{q}})^2 \delta p_{\mathbf{q}} \frac{\partial^2 f_0}{\partial \omega_{\mathbf{q}}^2} \frac{d^3 \mathbf{q}}{(2\pi)^3} \\ = -\sigma S_d \begin{cases} \xi_0, & \xi_0 \gg 1, \\ 3, & \xi_0 \ll 1, \end{cases} \quad (25)$$

where the thermal conductance drops with a positive electric field along \mathbf{P}_0 by electric “freeze-out” of the thermally excited ferrons. We also find

$$K' \equiv \frac{\partial K}{\partial E} = -\xi_0 [1 + f_0(\xi_0)] G S_b. \quad (26)$$

Thus the κ' (K') together with the L_d (L_b) allows one to access σ (G) and S_d (S_b).

Table II summarizes the numerical calculations of the integral expressions of transport coefficients derived above with the parameters given in Table I, in which the integrals are cut off by the Debye wave vector $q_D = (6\pi^2/V_0)^{1/3}$. We observe that the experimental thermal conductivities are much larger than the computed ones because they are dominated by the

TABLE II. The ferron gap (ω_0) and dipole moment (δp_0) at the Γ point and transport coefficients for the ferroelectrics in Table I at room temperature and zero field. The spontaneous electric dipole moment $p_0 = P_0 V_0 N$ with N the number of unit cells and experimental total thermal conductivities ($\kappa_{\text{tot}}^{\text{expt}}$) are given for comparison.

| | BaTiO ₃ | PbTiO ₃ | LiNbO ₃ | Units |
|-------------------------------------|--------------------|----------------------|----------------------|--------------------------------------|
| ω_0 | 20 | 32 | 47 | THz |
| δp_0 | -2.75 | -0.45 | -0.15 | $e\text{\AA}$ |
| p_0 | 1.09N | 2.97N | 14.8N | $e\text{\AA}$ |
| σ | 1.0 | 3.4×10^{-2} | 7.8×10^{-3} | 10^{-15} m/ Ω |
| G | 1.72 | 2.7×10^{-2} | 1.9×10^{-3} | 10^{-24} m ² / Ω |
| S_d | 0.16 | 0.72 | 1.94 | 10^7 V/(K m) |
| S_b | 0.04 | 0.32 | 1.18 | 10^7 V/(K m) |
| κ | 2.03 | 0.74 | 1.02 | W/(K m) |
| K | 0.75 | 0.47 | 0.34 | K_0 |
| κ' | -4.99 | -0.67 | -0.42 | 10^{-9} W/(K V) |
| K'/K_0 | -3.11 | -0.42 | -0.12 | 10^{-9} m/V |
| $\kappa_{\text{tot}}^{\text{expt}}$ | 6.5 [54] | 3.9 [55] | 8.5 [56] | W/(K m) |

acoustic phonons and that the κ' and K' agree well with the relations $\kappa' \approx -3\sigma S_d$ and Eq. (26), respectively.

The ferron dipole in BaTiO₃ is about six times (one order of magnitude) larger than in PbTiO₃ (LiNbO₃) because of a larger anharmonicity (β and λ) relative to the quadratic coefficient (α) in Eq. (10). Hence, the polarization transport coefficients and the field derivative of the thermal conductivity (conductance) κ' (K') are largest in BaTiO₃. A *negative* κ' can provide evidence for ferronic transport [57]. However, when comparing with experiments several competing mechanisms should be considered. While to leading order acoustic phonons do not carry an electric dipole, the electric field also modulates the elastic parameters including the sound velocities by electrostriction and thereby heat transport, which could be separated in principle by clamping the sample. A second-order effect of the electrostriction is a dynamical coupling of the acoustic phonons with the ferrons that preserves $\kappa' < 0$ at low temperatures [30]. Finally, electric fields suppress domain walls, which leads to an *increasing* thermal conductivity via a field-dependent relaxation time [55,58–60].

Electric dipole of ferron polaritons. Photons can hybridize with optical phonons to form phonon polaritons [61–67], that can show anharmonicities in ferroelectrics [68,69]. We may therefore consider “ferron polaritons” with a dispersion relation governed by [61]

$$\frac{c^2 k^2}{\omega^2} = \varepsilon(\omega), \quad (27)$$

where c , k , and $\varepsilon(\omega)$ are the light velocity, wave vector, and the dynamic (relative) permittivity in the long-wavelength limit, respectively. According to Eq. (7),

$$\varepsilon(\omega) - \varepsilon(\infty) \equiv \frac{\delta P_{\text{h}}}{\varepsilon_0 E_{\text{th}}} = \frac{1}{m_p \varepsilon_0 (\omega_0^2 - \omega^2 - i\omega\tilde{\gamma})}, \quad (28)$$

where $\tilde{\gamma} = \gamma/m_p$, while $\varepsilon(\infty)$ is the high-frequency permittivity. While this dispersion is identical to that of the phonon polaritons in normal ionic crystals [61,62], the ferron polaritons may transport electric dipoles below T_c . By Eq. (12), the

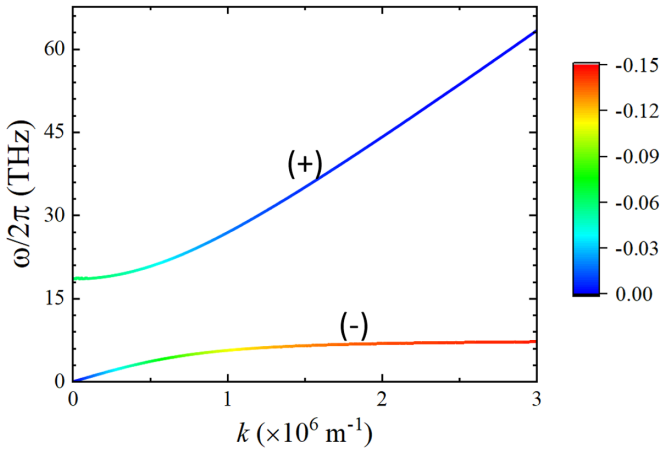


FIG. 2. The dispersion relations and the corresponding electric dipoles (represented by color) of two (\pm) of ferron polaritons branches in the absence of damping. The electric dipoles are in units of $e\text{\AA}$ with $\delta p_0 = -0.15 e\text{\AA}$. The parameters are for LiNbO_3 with $\varepsilon(\infty) = 5.5$.

electric dipole of ferron polaritons reads

$$\delta p_{\pm}(k) = - \left. \frac{\partial \hbar \omega_{\pm}(k)}{\partial E} \right|_{E \rightarrow 0} = \frac{\partial \omega_{\pm}(k)}{\partial \omega_0} \delta p_0, \quad (29)$$

where $+$ ($-$) indicates two (optical and ferronic) branches and $\delta p_0 = -\partial \hbar \omega_0 / \partial E$. Figure 2 gives the dispersion relations and the electric dipoles carried by the two branches for LiNbO_3 , in which the level repulsion renders the dipole of the ferronic branch smaller than δp_0 even at $k = 0$. Focused optical excitations at the optical phonon frequency of ferroelectrics can therefore be a source of coherent polarization currents and give rise to unique electro-optic properties such as electric field-controlled light propagation. The electric-dipolar interaction importantly affects the surface ferron-polariton dispersion relations [70].

Discussion and conclusions. We address displacive ferroelectrics by the Landau theory of a structural phase transition by condensation of a soft phonon. We identify the ferrons

as the quasiparticle excitations on top of the ordered state that, in contrast to conventional optical phonons, are endowed with a net electric dipole moment. The physical origin is the anharmonicity and the broken inversion symmetry of the ferroelectric order.

The anharmonicity of the Landau free energy as a function of polarization is essential when the system is far from equilibrium, e.g., during polarization switching, and is responsible for transient negative capacitances [71], while the interaction with high-frequency phonons enables ultrafast polarization reversal [72–74]. These processes may be accompanied by polarization loss due to ferron emission.

Goldstone-like (phason) and Higgs-like (amplitudon) excitations exist in any vector field and such as the ferroelectric [75,76] and ferromagnetic [77] orders. Transverse ferrons as discussed in Refs. [10,11] may be called phasonlike excitations. The ferrons in displacive ferroelectrics discussed here are fluctuations of the polarization modulus and therefore Higgs-like.

In conclusion, we identify the quasiparticle excitations of displacive ferroelectrics that carry heat and electric dipole currents and predict the associated low-temperature pyroelectric or electrocaloric coefficients, the (field-dependent) thermal conductivity, Peltier and Seebeck coefficients, and ferron polariton polarization. Thermally driven and electrically tunable ferronic transport in a broad class of ferroelectric materials may provide unique functionalities to thermal management and information technologies. Ferrons become observable by, e.g., a thermovoltage, a transient Peltier effect [10], and a magnetic stray field generated by the ferron current [11], a field-dependent thermal conductivity, and nonlocal dipolar drag effects [78].

Acknowledgments. We are grateful for enlightening discussions with Beatriz Noheda, Bart J. van Wees, Joseph P. Heremans, and Sergio Rezendes. JSPS KAKENHI Grant No. 19H00645 supported P.T. and G.B., while R.I. and K.U. acknowledge support by JSPS KAKENHI Grant No. 20H02609, JST CREST “Creation of Innovative Core Technologies for Nano-enabled Thermal Management” Grant No. JPMJCR17I1, and the Canon Foundation.

-
- [1] V. V. Kruglyak, S. O. Demokritov, and D. Grundler, *J. Phys. D* **43**, 264001 (2010).
- [2] A. V. Chumak, V. I. Vasyuchka, A. A. Serga, and B. Hillebrands, *Nat. Phys.* **11**, 453 (2015).
- [3] L. J. Cornelissen, J. Liu, R. A. Duine, J. B. Youssef, and B. J. van Wees, *Nat. Phys.* **11**, 1022 (2015).
- [4] L. J. Cornelissen, K. J. H. Peters, G. E. W. Bauer, R. A. Duine, and B. J. van Wees, *Phys. Rev. B* **94**, 014412 (2016).
- [5] K. Uchida, J. Xiao, H. Adachi, J. Ohe, S. Takahashi, J. Ieda, T. Ota, Y. Kajiwara, H. Umezawa, H. Kawai, G. E. W. Bauer, S. Maekawa, and E. Saitoh, *Nat. Mater.* **9**, 894 (2010).
- [6] J. Flipse, F. K. Dejene, D. Wagenaar, G. E. W. Bauer, J. Ben Youssef, and B. J. Van Wees, *Phys. Rev. Lett.* **113**, 027601 (2014).
- [7] S. Daimon, R. Iguchi, T. Hioki, E. Saitoh, and K. Uchida, *Nat. Commun.* **7**, 13754 (2016).
- [8] Y. Xu, *Ferroelectric Materials and Their Applications* (Elsevier, Amsterdam, 2013).
- [9] N. A. Spaldin, *Top. Appl. Phys.* **105**, 175 (2007).
- [10] G. E. W. Bauer, R. Iguchi, and K. Uchida, *Phys. Rev. Lett.* **126**, 187603 (2021).
- [11] P. Tang, R. Iguchi, K. Uchida, and G. E. W. Bauer, *Phys. Rev. Lett.* **128**, 047601 (2022).
- [12] R. Blinc and B. Žekš, *Adv. Phys.* **21**, 693 (1972).
- [13] W. Cochran, *Phys. Rev. Lett.* **3**, 412 (1959).
- [14] W. Cochran, *Adv. Phys.* **9**, 387 (1960).
- [15] K. Müller, Y. Luspin, J. Servoin, and F. Gervais, *J. Phys. Lett.* **43**, 537 (1982).
- [16] N. Dalal, A. Klymachyov, and A. Bussmann-Holder, *Phys. Rev. Lett.* **81**, 5924 (1998).
- [17] B. Zalar, V. V. Laguta, and R. Blinc, *Phys. Rev. Lett.* **90**, 037601 (2003).

- [18] A. Bussmann-Holder, H. Beige, and G. Völkel, *Phys. Rev. B* **79**, 184111 (2009).
- [19] A. F. Devonshire, *London, Edinburgh Dublin Philos. Mag. J. Sci.* **40**, 1040 (1949).
- [20] A. F. Devonshire, *London, Edinburgh Dublin Philos. Mag. J. Sci.* **42**, 1065 (1951).
- [21] E. Salje, *Ferroelectrics* **104**, 111 (1990).
- [22] W. Cao, *Ferroelectrics* **375**, 28 (2008).
- [23] P. Chandra and P. B. Littlewood, in *Physics of Ferroelectrics*, edited by K. M. Rabe, C. H. Ahn, and J.-M. Triscone, Topics in Applied Physics (Springer, Berlin, 2007), Vol. 105, p. 69.
- [24] K. Tani, *J. Phys. Soc. Jpn.* **26**, 93 (1969).
- [25] Y. Ishibashi, *Ferroelectrics* **98**, 193 (1989).
- [26] S. Sivasubramanian, A. Widom, and Y. N. Srivastava, *Ferroelectrics* **300**, 43 (2004).
- [27] A. Widom, S. Sivasubramanian, C. Vittoria, S. Yoon, and Y. N. Srivastava, *Phys. Rev. B* **81**, 212402 (2010).
- [28] L. D. Landau, E. M. Lifshitz, and L. P. Pitaevskii, *Statistical Physics, Part I*, 3rd ed. (Pergamon, New York, 1980).
- [29] T. Tadano and S. Tsuneyuki, *J. Phys. Soc. Jpn.* **87**, 041015 (2018).
- [30] P. Tang and G. E. W. Bauer (unpublished).
- [31] M. J. Haun, E. Furman, S. Jang, H. McKinstry, and L. Cross, *J. Appl. Phys.* **62**, 3331 (1987).
- [32] N. A. Pertsev, A. G. Zembilgotov, and A. K. Tagantsev, *Phys. Rev. Lett.* **80**, 1988 (1998).
- [33] D. A. Scrymgeour, V. Gopalan, A. Itagi, A. Saxena, and P. J. Swart, *Phys. Rev. B* **71**, 184110 (2005).
- [34] Y. Li, L. Cross, and L. Chen, *J. Appl. Phys.* **98**, 064101 (2005).
- [35] J. Hlinka and P. Marton, *Phys. Rev. B* **74**, 104104 (2006).
- [36] L. Liang, Y. Li, L.-Q. Chen, S. Hu, and G.-H. Lu, *Appl. Phys. Lett.* **94**, 072904 (2009).
- [37] R. Whatmore, *Rep. Prog. Phys.* **49**, 1335 (1986).
- [38] P. Muralt, *Rep. Prog. Phys.* **64**, 1339 (2001).
- [39] A. Mischenko, Q. Zhang, J. Scott, R. Whatmore, and N. Mathur, *Science* **311**, 1270 (2006).
- [40] B. Neese, B. Chu, S.-G. Lu, Y. Wang, E. Furman, and Q. Zhang, *Science* **321**, 821 (2008).
- [41] X. Li, S.-G. Lu, X.-Z. Chen, H. Gu, X.-s. Qian, and Q. Zhang, in *Progress in Advanced Dielectrics* (World Scientific, Singapore, 2020), pp. 329–367.
- [42] A. Glass and M. Lines, *Phys. Rev. B* **13**, 180 (1976).
- [43] S. B. Lang, L. H. Rice, and S. A. Shaw, *J. Appl. Phys.* **40**, 4335 (1969).
- [44] M. Born, *Rev. Mod. Phys.* **17**, 245 (1945).
- [45] B. Szigeti, *Phys. Rev. Lett.* **35**, 1532 (1975).
- [46] G. E. W. Bauer, P. Tang, R. Iguchi, and K. Uchida, *J. Magn. Magn. Mater.* **541**, 168468 (2022).
- [47] R. K. Behera, C.-W. Lee, D. Lee, A. N. Morozovska, S. B. Sinnott, A. Asthagiri, V. Gopalan, and S. R. Phillpot, *J. Phys.: Condens. Matter* **23**, 175902 (2011).
- [48] M. S. Richman, X. Li, and A. Caruso, *J. Appl. Phys.* **125**, 184103 (2019).
- [49] A. N. Morozovska, E. A. Eliseev, C. M. Scherbakov, and Y. M. Vysochanskii, *Phys. Rev. B* **94**, 174112 (2016).
- [50] $\tau \sim 1/\Delta\omega$ was estimated from the broadening ($\Delta\omega$) of the lowest $A_1(\text{TO})$ line in Raman-scattering spectra.
- [51] M. Fontana, K. Laabidi, and B. Jannot, *J. Phys.: Condens. Matter* **6**, 8923 (1994).
- [52] J. A. Sanjurjo, E. Lopez-Cruz, and G. Burns, *Phys. Rev. B* **28**, 7260 (1983).
- [53] A. Ridah, M. D. Fontana, and P. Bourson, *Phys. Rev. B* **56**, 5967 (1997).
- [54] Y. Suemune, *J. Phys. Soc. Jpn.* **20**, 174 (1965).
- [55] E. Langenberg, D. Saha, M. E. Holtz, J.-J. Wang, D. Bugallo, E. Ferreiro-Vila, H. Paik, I. Hanke, S. Ganschow, D. A. Muller *et al.*, *Nano Lett.* **19**, 7901 (2019).
- [56] G. Burkhardt and R. Rice, *J. Appl. Phys.* **48**, 4817 (1977).
- [57] B. L. Wooten, R. Iguchi, P. Tang, J. S. Kang, K. Uchida, G. E. W. Bauer, and J. P. Heremans (unpublished).
- [58] A. Mante and J. Volger, *Physica* **52**, 577 (1971).
- [59] G. A. Northrop, E. J. Cotts, A. C. Anderson, and J. P. Wolfe, *Phys. Rev. Lett.* **49**, 54 (1982).
- [60] M. Weilert, M. Msall, J. Wolfe, and A. Anderson, *Z. Phys. B* **91**, 179 (1993).
- [61] M. Born, K. Huang, and M. Lax, *Am. J. Phys.* **23**, 474 (1955).
- [62] U. Fano, *Phys. Rev.* **103**, 1202 (1956).
- [63] C. Henry and J. Hopfield, *Phys. Rev. Lett.* **15**, 964 (1965).
- [64] H. J. Bakker, S. Hunsche, and H. Kurz, *Phys. Rev. Lett.* **69**, 2823 (1992).
- [65] S. Kojima, N. Tsumura, H. Kitahara, M. W. Takeda, and S. Nishizawa, *Jpn. J. Appl. Phys.* **41**, 7033 (2002).
- [66] S. Kojima, N. Tsumura, M. W. Takeda, and S. Nishizawa, *Phys. Rev. B* **67**, 035102 (2003).
- [67] Y. Ikegaya, H. Sakaibara, Y. Minami, I. Katayama, and J. Takeda, *Appl. Phys. Lett.* **107**, 062901 (2015).
- [68] H. J. Bakker, S. Hunsche, and H. Kurz, *Phys. Rev. B* **50**, 914 (1994).
- [69] H. Bakker, S. Hunsche, and H. Kurz, *Rev. Mod. Phys.* **70**, 523 (1998).
- [70] S. M. Rezende and R. L. Rodríguez-Suárez (unpublished).
- [71] J. Íñiguez, P. Zubko, I. Luk'yanchuk, and A. Cano, *Nat. Rev. Mater.* **4**, 243 (2019).
- [72] A. Subedi, *Phys. Rev. B* **92**, 214303 (2015).
- [73] R. Mankowsky, A. von Hoegen, M. Först, and A. Cavalleri, *Phys. Rev. Lett.* **118**, 197601 (2017).
- [74] P. Chen, C. Paillard, H. J. Zhao, J. Íñiguez, and L. Bellaiche, *Nat. Commun.* **13**, 2566 (2022).
- [75] J. Mangeri, K. C. Pitike, S. P. Alpay, and S. Nakhmanson, *npj Comput. Mater.* **2**, 16020 (2016).
- [76] S. Prosandeev, S. Prokhorenko, Y. Nahas, A. Al-Barakaty, L. Bellaiche, P. Gemeiner, D. Wang, A. A. Bokov, Z.-G. Ye, and B. Dkhil, *Phys. Rev. B* **102**, 104110 (2020).
- [77] M. Grassi, M. Geilen, K. A. Oukaci, Y. Henry, D. Lacour, D. Stoeffler, M. Hehn, P. Pirro, and M. Bailleul, *Phys. Rev. B* **105**, 094444 (2022).
- [78] P. Tang, K. Uchida, and G. E. W. Bauer, *arXiv:2207.00240* (2022).