Polarization and Adiabatic Pumping in Inhomogeneous Crystals

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We develop a general theory of electric polarization in crystals with inhomogeneous order. We show that the inhomogeneity-induced polarization can be classified into two parts: a perturbative contribution stemming from a correction to the basis functions and a topological contribution described in terms of the Chern-Simons form of the Berry gauge fields. The latter is determined up to an uncertainty quantum, which is the second Chern number in appropriate units. Our theory provides an exhaustive link between microscopic models and the macroscopic polarization.

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In the study of dielectric and ferroelectric materials, it often happens that the system is in an inhomogeneous state, with the electric polarization strongly depending on the inhomogeneity. Classic examples include ferroelectric domain walls with induced polarization charge density [1] and flexoelectric polarization produced by a strain gradient [2,3]. Recently, another example of this type of problem has been found in a novel class of multiferroics, where the magnetic order varies in space and induces a spontaneous polarization [4]. A central quantity in the description of these phenomena is the inhomogeneity-induced polarization. However, despite its broad applications, the theory of polarization in inhomogeneous crystals remains primarily based on phenomenology [5].

Theoretically, it has been recognized that in an extended system only the change in polarization has physical meaning, and it can be quantified by using the Berry phase of the electronic wave functions [6–8]. For periodic insulators, the Berry-phase formula is conveniently expressed in terms of the Bloch orbitals, allowing one to compute the polarization from first principles. However, in inhomogeneous crystals the translational symmetry is broken, rendering previous methods based on Bloch's theorem inapplicable. To circumvent this, a supercell approach has been applied in numerical calculations [9]. But this approach has two shortcomings: If the inhomogeneity is incommensurate with the lattice, an enormous supercell is required to render an accurate result; furthermore, by its nature this approach is blind to the spatial variation within the supercell, making it difficult to investigate the role of inhomogeneity in the appearance of the polarization.

In this Letter, we present a general theory of electric polarization in inhomogeneous crystals that is exact up to first order in the spatial gradient. Our theory is based on the elementary relation between the change in polarization and the adiabatic current [7,8]. The latter can be evaluated using the semiclassical formalism of Bloch electron dynamics [10], a powerful framework for investigating the influence of slowly varying perturbations. We find that the inhomogeneity-induced polarization has two different origins: One results from a perturbative correction to the basis functions and is a direct generalization of previous work on insulators in finite electric fields [11,12]; the other is topological and is given in terms of the Chern-Simons form of the Berry gauge fields derived from the Bloch functions. Because of its topological nature, this contribution can be determined only up to an uncertainty quantum, which we identify as the second Chern number in appropriate units [13]. Our theory provides an exhaustive link between microscopic models and the macroscopic polarization, and it allows for a straightforward implementation in first-principles codes.

Let us consider an insulating crystal with an order parameter that varies slowly in space. We assume that, at least at the mean-field level, the system can be described as a perfect crystal under the influence of an external field $\boldsymbol{h}(\boldsymbol{r})$. Under this assumption, the Hamiltonian can be written as $\mathcal{H}[\boldsymbol{h}(\boldsymbol{r})]$, with $\mathcal{H}(\boldsymbol{h}=0)$ describing the unperturbed periodic crystal. If, for example, the order parameter is the magnetization, then $\boldsymbol{h}(\boldsymbol{r})$ can be chosen as the exchange field that yields the corresponding spin configuration $\boldsymbol{s}(\boldsymbol{r})$. Since we are interested in the inhomogeneity-induced polarization, we choose the initial state with a uniform $\boldsymbol{h}=\boldsymbol{h}_0$ and the final state with $\boldsymbol{h}(\boldsymbol{r})$ being fully turned on [14]. Our goal is to calculate the polarization difference between these two states.

As a first step, we make a local approximation, in which the system is described by a class of local Hamiltonians $\mathcal{H}_c[\boldsymbol{h}(\boldsymbol{r}_c)]$ which assume a constant value of the external field $\boldsymbol{h}(\boldsymbol{r}_c)$ at each position $\boldsymbol{r}_c$. Since $\mathcal{H}_c[\boldsymbol{h}(\boldsymbol{r}_c)]$ maintains the periodicity of the unperturbed crystal, its eigenstates still have the Bloch form: $|\psi_n(\boldsymbol{k},\boldsymbol{r}_c)\rangle = e^{i\boldsymbol{k}\cdot\boldsymbol{r}}|u_n(\boldsymbol{k},\boldsymbol{r}_c)\rangle$. Inserting $|u_n(\boldsymbol{k},\boldsymbol{r}_c)\rangle$ into the King-Smith and Vanderbilt formula [6] for periodic insulators, we obtain the zeroth-order contribution to the polarization:

$$\boldsymbol{P}^{\text{KS-V}} = -e\sum_n \int_{\text{BZ}} \frac{d\boldsymbol{k}}{(2\pi)^d} \langle u_{n\boldsymbol{k}} | i\boldsymbol{\nabla}_{\boldsymbol{k}} | u_{n\boldsymbol{k}}\rangle |_0^1, \tag{1}$$

where the sum is over occupied bands and 0 and 1 label the initial and final states, respectively. If the crystal structure is centrosymmetric and the uniform $\boldsymbol{h}$ does not break the inversion symmetry, then $\boldsymbol{P}^{\text{KS-V}}$ vanishes.

Next we look for first-order contributions. A natural step is to expand the Hamiltonian around $\boldsymbol{r}_c$:

$$\mathcal{H} = \mathcal{H}_c + (\nabla^r_\alpha h_\beta)(r_\alpha - r_{c,\alpha})\hat{s}_\beta, \tag{2}$$

where $\nabla^r_\alpha \equiv \partial/\partial r_\alpha$ and $\hat{s}_\beta \equiv \partial\mathcal{H}/\partial h_\beta$. (Summation over repeated indices is implied throughout our derivation.) Obviously, the gradient term in the Hamiltonian (2) will introduce a correction to the basis functions, i.e., $|\tilde{u}_{n\boldsymbol{k}}\rangle = |u_{n\boldsymbol{k}}\rangle + |\delta u_{n\boldsymbol{k}}\rangle$, where $|\tilde{u}_{n\boldsymbol{k}}\rangle$ is the modified basis and $|\delta u_{n\boldsymbol{k}}\rangle$ is proportional to the gradient. If one assumes that the polarization is still given by Eq. (1) but with $|u_{n\boldsymbol{k}}\rangle$ replaced by $|\tilde{u}_{n\boldsymbol{k}}\rangle$, then a first-order contribution can be obtained as

$$\delta\boldsymbol{P}^{\text{KS-V}} = 2e\sum_n \int_{\text{BZ}} \frac{d\boldsymbol{k}}{(2\pi)^d} \operatorname{Im}\langle \delta u_{n\boldsymbol{k}} | \boldsymbol{\nabla}_{\boldsymbol{k}} | u_{n\boldsymbol{k}}\rangle |_0^1. \tag{3}$$

The explicit form of $|\delta u_{n\boldsymbol{k}}\rangle$ can be derived using linear-response theory by taking the long wavelength limit [7,15]. In the special case of an applied electric field, the above formula reduces to the one obtained in Ref. [11].

However, the above derivation misses an important contribution due to the inhomogeneity-induced electron dynamics. As was emphasized in previous work [6–8], the proper calculation of the polarization relies on the elementary relation between the polarization and the adiabatic current [16], i.e.,

$$\boldsymbol{P} = \int_0^T dt\,\boldsymbol{j}(\boldsymbol{r}, t), \tag{4}$$

where $\boldsymbol{j}(\boldsymbol{r}, t)$ is the bulk current density as the system adiabatically evolves from the initial state ($t = 0$) to the final state ($t = T$). This process can be described by a smooth transformation of the Hamiltonian $\mathcal{H}[\boldsymbol{h}(\boldsymbol{r}; \lambda)]$, parametrized by a scalar λ. Following convention, we set $\lambda(0) = 0$ and $\lambda(T) = 1$. As we shall show below, the specific form of $\boldsymbol{h}(\lambda)$ is not important as long as the system remains an insulator during the process.

In order to find the current density $\boldsymbol{j}(\boldsymbol{r}, t)$, we adopt the formalism of wave packet dynamics of Bloch electrons [10]. In the following derivation, we shall consider only the case of nondegenerate bands and hence omit the band index n. It has been shown that the wave packet center satisfies the following equations of motion [10,17]:

$$\dot{r}_\alpha = \nabla^k_\alpha \varepsilon - \Omega^{kr}_{\alpha\beta}\dot{r}_\beta - \Omega^{kk}_{\alpha\beta}\dot{k}_\beta - \dot{\lambda}\Omega^{k\lambda}_\alpha, \tag{5a}$$

$$\dot{k}_\alpha = -\nabla^r_\alpha \varepsilon + \Omega^{rr}_{\alpha\beta}\dot{r}_\beta + \Omega^{rk}_{\alpha\beta}\dot{k}_\beta + \dot{\lambda}\Omega^{r\lambda}_\alpha, \tag{5b}$$

where ε is the electron energy. Here $\boldsymbol{\Omega}$ is the Berry curvature obtained from the gauge field $\mathcal{A}$ derived from $|\tilde{u}(\boldsymbol{k}, \boldsymbol{r}; \lambda)\rangle$. For example,

$$\mathcal{A}^k_\alpha = \langle \tilde{u} | i\nabla^k_\alpha | \tilde{u}\rangle, \qquad \mathcal{A}^r_\alpha = \langle \tilde{u} | i\nabla^r_\alpha | \tilde{u}\rangle, \tag{6}$$

$$\Omega^{kr}_{\alpha\beta} = \nabla^k_\alpha \mathcal{A}^r_\beta - \nabla^r_\beta \mathcal{A}^k_\alpha. \tag{7}$$

The Berry curvatures are antisymmetric tensors ($\Omega^{kr}_{\alpha\beta} = -\Omega^{rk}_{\beta\alpha}$).

The appearance of the modified basis $|\tilde{u}_{\boldsymbol{k}}\rangle$ in the equations of motion (5) via the Berry curvature is undesirable and, in fact, is unnecessary in most terms. Recall that we are aiming at a first-order calculation in the spatial gradient. A quick look of Eq. (5) reveals that there are two zeroth-order terms: $\nabla^k_\alpha \varepsilon$ and $\dot{\lambda}\Omega^{k\lambda}_\alpha$; the rest are at least first-order in the gradient. The term $\nabla^k_\alpha \varepsilon$ has no effect on our final result. Therefore only $\Omega^{k\lambda}_\alpha$ needs to be evaluated using $|\tilde{u}_{\boldsymbol{k}}\rangle$; for other Berry curvatures, it is sufficient to evaluate them using the unperturbed basis $|u_{\boldsymbol{k}}\rangle$. For the same reason, the term $\dot{\lambda}\Omega^{r\lambda}_\alpha$ should be kept in the derivation. In previous work [18,19], this term was dropped based on the reasoning that the time and spatial variations are treated at the same order. However, this is not true in the calculation of the polarization because of the explicit time integral in Eq. (4).

Now we can calculate the induced adiabatic current given by

$$\boldsymbol{j} = -e\int_{\text{BZ}} d\boldsymbol{k} D(\boldsymbol{k}, \boldsymbol{r})\dot{\boldsymbol{r}}, \tag{8}$$

where $D(\boldsymbol{r}, \boldsymbol{k})$ is the electron density of states, modified from its usual value of $1/(2\pi)^d$ in the presence of the Berry curvature [20]: $D(\boldsymbol{k}, \boldsymbol{r}) = (1 + \Omega^{kr}_{\alpha\alpha})/(2\pi)^d$. We solve for $\dot{r}_\alpha$ from Eq. (5) and then insert it into Eq. (8). It can be shown that only terms proportional to $\dot{\lambda}$ survive [21]. Physically, this result is required by the adiabaticity of the transformation. We find the total current is $\boldsymbol{j} = \boldsymbol{j}^{(1)} + \boldsymbol{j}^{(2)}$, where

$$j^{(1)}_\alpha = e\dot{\lambda}\int_{\text{BZ}} \frac{d\boldsymbol{k}}{(2\pi)^d} \tilde{\Omega}^{k\lambda}_\alpha \tag{9}$$

and

$$j^{(2)}_\alpha = e\dot{\lambda}\int_{\text{BZ}} \frac{d\boldsymbol{k}}{(2\pi)^d} (\Omega^{kk}_{\alpha\beta}\Omega^{r\lambda}_\beta + \Omega^{kr}_{\beta\beta}\Omega^{k\lambda}_\alpha - \Omega^{kr}_{\alpha\beta}\Omega^{k\lambda}_\beta). \tag{10}$$

We have added a tilde to $\tilde{\Omega}^{k\lambda}_\alpha$ to emphasize that it is evaluated using the modified basis $|\tilde{u}_{\boldsymbol{k}}\rangle$. The current $\boldsymbol{j}^{(1)}$ is given by the first Chern form of the Berry curvature, hence the superscript (1). It was first derived by Thouless in his study of charge pumping [22]. The current $\boldsymbol{j}^{(2)}$ is given by the second Chern form of the Berry curvature. It originates from the competition between the intrinsic lattice period and incommensurate external field, and it will vanish in a uniform system. $\boldsymbol{j}^{(2)}$ provides another route for adiabatic charge pumping through spatial inhomogeneity [13].

To understand the origin of the inhomogeneity-induced current $\boldsymbol{j}^{(2)}$, we examine the physical meaning of the individual terms in Eq. (10). The first term is a Hall current: The integration of $\Omega^{kk}_{\alpha\beta}$ gives the Hall conductivity [23], and $\Omega^{r\lambda}_{\beta}$ is the driving force due to the spatial variation. The second term is a spatially modulated current: $\Omega^{k\lambda}_{\alpha}$ is the electron velocity along the α direction, and $\Omega^{kr}_{\beta\beta}$, coming from the modified density of states, represents the change in the unit length along the β direction. The third term does not have an obvious interpretation, and it has to be obtained through the above derivation or its equivalent [17].

Once we obtain the expression for the adiabatic current $\boldsymbol{j}$, the polarization can be found by integrating $\boldsymbol{j}$ [Eq. (4)]. The integration of $\boldsymbol{j}^{(1)}$ gives $\boldsymbol{P}^{(1)} = \boldsymbol{P}^{\text{KS-V}} + \delta\boldsymbol{P}^{\text{KS-V}}$. This prompts us to name $\delta\boldsymbol{P}^{\text{KS-V}}$ the perturbative contribution since it is a correction to the original King-Smith and Vanderbilt formula. On the other hand, the integration of $\boldsymbol{j}^{(2)}$ gives a purely topological contribution $\boldsymbol{P}^{(2)}$. The difference between $\delta\boldsymbol{P}^{\text{KS-V}}$ and $\boldsymbol{P}^{(2)}$ can be seen by considering a cyclic change of the system. During this process, both $\boldsymbol{P}^{(1)}$ and $\boldsymbol{P}^{\text{KS-V}}$ can change only by an integer (in appropriate units). Since $\delta\boldsymbol{P}^{\text{KS-V}}$ is a perturbative contribution, it must vanish. In contrast, $\boldsymbol{P}^{(2)}$ can be nonzero and takes an integer value as discussed below. Since the general properties of $\boldsymbol{P}^{(1)}$ have been discussed thoroughly in previous work [6–8], we shall focus on the properties of $\boldsymbol{P}^{(2)}$ in what follows.

We first show that $\boldsymbol{P}^{(2)}$ has the desired property that it depends only on the initial and final states. The gauge invariance of Eq. (10) allows us to calculate $\boldsymbol{P}^{(2)}$ with any gauge choice. In order to carry out the integration over λ, we choose the path-independent gauge by requiring that the phase difference between $|u^{(\lambda)}(\boldsymbol{k}, \boldsymbol{r})\rangle$ and $|u^{(\lambda)}(\boldsymbol{k} + \boldsymbol{G}, \boldsymbol{r})\rangle$ does not depend on λ, where $\boldsymbol{G}$ is a reciprocal lattice vector [8]. Under this gauge, $\boldsymbol{P}^{(2)}$ is found as

$$P^{(2)}_{\alpha} = e\int_{\text{BZ}} \frac{d\boldsymbol{k}}{(2\pi)^d}(\mathcal{A}^k_{\alpha}\nabla^r_{\beta}\mathcal{A}^k_{\beta} + \mathcal{A}^k_{\beta}\nabla^k_{\alpha}\mathcal{A}^r_{\beta} + \mathcal{A}^r_{\beta}\nabla^k_{\beta}\mathcal{A}^k_{\alpha})\big|^1_0. \tag{11}$$

We recognize that the integrand in the above equation is of Chern-Simons form.

However, we have paid a price for carrying out the λ integration; namely, the spatially averaged polarization $\langle P^{(2)}_{\alpha}\rangle = (1/V)\int d\boldsymbol{r} P^{(2)}_{\alpha}$ resulting from this two-point formula (11) can be determined only modulo a quantum. Consider a cyclic change of the system with $\lambda(0) = \lambda(T)$, and assume $\boldsymbol{h}(\boldsymbol{r})$ is periodic in $\boldsymbol{r}$. The integral $\int d\boldsymbol{r}\int dt j^{(2)}_{\alpha}$ over a closed manifold spanned by $(k_{\alpha}, k_{\beta}, r_{\beta}, t)$ is an integer called the second Chern number [13]. Since Eq. (11) does not track the evolution of $\lambda(t)$, there is no information on how many cycles λ has gone through; hence $\langle P^{(2)}_{\alpha}\rangle$ can be determined only modulo a quantum. Assuming $\boldsymbol{h}(\boldsymbol{r})$ depends on y, we obtain the quantum for $P^{(2)}_x$ in a three-dimensional system:

$$\Delta\langle P^{(2)}_x\rangle = \frac{e}{l_y a_z}, \tag{12}$$

where l_y is the period of $\boldsymbol{h}(y)$ and a_z is the lattice constant along $\hat{z}$.

Next we discuss the general conditions on microscopic models [24,25] that display a nonzero $\boldsymbol{P}^{(2)}$. Since the Hamiltonian is assumed to have the form $\mathcal{H}[\boldsymbol{h}(\boldsymbol{r}, \lambda)]$, both λ and $\boldsymbol{r}$ dependence enter through $\boldsymbol{h}$. Using the relation $\nabla^r_{\alpha} = \nabla^r_{\alpha}h_{\mu}\nabla^h_{\mu}$ and $\nabla^{\lambda} = \partial_{\lambda}h_{\mu}\nabla^h_{\mu}$, we find

$$P^{(2)}_{\alpha} = e\int_{\text{BZ}} \frac{d\boldsymbol{k}}{(2\pi)^d}\int_0^1 d\lambda \nabla^{\lambda}h_{\mu}\nabla^r_{\beta}h_{\nu}(\Omega^{kh}_{\alpha\mu}\Omega^{kh}_{\beta\nu} - \Omega^{kh}_{\alpha\nu}\Omega^{kh}_{\beta\mu} + \Omega^{kk}_{\alpha\beta}\Omega^{hh}_{\mu\nu}). \tag{13}$$

Besides having the crystal be inhomogeneous, there are three general conditions for $\boldsymbol{P}^{(2)}$ to be nonzero according to Eq. (13): (i) The system must be two-dimensional or higher; (ii) the order parameter $\boldsymbol{h}(\boldsymbol{r})$ must have two or more components; and (iii) the wave function must depend on four or more *independent* parameters. Conditions (i) and (ii) are obtained by realizing that the integrand in Eq. (13) is antisymmetric in k_{α} and k_{β} and in h_{μ} and h_{ν}. Furthermore, since the integrand is actually the second Chern 4-form $\Omega \wedge \Omega$, it would vanish identically in three or fewer dimensions; hence condition (iii) follows. Based on condition (iii), we can further deduce that $\dim(\mathcal{H}) > 2$. If $\dim(\mathcal{H}) = 2$, $\mathcal{H}$ has four components. However, since shifting and scaling energy has no effect on wave functions, the wave function can depend on only two *independent* parameters (for example, the spherical coordinates on a 2-sphere S^2), and $\boldsymbol{P}^{(2)}$ vanishes in this case.

The Chern-Simons form of our theory also allows us to deduce the general form of $\boldsymbol{P}^{(2)}$. We first consider a two-dimensional "minimal" model with $\boldsymbol{h}(\boldsymbol{r})$ having two components. Because of its antisymmetric properties, we can write the integrand of Eq. (13) as $\epsilon_{\alpha\beta}\epsilon_{\mu\nu}\chi$. Then, by assuming $\boldsymbol{h}(\boldsymbol{r}, \lambda) = \lambda\boldsymbol{h}(\boldsymbol{r})$, we find Eq. (13) takes the following form:

$$\boldsymbol{P}^{(2)} = e\chi[(\boldsymbol{\nabla}\cdot\boldsymbol{h})\boldsymbol{h} - (\boldsymbol{h}\cdot\boldsymbol{\nabla})\boldsymbol{h}]. \tag{14}$$

Here χ, as a function of $\boldsymbol{h}(\boldsymbol{r})$, can be spatially dependent. Interestingly, if we identify $\boldsymbol{h}(\boldsymbol{r})$ with the magnetization order parameter $\boldsymbol{M}(\boldsymbol{r})$, the above result has the same form as that obtained from the Landau-Ginzburg approach [26–28]. However, unlike the Landau theories, Eq. (14) is a direct consequence of the minimal dimensionality, and we did not invoke any symmetry argument; in particular, the time-reversal invariance is irrelevant.

Next we consider three-dimensional systems with cubic symmetry. We start from Eq. (11) by making the variable substitution $\nabla^r_{\beta} = \nabla^r_{\beta}h_{\gamma}\nabla^h_{\gamma}$. By applying the antisymmetric properties of the Chern-Simons form, we can write $P^{(2)}_{\alpha} = \epsilon_{\beta\gamma\sigma}\nabla^r_{\beta}h_{\gamma}C_{\alpha\sigma}$, where $C_{\alpha\sigma}$ is a coefficient. Since the crystal has cubic symmetry, we have either (i) $C_{\alpha\sigma} = \delta_{\alpha\sigma}\chi$ or (ii) $C_{\alpha\delta} = \epsilon_{\eta\alpha\sigma}D_{\eta}$. In the former case, $P_\alpha^{(2)} = \epsilon_{\beta\gamma\alpha}\chi\nabla_\beta^r h_\gamma$. This is allowed only when $\boldsymbol{h}$ is invariant under time reversal. The antisymmetric tensor $\epsilon_{\beta\gamma\alpha}$ also prohibits its existence in two-dimensional systems. If $C_{\alpha\sigma} = \epsilon_{\eta\alpha\sigma}D_\eta$, then $\boldsymbol{D}$ must be pointing in the direction of $\boldsymbol{h}$, i.e., $D_\eta = \chi h_\eta$, and $P_\alpha^{(2)} = \chi(h_\beta\nabla_\beta^r h_\alpha - h_\alpha\nabla_\beta^r h_\beta)$, which again gives Eq. (14). For more complicated cases, one will have to carry out a careful symmetry analysis of the crystal structure to determine the general form of $\boldsymbol{P}^{(2)}$.

Finally, we discuss how to calculate $\boldsymbol{P}^{(2)}$ from a computational point of view. For simplicity, we again consider a two-dimensional system and assume $\boldsymbol{h}(\boldsymbol{r})$ is periodic in the y direction. After taking the spatial average, the two-point formula (11) for $P_x^{(2)}$ involves three nontrivial variables, namely, k_x, k_y, and y. We then make a tetrahedral mesh in the three-dimensional parameter space spanned by these variables. At each mesh point $\boldsymbol{R}_i = (k_{x_i}, k_{y_i}, y_i)$, one can solve the Kohn-Sham equation self-consistently with the constraint that the ground state energy is minimized for a constant $\boldsymbol{h}(y_i)$. In the case of multiferroics, this is equivalent to solving the Kohn-Sham equation with a fixed and uniform spin magnetization [29]. According to Ref. [30], the discretized version of the Chern-Simons action within each tetrahedron is given by

$$\frac{1}{6}(\phi_{12}\phi_{34} - \phi_{13}\phi_{24} + \phi_{14}\phi_{23}), \tag{15}$$

where ϕ_{ij} is the discretized Berry phase between two vertices labeled by i and j [31]:

$$\phi_{ij} = \operatorname{Im}\log\langle u_i \mid u_j\rangle. \tag{16}$$

The total polarization is then given by the sum over all tetrahedrons. The above process sketches the basic recipe for the calculation of $\boldsymbol{P}^{(2)}$, although for real crystals a more careful treatment is needed.

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Note added.—The formalism detailed in this paper was recently successfully applied by another group to magnetic field-induced polarization in topological insulators [32].

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