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Theoretical study of ferroelectric nanoparticles using phase reconstructed electron microscopy

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Ferroelectric nanostructures are important for a variety of applications in electronic and electro-optical devices, including nonvolatile memories and thin-film capacitors. These applications involve stability and switching of polarization using external stimuli, such as electric fields. We present a theoretical model describing how the shape of a nanoparticle affects its polarization in the absence of screening charges, and quantify the electron-optical phase shift for detecting ferroelectric signals with phase-sensitive techniques in a transmission electron microscope. We provide an example phase shift computation for a uniformly polarized prolate ellipsoid with varying aspect ratio in the absence of screening charges.

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I. INTRODUCTION

Ferroelectric nanostructures are fundamental components of modern electronic devices, such as ferroelectric random access memory [1] and ferroelectric field effect transistors [2]. These applications are based on the manipulation and control, through the use of electric fields, of the direction of the polarization in the ferroelectric material. The process of polarization switching involves the formation and growth of domains within the ferroelectric. To fully understand this switching process, it is necessary to study domain behavior, both static and dynamic, for example by obtaining quantitative maps of nanoscale electric fields associated with the polarization. A lot of progress has been made toward understanding nanoscale effects on ferromagnetic properties, however the formalism for describing finite size and shape effects on ferroelectric properties is less developed. There are various reports in the literature describing complete suppression of ferroelectric behavior at nanoscale sizes as well as unusual phase transitions in nanodisks [3–5]. An in-depth understanding can be obtained by observing simultaneously the polarization, shape, and size of the nanostructures. Such studies will not only provide insights into the fundamental ferroelectric behavior but may also facilitate the design of new devices and technology.

The transmission electron microscope (TEM) has been used frequently to study ferroelectric materials and ferroelectric domains. Pfister *et al.* [6] and Tanaka *et al.* [7] performed some of the earliest TEM studies on ferroelectrics; they were able to show the existence of ferroelectric domain boundaries by looking at the microstructure of the ferroelectric material. Since then, there have been numerous studies of such domain boundaries. In the majority of cases, the analysis involves interpretation of dynamical diffraction image contrast due to the lattice mismatch across a domain boundary or electron diffraction patterns from overlapping neighboring domains. Recent work made use of convergent beam electron diffraction to determine the polarity of ferroelectric domains [8]. However, these studies are qualitative and do not provide

direct quantitative information about, or images of, the polarization state of the ferroelectric. Recently, high resolution aberration-corrected TEMs have been employed to infer the ferroelectric polarization in PZT thin films by measuring atomic displacements and deviations from centrosymmetry at the unit cell level [9], or strain measurement using geometric phase analysis (GPA) [10] rather than by capturing the electric field that arises from polarization charges.

In a TEM experiment, the high energy electrons experience a phase shift due to the presence of electric and/or magnetic fields in and around the sample; thus, a polarized ferroelectric material with internal interfaces (e.g., between differently-oriented domains) generating boundary polarization charges is expected to induce a phase shift in the electron wave. Zhang *et al.* [11] used electron holography to recover the phase shift from ferroelectric materials and relate it to the polarization. However, their theoretical description and interpretation was not entirely correct, as Spence *et al.* [12] showed that the electrons are only sensitive to the polarization component perpendicular to the direction of propagation of the electrons. Lichte *et al.* [13,14] subsequently presented a basic framework for the investigation of ferroelectric domains using electron holography. Schofield *et al.* [15] performed holography experiments on BaTiO₃ to map out the electric fields. Szwarcman *et al.* [16] have also performed measurements of the phase shift from BaTiO₃ nanoparticles to correlate it with the local ferroelectric polarization. Recent work has showed that using the differential phase contrast technique, it is possible to map mesoscopic as well as atomic level electric fields in BaTiO₃ [17]. However, a clear theoretical relationship between the polarization state and the resulting electron phase shift is still lacking, making it difficult to interpret the phase contrast images and also hindering the design of suitable experiments to successfully map the field distribution.

In this paper, we present a theoretical model relating the phase shift of the electrons passing through a ferroelectric nanoparticle to its polarization charge density. We present a method to determine the spontaneous polarization of such ferroelectric nanoparticles. Then we analyze the effect of the shape and size on the expected value of the phase shift, and we present simulation results comparing the electron phase shift directly with the polarization charge of the nanoparticle.

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II. THEORETICAL MODEL

The phase shift of an electron wave interacting with a nonmagnetic sample in a TEM is proportional to the electrostatic potential within and around it, projected along the beam direction, according to the standard expression

$$\varphi(x, y) = C_E \int_{-\infty}^{+\infty} V(x, y, z) dz, \quad (1)$$

where the electrons travel along the z axis, and C_E is a constant equal to $6.53 \times 10^6 \text{ V}^{-1} \text{ m}^{-1}$ at an accelerating voltage of 300 kV. In general, there are several contributions to this potential: (i) the mean-inner potential V_0 which for nonhomogeneous samples may be a function of position and includes effects such as density or compositional changes, (ii) the potential of the electric field generated by polarization charges, (iii) net external charges originating from a variety of sources (primarily: emission of secondary electrons) together with their induced charges for neutrality, often present at the surface of an object, or at the surface of a conducting support, or, lacking everything else, somewhere on the closest grounded metallic element (TEM grid, or sample holder, or microscope column), (iv) ohmic potentials if currents are flowing, (v) band-bending effects at interfaces, with the associated charge transfer, and so forth. Our purpose is to isolate the ferroelectric phase shift of the nanoparticle and compare its magnitude with the only other potential which is always present: the mean-inner potential. Thus, we assume that no other electric field sources are present, other than the atoms and the polarization charges, so that the total phase shift can be written as

$$\varphi(x, y) = C_E V_0 t_p(x, y) + C_E \int_{-\infty}^{+\infty} V_{FE}(x, y, z) dz, \quad (2)$$

where $t_p(x, y)$ is the projected thickness at position (x, y) , and V_{FE} is the potential of the electric field due to the ferroelectric polarization $\mathbf{P}(\mathbf{r})$ of the nanoparticle. Nominally, the spontaneous polarization of the ferroelectric will be screened by the mobile charges within the material and/or adsorbed on the surface, to compensate for the strong depolarizing field generated by the polarization charges. In order for the nanoparticle to retain some degree of polarization, it is necessary for some relief mechanism to lower the electrostatic energy by partially compensating the depolarizing field; such mechanisms include embedding the nanoparticle in a dielectric matrix, compensating the charge through external electrodes, and elongating the particle along the polarization axis. In this paper, we will specifically consider the case of compensation of the depolarizing field due to the shape of the nanoparticle. We will compute the resulting potential from the polarization and use this potential to compute the electron phase shift. We will then analyze the variation of the observable phase shift as a function of various shape parameters.

The potential due to the ferroelectric polarization $\mathbf{P}(\mathbf{r})$ can be written as

$$V_{FE}(\mathbf{r}) = \frac{1}{4\pi\epsilon_0} \iiint d\mathbf{r}' \mathbf{P}(\mathbf{r}') \cdot \frac{\mathbf{r} - \mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|^3}, \quad (3)$$

where $\mathbf{r}$ and $\mathbf{r}'$ are position vectors. Using Fourier transforms, the potential distribution can be expressed as

$$V_{FE}(\mathbf{k}) = -\frac{i}{k^2\epsilon_0} \mathbf{P}(\mathbf{k}) \cdot \mathbf{k}, \quad (4)$$

where $\mathbf{k}$ is a Fourier space vector. For a uniformly polarized nanoparticle, the polarization can be written using the shape (or characteristic) function as $\mathbf{P}(\mathbf{r}) = P D(\mathbf{r}) \hat{\mathbf{p}}$, where P is the magnitude of the polarization, $\hat{\mathbf{p}} \equiv [p_x, p_y, p_z]$ represents a unit vector in the direction of the polarization, and $D(\mathbf{r})$ is the shape function, which equals 1 inside the nanoparticle and 0 outside. This equation can be written in Fourier space as $\mathbf{P}(\mathbf{k}) = P D(\mathbf{k}) \hat{\mathbf{p}}$. Substituting this in Eq. (4), we obtain

$$V_{FE}(\mathbf{k}) = -\frac{i P D(\mathbf{k})}{\epsilon_0 k^2} \hat{\mathbf{p}} \cdot \mathbf{k}. \quad (5)$$

The resulting electric field ($\mathbf{E} = -\nabla V_{FE}$) can be written in Fourier space as

$$\begin{aligned} \mathbf{E}_{FE}(\mathbf{k}) &= i \mathbf{k} V_{FE}(\mathbf{k}); \\ &= -\frac{P}{\epsilon_0} D(\mathbf{k}) \frac{\hat{\mathbf{p}} \cdot \mathbf{k}}{k^2} \mathbf{k}. \end{aligned} \quad (6)$$

It should be noted here that P differs from the spontaneous polarization of the bulk ferroelectric. This polarization value will depend on the depolarizing field and the resulting self energy of the nanoparticle. The self-energy density of the polarized nanoparticle can be written as

$$\begin{aligned} \mathcal{E}_s &= -\frac{1}{2V} \iiint \mathbf{P} \cdot \mathbf{E}_{FE} d^3\mathbf{r}, \\ &= \frac{P^2}{16\pi^3\epsilon_0 V} \iiint d^3\mathbf{k} \frac{|D(\mathbf{k})|^2}{k^2} (\hat{\mathbf{p}} \cdot \mathbf{k})^2, \end{aligned} \quad (7)$$

where V is the particle volume.

In the Ginzburg-Landau framework [18], the double-well potential with free energy density

$$\mathcal{F}_{FE} = -\frac{A}{2} P^2 + \frac{B}{4} P^4 + \frac{C}{6} P^6 \quad (8)$$

represents a simple model that captures the ferroelectric phase transition in a bulk uniaxial material. The values of the coefficients A, B, C for bulk BTO (BaTiO_3 , which we take here as a reference material) are: $A = 2.634 \times 10^8 \text{ J m/C}^2$, $B = 21.29 \times 10^8 \text{ J m}^5/\text{C}^4$, and $C = 273.1 \times 10^8 \text{ J m}^9/\text{C}^6$. The value of the bulk spontaneous polarization P_s is determined by finding the location of the energy minimum

$$P_s = \sqrt{\frac{B}{2C} \left(\sqrt{1 + \frac{4AC}{B^2}} - 1 \right)}, \quad (9)$$

which results in a nonvanishing value only if $A > 0$. For bulk BTO, we have $P_s = 0.258 \text{ C/m}^2$.

Next, we include the self-depolarizing energy density of the nanoparticle given by Eq. (7) which modifies the free energy density as

$$\mathcal{F}_{FE} = -\frac{(A - A_d)}{2} P^2 + \frac{B}{4} P^4 + \frac{C}{6} P^6, \quad (10)$$

with

$$A_d = \frac{1}{8\pi^3\epsilon_0 V} \iiint d^3\mathbf{k} \frac{|D(\mathbf{k})|^2}{k^2} (\hat{\mathbf{p}} \cdot \mathbf{k})^2. \quad (11)$$

It should be noted that A_d can be related to the depolarizing factor of the nanoparticle. We minimize this equation with respect to P to determine the conditions for shape effects to be sufficient to compensate for the depolarizing field and maintain a spontaneous polarization P_{np} in the nanoparticle. This value of P_{np} is given by

$$P_{np} = \sqrt{\frac{B}{2C} \left(\sqrt{1 + \frac{4(A - A_d)C}{B^2}} - 1 \right)}. \quad (12)$$

Once P_{np} is determined, we can compute the potential due to the polarization and the expected electron phase shift using Eqs. (3) and (2), respectively. Using the Fourier space representation, we can write the phase shift due to the ferroelectric charge density as

$$\varphi_{FE}(k_x, k_y) = -\frac{iC_E P_{np}}{\epsilon_0} \frac{D(k_x, k_y, 0)}{k_x^2 + k_y^2} \hat{\mathbf{p}} \cdot \mathbf{k}. \quad (13)$$

An inverse Fourier transform then produces the phase shift, $\varphi_{FE}(x, y)$, in real space.

III. POLARIZATION AND PHASE SHIFT OF ELLIPSOIDAL NANOPARTICLES

An elongated particle shape helps to reduce the effect of the depolarizing field. To quantify this elongation effect, we consider a uniformly polarized triaxial ellipsoid, described by three semi-axes a, b, c with $c > b > a$ and the parametric equations

$$\begin{aligned} x &= \frac{a}{c} r \cos \phi \sin \theta, \\ y &= \frac{b}{c} r \sin \phi \sin \theta, \\ z &= r \cos \theta. \end{aligned} \quad (14)$$

The shape function for such an ellipsoid can be determined in Fourier space as [19]

$$D(\mathbf{k}) = 4\pi abc \frac{j_1(q)}{q}, \quad (15)$$

where $j_1(q)$ is a spherical Bessel function and $q^2 = a^2 k_x^2 + b^2 k_y^2 + c^2 k_z^2$. If the polarization axis of the nanoparticle is along the longest semi-axis, i.e., along the z axis, then we have $\hat{\mathbf{p}} = \hat{\mathbf{z}}$. The spontaneous polarization of the particle can be computed using Eq. (12). Substituting the equation for the shape function, we determine A_d as

$$A_d = \frac{3abc}{2\pi^2\epsilon_0} \iiint d^3\mathbf{k} \frac{j_1^2(q)}{q^2} \frac{k_z^2}{k^2}. \quad (16)$$

The depolarizing factor of an ellipsoid is given by [19,20]

$$N_i = \frac{3abc}{2\pi^2} \iiint d^3\mathbf{k} \frac{j_1^2(q)}{q^2} \hat{k}_i^2. \quad (17)$$

Hence, the depolarizing energy coefficient A_d can be expressed in terms of the depolarizing factor N_z as $A_d = N_z(\tau_a, \tau_b)/\epsilon_0$, and N_z is given by

$$N_z(\tau_a, \tau_b) = \frac{1}{\tau_a \tau_b} \frac{F(k, m) - E(k, m)}{m \sin^3 k}, \quad (18)$$

where $k = \arcsin \sqrt{1 - \tau_a^{-2}}$, $m = \frac{1 - \tau_b^{-2}}{1 - \tau_a^{-2}}$, $\tau_a = c/a$, $\tau_b = c/b$, and $F(k, m)$ and $E(k, m)$ are incomplete elliptic integrals [21]. Next, we determine the conditions with respect to the ellipsoid aspect ratios under which the nanoparticle can sustain a spontaneous polarization and determine the value of the polarization. Figure 1(a) shows a 2D plot of the region where the spontaneous polarization of the nanoparticle, P_{el} , has a real solution as a function of τ_a and τ_b . The contours in the plot indicate the value of P_{el} for bulk BTO. It can be seen that there is no real solution for P_{el} for values of $\tau_a \leq 38$ and $\tau_b \leq 38$. Similarly, the upper bound for the region is given by $\tau_a = \tau_b$, which is the case of a spheroid with $a = b$. Figure 1(b) shows line plots of P_{el} for various values of τ_a and τ_b . The solid lines show P_{el} as a function of τ_b for fixed τ_a , and the dashed lines show the same for τ_a for a fixed value of τ_b . The red line shows P_{el} for the special case of a spheroid ($\tau_a = \tau_b$). From these line plots, we observe that, as the aspect

FIG. 1. (Color online) (a) 2D plot showing the region where a real solution for P_s exists (for bulk BTO) as a function of τ_a and τ_b , the contours indicate the value of P_s , and (b) shows line plots of P_s as a function of either τ_a or τ_b .

FIG. 2. (Color online) (a) The projection of a spheroid with $\tau_a = 40$ and $c = 200$ nm, (b) the total phase shift due to the ellipsoid, and (c) plot of the ferroelectric phase shift along the long axis of the ellipsoid.

ratio increases, P_{el} approaches 0.25 C/m^2 asymptotically. Now that we have determined the aspect ratio dependence of the spontaneous polarization in a triaxial ellipsoid, we can compute the expected electron phase shift due to the ferroelectric polarization charge density using Eq. (13).

To simplify the computation of the phase shift for a triaxial ellipsoid, we can assume without loss of generality that the ellipsoid is oriented such that the longest semi-axis is along the y direction. Thus we have the polarization of the ellipsoid given by $\hat{\mathbf{p}} = \hat{\mathbf{y}}$. Then by redefining the parametric equations for the ellipsoid and substituting for the shape function, the phase shift can be written as

$$\varphi_{FE}(k_x, k_y) = -\frac{4\pi iabcC_E P_{el}(a, b, c)}{\epsilon_0} \frac{j_1(q_{xy})}{q_{xy}} \frac{k_y}{k^2}, \quad (19)$$

where $q_{xy}^2 = b^2 k_x^2 + c^2 k_y^2$ and $k^2 = k_x^2 + k_y^2$.

Figure 2(a) shows a projection of a spheroid with long semi-axis $c = 200$ nm, and $a = b = 5$ nm, resulting in an aspect ratio of $\tau = 40$. Using the previous results, the spontaneous polarization of such a spheroid can be determined to be $P_{el} = 0.10 \text{ C/m}^2$. Figure 2(b) shows the total phase shift due to the polarized ellipsoid. The phase shift due to the mean inner potential (MIP) was determined by assuming $V_0 = 20$ V for BaTiO_3 . For such an ellipsoid, the effect of the polarization charge density on the electron phase shift is clearly visible. Figure 2(c) shows a plot of the ferroelectric component of the phase shift along the long axis through the center of the ellipsoid. It can be seen that the maximum magnitude of the phase shift due to the polarization ($|\varphi_{\max}|$) was calculated to be 2.4 radians. Due to the high aspect ratio of the spheroid, the phase shift is equivalent to that of an elongated dipole with the corrected value of polarization.

Furthermore, the gradient of the ferroelectric phase shift can be computed numerically, which then represents the thickness integrated electric field map. This is shown as a vector field map in Fig. 3(a). Here it should be noted that the gradient computed from the phase shift shows the direction of the electric field and not the polarization itself. Figure 3(b) shows the phase shift as a function of the aspect ratio for the special case of a spheroid with $a = b = 5$ nm. The plot shows the

FIG. 3. (Color online) (a) Gradient of the ferroelectric phase shift showing the electric field map in and around the ellipsoid, and (b) plot showing the variation of the phase shift due to ferroelectric polarization as a function of the aspect ratio τ (black), compared with the phase shift due to the mean inner potential. The line plot in red shows the value of the gradient of the ferroelectric phase shift at the center of the ellipsoid as a function of the aspect ratio.

maximum magnitude of the phase shift ($|\varphi|$) arising from the ferroelectric polarization charge density and that due to the mean inner potential of the nanoparticle. The ferroelectric polarization of the nanoparticle gives rise to a phase shift that is of the same order of magnitude as that due to the mean inner potential. The line plot in red shows the variation of the y component of the gradient at the center of the ellipsoid as a function of the aspect ratio. It can be seen that the gradient reaches a maximum value for $\tau = 51$ corresponding to $P_{el} = 0.185 \text{ C/m}^2$ and then decreases again.

IV. DISCUSSION

As shown in the previous sections, by accounting for the effect of shape on the compensation of the depolarizing field of ferroelectric nanoparticles within a Ginzburg-Landau framework, we can estimate the resulting spontaneous polarization of the nanoparticle. As mentioned previously, typically the depolarizing field due to ferroelectric polarization is very high, and an individual nanoparticle cannot sustain spontaneous polarization unless its effective strength is decreased. The formalism presented here shows how the shape of the particle can help reduce the strength of the depolarizing field. For example, for the case of the ellipsoid discussed in the previous section, if we assume P_{el} equal to the bulk value of 0.25 C/m^2 , then the maximum potential and the depolarizing electric field can be computed to be 11.6 V and 3.62 V/nm, respectively. If we consider an equal volume sphere that is uniformly polarized such that the total polarization charge density is the same, then the maximum potential and depolarizing field can be computed to be 156.9 V and 18.3 V/nm, respectively. A comparison of these numbers shows direct evidence of reduction in the depolarizing field due to elongation that can stabilize the polarization in uniformly polarized nanoparticles. These values are further reduced to 4.6 V and 1.44 V/nm, if we use the reduced $P_{el} = 0.10 \text{ C/m}^2$ derived based on the formalism presented here. With a triaxial ellipsoid as a model shape, we have shown a phase diagram indicating for which aspect ratio range the nanoparticle can sustain some degree of spontaneous polarization. This analysis can be thought of as the ferroelectric equivalent to the Stoner-Wohlfarth model for

ferromagnetism [22]. From our results, it is clear that, unless an ellipsoidal nanoparticle is highly elongated, it cannot sustain a spontaneous polarization.

It should be noted that the origin of the phase shift is not directly due to the polarization of the nanoparticle, but is in fact due to the potential generated in and around the nanoparticle by the ferroelectric polarization charges. Hence, computing the gradient of the phase shift gives the direction of the local electric field and not the direction of the ferroelectric polarization itself. Also, as shown in the previous section, the gradient of the phase shift is maximized for a certain aspect ratio. This can be understood from the fact that for lower values of τ , the value of P_{el} is small, resulting in a smaller phase gradient. For larger values of τ , the value of P_{el} increases, eventually getting closer to the bulk value, but the poles are further apart from each other, again resulting in a smaller phase gradient. Thus, by identifying this behavior, a sample consisting of a suitable aspect ratio of nanoparticles can be used to maximize the signal obtained from them.

Using the same formalism, we can compute the spontaneous polarization of a uniformly polarized sphere, for which we obtain $A_d = 3.38 \times 10^{10}$ Jm/C²; this value is significantly larger than A for a BaTiO₃ nanoparticle, and, as a result, P_{np} does not have a real solution for BTO. Thus, a uniformly polarized BTO sphere cannot sustain a uniform polarization, unless the depolarizing field is compensated by other mechanisms, such as screening charges. The same holds for other regular polyhedral shapes such as the cube, the octahedron, cuboctahedra, and so on. For such cases, it is necessary to account for the screening potential and then compute the net resulting potential, which can then be used to compute the electron phase shift. For the case of a uniformly polarized

sphere, this can be achieved using a Thomas-Fermi framework to describe the screening potential [23].

V. CONCLUSION

In conclusion, we have shown in this paper that in order to understand the origin of the electron phase shift due to ferroelectric nanoparticles, it is necessary to account for the effect of the depolarizing field. We have derived a formalism to determine the spontaneous polarization of nanoparticles using a combination of the Ginzburg-Landau framework and the shape function formalism to compute the depolarizing factors. We have analyzed the case of a triaxial ellipsoid, where we find that the polarization has a real solution only for high aspect ratios, and the resultant polarization value is smaller than the bulk value. Using this value, we have estimated the electron phase shift arising from the polarization charge density and shown that it is in a measurable range and of the same order of magnitude as the phase shift due to the mean inner potential. Additional simulations and modeling are necessary to determine the net potential and the polarization of other ferroelectric nanoparticle shapes, such as cubes, by accounting for the surface screening charges. Similarly, it is necessary to account for such screening effects when determining the phase shift from ferroelectric domain walls. Further work in this direction is in progress.

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- [1] E. Tokumitsu, G. Fujii, and H. Ishiwaru, *Appl. Phys. Lett.* **75**, 575 (1999).
 - [2] R. Naber, C. Tanase, P. Blom, G. Gelinck, A. Marsman, F. Touwslager, S. Setayesh, and D. De Leeuw, *Nat. Mater.* **4**, 243 (2005).
 - [3] I. I. Naumov, L. Bellaiche, and H. Fu, *Nature (London)* **432**, 737 (2004).
 - [4] W. L. Zhong, Y. G. Wang, P. L. Zhang, and B. D. Qu, *Phys. Rev. B* **50**, 698 (1994).
 - [5] A. N. Morozovska, E. A. Eliseev, and M. D. Glinchuk, *Physica B: Condensed Matter* **387**, 358 (2007).
 - [6] H. Pfisterer, E. Fuchs, and W. Liesk, *Naturwissenschaften* **49**, 178 (1962).
 - [7] M. Tanaka, N. Kitamura, and G. Honjo, *J. Phys. Soc. Jpn.* **17**, 1197 (1962).
 - [8] J. M. LeBeau, A. J. D'Alfonso, N. J. Wright, L. J. Allen, and S. Stemmer, *Appl. Phys. Lett.* **98**, 052904 (2011).
 - [9] C.-L. Jia, S.-B. Mi, K. Urban, I. Vrejoiu, M. Alexe, and D. Hesse, *Nat. Mater.* **7**, 57 (2008).
 - [10] P. Gao, J. Britson, J. R. Jokisaari, C. T. Nelson, S.-H. Baek, Y. Wang, C.-B. Eom, L.-Q. Chen, and X. Pan, *Nat. Commun.* **4**, 2791 (2013).
 - [11] X. Zhang, T. Hashimoto, and D. C. Joy, *Appl. Phys. Lett.* **60**, 784 (1992).
 - [12] J. C. H. Spence, J. M. Cowley, and J. M. Zuo, *Appl. Phys. Lett.* **62**, 2446 (1993).
 - [13] H. Lichte, M. Reibold, K. Brand, and M. Lehmann, *Ultramicroscopy* **93**, 199 (2002).
 - [14] A. Rother, M. Reibold, H. Lichte, T. Leisegang, A. A. Levin, P. Paufler, D. C. Meyer, S. Gemming, I. Chaplygin, G. Seifert, A. Ormeci, and H. Rosner, *Phys. Rev. B* **74**, 134116 (2006).
 - [15] M. A. Schofield, L. Wu, and Y. Zhu, *Microsc. Microanal.* **14**, 238 (2008).
 - [16] D. Szwarcman, A. Lubk, M. Linck, K. Vogel, Y. Lereah, H. Lichte, and G. Markovich, *Phys. Rev. B* **85**, 134112 (2012).
 - [17] N. Shibata, S. D. Findlay, Y. Kohno, H. Sawada, Y. Kondo, and Y. Ikuhara, *Nat. Phys.* **8**, 611 (2012).
 - [18] C. Kittel, *Introduction to solid state physics*, 7th ed. (John Wiley & Sons, Singapore, 1995).
 - [19] M. Beleggia, M. De Graef, and Y. Millev, *Philos. Mag.* **86**, 2451 (2006).
 - [20] J. Osborn, *Phys. Rev.* **67**, 351 (1945).
 - [21] M. Abramowitz and I. Stegun, *Handbook of Mathematical Functions* (Dover, New York, 1972).
 - [22] E. Stoner and E. Wolfarth, *Phil. Trans. Roy. Soc. London A* **240**, 599 (1948).
 - [23] J.-N. Chazalviel, *Coulomb Screening by Mobile Charges: Applications to Materials Science, Chemistry, and Biology* (Birkhäuser, Boston, 1999).