

Synchrotron x-ray diffraction study of inversion symmetry breaking in bulk black phosphorus

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X-ray diffraction study of black phosphorus (BP) shows forbidden reflections, which imply a broken inversion symmetry with atomic distortion in the orthorhombic lattice. The unexpected distortion occurs throughout the entire bulk crystal, rather than being confined to just the top-surface layer. Thus our observation suggests that this distortion is an intrinsic bulk property, in contrast to earlier studies which attributed the distortion to surface effects or defects. Our diffusion quantum Monte Carlo calculation predicts the same asymmetric structure. Density functional theory calculation incorporating Hubbard correction attributes the symmetry breaking to intrinsic electronic interaction in *sp* hybridized orbitals. We propose that the asymmetric lattice distortion in BP could enable stable two-dimensional ferroelectricity.

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Structural symmetry has been a central concept of space groups in solid and molecular systems [1]. It provides guidelines for determining atomic structure and identifying electronic states. Black phosphorus (BP) has strong anisotropic properties that are exploited to tailor optoelectronic, spintronic, and thermoelectric devices to meet practical requirements [2–5]. BP has peculiar electronic properties such as thickness-dependent band gap [6,7], pressure or strain-induced electronic transition [8–10], and Dirac- or Weyl-like semimetallic behavior [11,12]. Four phosphorus atoms form a covalent monolayer which is also stacked periodically by van der Waals (vdW) interaction. The structure is commonly accepted to be a symmetric puckered layer [13,14].

The crystal structure of BP is distinguished topologically by glide mirror planes in addition to inversion symmetry [11,12,15]. Apparent crystal symmetry of BP is generally preserved except when strong strain field or high pressure is applied [9,16]. We will here propose the asymmetric distortion for a true stable structure of BP and for the physical implication. Some other elements (As, Sb, Bi) in group V also favor buckled structures, which might yield two-dimensional (2D) ferroelectricity [17–20].

Despite the tendency for elements in this group to form buckled structures, the standard density functional theory (DFT) calculations have predicted symmetric BP without

any atomic distortion [21–23]. Although a few earlier reports showed an interest in structural distortion after it was first observed [24], it has been treated just as a surface-limited phenomenon that is a result of structural defects [24–28]. However, our x-ray diffraction measurement suggests it should be a characteristic bulk structure, rather than a surface phenomenon.

In this study, the atomic structure of BP was explored in detail by using synchrotron x-ray diffraction, which is not hampered by the multiple scattering effect [29,30] (Fig. S1, Supplemental Material, Sec. A [31]). Thus we report clear experimental evidence of lattice inversion symmetry breaking in bulk BP. To focus our effort on determination of lattice symmetry, we have analyzed forbidden reflections and investigated the lattice structural feature by using diffusion Monte Carlo (DMC) and DFT calculations.

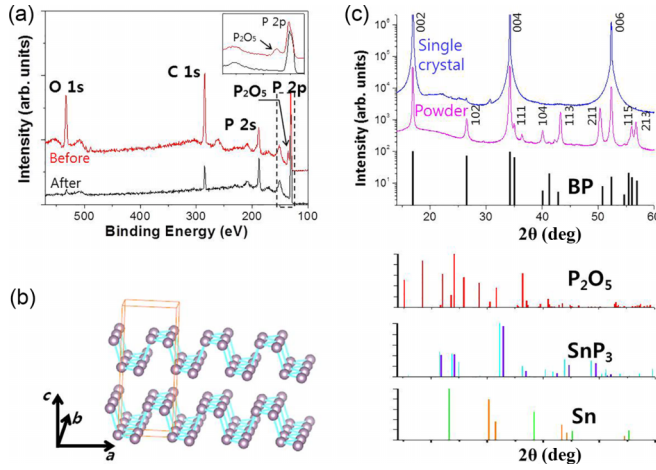
Prior to the measurement, surface layers of the sample were peeled off to make it clean. X-ray photoemission spectroscopy spectra confirm the cleanliness [Fig. 1(a)] [32]. X-ray diffraction measurements were performed at room temperature on several samples, provided by two different manufacturers: HQ Graphene and 2D Semiconductors [33]. The orthorhombic crystal structure of BP has the lattice parameters $a = 4.38(4) \text{ \AA}$, $b = 3.31(7) \text{ \AA}$, and $c = 10.48 \text{ \AA}$ [34]. The a , b , and c crystal axes are defined as the armchair (AC), zigzag (ZZ), and stacking direction, respectively, and the corresponding reciprocal lattices are defined as (hkl) . A single layer of BP consists of two atomic planes, which form a puckered honeycomb lattice [Fig. 1(b)].

We first performed a wide scan along the specular direction that produces (00ℓ) ($\ell = 2, 4, 6, \dots$) and diffraction profiles at several Bragg points [Fig. 1(c)]. The (004) Bragg peak showed a full width at half maximum (FWHM) $\sim 0.002 \text{ \AA}^{-1}$, which indicates that BP has high crystalline quality. No structural changes due to stacking sequence faults were detected

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in out-of-plane Bragg reflections. Moreover, absence of the in-plane (110) Bragg peak ensures that BP has a single type of sequence of layers, i.e., AB stacking. AA-stacked BP would have produced considerable intensities at the (110) Bragg position. According to the DFT calculations, depending on the stacking order [35], the lattice constant c increases by $\sim 0.4 \text{ \AA}$ (4%) due to the elongated vdW interlayer distance, which would be sufficiently observable if it were to actually expand.

We performed a series of radial scans passing through Bragg peaks of bulk BP (Fig. 2). The figure confirms a few structural features of BP. First, absence of the (210) and (110) reflections indicates that a periodic unit consists of two identical asymmetric layers in AB-stacking order. Also, absence of the (010) reflection implies that no shift in the ZZ direction occurred; that is, symmetry was preserved, as seen in scanning tunneling microscope (STM) images [24,25]. However, our measurements show two forbidden reflections of (100) and (011) which should disappear in symmetric bulk structure with the high symmetry. These forbidden peaks had been alluded to by transmission electron microscope (TEM) studies of few-layer BP [26,27]. Notably here intensities of the surface peak (100) and the completely forbidden bulk Bragg peak (011) are detected to be three orders of magnitude smaller than those of bulk Bragg reflections. Their existence is clear evidence that the lattice symmetry is broken in the sample. In particular, the presence of the completely forbidden (011) reflection suggests that the lattice should be buckled to create the asymmetric heights as in the earlier observations [28].

We have simulated such a series of diffraction peaks (Fig. 3). The simulation was simplified by considering a finite volume of $30 \times 30 \times 30 = 27\,000$ unit cells (Fig. S2,

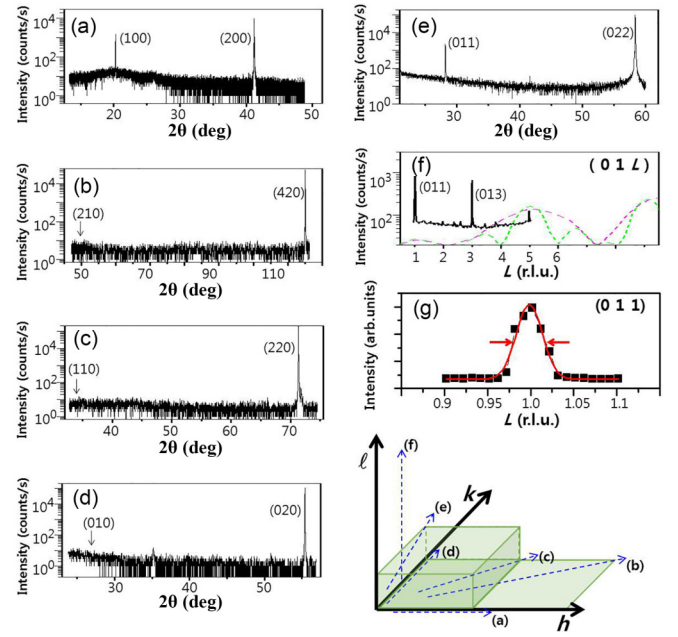


FIG. 2. Several x-ray diffraction scans of BP. (a–d) In-plane scans in the radial direction. (e) A radial scan in the (022) direction. (210), (110), and (010) in (b–d) are negligible differently from (100) in (a) and from (011) in (e). (f) Rod (01 ℓ) measured along the surface normal direction (solid line). Dotted lines: simulations of surface reconstruction with a single top plane only (magenta) or a monolayer (green). (g) Detailed line shape of the (011) forbidden reflection.

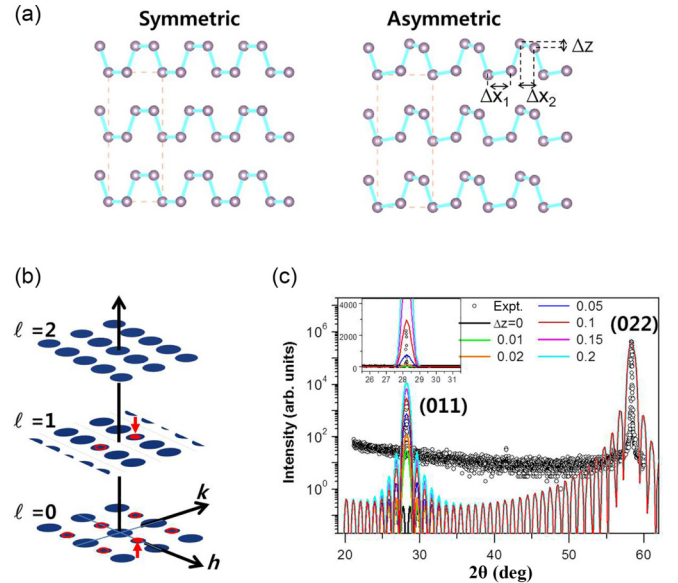


FIG. 3. Diffraction simulations. (a) Schematics of symmetric BP and asymmetric buckled structure. (b) Distribution of simulated Bragg reflections including in-plane and reflections with finite ℓ in the reciprocal space. The intensities are logarithmically proportional to the size of the circles. The forbidden (011) and (100) are directed by arrows. The buckling height ($\Delta z = 0.1 \text{ \AA}$) and the lateral distortion ($\Delta x_1 - \Delta x_2 = 0.02 \text{ \AA}$) are assumed for the asymmetric structure. (c) The radial scan in the (022) direction is simulated with different values of Δz on the buckled model. The simulated (011) peak intensities (solid curves) are compared with the experimental intensities of Fig. 2(e) (circles).

Supplemental Material, Sec. B [31]). The scattering amplitude was calculated [36] as $F(\mathbf{q}) = \sum_j \theta_j f_j \exp[-B_j q^2 / (16\pi^2)] \exp[-i(\mathbf{q} \cdot \mathbf{r}_j)]$, where the sum is over all the atoms with atomic scattering factor f_j , Debye parameter B_j , and atomic occupancy θ_j . Here, for simplicity, the scattering amplitude can be reduced to the structure factor $F(\mathbf{q}) \propto S(\mathbf{q}) = \sum_j \exp[-i(\mathbf{q} \cdot \mathbf{r}_j)]$. In the calculation, the attenuation factor is ignorable if the calculation considers a large penetration depth $\mu^{-1} \approx 100 \mu\text{m}$.

To reproduce the experimental scattering intensity, atomic positions were determined. Diffraction profiles of the (01 ℓ) rod passing through the (011) peak were first calculated for surface reconstruction with a single top plane only, or a monolayer. This rod generally reflects the detailed buckling geometry on surface or interface most sensitively. The simulated rods for the surface reconstruction only do not match the bulk Bragg-like experimental reflections [Fig. 2(g)]. As determined by the FWHM of $\sim 0.02 \text{ \AA}^{-1}$ of the (011) peak [Fig. 2(g)], the buckling exists even quite deep in the bulk with the correlation length of $\sim 300 \text{ \AA}$.

Then the radial scan in the (022) direction was simulated with different values of distorted buckling height Δz on the asymmetric buckled model (Fig. 3); then the simulated (011) peak intensities were compared with the experimental intensity [Fig. 3(c)]. Here the atomic distortion deviates from that of the bulk by less than a few percent of a bond length. The Δz between two atoms is estimated as $\sim 0.1 \text{ \AA}$.

The presence of the (100) peak breaks the translation symmetry of a half shift of a lattice unit ($a/2$). In-plane arrangements in a single layer should exhibit another asymmetry between bond lengths in upper and lower planes, i.e., $\Delta x_1 \neq \Delta x_2$, but they do not show it. The absence of this asymmetry might be unexplainable if the in-plane asymmetry spreads out over the whole bulk. Just like the surface reconstruction in the generally asymmetric solid-vacuum interface, we would restrict the (100) Bragg reflection to result from atomic rearrangements in the BP surface layer. Taking into account the reduced penetration depth of $<1 \mu\text{m}$ in grazing incidence geometry of $\alpha \leq 0.5^\circ$, the three orders of magnitude smaller intensity could be understood. We estimate that a surface bilayer occupies the same ratio of amount, i.e., 10^{-3} , times the volume of the penetration depth of $1 \mu\text{m}$. Measurements on an air-exposed sample confirmed that the (100) in-plane reflection is related to surface destruction. On a severely oxidized surface, the (100) in-plane reflection disappeared, but the (011) bulk reflection survived.

To investigate the cause of the possible lattice symmetry breaking in the BP sample, we first considered the antiphase domain boundary [36] as one of the causes. In fact, the antiphase domain boundary of BP is the same as the bilayer shift between the vdW gaps, i.e., a change in stacking order. For another case, we performed simulations on various defect-related lattice models (Supplemental Material, Sec. B [31]). The results indicate that point defects or adatoms on surfaces contribute little to the long-range order [36]. To create a measurable (011) peak, the vacancy concentration must be at least 30%. Such a large value seems unreasonable when compared to those assigned by considering STM measurements [24,25,33]. Because of this unreasonably

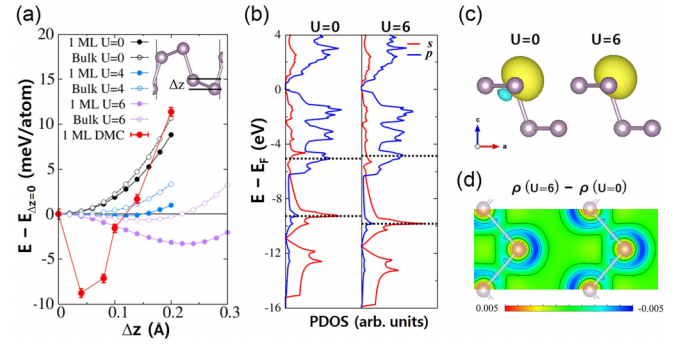


FIG. 4. Calculations. (a) Relative potential energy curves for 1 monolayer (ML) and bulk BP as a function of buckling height (Δz) by DFT+ U and DMC calculations. Asymmetric distortion arises at finite Δz . (b) PDOS of s - and p orbitals of the symmetric 1 ML ($\Delta z = 0$) at $U = 0$ and 6. The separation between s and p orbitals increases with increasing U . (c) Wannier orbitals associated with lone pairs of $U = 0$ and 6. Blue and yellow represent the isosurfaces of negative and positive levels, respectively, of $\pm 0.005 e \text{ \AA}^{-3}$. (d) Electron density difference map between $U = 0$ and 6, on the plane of the phosphorus zigzag chain.

large defect concentration, we reject the defect model as implausible.

At this stage, the slightly buckled structure above agrees well with our experimental result. We thus conclude with confidence that our asymmetrically buckled model gives a good description of the atomic structure of BP. Indeed, our DMC calculation [37–43] (Supplemental Material, Sec. C [31]) demonstrates that the asymmetrically buckled BP is a true stable structure. The potential energy curves are plotted [Fig. 4(a)] as a function of buckling height Δz for monolayer and bulk. Asymmetric distribution of p electrons caused by buckling is energetically favored against local distortion at small values of Δz .

We also performed DFT calculations using the VASP package [44,45] to understand why the distorted structure is favored. The PBE exchange-correlation functional was considered. The experimental lattice constants mentioned above [34] were used for our DFT calculations (Supplemental Material, Sec. D [31]). We included the on-site Hubbard correction U applied to p -orbital electrons using Dudarev's scheme [46] to properly describe electron-electron interactions which might be critical for our study.

For $U = 0$ eV, the minimum occurs at $\Delta z = 0.0 \text{ \AA}$. When $U = 6$ eV, the minima occurs at nonzero values of $\Delta z \approx 0.2 \text{ \AA}$ for monolayer and $\Delta z \approx 0.15 \text{ \AA}$ for the bulk, which is slightly larger than $\Delta z \approx 0.05 \text{ \AA}$ obtained by the DMC calculation. Our results with finite values of U manifest the asymmetric buckling structure of BP. We note that our predicted U value, obtained from the constrained local density approximation (LDA) calculation, is approximately 4 eV, which favors the buckled structure shown in Fig. 4(a). Nevertheless, we considered a range of U values from 0 to 6 eV to qualitatively assess the effects of electron-electron interactions.

The effect of U on the orbital electrons is analyzed by investigating the projected density of states (PDOS) for the symmetric monolayer [Fig. 4(b)]. As U increases, the

p -orbital band is overall shifted upward and the s -orbital band shifts downward. The separation between the s - and p -orbital bands increases compared to the case of $U = 0$. This tendency is a result of the on-site Hubbard correction U . As a result, as U increased, the overlap of the s and p orbitals is reduced, so the hybridization strength weakens.

Figure 4(c) illustrates how the Wannier orbitals associated with lone pairs become less anisotropic as U increases. Such a change of the orbital shape indicates that the lone pair begins to resemble the s orbital due to the decoupling of s - p orbitals. Figure 4(d) shows the electron density difference map of $U = 0$ and $U = 6$. As U increases, the electron density decreases in the region where lone pair electrons are concentrated, indicated in blue. In contrast, there is an increase in electron density near the atomic center, as shown in red. We conclude that a primary effect of U is to weaken s - p hybridization, leading to a more isotropic distribution of lone pair electrons. The resulting electron distribution around the atomic center is found to give a result consistent with DMC by DFT+ U , addressing delocalization error inherent in standard DFT calculations. Here we note that other elements in group V such as Bi have the s and p bands decoupled (Fig. S3, Supplemental Material, Sec. E [31]) and their buckled structures are well produced from normal DFT calculations without Hubbard correction U .

On the other hand, the hybrid functional (HSE06), which is known to describe band structure consistently with the experiment [47], does not allow us to infer the qualitative feature with preferred distortion in the potential energy curve (Fig. S4, Supplemental Material, Sec. F [31]). This failure suggests that, to achieve an appropriate description of electron

distribution, the Hubbard correction for p -orbital subspace rather than Kohn-Sham orbitals is essential. Lastly, it may be useful to notice that we did not observe any phase transition from our additional x-ray measurements in a wide range of temperature, i.e., 10 – 600 K (Fig. S5, Supplemental Material, Sec. G [31]).

In summary, we have shown an unusual asymmetric lattice distortion in BP both experimentally and theoretically. Observation of the forbidden reflection (011) and DMC calculation demonstrate that lattice symmetry breaks due to intrinsic electronic interaction rather than to any kinds of defects or multiple scattering. Our DFT calculation with finite U explains successfully the electronic origin of unexpected distortion. The result may also provide a clue to understand the intriguing electronic feature of BP. Such a lattice distortion functions as an electronic perturbation to the asymmetric charge redistribution in BP by the charge transfer of $\sim 0.1 e$. We thus assert the possibility of 2D ferroelectricity in BP as has been pursued previously [16,22,23].

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