A metastable phase of body-centered-tetragonal ruthenium (bct Ru) is identified to exhibit a large perpendicular magnetocrystalline anisotropy (PMCA), whose energy $E_{\text{MCA}}$ is as large as 150 μeV/atom, which is two orders of magnitude greater than those of 3d magnetic metals. Further investigation over the range of tetragonal distortion suggests that the appearance of magnetism in the bct Ru is governed by the Jahn-Teller split $e_g$ orbitals. Moreover, from band analysis, MCA is mainly determined by an interplay between two $e_g$ states, $d_{3z^2-r^2}$ and $d_{yz}$ states, as a result of level reversal associated with tetragonal distortion.

As the electronic structure of magnetic materials with non-negligible MCA is mainly dominated by $d$ electrons, it would be worthwhile to see how the energy levels of $d$ orbitals evolve in different crystal symmetries, as illustrated in Fig. 1. For bcc Ru with $c/a = 1$, the cubic symmetry splits five $d$ orbitals into singlets ($e_g$) and triplets ($t_{2g}$). When the lattice changes from high-symmetric body-centered to tetragonal with lower symmetry, additional Jahn-Teller splitting may offer more freedom to provide more energy differences in Eq. (1). More specifically, the tetragonal distortion further splits these $e_g$ and $t_{2g}$ levels into two irreducible representations: $e_g$ into two singlets $d_1 (d_{3z^2})$ and $b_1 (d_{y^2-x^2})$, and $t_{2g}$ into a singlet $b_2 (d_{xz})$ and a doublet $e (d_{yz}, d_{xy})$, where their relative order is determined by $c/a$, which is either larger or smaller than unity.

Metals with 4$d$ and 5$d$ valence electrons possess inherently larger SOC than conventional 3$d$ metals. The search for magnetism in these transition metals has a long history. The fact that Pd and Pt barely miss the Stoner criteria to become ferromagnetic (FM) has incurred enormous efforts to realize magnetism in several multilayers and interfaces of 4$d$ metals by adjusting the volumes or lattice constants, thereby, increasing the density of states (DOS) at the Fermi level ($E_F$). $N(E_F)$, due to a narrowed bandwidth, would meet the Stoner criteria. Hence, 4$d$ and 5$d$ metals with large SOC as well as magnetism would be favorable candidates to realize large MCA.

A previous theoretical study has suggested that ferromagnetism in Ru is feasible in a body-centered-cubic (bcc) structure when the lattice is expanded by 5% [8]. Other studies predicted that magnetism can occur in Rh and Pd with volume changes [9,10]. However, theoretically proposed magnetism associated with volume changes in 4$d$ metals has not been fully confirmed experimentally. Nevertheless, with remarkable advances in current fabrication techniques, various types of lattices are now accessible with a diverse choice of substrates. In particular, the bct Ru film has been successfully fabricated on the Mo (110) substrate, whose lattice constants are $a = 3.24$ Å and $c/a = 0.83$, as identified by x-ray electron diffraction [11]. Later, a theoretical calculation argued that magnetism can exist in bct Ru for $c/a = 0.84$ with a moment of 0.4$\mu_B$/atom [12].
In this paper, we present that in an identified metastable phase of bct Ru, $E_{\text{MCA}}$ can be as large as 150 $\mu$eV/atom, which is two orders of magnitude greater than those in 3d magnetic metals. The magnetic instability driven by this tetragonal distortion is discussed in connection with the Stoner criteria. Furthermore, we show that magnetism as well as MCA are governed mainly by the Jahn-Teller split $e_g$ orbitals.

II. COMPUTATIONAL DETAILS

Density functional calculations were performed using the highly precise full-potential linearized augmented plane wave (FLAPW) method [13]. For the exchange-correlation potential, the generalized gradient approximation (GGA) was employed as parameterized by Perdew, Burke, and Ernzerhof (PBE) [14]. Energy cutoffs of 16 and 256 Ry were used for wave function expansions and potential representations. Charge densities and potential inside muffin-tin (MT) spheres for wave function expansions and potential representations.

Charge densities and potential inside muffin-tin (MT) spheres for wave function expansions and potential representations. In the cubic symmetry, such as bcc ($c/a = 1$), the $d$ orbital splits into doublets ($e_d$) and triplets ($t_{2g}$). Tetragonal distortion further splits $e_d$ into $a_1$ and $b_1; t_{2g}$ splits into a singlet $b_2$ and a doublet $e$, where their relative order is shown depending on whether $c/a$ is greater or smaller than unity.

FIG. 1. (Color online) Schematic presentation of the Jahn-Teller splitting of $d$ electrons. In the cubic symmetry, such as bcc ($c/a = 1$), the $d$ orbital splits into doublets ($e_d$) and triplets ($t_{2g}$). Tetragonal distortion further splits $e_d$ into $a_1$ and $b_1; t_{2g}$ splits into a singlet $b_2$ and a doublet $e$, where their relative order is shown depending on whether $c/a$ is greater or smaller than unity.

III. RESULTS AND DISCUSSION

Equilibrium lattice constants of hexagonal-closed-packed (hcp), face-centered-cubic (fcc), and bcc Ru are summarized in Table I, which are in good agreement with experiments [11,24] and previous work [12]. The hcp structure is the most stable phase, as Ru crystallizes in hcp. However, the energy difference between hcp and fcc, 0.07 eV/atom, is very small, which reflects the feature of the closed packed structures of the two but with different stacking sequences. In Fig. 2(a), the total energy of nonmagnetic (NM) bct Ru as a function of tetragonal distortion ($c/a$) is plotted for a fixed volume of the equilibrium bcc structure. Our result reproduces that given by Watanabe et al. [12]: There is a global minimum at $c/a = 1.41$ corresponding to the fcc structure. There are two other extrema, a local maximum and minimum at $c/a = 1$ and $c/a = 0.84$, respectively. In particular, the local minimum at $c/a = 0.84$ suggests the existence of a metastable phase, as discussed in Ref. [12]. Further calculations of total energy of the bct structure as a function of both $a$ and $c/a$ confirm that the local minimum is at $a = 3.25$ Å and $c/a = 0.84$, consistent with the fixed volume calculation of the bcc structure.

On the other hand, as shown in Fig. 2(c), the energy difference between the NM and FM states ($\Delta E = E_{\text{FM}} - E_{\text{NM}}$) and the magnetic moment reveal almost the same trends as $c/a$ changes. $\Delta E$ of the bcc and fcc phases are negligibly small, thus both phases are nonmagnetic. When $c/a < 1.1$ but $c/a \neq 1$, the bct Ru is magnetic ($\Delta E > 0$), whereas when $c/a > 1.1$, it is nonmagnetic. In particular, $c/a = 0.84$ gives $\Delta E = 35$ meV/atom with a magnetic moment as high as 0.6$\mu_B$, which is larger than 0.40$\mu_B$ in Ref. [12]. Interestingly,

TABLE I. Calculated equilibrium lattice parameters, $a$ (in Å) and $c/a$, and total energy difference $\Delta E$ (in eV/atom) of hcp, fcc, bcc, and bct Ru with respect to the total energy of the hcp structure. Experimental and previous theoretical results are also given for comparison.

|     | hcp       | fcc       | bcc       | bct       |
|-----|-----------|-----------|-----------|-----------|
| $a$ | Present   | 2.70      | 3.84      | 1.00      | 3.25      |
|     | Experiment | 2.70      | 3.84      | 1.00      | 3.25      |
| $c/a$ | Present | 1.58      | 1.09      | 0.56      | 0.84      |
|     | Previous  | Previous  | Previous  | Previous  | Previous  | Previous  |       |
|     |           |           |           |           |       |
| $\Delta E$ | Present | 0.07      | 0.13      | 0.65      | 0.48      | 0.55      |
|     | Previous  | Previous  | Previous  | Previous  | Previous  | Previous  |       |
|     |           |           |           |           |       |

$^a$Shiiki et al. [11].

$^b$Watanabe et al. [12].
the magnetic moment of the bct Ru exhibits a reentrance behavior for \(c/a > 1\), as predicted by Schönecker et al. [25]. In region A \((c/a < 1)\), the magnetic moment decreases as \(c/a\) increases, whereas magnetism reappears when \(c/a\) just passes unity, which eventually vanishes for \(c/a > 1.1\).

The total DOS and those from \(e_g\) orbitals at \(E_F\) as a function of \(c/a\) are plotted in Fig. 2(d) for the NM bct Ru. Most contributions come from the Jahn-Teller split \(e_g\) orbitals, whose difference in DOS is also plotted: It resembles the magnetic moment shown in Fig. 2(c). Moreover, among the Jahn-Teller split \(e_g\) orbitals, \(d_{z^2} - \gamma^2\) dominates the other for \(c/a < 1\) (\(c/a > 1\)).

The partial DOS (PDOS) of \(d\) orbitals are shown in Fig. 3 for the spin-polarized cases, where the trivial \(c/a = 1\) is omitted. The prominent peaks at \(c/a = 0.84\) are mainly from the \(d_{x^2 - y^2}\) states with occupied (unoccupied) peaks in the majority (minority) spin bands, while the peaks in the \(d_{z^2}\) states evolve as \(c/a\) increases. Contributions from the \(t_{2g}\) states are rather featureless.

For simplicity, we assign the energy difference of the peaks in the \(e_g\) states, \(d_{z^2} - \gamma^2\) for \(c/a < 1\) and \(d_{z^2}\) for \(c/a > 1\), respectively, as the exchange splitting. Then, as \(c/a\) increases, the exchange splittings are 1.02, 1.05, 0.80, and 0.66 eV for \(c/a = 0.84, 0.90, 0.96,\) and 1.06, respectively, which qualitatively reflects magnetism of the bct Ru. From this, the exchange splitting is mainly determined by one of the Jahn-Teller split \(e_g\) orbitals.

In addition to magnetism, the bct Ru exhibits large MCA. The angle-dependent total energy in a tetragonal symmetry is expressed in the most general form, \(E_{tot}(\theta, \varphi) = E_0 + k_1 \sin^2 \theta + k_2 \sin^2 \theta + k_3 \sin^3 \theta \cos 4\varphi\), where \(\theta\) and \(\varphi\) are polar and azimuthal angles, respectively, and \(k_1 = 100, k_2 = -1,\) and \(k_3 \ll 1 \text{ eV}\). The small value of \(k_3\) indicates a negligible \(\varphi\) dependence. \(E_{MCA} = E_{tot}(\theta = 90^\circ) - E_{tot}(\theta = 0^\circ)\) as a function of the tetragonal distortion \(c/a\) is shown in Fig. 4(a). Here, \(E_{MCA} = 150 \text{ eV/atom at } c/a = 0.80,\) and \(E_{MCA} = 100 \text{ eV/atom for the local minimum } (c/a = 0.84),\) which is two orders of magnitude greater than conventional 3d magnetic metals. As the strength of the tetragonal distortion \(c/a\) changes, \(E_{MCA}\) changes not only in magnitude but also in sign. In region A, \(E_{MCA}\) becomes negative near \(c/a \approx 0.9\) and reaches \(-100 \text{ eV/atom} \approx 0.96,\) whereas in region B, \(E_{MCA} > 0\); PMCA is restored. Hence, the strength of the tetragonal distortion \(c/a\) influences the magnetic moments as well as \(E_{MCA}\).

\(E_{MCA}\) is decomposed into different spin channels following Eq. (1), as shown in Fig. 4(b) for bct Ru with \(c/a = 0.84, 0.90, 0.96,\) and 1.06, respectively. For \(\sigma \sigma' = \uparrow \uparrow\) or \(\downarrow \downarrow\), the...
positive (negative) contribution to $E_{MCA}$ is determined by the SOC interaction between the occupied and unoccupied states with the same (different by one) magnetic quantum number ($m$) through the $\ell_Z$ ($\ell_X$) operator. For $\sigma \sigma' = \uparrow \downarrow$, Eq. (1) has opposite sign, so the positive (negative) contribution comes from the $\ell_X$ ($\ell_Z$) coupling.

From the spin-channel decomposition of $E_{MCA}$, one notes that there is no dominant spin channel. This feature differs from the 3$d$ transition metals, where a particular spin channel, i.e., the $\downarrow \downarrow$ channel, dominantly contributes to the positive value through the SOC matrix $\langle x^2 - y^2 | \ell_Z | xy \rangle$, with negligible ones from the $\ell_X$ matrices [7,26]. When $c/a = 0.84$, the $\downarrow \downarrow$ channel gives the largest contribution, while those from other channels are smaller than half of the $\downarrow \downarrow$ channel with opposite signs. As $c/a$ increases, the $\downarrow \downarrow$-channel contribution is reduced, which turns negative for $c/a > 1$. MCA almost vanishes for $c/a =$
0.90 and becomes negative for $c/a = 0.96$. On the other hand, for $c/a = 1.06$, the $\uparrow\downarrow$ and $\downarrow\downarrow$ channels contribute almost the same magnitudes with opposite signs, so just the $\uparrow\uparrow$-channel contribution remains.

To obtain more insights, the band structure is plotted in Fig. 5 with $d$-orbital projection, where the size of the symbols is proportional to their weights. All the bands along $\Gamma-Z-X$ are highly dispersive, whereas those along $X-P-N-\Gamma-X$ are less dispersive with a rather flat feature from the $d_{x^2-y^2}$ and $d_{z^2}$ states. The level reversals between $e_g$ states, $d_{x^2-y^2}$ and $d_{z^2}$, are well manifested, while $t_{2g}$ states are relatively rigid with respect to tetragonal distortion. It is a formidable task to identify the role of each individual SOC matrix for each $c/a$. However, from the spin-channel decomposed MCA [Fig. 4(b)], each spin channel changes its sign when $c/a$ becomes greater than unity, where the level reversal occurs between $d_{x^2-y^2}$ and $d_{z^2}$. 

FIG. 5. (Color online) Band structures of bct Ru for $c/a = 0.84$, 0.90, 0.96, and 1.06 for the majority and minority spin states. The $d$-orbital states are shown in different colors: red ($d_{z^2}$), black ($d_{x^2-y^2}$), blue ($d_{xy}$), orange ($d_{xz}$), and green ($d_{yz}$), respectively.
For a simple analysis, we express the $\downarrow\downarrow$ channel as

$$E(\downarrow\downarrow) = \frac{|(x^2 - y^2)[\epsilon_{\chi}x y]|^2}{\epsilon_{x^2-y^2} - \epsilon_{xy}} - \frac{|(x^2 - y^2)[\epsilon_{\chi}x z]|^2}{\epsilon_{x^2-y^2} - \epsilon_{xz}}$$

$$= \frac{|c z^2[\epsilon_{\chi}x z]|^2}{\epsilon_{c^2} - \epsilon_{xz}}.$$  

(2)

We focus along $X-P-N-\Gamma-X$, where $\epsilon_{\chi}$'s are unoccupied. The $(yz)[\epsilon_{\chi}(x z)]$ contributions are neglected due to the rigidity of the $x_{\pm}$ states as well as their small contribution to $E_{\text{MCA}}$ owing to the large energy denominator. From the fact that $E(\downarrow\downarrow) > 0$ when $c/a = 0.84$ with the largest value, we can infer that the first term in Eq. (2) should be larger than the other two, where the largest occurs along $P-N$. [See the Supplementary Material (SM) for the $k$-resolved MCA analysis [27].]

As $c/a$ increases but $c/a < 1$, the empty $d_{z^2}$ band moves downward while the empty $d_{x^2-y^2}$ band goes upward with respect to $E_F$. As a result, the third term is enhanced due to the rigidity of a smaller energy denominator. Hence, $E(\downarrow\downarrow)$ decreases but remains positive. When $c/a > 1$, however, the level reversal between $\epsilon_{\chi}$ states pushes $E_F$ and $d_{x^2-y^2}$ below $E_F$ along $N-\Gamma-X$. The former provides an additional negative contribution while the latter reduces the positive contribution. As a consequence, $E(\downarrow\downarrow) < 0$ for $c/a > 1$. The sign behavior of the $\uparrow\downarrow$ component, $E(\uparrow\downarrow)$, is completely opposite to $E(\downarrow\downarrow)$, as all terms in Eq. (2) take opposite signs [7]. For the $\uparrow\downarrow$ component when $c/a < 1$, we focus near $P-N$. The largest positive contribution in the $\downarrow\downarrow$ component is significantly reduced in the $\uparrow\uparrow$ channel because the empty $d_{x^2-y^2}$ band in the minority spin is occupied in the majority spin, and the empty $d_{z^2}$ band contributes negatively. Thus, $E(\uparrow\uparrow) < 0$. When $c/a > 1$, the occupancies of the $\epsilon_{\chi}$ states are reversed again due to the level reversal, therefore $E(\uparrow\uparrow) > 0$. We want to point out that the level reversal between the $d_{x^2-y^2}$ and the $d_{z^2}$ states not only affects the sign behavior of MCA but also the exchange splitting in DOS. The above argument of the sign behavior is more clearly supported by the $k$-resolved MCA analysis. (See SM Figs. S1–S5 [27].)

IV. CONCLUSION

In summary, a metastable phase of bct Ru has been identified to exhibit a large PMCA, which is two orders of magnitude greater than conventional magnetic metals. In the context of spintronics applications, this large anisotropy, along with low magnetization and small volume, would be key factors to realize materials with a low switching current and high thermal stability. Magnetism of bct Ru is mainly governed by the Jahn-Teller split $\epsilon_{\chi}$ states. As the strength of the tetragonal distortion changes, the magnetism of bct Ru shows an interesting reentrance behavior for $1 < c/a < 1.1$. The tetragonal distortion accompanies MCA changes in both magnitudes and signs, as a result of the level reversal between $d_{x^2-y^2}$ and $d_{z^2}$.

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