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Intrinsic origin of interfacial second-order magnetic anisotropy in ferromagnet/normal metal heterostructures

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Abstract

Interfacial perpendicular magnetic anisotropy, which is characterized by first-order (K_1) and second-order (K_2) anisotropy, is the core phenomenon for nonvolatile magnetic devices. A sizable K_2 satisfying a specific condition stabilizes the easy-cone state, where equilibrium magnetization forms at an angle from the film normal. The easy-cone state offers intriguing possibilities for advanced spintronic devices and unique spin textures, such as spin superfluids and easy-cone domain walls. Experimental realization of the easy-cone state requires understanding the origin of K_2 , thereby enhancing K_2 . However, the previously proposed origins of K_2 cannot fully account for the experimental results. Here, we experimentally show that K_2 scales almost linearly with the work function difference between the Co and X layers in Pt/Co/X heterostructures ($X = \text{Pd, Cu, Pt, Mo, Ru, W, and Ta}$), suggesting the central role of the inversion asymmetry in K_2 . Our result provides a guideline for enhancing K_2 and realizing magnetic applications based on the easy-cone state.

Introduction

Magnetic anisotropy describes a magnetization-angle-dependent change in magnetic energy and stabilizes the magnetization in specific directions. Its angular dependence is determined by the symmetry of the crystal or structure. In thin-film heterostructures such as ferromagnet/normal metal bilayers where the structural inversion symmetry is broken at the interface, the magnetic anisotropy is dominated by interfacial contributions, as follows (up to the second order):

$$E(\theta) = K_1^{\text{eff}} \sin^2 \theta + K_2 \sin^4 \theta \quad (1)$$

where $K_1^{\text{eff}} (= K_1 - 2\pi M_s^2)$ is the effective first-order anisotropy energy density that comprises the demagnetization

energy density (with K_1 and M_s being the first-order anisotropy energy density and saturation magnetization, respectively), K_2 is the second-order anisotropy energy density, and θ is the polar angle of the magnetization. The magnetic phase diagram as functions of K_1^{eff} and K_2 (Fig. 1a) shows several distinct magnetic states¹. Among them, the out-of-plane state originating from perpendicular magnetic anisotropy (PMA) has been a main focus of spintronics research² because it offers scalable magnetic random-access memories (MRAMs)³.

Recently, interest in another state—the easy-cone state, where the equilibrium magnetization direction is tilted from the film normal and forms a cone—has increased for the following reasons. It provides improved functionalities of various spintronic devices, such as low-power operation of spin-transfer torque (STT) MRAMs^{4–6} and zero-field precession of STT oscillators⁷. Moreover, it hosts spin superfluids associated with spontaneous breaking of $U(1)$ spin-rotational symmetry^{8,9} and allows unique easy-cone domain wall dynamics¹⁰. The existence of the easy-cone state was experimentally verified in various layered

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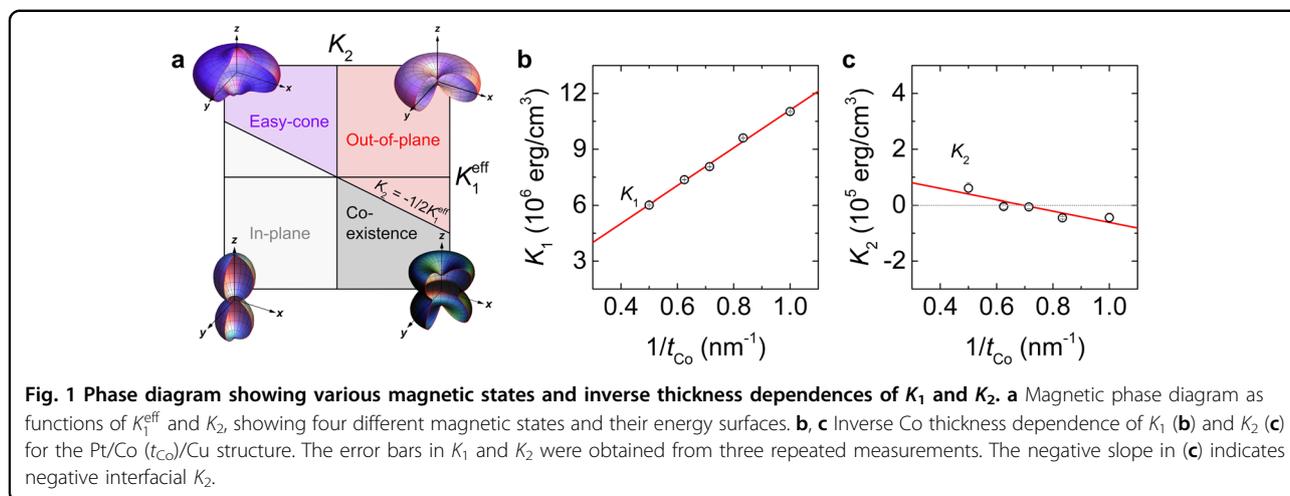
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structures^{6,11,12}. However, the design window for forming a stable easy-cone state is very narrow^{6,11,12}, which presents a critical challenge for realizing magnetic devices utilizing the easy-cone state.

In contrast to the out-of-plane state that can form with K_1 alone, the easy-cone state requires a large K_2 value; it is formed for $K_1^{\text{eff}} < 0$ and $K_2 > -1/2K_1^{\text{eff}}$ (Fig. 1a). To actively employ the easy-cone state in various applications, therefore, it is of crucial importance to find a way of enhancing K_2 , which necessitates a fundamental understanding of its origin. The origin of K_1 has long been a subject of extensive theoretical and experimental research. It was found to depend on the orbital anisotropy¹³, spin-orbit interaction of electronic structures near the Fermi level¹⁴ or Rashba-type spin-orbit interaction at the interface associated with the inversion symmetry breaking^{15–17}. Concerning the origin of K_2 , three mechanisms have been proposed: (1) spatial fluctuations of K_1 ¹⁸, (2) interfacial PMA combined with a gradual weakening of the exchange energy along the thickness direction¹⁹, and (3) the mixture of bulk magnetocrystalline cubic anisotropy and interfacial uniaxial anisotropy²⁰. The first and second mechanisms predict only positive K_2 and fail to explain the negative K_2 observed in experiments^{21,22}. The third mechanism predicts both signs of K_2 depending on the *nature* of the bulk cubic anisotropy. Our measurement of K_2 for a Pt/Co/Cu structure, however, shows that K_2 is inversely proportional to the Co thickness (thus, the interface origin) and is negative for thin Co layers (see Fig. 1c and Supplementary Note 1 for details). As the third mechanism cannot account for the origin of the negative K_2 of the interface, none of the three aforementioned mechanisms can explain this experimental observation; thus, a new origin of K_2 must be identified.

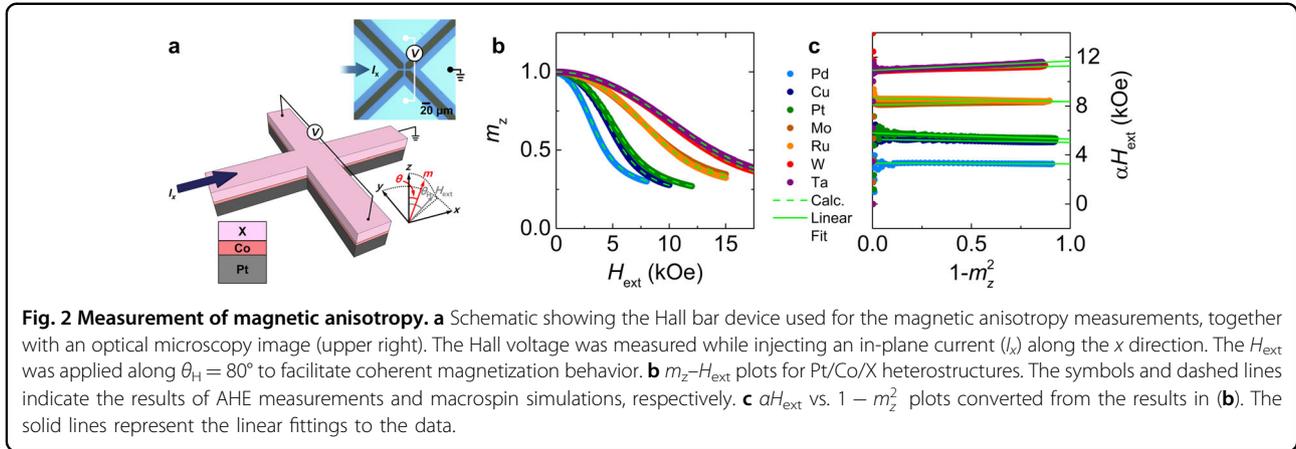
In this study, we focus on the role of the inversion symmetry breaking in K_2 for the following two reasons.

First, recent theoretical and experimental studies indicated the important role of the inversion asymmetry in K_1 for ferromagnet–normal metal heterostructures^{15–17}. As K_1 and K_2 are the order-expanded coefficients of the net magnetic anisotropy [Eq. (1)], it is reasonable to expect that they share the same origin. Second, our measurements of K_1 and K_2 for Pt/Co/Cu and Pt/Co/MgO stacks over a wide range of Co thickness (t_{Co}) show that for both K_1 and K_2 , the interfacial contribution is dominant compared with the bulk contribution (Supplementary Note 1), indicating the important role of the inversion asymmetry at the interface in the anisotropy.

Materials and methods

Sample preparation

To investigate the correlation between the inversion asymmetry and K_2 , we examine various sputtered Pt/Co/X stacks, with X = Pd, Cu, Pt, Mo, Ru, W, and Ta. The stacks investigated in this study had the structure of Si substrate (wet-oxidized)/Ta (5 nm)/Pt (5 nm)/Co (1 nm)/X (3 nm)/Ta (3 nm) and were fabricated using an ultrahigh-vacuum magnetron sputtering system with a base pressure of 8×10^{-8} Torr. All metallic layers were deposited under an Ar pressure of 2×10^{-3} Torr. The Ta under- and upper-layers were introduced to improve the surface roughness and prevent the oxidation of the stacks, respectively. For X = Ta, Pt (3 nm) was used as the upper layer. Pt/Co/MgO (2 nm) stacks were also prepared, followed by post-annealing at 400 °C for 30 min to maximize the interfacial PMA at the Co/MgO interface^{23–25}. Details regarding the fabrication and annealing are provided in Supplementary Note 5. The continuous samples were patterned into a Hall bar structure via photolithography and inductively coupled plasma etching. The current-injection line and the voltage branch had dimensions of 5 μm (width) \times 35 μm (length). A 50-nm-thick Pt layer was



deposited on top of the patterned structure as a contact pad for magnetotransport characterization (Fig. 2a).

Measurement of magnetic anisotropy

The magnetic anisotropies (K_1 and K_2) were characterized by the anomalous Hall effect (AHE) in a standard four-probe Hall geometry. The Hall bar device was mounted on a rotatable sample stage placed in the gap of an electromagnet. The AHE measurements involved injecting an in-plane current ($I_x = 5$ mA) along the x direction and sensing the Hall voltage induced along the y direction. The external magnetic field (H_{ext}) was applied at a polar angle (θ_H) of 80° to facilitate coherent magnetization behavior (Fig. 2a). The generalized Sucksmith–Thompson method was used to accurately determine the effective first- and second-order anisotropy fields (denoted as $H_{K1}^{\text{eff}} = 2K_1/M_s - 4\pi M_s$ and $H_{K2} = 4K_2/M_s$, respectively)²⁶. The key to this method is the use of the following equations, which can be derived from the total magnetic energy equation [Eq. (1), considering the Zeeman energy ($-\mathbf{M} \cdot \mathbf{H}_{\text{ext}}$)]:

$$\alpha H_{\text{ext}} = H_{K1}^{\text{eff}} + H_{K2}(1 - m_z^2), \quad (2)$$

$$\alpha \equiv \frac{m_z \sin \theta_H - \sqrt{1 - m_z^2} \cos \theta_H}{m_z \sqrt{1 - m_z^2}}. \quad (3)$$

The AHE results were normalized with respect to the anomalous Hall voltages to obtain m_z - H_{ext} curves (Fig. 2b), and then αH_{ext} was plotted with respect to $1 - m_z^2$ to extract H_{K1}^{eff} and H_{K2} from the intercept and slope, respectively [Eq. (2) and Fig. 2c]. We observed a slight misalignment in θ_H from its nominal value (mostly within 2°), which was adjusted to maximize the linearity of the αH_{ext} vs. $1 - m_z^2$ plot. To confirm the accuracy of the anisotropy constants, the measured m_z - H_{ext} curves were compared with those from macrospin simulations using the obtained H_{K1}^{eff} and H_{K2} values as inputs (Fig. 2b). The M_s values of the continuous samples were measured using a vibrating

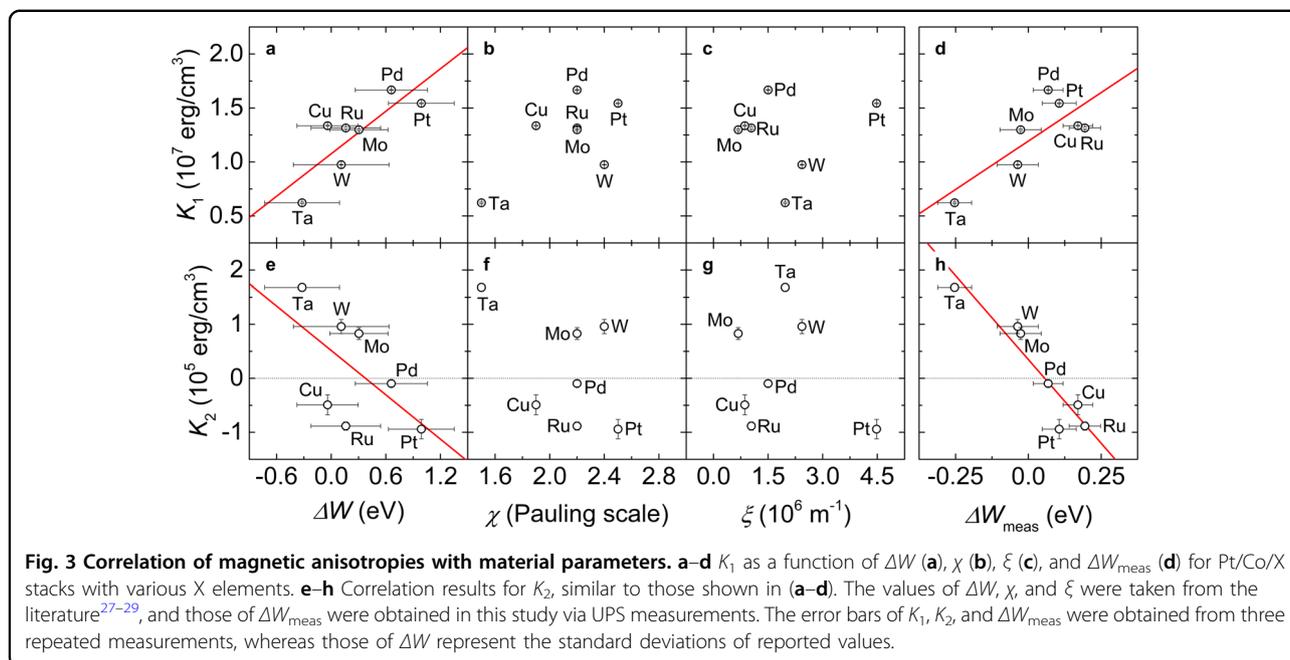
sample magnetometer. The anisotropy constants were then obtained from the relationships $K_1 = M_s H_{K1}^{\text{eff}}/2 + 2\pi M_s^2$ and $K_2 = M_s H_{K2}/4$. All measurements were performed at room temperature.

Measurement of work function

To measure the work functions of metals and MgO, ultraviolet photoelectron spectroscopy (UPS) measurements were performed for separately prepared stacks of Si substrate (wet-oxidized)/X (5 nm) (including Co). The UPS measurements were performed using He I radiation ($h\nu = 21.2$ eV) from a gas-discharge lamp. The base pressure of the chamber was 2×10^{-8} Torr. Prior to the measurement, Ar ion sputtering was performed to remove any native oxides formed during the exposure to air. The metallic films were sputtered repeatedly until the Fermi edge was observed. More details on the measurement of the work function and the photoemission spectra are provided in Supplementary Note 2.

Results and discussion

In Fig. 3a–c, K_1 is plotted as a function of the work function (W), electronegativity (χ), and spin–orbit coupling constant (ξ), all of which are taken from the literature^{27–29}. We choose these material parameters because of their potential correlation with the inversion asymmetry or Rashba effect at the Co/X interface^{30–32}. To estimate the strength of the correlation, we calculated Pearson’s r for all the plots. Pearson’s r is close to ± 1 (0) for a strong (weak) correlation. We obtain correlation coefficients of 0.82, 0.63, and 0.07 for the plots in Fig. 3a–c, respectively, indicating the strongest correlation between K_1 and ΔW ($\equiv W_X - W_{\text{Co}}$). K_1 also appears to be correlated with χ (Fig. 3b). This is expected because the difference in χ between two elements is proportional to the charge transfer³³, which could be driven by the potential gradient at the Co/X interface in our samples. We note that this correlation feature is in accordance with



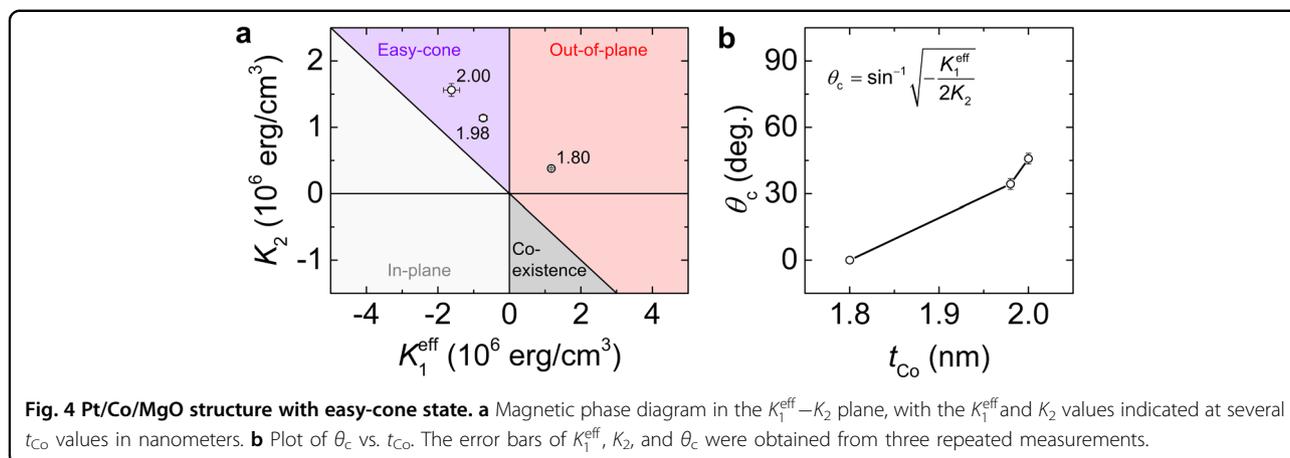
a recent experimental observation for the interfacial Dzyaloshinskii–Moriya interaction originating from inversion asymmetry²⁷. We also plot K_1 as a function of ΔW measured for our samples by UPS (denoted as ΔW_{meas}) (see Fig. 3d, Methods, and Supplementary Note 2 for details) and find a similar correlation between the two parameters (K_1 and ΔW_{meas}) with a correlation coefficient of 0.78. This result shows that the inversion asymmetry at the interface plays an important role in the K_1 of Pt/Co/X heterostructures.

Figure 3e–h shows the results for K_2 , which are similar to those for K_1 shown in Fig. 3a–d. The correlation coefficients for K_2 are -0.59 , -0.51 , and -0.18 for literature values of ΔW , χ , and ξ , respectively. Similar to K_1 , K_2 exhibits meaningful correlations with ΔW and χ . The correlation coefficient of K_2 with ΔW_{meas} is substantially improved to -0.94 (Fig. 3h), suggesting a strong correlation. Importantly, K_2 changes its sign depending on the type of material X but still shows an almost linear correlation with ΔW_{meas} . According to theoretical work, the Rashba spin–orbit coupling is known to be proportional to the surface potential (seen by electrons) and electron density distribution³⁴. Since the surface potential of a metal–metal interface is equivalent to ΔW_{meas} , the good correlation observed in Fig. 3h suggests that the inversion asymmetry is an intrinsic origin of K_2 in Pt/Co/X heterostructures. We call it intrinsic because this mechanism is distinct from the first (spatial fluctuations of K_1 ¹⁸) and second (interfacial PMA combined with a gradual weakening of the exchange energy along the thickness direction¹⁹) mechanisms, which are extrinsic. Furthermore, our simple tight-binding model calculation with Rashba

spin–orbit coupling supports this conclusion, as it shows that K_2 can have both positive and negative signs depending on the band filling even though K_1 is positive (i.e., PMA) (Supplementary Note 3). It is worth noting that the linear correlation, observed in Fig. 3d, h, persists even with the structural disordering taken into account (Supplementary Note 4). This indicates that the effect of the inversion asymmetry on the magnetic anisotropy can still be valid in intermixed thin-film structures¹⁷.

The linear correlation between K_2 and ΔW_{meas} however, appears to be somewhat unreasonable, considering that the magnetic anisotropy is known to originate from the second-order perturbative treatment of spin–orbit coupling near the Fermi level^{13,16}. The following explanation can be given to understand the observed linear correlation. The effective electric field (E_0) formed at the metal–metal interface will be large when the work-function difference between the two metals (e.g., Co and normal metal) is large. The use of a different normal metal will result in the modulation of E_0 , dE , with a resultant E_0 value of $E_0 + dE$. Since the magnetic anisotropy is quadratic in the Rashba parameter (i.e., $E_0 + dE$)¹⁶, the variation of the magnetic anisotropy with a differing normal metal can be simply expressed as $(E_0 + dE)^2 \approx E_0^2 + 2E_0 dE$. It is then possible to explain our experimental results (Fig. 3d, h) that the modulation of the work function can give rise to the linear variation of the magnetic anisotropy.

The correlation result suggests that a large negative ΔW results in a large positive K_2 , which is needed to form the easy-cone state. For experimental realization, we replace the metallic X layer with a MgO layer (see Supplementary Note 5). We choose MgO for the following two reasons.



First, strong Rashba splitting was observed at metal–oxide interfaces^{31,32}. Our ΔW_{meas} value at the Co/MgO interface is consistent with this expectation: it is -0.36 eV (Supplementary Note 5), which is more negative than the value (-0.25 eV) for the Co/Ta interface, which exhibits the most negative ΔW_{meas} among all the metallic Co/X interfaces. Second, MgO is widely adopted in various spintronic devices³. For a Pt/Co (1.0 nm)/MgO stack, we obtain a K_1 of 1.47×10^7 erg/cm³ and K_2 of 2.61×10^6 erg/cm³. Compared with the all-metallic structures, the K_2 of the Pt/Co/MgO structure is larger by an order of magnitude, which is in accordance with our conclusion in this work; the inversion asymmetry is an intrinsic origin of K_2 . However, previously proposed mechanisms^{18–20} not considering the role of the inversion asymmetry are unable to explain the enhanced K_2 (see Supplementary Note 7 for details). Nonetheless, we note that the simple linear correlation between K_2 and ΔW_{meas} describes the enhanced K_2 of the Pt/Co/MgO structure only qualitatively, not quantitatively. Extrapolation of the linear line in Fig. 3h gives a K_2 value of approximately 0.27×10^6 erg/cm³, which is significantly smaller than the measured value of 2.61×10^6 erg/cm³. A similar behavior is observed for K_1 ; in this case, the extrapolation gives a value of 0.55×10^7 erg/cm³, which is approximately one third of a measured value of 1.47×10^7 erg/cm³. These deviations may indicate that ΔW_{meas} is not the sole factor determining the inversion asymmetry for a metal–oxide interface. A recent experimental work combined with a first-principles study found that the asymmetric charge-density distribution (or the charge transfer) at a metal–oxide interface has a larger effect on the Rashba splitting than the work-function difference (or the potential gradient)³².

This large and positive K_2 allows the easy-cone state to be formed in Pt/Co/MgO structures at t_{Co} near the spin reorientation transition¹. The formation of the easy-cone state is validated by both vibrating sample magnetometry and AHE measurements (Supplementary Note 8). The

K_1^{eff} and K_2 values for the Pt/Co (1.8–2.0 nm)/MgO structures are overlaid on a magnetic phase diagram (Fig. 4a). The cone angle (θ_c) is estimated according to the relationship $\theta_c = \sin^{-1}\left(\sqrt{-K_1^{\text{eff}}/2K_2}\right)$. We find that θ_c can be engineered by controlling t_{Co} (Fig. 4b), which is beneficial for device applications of the easy-cone state.

Conclusion

We investigated the origin of K_2 in Pt/Co/X heterostructures and found that inversion asymmetry plays an important role in K_2 . Among the material parameters considered in this study, the work-function difference at the Co/X interface shows the strongest correlation with both K_1 and K_2 . Replacing the metallic X layer with MgO, whose interface with Co has a strong inversion asymmetry, we obtain greatly enhanced K_2 , allowing the easy-cone state. The intrinsic origin of K_2 revealed in this study will contribute to the control of its values and therefore allow various easy-cone states suitable for a wide variety of spintronic applications.

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Author contributions

H.K.G. and S.H.L. planned and designed the experiment. H.K.G. prepared the samples and performed measurements. H.-J.P., K.-W.K., and K.-J.L. performed the theoretical analysis. All authors discussed the results and contributed to the manuscript.

Conflict of interest

The authors declare that they have no conflict of interest.

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