Metallic cobalt (Co) has been widely studied as an important magnetic material and its magnetic properties can vary significantly depending on its structures.[21] the face centered cubic (FCC, stable above 450 °C) phase shows good soft magnetic behaviors, and amorphous CoSiB materials based on the structure (with a general composition at ca. Co80(Si,B)20) are one of the best soft magnetic materials, used in many high-performance electric devices;[22] the hexagonal close-packed (HCP, stable below 450 °C) Co shows hard magnetic behavior because of the structural anisotropy, and its compounds with rare earth (RE) elements (e.g., SmCo5) or noble metals (e.g., CoPt) do show significantly enhanced hard magnetic behaviors due to the high anisotropy of RE elements or strong 3d–5d hybridizations.[3,4,12] The high cost of these materials inhibits their applications as permanent magnets in many cases. On another hand, many of these compounds show unsatisfactory mechanical performance and poor processing ability. In many cases, polymer composites of these materials were used.[5] The fabrication of nanomaterials especially nanowires does improve the hard magnetic behaviors significantly,[6,7] but the complex process and ease of oxidation are the main drawbacks.

In metallic glasses, it is generally agreed that there are one or two kinds of atomic clusters (short-range orders) dominating the structure and thus controlling the physical properties.[8] It is reported that based on different dominant clusters, CoSiB metallic glasses with very similar compositions can have significantly different structure and magnetic behaviors (from ferromagnetism to antiferromagnetism) can be achieved.[9,10] In solid state solutions, it is also found that their atomic structures are not completely disordered in all length scales. Instead, dominant atomic clusters determining the magnetic properties exist in these compounds, and can vary depending on the compositions.[6,7,11] It is therefore possible to design this kind of magnetic compounds based on the dominant atomic clusters by using the atomic cluster model previously developed for amorphous alloys.[9]

CoB/CoSiB metallic glasses are widely studied in both structure and magnetic properties since 1970s. The atomic clusters favoring glassy formation have to be avoided, because the absence of anisotropy in glassy states will deteriorate the hard magnetism. According to Co-B phase diagram,[10] a Co rich FCC phase, Co23B6, is stable at high temperature. Thus the cluster favoring the FCC structure, Co0B polyhedral (see the inset structure in Figure 1a), can be extracted from this compound.[12] In order to reduce the cost and increase the magnetic anisotropy, it is better to include Si and B as much as possible while retaining the FCC or HCP Co-type structure. The maximum solubility of Si is 10 at.% (Co:Si=9:1) in HCP Co and 18 at.% in FCC Co.[11] Si concentration exceeding the maximum solubility may favor the amorphous state instead of crystalline Co structure. Thus the composition is designed as Co0.68Si0.32B0.1, normalized as Co9Si1.8B0.1. The synthesized structure is expected to be FCC Co type, because the dominant cluster is from FCC Co23B6. As a result, we obtained low-cost FCC CoSiB ribbons with high magnetcocrystalline anisotropy successfully in this work. The structural stability and magnetic behaviors of the compound can also be understood based on experimental electronic structures.

The X-ray diffraction (XRD) pattern in Figure 1a shows the dominant (111) reflection of the FCC phase with no visible trace

**Face Centered Cubic Co\textsubscript{81.8}Si\textsubscript{9.1}B\textsubscript{9.1} With High Magnetocrystalline Anisotropy**

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By using the atomic cluster model, face centered cubic (FCC) Co\textsubscript{81.8}Si\textsubscript{9.1}B\textsubscript{9.1} compound is designed and synthesized as ductile single-phase ribbons successfully. These ribbons show strong orientation along [111] and high magnetocrystalline anisotropy with a coercivity of 430 Oe and squareness of 0.82 at room temperature. The large spin–orbit coupling also contributes to the delocalization of Co 3d band and increased character of itinerant electrons which account for the structural stability and magnetic behaviors. The experimental electronic structure indicates that the magnetic performance can be improved further. This work not only develops a low-cost Co-based material for hard magnetic applications, but also extends the atomic cluster model into the design of new crystalline materials.

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of amorphous hump, affirming the single-phase nature of the as-made ribbons. The absence of other reflections suggests the strong orientation along (111). The morphologies of these ribbons indicate the good ductility of these samples, as shown in the inset of Figure 1(a). The lattice parameter estimated from the (111) reflection is \( a = 3.514 \text{ Å} \), smaller than the value 3.537-3.558 Å of FCC Co at room temperature.\(^{[13]}\) It is in agreement with the small atomic size of the substituting elements B and Si.

The (111) reflection peak is broadened obviously, suggestive of the nanocrystalline nature. The apparent crystallite size was estimated to be approximately 92 nm using the Scherrer’s formula.\(^{[14]}\) The nanocrystals of Co\(_{81.8}\)Si\(_{9.1}\)B\(_{9.1}\) were confirmed by transmission electron microscopy, as shown in Figure 1b. All observed crystals are less than 100 nm in critical size, in agreement with XRD results. No diffuse ring was observed in electron diffraction (see the inset in Figure 1b) and this confirms the absence of amorphous phases in the samples. Most of the grains are not spherical but elongated along the spinning direction. The anisotropic shape surely benefits the hard magnetic behaviors.

Magnetic hysteresis loops were measured under applied fields along longitudinal direction and perpendicular to the ribbon plane, respectively, at room temperature. As shown in Figure 2, Co\(_{81.8}\)Si\(_{9.1}\)B\(_{9.1}\) exhibits high magnetocrystalline anisotropy with [111] easy direction, with the coercivity \( (H_c) \) of around 430 Oe, in both easy and hard directions. Such high anisotropy was mainly observed in nanoscale thin film or nanomaterials of anisotropic shapes.\(^{[7,15]}\)

The magnetization is almost saturated at 5000 Oe along the easy direction, which is close to the field for saturating soft CoB/CoSiB amorphous alloys, and at 15000 Oe along the perpendicular direction, which is close to the field for bulk and nanoscale Co in both FCC and HCP structures. The saturation magnetization \( (M_s) \) is only 31.7 emu g\(^{-1}\), corresponding to 36 emu per Co gram, which is much smaller than the reported \( M_s \) in bulk Co and most nanoscale Co.\(^{[16,17]}\) However, the saturation remanence \( (M_r) \) is still up to 26 emu g\(^{-1}\) with a high squareness ratio \( (M_r/M_s) \) of 0.82. The small \( M_r \) is not likely due to the dilution effect of the substituted elements. Such reduced \( M_s \) was also observed in many CoPt and FePt nanoparticles.\(^{[18–20]}\)

It is also reported the \( M_s \) could be increased significantly in FePt by tuning the 3d-5d interaction via the minor addition of Au.\(^{[20]}\) Thus the reduced \( M_s \) should result from the partial delocalization of Co 3d electrons likely induced the strong interaction with B or Si. Such strong interaction may also contribute to the high magnetic anisotropy as in the case of CoPt.\(^{[18]}\)

For a cubic system, the magnetocrystalline anisotropy energy can be expressed as\(^{[21]}\)

\[
E_K = K_0 + K_1 (a_1^2 a_2^2 + a_2^2 a_3^2 + a_1^2 a_2^2) + K_2 a_1^2 a_2^2 + \cdots, \tag{1}
\]

where \( a_1, a_2, \) and \( a_3 \) are the cosines of angles between \( M_s \) and crystal axes. \( K_0, K_1, \) and \( K_2 \) are anisotropic constants. Higher powers and sometimes \( K_2 \) are so small that the terms involving them can be neglected. The first term, \( K_0 \), is independent of angle and is usually ignored. The easy direction (111) indicates that \( K_1 \) is negative like in many FCC metals. This is not
surprising because here the Co$_{81.8}$Si$_{9.1}$B$_{9.1}$ adopts FCC structure. The field required to saturate in the (111) direction is \[ H = \frac{4(3K_1 + K_2)}{9M_S}. \] (2)

In the case that $K_2$ is negligible, the $K_1$ value can be estimated as $1.19 \times 10^5$ J m$^{-3}$.

To reveal the origin of the improvement in the hard magnetic properties, magnetic domains in the samples were observed by magnetic force microscopy (MFM). The samples show (see Figure 3) distinctive feature of dark and bright stripe magnetic domain structure. The stripe domains are often observed in thin ferromagnetic films and platelets with weak perpendicular or oblique anisotropy. \[22\] In ferromagnetic films, the periodic width of strip domains is comparable to the film thickness. \[22\] However, the strip domain width in the Co$_{81.8}$Si$_{9.1}$B$_{9.1}$ ribbon is $\approx 90$ nm, which is much less than the thickness of the ribbon ($\approx 20$ μm). Instead, the period is very close to the longitudinal size of the nanocrystal grains. The stripe magnetic domains in the Co$_{81.8}$Si$_{9.1}$B$_{9.1}$ ribbons here should therefore mainly result from the anisotropic shape of CoSiB nanocrystals. As a result, the hard magnetic behavior of the materials can be further improved by tuning grain sizes.

For strip/slab-like domains, the domain thickness can be expressed as \[ D = \sqrt{\frac{\sigma L}{0.85M_S^2}}, \] (3)

where $\sigma$ is the domain wall energy per unit area and $L$ is the thickness of crystal (here the ribbon). The total energy for multi-domain structure is \[ E = 2M_S\sqrt{0.85}\sigma L = 1.7DM_S^2. \] (4)

Note that Co-based nanomaterials or thin films generally have similar domain thickness but much larger saturated moment, leading to higher energy. Thus the present compound has a more stable domain structure.

To understand the origin of the special structure and magnetism of the present Co$_{81.8}$Si$_{9.1}$B$_{9.1}$ phase, the electronic structures around Fermi level of Co$_{81.8}$Si$_{9.1}$B$_{9.1}$ phase, HCP Co and a soft magnetic CoSiB alloy Co$_{63.1}$B$_{27}$Si$_{9.9}$ were measured. Because the major phase after crystallization of soft magnetic CoSiB amorphous alloy is generally the FCC Co structure, the electronic structure of soft magnetic CoSiB amorphous alloy should be similar to that of FCC Co. \[9,23\]

Compared with the electronic structures of HCP Co (see Figure 4), many soft magnetic CoSiB alloys show similar feature around the Fermi level, viz. peak electronic density of state (DOS, N(E)) at Fermi level. \[9,23\] Both HCP Co and CoSiB amorphous alloy have large DOS close to the peak value at their Fermi level, while the FCC Co$_{81.8}$Si$_{9.1}$B$_{9.1}$ exhibits a small DOS at the Fermi level. It is evident that the FCC Co$_{81.8}$Si$_{9.1}$B$_{9.1}$ is more stable than both HCP Co and amorphous CoSiB alloys. As the electronic
structure around the Fermi level determines the magnetic behaviors, the Co atoms in both HCP Co and amorphous CoSiB show similar magnetic moment, in agreement with literatures. For the FCC Co$_{91.8}$Si$_{9.1}$B$_{9.1}$, the shift of peak towards high binding energy indicates that the strong interactions between Co and B/Si leads to the delocalization of Co 3d electrons and thus low Co moments. Such delocalization yielding significantly reduced magnetic moments was also observed in FeBY glassy alloys.[24]

Magnetocrystalline anisotropy results from mainly spin–orbit coupling.[25] Due to the large magnetocrystalline anisotropy, the spin–orbit coupling will enhance the Co 3d band splitting (lower the occupied orbits and elevate the unoccupied orbits) and thus the spin–spin interaction will also be reduced. The dilute effects of Co and Si may also reduce the Co-Co interactions, and thus exchange interaction in the Co$_{91.8}$Si$_{9.1}$B$_{9.1}$ compound will be smaller than Co or other Co-based materials and less 3d electrons can be excited into spin up state. As a result, more 3d electrons will take the orbits of the lowest energy and act as itinerant electrons. It will lead to a low electronic density of states at Fermi level as observed in Figure 4, accounting for significantly reduced Ms and enhanced structural stability of the phase. However, the spin–orbit coupling is mainly determined by crystal field and can be tuned by the symmetry or distortion of atomic clusters by controlling the compositions, because the N(E$_f$) of Co$_{91.8}$Si$_{9.1}$B$_{9.1}$ is much lower than that of Co or CoSiB amorphous materials.

In conclusion, based on the Co$_{9}$B cluster extracted from FCC Co$_{92}$B$_{9}$, the low-cost FCC Co$_{91.8}$Si$_{9.1}$B$_{9.1}$ ribbon was successfully produced. Despite the high content of metalloid Si and B, the as-spun ribbons are ductile and show significantly enhanced hard magnetic behaviors with a room-temperature coercivity of 430 Oe. The domain structure with a thickness close to the critical grain size is more stable than Co-based nanomaterials and thin film. The structural stability and special magnetism of the present materials are related to the delocalization of Co 3d band as revealed by the experimental electronic structures. The results also show that the hard magnetic behaviors can be further improved without destruction of the structure, although a balance between structural stability and magnetic performance has to be taken into account.

**Experimental Section**

**Synthesis of FCC Co$_{81.8}$Si$_{9.1}$B$_{9.1}$:** The mixtures (10 g) of pure constituent elements Co (99.9 wt.%), Si (99.9 wt.%), and B particles (99.9 wt.%) were melted under a Ti-gettered argon atmosphere. The alloy ingots were remelted four times to improve compositional homogeneity. Using these master ingots, at气氛. The alloy ingots were remelted four times to improve compositional homogeneity. Using these master ingots, constituent elements Co (99.99 wt.%), Si (99.99 wt.%), and B (99.9 wt.%) were produced by a single roller melting-spinning apparatus at a wheel surface velocity of 40 m s$^{-1}$. Ribs were produced by a single roller melting-spinning apparatus at a wheel surface velocity of 40 m s$^{-1}$. Ribs were thinned by twin-jet electropolishing using a HClO$_4$-C$_2$H$_5$OH solution (volume ratio 1:8) at $\approx$ 30 $^\circ$C. These specimens were finally cleaned by low-angle ion milling for no more than 5 min for TEM observation. Magnetic measurements were carried out using an X-ray photoelectron spectroscopy (XPS) with a monochromatized Al Kα radiation (1486.6 eV) in an ULVAC-PHI 5802 system (Kanagawa, Japan). Before the measurement, depth profiling up to 270 nm was done to inspect the depth for stable states (120 nm for Co$_{81.8}$Si$_{9.1}$B$_{9.1}$).

**Conflict of Interest**

The authors declare no conflict of interest.

**Keywords**

atomic cluster, cobalt, magnetization, magnetocrystalline anisotropy

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