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# **Anisotropic Elastic Constants and Thermal Expansivities in Monocrystal CrB<sub>2</sub>, TiB<sub>2</sub>, and ZrB<sub>2</sub>**

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## **Abstract**

The elastic constants and thermal expansivities in monocrystals of three transition-metal diborides with the AlB<sub>2</sub> structure, CrB<sub>2</sub>, TiB<sub>2</sub> and ZrB<sub>2</sub> have been investigated in the temperature range from 300 to 1373K and from 300 to 1073K, respectively. The anisotropic parameters deduced from the measured elastic constants and thermal expansivities indicate that of the three diborides, the anisotropy is the most and least significant in CrB<sub>2</sub> and ZrB<sub>2</sub>, respectively. The factors determining the significance in anisotropy in atomic bonding in AlB<sub>2</sub>-type diborides are analyzed by an approach similar to the valence-force-field method and are discussed in terms of the deformation of the electronic charge around the metal atoms occurring to fit themselves in the (0001) basal plane.

**Keywords:** Borides; Transition-metals; Monocrystals; Anisotropy; High temperatures

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## 1. Introduction

Many transition-metal diborides,  $MB_2$  (M: transition-metal atom) with the hexagonal  $AlB_2$  structure (space group:  $P6/mmm$ ) exhibit a wide variety of attractive properties such as high melting temperature, high stiffness and hardness, and high electrical and thermal conductivity [1-3] and thus have many different applications. For example,  $TiB_2$  has often been used as reinforcements in various composite materials such as steel [4].  $TiB_2$  has also been considered in applications in diffusion barriers for preventing electromigration in very large-scale integrated (LSI) circuits because of the very low diffusion coefficient [5].  $ZrB_2$  and  $HfB_2$  have long been used as refractory crucibles and sheaths in steel making industries because of their high corrosion-resistance [6]. In addition,  $ZrB_2$  is recently under consideration for the use as a substrate for heteroepitaxial growth of GaN because of small mismatches in lattice constants and thermal expansivities with GaN [7-12].

The hexagonal  $AlB_2$  structure, into which these transition-metal diborides crystallize, is build up of hexagonal nets of pure transition-metal atoms and triangle nets of pure boron atoms, which are alternately stacked along the  $c$ -axis, as shown in Fig. 1. The crystal structure can hence be regarded as a layered structure. If we describe the crystal structure as a packing of touching spheres with  $R_M$  and  $R_B$  (radii of M and B atoms), simple geometrical consideration gives the M-M distance ( $=2R_M$ ) as  $a$ , the B-B distance ( $=2R_B$ ) as  $a/3^{1/2}$  and the M-B distance ( $=R_M + R_B$ ) as  $(a^2/3 + c^2/4)^{1/2}$ , where  $a$  and  $c$  denote the lattice constants along the  $a$ - and  $c$ - axes, respectively. Hence, the ideal  $c/a$  axial ratio of 1.0746 ( $=(4/3)^{1/4}$ ) is deduced together with the ideal atomic size ratio  $R_M/R_B = 3^{1/2} = 1.732$ . In fact,  $c/a$  axial ratios for many transition-metal diborides are close to the above ideal value as shown in the left-hand side of Fig. 2 [13] while those for lanthanoid-metal diborides are larger than the ideal value as shown in the right-hand side of the figure. Close examination of the  $c/a$  axial ratios indicates that the  $c/a$  axial ratios of some diborides formed with, for example, Cr, V and

Ta are a little smaller than the ideal value, while those of other diborides formed with, for example, Hf, Zr and most of lanthanoid-metals are a little larger than the ideal one, and that diborides formed with Al, Ti and Nb possess the  $c/a$  axial ratios very close to the ideal value. When considering the fact that the crystal structure can be regarded as a layered structure, physical properties are expected to be highly anisotropic and the extent of the anisotropy varies from diboride to diboride, depending on their  $c/a$  axial ratios. However, because mainly of the inherent difficulty in growing monocrystals of transition-metal diborides due to their high melting points (usually exceeding 2500 K, see Table 1) [14-16], almost nothing is known about how their physical properties vary with crystallographic directions (anisotropy) and how the extent of anisotropy varies from diboride to diboride for most of these transition-metal diborides.

In the present study, we investigate monocrystal elastic constants and thermal expansivities as a function of crystal orientation with the use of monocrystals of  $\text{CrB}_2$ ,  $\text{TiB}_2$  and  $\text{ZrB}_2$ , whose  $c/a$  axial ratios are smaller than, almost identical with and larger than the ideal value, respectively, as shown in Fig. 2 and Table 1. We discuss anisotropy in physical properties of these transition-metal diborides in terms of chemical bondings.

## 2. Experimental procedures

Monocrystals of  $\text{CrB}_2$  were grown with an optical floating-zone furnace while those of  $\text{TiB}_2$  and  $\text{ZrB}_2$  were grown with a radio-frequency (RF) heated floating-zone furnace as described previously [17, 18]. After determining the crystallographic orientations by the X-ray back reflection Laue method, specimens with a rectangular parallelepiped shape having three orthogonal faces parallel to the  $(0001)$ ,  $(11\bar{2}0)$  and  $(1\bar{1}00)$  planes were cut from the crystals by spark-machining. Then, the specimen surface was mechanically polished with diamond paste. The maximum error in parallelism for each face was at most  $3\ \mu\text{m}/\text{mm}$ . The

deviation from the respective crystallographic orientation was smaller than  $0.2^\circ$  for each face. The dimensions of specimens used for the measurements of elastic constants and thermal expansivities are summarized in Table 2.

Measurements of elastic constants were carried out by the rectangular parallelepiped resonance (RPR) method [19] in the temperature range from room temperature to 1373K. In this method, all elastic constants are derived from the frequencies of resonance vibrations of specimen [19]. Measurements of thermal expansivities were carried out with a push-rod type differential dilatometer (Shimadzu TMA-60) in the temperature range from room temperature to 1073 K at the heating rate of 5 K per minute under an Ar gas flow.

### 3. Results

#### 3.1. Monocrystal elastic constants

Monocrystal elastic constants of  $\text{CrB}_2$ ,  $\text{TiB}_2$  and  $\text{ZrB}_2$  are plotted respectively in Figs. 3(a)-(c) as a function of temperature. Values of  $c_{11}$ ,  $c_{33}$  and  $c_{44}$  decrease monotonically with the increase in temperature, while those of  $c_{12}$  and  $c_{13}$  are virtually temperature independent for all transition-metal diborides investigated. Although actual temperature dependence of elastic constants is slightly nonlinear even in very-well-behaved materials, these data points for each of the five elastic constants are fitted to a linear equation in the form of

$$c_{ij} = c_{ij(300K)} + k(T - 300), \quad (1)$$

where  $c_{ij(300K)}$ ,  $k$  and  $T$  stand respectively for the elastic constant at 300 K, numerical constant and temperature in Kelvin, as tabulated in Table 3. The values of elastic constants for  $\text{TiB}_2$  determined in the present study agree well with those previously reported by Spoor et al. [20] but not completely with those reported by Gilman et al. [21]. In particular, the values of  $c_{12}$  and  $c_{13}$  determined in the present study are considerably smaller than those reported by Gilman et al. [21]. While the values of  $c_{12}$  and  $c_{13}$  for  $\text{CrB}_2$  are comparable to that of  $c_{44}$ , those

of  $c_{12}$  and  $c_{13}$  for  $\text{TiB}_2$  and  $\text{ZrB}_2$  are notably smaller than those of the other constants, indicating the brittleness of  $\text{TiB}_2$  and  $\text{ZrB}_2$ . The values of anisotropic parameters defined in crystals with the hexagonal symmetry as  $c_{33}/c_{11}$  and  $c_{44}/c_{66}$  are both the largest for  $\text{ZrB}_2$  and the smallest for  $\text{CrB}_2$ , as tabulated in Table 3.

The orientation dependence of Young modulus on  $(1\bar{1}00)$  prism plane at 300 and 1373 K is depicted in Fig. 4(a) for  $\text{CrB}_2$ ,  $\text{TiB}_2$  and  $\text{ZrB}_2$ . The curves in Fig. 4(a) are calculated with the following equation [22]:

$$1/E = s_{11} \cdot \sin^4 \theta + s_{33} \cdot \cos^4 \theta + (s_{44} + 2s_{13}) \sin^2 \theta \cdot \cos^2 \theta, \quad (2)$$

where  $\theta$  is the angle between the corresponding loading direction and the  $c$ -axis,  $E$  is Young modulus along the loading direction, and  $s_{ij}$  is elastic compliance constants. The values of Young modulus increase monotonically as the angle  $\theta$  increases for  $\text{CrB}_2$  and  $\text{TiB}_2$ , whereas those for  $\text{ZrB}_2$  exhibit a maximum along a direction approximately  $\theta=60^\circ$  at both 300 and 1373 K. The values of Young modulus along the  $a$ - ( $E_a$ ) and  $c$ -axes ( $E_c$ ) at 300 K as well as their ratio ( $E_c/E_a$ ) are tabulated in Table 4 for  $\text{CrB}_2$ ,  $\text{TiB}_2$  and  $\text{ZrB}_2$ . The value of  $E_c/E_a$  increases in the order of  $\text{CrB}_2$ ,  $\text{TiB}_2$  and  $\text{ZrB}_2$ . The values of  $E_a$  and  $E_c$  are both the largest for  $\text{TiB}_2$  and the smallest for  $\text{CrB}_2$ , but the value of  $E_c/E_a$  is the largest for  $\text{ZrB}_2$  and the smallest for  $\text{CrB}_2$ .

Linear compressibilities along the  $a$ - and  $c$ -axes,  $\beta_a$  and  $\beta_c$ , for a hexagonal crystal can be defined with the following equations [22];

$$\beta_a = s_{11} + s_{12} + s_{13}, \quad (3)$$

$$\beta_c = 2s_{13} + s_{33}. \quad (4)$$

The reciprocal values of  $\beta_a$  and  $\beta_c$  and their ratio at 300 K are tabulated in Table 4 for  $\text{CrB}_2$ ,  $\text{TiB}_2$  and  $\text{ZrB}_2$ . The value of  $\beta_a^{-1}$  is the largest for  $\text{CrB}_2$  and is the smallest for  $\text{ZrB}_2$ , but that of  $\beta_c^{-1}$  is the largest for  $\text{ZrB}_2$  and is the smallest for  $\text{CrB}_2$ . The value of  $\beta_c^{-1}/\beta_a^{-1}$  is the largest for  $\text{ZrB}_2$  and the smallest for  $\text{CrB}_2$ .

### 3.2. Polycrystalline elastic moduli

Polycrystalline elastic moduli are evaluated from the monocrystal elastic constants by the Hill's method [23]. The temperature dependence of Young ( $E$ ), bulk ( $B$ ) and shear ( $G$ ) moduli as well as that of Poisson ratio are illustrated in Figs. 5(a)-(c) respectively for  $\text{CrB}_2$ ,  $\text{TiB}_2$  and  $\text{ZrB}_2$ . As in the case of monocrystal elastic constants, the values of Young, bulk and shear moduli all decrease monotonically with increasing temperature. While the values of shear modulus are comparable with those of bulk modulus for  $\text{TiB}_2$  and  $\text{ZrB}_2$ , those of shear modulus are smaller than those of Young and bulk moduli for  $\text{CrB}_2$ . This is because of the exceptionally small values of  $c_{44}$  for  $\text{CrB}_2$  as shown in Fig. 3(a). Although the bulk moduli of the pure transition metals differ considerably [Cr: 190; Ti: 105; Zr: 83 (GPa)] [24], those of the boride compounds are similar, indicating the strong role of covalent B-B bonding. The values of Poisson ratio generally increase with increasing temperature and range from 0.206 to 0.230, from 0.112 to 0.123, and from 0.133 to 0.151 for  $\text{CrB}_2$ ,  $\text{TiB}_2$  and  $\text{ZrB}_2$ , respectively. The small values of Poisson ratio again indicate the strong covalence in these diborides. The data points for each of these polycrystalline elastic moduli as well as Poisson ratio are fitted to a linear equation in the form of Eq. (1). The values of polycrystalline elastic moduli and Poisson ratio at 300 K are tabulated in Table 5 for  $\text{CrB}_2$ ,  $\text{TiB}_2$  and  $\text{ZrB}_2$ , together with the numerical constants in the fitting equation.

### 3.3. Thermal expansivities

Thermal expansivity data obtained along the  $a$ - and  $c$ -axes as relative elongation with respect to the original specimen length at room temperature were fitted with a quartic function. Thermal expansivities were, then, derived by differentiating the fitted quartic function with respect to temperature. The values of thermal expansivities thus determined are plotted in Figs.



6(a)-(c) as a function of temperature for CrB<sub>2</sub>, TiB<sub>2</sub> and ZrB<sub>2</sub>, respectively. For CrB<sub>2</sub>, the value of thermal expansivity along the *a*-axis ( $\alpha_a$ ) is as large as  $14.0 \times 10^{-6} \text{ K}^{-1}$  at room temperature and rapidly decreases with increasing temperature up to around 700K, followed by a slight increase at higher temperatures. On the other hand, the value of thermal expansivity along the *c*-axis ( $\alpha_c$ ) for CrB<sub>2</sub> is as small as  $2.9 \times 10^{-6} \text{ K}^{-1}$  at room temperature and monotonically increases with increasing temperature. We consider that the unusual temperature dependence of thermal expansivities for CrB<sub>2</sub> may be related to the magnetic thermal expansion due to the antiferromagnetism of CrB<sub>2</sub> as reported by Nishihara et al. [25]. On the other hand, the temperature dependence of thermal expansivities along the *a*- and *c*-axes for TiB<sub>2</sub> and ZrB<sub>2</sub> is rather small when compared to that for CrB<sub>2</sub>. The value of thermal expansivity along the *c*-axis is considerably larger (by almost 50 %) than the corresponding value along the *a*-axis for TiB<sub>2</sub>. For ZrB<sub>2</sub>, on the other hand, the value of thermal expansivity along the *c*-axis is slightly larger than the corresponding value along the *a*-axis at temperatures below around 700K while they are virtually identical to each other at higher temperatures. The values of thermal expansivities averaged over the temperature range from 300 to 1073 K are tabulated in Table 6, together with the ratio of the thermal expansivities along the *a*- and *c*-axes.

#### 4. Discussion

The anisotropic parameters in elasticity,  $c_{33}/c_{11}$ ,  $c_{44}/c_{66}$ ,  $E_c/E_a$  and  $\beta_c^{-1}/\beta_a^{-1}$  for CrB<sub>2</sub>, TiB<sub>2</sub> and ZrB<sub>2</sub> are plotted in Fig. 7 as a function of the magnitude of their *a*-axis lattice constant together with those in thermal expansivity,  $\alpha_c/\alpha_a$ . All the anisotropic parameters in elasticity are smaller than unity whereas those of thermal expansivity are larger than unity (except for the  $\alpha_c/\alpha_a$  value for CrB<sub>2</sub>), indicating that atomic bonding along the *a*-axis is stronger than that along the *c*-axis for all the diborides, which is consistent with the fact that

the  $AlB_2$ -type crystal structure is of the layered-type, in which hexagonal nets of pure transition-metal atoms and pure boron atoms stacked alternatively along the  $c$ -axis. Of the three diborides, the anisotropy is the least significant in  $ZrB_2$  since the values of  $c_{44}/c_{66}$  and  $\alpha_c/\alpha_a$  are close to unity. This is somewhat surprising when considering the fact that  $ZrB_2$  exhibits the largest value of the  $c/a$  axial ratio, since the ratio of the strength of atomic bonding along the  $c$ -axis to that along the  $a$ -axis is considered to be the smallest on the rough assumption that the atomic bond strength decreases with the increase in the bond distance. In the following, we will discuss some possible reasons why  $ZrB_2$  with the largest  $c/a$  axial ratio exhibits the least significant anisotropic behavior and vice versa.

If the B-B distance in the (0001) plane of an  $AlB_2$ -type metal diboride is assumed to be identical with the covalent bonding distance of B atoms in pure  $\alpha$ -boron (0.176 nm) [26], the magnitude of the  $a$ -axis lattice constant of the diboride should be 0.305 nm since the B-B distance ( $=2R_B$ ) corresponds to  $a/3^{1/2}$ , as described in Introduction section. On the basis of a packing of touching spheres of M and B atoms in describing the crystal structure, the Goldschmidt radius ( $R_{M(G)}$ ) of the M atom should be 0.152 nm as the M-M distance ( $=2R_M$ ) corresponds to  $a$ . This value of the Goldschmidt radius ( $R_{M(G)}$ ) for the M atom is designated as the ideal Goldschmidt radius ( $R_{M(ideal)}$ ). In this circumstance, the ideal  $c/a$  axial ratio of 1.0746 ( $=(4/3)^{1/4}$ ) is achieved with the ideal atomic size ratio  $R_M/R_B = 3^{1/2}=1.732$ . This is almost completely achieved for  $TiB_2$  with the Goldschmidt radius ( $R_{Ti(G)}$ ) of 0.146 nm [27]. However, if the constituent M atom in a metal diboride possesses  $R_{M(G)}$  larger than the ideal value ( $R_{M(ideal)}=0.152$  nm), the diboride should expand along the  $a$ -axis in the (0001) plane so as to make the B-B distance larger than 0.176 nm. This corresponds to the case of  $ZrB_2$ , in which the B-B distance is 0.1807 nm. However, this expansion along the  $a$ -axis is not sufficient to allow Zr atoms packed hexagonally in the (0001) plane in  $ZrB_2$  and there still exist the overlapping of Zr atom spheres, as shown in Fig. 8(a). Then, the electronic charge

around Zr atoms in ZrB<sub>2</sub> is considered to deform to elongate along the *c*-axis (Fig. 8(b)). As a result, the interaction along the *c*-axis is expected to become relatively stronger in spite of the *c/a* axial ratio (1.129) larger than the ideal one (1.0746). The atomic bonding in ZrB<sub>2</sub> is thus considered to be more isotropic than that in TiB<sub>2</sub>.

On the other hand, if the constituent M atom of a metal diboride possesses  $R_{M(G)}$  smaller than the ideal value, the diboride should contract along the *a*-axis in the (0001) plane. This corresponds to the case of CrB<sub>2</sub> whose *a*-axis lattice constant (0.2973 nm) [13] is smaller than the ideal one (0.305 nm). This contraction along the *a*-axis for CrB<sub>2</sub> is not sufficient for hexagonally-arranged spheres of Cr atoms to touch each other in the (0001) plane and the Cr atom spheres are left separated in the (0001) plane, as shown in Fig. 8(c). Then, the electronic charge around Cr atoms in CrB<sub>2</sub> is considered to deform to elongate along the *a*-axis (Fig. 8(d)). As a result, the interaction along the *c*-axis is expected to become relatively weaker in spite of the *c/a* axial ratio (1.033) smaller than the ideal one (1.0746). The anisotropy in atomic bonding is thus considered to be more significant in CrB<sub>2</sub> than in TiB<sub>2</sub>.

The fact that the relative atomic bond strength in basal plane (along the *a*-axis) with respect to that out of basal plane (along the *c*-axis) increases in the order of ZrB<sub>2</sub>, TiB<sub>2</sub> and CrB<sub>2</sub> can be quantitatively validated by deriving force constants both in and out of basal plane from their elastic constants. These force constants are analyzed by adopting an approach similar to the valence-force-field method [28-31]. In this approach, all interatomic forces are resolved into bond-stretching and bond-bending forces and the elastic properties are described with the force constants corresponding to these two forces. Because of the strong role of covalent B-B bonding, the bond-bending (non-central) forces in CrB<sub>2</sub>, TiB<sub>2</sub> and ZrB<sub>2</sub> are considered to be significant. However, we here consider only the bond-stretching (central) interaction between a given atom and its first-nearest-neighbor atoms in order to deduce the bond-stretching force constants in and out of basal plane from the experimentally determined

elastic constants [32]. If we ignore the bond-bending interaction, the total elastic energy of a metal diboride,  $U$  can be written as follows,

$$U = k_a \sum_i (\Delta r_i)^2 + k_c \sum_i (\Delta r_i)^2, \quad (5)$$

where  $k_a$  and  $k_c$  are the force constants in and out of basal plane, respectively, and  $\Delta r_i$  is the change in the bond length between the given atom and the  $i$ th first-nearest-neighbor atom. The magnitude of  $\Delta r_i$  is calculated for the deformation matrix  $\boldsymbol{\varepsilon}$  by the following equation,

$$\Delta r_i = \frac{\mathbf{r}_i \cdot \boldsymbol{\varepsilon} \cdot \mathbf{r}_i^t}{|\mathbf{r}_i|^2}, \quad (6)$$

where  $\mathbf{r}_i$  is a position (row) vector for the  $i$ th first-nearest-neighbor atom while  $\mathbf{r}_i^t$  is the transposed (column) vector of  $\mathbf{r}_i$ . The elastic constants are derived as the second derivative of Eq. (5) as follows,

$$c_{ij} = \frac{d^2}{d\varepsilon^2} U(\boldsymbol{\varepsilon}), \quad (7)$$

where  $\varepsilon$  is the magnitude of strain corresponding to  $c_{ij}$ . We will express  $c_{44}$  and  $c_{66}$  with the force constants, since the change in anisotropy in elastic properties for  $\text{CrB}_2$ ,  $\text{TiB}_2$  and  $\text{ZrB}_2$  is best described with the  $c_{44}/c_{66}$  ratio (Fig. 7) although hexagonal crystals provide anisotropic parameters of  $c_{13}/c_{12}$ ,  $c_{33}/c_{11}$ ,  $c_{44}/(c_{11}-c_{12})$  and so forth other than  $c_{44}/c_{66}$ . If the following deformation matrices are used,

$$\boldsymbol{\varepsilon}(c_{44}) = \frac{1}{2} \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & \varepsilon \\ 0 & \varepsilon & 0 \end{pmatrix}, \quad \boldsymbol{\varepsilon}(c_{66}) = \frac{1}{2} \begin{pmatrix} 0 & \varepsilon & 0 \\ \varepsilon & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \quad (8)$$

the elastic constants  $c_{44}$  and  $c_{66}$  are deduced with the force constants  $k_a$  and  $k_c$  as follows,

$$c_{44} = 0k_a + 48 \left( \frac{\sqrt{3}(c/a)}{4 + (c/a)^2} \right)^2 k_c, \quad (9)$$

$$c_{66} = 3k_a + 16 \left( \frac{\sqrt{3}}{4 + (c/a)^2} \right)^2 k_c. \quad (10)$$

The constants of the second term in Eqs. (9) and (10) vary with the  $c/a$  axial ratio and the values for  $\text{CrB}_2$ ,  $\text{TiB}_2$  and  $\text{ZrB}_2$  are tabulated in Table 7. The ratio of  $k_a/k_c$  with which the value of  $c_{44}/c_{66}$  coincides with the experimentally determined value is tabulated in Table 7. The ratio of  $k_a/k_c$  is the largest for  $\text{CrB}_2$  and is the smallest for  $\text{ZrB}_2$ , which is consistent with our qualitative expectation that the ratio of the atomic bond strength in basal plane to that out of basal plane is the largest for  $\text{CrB}_2$  and is the smallest for  $\text{ZrB}_2$ .

The value of  $R_{\text{M(G)}}-R_{\text{M(ideal)}}$  is thus considered to be a good indicator for predicting the extent of the anisotropy in atomic bonding in metal diborides with the  $\text{AlB}_2$  structure. The values of the anisotropic parameters  $c_{44}/c_{66}$  derived by ab-initio calculations by Shein et al. [33] are plotted in Fig. 9 as a function of the value of  $R_{\text{M(G)}}-R_{\text{M(ideal)}}$ . The experimental values of  $c_{44}/c_{66}$  for  $\text{CrB}_2$ ,  $\text{TiB}_2$  and  $\text{ZrB}_2$  determined in the present study are also plotted with solid circles in the figure. The values of  $c_{44}/c_{66}$  for all the metal diborides except for  $\text{MgB}_2$  and  $\text{AlB}_2$  generally increase with the increase in the value of  $R_{\text{M(G)}}-R_{\text{M(ideal)}}$ . This is consistent with what is discussed in the present paper in terms of the anisotropy in atomic bonding of  $\text{AlB}_2$ -type borides; the significance in anisotropy in atomic bonding is reduced as the Goldschmidt radius ( $R_{\text{M(G)}}$ ) of the M atom and thereby the  $c/a$  axial ratio of the  $\text{AlB}_2$ -type borides increases due to the occurrence of the elongation of the electronic charge around the M atom along the  $c$ -axis by an amount corresponding to the value of  $R_{\text{M(G)}}-R_{\text{M(ideal)}}$ . The values of  $c_{44}/c_{66}$  for  $\text{MgB}_2$  and  $\text{AlB}_2$  are exceptionally small. This may be because the bonding nature for metal diborides without  $d$  electrons is quite different from that for metal diborides with  $d$  electrons.

## 5. Conclusions

(1) All the five independent monocrystal elastic constants of  $\text{CrB}_2$ ,  $\text{TiB}_2$  and  $\text{ZrB}_2$  have been determined in the temperature range from 300 to 1373K. The anisotropic parameters of  $c_{33}/c_{11}$

and  $c_{44}/c_{66}$  as well as the ratios of the Young moduli and reciprocals of linear compressibilities along the  $a$ - and  $c$ -axes ( $E_c/E_a$ ,  $\beta_c^{-1}/\beta_a^{-1}$ ) are smaller than unity. These anisotropic parameters decrease in the order of ZrB<sub>2</sub>, TiB<sub>2</sub> and CrB<sub>2</sub>. The small values of Poisson ratio (CrB<sub>2</sub>: 0.207, TiB<sub>2</sub>: 0.111, ZrB<sub>2</sub>: 0.135 at 300 K) indicate the strong covalence in these diborides.

(2) The values of thermal expansivities along the  $a$ - and  $c$ -axes of CrB<sub>2</sub>, TiB<sub>2</sub> and ZrB<sub>2</sub> have been determined in the temperature range from 300 to 1073K. The temperature dependence of the thermal expansivities along the  $a$ - and  $c$ -axes for CrB<sub>2</sub> is considerably large whereas that for TiB<sub>2</sub> and ZrB<sub>2</sub> is relatively small. The ratio of the thermal expansivities along the  $a$ - and  $c$ -axes ( $\alpha_c/\alpha_a$ ) for TiB<sub>2</sub> is larger than that for ZrB<sub>2</sub>.

(3) The ratio of the bond strength out of basal plane to that in basal plane increases in the order of CrB<sub>2</sub>, TiB<sub>2</sub> and ZrB<sub>2</sub>, as evidenced with the force constant ratio of  $k_a/k_c$  calculated by an approach similar to the valence-force-field method. The significance in anisotropy in atomic bonding in AlB<sub>2</sub>-type diborides is reduced as the Goldschmidt radius ( $R_{M(G)}$ ) of the M atom and thereby the  $c/a$  axial ratio of the AlB<sub>2</sub>-type borides increases due to the occurrence of the elongation of the electronic charge around the M atom along the  $c$ -axis by an amount corresponding to the value of  $R_{M(G)} - R_{M(\text{ideal})}$ .

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force constants becomes as many as six, which is larger than that of independent elastic constants (five) so that the force constants cannot be deduced from the experimentally determined elastic constants. We can consider six different bond-bending terms: M-M-M, B-B-B, B-M-B, M-B-M, M-M-B and B-B-M. The force constants in the first and second terms are linearly dependent, and so are those in the third and fourth terms. However, the force constants in the fifth and sixth terms are linearly independent. Thus, the number of independent force constants for bond-bending terms is four, producing six in total including force constants for bond-stretching terms (two independent force constants as stated in the text).

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## Figure captions

- Fig. 1. (Color online) (a) Crystal structure of metal diborides with the hexagonal  $AlB_2$  structure. The frame indicates a unit cell. Projection of the crystal structure along the (b)  $[0001]$  and (c)  $[11\bar{2}0]$  directions.
- Fig. 2. Experimental lattice constants of various metal diborides with the  $AlB_2$  structure. Data are taken after Ref. 13.
- Fig. 3. (Color online) Five independent monocrystal elastic constants of (a)  $CrB_2$ , (b)  $TiB_2$  and (c)  $ZrB_2$  plotted as a function of temperature. Experimental error bars are smaller than the symbol sizes.
- Fig. 4. (Color online) Orientation dependence of Young modulus at 300 and 1373 K on  $(1\bar{1}00)$  prism plane for  $CrB_2$ ,  $TiB_2$  and  $ZrB_2$ .
- Fig. 5. (Color online) Young, bulk, shear moduli and Poisson ratio for polycrystals of (a)  $CrB_2$ , (b)  $TiB_2$  and (c)  $ZrB_2$  plotted as a function of temperature. Experimental error bars for moduli are smaller than the symbol sizes.
- Fig. 6. (Color online) Thermal expansivities for (a)  $CrB_2$ , (b)  $TiB_2$  and (c)  $ZrB_2$  along the  $a$ - and  $c$ -axes plotted as a function of temperature.
- Fig. 7. (Color online) Anisotropic parameters in elasticity,  $c_{33}/c_{11}$ ,  $c_{44}/c_{66}$ ,  $E_c/E_a$  and  $\beta_c^{-1}/\beta_a^{-1}$  for  $CrB_2$ ,  $TiB_2$  and  $ZrB_2$  as well as those in thermal expansivities,  $\alpha_c/\alpha_a$ , plotted as a function of the magnitude of their  $a$ -axis lattice constant. Experimental error bars are smaller than the symbol sizes.
- Fig. 8. (Color online) Schematics of the distribution of the electronic charge around M atoms in the  $(0\bar{1}10)$  plane. The value of  $R_{M(G)} - R_{M(ideal)}$  is (a,b) positive and (c,d) negative. (a,c) Uniform and (b,d) non-uniform distributions of the electronic charge around the M atoms are assumed.
- Fig. 9. Anisotropic parameters of  $c_{44}/c_{66}$  for several metal diborides derived by ab-initio

calculations [33] (open circles) and those for CrB<sub>2</sub>, TiB<sub>2</sub> and ZrB<sub>2</sub> experimentally determined in the present study (solid circles) plotted as a function of the value of  $R_{M(G)} - R_{M(ideal)}$ . Experimental error bars are smaller than the symbol sizes.

Table 1. Lattice constants,  $c/a$  axial ratio, B-B atomic distance, melting temperature, Goldschmidt radius of the constituent metal atom,  $R_{M(G)}$ , and the difference between the Goldschmidt radius of the metal atom and the ideal one ( $R_{M(ideal)}$ ) for  $CrB_2$ ,  $TiB_2$ ,  $ZrB_2$ , and the ideal diboride.

	$a$ (nm)	$c$ (nm)	$c/a$	B-B (nm)	$T_m$ (K)	$R_{M(G)}$ (nm)	$R_{M(G)}-R_{M(ideal)}$ (nm)
$CrB_2$	0.2973 <sup>a</sup>	0.3072 <sup>a</sup>	1.033	0.1716	2473 <sup>b</sup>	0.128 <sup>f</sup>	-0.024
$TiB_2$	0.3038 <sup>a</sup>	0.3239 <sup>a</sup>	1.066	0.1754	3193 <sup>c</sup>	0.146 <sup>f</sup>	-0.006
$ZrB_2$	0.3130 <sup>a</sup>	0.3533 <sup>a</sup>	1.129	0.1807	3518 <sup>d</sup>	0.160 <sup>f</sup>	+0.008
Ideal	0.305	0.328	1.0746	0.176 <sup>e</sup>	-	0.152	0

<sup>a</sup> Ref. 13.

<sup>b</sup> Ref. 14.

<sup>c</sup> Ref. 15.

<sup>d</sup> Ref. 16.

<sup>e</sup> Ref. 26.

<sup>f</sup> Ref. 27.

Table 2. Dimensions of specimens used for the measurements of elastic constants and thermal expansivities.

Dimensions (mm)		CrB <sub>2</sub>	TiB <sub>2</sub>	ZrB <sub>2</sub>
Elastic constants	[0001]	2.819	2.395	3.762
	[11 $\bar{2}$ 0]	2.792	3.752	3.673
	[1 $\bar{1}$ 00]	2.452	2.788	3.694
Thermal expansivities (longitudinal axis)	<i>a</i> -axis	6.142	6.245	6.862
	<i>c</i> -axis	8.709	7.244	7.910

Table 3. Monocrystal elastic constants at 300 K in the form of  $c_{ij} = c_{ij(300K)} + k(T - 300)$  where  $c_{ij(300K)}$ ,  $k$  and  $T$  stand for the elastic constant at 300 K, numerical constant and temperature in Kelvin, respectively, and anisotropic parameters ( $c_{33}/c_{11}$  and  $c_{44}/c_{66}$ ) at 300 K. The numerical constants are shown in the parentheses. Previously reported monocrystal elastic constants for  $\text{TiB}_2$  are also tabulated for comparison [20, 21].

	$c_{11}$ (GPa)	$c_{33}$ (GPa)	$c_{12}$ (GPa)	$c_{13}$ (GPa)	$c_{44}$ (GPa)	$c_{66}^*$ (GPa)	$c_{33}/c_{11}$	$c_{44}/c_{66}$
$\text{CrB}_2$	583.7 (-0.0586)	343.3 (-0.0311)	117.3 (0.0044)	119.7 (-0.0044)	143.1 (-0.0284)	233.2 (-0.0315)	0.588	0.614
$\text{TiB}_2$	654.5 (-0.0412)	454.5 (-0.0305)	56.5 (0.0060)	98.4 (-0.0016)	263.2 (-0.0253)	299.0 (-0.0236)	0.694	0.880
$\text{TiB}_2^a$	660	432	48	93	260	306	0.655	0.850
$\text{TiB}_2^b$	690	440	410	320	250	140	0.638	1.786
$\text{ZrB}_2$	567.8 (-0.0431)	436.0 (-0.0294)	56.9 (0.0051)	120.5 (-0.0022)	247.5 (-0.0261)	255.4 (-0.0241)	0.768	0.969

\*  $c_{66} = (c_{11} - c_{12})/2$

<sup>a</sup> Ref. 20.

<sup>b</sup> Ref. 21.

Table 4. Values of Young moduli and reciprocals of linear compressibilities along the  $a$ - and  $c$ -axes at 300 K.

	Young moduli			Reciprocals of linear compressibilities		
	$E_a$ (GPa)	$E_c$ (GPa)	$E_c/E_a$	$\beta_a^{-1}$ (GPa)	$\beta_c^{-1}$ (GPa)	$\beta_c^{-1}/\beta_a^{-1}$
CrB <sub>2</sub>	531.4	302.4	0.569	948.2	459.3	0.484
TiB <sub>2</sub>	631.2	427.2	0.677	853.1	590.8	0.692
ZrB <sub>2</sub>	533.3	387.7	0.727	772.1	631.3	0.818

Table 5. Values of polycrystalline elastic moduli (Young ( $E$ ), bulk ( $B$ ), shear ( $G$ )) and Poisson ratio ( $\nu$ ) at 300 K obtained by linear fitting with Eq. (1). The numerical constants obtained by linear fitting are shown in the parentheses.

	$E$ (GPa)	$B$ (GPa)	$G$ (GPa)	$\nu$
$\text{CrB}_2$	422.5 (-0.0594)	240.2 (-0.0170)	175.0 (-0.0273)	0.206 ( $2.21 \times 10^{-5}$ )
$\text{TiB}_2$	583.5 (-0.0450)	250.0 (-0.0125)	262.6 (-0.0226)	0.111 ( $1.10 \times 10^{-5}$ )
$\text{ZrB}_2$	526.0 (-0.0457)	240.1 (-0.0127)	231.7 (-0.0225)	0.135 ( $1.32 \times 10^{-5}$ )



Table 6. Values of thermal expansivities averaged over the temperature range from 300 to 1073 K and the ratio of the thermal expansivities along the *a*- and *c*-axes.

	$\alpha_a$ ( $\times 10^{-6}$ [K <sup>-1</sup> ])	$\alpha_c$ ( $\times 10^{-6}$ [K <sup>-1</sup> ])	$\alpha_c/\alpha_a$
CrB <sub>2</sub>	9.66	8.81	0.91
TiB <sub>2</sub>	6.35	9.30	1.46
ZrB <sub>2</sub>	6.66	6.93	1.04

Table 7. Values of the coefficients of the second term in Eqs. (9) and (10) and the ratio of  $k_a/k_c$  with which the value of  $c_{44}/c_{66}$  coincides with the experimentally determined value.

	$c_{44}$	$c_{66}$	$k_a/k_c$
CrB <sub>2</sub>	2.963	0.925	1.30
TiB <sub>2</sub>	2.981	0.874	0.84
ZrB <sub>2</sub>	2.998	0.784	0.77

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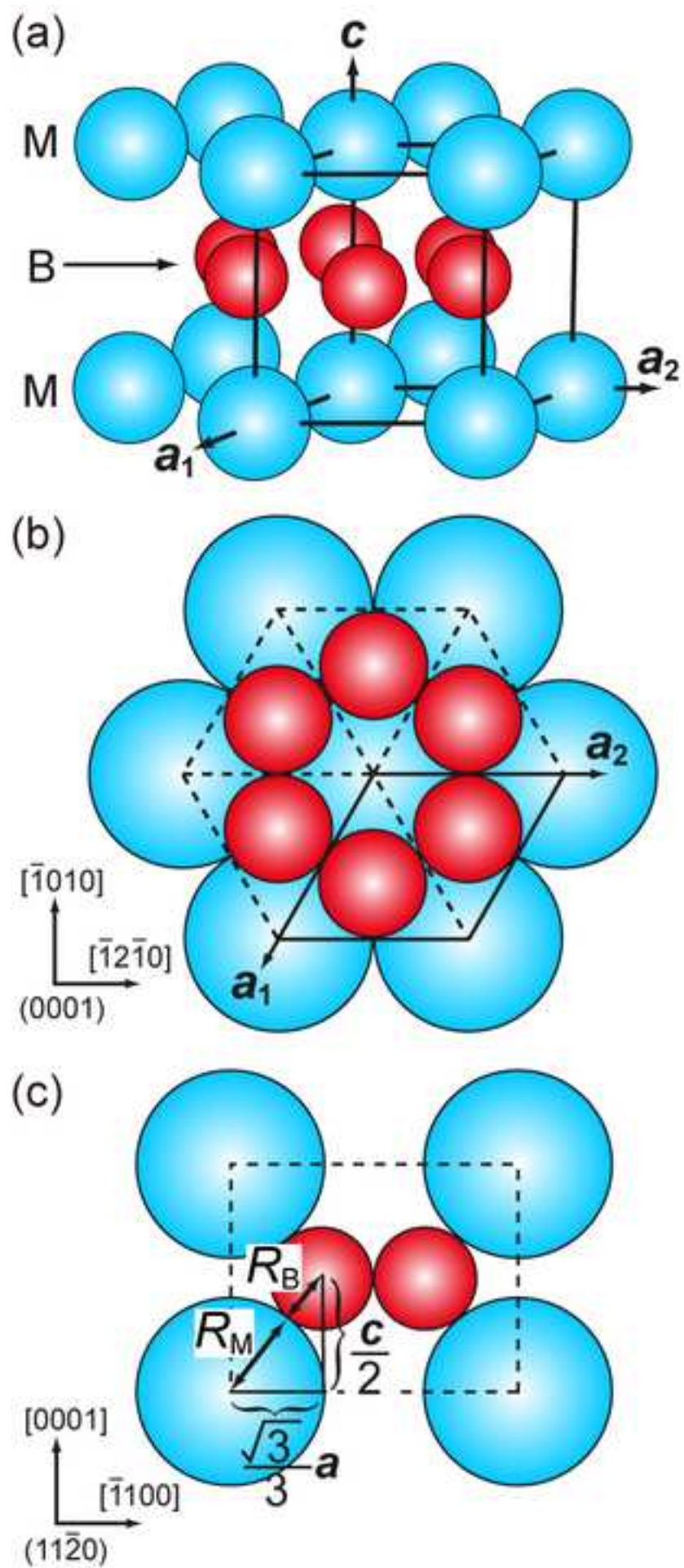


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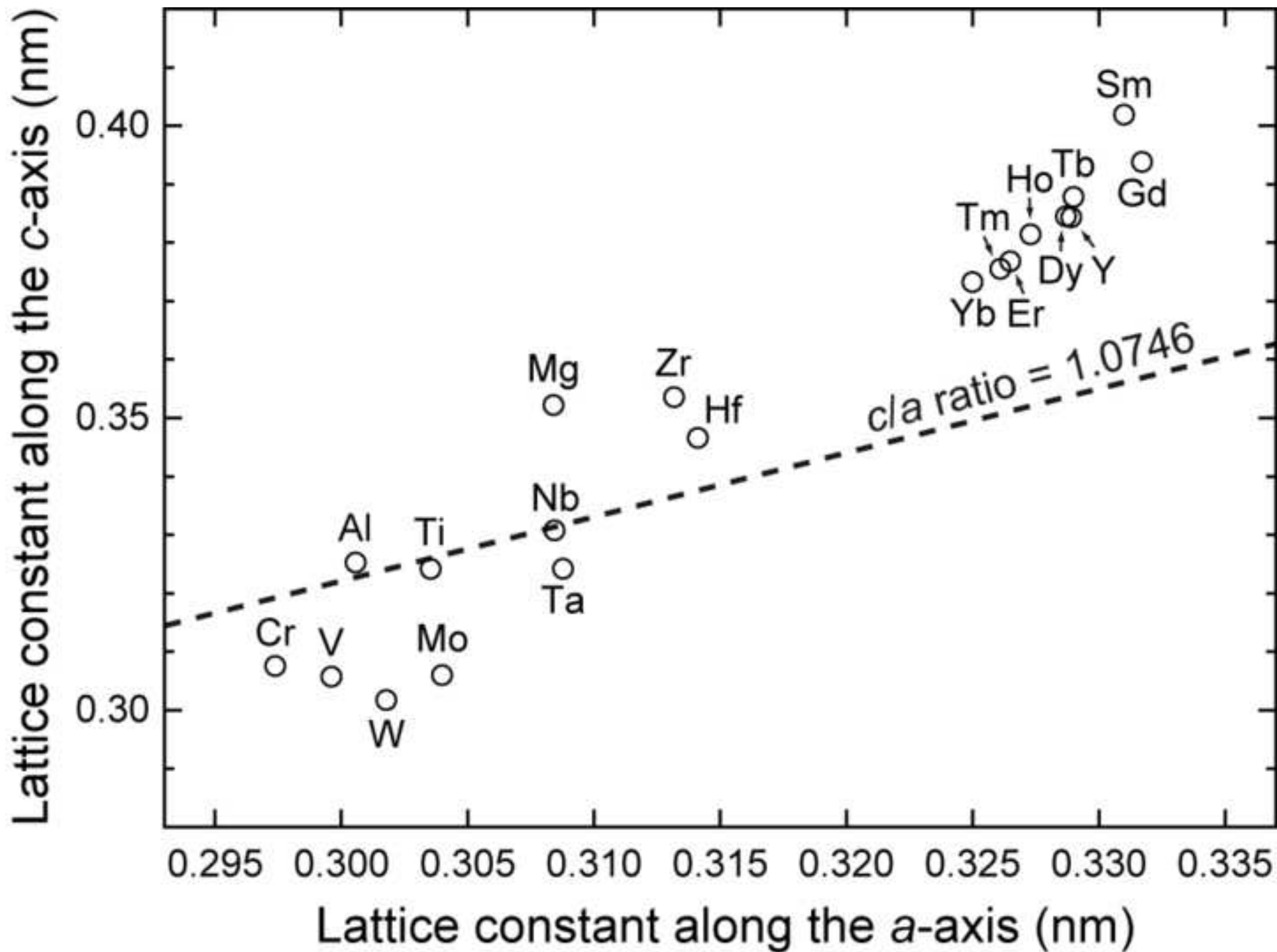


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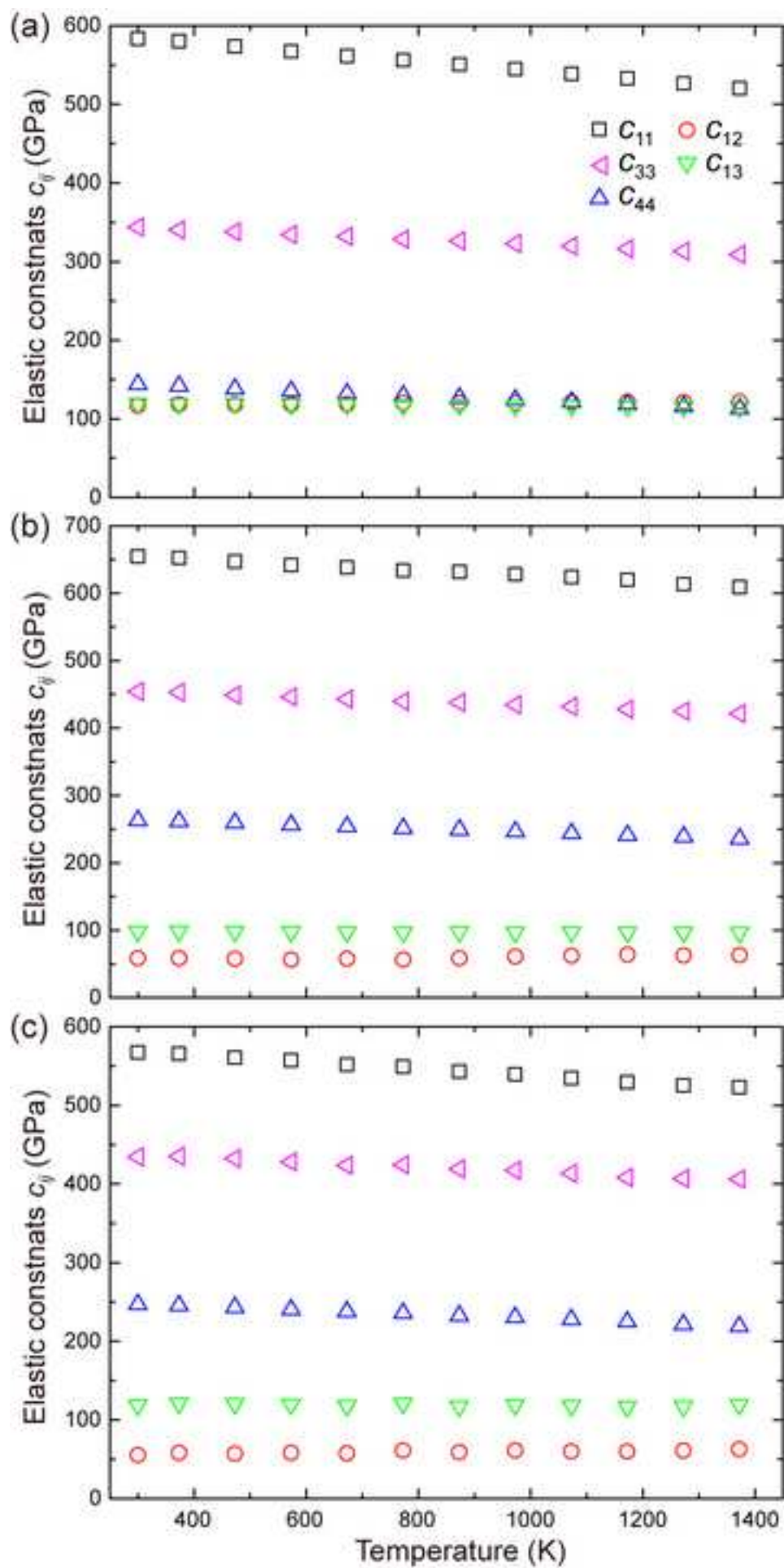


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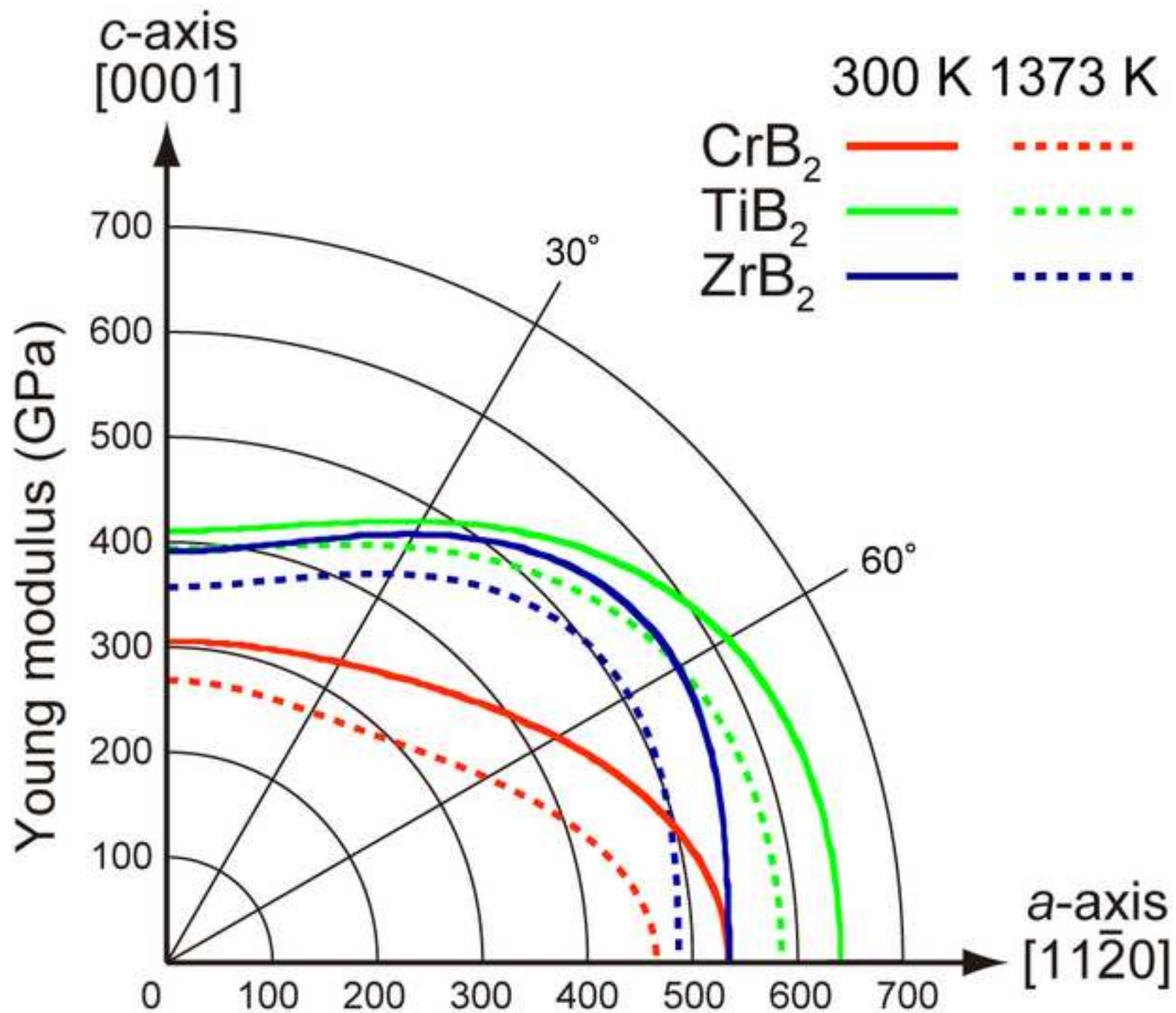


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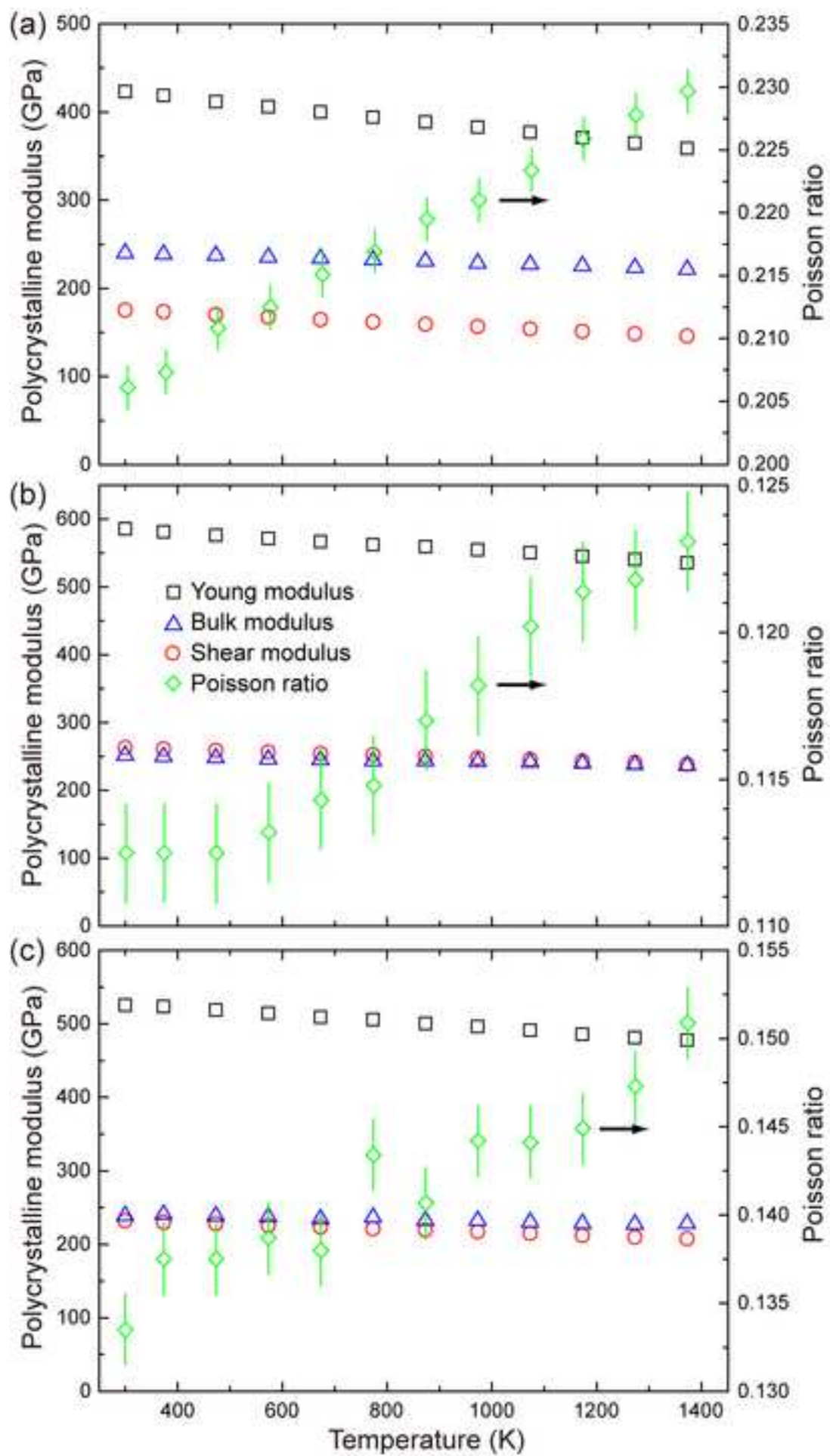


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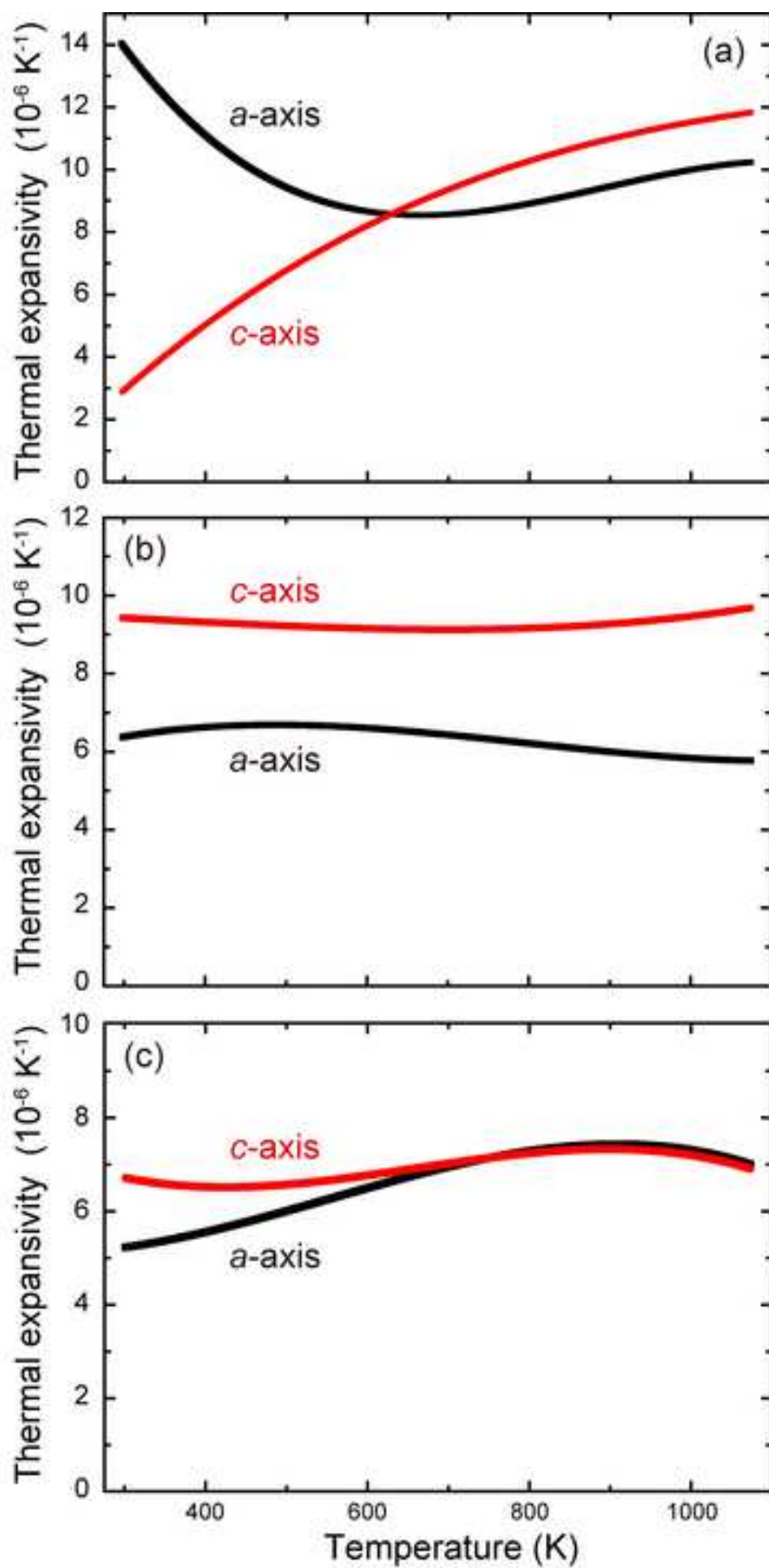




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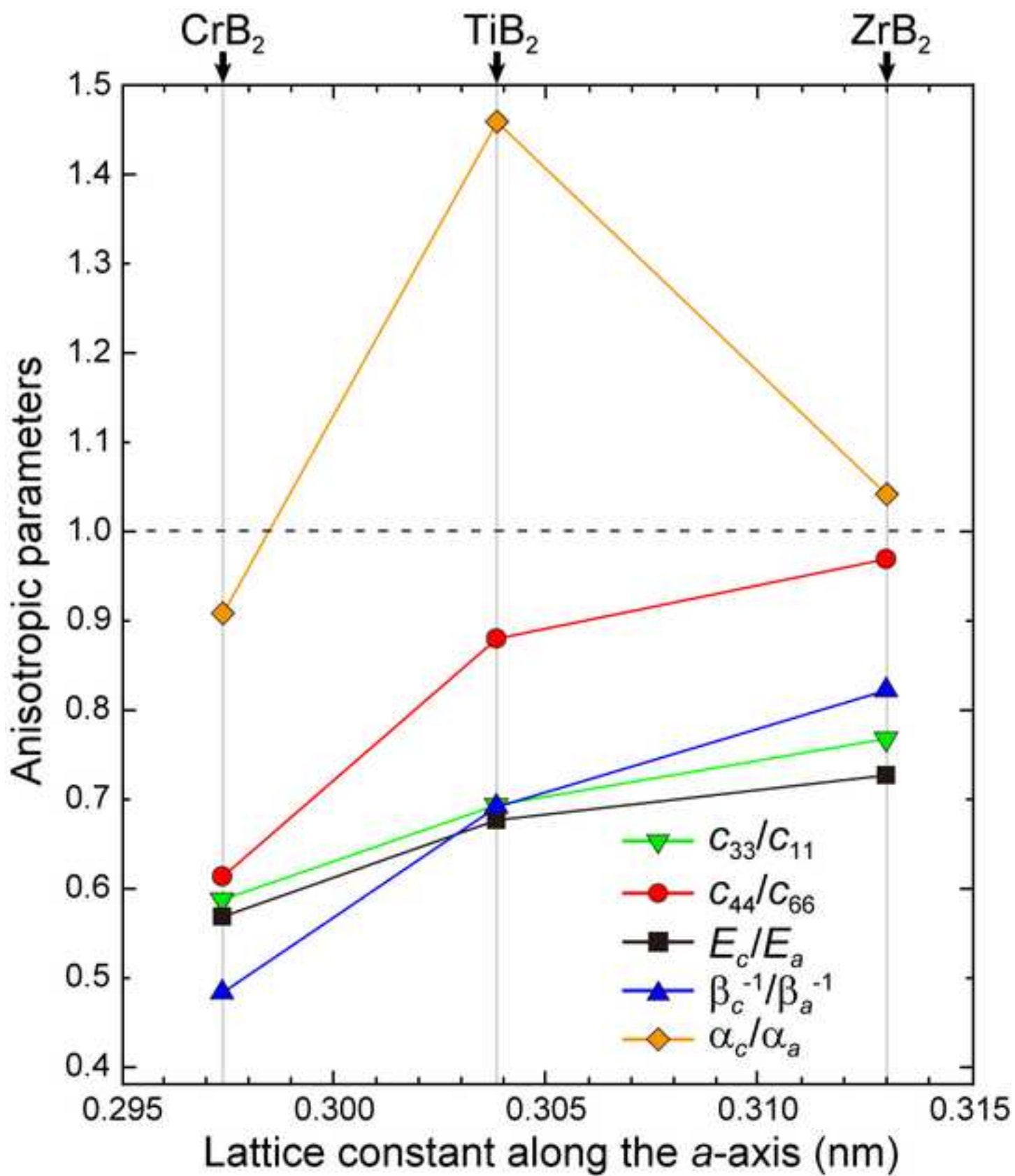


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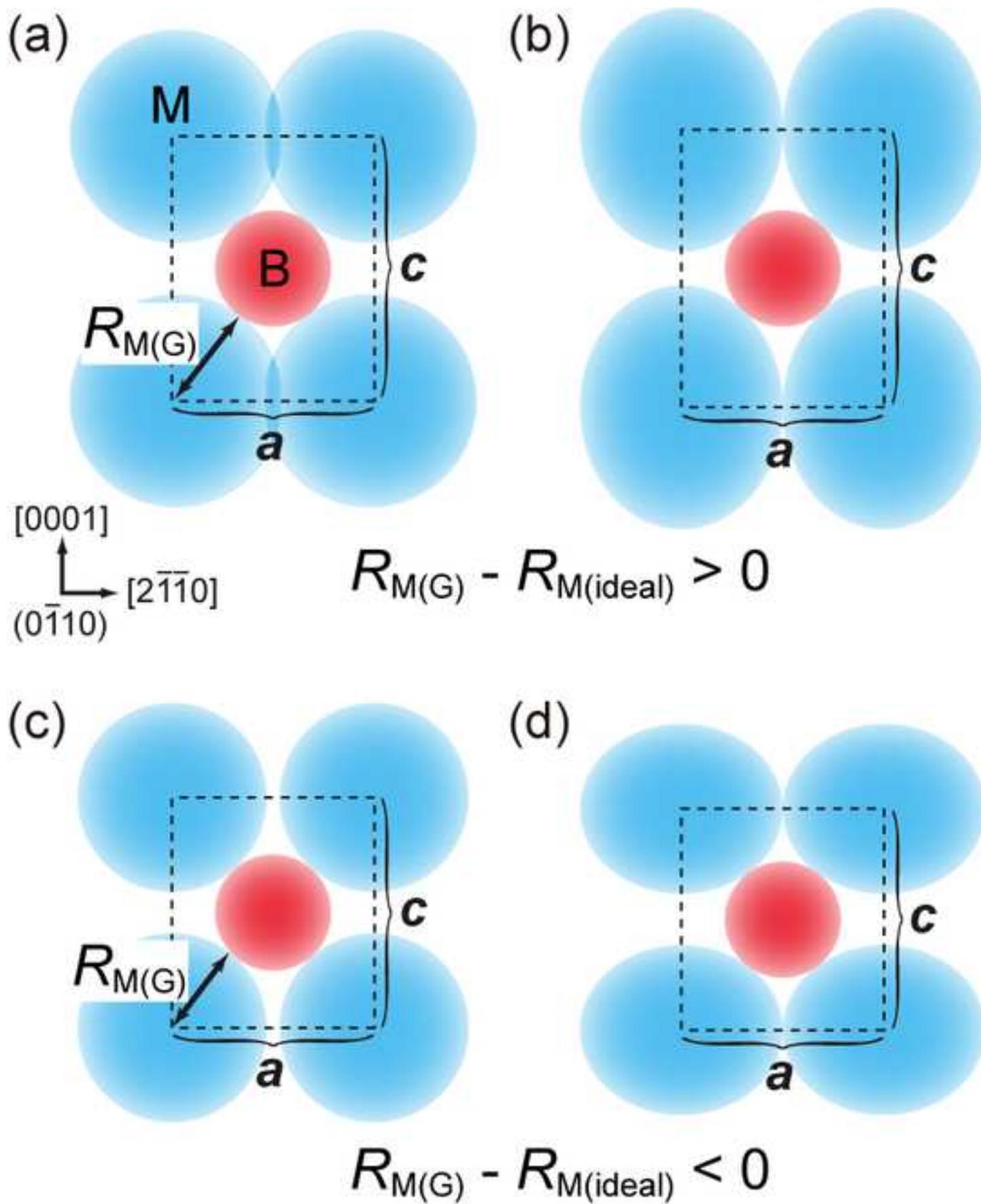


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