

Elastic Constants and Properties of B2-type FeAl and Fe–Cr–Al Alloys from First-Principles Calculations

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Abstract. The elastic constants (c_{ij}) and elastic properties of B2-phase FeAl intermetallic compounds and Fe–Cr–Al ternary alloys are studied by performing first-principles density functional theory calculations. The stable structures of Fe–Cr–Al and the elastic constants of FeAl and Fe–Cr–Al are predicted within the local density approximation (LDA) and PBE formulations of the generalized gradient approximation (GGA). It is found that more precise calculations of the c_{ij} values of Fe–Cr–Al can be performed using the GGA-PBE method by comparing with experimental results. The predicted c_{ij} values of Fe–Cr–Al will help in predicting the elastic properties of Fe–Cr–Al. The electronic structures of FeAl and Fe–Cr–Al are analyzed to determine the micro mechanism of the two compounds.

Introduction

Important signatures of Fe–Al intermetallic compounds are heat corrosion and erosion resistance, high-temperature oxidation resistance, sulfidation, and low cost. However, the shortage of room-temperature ductility and low high-temperature strength of FeAl hinder its industrial use.^[1] Alloying is a stable method used to intensify room-temperature ductility and strength of iron aluminides. Cr is one of the most popular alloy elements for solid-solution strengthening.^[2, 3] It is essential to obtain the elastic stiffness constants (c_{ij}) of FeAl and Fe–Cr–Al to determine the Cr alloying effects on the mechanical properties of iron aluminides.

In this work, the c_{ij} values of B2-FeAl and Fe–Cr–Al were calculated based on first-principles. The cohesive energies were calculated for structures with the alloying Cr replacing both Fe and Al atoms to determine the preferred occupation sites of Cr in FeAl. The elastic modulus calculated by c_{ij} , such as the Pugh ratio, the Poisson's ratio, and the Cauchy pressure, can be used to forecast the elastic properties of the two compounds. Based on the values obtained, the accuracy of the calculation method can be determined.

Methodology

Calculations were performed using the Cambridge Sequential Total Energy Package (CASTEP)^[4] based on the density functional theory. Both the generalized gradient approximation (GGA) PBE scheme^[5] and the local density approximation (LDA)^[6] were employed as the exchange correlation functions. Lattice parameter optimizations were performed using the Broyden–Fletcher–Goldfarb–Shanno (BFGS) method. The ultra soft pseudo-potential was used as the all atomic pseudo-potential. The cut-off energy was set to 420 eV, and the k-points were set to 22

$\times 22 \times 22$. The total energy convergence was set to 1.0×10^{-5} eV·atom⁻¹, the force acting convergence was set to 0.05 eV·Å⁻¹, the stress deviation was set to 0.1 GPa, and the maximum displacement convergence was set to 0.002 Å. The spin polarization was performed.

Results and Discussions

Effect of Cr on Structural Stability

The FeAl has a symmetrical structure belonging to the Pm-3m space group. The 16-atom supercell model was adopted in this work containing $2 \times 2 \times 2$ FeAl unit cells, denoted as Fe₈Al₈. The crystal structure models of FeAl, Fe₈CrAl₇, and Fe₇CrAl₈ are shown in Fig.1. The cohesive energies were calculated to predict the substituting location of Cr. The calculation equation for Fe–Cr–Al is by Eq. (1), in which every energy is the static energy calculated after the geometric optimization. In Eq. (1), E_{coh} (Fe_aCr_bAl_c) refers to the cohesive energy of Fe–Cr–Al; E_{tot} (Fe_aCr_bAl_c) refers to the total energies of Fe–Cr–Al, $E(\text{Fe})$, $E(\text{Cr})$, and $E(\text{Al})$ respectively refer to the energies of Fe, Cr, and Al, respectively. Moreover, a and b refer to the numbers of Fe, and Al atoms, respectively, and the Cr atom number in the supercell is 1.

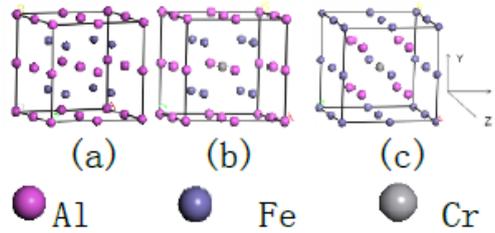


Figure1. Crystal structure models of the (a) FeAl supercell Fe₈Al₈, (b) Fe₈CrAl₇ and (c) Fe₇CrAl₈

$$E_{coh}(\text{Fe}_a\text{CrAl}_b) = \frac{E_{tot}(\text{Fe}_a\text{CrAl}_b) - aE(\text{Fe}) - E(\text{Cr}) - bE(\text{Al})}{a + 1 + b} \quad (1)$$

Table 1 shows the cohesive energy of the replaced atom in the structures of supercells in which Cr is substituted for a Fe or Al atoms, calculated by GGA-PBE and LDA. These results illustrate that the structures in which Cr is substituted for an Al atom in the supercell are the more stable. Hence, the Fe₈CrAl₇ model was used in the following calculations. In the model the Cr centration is 6.25 at%.

Table 1 Cohesive energy (eV) and replaced atom.

Phase	Cohesive Energy (eV)		Replace d Atom
	GGA-PBE	LDA	
Fe ₈ CrAl ₇	-7.34	-5.101	Al
Fe ₇ CrAl ₈	-6.952	-5.02	Fe

Effect of Cr on the Elastic Modulus

The efficient strain–stress method^[7] was used to predict the elastic constants of FeAl and Fe–Cr–Al crystals. A strain $\boldsymbol{\varepsilon}$ is imposed on a crystal with lattice vector \mathbf{R} , and the produced stress is $\boldsymbol{\sigma}$. The strain $\boldsymbol{\varepsilon}$ and stress $\boldsymbol{\sigma}$ are both tensors composed of nine components. However, because the strain and stress tensors have symmetry, they can be expressed in Voigt notation as Eqs. (2) and (3):

$$\boldsymbol{\varepsilon} = \begin{pmatrix} \varepsilon_1 & \varepsilon_6/2 & \varepsilon_5/2 \\ \varepsilon_6/2 & \varepsilon_2 & \varepsilon_4/2 \\ \varepsilon_5/2 & \varepsilon_4/2 & \varepsilon_3 \end{pmatrix} \quad (2)$$

$$\boldsymbol{\sigma} = \begin{pmatrix} \sigma_1 & \sigma_6 & \sigma_5 \\ \sigma_6 & \sigma_2 & \sigma_4 \\ \sigma_5 & \sigma_4 & \sigma_3 \end{pmatrix} \quad (3)$$

The 3×3 deformed matrix \mathbf{R}' is obtained as $\mathbf{R}' = \mathbf{R}(\mathbf{I} + \boldsymbol{\varepsilon})$, in which \mathbf{R} is the undeformed vector, \mathbf{I} is the 3×3 unit matrix, and $\boldsymbol{\varepsilon}$ is the strain matrix expressed as Eq. (2). \mathbf{R}' is expressed as Eq. (4):

$$\mathbf{R}' = \mathbf{R} \begin{pmatrix} 1 + \varepsilon_1 & \varepsilon_6/2 & \varepsilon_5/2 \\ \varepsilon_6/2 & 1 + \varepsilon_2 & \varepsilon_4/2 \\ \varepsilon_5/2 & \varepsilon_4/2 & 1 + \varepsilon_3 \end{pmatrix} \quad (4)$$

The generalized Hooke's law can be expressed as in Eq. (5).

$$\sigma_i = C_{ij}\varepsilon_j \quad (5)$$

In Eq. (5), C_{ij} is an element of the 6×6 elastic constant matrix. Eq (6) is the expansion of Eq. (5):

$$\begin{pmatrix} \sigma_{11} \\ \sigma_{22} \\ \sigma_{33} \\ \sigma_{23} \\ \sigma_{31} \\ \sigma_{12} \end{pmatrix} = \begin{pmatrix} c_{11} & c_{12} & c_{13} & c_{14} & c_{15} & c_{16} \\ c_{21} & c_{22} & c_{23} & c_{24} & c_{25} & c_{26} \\ c_{31} & c_{32} & c_{33} & c_{34} & c_{35} & c_{36} \\ c_{41} & c_{42} & c_{43} & c_{44} & c_{45} & c_{46} \\ c_{51} & c_{52} & c_{53} & c_{54} & c_{55} & c_{56} \\ c_{61} & c_{62} & c_{63} & c_{64} & c_{65} & c_{66} \end{pmatrix} \begin{pmatrix} \varepsilon_{11} \\ \varepsilon_{22} \\ \varepsilon_{33} \\ 2\varepsilon_{23} \\ 2\varepsilon_{13} \\ 2\varepsilon_{12} \end{pmatrix} \quad (6)$$

In the cubic crystal structure, symmetric relations such as $c_{11} = c_{22} = c_{33}$, $c_{12} = c_{23} = c_{31}$, and $c_{44} = c_{55} = c_{66}$ hold, hence the elastic constant matrix \mathbf{C} can be expressed as Eq. (7).

$$\mathbf{C} = \begin{pmatrix} c_{11} & c_{12} & c_{12} & 0 & 0 & 0 \\ c_{12} & c_{11} & c_{12} & 0 & 0 & 0 \\ c_{12} & c_{12} & c_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & c_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & c_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & c_{44} \end{pmatrix} \quad (7)$$

In this work, CASTEP was used to calculate the elastic constants of FeAl and Fe–Cr–Al. Strains of $(x, 0, 0, 0, 0, 0)$ with $x = \pm 0.001$ and ± 0.003 were chosen to obtain sufficient stress values and accurate elastic constants.

Table 2 lists the calculated and reference lattice parameters of FeAl and the elastic constants, bulk modulus, and shear modulus of FeAl and Fe–Cr–Al calculated by the GGA-PBE and LDA formulations. The bulk modulus, and shear modulus were calculated using the Hill calculation method [8], B denotes the bulk moduli and G denotes the shear moduli.

Table 2 Lattice parameters (Å), elastic constants (GPa), shear moduli (GPa) G and bulk moduli (GPa) B of Fe_8Al_8 and Fe_8CrAl_7 .

		Lattice Parameter (Å)	C_{11} (GPa)	C_{12} (GPa)	C_{44} (GPa)	G (GPa)	B (GPa)
Fe_8Al_8	GGA-PBE	5.71	274.24	138.5	151.36	109.7	183.75
	LDA	5.57	330.38	151.15	176.88	134.64	210.89
	Ref.	5.72 ¹⁰	290 ¹⁰	130 ¹⁰	166 ¹⁰		177 ¹¹
Fe_8CrAl	GGA-PBE		332.08	151.86	146.4	120.51	211.93
	LDA		348.82	135.24	167.71	139.95	206.43

For FeAl crystals, Table 2 shows that the LDA calculation predicts denser structures than the GGA-PBE calculations, as represented by the smaller lattice parameters. Furthermore, Table 2 also shows that the c_{ij} values predicted by the LDA calculation are generally larger than those predicted by the PBE calculations.

The elastic stabilities of the cubic crystal structures need to satisfy the mechanical equilibrium conditions under ambient conditions^[9], expressed as Eq. (8).

$$c_{11} > 0, c_{11} > |c_{12}|, c_{44} > 0, c_{11} + 2c_{12} > 0, c_{11} > B > c_{12} \quad (8)$$

For the elastic constants listed in Table 2, the FeAl and Fe–Cr–Al structures satisfy the mechanical equilibrium standards, illustrating that these are stable structures. The good agreement between the c_{ij} values of FeAl calculated by GGA-PBE and those measured experimentally^[10] shows that the GGA-PBE can be used for the Fe–Cr–Al structures. The Hill's calculation method[8] is as follows: the bulk modulus B is calculated by the expression $B = (C_{11} + 2C_{12})/3$, the shear modulus G is the average value of G_V and G_R , G_V is calculated by the expression $G_V = (C_{11} - C_{12} + 3C_{44})/5$, and G_R is calculated by the expression $G_R = [5(C_{11} - C_{12})C_{44}]/[4C_{44} + 3(C_{11} - C_{12})]$. From Table 2 the GGA-PBE calculations predicting the bulk and shear moduli of FeAl are closer to the experimental data^[11] than the LDA calculations.

The Pugh ratio (B/G),^[12] Poisson's ratio $((3B - 2G)/2(3B + G))$,^[13] and Cauchy pressure $(c_{12} - c_{44})$ ^[14] are normally used to predict the brittleness or ductility of materials; the larger the values, the more ductile the material. In Fig. 2, the Pugh ratio, the Poisson's ratio and Cauchy pressure line charts of Fe_8Al_8 and Fe_8CrAl_7 , calculated by GGA-PBE and LDA, show the same tendencies. The values calculated by LDA show that Cr addition lowers the ductility of FeAl, which is contradictory to the results of previous studies.^[3] In addition, large errors in the FeAl c_{ij} values are obtained when the LDA method is used together with experimental and other calculated values.

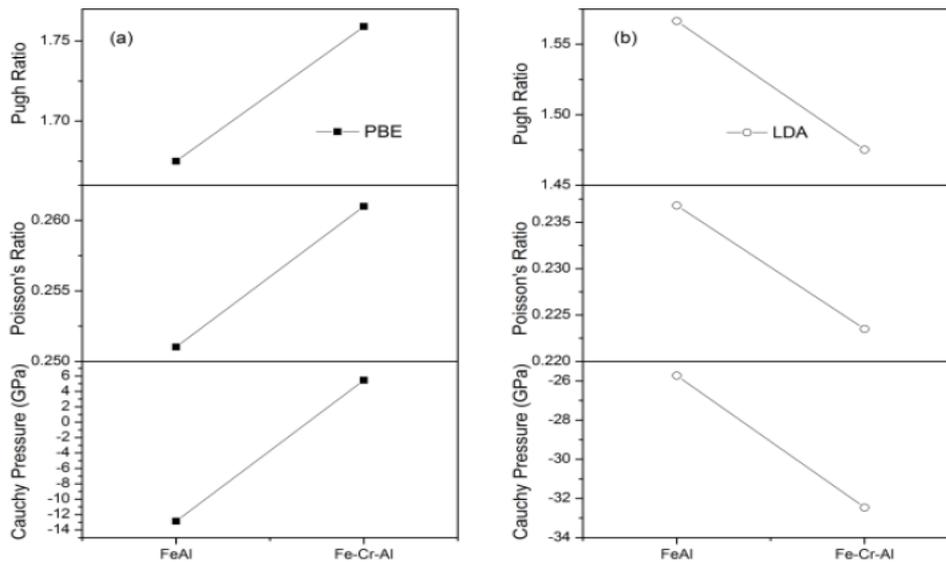


Figure 2. Pugh ratio, Poisson's ratio, and Cauchy pressure (GPa) of Fe_8Al_8 and Fe_8CrAl_7 calculated by GGA-PBE (a) and LDA (b).

The elastic properties calculated by GGA-PBE and LDA are different. Cr is predicted by GGA-PBE to increase the ductility of FeAl, while it is predicted by LDA to decrease the ductility of FeAl. The Fe-Cr-Al elastic constants and the elastic properties predicted by LDA deviate from the existing experimental results.^[11] In contrast, the calculations by GGA-PBE can be considered to be precise since the elastic constants and properties predicted by this method are consistent with existing research results.

Electronic Properties Analysis

In order to clarify the effects of the Cr alloying element on the electronic properties, the density of states (DOS), containing the total density of states (TDOS) and the partial density of states (PDOS), were calculated by GGA-PBE and the results are shown in Fig. 3. Fig. 2 (a) illustrates the TDOS and PDOS of Fe_8Al_8 . In Fe_8Al_8 , the bonding peak is mainly contributed from the valence electrons of Fe

and Al. The bonding originates from Fe (3d)(4s)(3p) and Al (3s)(3p), particularly from Fe(3d). From the DOS of FeAl alloys, the bonding property can be considered mainly a valence property, illustrating that this is the reason for the brittleness of FeAl. Fig. 2 (b) displays the DOS of Fe₈CrAl₇, in which three the bonding peaks occur, two of which originate from Cr (4s) and Cr (3p) under the fermi energy level. The bonding peak is mainly contributed from the valence electrons of Fe, Al, and Cr. The hybrid bonding mainly originates from Fe (3d) and Cr (3d). The number of bonding peaks of Fe₈CrAl₇ is greater than that of Fe₈Al₈, which can be considered one result of the improved cohesive capacity of FeAl caused by Cr.

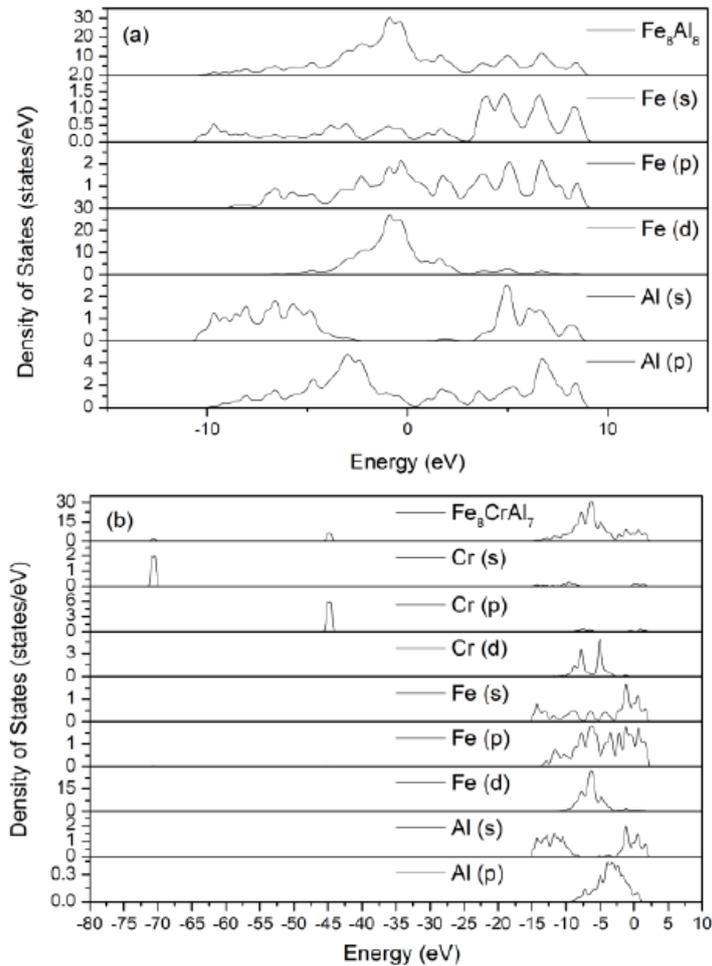


Figure3. Density of states of Fe₈Al₈ (a) and Fe₈CrAl₇ (b)

Electron Densities Analysis

Difference electron density can be performed to visually illustrate the electron configuration. Fig. 4 (a) and (b) display the difference electron densities in the (110) plane for Fe₈Al₈ and Fe₈CrAl₇, calculated by the GGA-PBE method. In Fe₈CrAl₇, Cr rearranges the electron distribution near the Fe and Al atoms, and the overlapped electrons between Cr and Fe are heavier than those between Al and Fe in Fe₈Al₈. The results are compatible with the above analysis of elastic properties and DOS.

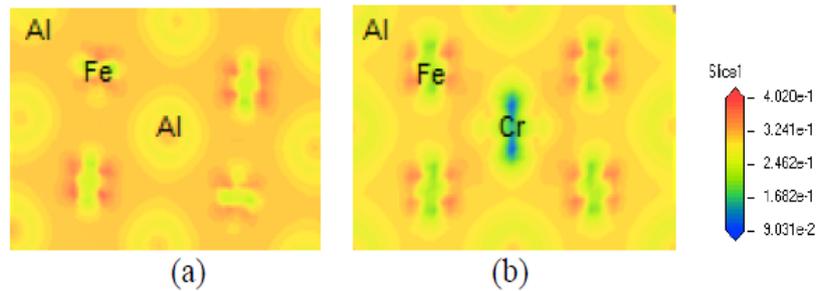


Figure 4. Difference electron densities of (110) plane in Fe₈Al₈(a) and Fe₈CrAl₇(b).

Conclusions

- (1) The elastic constants c_{ij} of B2-phase FeAl intermetallic compounds and Fe-Cr-Al computed using the strain-stress method with GGA-PBE is more accurate than those computed using LDA.
- (2) Alloy elements such as Cr increase the ductility of FeAl.
- (3) The alloying elements affect the c_{ij} values of FeAl as they affect the density of states and electron density.

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