Theoretical calculation of elastic properties and electronic structure of B2 iron aluminides and ternary iron–aluminum alloys

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Keywords: FeAl intermetallic compound, density functional theory, elastic properties, electronic structure, empirical electron theory of solids and molecules

Abstract

The mechanical properties of FeAl and ternary Fe–X–Al (X = Cr, Mo) alloys are investigated using first-principles density functional theory (DFT), with the valence electron structures also being determined using the empirical electron theory of solids and molecules. The structural attributes of FeAl are fitted using an E–V curve, and the stable structures of the ternary alloys are systematically predicted along with their respective elastic constants and phonon frequencies. The bonding nature in FeAl is partly defined by covalence with orbital hybridization, which explains its intrinsic brittleness. The micro-mechanism by which the ductility of FeAl is improved by Cr or Mo addition is as follows: Cr or Mo addition increases the cohesive capacity of the bonds in FeAl; s, p, and d orbital electrons of the alloying element are mainly involved in the hybridization of FeAl; and the alloying elements increase the electron density of Fe and Al atomic bonding.

1. Introduction

Iron aluminate (FeAl) intermetallic compounds have been widely studied because of their excellent resistance to thermal corrosion/erosion, high-temperature oxidation, and sulfidation, combined with their low density and low cost relative to those of other intermetallic compounds; however, their lack of room-temperature ductility and low high-temperature strength have proven to be major obstacles to their extensive commercial application [1, 2]. Commonly used methods for enhancing the high-temperature strength and room-temperature ductility of iron aluminides include precipitation strengthening, solid-solution strengthening by alloying with Cr, Mo, Ti or Mn [3–6], and the use of nanotechnology to add Cr [7].

Although the effects of such alloying processes on the mechanical properties of FeAl have been investigated experimentally, their exact functional mechanisms have not yet been detailed at the microscopic level.

First-principles density functional theory (DFT) calculations play a key role in obtaining the mechanical properties through the simulation of tensile tests in nanowire materials to confirm the experimental results [8]. First-principles DFT can also precisely calculate the elastic constants (cij), which can be used to predict the elastic properties including ductility and stiffness. The elastic constants of FeAl, calculated by DFT, are in good agreement with experimental results [9, 10]. Zheng et al [11] systematically calculated the elastic constants of 15 B2 type FeAl–X ternary alloys doped with Co, Cr, Ti, V, and others, and further analyzed the effects of these alloy elements on mechanical properties and electronic structures of FeAl. The method to calculate the elastic constants and elastic modulus by DFT to predict ductility is based on additional criteria, such as the Cauchy pressure [12, 13], Pugh ratio [13, 14], and Poisson’s ratio [13, 15, 16]. However, inconsistencies can occur when using only this method. The predicted effect of Mo and W on mechanical properties of FeAl differs depending on the criteria used [9, 11].
To understand the structural stability of B2-FeAl and Fe3.1. Effect of Cr and Mo on the structural stability of FeAl

Results and discussion

First-principles calculations were performed using a plane-wave pseudo-potential method based on DFT and implemented using the Cambridge Sequential Total Energy Package (CASTEP) [22, 23]. A generalized gradient approximation (GGA-PW91) scheme [24] was adopted for the exchange correlation, a self-consistent field (SCF) iteration was used to calculate the electronic structure, and an ultrasoft pseudo-potential was used for all atomic pseudo-potentials on the fast Fourier-transform (FFT) grid. A Broyden–Fletcher–Goldfarb–Shanno (BFGS) scheme was used for the cell optimization calculations using the following parameters: a 520 eV cut-off energy, a total energy convergence of less than $1.0 \times 10^{-9}$ eV atom$^{-1}$, a force acting on each atom of less than 0.05 eV Å$^{-1}$, a stress deviation of less than 0.1 GPa, and a maximum displacement of 0.002 Å. It was found that the total energy was independent of the number of k-points when the Monkhorst–Pack grid was more than $16 \times 16 \times 16$ k-points in size, and that the error in the total energy was less than $1 \times 10^{-10}$ eV. The cell was optimized during geometry optimization, and the spin polarization was fixed for all calculations. The finite displacement method was employed for the phonon frequency calculation.

The symmetric B2-type crystal structure of FeAl shown in figure 1(a) has a Pm-3m space group, with a 16-atom supercell model consisting of $2 \times 2 \times 2$ FeAl unit cells (figure 1(b)) being used to represent Fe8Al8 in this study. Considering the cohesive energy results for Cr or Mo substitution of Fe or Al atoms in Fe8Al8, as analyzed in section 3.1, the established model replaced the Al atom of the supercell with 6.25 at% alloying element content, thereby giving the crystal structure model shown in figure 1(c) of Fe8XAl7 (where $X = \text{Cr, Mo}$). All supercell structures are fully relaxed during geometry optimization.

The electronic configurations of the ground state of Fe, Al, Cr and Mo involving in our study are as the below: $1s^22s^22p^63s^23p^64s^23d^6$ (Fe), $1s^22s^22p^63s^23p^1$ (Al), $1s^22s^22p^63s^23p^64s^13d^5$ (Cr), and $1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^14d^5$ (Mo).

2. Methodology and models

3. Results and discussion

3.1. Effect of Cr and Mo on the structural stability of FeAl

To understand the structural stability of B2-FeAl and Fe–X–Al ($X = \text{Cr, Mo}$), the location of the substituting alloying elements within the crystal lattice was determined based on the cohesive energies that were calculated using the static energy after geometry optimization:

![Crystal structure of FeAl, Fe8CrAl7, and Fe8MoAl7](image-url)
where \( E_{\text{coh}}(\text{Fe}_a\text{X}_b\text{Al}_c) \) and \( E_{\text{tot}}(\text{Fe}_a\text{X}_b\text{Al}_c) \) represent, respectively, the cohesive and total energies of Fe–X–Al; \( E(\text{Fe}) \), \( E(\text{X}) \), and \( E(\text{Al}) \) indicate Fe, X, and Al single atomic energies respectively; and \( a \), \( b \), and \( c \) indicate the number of individual atoms of each element within the cell.

The cohesive energy values obtained are listed in table 1 alongside the replaced atom in the supercell structure, from which we see that structures in which the alloying element replaces Al atoms are the most stable. Based on this, models of Fe\(_8\)Cr\(_7\)Al\(_7\) and Fe\(_8\)Mo\(_7\)Al\(_7\) were used in the calculations presented in the sections that follow.

3.2. Lattice parameters, mechanical stability, and dynamical stability

The lattice parameters and bulk modulus of B\(_2\)-FeAl determined from the energy versus volume (\( E-V \)) equation of state (EOS) were more accurate values than those calculated indirectly from first-principles calculations. The EOS can be used to determine equilibrium properties such as the lattice parameters and bulk moduli; hence, a four-parameter Birch–Murnaghan EOS \(^{[25]}\) was used to fit the \( E-V \) data points obtained from first-principles calculations (equation (2)). Figure 2 presents the \( E-V \) curve of FeAl calculated by this EOS, which obtained a good fit to the energies calculated by first principles (average deviation of \( 3.4 \times 10^{-4} \) eV). This suggests that the results obtained through first-principles calculation are reliable.

Table 2 summarizes of the calculated and reference lattice parameters for FeAl, as well as the elastic constants. The calculated equilibrium lattice constants of Fe\(_8\)Al\(_8\) matched well with the value obtained by fitting with the \( E-V \) equation of state (5.7062 Å) and the experimental result of 5.7223 Å \(^{[26]}\), with deviations of just 0.12% and 0.4%, respectively. Therefore, the calculated lattice constants can be considered accurate.

Under ambient conditions, the following mechanical equilibrium conditions \(^{[27, 28]}\) can be used as the elastic stability criteria of a cubic crystal structure:

![Figure 2. E–V curve of B\(_2\)-FeAl.](image)
All alloys listed in table 2 have elastic constants that satisfy these equilibrium conditions, indicating that their structures were stable and that there is excellent agreement between the calculated and measured $c_{ij}$ values \[29, 30\] of FeAl. The deviation of $c_{11}$ is 2.23% and 2.9%, whereas that of $c_{12}$ is less at 6.29% and 1.6%. The deviation of $c_{44}$ is 7.5% and 6.95%, but as these are both still less than 10%, the calculation is precise, and the results are reliable.

To further confirm the dynamical stability of FeAl, Fe$_8$CrAl$_7$ and Fe$_8$MoAl$_7$, their phonon frequencies were calculated. From the obtained phonon dispersion curves (figure 3) for these three materials, no imaginary frequency was observed throughout the entire Brillouin zone, indicating that FeAl, Fe$_8$CrAl$_7$ and Fe$_8$MoAl$_7$ all exhibit dynamical stability at the ground state.

Because the calculations are performed for a temperature of 0 K, the zero-point vibrational energy is considered. Equation (3) \[31\] is the computational formula for the zero-point vibrational energy, in which $F(\omega)$ is the phonon density of states and $h$ is Planck’s constant. The zero-point vibrational energies thus calculated for FeAl, Fe$_8$CrAl$_7$ and Fe$_8$MoAl$_7$ were 0.842 eV, 0.831 eV and 0.830 eV, respectively. These zero-point vibrational energy values are much smaller in magnitude than the total energy of these three phases: $-7396.286$ eV, $-9808.854$ eV and $-9277.911$ eV, respectively. In addition, the total energy calculated in this study did not include the zero-point vibrational energy.

$$E_{zp} = \frac{1}{2} \int F(\omega) h \omega d\omega$$

### 3.3. Effect of Cr and Mo on the ductility of FeAl

#### 3.3.1. Analysis by density functional theory

Many mechanical parameters such as the bulk modulus ($B$), shear modulus ($G$), Young’s modulus ($E$), Pugh modulus ($B/G$), Poisson’s ratio ($\nu$), and Cauchy pressure ($C_p$) are directly related to the macroscopic mechanical properties of materials. As such, these parameters can be obtained from the elastic constants. The bulk modulus, shear modulus and Young’s modulus of FeAl and Fe–X–Al were calculated using the Hill method [32], as outlined in equation (5) to equation (9). The Cauchy pressure and Poisson’s ratio were then calculated from the elastic constants, bulk modulus and shear modulus using equations (10) and (11).

$$B = \frac{C_{11} + 2C_{12}}{3}$$

$$G_V = \frac{C_{11} - C_{12} + 3C_{44}}{5}$$
Using the Voigt method

Here, $B$ is the bulk modulus; $G$ is the shear modulus, which is the average value of the shear moduli calculated using the Voigt method ($G_V$) and the shear modulus calculated by the Reuss method ($G_R$); $E$ is the Young’s modulus; $v$ is Poisson’s ratio and $C_p$ is the Cauchy pressure. The bulk modulus values calculated using this method and EOS fitting were close to their respective reference values [33, 34] (the bulk modulus is hereafter referred to as $B_{\text{Hill}}$ and $B_{\text{EOS}}$, respectively).

When a material is subjected to an overall pressure, equivalent to a volume stress in materials, the ratio of the bulk stress and volumetric strain of the material under stress is the bulk modulus. Because the total volume of the object is always greater than the volume under pressure, the bulk modulus is always positive, and a higher value typically indicates higher material strength. However, if the atoms of a material are stronger then it is more difficult to compress, thus exhibiting a higher modulus value.

Table 3 shows the bulk modulus fitted through the $E$–$V$ equation of state ($B_{\text{EOS}}$), the experimental bulk modulus ($B$) reported by other researchers, and the calculated bulk ($B_{\text{Hill}}$), shear ($G_{\text{Hill}}$) and Young’s moduli ($E_{\text{Hill}}$) using the Hill’s algorithm. The calculated bulk moduli ($B_{\text{Hill}}$) of FeAl were found to correlate well with the experimental data [26, 34], with deviations of 4.29% and 5.44%, respectively, which, at less than 10%, can be considered to be within a reliable range. However, the deviation with the calculated and fitted FeAl bulk modulus was 10.47%, which is slightly over 10%. After Cr and Mo were added to FeAl, its bulk modulus, shear modulus, and Young’s modulus all changed in the order of: Fe$_8$CrAl$_7$ > Fe$_8$MoAl$_7$ > Fe$_8$Al$_{16}$, from largest to smallest. The above description of these moduli (i.e., that the shear modulus and Young’s modulus can be used to judge the nature of a material) clearly demonstrate that both Cr and Mo improve the strength and rigidity of FeAl.

The Pugh modulus ($B/G$), which is the ratio of the bulk modulus to the shear modulus, can be used to determine whether a material is brittle (<1.75) or ductile (>1.75) [14, 15]. Figure 4(a) demonstrates that Cr increases the ductility of FeAl, but Mo decreases the ductility of FeAl.

The ratio of the absolute value of the lateral strain to the axial strain when the crystal is stretched or compressed under the uniaxial stress (Poisson’s ratio, $v$) can be used to predict the shear stress stability of crystals [15] as equation (10). This gives an indication of the ductility of a crystal, with a larger value of $v$ suggesting a
more ductile material [16]. Thus, much like the Pugh ratio, the Poisson’s ratio values in figure 4(b) indicate that Cr increases the ductility of FeAl, but Mo decreases the ductility of FeAl.

The Cauchy pressure, \( C_p \), is an interesting parameter used to describe the angular property of materials as equation (11). This can also be used to predict the ductility of a material [12, 13], with a positive value indicating metallic bonding, whereas a negative value is consistent with covalent bonding. The calculated Cauchy pressure values for Cr in figure 4(c) show a similar relation to the Pugh ratio and the Poisson’s ratio, again indicating that Cr improves the ductility of FeAl. However, the Cauchy pressure indicates that Mo slightly improves the ductility of FeAl, which is different than that suggested by analysis using the Pugh ratio and the Poisson’s ratio.

The observation that Cr addition can reduce the inherent brittleness of FeAl is consistent with past research [1–4]; however, in terms of the effect of adding Mo on FeAl ductility, different results were obtained according to the three indicators, i.e., the Pugh ratio, Poisson’s ratio and Cauchy pressure. On the other hand, some experimental reports on the solid solution strengthening of FeAl with Mo [3, 5] have shown that Mo addition can increase the ductility of FeAl. In order to solve the inconsistency between the Pugh ratio, Poisson’s ratio, and Cauchy pressure indicators and to quantify the ductility, we propose a method using the EET based on the results calculated using DFT above.

### 3.3.2. Analysis by empirical electron theory of solids and molecules

The EET of solids and molecules describes the VES of a crystal by assuming that each atom is composed of multiple discontinuous hybrid states, each with its own number of covalent electrons \( n_{c} \), lattice electrons \( n_{l} \), single bond radius \( R \), etc. This information is listed in table 4. The EET also provides a method called the bond length difference (BLD), which was used to calculate the VES from the qualified hybrid state of each atom [17, 18] using the following equations:

\[
\begin{align*}
&D_{\alpha}(n_{\alpha}) = R_{\alpha}(1) + R_{\alpha}(1) - \beta \log n_{\alpha} \quad (\alpha = B, C, D, \ldots, N) \\
&D_{\alpha'}(n_{\alpha'}) = R_{\alpha}(1) + R_{\alpha}(1) - \beta \log n_{\alpha'} \quad (\alpha' = B, C, D, \ldots, N) \\
&\log \frac{n_{\alpha'}}{n_{\alpha}} = \frac{D_{\alpha}(n_{\alpha}) - D_{\alpha}(n_{\alpha'}) + R_{\alpha}(1) + R_{\alpha}(1) - R_{\alpha'}(1) - R_{\alpha'}(1)}{\beta} \\
&\sum n_{c} = \sum I_{c} n_{i} = n_{A} \left( I_{A} + \frac{I_{B}}{n_{A}} + \ldots + \frac{I_{N}}{n_{A}} \right) \\
&n_{c'} = n_{A} \cdot \frac{n_{\alpha'}}{n_{\alpha}} \\
&D_{\alpha'}(n_{\alpha'}) = R_{\alpha}(1) + R_{\alpha}(1) - \beta \log n_{\alpha}
\end{align*}
\]

With the BLD method, equations for the experimental bond length were established by expanding equation (11) to form N equations, in which A denotes the strongest covalent bond of the material and \( \alpha' \) denotes the remaining N−1 bonds. The \( D(n_{\alpha}) \) values obtained from the DFT calculation using the methodology presented in section 2, and which are listed in table 4, were then substituted for the corresponding bond’s \( D_{\alpha}(n_{\alpha}) \) or \( D_{\alpha'}(n_{\alpha'}) \). Calculation of the experimental bond length difference between one random bond and the strongest covalent bond produced equation (13), which is then expanded into N−1 equations that are solved to obtain the value of \( \frac{n_{\alpha'}}{n_{\alpha}} \). Next, equation (14) was established as a function of \( n_{\alpha} \), with the values of \( I_{c} \) given in...
Table 4. Hybridization tables of Fe, Al, Cr and Mo [18].

| Fe    | σ  | 1  | 2  | 3  | 4  | 5  | 6  |
|-------|----|----|----|----|----|----|----|
| nₐ   | 3  | 3.0024 | 3.0095 | 3.0133 | 3.0753 | 3.2826 |
| nᵦ   | 2  | 1.9984 | 1.9937 | 1.9911 | 1.9498 | 1.8116 |
| R(1)/Å | 1.161 | 1.1609 | 1.0607 | 1.1606 | 1.159 | 1.1535 |
| σ    | 7  | 1.3096 | 1.3314 | 1.3823 | 1.5709 | 4.0021 | 4.24 |
| nₐ   | 1.7936 | 1.7791 | 1.7451 | 1.6194 | 1.3319 | 1.1734 |
| R(1)/Å | 1.1527 | 1.1522 | 1.1508 | 1.1458 | 1.1343 | 1.1279 |
| σ    | 13 | 4.461 | 4.7144 | 5.371 | 5.8436 | 5.9153 | 6 |
| nₐ   | 1.026 | 0.8571 | 0.4194 | 0.1043 | 0.0565 | 0 |
| R(1)/Å | 1.122 | 1.1153 | 1.0978 | 1.0852 | 1.0833 | 1.081 |

| Al   | σ  | 1  | 2  | 3  | 4  | 5  | 6  |
|------|----|----|----|----|----|----|----|
| nₐ   | 1  | 1.033 | 1.1734 | 2.5296 | 2.897 | 3 |
| nᵦ   | 2  | 1.967 | 1.8266 | 0.4704 | 0.103 | 0 |
| R(1)/Å | 1.19 | 1.19 | 1.19 | 1.19 | 1.19 | 1.19 |

| Cr   | σ  | 1  | 2  | 3  | 4  | 5  | 6  |
|------|----|----|----|----|----|----|----|
| nₐ   | 4  | 3.9851 | 3.9515 | 3.9369 | 3.8779 | 3.6807 |
| nᵦ   | 2  | 1.9702 | 1.9029 | 1.8739 | 1.7558 | 1.3614 |
| R(1)/Å | 1.087 | 1.0695 | 1.0751 | 1.0775 | 1.0874 | 1.1202 |
| σ    | 7  | 3.6487 | 3.6177 | 3.3972 | 3.3538 | 3.2932 | 3.1635 |
| nₐ   | 1.2974 | 1.2354 | 0.7945 | 0.7075 | 0.5865 | 0.3269 |
| R(1)/Å | 1.1256 | 1.1307 | 1.1675 | 1.1747 | 1.1848 | 1.2065 |
| σ    | 13 | 3.129 | 3.0222 | 3.0025 | 3.0006 | 3.0002 | 3 |
| nₐ   | 0.258 | 0.0444 | 0.0049 | 0.0013 | 0.0005 | 0 |
| R(1)/Å | 1.2122 | 1.23 | 1.2333 | 1.2336 | 1.2337 | 1.2337 |

| Mo   | σ  | 1  | 2  | 3  | 4  | 5  | 6  |
|------|----|----|----|----|----|----|----|
| nₐ   | 4  | 4  | 4  | 4  | 4  | 4  | 4  |
| nᵦ   | 4  | 4  | 4  | 4  | 4  | 4  | 4  |
| R(1)/Å | 1.2295 | 1.2336 | 1.2389 | 1.2427 | 1.2466 | 1.2588 |
| σ    | 7  | 4  | 4  | 4  | 4  | 4  | 4  |
| nₐ   | 4  | 4  | 4  | 4  | 4  | 4  | 4  |
| nᵦ   | 4  | 4  | 4  | 4  | 4  | 4  | 4  |
| R(1)/Å | 1.7095 | 1.479 | 1.0879 | 0.914 | 0.7789 | 0.5225 |

Table 5 denoting the number of each kind of bond and $\sum n_i$ representing the sum of all covalent electrons. The solution of equation (14), $n_i$, and the result of equation (15), $n_{i'}$, are then substituted into equation (16) to obtain the multiple values of the theoretical bond lengths $D_{theo}(n_i)$; the variables $u$, $v$, $s$, and $t$ representing the different atoms which may be same or different atom types. Finally, the difference between the theoretical and experimental bond length, $\Delta D_{theo}$, was calculated. Because Fe, Cr and Mo have 18 hybrid levels and Al has 6, each single bond radius $R(1)$ and the number of covalent electrons $n_i$ for each hybrid level needs to be substituted into equations (12) to (16). As a result, both $\Delta D_{theo}$ and $n_i$ have multiple values, which makes the amount of calculation needed very large. A system was therefore developed in which, according to EET, $\Delta D_{theo} < 0.005$ Å is considered to correspond to an actual possible atomic state and the theoretical value closest to the experimental value is selected as an optimal value from table 3. Since this has the potential to introduce error into the determined value, it was fitted to similar structures for comparison [30].

Using the EET and BLD methods described above to calculate the Fe₈Al₈, Fe₈CrAl₇ and Fe₈MoAl₇ structures, the hybrid state of each atom, the difference between the theoretical and experimental bond lengths, the most covalent electrons, and the number of lattice electrons were obtained (table 6). The bond population listed in table 6 will be further referenced in section 3.4. According to the EET analysis, a higher lattice electrons number...
in the system indicates a more ductile material \[17\], which confirms that Mo can improve the ductility of FeAl; this result is consistent with the experimental results and Cauchy pressure results in section 3.3.1. In addition, Cr more effectively increases the ductility of FeAl than Mo, which is also consistent with these Cauchy pressure results.

### 3.4. Electronic properties of B2-FeAl ternary alloys

Analyzing the Mulliken and bond populations can produce quantitative results that can indicate certain chemical bonding properties. Table 7 lists Mulliken populations of Fe₈Al₈, Fe₈CrAl₇, and Fe₈MoAl₇ calculated by DFT, which indicate that charge transfers occur in each of these three phases. In Fe₈Al₈, Fe atoms gained 1.28e charge from Al atoms. In Fe₈CrAl₇, the addition of Cr increased the transferred charge amount to 1.44e, similarly, in Fe₈MoAl₇, the addition of Mo increased the transferred charge amount to 1.92e. This increase indicates that there are stronger ionic interactions between Fe, Al, and Cr or Mo in Fe₈CrAl₇ or Fe₈MoAl₇ than in Fe₈Al₈.

Table 5 summarizes the bond population and bond length for the nearest neighbors of Fe₈Al₈, Fe₈CrAl₇, and Fe₈MoAl₇ calculated by DFT. Positive and negative bond population values represent bonding and antibonding states, respectively, and a positive value indicates that the two atoms are covalently bonded, whereas a bond population value close to zero indicates that the two atoms exhibit a weak covalent interaction \[11, 37\].

| No. | Bond name | D(\(n_α\)) (Bond length) | Bond population | \(I_α\) |
|-----|-----------|---------------------------|-----------------|--------|
| A   | Al–Fe     | 2.46799                   | 0.09            | 64     |
| B   | Fe–Fe     | 2.84979                   | −0.19           | 12     |
| C   | Al–Al     | 2.84979                   | 0.2             | 12     |

| No. | Bond name | D(\(n_α\)) (Bond length) | Bond population | \(I_α\) |
|-----|-----------|---------------------------|-----------------|--------|
| A   | Cr–Fe     | 2.42669                   | −0.83           | 8      |
| B   | Al1–Fe    | 2.4481                    | 0.15            | 8      |
| C   | Al2–Fe    | 2.46934                   | 0.2             | 24     |
| D   | Al3–Fe    | 2.49039                   | 0.03            | 24     |
| E   | Fe–Fe     | 2.8021                    | −0.05           | 12     |
| F   | Al1–Al2   | 2.83887                   | 0.2             | 3      |
| G   | Al2–Al3   | 2.83887                   | 0.31            | 6      |
| H   | Al3–Cr    | 2.83887                   | −0.22           | 3      |

| No. | Bond name | D(\(n_α\)) (Bond length) | Bond population | \(I_α\) |
|-----|-----------|---------------------------|-----------------|--------|
| A   | Mo–Fe     | 2.48176                   | −0.98           | 8      |
| B   | Al1–Fe    | 2.47731                   | 0.04            | 8      |
| C   | Al2–Fe    | 2.47879                   | 0.22            | 24     |
| D   | Al3–Fe    | 2.48027                   | 0.17            | 24     |
| E   | Fe–Fe     | 2.86055                   | −0.01           | 12     |
| F   | Al1–Al2   | 2.86312                   | 0.18            | 3      |
| G   | Al2–Al3   | 2.86312                   | 0.29            | 6      |
| H   | Al3–Mo    | 2.86312                   | −0.22           | 3      |

Table 6. Valence electron structure of Fe₈Al₈, Fe₈CrAl₇, and Fe₈MoAl₇.

| Phase         | Fe(\(σ\)) | Al1(\(σ\)) | Al2(\(σ\)) | Al3(\(σ\)) | X(\(σ\)) | \(\Delta D\) | \(n_α\) | \(\sum n_α\) |
|---------------|------------|-------------|-------------|-------------|---------|-------------|--------|--------------|
| Fe₈Al₈        | 4          | 4           | 4           | 4           | 4.5 \(10^{-5}\) | 0.637 | 19.692      |
| Fe₈CrAl₇      | 6          | 6           | 6           | 18          | 2.34 \(10^{-5}\) | 0.839 | 20.999      |
| Fe₈MoAl₇      | 3          | 5           | 2           | 14          | 2.82 \(10^{-4}\) | 1.676 | 20.889      |
to zero, indicating that both doping elements decreased the interaction among Fe atoms; Al–Fe bonds maintained bonding states, but the bond population values were differentiated into three states, in which two bond populations increased and the third decreased to approach zero; Al–Al bonds maintained bonding states, but the bond population value increased, indicating that both doping elements increased the covalent interaction among Al atoms.

The total density of states and partial density of states of Fe₈Al₈, Fe₈CrAl₇ and Fe₈MoAl₇ are presented in figures 5(a)–(c), respectively. Figures 5(d)–(f) clearly exhibit the same main bonding range for Fe₈CrAl₇ and Fe₈MoAl₇ as is shown by Fe₈Al₈ of figure 5(a). The figure also shows that the total density of states of all three phases passed through the Fermi levels marked by the dashed lines. These results indicate that free electrons exist near the Fermi level and that the three phases have metallic characteristics [38].

In the case of Fe₈CrAl₇ (figure 5(b)), the bonding energy of the electrons is mainly distributed in three distinct ranges: −72.532 to −71.682 eV, −44.004 to −42.814 eV, and −9.964 to 8.842 eV. As shown in figure 5(e),

![Figure 5](image_url)

**Table 7. Mulliken population of Fe₈Al₈, Fe₈CrAl₇ and Fe₈MoAl₇.**

| Species     | Number | s     | p     | d     | Total  | Charge (e) |
|-------------|--------|-------|-------|-------|--------|------------|
| Fe₈Al₈      | 8      | 0.88  | 1.96  | 0     | 2.84   | 0.16       |
| Al          | 8      | 0.34  | 0.75  | 7.07  | 8.16   | −0.16      |
| Fe₈CrAl₇    | 1      | 0.91  | 2     | 2.92  | 3.00   | 0.08       |
| Al          | 3      | 0.89  | 1.96  | 2.85  | 4.64   | 0.15       |
| Al          | 3      | 0.87  | 1.93  | 2.81  | 4.62   | 0.19       |
| Fe          | 8      | 0.39  | 0.78  | 7.01  | 8.18   | −0.18      |
| Cr          | 1      | 2.61  | 6.04  | 5     | 13.64  | 0.36       |
| Fe₈MoAl₇    | 1      | 0.92  | 2.01  | 2.93  | 5.86   | 0.07       |
| Al          | 3      | 0.89  | 1.95  | 2.84  | 4.68   | 0.16       |
| Al          | 3      | 0.88  | 1.95  | 2.82  | 4.65   | 0.18       |
| Fe          | 8      | 0.4   | 0.81  | 7.03  | 8.24   | −0.24      |
| Mo          | 1      | 2.61  | 5.62  | 4.95  | 13.18  | 0.82       |
the -5.6 to 2.86 eV energy range represents the strong bonding range of Fe, Al, and Cr atoms, indicating that Fe-
d, Al-p, and Cr-d orbital electrons contribute primarily to bonding, while other orbital electrons participate in
hybrid bonding. With Fe₈MoAl₇ (figure 5(c)), the bonding energy of the electrons is mainly distributed in the ranges of: −61.447 to −60.745 eV, −35.729 to −34.77 eV, and −9.905 to 8.843 eV. As shown in figure 5(f), the
−5.62 to 3.37 eV energy range represents the strong bonding range of Fe, Al, and Mo atoms, suggesting that Fe-
d, Al-p and Mo-d orbital electrons are the main contributors to bonding, while other orbital electrons
participate in hybrid bonding. The peaks of both Cr and Mo occur to the right side of the Fermi energy level,
indicating that Cr or Mo associations with Fe or Al are all characterized by antibonding states, based on the above
bond population analysis.

In ternary Fe–Al alloys containing either Cr or Mo, it is the Cr-d/Mo-d orbital electrons; s, p, and d orbital
electrons of Fe; and s and p orbital electrons of Al that participate in hybrid bonding. This results in the two low-
level peaks under the Fermi energy that are observed in the case of Fe₈CrAl₇ and Fe₈MoAl₇, which means that Cr
and Mo are both capable of improving the cohesive capacity of FeAl. This would also explain the greater ductility
of Fe₈CrAl₇ and Fe₈MoAl₇ compared to Fe₈Al₈ that was identified in sections 3.2 and 3.3.

3.5. Electron density difference
Electron density difference is with respect to a linear combination of the atomic densities, which can illustrate
the charge redistribution due to chemical bonding. Electron density difference maps are often used to show the
distribution of electrons around atoms as they form existing structures [39, 40].

Figure 6 shows the electron density difference map in the (110) plane of Fe₈Al₈, Fe₈CrAl₇ and Fe₈MoAl₇,
clearly demonstrating how the alloying elements change the electron distribution around the Fe and Al atoms.
The plotted density values are selected from −0.7 to 0.3 e Å⁻³ for the clarity of the three maps, and positive value
(red color) and negative value (blue color) respectively represent the charge accumulation and depletion
between atoms. As shown in all three maps in figure 6, a charge cloud is completely distributed among Fe, Al,
and Cr or Mo atoms. This finding can be considered to demonstrate the metallic characteristics of FeAl,
Fe₈CrAl₇, and Fe₈MoAl₇. In addition, figure 6(a) shows the hybridization of Al s orbital, Fe p orbitals, and Fe d
orbitals, which indicate that covalent bonding interactions partly exist in FeAl. Similar to those in FeAl, the
hybridizations of Al-s, Fe-p, Fe-d, and Cr- or Mo-d orbitals can be observed in figures 6(b) and (c). A greater
density of electrons is seen between Cr or Al and Fe from figure 6(b) and between Mo or Al and Fe from
figure 6(c) than between Al and Fe from figure 6(a). No obvious difference is apparent in the electron densities of
Cr–Fe bond in figure 6(b) or Mo–Fe bond in figure 6(c) and the Al–Al bond in figure 6(a). Considered in
conjunction with the bond population results, doping with Cr or Mo forms antibonding state with Fe, increases
the electron density between Al and Fe, and changes the electron configuration between Cr or Mo and Al but not
the electron density between Cr or Mo and Al. These electron structures can be attributed to the increased
toughness of the FeAl induced by Cr or Mo doping.
4. Conclusions

In summary, the following conclusions can be drawn:

(1) The alloying elements Cr and Mo both preferentially substitute for Al in the FeAl lattice.

(2) Both Cr and Mo addition increase the ductility of FeAl, but Cr produces a more pronounced effect.

(3) The addition of Cr or Mo improves the cohesive capacity of FeAl, as the orbital electrons of the alloying element become involved in hybrid bonding.

(4) Alloying with Cr or Mo increases the electron density of Fe–Al atomic bonding, as the electron density of Cr–Fe, Mo–Fe, and partial Fe–Al atomic bonding in Fe–Al–Cr or Fe–Al–Mo is higher than that of Fe–Al atomic bonding in FeAl.

Acknowledgments

This work was financially supported by the National Natural Science Foundation of China (Grant No. 51371097), under the Six Top Talent Peak Project funded by Jiangsu Province (Grant No. XCL-044), the Qing Lan Project of the Jiangsu Province, the Jiangsu Province Higher Visiting Scholars Program (Grant No. 2017GRGDYX024), the Jiangsu Precision Manufacturing Engineering Technology Research and Development Center Foundation (Grant No. ZK16-01-04), and the Scientific Research Foundation of Nanjing Institute of Industry Technology (Grant No. Yk18-07-02). The funders had no role in the study design; in the collection, analysis and interpretation of data; in the writing of the report; and in the decision to submit the article for publication.

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