Effect of intrinsic point-defect complex on elastic properties of $\gamma'$-Ni$_3$Al phases

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Abstract

The effect of the intrinsic point-defect complex on the elastic properties of the $\gamma'$-Ni$_3$Al phases was investigated through first-principles calculations. The formation enthalpies show that Al$_{Ni}$ and Ni$_{Al}$ defects dominate in the off-stoichiometric $\gamma'$-Ni$_3$Al phases, and the Al$_{Ni}$ + Al$_{Ni}$ and Ni$_{Al}$ + Ni$_{Al}$ point-defect complexes most likely emerge in Al-rich and Ni-rich systems, respectively. Our computational results suggest that the shear modulus $G$, Young’s modulus $E$, and melting point $T_m$ of the Ni$_3$Al phases increase when single anti-site defects form, but decrease when intrinsic point defects combine. With variations in the electronic structures caused by point defects, we explained the adverse effect of the intrinsic point-defect complex on the strength of the $\gamma'$-Ni$_3$Al phases.

1. Introduction

Nickel-based single-crystal (SC) superalloys are widely used in gas turbines and aero-engine blades owing to their high-temperature strength, excellent antioxidation, and corrosion resistance [1]. These properties benefit from a high volume fraction of the L1$_2$ Ni$_3$Al strengthening phase coherently embedded in the face-centered cubic (FCC) Ni matrix phase [2]. The performance of nickel-based SC superalloys strongly depends on the size, volume fraction, and solution strengthening degree of the $\gamma'$-Ni$_3$Al phases [3–5]. The addition of extra alloying elements increases the manufacturing cost of nickel-based SC superalloys. Therefore, the mechanical properties of off-stoichiometric $\gamma'$-Ni$_3$Al crystals with intrinsic point defects have received great attention [6–11].

Many studies have shown that the strengths of the off-stoichiometric $\gamma'$-Ni$_3$Al phases are greater than those of stoichiometric systems. In off-stoichiometric systems, the formation of anti-site point defects, Al$_{Ni}$ or Ni$_{Al}$, emerges more easily than vacancy defects [6, 12], $V_{Ni}$ or $V_{Al}$, and the anti-site point defects have been considered as a reinforcing factor for the $\gamma'$-Ni$_3$Al phases [7, 8]. For example, the flow stress-temperature curves of off-stoichiometric $\gamma'$-Ni$_3$Al phases were first determined by Lopez and Hancoc [13] for temperatures in the range 77–1273 K. For temperatures below 1173 K, there was a dramatic improvement in the strength of the Al-rich compound [13]. Noguchi et al [14] also observed that Al-rich off-stoichiometric $\gamma'$-Ni$_3$Al phases produce more significant strengthening effects than those of Ni-rich systems and the strength was the lowest for a stoichiometric composition in compression tests for temperatures in the range 77–1000 K. Furthermore, a comparison of stoichiometric Ni$_3$Al (Ni–25 at.\% Al) and Al-rich $\gamma'$-Ni$_3$Al single crystals (Ni–26 at.\% Al and Ni–27 at.\% Al) performed by Golberg et al [8] indicated that the former is weaker and has a lower yield stress than that of the latter below the peak temperature (1073 K) of the yield stress anomaly. Miura et al [10] explored the hardening of Al-rich and Ni-rich Ni$_3$Al at 77 K and found that Al-rich compounds have higher strengths than Ni-rich compounds [9]. Thus, they concluded that the hardening effect of the off-stoichiometric composition was caused by the anti-site point defects, Al$_{Ni}$ or Ni$_{Al}$, and the effect of the Al$_{Ni}$ point defect was better.

However, the attractive hardening effect in Al-rich $\gamma'$-Ni$_3$Al crystals only occurred at low temperatures, and the strength of stoichiometric Ni$_3$Al was higher than that of Al-rich Ni$_3$Al at high temperatures. Lopez et al [13]...
demonstrated that the yield stress of Al-rich Ni$_3$Al was lower than that of Ni-rich Ni$_3$Al above 1173 K, and the stoichiometric compound was the highest. Hayashi et al.\cite{7} investigated the effect of off-stoichiometry on the creep resistance of binary and ternary Ni$_3$Al. These results showed that the creep strengths of the $\gamma'$-Ni$_3$Al phases increased with increasing Ni concentration above 1123 K, except for the stoichiometric $\gamma'$-Ni$_3$Al crystals\cite{7}. Thus, it was observed that anti-site point defects do not always enhance the $\gamma'$-Ni$_3$Al phases at high temperatures, which may originate from the intrinsic point-defect complex related to the diffusion mechanisms in the $\gamma'$-Ni$_3$Al phases\cite{11,15,16}.

The first molecular dynamics simulations of diffusion mechanisms in stoichiometric and off-stoichiometric Al-rich Ni$_3$Al were performed by Duan\cite{11,17}. These results showed that Al atoms were diffused via the anti-structural bridge and intra-sublattice mechanism, resulting in the formation of intrinsic point-defect complexes\cite{11,17}. For off-stoichiometric $\gamma'$-Ni$_3$Al crystals, Hu et al\cite{16} found that Ni diffusion coefficients decreased monotonically with increasing Ni content, and the Al diffusion coefficients increased with increasing Al content. In addition, the diffusion coefficients of the Ni and Al atoms in the $\gamma'$-Ni$_3$Al crystals increased with increasing temperature\cite{16,18}. Consequently, the impact of the intrinsic point-defect complex on the elastic properties of the $\gamma'$-Ni$_3$Al phases should not be ignored at high temperatures.

This study aimed to discuss the effect of intrinsic point-defect complexes on the elastic properties of $\gamma'$-Ni$_3$Al crystals by employing a series of constructed models. In this study, the formation enthalpies of various point-defect complexes and their corresponding elastic properties were calculated using supercell models. In addition, supercells with four single intrinsic point defects were also constructed and calculated. Finally, an analysis of intrinsic point-defect complexes and their influence on the mechanical properties of the $\gamma'$-Ni$_3$Al phases was conducted. Moreover, the variation in the electronic structures caused by the point defects was examined.

### 2. Calculation details

First-principles calculations were performed using the Vienna \textit{ab initio} simulation package (VASP)\cite{19,20}. The VASP was based on density functional theory, in which a plane-wave basis set with a projector augmented wave\cite{21} was adopted to characterize the ion-electron interaction, and the exchange-correlation term was described within the generalized gradient approximation, which was parameterized by the Perdew–Burke–Ernzerhof functional\cite{22}. In our self-consistent field (SCF) calculations, the cutoff energy of the plane-wave functions was set at 350 eV, and the sampling of irreducible wedges of the Brillouin zones was performed with $4 \times 4 \times 4$ regular Monkhorst-Pack grids\cite{23}. The calculations of the total energies and electronic structures were performed after the volume and atomic position optimizations using an SCF tolerance of $1 \times 10^{-6}$ eV.

A series of supercells were constructed for the defective system, which was $3 \times 3 \times 3$ of the $\gamma'$-Ni$_3$Al crystallographic cell (see figure 1(b)), consisting of 27 Al and 81 Ni sites. The single intrinsic point defects were indicated as Al$_{Ni}$, V$_{Ni}$, Ni$_{Al}$ or V$_{Al}$, which corresponded to the Al anti-site, Ni vacancy, Ni anti-site, and Al vacancy defects, respectively. As the two intrinsic point defects were simultaneously added to the Ni$_3$Al models, we constructed seven point-defect complex models in the investigations: Al$_{Ni}$ + Al$_{Ni}$, Al$_{Ni}$ + Ni$_{Al}$, Al$_{Ni}$ + V$_{Ni}$, Al$_{Ni}$ + V$_{Al}$, Ni$_{Al}$ + V$_{Ni}$, Ni$_{Al}$ + V$_{Al}$, Al$_{Ni}$ + Ni$_{Al}$ + V$_{Ni}$, Ni$_{Al}$ + Ni$_{Al}$ + V$_{Al}$, and Ni$_{Al}$ + Ni$_{Al}$ + V$_{Al}$. The orientation and distance between the lattice points occupied by the defects in the Ni$_3$Al crystals are shown in figure 1(a); the distances are $\sqrt{2}/2$-a and a, where a is the equilibrium lattice parameter.

The elastic properties of Ni$_3$Al, with and without various defects, were calculated to investigate the effects of the point-defect complexes on the mechanical properties. The elastic tensor for the equilibrium volume was determined by performing seven finite distortions of the lattice and deriving the elastic constants from the strain–stress curves\cite{24,25}. There were three independent components, $C_{11}$, $C_{12}$, and $C_{44}$, in the cubic L1$_2$ Ni$_3$Al crystals\cite{25}. Therefore, the bulk modulus B, shear modulus G, Young’s modulus E, and Poisson’s ratio $\nu$ can be directly obtained using the elastic constants via the Voigt–Reuss–Hill method\cite{26}. These were calculated for the cubic crystals using the following expressions:

\begin{align}
B &= (C_{11} + 2C_{12})/3 \\
G_V &= [(C_{11} - C_{12}) + 3C_{44}]/5 \\
G_R &= [5C_{44}(C_{11} - C_{12})]/[3(C_{11} - C_{12}) + 4C_{44}] \\
G &= G_{HH} = (G_V + G_R)/2 \\
E &= 9BG/(3B + G) \\
\nu &= (3B - 2G)/(2(3B + G))
\end{align}

Table 1 lists the elastic constants, bulk modulus B, shear modulus G, and Young’s modulus E of the perfect $\gamma'$-Ni$_3$Al crystals, which are consistent with previous theoretical\cite{27} and experimental\cite{28} results, indicating that the parameters were sufficient to achieve the accuracy required in the current calculations.
3. Results and discussion

3.1. Formation enthalpy of point defect

The calculated equilibrium lattice parameter $a$ of the $\gamma'$-Ni$_3$Al crystals was 3.566 Å, which was consistent with the experimental value of 3.572 Å [29]. Furthermore, the formation enthalpies of the point defects $H_d$ [30, 31] in defective systems were calculated using

$$H_d = E_{Ni_{1-x}Al_{x}} - E_{Ni_{1-x}Al_{x}} + x \cdot E(Ni) + y \cdot E(Al)$$

where $E_{Ni_{1-x}Al_{x}}$ and $E_{Ni_{1-x}Al_{x}}$ are the total energies of the defective and perfect Ni$_3$Al crystals, respectively. $x$ and $y$ are the numbers of Ni and Al sites replaced by point defects, respectively; these can be $-2$, $-1$, 0, 1, or 2, depending on the type of point defect in the supercell models. For example, the combination of $x = 1$ and $y = -1$ represents an Al anti-site defect (i.e., Al$_{Ni}$); the combination of $x = 1$ and $y = 0$ represents a vacancy on the Ni site (i.e., $V_{Ni}$) or a complex with an Al anti-site defect and vacancy on the Al site (i.e., Al$_{Ni}$ + $V_{Al}$). In this case, the two configurations may yield different $H_d$ values for the point defects, despite their expressions being the same. $E(Ni)$ and $E(Al)$ are the energies per atom in the FCC-Ni and FCC-Al unit cells, respectively.

Using the Al$_{Ni}$ + Al$_{Ni}$ complex as an example, a comparison of the calculated $H_d$ values obtained for different sized supercell models is plotted in figure 2. It is clear that the 3 $\times$ 3 $\times$ 3 supercell models were sufficient in this study.

The calculated $H_d$ values of the point defects are listed in table 2. As for the single point defect, $H_d$ of the Al anti-site defects ($-0.968$ eV) is much lower than that of the Ni vacancy defect ($1.624$ eV) in the Al-rich alloys, and $H_d$ of the Ni anti-site ($2.008$ eV) is much lower than that of the Al vacancy defect ($3.638$ eV) in the Ni-rich alloys. These results clearly indicate that the anti-site point defects were dominant in the off-stoichiometric Ni$_3$Al crystals, which is consistent with previous theoretical and experimental results [27, 32, 33]. Furthermore, a negative $H_d$ of Al$_{Ni}$ indicates that the formation of a single Al anti-site defect is an exothermic reaction, which means that the Al anti-site defect was the easiest to form in the Ni$_3$Al intermetallic compounds.

For the point-defect complex in the Al-rich Ni$_3$Al crystals, $H_d$ of the Al$_{Ni}$ + Al$_{Ni}$ complexes were the lowest, followed by those of the Al$_{Ni}$ + $V_{Ni}$ and Al$_{Ni}$ + $V_{Al}$ complexes. This clearly reveals that the dominance of the Al anti-site defects in the Al-rich systems did not have a significant effect, despite the extra point defect, and the

| Alloys      | $C_{11}$/GPa | $C_{12}$/GPa | $C_{44}$/GPa | $B$/GPa | $G$/GPa | $E$/GPa |
|-------------|--------------|--------------|--------------|---------|---------|---------|
| Ni$_3$Al    | 232          | 157          | 122          | 182     | 76      | 201     |
| Ni$_3$Al [27] | 242          | 152          | 125          | 182     | 83      | 217     |
| Ni$_3$Al [28] | 225          | 149          | 124          | 174     | 77      | 202     |

![Figure 1](image-url)
Al$_{Ni}$ + Al$_{Ni}$ point-defect complexes were the most likely to emerge. The $H_d$ values of the point-defect complex were larger in the Ni-rich phases compared with those of the Al-rich phases. Specifically, $H_d$ of the Ni$_{Al}$ + V$_{Ni}$ complex (5.614 eV) was higher than that of the Al$_{Ni}$ + V$_{Ni}$ complex (0.705 eV) at the same orientation and distance, $\frac{1}{2}(110)$. This indicates that point defects can hardly be complex in Ni-rich crystals. Despite this, the Ni$_{Al}$ + Ni$_{Al}$ defect was dominated by the smallest $H_d$ in the Ni-rich system. These results demonstrate that the complex of anti-site point defects was dominant in the off-stoichiometric Ni$_3$Al crystals, as concluded previously. For the Al$_{Ni}$ + Ni$_{Al}$ complex, $H_d = 0.781$ eV, which is less than that of both the point-defect complex in Ni-rich Ni$_3$Al and a single Ni$_{Al}$ defect, indicating that the exchange point-defect complex can be formed in stoichiometric Ni$_3$Al phases.

By considering the distance between the point defects, it was found that their interaction had a significant impact on the formation ability of defects in the same complex. For example, the distances in the Al$_{Ni}$ + Al$_{Ni}$ complexes with the (100) and $\frac{1}{2}(110)$ configurations were $a$ and $\frac{\sqrt{2}}{2}a$, with $H_d$ values of $-1.789$ and $-1.579$ eV (table 2), respectively. In this case, a larger distance in the former configuration implies a weaker interaction between the point defects [31, 34]. Thus, a large interaction between point defects is unfavorable for the formation of a point-defect complex. As a result, the point defects tended to separate from each other in the Ni$_3$Al crystals at low temperatures. However, the diffusion of Al and Ni atoms also became stronger with increasing temperature [16], and a growing number of point-defect complexes were inevitable in the $\gamma'$-Ni$_3$Al crystals. Hence, the investigation of the impact of point-defect complexes on the mechanical properties can provide an in-depth perspective for understanding the high-temperature strength of off-stoichiometric $\gamma'$-Ni$_3$Al phases.

3.2. Elastic properties

The values of the elastic constants of the defect systems are listed in table 2. The mechanical stability criterion, i.e., the Born criterion, for the elastic constants is $C_{11} - C_{12} > 0$, $C_{44} > 0$, and $C_{11} + 2C_{12} > 0$ [35, 36]. As seen in table 2, all elastic constants met these criteria, indicating that the L1$_2$-Ni$_3$Al crystals, both with and without various point defects, were mechanically stable. Meanwhile, $C_{11}$ and $C_{12}$ were significantly affected by the point defects, while $C_{44}$ was insensitive.

Table 2 further provides the values of the bulk modulus $B$, shear modulus $G$, Young’s modulus $E$, $B/G$, and Poisson’s ratio $\nu$. For the $\gamma'$-Ni$_3$Al crystals with single point defects, other calculation values were also employed and determined in line with our results [27]. Generally, $B/G$ is associated with the ductility (brittleness) of a material [37, 38]. If $B/G < 1.75$, a material is a brittle substance, otherwise it is ductile. $B$, $G$, and $E$ determine the resistance to fracture, resistance to plastic deformation, and evaluation of the stiffness of the solid, respectively [39]. Moreover, the ductility or brittleness behavior of materials can also be characterized using Poisson’s ratio $\nu$ [40], in which $\nu < 0.26$ and $\nu > 0.26$ corresponds to brittle and ductile materials, respectively [41].

Single anti-site defects have a strengthening effect on the mechanical properties of $\gamma'$-Ni$_3$Al crystals relative to single vacancy defects, that is, Al$_{Ni}$ and Ni$_{Al}$ defects are beneficial, while V$_{Ni}$ and V$_{Al}$ defects are detrimental [27]. For example, in table 2 $G$ is 80 and 78 GPa in the Al$_{Ni}$ and Ni$_{Al}$ models, respectively, which are both greater than 76 GPa in the defect-free model. Similarly, the $E$ increased to 208 and 205 GPa in the Al$_{Ni}$ and Ni$_{Al}$ models,
Table 2. Formation enthalpies of the point defects (\(H_d\)) and elastic properties of the Ni$_3$Al models with various point defects.

| Component      | Point defects | orientation and distance | \(H_d\)/eV | \(C_{11}\)/GPa | \(C_{12}\)/GPa | \(C_{44}\)/GPa | \(B$/GPa$ | \(G$/GPa$ | \(E$/GPa$ | \(B$/G| \(v| References |
|----------------|---------------|--------------------------|------------|-----------------|-----------------|----------------|----------|----------|----------|----------|--------|---------|
| Al-rich        | V$_{Ni}$      | —                        | 1.624      | 227             | 155             | 120             | 179       | 74       | 196       | 2.41     | 0.32   | This work |
|                |               |                          | 1.48       | 220             | 155             | 155             | 177       | 69       | 183       | 2.56     | 0.33   | [27]     |
|                | Al$_{Ni}$     | —                        | −0.968     | 236             | 153             | 123             | 181       | 80       | 208       | 2.27     | 0.31   | [32],[33] |
|                |               |                          | −1.00      | 233             | 152             | 121             | 179       | 77       | 203       | 2.31     | 0.32   | This work |
|                | Al$_{Ni}$ + Al$_{Ni}$ (100) |                     | −1.789     | 214             | 168             | 122             | 183       | 64       | 171       | 2.88     | 0.34   | This work |
|                | Al$_{Ni}$ + Al$_{Ni}$ (100) |                     | −1.579     | 200             | 191             | 122             | 191       | 43       | 120       | 4.53     | 0.40   | This work |
|                | Al$_{Ni}$ + Al$_{Ni}$ (100) |                     | 0.671      | 222             | 156             | 120             | 178       | 72       | 190       | 2.48     | 0.32   | This work |
|                | Al$_{Ni}$ + Al$_{Ni}$ (100) |                     | 0.705      | 222             | 156             | 120             | 178       | 72       | 190       | 2.48     | 0.32   | This work |
|                | Al$_{Ni}$ + Al$_{Ni}$ (100) |                     | 2.307      | 227             | 154             | 120             | 178       | 75       | 196       | 2.39     | 0.32   | This work |
| Stoichiometric | Al$_{Ni}$ + Ni$_{Al}$ (110) |                     | 0.781      | 232             | 156             | 122             | 181       | 77       | 201       | 2.37     | 0.32   | This work |
|                | Defect free   |                          | —          | 232             | 157             | 122             | 182       | 76       | 201       | 2.39     | 0.32   | This work |
| Ni-rich        | V$_{Al}$      | —                        | 3.638      | 228             | 156             | 120             | 180       | 74       | 196       | 2.42     | 0.32   | This work |
|                |               |                          | 3.42       | 221             | 150             | 120             | 174       | 74       | 194       | 2.35     | 0.32   | [27]     |
|                | Ni$_{Al}$     | —                        | 2.008      | 236             | 156             | 122             | 183       | 78       | 205       | 2.34     | 0.31   | This work |
|                |               |                          | 2.06       | 242             | 149             | 123             | 180       | 83       | 216       | 2.17     | 0.30   | [27]     |
|                | Ni$_{Al}$ + V$_{Ni}$ (110) |                     | 5.614      | 57              | 39              | 120             | 45        | 48       | 106       | 0.94     | 0.11   | [32],[33] |
|                | Ni$_{Al}$ + V$_{Al}$ (100) |                     | 3.982      | 228             | 156             | 119             | 180       | 74       | 195       | 2.44     | 0.32   | This work |
|                | Ni$_{Al}$ + Ni$_{Al}$ (100) |                     | 3.613      | 234             | 157             | 120             | 183       | 76       | 201       | 2.40     | 0.32   | This work |
respectively. $B$, $G$, and $E$ decreased to 179, 74, and 196 GPa in the $V_{Ni}$ model and 180, 74, and 196 GPa in the $V_{Al}$ model, respectively. Furthermore, the values of $B/G$ and $v$ were all greater than the 1.75 and 0.26 criteria, respectively. These results indicate that the $\gamma'$-$Ni_3Al$ crystals, both with and without single point defects, were ductile in all cases, and the anti-site defect decreased the ductility of the materials because the values of $B/G$ and $v$ were reduced compared to those of perfect materials.

The bulk modulus $B$, shear modulus $G$, Young’s modulus $E$, $B/G$, and Poisson’s ratio $v$ for the point-defect complex systems are shown in Figure 3; the values of the perfect Ni$_3$Al and single point defect models are also plotted for comparison. In the Al-rich models, $B$ was in the range 183–191 GPa for the Al$_{Ni}$ + Al$_{Ni}$ complex models, which were the largest among all point-defect complex models, and significantly higher than that of the Al$_{Ni}$ model (181 GPa). This indicates that a double Al$_{Ni}$ defect configuration can further improve the resistance

![Figure 3. Bulk modulus $B$, shear modulus $G$, Young’s modulus $E$, $B/G$, and Poisson’s ratio $v$ of $\gamma'$-$Ni_3Al$ crystals with a point-defect complex.](image-url)
Table 3. Melting point $T_m$ and $G_{11}$ of Ni$_3$Al crystals with various point defects.

| Component     | Point defects | Orientation and distance | $G_{11}$/GPa | $T_m$/K | References |
|---------------|---------------|--------------------------|--------------|---------|------------|
| Al-rich       | $V_{Ni}$      | —                        | 227          | 1595    | This work  |
|               | $Al_{Ni}$     | —                        | 236          | 1647    | This work  |
|               | $Al_{Ni} + Al_{Ni}$ | $\frac{1}{2}(110)$   | 214          | 1517    | This work  |
|               | $Al_{Ni} + V_{Ni}$ | $\frac{1}{2}(110)$   | 222          | 1565    | This work  |
| Stoichiometric| $Al_{Ni} + V_{Al}$ | $\frac{1}{2}(110)$   | 227          | 1594    | This work  |
| Ni-rich       | $V_{Al}$      | —                        | 228          | 1600    | This work  |
|               | $Ni_{Al}$     | —                        | 236          | 1648    | This work  |
|               | $Ni_{Al} + V_{Ni}$ | $\frac{1}{2}(110)$   | 57           | 590     | This work  |
|               | $Ni_{Al} + V_{Al}$ | (100)               | 228          | 1600    | This work  |
|               | $Ni_{Al} + Al_{Al}$ | (100)               | 234          | 1635    | This work  |

To fracture of $\gamma'$-Ni$_3$Al crystals. However, as shown in figure 3, $G$ and $E$ in the $Al_{Ni} + Al_{Ni}$ complex models were the lowest for all Al-rich systems, which were not only smaller than that of perfect Ni$_3$Al, but also smaller than that of the $V_{Ni}$ model, indicating that the resistance to plastic deformation and stiffness of the materials were significantly weaker. Conversely, the ductility of the materials was enhanced as a result of having the highest $B/G$ and $\psi$ in a series of models. Similar to the $Al_{Ni} + Al_{Ni}$ complex models, $B$, $G$ and $E$ of the $Al_{Ni} + V_{Ni}$ and $Al_{Ni} + V_{Al}$ complex models were less than those of the $Al_{Ni}$ model and perfect Ni$_3$Al. This phenomenon resulted in a low high-temperature strength of Al-rich Ni$_3$Al compared to that of stoichiometric Ni$_3$Al [13]. Compared to the $Al_{Ni} + Al_{Ni}$ complex models, $B$ was large (183 GPa) and greater than that of perfect Ni$_3$Al for the $Ni_{Al} + Ni_{Al}$ complex model (figure 3). $G$ and $E$ of the $Ni_{Al} + Ni_{Al}$ complex model did not improve compared to that of perfect Ni$_3$Al, and were less than those of the $Ni_{Al}$ model. This result clearly indicates that the anti-site point-defect complex in Ni-rich Ni$_3$Al has an indirect reinforcement effect on the $\gamma'$-Ni$_3$Al crystals. In addition, $E = 195$ GPa for the $Ni_{Al} + V_{Al}$ complex model, which is less than that of the $V_{Al}$ model; and $B$, $G$, and $E$ in the $Ni_{Al} + V_{Ni}$ complex model were the smallest among all models. Consequently, the high-temperature strength of Ni-rich Ni$_3$Al is less than that of stoichiometric Ni$_3$Al [7, 13].

Thus, we conclude that although a single anti-site defect is helpful in improving strength, the point-defect complexes due to atomic diffusion [16] are harmful for the strengthening of $\gamma'$-Ni$_3$Al crystals.

### 3.3. Melting point $T_m$

To understand the effect of the point-defect complex on the heat resistance of the $\gamma'$-Ni$_3$Al crystals, their melting point $T_m$ was calculated using an empirical formula. The relationship between the elastic constant $G_{11}$ and $T_m$ for Ni–X binary systems is as follows [42, 43]:

$$T_m = 553 + 5.91G_{11} - 300(K) \quad (8)$$

The calculated $T_m$ values for the Ni$_3$Al crystals with various point defects are listed in table 3. For the defect-free Ni$_3$Al crystals, $T_m = 1624$ K, which is consistent with experimental results [29], indicating that the $T_m$ computational method is reliable. For the $\gamma'$-Ni$_3$Al crystals with single point defects, $T_m$ decreased from 1624 to 1600 and 1595 K, corresponding to the effects of the $V_{Al}$ and $V_{Ni}$ defects, respectively. In contrast, $T_m$ increased to 1647 and 1648 K in the $\gamma'$-Ni$_3$Al crystals with $Al_{Ni}$ and $Ni_{Al}$ defects, respectively. These results clearly suggest that single anti-site defects are favorable for the improvement of $T_m$ in $\gamma'$-Ni$_3$Al crystals and single vacancy defects are disadvantageous. For Ni$_3$Al with point-defect complexes, the values were reduced to the range 590–1600 K, except for the $Al_{Ni} + Ni_{Al}$ and $Ni_{Al} + Ni_{Al}$ complexes, which demonstrated that the point-defect complexes had a detrimental effect on $T_m$ of the $\gamma'$-Ni$_3$Al crystals. This may explain the reduction in the high-temperature strength of the off-stoichiometric Ni$_3$Al, especially that of Al-rich systems [7, 13].

### 3.4. Electronic density

To understand the impact of the point-defect complex on the elastic properties of the $\gamma'$-Ni$_3$Al phases, the electronic density contours of the typical (001) and (002) planes are plotted in figure 4. The variations in the elastic properties of the $\gamma'$-Ni$_3$Al crystals resulting from point defects can be explained using the electronic density [44]. The greater the electronic density, the stronger the bonds formed between the Ni and Al atoms [45],

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and materials with nearly spherical electronic structures are prone to deformation owing to their relatively shorter shear deformation ranges [46].

Figure 4(c) shows that the single AlNi defect affected the electronic densities between its nearest neighboring Al-Ni atoms, making the electronic structure around point defects from nearly spherical (figure 4(a)) to nearly square (figure 4(c)). For the NiAl model, as shown in figure 4(d), the electronic density between the nearest neighboring Ni-Ni atoms was significantly increased compared to that between the Al and Ni atoms, and the electronic structure around the point defect became nearly square from nearly spherical. Therefore, single anti-site AlNi and NiAl defects enhance the strength of γ′-Ni3Al crystals [27].

For the point-defect complex systems, the electronic density contours of the (002) plane in the AlNi + AlNi\textsubscript{1/2}(110) and (001) planes in the NiAl + V\textsubscript{Ni}\textsubscript{1/2}(110) models are also plotted in figures 4(e) and (f), respectively. For the AlNi + AlNi model, when the nearest neighboring Ni atoms were simultaneously replaced by two Al atoms, the electronic structure between the point defects changed from nearly square (figure 4(b)) to nearly spherical (figure 4(e)), and the electronic density between the Al and Al atoms (figure 4(e)) was less than that between the Ni and Ni atoms (figure 4(b)). Thus, the AlNi + AlNi complex reduced the strength of the γ′-Ni3Al crystals, as opposed to further strengthening it. For the NiAl + V\textsubscript{Ni} model, the anti-site Ni atom and its nearest-neighbor Ni vacancy occurred simultaneously. The Ni vacancy (figure 4(f)) caused the electronic density to decrease significantly in the γ′-Ni3Al crystals, and the electronic structure around the anti-site Ni atom became nearly spherical owing to the effect of the Ni vacancies. Therefore, the strength of the γ′-Ni3Al crystals was significantly reduced (see figure 3).

4. Conclusions

Density functional theory calculations were performed to study the effect of various point defects on the elastic properties of the L12 Ni3Al phases. Furthermore, the forming abilities of point defects were also investigated. The analysis of the formation enthalpy implied that single anti-site point defects were dominant in the off-stoichiometric γ′-Ni3Al crystals, which is consistent with previously reported theoretical and experimental results. In the case of the point-defect complex, AlNi + AlNi and NiAl + NiAl complexes tended to occur in the Al-rich and Ni-rich Ni3Al, respectively. These results demonstrate that the anti-site point defects are predominant, both at low and high temperatures, for off-stoichiometric Ni3Al. In addition, the calculation
results of the elastic properties showed that the single AlNi and NiAl point defects were beneficial to the strengthening of the $\gamma'$-Ni$_3$Al phases, while the AlNi + AlNi and NiAl + NiAl point-defect complexes were harmful. Furthermore, single anti-site point defects and point-defect complexes can increase and reduce the melting point $T_m$ of the $\gamma'$-Ni$_3$Al crystals, respectively. In other words, with increasing temperature service conditions, stoichiometric $\gamma'$-Ni$_3$Al crystals are more likely to achieve excellent high-temperature strengths. At low temperatures, the $\gamma'$-Ni$_3$Al phases should deviate from the stoichiometric ratio and form anti-site point defects, thereby increasing their strength. These results provide some explanations for the reduction in the high-temperature strength of off-stoichiometric systems. A careful analysis of the electronic densities revealed that the increase in the strength of the AlNi and NiAl models resulted mainly from the nearly square electronic structure around the anti-site point defects and the higher strength of the Ni–Ni bonding compared to that of the Al–Ni bonding in the NiAl model. Furthermore, the nearly spherical electronic structures around the point defects and the lower strength of the Al–Al bonding relative to that of the Ni–Al bonding resulted in the weakening of the $\gamma'$-Ni$_3$Al crystals with the AlNi + AlNi complex.

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**Data availability statement**

All data that support the findings of this study are included within the article (and any supplementary files).

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