The Influence of Doping by Transition Metal Elements on the Vacancy Formation Energy in Fe-Al *B*2 Phase

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Based on ab initio calculations for Fe-Al *B*2 phase with and without the vacancies, the authors studied the influence of alloying by Ni, Cr, and V on the energy of vacancy formation. The authors predict that the presence of these alloying elements in the vicinity of the vacancy on the Fe site increases the energy of the vacancy formation. The present article discusses the changes of the electron charge redistribution in the vicinity of the vacancy in Fe-Al alloyed with these transition metals and link the preference of their site occupation with the peculiarities of the electron density redistribution. In addition, the authors report on the results of calculations of different types of antisite defects in Fe-Al and show that the formation of the antisite on the Al site is the energetically preferable configuration for this defect. The obtained results are in agreement with the experimental data.

1. Introduction

Several experimental studies together with theoretical studies, particularly those based on ab initio methods, have concentrated their efforts on understanding the influence of point defects, such as vacancies and ternary additives, on the mechanical and electrical properties of intermetallic compounds. It has been shown that Fe-Al has a high concentration of point defects, one of the most prominent being thermal vacancies. Therefore, much research, since the pioneering work began in the 1970s,[1-3] has been pointed toward understanding the influence of the vacancy formation on the properties of this intermetallic compound. For example, a study of equilibrium point defects in Fe-Al and Ni-Al,[4] based on local-density functional (LDF) equations within the mixed-basis pseudopotential method, predicted a strong tendency for vacancy clustering in Fe-Al and explained the differing mechanical behaviors of Fe-Al and Ni-Al by shedding some light on the dissimilarity of the defects that formed in these intermetallics. Vacancies cause hardening,[5,6] and an increase in their concentration depends on temperature and Al concentration.[4,7] The alloying of iron aluminides by Ni slows down the removal of thermal vacancies.[8] In contrast, boron increases the rate of vacancy elimination.[9] The study of the site preference of ternary alloying additions, by ab initio calculations with LDF equations,[10] shows that in Fe-Al Cr and Ti occupy the Al sublattice whereas Ni has a distinct preference for the Fe sublattice. Also, using the transmission electron microscope-based technique atom location by channeling enhanced microanalysis it was shown that Cu atoms occupy

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the Fe sublattice in Fe-45at.%Al-5at.%Cu, but Cr atoms mostly occupy the Al sublattice in Fe-45at.%Al-5at.%Cu and in Fe-40at.%Al-5at.%Cu.[11] It has also been found that the strain-induced ferromagnetism in B2-structured Fe-Al is a function of composition and of deformation degree.[12] Other major structural defects in B2-type iron aluminides are antistructure atoms that form on both sublattices.[13-16] Because intermetallic compounds, and the Fe-Al *B*2 phase in particular, are candidate high-temperature structural materials, diffusion in them and factors that affect the diffusion mechanism have been actively investigated.[17-19] One of the conditions for the diffusion of atoms is a vacancy formation on the nearest or second-nearest neighbor site. Therefore, diffusivity depends on the vacancy concentration.[18]

Alloying elements affect the energy of the vacancy formation, and therefore they influence the diffusion mechanics.[20] In the present article, we report the results of our study of the influence of Ni, Cr, and V on the energy of vacancy formation on both Fe and Al sites in Fe-Al.

2. Computational Method

The authors performed ab initio calculations with density-functional theory in the generalized gradient approximation for the exchange correlation functional.[21] It was found that a k-mesh value of ~800 points in the first Brillouin zone makes the total amount of energy independent of the number of k-points. The augmented plane wave-plus-local orbitals (APW + lo) basis for all valence orbitals was used. The basis-set size $R_{mt}K_{max} = 6.5$ was used, while a chosen radius of muffin-tin spheres, R_{mt}, both for Fe and Al atoms, was taken equal to 2.2 atomic units. The energy cutoff, separating the core and valence states, was chosen equal to −7.0 rydbergs, and the maximal wave vector G was chosen equal to 14 (in units $2\pi/a$, where a is the lattice parameter). The WIEN2k package[22] was applied. All calculations were performed in relativistic approximation for Fe-Al with and without defects.

Table 1 Comparison of the calculated results for the enthalpy of formation, for the lattice parameter, and for the energies of the vacancy formation $E_v(A)$ on the A-atom site

Study	ΔH, eV/atom	a(Å)	E_v(Fe), eV	E_v(Al), eV
This work	−0.324	2.88	0.869	3.537
Hultgren et al.[23]	−0.33	…	…	…
Smithels[24]	−0.28	2.86	…	…
Fu[25]	…	…	0.82	4.00
Kerl et al.[26]	…	…	0.85	…
Kass et al.[27]	…	…	0.934	…

Table 2 Energy of the vacancy formation $E_v(A)$ at the A-atom site in FeAl without and with alloying elements

FeAl alloyed with	E_v(Fe), eV	E_v(Al), eV
Without alloying element	0.869	3.537
Cr on the Fe site	0.910	4.510
Cr on the Al site	2.166	3.887
V on the Fe site	0.902	3.354
V on the Al site	1.261	3.963
Ni on the Fe site	1.928	4.848
Ni on the Al site	0.993	3.333

With a 54-atom supercell, our calculations indicated that the energy of vacancy formation differs by ~10% compared with the results for a 16-atom supercell, but increases the computation time drastically. In this study the authors used a 16-atom supercell that included one point defect of any kind (e.g., vacancy, antistructure atom, or ternary element).

3. Results

In the studies for simple metals, it was shown that the vacancy formation is followed by significant shifts of the atoms in the vicinity of the vacancies. In the case of intermetallic compounds, not only metallic bonds (as in the case of a simple metals), but also 30 to 40% of covalent bonds are present, which are known to be much stronger than a metallic bonds. In this investigation, a $2 \times 2 \times 2$ supercell was used; therefore, the displacements around the vacancy only of its nearest neighbors could be checked. It was found that the local relaxation around the vacancy is an inward shift of the first neighbors of the vacancy. This value is 0.4% of the equilibrium lattice parameter of the extended Fe-Al $B2$ phase with the vacancy. When this local relaxation is taken in account, the energy of vacancy formation is negligibly decreased by about 0.43%. This value is much smaller than values that had been reported for simple metals. The reason for the small value of local relaxation in this case compared with that for simple metals follows from the presence of highly localized covalent bonds in Fe-Al. The highly localized electronic charge makes the lattice of the intermetallic compound very rigid and only slightly sensitive with respect to the formation of the hollow site. The elastic field around the vacancy in Fe-Al is of a rather short range. The elastic field has a negligible effect on second-nearest neighbors of the vacancy on the Fe site. Therefore, we have omitted the local relaxations in our additional calculations.

The quality of the calculations is shown in Table 1. The enthalpy of formation ΔH and the lattice parameter a are in good agreement with the calorimetric measurements.[23,24] The energies of the vacancy formation in the stoichiometric Fe-Al $B2$ phase on the Fe and Al sites, E_v(Fe) and E_v(Al), respectively, are in good agreement with the values calculated by the full-potential linearized augmented waves

(FLAPWs) method with spin polarization[25] and with experimental measurements.[26,27]

3.1 The Preference of Site Occupation of the Alloying Elements

It was found that the preferred site for occupation by Ni in Fe-Al with and without the vacancies was the Fe site. This analysis was based on a comparison of the mixing energies following the scheme presented in previous work.[20] It was also reported that Cr and V occupy the Al site in the ideal Fe-Al $B2$ phase. In the case of a vacancy on the Fe site in Fe-Al, V occupies the Al site and Cr occupies the Fe site nearest to the vacancy.

3.2 Energy of Vacancy Formation

The vacancies in the Fe-Al $B2$ phase are formed mainly on the Fe sublattice[20]; therefore, it is of interest to check the influence of the alloying transition metal (TM) on the preference site for the vacancy formation. The calculated results are summarized in Table 2.

One can see that the energy of the vacancy formation on the Al site remains approximately four times higher than this on the Fe site also after alloying. Therefore, the vacancies are also formed mainly at Fe sites when TM-alloying elements are present in their vicinity. In addition, alloying by Cr on the Al site and by Ni on the Fe site doubles the energy of the vacancy formation on the Fe site. Alloying by V increases the energy of vacancy formation by 1.5 times.

3.3 Energy of Antisite Formation

Other structural defects that were studied are the antisite defects on both sublattices. For Fe-Al, relatively low antisite formation energy during stoichiometry was found. The calculated results are given in Table 3 and are compared with other relativistic[25] and nonrelativistic ab initio calculations.[4,28] The results for antisite energy formation differ slightly from the previous ab initio calculations. The previous results for the antisite formation energies at the Fe and Al sublattices are almost the same, while our calculations show a much more significant difference in the formation energies of antisites at the Fe and Al sites. The

results were confirmed experimentally by Mössbauer spectroscopic experiments[29] that showed that Fe-Al $B2$ phase contains predominately antisites at the Al sublattice and vacancies at the Fe sublattice. Only a negligible number of defects, such as antisites on the Fe sublattice and vacancies on the Al sublattice, were detected in these experiments.

It is interesting to note that Fe-Al has relatively low antisite formation energy at the Fe site, but very high vacancy formation at the Al sites. Therefore, it is easier to add an Al atom than to remove an Al atom. Actually, the antisite defects at the Fe sites become the dominant type of defect for Al-rich Fe-Al. But for the Fe-rich Fe-Al the dominant defects are vacancies at the Fe sites and antisites at the Al sites.

3.4 Equilibrium Lattice Parameter

The total energy in the APW + lo calculations has also been minimized for the defect supercell systems. The corresponding equilibrium lattice constants are given in Table 4 and are compared with the results of the previous tight-binding linear muffin-tin orbital (TB-LMTO) calculations.[30]

3.5 Charge Distribution

To understand the preferential occupancy of particular sites by of the alloying elements in Fe-Al $B2$ with and without vacancies, the charge redistribution in the real space was studied. The authors compared the differential charge distribution (i.e., the difference between the electron distribution in the intermetallic compound and that of the constituent atoms) in Fe-Al, as shown in Fig. 1 and 2.

For the case without the vacancy (Fig. 1), a comparison was made of the charge transfer in the vicinity of the alloying elements on the Fe site (Fig. 1a-c) and the charge transfer when the alloying elements occupy the Al site (Fig. 1d-f). The isodensity curves in Fig. 1 and 2 are drawn with increments of 0.001 e/angstom³.

When Cr or V occupies the Al site (Fig. 1d and f, respectively), the electron density between these ternary elements and their nearest neighbors, the Fe atoms, is relatively high. In the case of Cr, the value was 16, and in the case of V it was 14 (in units of 0.001 e/′³ here and in further discussion). On the contrary, when Cr or V occupies the Fe site the electron density is relatively low between ternary elements and their nearest neighbors, the Al atoms. The corresponding values are 4 between Cr and Al atoms, and 3 between V and Al atoms. Thus, strong directional bonds are formed between these ternary elements and Fe atoms, and therefore these ternary elements prefer to occupy the Al site, which is in agreement with results for the mixing energy.[20] When Ni occupies the Al site, the value of the electron density in the vicinity of the ternary element is only 6. This means that no strong directional bonds are formed between Ni and its nearest neighbors, the Fe atoms. When Ni occupies the Fe site, the electron density in the vicinity of Ni is almost homogeneously distributed and relatively low, and the differential charge distribution changes from 2 to 3. Therefore, in this case the uniform distribution of the charge makes the compound more stable.

A similar comparison of the charge transfer has been done for the case with the vacancy on the Fe site in Fe-Al with alloying elements (Fig. 2). When the alloying elements occupy the Fe site, the second-nearest neighbor of the vacancy (Fig. 2a-c), called the *vacancy pocket*, is nearly sym-

Table 3 Anti-site formation energies of FeAl at stoichiometry, $E_{\text{anti}}(A)$, at A-atom sites

Method	$E_{\text{anti}}(\text{Fe})$, eV	$E_{\text{anti}}(\text{Al})$, eV
This work	1.054	0.699
FLAPW[25]	0.68	0.65
FLAPW[4]	1.03	0.95
Pseudopotentials[28]	0.99	0.99

Table 4 Equilibrium lattice constant for the FeAl supercell with defects

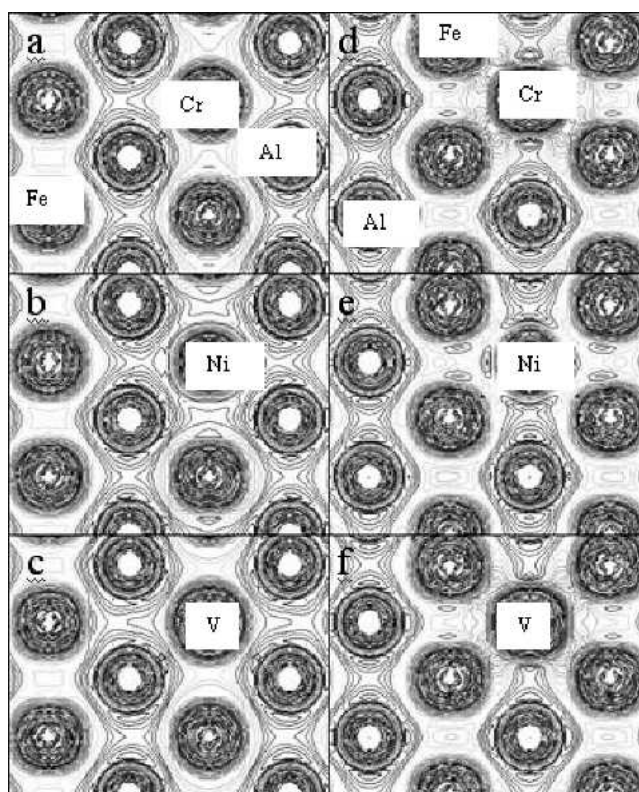| Variables	This work	TB-LMTO[30]
Vacancy on Fe sublattice	5.715	5.719
Vacancy on Al sublattice	5.715	5.716
Fe antistructure atom	5.760	5.701
Al antistructure atom	5.800	5.741

Fig. 1 Differential charge distribution for electrons in the spin-up state for the Fe-Al $B2$ phase alloyed by (a) Cr, (b) Ni, and (c) V on the Fe site, and by (d) Cr, (e) Ni, and (f) V on the Al site in the (110) plane
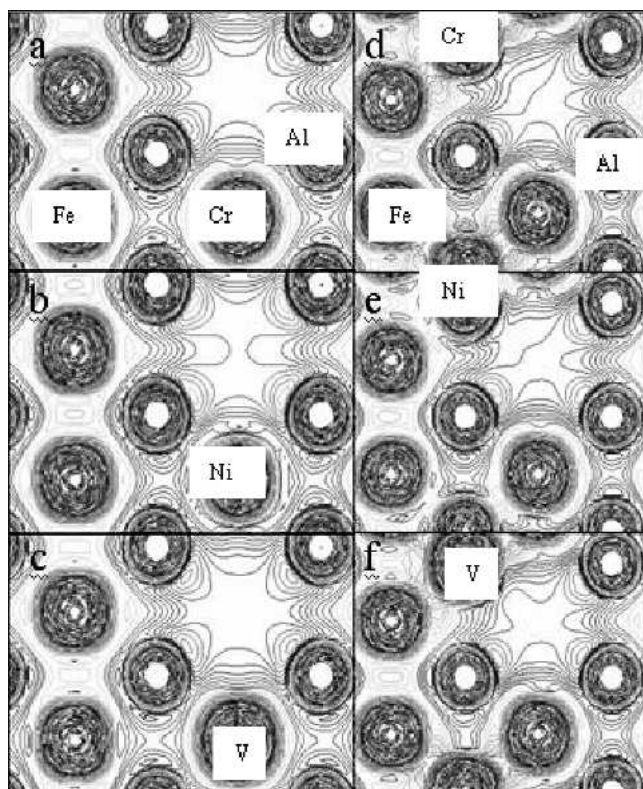
Fig. 2 Differential charge distribution for electrons in the spin-up state for the Fe-Al *B*2 phase with the vacancy on the Fe site (the second-nearest neighbor of the vacancy) alloyed by (a) Cr, (b) Ni, and (c) V on the Fe site, and by (d) Cr, (e) Ni, and (f) V on the Al site in the (110) plane

metric. This symmetry is distorted when the alloying elements occupy the Al site, the nearest vacancy neighbor (Fig. 2d-f). In the cases of alloying by Cr and Ni (Fig. 2a, b), the distortion is more pronounced than in the case of alloying by V (Fig. 2c). When Cr or V atoms occupy the Al sites, high electron density was detected between these alloying elements and Fe atoms (Fig. 2d, f, respectively), the differential charge density was 16. This high charge density was not detected in the case with Ni as the alloying element (Fig. 2e). In that case, the highest value of differential charge density between these atoms was 7. Similar to the case without the vacancy, when Ni occupies the Fe site, the electron density in its vicinity is relatively low. It is possible to explain the site preference of these alloying elements in Fe-Al with vacancies based on the competition between the strong directional bond formation and the symmetry in charge distribution. When Cr or Ni occupies the Al site, the symmetry distortion is very high, and therefore these alloying elements prefer to occupy the second-nearest neighbor sites of the vacancy, which is an Fe atom site. When V occupies the Al site, strong directional bonds are formed between the TMs. This effect compensates for the distortion of the differential charge density in the vicinity of the vacancy; therefore, V prefers to occupy the Al site.

Whether the alloying elements occupy the Fe sublattice or the Al sublattice, the differential charge density in the

center of the vacancy pocket in the cases with Ni and Cr is −4, and in the case with V it is −3. In the vicinity of the Al atoms, this value drops to −6 in the cases with Cr and V, and to −7 in the case with Ni. Therefore, we found here a charge transfer from Al atoms to TM atoms.

4. Summary

The energy of vacancy formation increases when the alloying elements in the vicinity of the vacancy occupy an Fe site. In addition, the alloying of Fe-Al by Cr, Ni, or V does not decrease the energy of the vacancy formation on the Al site. Therefore, due to the high energy of vacancy formation in alloyed Fe-Al, vacancies are formed mainly on the Fe site.

The analysis of preferential occupation of sites by Ni, V, and Cr in Fe-Al was performed on the basis of the study of electron density distribution. According to our results, Ni occupies the Fe sites both in ideal Fe-Al and in Fe-Al with the vacancy on the Fe site. Transition metals with atomic numbers lower than those for Fe are V and Cr, and these occupy the Al sublattice in ideal Fe-Al, which is in agreement with our previous work,[20] in which the analysis was performed on the basis of energy considerations.

It was shown that in Fe-Al Cr prefers to occupy the Fe site closest to the vacancy. The authors link this amphoteric property of Cr with the peculiarities of the electron density distribution.

The calculated energies of the antisite formation on both sublattices are relatively low. The energy of formation of the antisite on an Al site is lower than that of the antisite on an Fe site, showing the preference of this configuration of defect to be in agreement with the experimental data.

References

1. N. Junqua, J.C. Desoyer, and P. Moine, Electron Microscopy Observation of Quenching Defects in an Ordered Alloy of B2 Type: Fe-40 at% Al, *Phys. Status Solidi A,* Vol 18, 1973, p 387-395
2. D. Paris, P. Lesbats, and J. Levy, An Investigation of the Distribution of Vacancies in an Ordered Fe-Al Alloy by Field Ion Microscopy, *Scr. Metall.,* Vol 9, 1975, p 1373-1378
3. K. Ho and R.A. Dodd, Point Defects in FeAl, *Scr. Metall.,* Vol 12, 1978, p 1055-1058
4. C.I. Fu, Y.-Y. Ye, M.H. Yoo, and K.M. Ho, Equilibrium Point Defects in Intermetallics with B2 Structure: NiAl and FeAl, *Phys. Rev. B: Solid State,* Vol 48, 1993, p 6712-6715
5. Y.A. Chang, L.M. Pike, C.T. Liu, A.R. Bilbrey, and D.S. Stone, Correlation of the Hardness and Vacancy Concentration in FeAl, *Intermetallics,* Vol 1, 1993, p 107-115
6. P. Nagpal and I. Baker, Effect of Cooling Rate on Hardness of

FeAl and NiAl, *Metallurgical Transactions A,* Vol 21, 1990, p 2281-2282

7. J.H. Schneibel and L.M. Pike, A Technique for Measuring Thermal Vacancy Concentration in Stoichiometric FeAl, *Intermetallics,* Vol 12, 2004, p 85-90

8. J.H. Schneibel, Strengthening of Iron Alu-Minides by Vacancies and/or Nickel, *Mater. Sci. Eng., A,* Vol 258, 1998, p 181-186

9. A. Fraczkiewicz, A.S. Gay, and M. Biscondi, On the Boron Effect in FeAl (B2) Intermetallic Alloys, *Mater. Sci. Eng., A,* Vol 258, 1998, p 108-114

10. C.L. Fu and J. Zou, Site Preference of Ternary Alloying Additions in FeAl and NiAl by First-Principles calculations, *Acta Mater.,* Vol 44, 1996, p 1471-1478

11. I.M. Anderson, ALCHEMI Study of Site Distributions of 3D Transition Metals in B2-Ordered Iron Aluminides, *Acta Mater.,* Vol 45, 1997, p 3897-3909

12. D. Wu, I. Baker, and P.R. Munroe, The Effect of Substitutional Elements on the Strain-Induced Ferremagnetism in B2-Structured Fe-Al Single Crystals, *Intermetallics,* Vol 12, 2004, p 851-858

13. M. Kogachi, T. Tanahashi, Y. Shirai, and M. Yamaguchi, Determination of Vacancy Concentration and Defect Structure in the B2 Type NiAl β-Phase Alloys, *Scr. Mater.,* Vol 34, 1996, p 243-248

14. M. Kogachi, T. Haraguchi, and S.M. Kim, Point Defect Behaviour in High Temperature Region in the B2-Type Intermetallic Region Compound FeAl, *Intermetallics,* Vol 6, 1998, p 499-510

15. M. Kogachi and T. Haraguchi, Possibilities of Random Vacancy Distribution and Antisite Atom Recovering in the Point Defect Mechanism in B2-Type Intermetallics, *Intermetallics,* Vol 7, p 1999, 289-300

16. R. Krachler, H. Ipser, B. Sepiol, and G. Vogl, Diffusion Mechanism and Defect Concentrations in β'-FeAl, an Intermetallic Compound with B2 Structure, *Intermetallics,* Vol 3, 1995, p 83-88

17. R. Nakamura, K. Takasawa, Y. Yamazaki, and Y. Iijima, Single-Phase Interdiffusion in the B2 Type Intermetallic Compounds NiAl, CoAl and FeAl, *Intermetallics,* Vol 10, 2002, p 195-204

18. C.R. Kao and Y.A. Chang, On the Composition Dependencies of Self-Diffusion Coefficients in B2 Intermetallic Compounds, *Intermetallics,* Vol 1, 1993, p 237-250

19. H. Mehrer, M. Eggersmann, M. Salamon, and B. Sepiol, Diffusion in Intermetallic Phase of the Fe-Al and Fe-Si Systems, *Mater. Sci. Eng., A,* Vol 239-240, 1997, p 889-898

20. D. Fuks, A. Strutz, and A. Kiv, Bonding of Cr and V in FeAl B2 Phase, *Int. J. Quantum Chem.,* Vol 102, 2005, p 606-611

21. J.P. Perdew, S. Burke, and M. Ernzerhof, Generalized Gradient Approximation Made Simple, *Phys. Rev. Lett.,* Vol 77, 1996, p 3865-3868

22. P. Blaha, K. Schwarz, G. Madsen, D. Kvasnicka, and J. Luitz, *WIEN2k,* Institute of Materials Chemistry, Vienna University of Technology, 2001

23. R. Hultgren, P.D. Desai, D.T. Hawkins, M. Gleiser, and K.K. Kelley, *Selected Values of the Thermodynamic Properties of Binary Alloys;* American Society for Metals, 1973

24. C.J. Smithels, *Metals Reference Book, Vol II*, Butterworth, London, 1962

25. C.L. Fu, Origin of Ordering in *B*2-Type Transition-Metal Aluminides: Comparative Study of the Defect Properties of PdAl, NiAl, and FeAl, *Phys. Rev. B: Condens. Matter,* Vol 52, 1995, p 3151-3158

26. R. Kerl, J. Wolff, and Th. Hehekamp, Equilibrium Vacancy Concentration in FeAl and FeSi Investigated with an Absolute Technique, *Intermetallics,* Vol 7, 1999, p 301-308

27. M. Kass, Ch.R. Brooks, D. Falcon, and D. Basak, The Formation of Defects in Fe-Al Alloys: Electrical Resistivity and Specific Heat Measurements, *Intermetallics,* Vol 10, 2002, p 951-966

28. M. Fähnle, J. Mayer, and B. Mayer, Theory of Atomic Defects and Diffusion in Ordered Compounds, and Application to B2-FeAl, *Intermetallics,* Vol 7, 1998, p 315-323

29. G.S. Collins and L.S.J. Peng, Point Defects in FeAl, *Il Nuovo Cimento,* Vol 18D, 1996, p 329-337

30. N.I. Kulikov, A.V. Postnikov, G. Borstel, and J. Braun, Onset of Magnetism in *B*2 Transition-Metal Aluminides, *Phys. Rev. B: Condens. Matter,* Vol 59, 1999, p 6824-6833