RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 33, NUMBER 2 15 JANUARY 1986

Vacancies in CsCl-type intermetallic compounds: Structural versus thermal

S. M. Kim
Atomic Energy of Canada Research Company, Chalk River Nuclear Laboratories, Chalk River, Ontario, Canada K0J 1J0

(Received 20 August 1985)

For many years it has been widely believed that structural vacancies exist in NiAl, CoGa, NiGa, and other CsCl-type intermetallic compounds. In formulating a theory of vacancy formation in ordered nonstoichiometric bcc alloys, we have found that such structural vacancies may not necessarily exist. It is shown that in CoGa structural vacancies are indeed extremely unlikely and that purely thermal vacancies can account satisfactorily for the observed composition dependence of vacancy concentration.

While studying the structure of nickel-aluminum alloys, Bradley and Taylor discovered that in Al-rich *B*2 (CsCl structure) NiAl the excess Al atoms do not substitute in the usual way on the Ni sublattice, but instead vacancies are created on this sublattice.[1] Such vacancy populations, determined by composition and not temperature, have since been distinguished as structural (or constitutional) vacancies. In recent years considerable effort has been made to understand the vacancy properties in NiAl as well as many other *B*2 intermetallic compounds.[2-19] In NiAl, CoAl, NiGa, and CoGa very large vacancy concentrations were detected on the Ni or Co sublattices in slowly cooled specimens, and these vacancies were attributed to be mainly structural vacancies. In this paper we formulate a theory of vacancy formation in highly ordered nonstoichiometric bcc alloys using the nearest-neighbor bond-energy model. It will be shown that structural vacancies may not exist in these alloys and that the observed vacancies are most likely frozen-in thermal vacancies.

Before presenting the theory we examine closely some of the pertinent experimental observations. The observed composition dependence of vacancy concentrations in NiAl,[3] CoAl,[5] NiGa,[8] and CoGa,[7] slowly cooled to room temperature after equilibrating at 1073 K or above, is shown in Fig. 1(a). It is seen that even in the stoichiometric composition as well as on the Ni- or Co-rich side of stoichiometry, these alloys contain appreciable vacancy concentrations. Since structural vacancies cannot be present at these compositions, these vacancies were thought to be frozen-in thermal vacancies. The observed vacancy concentrations on the Al- or Ga-rich side of stoichiometry, on the other hand, were believed to be mainly structural vacancies. Thus it is clear that, although the existence of structural vacancies has been widely accepted, the experimental evidence is not very persuasive. From the theoretical viewpoint, as will be discussed later, it is also unconvincing since most of the models and theories advanced thus far[9,11,12,20-22] have involved a variety of unrealistic assumptions.

The present theory is based on the nearest-neighbor bond-energy model, which has provided valuable theoretical descriptions of the statistical thermodynamic properties of alloys such as the order-disorder transition[21,23] and alloy mixing.[23] Although this model is not free from difficulties,[24] it is quite satisfactory in many respects and theories based on this model have also enabled a clear understanding of vacancy properties in highly ordered stoichiometric bcc al-

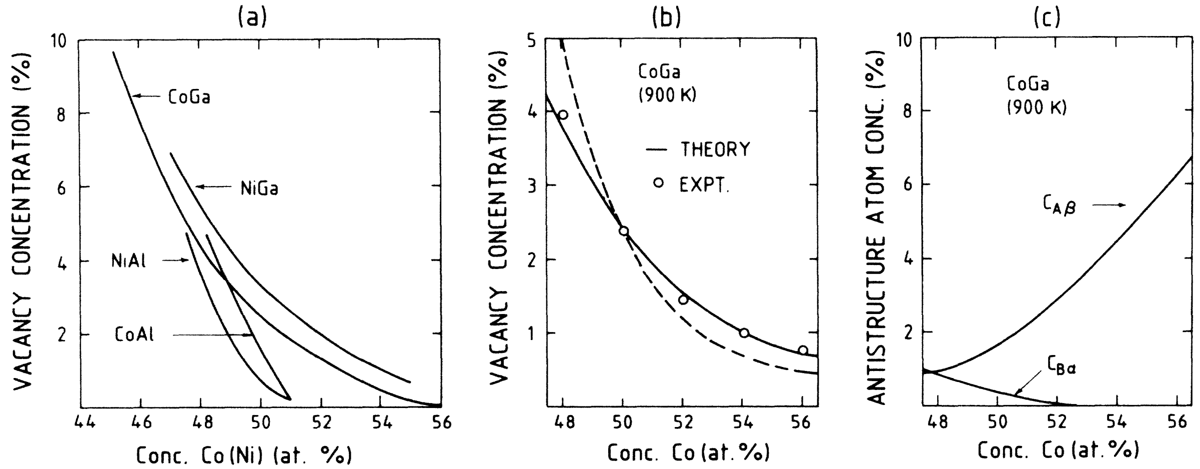

FIG. 1. (a) The observed composition dependence of vacancy concentrations on the Co(Ni) sublattice in slowly cooled NiAl (Ref. 3), CoAl (Ref. 5), NiGa (Ref. 8), and CoGa (Ref. 7). (b) The composition dependence of vacancy concentrations on the Co sublattice (C_{V_α}) in CoGa at 900 K. The full line is from the present theory and open circles are experimental values (Ref. 16). The dashed line is the theoretical predictions obtained with $\epsilon_{BB}=0$. (c) The composition dependence of Co($C_{A\beta}$) and Ga($C_{B\alpha}$) antistructure atom concentrations in CoGa at 900 K obtained from the present theory.

loys[25] as well as in disordered alloys.[24,26] The AB alloy is assumed to consist of α and β sites (or sublattices) occupied by two atomic species, A and B, as well as vacancies, V. We define $N+n=$ number of α (or β) sites, $N(1-\delta)$ $=$ number of A atoms, $N(1+\delta)=$ number of B atoms, $N_{ij}=$ number of ith species on jth sites. We then have

$$N_{A\alpha}=N(1-\delta)-N_{A\beta}\ , \tag{1a}$$

$$N_{B\beta}=N(1+\delta)-N_{B\alpha}\ , \tag{1b}$$

$$N_{V\alpha}=n+N\delta+N_{A\beta}-N_{B\alpha}\ , \tag{1c}$$

$$N_{V\beta}=n-N\delta-N_{A\beta}+N_{B\alpha}\ . \tag{1d}$$

The configurational free energy at a temperature T is given by

$$F=E-TS\ , \tag{2}$$

where E is the total bond energy for a given configuration and S is the configurational entropy. If we denote the bond energy between the ith and jth atoms as ϵ_{ij}, we have $\epsilon_{AB}=(\epsilon_{AA}+\epsilon_{BB})/2+\epsilon$, where ϵ is the ordering energy.

We assume that the vacancy and antistructure atom (atoms at wrong sites) concentrations are small compared with the number of lattice sites so that all the defects are essentially isolated from each other. We also restrict the discussion to alloys where the deviation from stoichiometry is small, $0<\delta/2<<1$, and $\epsilon_{AA}>\epsilon_{BB}$. It can be readily shown that if $\epsilon_{BB}>0$ the ground state at $T=0$ K will contain only antistructure B atoms. Only for alloys where ϵ_{BB} is repulsive and small, $-2\epsilon<\epsilon_{BB}<0$, will structural vacancies be present at $T=0$ K. If $\epsilon_{BB}<-2\epsilon$ the alloy will be unstable against vacancy formation on both A and B atom sites on the α sublattice. Thus it is clear that not too many alloys, if any, would contain structural vacancies. At finite temperatures vacancies and antistructure atoms will be present at both sublattices regardless of the ground state at $T=0$ K. A detailed examination of the various vacancy and antistructure atom formation processes at $T>0$ K, similar to those described previously,[25] shows that the bond energy change when these defects are created is the same for A and B atom sites on the α sublattice. This result greatly simplifies the expression for the configurational entropy. Since the A and B atoms on α sublattice are surrounded on the average by 8 $N_{A\beta}/(N+n)$ A atoms and 8 $N_{B\beta}/(N+n)$ B atoms, the total bond energy for the alloy containing small defect concentrations can be well approximated by writing

$$\begin{aligned}E&=-\frac{8}{N+n}[N_{A\alpha}N_{A\beta}\epsilon_{AA}+(N_{A\alpha}N_{B\beta}+N_{B\alpha}N_{A\beta})\epsilon_{AB}+N_{B\alpha}N_{B\beta}\epsilon_{BB}]\\&\simeq-8(N-n)[\epsilon_{AB}+\delta(\epsilon_{BB}-\epsilon_{AB})]-8N_{A\beta}(1-\delta)(\epsilon_{AA}-\epsilon_{AB})-8(N_{B\alpha}-N\delta)(1-\delta)(\epsilon_{BB}-\epsilon_{AB})\ .\end{aligned} \tag{3}$$

The corresponding configurational entropy can be described by

$$S=k_B\ln\left[\frac{(N+n)!}{N_{A\alpha}!N_{B\alpha}!N_{V\alpha}!}\right]\frac{(N+n)!}{N_{A\beta}!N_{B\beta}!N_{V\beta}!}\ , \tag{4}$$

where $N_{A\alpha}$, $N_{B\beta}$, $N_{V\alpha}$, and $N_{V\beta}$ are given by Eqs. (1a)–(1d). Substituting Eqs. (3) and (4) in Eq. (2), and minimizing the free energy with respect to n, $N_{A\beta}$, and $N_{B\alpha}$, we obtain after some algebraic manipulations,

$$\frac{N_{V\alpha}}{N+n}=\left(\frac{N_{A\alpha}N_{B\alpha}}{N_{A\beta}N_{B\beta}}\right)^{1/4}e^{-4[\epsilon_{BB}+(1-\delta)\epsilon]/k_BT}\ , \tag{5}$$

$$\frac{N_{V\beta}}{N+n}=\left(\frac{N_{A\beta}N_{B\beta}}{N_{A\alpha}N_{B\alpha}}\right)^{1/4}e^{-4[\epsilon_{AA}+\epsilon-\delta(\epsilon_{AA}-\epsilon_{BB}+\epsilon)]/k_BT}\ , \tag{6}$$

$$\left.\begin{matrix}\dfrac{N_{A\beta}}{N+n}\\ \dfrac{N_{B\alpha}}{N+n}\end{matrix}\right\}=\left[\frac{1}{16}\left(\frac{N_{V\alpha}-N_{V\beta}}{N+n}-\frac{2N\delta}{N+n}\right)^2+\frac{N_{A\alpha}N_{B\beta}}{(N+n)^2}e^{-16\epsilon(1-\delta)/k_BT}\right]^{1/2}\pm\frac{1}{4}\left(\frac{N_{V\alpha}-N_{V\beta}}{N+n}-\frac{2N\delta}{N+n}\right)\ . \tag{7}$$

From Eqs. (1a)–(1d) and (5)–(7) it can be shown that $N_{V\alpha}>N_{V\beta}$ for alloys where $\epsilon_{AA}>\epsilon_{BB}$, and $N_{V\alpha}<N_{V\beta}$ for alloys where $\epsilon_{AA}<\epsilon_{BB}$. Since the pre-exponential factors in Eqs. (5) and (6) are slowly varying functions of $N_{A\alpha}N_{B\alpha}/N_{A\beta}N_{B\beta}$, Eqs. (5)–(7) can be readily solved by trial and error.

In the light of the present work, we examine briefly the shortcomings in the previous theories of vacancy formation in ordered nonstoichiometric bcc alloys. In the model of Girifalco,[20] as well as in the simple displacement model and the modified vacancy energy model of Cheng, Wynblatt, and Dorn,[22] the combined creation of vacancies and antistructure atoms has not been taken into account, and thus these models are unrealistic, as pointed out already.[25] In the models of Krivoglaz and Smirnov,[21] as well as in the smeared displacement model of Cheng *et al.*,[22] an assumption $N_{A\beta}=N_{B\alpha}-N\delta$ has been made, so that these models are applicable only to alloys where $N_{V\alpha}\simeq N_{V\beta}$. In the model of Neumann, Chang, and Lee,[9] an assumption $N_{B\alpha}$ $=N_{V\beta}=0$ has been made in the free-energy expression for NiAl-type alloys. Since the condition $N_{B\alpha}=0$ is satisfied only in alloys where ϵ is infinite, the validity of their calculation on real alloys is not easily determined. Their other assumption, $\epsilon_{AV}\neq 0$ and $\epsilon_{BV}\neq 0$, is also difficult to justify, since their model is based on the nearest-neighbor bond-energy concept. In the model of Bakker and van Ommen,[11] the same assumptions, $N_{B\alpha}=N_{V\beta}=0$ and $\epsilon_{AV}\neq\epsilon_{BV}\neq 0$, have been made for NiAl-type alloys. Their further assumption that an alloy can be thought of as a mixture of solid and gases is also difficult to justify. In the nearest-neighbor bond-energy model of Edelin[12] for NiAl-type alloys, an unreasonable assumption, $4(\epsilon_{AB}-2\epsilon_{AV}) >> 4(\epsilon_{AB}-2\epsilon_{BV})$, has been made. Unlike the above models and theories, the only assumption made in our theory is that of small defect concentrations.

We now compare the theory with experiments in a typical $B2$ intermetallic compound, CoGa, for which equilibrium vacancy concentrations have been determined as a function of composition by means of lattice parameter, length, and density measurements.[16] For the sake of brevity, we will make the following simplifying assumptions without much elaboration. First, we assume that the nonconfigurational entropy in CoGa is $1.5k_B$, similar to the values in pure metals, so that the total vacancy concentration is $C_V = 4.48\ C_V^f$, where C_V^f is the vacancy concentration from the configurational free energy of Eq. (2). We assume that the bond energy between two Co atoms in this alloy, ϵ_{AA}, is the same as that in hcp Co metal. The latter can be obtained from positron annihilation data for hcp Co by means of the relation $E_f = 15k_BT_t$, where $E_f = 6\epsilon_{AA}$ is the vacancy formation energy and T_t is the threshold temperature:[27-30] The value is $\epsilon_{AA} = 0.275$ eV. For the bond energy between two Ga atoms we use the value $\epsilon_{BB} \simeq 0.042$ eV, determined from the analysis on stoichiometric NiGa.[25] The ordering energy ϵ in CoGa has not been measured, but is expected to be similar to that in NiGa, $\simeq 0.036$ eV, since the observed vacancy concentrations in CoGa are similar to corresponding values in NiGa.[7,8,10,13,16,17] We find that a value of 0.039 eV is most appropriate. We define $C_{ij} = N_{ij}/2(N+n)$, where C_{ij} denotes various defect concentrations.

The vacancy concentration on the Co sublattice, $C_{V\alpha}$, and the antistructure atom concentrations, $C_{A\beta}$ and $C_{B\alpha}$, in CoGa at 900 K, calculated from the present theory using the above parameter values, are shown in Figs. 1(b) and 1(c). The vacancy concentration on the Ga sublattice, $C_{V\beta}$, was found to be entirely negligible ($C_{V\beta} < 10^{-6}$). The observed composition dependence of vacancy concentration on the Co sublattice in CoGa at 900 K (Ref. 16) is also shown in Fig. 1(b). It is seen that the agreement between the theory and experiment is excellent. The antistructure atom concentrations in CoGa have not yet been determined experimentally. It is seen that while $C_{A\beta}$ describes the dominant defects, both $C_{A\beta}$ and $C_{B\alpha}$ are quite appreciable on the Ga-rich side of stoichiometry. The composition dependence of vacancy concentration in CoGa has also been calculated assuming that structural vacancies exist in this alloy. The dashed line in Fig. 1(b) shows the results obtained by setting $\epsilon_{BB} = 0$. It is clear that the observed vacancy concentrations cannot be described with negative values of ϵ_{BB}. Thus the existence of structural vacancies in CoGa is extremely unlikely. It is known that the activation energy of self-diffusion in CoGa is large, 4.4 eV $\geqslant Q_{\mathrm{SD}} \geqslant$ 2.4 eV, and increases substantially with Ga concentration.[31] Since the formation energy of vacancies in CoGa estimated from Eq. (5) is small, of order $4[\epsilon_{BB} + (1-\delta)\epsilon] \simeq 0.3$ eV, the migration energy of vacancies is expected to be high and also would increase with Ga concentration. Thus it would not be surprising to find that a large fraction of thermal vacancies is retained even in slowly cooled specimens, giving rise to the behavior shown in Fig. 1(a). Indeed, the measurements of vacancy concentrations in quenched (from 1173 K) and slowly cooled CoGa show that while only a small fraction of vacancies is retained in very Co-rich compositions, in the extreme Ga-rich compositions fully 90% of the vacancies are retained in the slowly cooled specimens.[7]

We conclude that structural vacancies may not necessarily exist in all the NiAl-type intermetallic compounds and that purely thermal vacancies can satisfactorily account for the observed composition dependence of vacancy concentrations in a typical $B2$ intermetallic compound CoGa. It is suggested that additional precise equilibrium measurements be made on NiAl, CoAl, and other alloys for further testing of the present theory.

---

[1] A. J. Bradley and A. Taylor, Proc. R. Soc. London **159**, 56 (1937).

[2] T. Hughes, E. P. Lautenschlager, J. B. Cohen, and J. O. Brittain, J. Appl. Phys. **42**, 3705 (1971).

[3] H. Jacobi and H. J. Engell, Acta Metall. **19**, 701 (1971).

[4] A. Taylor and N. J. Doyle, J. Appl. Crystallogr. **5**, 201 (1972); **5**, 210 (1972).

[5] E. Wachtel, V. Linse, and V. Gerold, J. Phys. Chem. Solids **34**, 1461 (1973).

[6] D. Fort, R. E. Smallman and I. R. Harris, J. Less-Common Met. **31**, 263 (1973).

[7] D. Berner, G. Geibel, V. Gerold and E. Wachtel, J. Phys. Chem. Solids **36**, 221 (1975).

[8] A. T. Donaldson and R. D. Rawlings, Acta. Metall. **24**, 811 (1976).

[9] J. P. Neumann, Y. A. Chang, and C. M. Lee, Acta Metall. **24**, 593 (1976).

[10] K. Ho, M. A. Quader, F. Lin, and R. A. Dodd, Scr. Metall. **11**, 1159 (1977).

[11] H. Bakker and A. H. van Ommen, Acta Metall. **26**, 1047 (1978).

[12] G. Edelin, Acta Metall. **27**, 455 (1979).

[13] J. P. Neumann and Y. A. Chang, Z. Metallkd. **70**, 118 (1979).

[14] S. M. Kim and W. J. L. Buyers, Phys. Rev. Lett. **45**, 383 (1980).

[15] J. P. Neumann, Acta Metall. **28**, 1165 (1980).

[16] A. H. van Ommen, A. Waegemaekers, A. C. Moleman, H. Schlatter, and H. Bakker, Acta Metall. **29**, 123 (1981).

[17] A. H. van Ommen, Phys. Status Solidi (a) **72**, 273 (1982).

[18] H. G. Müller and H. Hahn, Philos. Mag. A **50**, 71 (1984).

[19] A. Parthasarathi and H. L. Fraser, Philos. Mag. A **50**, 89 (1984).

[20] A. Girifalco, J. Phys. Chem. Solids **24**, 323 (1964); *Statistical Physics of Materials* (Wiley, New York, 1973), pp. 274–289.

[21] M. A. Krivoglaz and A. Smirnov, *The Theory of Order-Disorder in Alloys* (MacDonald, London, 1964), pp. 1–280.

[22] C. Y. Cheng, P. P. Wynblatt, and J. E. Dorn, Acta Metall. **24**, 811 (1976).

[23] E. A. Guggenheim, *Mixtures* (Clarendon, Oxford, 1952), pp. 23–143.

[24] S. M. Kim, Phys. Rev. B **30**, 4829 (1984).

[25] S. M. Kim, Phys. Rev. B **29**, 2356 (1984).

[26] S. M. Kim, in *Proceedings of the Seventh International Conference on Positron Annihilation* (World Scientific, Singapore, in press).

[27] S. M. Kim and W. J. L. Buyers, J. Phys. F **8**, L103 (1978).

[28] R. N. West, in *Positrons in Solids,* edited by P. Hautojärvi, Topics in Current Physics, Vol. 12 (Springer, New York, 1979), pp. 89–144.

[29] S. M. Kim and W. J. L. Buyers, Can. J. Phys. **61**, 140 (1983).

[30] C. W. Schulte and J. L. Campbell, Appl. Phys. **19**, 269 (1979).

[31] N. A. Stolwijk, M. van Gend, and H. Bakker, Philos. Mag. A **42**, 783 (1980).