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Atomic defects in the ordered compound B2-CoAl: A combination of *ab initio* electron theory and statistical mechanics

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For an ideal model of a homogeneous thermodynamically stable ordered compound $B2\text{-Co}_x\text{Al}_{1-x}$, the effective formation energies of vacancies and antistructure atoms on both sublattices are calculated by a combination of *ab initio* electron theory and statistical mechanics. The results are compared with data for FeAl and NiAl obtained by the same procedure and with experimental results. The structural defects in $\text{Co}_x\text{Al}_{1-x}$ are Co antistructure atoms (for $x>0.5$) and Co vacancies (for $x<0.5$), albeit these latter defects are only slightly more favorable than Al antistructure atoms. This near balance possibly is responsible for conflicting experimental results obtained in real Al-rich samples. The dominant thermal excitations are also discussed. [S0163-1829(99)01445-9]

I. INTRODUCTION

Intermetallic phases with a $B2$ structure form a large group of intermetallics, and some representatives, e.g., FeAl, CoAl, NiAl, and mixed phases of these compounds are considered as promising candidates for high-temperature applications.[1] Thereby, the mechanical properties of these materials are influenced by the type of structural defects, i.e., by those defects which survive at zero temperature in order to maintain the deviations from stoichiometry, and sometimes also by the thermally excited defects.[2]

It is generally accepted from experiments[3] that in Fe-rich FeAl, Fe antistructure atoms on the Al sublattice constitute the structural defects. Al-rich samples exist only very close to stoichiometry. Therefore, only few data are available and there is no consensus concerning the structural defects. Measurements of the lattice parameter as function of composition were taken as hints to structural Fe vacancies.[3] Kogachi and Haraguchi[4] concluded from their study of the intensities of x-ray diffraction lines that the structural defects in Al-rich samples are Al antistructure atoms.

For NiAl, most of the data obtained by a simultaneous study of x-ray density and bulk density (see, e.g., Ref. 3) are compatible with the notion that the structural defects are Ni antistructure atoms in Ni-rich samples and Ni vacancies in Al-rich samples. Kogachi *et al.*[5] pointed out that the measurements of the bulk density may be critical because of the formation of microvoids which may pretend a vacancy concentration that is too large, and they tried to avoid this effect by using powder samples. In their analysis, they found that the total vacancy concentration in Al-rich samples is a bit smaller than the one which would arise if the deviation from stoichiometry was totally maintained by structural vacancies, and this observation was confirmed by a study of the intensities of x-ray diffraction peaks by the same authors.[5] Xiao and Baker[6] found even smaller vacancy concentrations in Al-rich samples utilizing diffracted x-ray intensity measurements. Both studies concluded that there is a considerable concentration of Al antistructure atoms in Al-rich samples in addition to the vacancies, and in the study of Kogachi *et al.*[5] Al vacancies were also found close to the stoichiometric composition.

For CoAl, which is between FeAl and NiAl in the periodic table, and which is very similar to NiAl with respect to density, thermal expansion behavior, melting temperature, and phase diagram (see references given in Ref. 1), the situation is also not yet clear. Again, most studies[3,7] of the x-ray and bulk density are essentially compatible with the notion that the structural defects are Co antistructure atoms in Co-rich samples and Co vacancies in Al-rich samples, whereas the more recent experiment of Kogachi and Tanahashi[8] yielded a smaller total vacancy concentration than expected if the deviation from stoichiometry was totally maintained by structural vacancies. As in the case of NiAl, the diffraction x-ray intensity measurements[6,8] indicated for Al-rich samples considerable concentrations of Al antistructure atoms, and also a high concentration of Al vacancies which increases with increasing Al content.[8] (The x-ray and bulk density measurements of Fleischer[9] indicated the existence of considerable vacancy concentrations at low temperatures even in Co-rich samples, a result which was not found in all of the other experiments.) Altogether, it can be concluded that there is a wide consensus for FeAl, CoAl, and NiAl concerning the structural defect in the Al-poor samples (Fe, Ni, and Co antistructure atoms), whereas for Al-rich samples, the appearance of Al antistructure atoms and (for CoAl and NiAl) Al vacancies already at low temperatures in addition to structural transition-metal vacancies is under discussion.

It has been pointed out in Ref. 10 that differences between various experiments may arise from the fact that the samples are in different states concerning purity, homogeneity, thermodynamical stability, and composition. In contrast, the theory (e.g., combination of statistical mechanics with *ab initio* electron theory) is able to deal with ideal reference systems, i.e., with ordered homogeneous thermodynamically stable compounds free of impurities and with exactly defined composition, and it therefore may provide reference data for these ideal systems. For FeAl, such calculations (see Ref. 11 and references therein) revealed antistructure atoms as structural defects on both sides of the stoichiometric composition, albeit on the Al-rich side, the Al antistructure atom is only

TABLE I. The effective formation energies for the $B2$ structures A_xB_{1-x} with $A=$Fe (Refs. 11,13,25), Ni (Ref. 12), and Co as obtained by a combination of statistical mechanics with *ab initio* electron theory.

	$x>0.5$			$x=0.5$			$x<0.5$		
	FeAl	CoAl	NiAl	FeAl	CoAl	NiAl	FeAl	CoAl	NiAl
$\tilde{E}_V^\alpha$	1.56	1.93	1.11	1.06	1.29	0.74	0.56	0.0	0.0
$\tilde{E}_V^\beta$	2.96	1.59	1.60	3.46	2.23	1.97	3.96	3.51	2.71
$\tilde{E}_A^\beta$	0.0	0.0	0.0	0.99	1.29	0.74	1.98	3.85	2.22
$\tilde{E}_B^\alpha$	1.98	4.19	3.10	0.99	2.91	2.36	0.0	0.36	0.88

slightly more favorable than the Fe vacancy. For NiAl, the structural defects were found[12] to be Ni antistructure atoms for the Ni-rich samples, and Ni-vacancies for the Al-rich samples. It will be shown in the present paper that CoAl yields the same types of structural defects as NiAl, albeit on the Al-rich side the Co vacancy is only slightly more favorable than the Al antistructure atom. Results for the thermally excited defects will also be reported.

II. CALCULATIONAL PROCEDURE

The calculations were performed by a combination of statistical mechanics with *ab initio* electron theory described in detail in Refs.11–13, which is valid for small defect concentrations. The *ab initio* electron theory within the density functional theory in local-density approximation[14] and the *ab initio* pseudopotential method[15] with a mixed basis set consisting of plane waves and five localized and nonoverlapping d orbitals per Co atom[16] was used. To test the reliability of the local-density approximation, calculations of the vacancy formation energies have been performed in the literature for those simple metals and transition metals for which accurate experimental data are available. In all cases, the agreement between theory and experiment was excellent (see, for instance, Table I of Ref. 13, and Ref. 17). Because there is no reason why the local-density approximation should work less reliably in intermetallic compounds, we refrained from going beyond the local-density approximation by using, for instance, gradient-corrected exchange-correlation functionals, especially in view of the fact that these functionals do not necessarily guarantee a consistent improvement over the predictions of the local-density approximation.[18] The *ab initio* calculations provide the so-called defect formation parameters ε_i^ν, s_i^ν, and ΔV_i^ν for the defects (i,ν), where the index i stands for a vacancy or an antistructure atom and the superscript ν denotes the α (i.e., Co) or β (i.e., Al) sublattice of the $B2$ structure. These defect formation parameters describe the change in total energy, vibrational entropy, and volume of the system when an atom is removed from the system (in the case of vacancies) or replaced by another kind of atom (in the case of antistructure atoms). In the present study the defect formation parameters were calculated by a supercell approach[11–13] with supercells containing 54 sites, and the structural relaxation of the atoms surrounding the defects as well as the volume relaxation of the supercell were fully taken into account. Furthermore, the electron theory gives the energy ε_0, the vibrational entropy s_0, and the volume Ω_0 per formula unit of the perfectly ordered stoichiometric compound. Based on this microscopic information, the statistical mechanics[11–13] yield the concentration c_i^ν for the various defects, which may be written as

$$c_i^\nu = \tfrac{1}{2} e^{\tilde{S}_i^\nu/k_B} e^{-(\tilde{E}_i^\nu + p\tilde{\Omega}_i^\nu)/k_B T}. \tag{1}$$

Here, $\tilde{S}_i^\nu$, $\tilde{E}_i^\nu$, and $\tilde{\Omega}_i^\nu$ denote the effective formation entropy, energy, and volume. Because in ordered compounds, inevitably various types of atomic defects must be created simultaneously by thermal excitation in order to conserve the homogeneity of the sample,[11–13] these effective defect formation quantities do not just depend on the defect formation parameters of the considered defect (i,ν), but on the whole set of defect formation parameters of all defects involved in the thermal excitation (and on ε_0, s_0, and Ω_0). The analytical expressions for the effective defect formation quantities of the $B2$ structure are all given in Appendix A of Ref. 12. These expressions hold if the concentrations of thermal defects are much smaller than the concentration of the structural defect in the case of nonstoichiometric compounds, and if the defect concentrations are small and two types of defects dominate strongly in the case of stoichiometric compounds. The structural defect is the one for which (at pressure $p=0$) the effective formation energy is zero. In the present study we did not determine the defect entropy parameters and therefore we cannot discuss the absolute values of the defect concentrations. Furthermore, we neglected the effect of the spin polarization, although the Co antistructure atom exhibits a localized magnetic moment (see Ref. 19 and references therein; a discussion of analogous magnetic effects in FeAl is given in Refs. 11 and 13).

III. RESULTS

Concerning the cohesive properties of ideal stoichiometric CoAl, we determined a lattice parameter of $a_0=2.799$ Å and a bulk modulus of $B_0=204$ GPa, in good agreement with plane-wave pseudopotential calculations[20] based on a Co pseudopotential of Ref. 21 ($a_0=2.805$ Å, $B_0=199$ GPa) and with linear-augmented-plane-wave calculations[22] ($a_0=2.80$ Å, $B_0=207$ GPa). Experiments at room temperature (see Refs. given in 20) yield $a_0=2.861$ Å and $B_0=162$ GPa, i.e., we obtain a slight overbinding, as is usual for the local-density approximation.

Table I represents our results for the effective formation energies. (Concerning the numerical accuracy we have performed the same convergence tests as in Ref. 12 with respect to the convergence parameters of the *ab initio* method.) It becomes obvious that the defect properties in CoAl are very similar to those in NiAl. For the Co-rich systems, the structural defects are Co antistructure atoms on the Al sublattice, in agreement with experimental data. For the Al-rich systems, the structural defects are Co vacancies, but the Co vacancies are only slightly more favorable than the Al antistructure atoms on the Co sublattice. We think that this near balance is also reflected in the experiments (see above): All of them find Co vacancies in the Al-rich samples, but there are also hints of Al antistructure atoms. We can imagine that deviations of the real samples from the ideal reference state considered in the theory, i.e., slight differences of the samples concerning homogeneity or thermodynamical stability may favor Co vacancies or Al antistructure atoms. Because of their very high effective formation energy, we cannot imagine that the Al vacancies are of some importance at low temperatures, in contrast to the conjecture of Kogachi and Tanahashi.[8] For NiAl the calculations[12] yielded the same type of structural defects as for CoAl, but in Al-rich NiAl, the Ni vacancies are much more favorable than the Al antistructure atoms. For Al-rich FeAl, the calculations[11] obtained Al antistructure atoms as structural defects, which are only slightly more favorable than structural Fe vacancies, and again this near balance is reflected in the experiments.

Concerning the formation of thermal defects for the stoichiometric composition ($x=0.5$), the triple defect formation according to

$$0 \rightarrow 2V^{\alpha} + \mathrm{Co}^{\beta} + \mathrm{CoAl}; \quad \tilde{E}_V^{\alpha} = 1.29 \ \mathrm{eV} \tag{2}$$

is the dominant thermal excitation, as in NiAl. Here, V^{α} and Co^{β} stand for the vacancy on the α (i.e., Co) sublattice and the Co antistructure atom on the β (i.e., Al) sublattice, and CoAl denotes the formation of a new unit cell during the triple defect excitation. At least at high temperatures there is possibly also a contribution of thermal Al vacancies. According to Appendix A of Ref. 12, the formation of Al vacancies in the stoichiometric triple defect compound CoAl proceeds via the reaction

$$\mathrm{Co}^{\beta} \rightarrow 3V^{\beta} + V^{\alpha} + 2\mathrm{CoAl}; \quad \tilde{E}_V^{\mathrm{Al}} = 2.23 \ \mathrm{eV}, \tag{3}$$

i.e., via an annihilation of Co antistructure atoms. Because we do not know the defect entropy parameters and hence the absolute values of the concentrations, we cannot figure out how strongly reaction (3) contributes to the formation of thermal defects at experimental temperatures. In contrast to CoAl and NiAl, stoichiometric FeAl is not a nearly pure triple defect system, but there might be considerable thermal concentrations of Fe vacancies and antistructure atoms on both sublattices.

For Co-rich samples ($x > 0.5$), we obtain the formation of vacancies on both sublattices according to the appendix of Ref. 12,

$$\mathrm{Co}^{\beta} \rightarrow 2V^{\beta} + \mathrm{CoAl}; \quad \tilde{E}_V^{\beta} = 1.59 \ \mathrm{eV}. \tag{4}$$

$$0 \rightarrow 2V^{\alpha} + \mathrm{Co}^{\beta} + \mathrm{CoAl}; \quad \tilde{E}_V^{\alpha} = 1.93 \ \mathrm{eV}. \tag{5}$$

Because of the formation of vacancies on both sublattices, the self diffusion in Co-rich CoAl in principle may proceed by nearest-neighbor jumps between the two sublattices, as in the case of NiAl. The situation is totally different in FeAl where there are only extremely few vacancies on the Al sublattice so that the diffusion mechanisms must be more complicated.[11,13] Reaction (4) describes a replacement of the Co antistructure atoms by Al vacancies. However, we do not think that this reaction may explain the observation of Fleischer[9] of the existence of considerable vacancy concentrations in Co-rich samples because Fleischer's experiment was performed at low temperatures.

For the Al-rich system ($x < 0.5$), the excitation with the smallest effective formation energy is the excitation of an Al antistructure atom on the Co sublattice with a simultaneous annihilation of two Co vacancies, according to (appendix of Ref. 12)

$$2V^{\alpha} + \mathrm{CoAl} \rightarrow \mathrm{Al}^{\alpha}; \quad \tilde{E}_{Al}^{\alpha} = 0.36 \ \mathrm{eV}, \tag{6}$$

leading to a shrinkage of the sample with increasing temperature. It can be shown[23] that the effective formation entropy for this process is very large and negative, expecially when approaching the stoichiometric composition, so that the corresponding defect concentrations at typical measuring temperatures are very small in spite of the very small effective formation energy. As noted above, the situation might be different in real samples deviating from the ideal reference state where inhomogeneities or deviations from thermodynamic stability could favor the formation of structural Al antistructure atoms. Because $\tilde{E}_V^{\beta}$ and $\tilde{E}_A^{\beta}$ are very high, the thermal concentrations of the corresponding defects are very small, in spite of the large positive effective formation entropies.[23] We therefore conclude that in the ideal reference systems of Al-rich CoAl there should be only few thermally excited defects at any temperature. For NiAl the effective formation energy of the Al antistructure atom is larger and hence, the concentration of this defect is probably even smaller than in CoAl. On the other hand, the effective formation energy for the A (i.e., Ni) antistructure atom, which in the Al-rich system is also formed by a triple defect excitation according to reaction (2) (as in the stoichiometric system) is smaller than in CoAl, so that the creation of the two Ni vacancies during the triple defect formation possibly may be responsible for the experimentally observed expansion of Al-rich NiAl with increasing temperature.[24]

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