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Atomic defects in FeCo: Stabilization of the $B2$ structure by magnetism

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The effective formation energies of atomic defects in the $B2$ phase of FeCo are calculated by a combination of the statistical mechanics with the *ab initio* density-functional electron theory with the local-spin-density approximation and the generalized-gradient approximation for the exchange-correlation functional. The effect of magnetism is required to stabilize the system against a spontaneous formation of antistructure atoms even in the stoichiometric case. The structural defects are antistructure atoms, and the effective energy for the formation of thermal antistructure atoms is much smaller than the effective formation energies for Fe and Co vacancies. The behavior of the atomic defects in this system consisting of two quite similar constituents appears to be much simpler than in the $B2$ transition-metal aluminides consisting of quite dissimilar constituents.

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I. Introduction. Binary intermetallic phases A_xB_{1-x} with $B2$ structure composed of two interpenetrating simple cubic sublattices (α for the A atoms and β for the B atoms) form a large group of intermetallics. Thereby, the subgroup of transition-metal (TM) aluminides has some representatives which are considered as candidates for high-temperature applications,[1] e.g., FeAl, CoAl, NiAl, and ternary mixtures of them. The physical properties of these materials are strongly influenced by the fact that the two constituents are quite different: The calculated lattice constant of Al in the bcc phase is about 14% larger than the calculated lattice constants of Fe, Co, Ni in this phase, i.e., the Al atom is bigger than the TM atoms. Furthermore, the electronic properties are quite different: Al, which is more electropositive, is a simple metal with delocalized s and p electronic states, whereas Fe, Co, and Ni are transition metals with well localized $3d$ states. As a result, the corresponding $B2$ phases exhibit a coexistence of metallic, ionic, and covalent bonding.[2,3] Especially CoAl and NiAl have a very strong ordering tendency; the thermal disorder is small up to the melting temperatures and the structural atomic defects, i.e., the defects which survive in thermodynamic equilibrium when approaching zero temperature in order to compensate the deviations $(x-0.5)$ from the stoichiometric composition, are TM antistructure atoms on the Al sublattice for TM-rich systems and vacancies on the TM sublattice for Al-rich systems.[4,5] In addition, thermal defects are produced at elevated temperatures, and it is characteristic for the TM aluminides that the effective defect formation energies are strongly different for $x<0.5$, $x=0.5$, and $x>0.5$.

Another subgroup of $B2$ phases consists of, respectively, two transition metals. A special representative is FeCo because Fe and Co are neighbors in the periodic table, and therefore in the $B2$ phase the two constituents should be more similar than the TM atoms and the Al atom. It is therefore expected that it costs little energy to exchange Fe and Co atoms between the two sublattices to produce Fe and Co antistructure atoms, so that the structural defects are antistructure atoms on both sides of the stoichiometric composition. This conjecture is supported by the low critical temperature of about 1000 K for the transition from the ordered $B2$ phase to the disordered $A2$ phase. Furthermore, it has been shown[6] that the lattice constant of FeCo increases monotonically with increasing amount of the bigger Fe atom through the stoichiometric composition (with a slightly slower rate for the Fe-rich samples), a behavior which also suggests that antistructure atoms are the structural defects in FeCo. Experimental information on the properties of thermally excited atomic defects is completely missing. In the present paper we therefore calculate the effective formation energies of atomic defects by the *ab initio* statistical mechanics to investigate the defect properties of a $B2$ phase for which the constituent atoms are more similar than in the TM aluminides.

Another important aspect is the role of magnetism. It has been shown by electron theory[7] that the spin polarization stabilizes the $B2$ structure of FeCo because it leads to a change of sign of the most relevant pair-interaction parameters. Therefore it will be interesting to figure out the role of magnetism on the properties of atomic defects.

II. Calculational procedure. It is well known (see, e.g., Refs. 4, 5, 8, and 9) that in ordered compounds A_xB_{1-x} inevitably various types of atomic defects must be created simultaneously by thermal excitation in order to conserve the homogeneity of the sample. For instance, in pure antistructure-type systems the thermal excitation consists of a simultaneous creation of A and B antistructure atoms on the two sublattices. In pure triple defect systems two A atom vacancies on the α sublattice, an A antistructure atom on the β sublattice, and a new unit cell AB are generated. In general, various types of such elementary excitations appear simultaneously with a respective statistical weight.

This coexistence of various types of atomic defects may be described by the *ab initio* statistical mechanics (for details see, e.g., Refs. 4, 5, 8, and 9) by a formalism which is valid at small defect concentrations. The defect concentrations are obtained by minimizing an appropriate ansatz for the Gibbs free energy G with respect to the numbers N_i^ν of various grand-canonical defects which are introduced in the originally perfectly ordered stoichiometric compound. The index i

denotes the type of defect (i.e., vacancy or antistructure atom), whereas ν labels the sublattice (α or β) on which the defect appears. The grand-canonical defects are grand-canonical vacancies which are obtained by totally removing an atom from the system, and grand-canonical antistructure atoms where an atom on its own sublattice is replaced by an atom of the other type. During the introduction of such a grand-canonical defect the energy, vibrational entropy, and volume of the system changes by ε_i^ν, s_i^ν, and ΔV_i^ν (defect formation parameters). The concentrations $c_i^\nu = N_i^\nu/2M$ (where M is the number of unit cells) are obtained by minimizing G with respect to N_i^ν whereby the conservation of particle numbers is guaranteed by means of Lagrangian parameters ($\mu_{\mathrm{Fe}}, \mu_{\mathrm{Co}}$) which for the thermodynamic equilibrium have the meaning of chemical potentials. This yields the concentrations as functions of temperature T, pressure p, and chemical potentials μ_{Fe}, μ_{Co}. The chemical potentials then are obtained from the Gibbs-Duhem relation and from the demand $N_{\mathrm{Fe}}/N_{\mathrm{Co}} = x/(1-x)$, which represent a set of nonlinear coupled equations which in general have to be solved numerically. Under certain circumstances which are fulfilled in many materials the defect concentrations then may be written in the form

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

Here, $\tilde{S}_i^\nu$, $\tilde{E}_i^\nu$, $\tilde{\Omega}_i^\nu$ denote the effective formation entropy, energy, and volume. Because of the above discussed simultaneous generation of various atomic defects, 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. If one special type of elementary excitation dominates strongly (e.g., the generation of A and B antistructure atoms, or the triple defect formation) then analytical expressions for the effective defect formation quantities may be obtained (see Appendix A of Ref. 5). For $\mathrm{Fe}_x\mathrm{Co}_{1-x}$ our numerical calculations have shown that the simultaneous generation of Fe and Co antistructure atoms represents the strongly dominating thermal excitation. The analytical results for the effective defect formation energies for this case are given by Eqs. (A7)–(A9) of Ref. 5 for the stoichiometric composition and by Eqs. (A15)–(A17) for nonstoichiometric compositions. Please note the well-known discontinuity in the values of the effective formation energies when going from Fe-rich to Co-rich systems.[4,5,8,9] The reason for this is very simple: For Fe-rich compounds the structural defect (which is the one with zero effective formation energy) is the Fe antistructure atom, whereas for the Co-rich compounds it is the Co antistructure atom. This abrupt change in the kind of the structural defect is reflected in a discontinuity of the chemical potentials which enter the effective defect formation energies and which thus produce a discontinuity of these.

The defect energy parameters ε_i^ν were calculated by the supercell approach,[4,5,8,9] i.e., large supercells containing N sites and one grand-canonical defect (i,ν), respectively, are repeated periodically. We used $N=16$ and $N=32$, and a comparison of the results shows that the data for $N=32$ are already well converged with respect to N. The energies of the supercells were calculated by the *ab initio* density-functional electron theory in local spin-density approximation (LSDA) for the exchange-correlation energy.[10] In addition, the generalized-gradient approximation[11] (GGA) for the exchange-correlation energy was used because it is known[12] that for bcc Fe the GGA vacancy formation energy agrees better with the experimental value than the LSDA energy. The calculations were performed with the *ab initio* pseudopotential method[13] and the mixed-basis pseudopotential code[14] (MB-PP) where the wave functions are evaluated into plane waves and five localized and nonoverlapping d orbitals per Fe and Co atom and where the spin polarization of the system was neglected, and with the WIEN 97 code[15] based on the full-potential linearized augmented plane-waves method (FLAPW), using local orbitals[16] for the $3p$ states. In all calculations the structural relaxations of the atoms around the defects were taken into account, whereas the volume relaxations of the supercells with the defects were generally neglected (see below). We also did not calculate the defect entropy parameters s_i^ν and therefore must confine ourselves to a discussion of the effective defect formation energies whereas no data for the absolute values of the defect concentrations can be given.

TABLE I. Lattice parameter a_0 and bulk modulus B_0 for stoichiometric $B2$ FeCo. The experimental lattice parameter is for $T=25$ °C. The symbols nsp and sp denote calculations without and with the effect of spin polarization.

	Experiment	MB-PP	FLAPW			
		LDA	LDA nsp	LSDA sp	GGA nsp	GGA sp
a_0 [Å]	2.8562	2.726	2.703	2.766	2.763	2.843
B_0 [GPa]		289	324	258	268	196

III. Results. Table I represents our results for the lattice parameter and the bulk modulus of perfectly ordered stoichiometric FeCo. It is remarkable that we need a combination of the GGA and the spin polarization to get a good agreement with the experimental lattice constant. Unfortunately, there is no experimental result for the bulk modulus of a single crystal for comparison.

Table II represents the effective defect formation energies for stoichiometric FeCo as calculated by the MB-PP method, neglecting the effect of spin polarization. There are two major and surprising points: First, the very large relaxations of the atoms around the vacancies which have a very strong effect on the effective vacancy formation energies. Second, the negative values of the effective formation energies for the antistructure atoms, which means that stoichiometric unpolarized $B2$ FeCo is unstable against the spontaneous formation of antistructure atoms. Very similar results were obtained for calculations including the volume relaxation of the supercells.

The situation seems to be similar to the case of $\mathrm{Fe_3Si}$ which crystallizes in the $D0_3$ structure and for which our calculations neglecting spin polarization also revealed an in-

TABLE II. The effective defect formation energies (in eV) for stoichiometric FeCo as calculated by the MB-PP code, neglecting the effect of spin polarization. The calculations were performed for supercells with $N=32$ sites, and the structural relaxation of the atoms around the defects were neglected (unr) or taken into account (r). The last line represents the calculated atom displacements in percent of the lattice parameter for the atoms in the first three neighbor shells around the defect. The minus and plus sign denotes a displacement towards or away from the defect, respectively.

	$\tilde{E}_V^{\alpha}$	$\tilde{E}_V^{\beta}$	$\tilde{E}_{\mathrm{Fe}}^{\beta}$	$\tilde{E}_{\mathrm{Co}}^{\alpha}$
unr	1.65	1.57	−0.05	−0.05
r	0.13	0.34	−0.06	−0.06
	−9.3/+4.3/−0.4	−9.0/+0.7/+0.5	+0.8/−0.4/−0.1	−1.4/+2.0/−0.2

stability against the spontaneous formation of defects.[17] It was our conjecture[17] that Fe_3Si is stabilized in the $D0_3$ structure by magnetic effects. As outlined in the introduction, the $B2$ structure of FeCo is also stabilized by magnetic effects. We therefore tried to remove the negative effective formation energies for antistructure atoms by performing spin-polarized FLAPW calculations.

Table III represents the effective defect formation energies for stoichiometric FeCo as obtained by the FLAPW calculations. When neglecting the spin polarization the FLAPW calculations reveal the same surprising features as the MB-PP calculations, i.e., a very strong effect of structural relaxations and negative values for the effective formation energies for antistructure atoms. When taking into account spin polarization, both peculiarities are removed, i.e., the structural relaxations are much smaller (compare the last lines of Tables II and III) so that the effective formation energies are only little affected by the relaxations, and the effective formation energies for the antistructure atoms are positive. The results are very similar for supercells with $N=16$ or $N=32$ sites, and therefore they appear to be well converged with respect to the supercell size. Furthermore, there is only little difference between the respective results from LSDA and spin-polarized GGA calculations, in contrast to the case of pure bcc Fe where the vacancy formation energy depends sensitively on the choice of the exchange-correlation functional.[12]

The stabilization of the $B2$ structure of FeCo by magnetic effects may be interpreted in the following way. An Fe atom in the perfectly ordered $B2$ structure is surrounded by eight Co atoms, and it exhibits (according to our LSDA calculations) a magnetic moment of $2.6\mu_B$ which is considerably larger than the atomic magnetic moment of bcc Fe $(2.22\mu_B)$. The corresponding gain in intra-atomic exchange energy sta-

TABLE III. The effective defect formation energies (in eV) for stoichiometric FeCo as calculated by the FLAPW code, without (nsp) and with (sp) the effect of spin polarization, without (unr) and with (r) the structural relaxation, and in LDA or LSDA as well as in GGA. The last line gives the calculated atom displacements in percent of the lattice parameter for the atoms in the first three neighbor shells around the defect, for the GGA32 spr calculation. The minus and plus sign denotes a displacement towards or away from the defect, respectively. The numbers 16 and 32 denote the number of sites in the supercells.

		$\tilde{E}_V^{\alpha}$	$\tilde{E}_V^{\beta}$	$\tilde{E}_{\mathrm{Fe}}^{\beta}$	$\tilde{E}_{\mathrm{Co}}^{\alpha}$
nsp, unr	LDA 16	1.72	1.69	−0.07	−0.07
	LDA 32	1.72	1.72	−0.07	−0.07
	GGA 16	1.52	1.52	−0.06	−0.06
nsp, r	LDA 16	0.24	0.03	−0.07	−0.07
	LDA 32	0.11	0.30	−0.08	−0.08
	GGA 16	0.21	0.02	−0.07	−0.07
sp, unr	LSDA 16	1.75	2.03	0.11	0.11
	LSDA 32	1.69	2.01	0.10	0.10
	GGA 16	1.72	1.87	0.17	0.17
	GGA 32	1.67	1.90	0.17	0.17
sp, r	LSDA 16	1.71	1.86	0.10	0.10
	LSDA 32	1.65	1.75	0.07	0.07
	GGA 16	1.70	1.73	0.17	0.17
	GGA 32	1.65	1.68	0.15	0.15
		−0.2/−0.5/+0.1	−3.3/+1.4/−0.7	−0.06/+0.9/−0.09	+0.4/−0.7/+0.06

TABLE IV. The effective formation energies (in eV) for FeCo as obtained from calculations for supercells with 32 sites, including spin polarization and atomic relaxations.

		$\tilde{E}_V^{\alpha}$	$\tilde{E}_V^{\beta}$	$\tilde{E}_{\mathrm{Fe}}^{\beta}$	$\tilde{E}_{\mathrm{Co}}^{\alpha}$
$x=0.5$	LSDA	1.65	1.75	0.07	0.07
	GGA	1.65	1.68	0.15	0.15
$x<0.5$	LSDA	1.61	1.78	0.15	0
	GGA	1.57	1.75	0.30	0
$x>0.5$	LSDA	1.69	1.71	0	0.15
	GGA	1.72	1.60	0	0.30

bilizes the $B2$ structure. In contrast, an Fe antistructure atom is surrounded by eight Fe atoms as in bcc Fe, and we therefore obtained a reduced magnetic moment of $2.32\mu_B$. The corresponding loss of intra-atomic exchange energy leads to a positive value for the formation energy of an Fe antistructure atom. A Co antistructure atom has the same effective formation energy [Eq. (A7) of Ref. 5] because the elementary thermal excitation is given by a simultaneous excitation of an Fe and a Co antistructure atom. To explain the reduction of the very strong relaxation effects by the magnetism we have performed spin-polarized calculations for the atom positions obtained by nonpolarized calculations. We found that for these positions the magnetic moments are much smaller than for the unrelaxed positions, leading to a big loss of intra-atomic exchange energy. The strive to attain large magnetic moments and hence large intra-atomic exchange energies drives the atoms back until they are close to their unrelaxed positions.

Table IV represents our final results for the effective formation energies for stoichiometric and nonstoichiometric $B2$ FeCo. This material is of antistructure type, i.e., the structural defects are Fe antistructure atoms for the Fe-rich compositions and Co antistructure atoms for the Co-rich compositions, and the effective formation energies for antistructure atoms are much smaller than those for vacancies. The low effective formation energy for antistructure atoms is consistent with the relatively low critical temperature of about 1000 K for the transition from the $B2$ phase to the disordered $A2$ phase. It results from the fact that Fe and Co in the bcc phase are quite similar: For instance, according to our calculations the lattice constants of bcc Fe and Co differ by less than 1% and the electronic structure is also similar because Fe and Co are neighbors in the periodic table. In contrast, for the transition-metal aluminides FeAl, CoAl, and NiAl with $B2$ structure the lattice constant of bcc Al is about 14% larger than the ones of Fe, Co, and Ni in the bcc phase, and the two constituents are electronically very different (mainly d character in the transition metals and s, p character in Al). As a result, there is a much stronger tendency to preserve the atomic order for the transition-metal aluminides than for FeCo.

The effective formation energies for Fe and Co vacancies are very similar which again results from the similarity of the constituent atoms, in contrast to the behavior of the transition-metal aluminides. For instance, for stoichiometric $B2$ FeAl the effective formation energy for the Al vacancy is a factor of 3.5 larger than the one for the Fe vacancy.[8,9,17] Because in FeCo the vacancies are available on both sublattices, the self-diffusion may proceed by a random walk of nearest-neighbor jumps of vacancies, whereas in FeAl probably cooperative jumps of Fe and Al atoms occur to avoid the generation of a fully developed Al vacancy.[8,9,17] Furthermore, it is striking that the effective formation energies for the various defects vary only little when going from the Fe-rich to the stoichiometric to the Co-rich compounds. In contrast, for the transition-metal aluminides there is a big variation of effective formation energies with composition.[4] Altogether, it appears that the $B2$ phase FeCo consisting of two rather similar constituents exhibits a much simpler behavior of the atomic defects than the transition-metal aluminides consisting of strongly dissimilar constituents.

Unfortunately, there are no direct experimental results for comparison. From the enthalpy of formation an effective formation energy for antistructure atoms of 0.34 eV was estimated[6] but no details on the underlying assumptions are given. This value would agree rather well with our calculated GGA value for nonstoichiometric compounds.

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