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Short communication

Dominant thermal defects in B2–FeAl

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Abstract

It is shown within the framework of the ab initio statistical mechanics that the triple defect formation is not the dominant thermal excitation in stoichiometric B2–FeAl, at least at low temperatures. Therefore the customary type of analysis of magnetic susceptibility measurements exclusively in terms of triple defects may yield erroneous results for the concentration of Fe vacancies.
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There are numerous hints from experiments [1–3] and from theory [4–8] that the stoichiometric compound B2–FeAl exhibits a hybrid behavior between an antistructure type system and a triple defect type system. In an antistructure type system the dominant thermal excitation is the simultaneous formation of antistructure atoms on both sublattices according to the reaction

$$0 \rightarrow \mathrm{Fe_{Al}} + \mathrm{Al_{Fe}} \tag{1}$$

whereas in a triple defect system the triple defect formation according to

$$0 \rightarrow 2\mathrm{V_{Fe}} + \mathrm{Fe_{Al}} + \mathrm{FeAl} \tag{2}$$

dominates. The theoretical arguments [4–8] were based on the calculation of the effective formation energy for these two types of defects. It has been shown in Refs. [9,10] that the defect vibrational entropies may play a very important role in intermetallic compounds so that at elevated temperatures the dominant thermal excitation is not necessarily the one with the smallest effective formation energy. In the present contribution we therefore recalculate the defect concentrations in stoichiometric FeAl, taking into account reliable estimates for the defect vibrational entropies [9,10]. Furthermore, we include the effect of magnetism. The perfectly ordered stoichiometric FeAl is paramagnetic, whereas an Fe antistructure atom on the Al sublattice, together with the surrounding Fe atoms, exhibits an effective magnetic moment [11–13]. The influence of magnetism on the effective formation energies has been considered previously [6]. We now take into account both the defect vibrational entropies and the effect of magnetism on the absolute values of the defect concentrations.

Our results are based on calculations of the defect concentrations within the framework of the ab-initio statistical mechanics. This approach has been described extensively in the literature (eg, Ref. [14]), so that we discuss in short only the basic ingredients. In this generalized grand-canonical formalism the concentration c_i^ν of defects (i denotes the type of defect, ie, vacancy or antistructure atom, and ν labels the sublattice) is obtained by minimizing the Gibbs free energy for given temperature T and pressure p with respect to the numbers N_i^ν of various 'grand-canonical defects' which are introduced into the originally perfectly ordered stoichiometric compound. The conservation of particle numbers N_{Fe} and N_{Al} in thermal equilibrium is

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guaranteed by means of Lagrangian parameters μ_{Fe} and μ_{Al} which have the meaning of chemical potentials. 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^v, s_i^v and ΔV_i^v (defect formation parameters). The minimization of the Gibbs free energy yields expressions for c_i^v $(T, p, \mu_{Fe}, \mu_{Al})$ which contain the defect formation parameters of all defects (i,v). The chemical potentials μ_{Fe} and μ_{Al} have to be obtained from two coupled nonlinear equations (Gibbs–Duhem relation, and the demand for the correct composition). In general, these equations have to be solved numerically, and then numerical results for c_i^v are obtained. If one specific type of thermal excitation (ie, the triple defect formation) dominates strongly over all other possible thermal excitations which conserve the homogeneity of the sample, the two equations may be solved analytically, and the c_i^v may be represented as

$$c_i^v = \frac{1}{2}\, e^{\tilde{S}_i^v/k_B}\, e^{-(\tilde{E}_i^v + p\tilde{\Omega}_i^v)/k_B T}, \tag{3}$$

with the effective defect formation energy $\tilde{E}_i^v$, formation entropy $\tilde{S}_i^v$ and formation volume $\tilde{\Omega}_i^v$ which depend in an analytical way on the defect formation parameters of the defects involved in the dominant thermal excitation (all these dependences are given in Appendix A of Ref. [14]). The structural defect, ie, the defect which survives when going to zero temperature in order to compensate possible deviations from stoichiometry, is the one for which $\tilde{E}_i^v = 0$ for zero p.

To calculate the defect formation parameters a supercell approach was used, ie, large supercells containing N sites and one defect, respectively, were arranged periodically, and ε_i^v or ΔV_i^v were determined from the difference in energies or equilibrium volumes of the cells with and without the defect, thereby taking into account the structural relaxation of the atoms around the defects. So far we did not calculate ab initio the defect entropy parameters s_i^v, and in the present study we neglect them or make reasonable estimates for their numerical values as discussed in Refs. [9,10]. The comparison of the results for the two types of calculations reveals the contribution of the s_i^v to the absolute values of the defect concentrations. To estimate the defect entropy parameters it was assumed [10] that the essential features of the phonon density of states originate from high-frequency vibrations of low-mass Al atoms in a cubic cage of eight surrounding Fe atoms and from low-frequency vibrations of high-mass Fe atoms, and that at not too high temperatures the entropy is dominated by the low-frequency Fe vibrations. When removing an atom from the system, the number of vibrational degrees of freedom is reduced and hence the entropy decreases, the decrease being stronger for the removal of a Fe atom than for the removal of an Al atom. Accordingly, when replacing a Fe(Al) atom by an Al(Fe) atom, the entropy decreases (increases). It was shown in Ref. [10] that we can reconcile our theoretical result for $\tilde{S}_{V_{Fe}}$ with the experimental result from positron annihilation experiments [15] by the choice $s_{Fe_{Al}} = -s_{Al_{Fe}} = 3\ k_B$ and $s_{V_{Fe}} = 2\ s_{V_{Al}} = -0.96\ k_B$. Because different combinations of atomic defects are involved in reactions (1) and (2), it becomes obvious that the effect of the defect vibrational entropies will be different for the two reactions.

The supercell calculations were performed by the ab initio density functional electron theory in local density approximation [16]. The great success of this type of electron theory for investigations of atomic defects in intermetallic compounds is discussed in Ref. [17]. Two sets of data are obtained. For the first set [7,18] the supercells contain $N = 54$ sites, and the effect of spin polarization is totally neglected. For the second set [6] the supercells contain $N = 32$ sites, and spin polarization is taken into account.

It should be noted that the spin-polarized calculations yield a weak ferromagnetic ground state for the perfect stoichiometric phase which is observed to be paramagnetic in experiments, and therefore the LDA calculations may give only an approximate estimate of the effect of magnetism on c_i^v. Nevertheless, the theory agrees with experiments concerning the fact that a large moment is induced at the Fe antistructure atoms. While the magnetism plays a role in the formation energies of defects, it will be shown below that our basic statements are not affected by the question whether we take into account the spin polarization or not.

In our calculations it turns out that the triple defect formation is the dominant thermal excitation only for Fe-rich systems. For Al-rich systems, the dominant thermal excitation is the annihilation of an Al antistructure atom, Al_{Fe}, with the simultaneous generation of two Fe vacancies according to

$$Al_{Fe} \rightarrow 2V_{Fe} + FeAl, \tag{4}$$

whereas the formation of Fe antistructure atoms via triple defects corresponds to a much larger effective formation energy. Finally, for the stoichiometric system the dominant thermal excitation at low temperatures is the exchange of Fe and Al atoms according to reaction (1). However, the effective formation energy of this process is only slightly smaller than the one for the formation of Fe vacancies via triple defects, reaction (2). At elevated temperatures therefore both processes are relevant, ie, stoichiometric FeAl is indeed neither a pure antistructure type system nor a pure triple defect type system. The concentrations c_i^v then can be calculated only numerically (see above).

Fig. 1 shows for $Fe_{50}Al_{50}$ the calculated ratio $r = c_{V_{Fe}}/c_{Fe_{Al}}$ which is zero for a pure antistructure type system and 2 for a pure triple defect type system. This ratio gradually increases from zero at very low temperatures towards 2 at elevated temperatures, demonstrating clearly the hybrid character of the system. Inclusion of the spin polarization supports the formation of Fe antistructure atoms because of the gain of intraatomic exchange energy when a high magnetic moment is formed. Inclusion of the defect entropy parameters supports the triple defect formation. In any case, the generation of Fe and Al antistructure atoms dominates the triple defect formation at low temperatures. Fig. 2 shows the ratio $r' = c_{Al_{Fe}}/c_{Fe_{Al}}$ which is 1 for a pure antistructure type system but zero for a pure triple

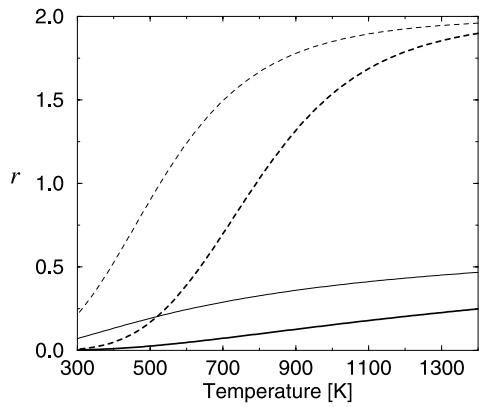

Fig. 1. The calculated ratio $r = c_{V_{Fe}}/c_{Fe_{Al}}$ as function of temperature for the defect formation parameters of set 1 (thin lines) where the spin polarization is neglected and for set 2 (thick lines) where the spin polarization is taken into account. The solid lines are obtained when the defect entropy parameters s_t^v are neglected whereas for the calculation of the dashed lines reasonable estimates for s_t^v according to Refs. [9,10] are inserted.

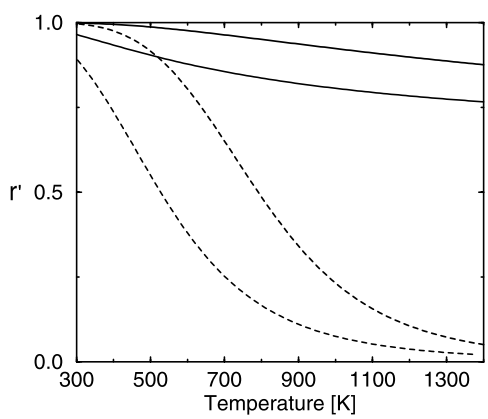

Fig. 2. The calculated ratio $r' = c_{Al_{Fe}}/c_{Fe_{Al}}$ as function of temperature for the defect formation parameters of set 1 (thin lines) where the spin polarization is neglected and for set 2 (thick lines) where the spin polarization is taken into account. The solid lines are obtained when the defect entropy parameters s_t^v are neglected whereas for the calculation of the dashed lines reasonable estimates for s_t^v according to Refs. [9,10] are inserted.

defect system. Again, the hybrid character of stoichiometric B2 FeAl becomes obvious.

Altogether, our calculations underpin the former claim [1–8] that stoichiometric FeAl exhibits a hybrid behavior. The relative weights of the triple defect formation and of the antisite defect formation are strongly determined by the defect vibrational entropies which favor the triple defect formation. In any case, there is a considerable amount of Al antistructure atoms which has to be taken into account when interpreting the physical properties (see below).

The present results have important consequences for the interpretation of magnetic susceptibility experiments, where the concentration of Fe antistructure atoms is monitored via a nonvanishing Curie constant [13]. Two variants of susceptibility experiments are conceivable. In the first variant, the system is prepared at high temperatures in thermodynamic equilibrium and then rapidly quenched to very low temperatures where the defects are frozen in. The concentration of Fe antistructure atoms then is obtained from the Curie constant measured at such low temperatures that the defects are not yet mobile. From the Curie constants found after quenching from various high temperatures T_q the equilibrium concentrations $c_{Fe_{Al}}(T_q)$ can be obtained. In a second variant the sample is again quenched from high temperatures, but then the susceptibility is measured for a larger temperature range, including temperatures for which the defects become mobile. The recovery behavior of the Fe antistructure atoms then may be monitored by a modification of the Curie constant, and from this modification as function of temperature and annealing time the activation energy for the elimination of Fe antistructure atoms may be obtained [13].

Problems for the interpretation of susceptibility measurements arise as soon as it is attempted to relate the concentrations of Fe antistructure atoms to the concentration of Fe vacancies. To do this it is assumed [13] that FeAl is a pure triple defect system. For the first variant of experiments this would yield $c_{V_{Fe}}(T_q)/c_{Fe_{Al}}(T_q) = r(T_q) = 2$, which is not correct according to Fig. 1. The errors for the concentration of Fe vacancies thereby are relatively small at elevated temperatures if the true defect entropy parameters are close to our estimated values, they are considerably larger if the defect entropy parameters are actually smaller. For the interpretation of the recovery experiments, however, the problem is much more serious. The elimination of Fe antistructure atoms may occur via the inverse of reaction (2). Alternatively, it may proceed via the inverse of reaction (1). Thereby the exchange of Fe and Al atoms requires Fe vacancies as a vehicle (Fig. 3), but the concentration of Fe vacancies is not at all affected by this elimination mode of antistructure atoms. Therefore, is is impossible to relate the decrease of the

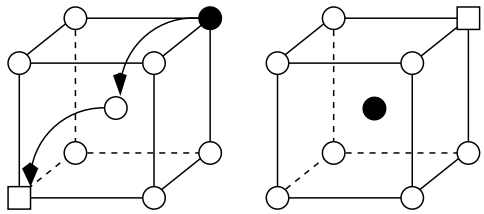

Fig. 3. A possible mechanism for the elimination of Fe antistructure atom according to the inverse of Eq. (1). The elimination involves a short-range migration of a vacancy, but the vacancy concentration is not affected by the elimination of Fe antistructure atoms. Note that the process requires a cooperative jump [7,17] of the Fe and the Al atom so that no fully developed Al vacancy (which corresponds to a very high energy [4–7]) occurs in an intermediate step. The open (solid) circles denote Fe (Al) atoms and the open squares vacant lattice sites.

concentration of Fe antistructure atoms to the decrease of the concentration of Fe vacancies. If this is done by assuming $r = 2$ for the interpretation of magnetic measurements, the so-obtained decrease in the concentration of Fe vacancies after annealing may be totally different from the one found in positron annihilation experiments [15] or in thermal expansion measurements [19].

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References

[1] Y.A. Chang, J.P. Neumann, Prog. Solid St. Chem. 14 (1982) 221.
[2] R. Krachler, H. Ipser, B. Sepiol, G. Vogl, Intermetallics 3 (1994) 83.
[3] X. Ren, K. Otsuka, M. Kogachi, Scripta Mater. 41 (1999) 907.
[4] C.L. Fu, Y.-Y. Ye, M.H. Yoo, K.M. Ho, Phys. Rev. B 48 (1993) 6712.
[5] J. Mayer, C. Elsässer, M. Fähnle, Phys. Stat. Sol. (b) 191 (1995) 283.
[6] C.L. Fu, Phys. Rev. B 52 (1995) 3151.
[7] M. Fähnle, J. Mayer, B. Meyer, Intermetallics 7 (1999) 315.
[8] M. Fähnle, B. Meyer, G. Bester, Intermetallics 7 (1999) 1307.
[9] B. Meyer, M. Fähnle, Phys. Rev. B 60 (1999) 717.
[10] M. Fähnle, G. Bester, B. Meyer, Scr. Mater. 39 (1998) 1071.
[11] G.R. Caskey, J.M. Franz, D.J. Sellmyer, J. Phys. Chem. Solids 34 (1973) 1179.
[12] H. Domke, L.K. Thomas, J. Magn. Magn. Mater. 45 (1984) 305.
[13] S. Zaroual, O. Sassi, J. Aride, J. Bernardini, G. Moya, Mat. Sci. Eng. A 279 (2000) 282.
[14] B. Meyer, M. Fähnle, Phys. Rev. B 59 (1999) 6072.
[15] R. Würschum, C. Grupp, H.-E. Schaefer, Phys. Rev. Lett. 75 (1995) 97.
[16] W. Kohn, L.J. Sham, Phys. Rev. 140 (1965) A1133.
[17] M. Fähnle, B. Meyer, J. Mayer, J. Oehrens, G. Bester, Mat. Res. Soc. Symp. Proc. 527 (1998) 23.
[18] B. Meyer, PhD thesis, Universität Stuttgart, 1998.
[19] H.-E. Schaefer, K. Frenner, R. Würschum, Phys. Rev. Lett. 82 (1999) 948.