

Stabilization of itinerant (band) magnetism in FeAl by Ga substitution for Al

D. A. Papaconstantopoulos, I. I. Mazin, and K. B. Hathaway^{a)}
 Naval Research Laboratory, Washington, DC 20375-5320

Band structure calculations of $\text{FeGa}_{1-x}\text{Al}_x$ have been performed, to further investigate the stability of ferromagnetism in FeAl. The Stoner parameter increases by about 20% at the FeGa end. This is also confirmed by our spin-polarized calculations. We conclude that Ga substitution for Al is likely to stabilize the elusive (or illusive) ferromagnetic state in FeAl. © 2001 American Institute of Physics. [DOI: 10.1063/1.1357838]

The CsCl ($B2$) structure transition metal aluminides have attracted substantial theoretical attention. It has been known since 1986 that the local spin density calculations for FeAl produce a ferromagnetic ground state, if performed at the experimental lattice parameter (5.41 a.u.).¹ It has been pointed out² that FeAl has a Stoner parameter (NI) very close to the critical value of 1.0 for which a stable ferromagnetic state would be expected to occur in the Stoner theory. Moreover this parameter was shown to be very sensitive to both changes in lattice constant and in band filling. Decreasing the band filling by substituting Mn for Fe in the amount of 40% also increases the Stoner factor to above 1.0. Experimentally FeAl in well-ordered samples has never been observed to be ferromagnetic, although quenched disorder does produce an observable magnetization. These experimental facts, together with the closeness of the Stoner parameter to the critical value, suggest that this system is on the verge of *itinerant* ferromagnetic instability and can be easily pushed over the border by small changes in crystal structure and/or composition.

Since the effect of substituting for Fe was investigated in earlier studies, it was of interest to determine the effect of substituting Ga for Al on the magnetization. Figure 1 shows the Stoner factor for $\text{FeGa}_{1-x}\text{Al}_x$ for a series of hypothetical ordered alloys³ (the calculated equilibrium lattice parameter 5.34 a.u. was used). The Stoner factor increases with Ga concentration, well exceeding 1.0 for pure FeGa, and increasing by about 20% over the composition range from FeAl to FeGa. The larger part of the 20% enhancement (12%) is due to an increase in the density of states, $N(E_F)$, at the Fermi level and the remainder is due to an increase in the value of the Stoner exchange integral I . Although the compound FeGa is not a stable compound on the Fe-Ga phase diagram, it is interesting to compare the band structures of FeAl and FeGa to determine what is responsible for this increase in Stoner factor. The d bands of FeGa near the Fermi energy are observed to be slightly flatter for FeGa than for FeAl, leading to a larger density-of-states (DOS), and thus to a larger Stoner factor. This band flattening is due to a reduction of the p -metal participation in the electronic states at the Fermi level, which leads to a narrowing of the $\text{Fe}(t_{2g})$

band, thus increasing the values of both $N(E_F)$ and I . Hence, we conclude that the Stoner factor increase with Ga doping results from a reduced hybridization between the $\text{Fe}(t_{2g})$ and $\text{Ga}(sp)$ states.

Spin-polarized calculations for FeAl and FeGa confirm the increased stabilization of ferromagnetism in FeGa. Figure 2 compares the total energy for FeAl and FeGa in the paramagnetic and ferromagnetic states as a function of volume. The energy differences between the paramagnetic and ferromagnetic minima provide a measure of the stability of the ferromagnetism. These energy differences are 0.35 mRy (55 K) for FeAl and 1.05 mRy (165 K) for FeGa. In both cases this is a rather weakly stabilized magnetic state (in agreement with the fact that paramagnetic calculations produce the Stoner factor close to 1 in both cases, but clearly larger for FeGa): for example, the magnetic energy stabilization of Fe is 60 mRy, corresponding to a temperature of 10 000 K. This temperature is an order of magnitude higher than the experimental Curie temperature of Fe so, by analogy, we could think that a stable magnetic state of FeAl would only be observed at temperatures well below 50 K.

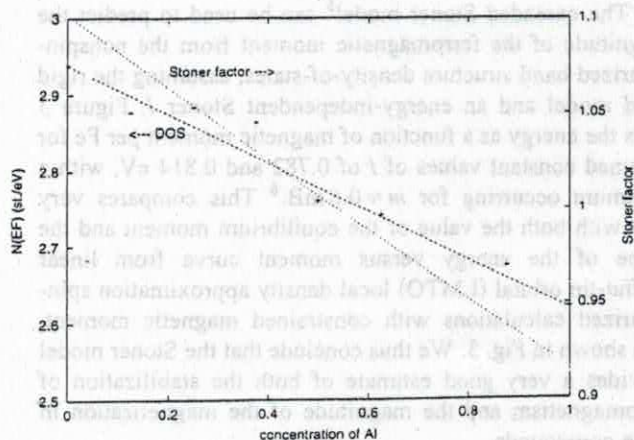


FIG. 1. Density of states at the Fermi level for a number of ordered Fe(Al, Ga) compounds as a function of the relative concentration of Al at the (Al, Ga) site (+). Artificial ordering introduces deviations from the straight line, which is probably a good approximation for the DOS in disordered $\text{FeAl}_x\text{Ga}_{1-x}$ alloys. The line showing the Stoner factor NI was produced using this linear dependence of DOS, and I (calculated as in Ref. 7) was also linearly interpolated between FeAl and FeGa (Ref. 1).

^{a)} Author to whom correspondence should be addressed; electronic mail: hathaway@anvil.nrl.navy.mil

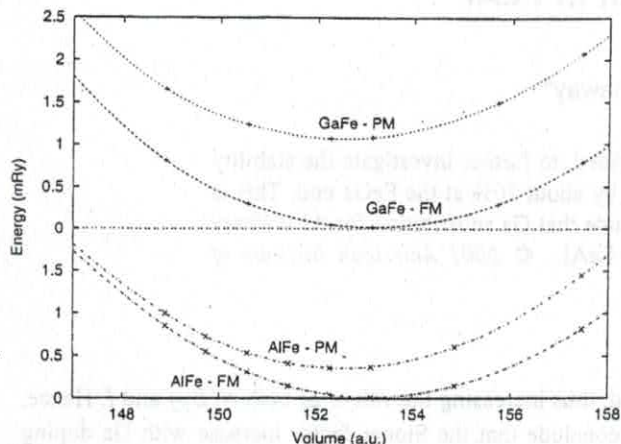


FIG. 2. Total energy as calculated by the LMTO method for stoichiometric FeAl and FeGa compound.

However, our calculations show FeAl to be analogous to Ni, and not to Fe, in the sense that like Ni FeAl appears to be an *itinerant* ferromagnet. Unlike pure Fe, where both ferro- and antiferromagnetic solutions exist, and the energy difference between the two is comparatively small, the antiferromagnetic state in FeAl cannot be stabilized in the calculations, like in Ni. Thus the magnetism should be destroyed by Stoner excitations with the characteristic energy of ≈ 50 K, and not by Heisenberg type fluctuations operative in Fe. In any event, the calculations show that the paramagnetic and the ferromagnetic ground state of FeAl differ in energy by very little and thus it may be that the clean, well ordered samples are in fact magnetic at some very low temperature. Another consequence of the itinerant character of magnetism in FeAl is that numerous model studies of this system, based on localized moments and Heisenberg interaction (e.g., Ref. 4), are irrelevant for the real material.

The extended Stoner model⁵ can be used to predict the magnitude of the ferromagnetic moment from the nonspin-polarized band structure density-of-states, assuming the rigid band model and an energy-independent Stoner I . Figure 3 plots the energy as a function of magnetic moment per Fe for assumed constant values of I of 0.782 and 0.814 eV, with a minimum occurring for $m = 0.6$ mB.⁶ This compares very well with both the value of the equilibrium moment and the shape of the energy versus moment curve from linear muffin-tin orbital (LMTO) local density approximation spin-polarized calculations with constrained magnetic moment, also shown in Fig. 3. We thus conclude that the Stoner model provides a very good estimate of both the stabilization of ferromagnetism and the magnitude of the magnetization in these compounds.

We have used the Stoner model with the same parameter I to study the role of defects in the stability of ferromagnetism in FeAl. It is known that quenched highly disordered samples show weak ferromagnetism.⁸ It is often deduced from this that defects are beneficial for magnetism in this system. We disagree with this. Quenched and cold-worked FeAl has a large amount of vacancies, which naturally create localized spins at neighboring Fe atoms. Localized spin den-

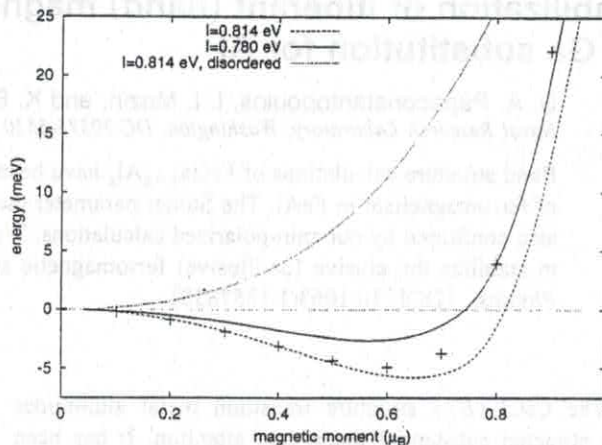


FIG. 3. Constrained LMTO fixed magnetic moment calculations for FeAl (+), compared to the extended Stoner model predictions with adjusted Stoner integrals (dashed and solid lines). The extended Stoner model prediction for the antisite disorder model is shown by a dotted line.

sity approximation (LSDA) calculations, on the other hand, suggest an itinerant magnetic state in the perfectly ordered material. It is plausible that easily formed antisite defects destroy itinerant magnetism, while further deviation from the perfect crystal, in the form of vacancies and/or clustering of iron, create localized magnetic moments. To test this idea, we performed a nonspin-polarized LMTO calculation of FeAl with an antisite defect⁹ in one out of every eight unit cells. The resulting density of states at the Fermi level is 17% lower than that for perfectly ordered FeAl, thus making the Stoner factor smaller than 1 and eliminating itinerant magnetism in the system. Extended Stoner model calculations, also shown in Fig. 3, indicated that, in agreement with the above, the energy increases monotonically away from the nonmagnetic state, with no stable nonzero moment.

To summarize:

- (1) We have shown that the predicted weak ferromagnetic order in Fe(Al, Ga) may be stabilized by (i) increasing the ratio of Ga to Al or (ii) decreasing the band filling by substituting Mn, for example for Fe (shown in a previous article).²
- (2) The Curie temperature, even in the perfect samples, should be low (< 70 K in FeAl and < 190 K in FeGa).
- (3) The predicted magnetic state is itinerant (no stable antiferromagnetic solution for either compound) and easily destroyed by weak disorder, while stronger disorder seemingly generates a localized magnetic moment on Fe.

¹B. I. Min, T. Oguchi, H. J. F. Jansen, and A. J. Freeman, *J. Magn. Mater.* **54**, 1091 (1986).

²D. A. Papaconstantopoulos and K. B. Hathaway, *J. Appl. Phys.* **87**, 5872 (2000).

³We used either the augmented plane wave muffin tin method or the linear muffin tin orbitals method in the calculations. Both methods produce the same results for the same crystal structures and compositions.

⁴J. A. Plascak, L. E. Zamora, and G. A. P. Alcazar, *Phys. Rev. B* **61**, 3188 (2000).

⁵G. L. Krasko, *Phys. Rev. B* **36**, 8565 (1987), and references therein.

⁶Stoner integral I can be estimated from paramagnetic calculations by in-

tegrating the LSDA exchange interaction over the unit cell or from the atomic part of an LMTO calculations. The two methods give close values of 0.70–0.72 eV. However, the value that fits the fixed moment calculations the best is larger (≈ 0.8 eV). In the spirit of the Stoner theory, we used this value in Fig. 3.

⁷J. F. Janak, Phys. Rev. B **16**, 255 (1977).

⁸M. J. Besnus, A. Herr, and A. J. P. Meyer, J. Phys. F: Met. Phys. **5**, 2138 (1975), and references therein.

⁹We call here an antisite defect the situation when one Fe and one Al interchange sites without violation of stoichiometry, unlike, say, in N. I. Kulikov, A. V. Postnikov, G. Borstel, and J. Braun, Phys. Rev. B **59**, 6824 (1999).

