

Ferromagnetism and crystal lattice stability of bcc and fcc iron

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The Stoner theory of itinerant ferromagnetism was used in calculating the magnetic properties of iron within the self-consistent linear muffin-tin orbital approach. The Stoner exchange parameter, I , was found from the linear-response theory as a function of volume and then adjusted by a constant enhancement factor determined by fitting the equilibrium atomic volume of the ferromagnetic (FM) bcc phase. No other adjustments of any quantities were performed. The calculations revealed a somewhat unusual behavior of phases. The nonmagnetic (NM) bcc phase is unstable with respect to spontaneous magnetization. Moreover, the enthalpy of the NM phase exhibits a monotonic decrease with c/a along the so-called Bain deformation path, the bcc modification being unstable with respect to the shear deformation. Ferromagnetism stabilizes the bcc phase. However, the FM fcc phase is unstable with respect to the shear deformation. The enthalpy curve along the deformation path has a cusp corresponding to a first-order phase transition between FM and NM states. The FM contributions to the energy versus atomic volume for different c/a values are tabulated.

I. INTRODUCTION

In recent years iron has been the object of extensive study by various first-principles methods (for references and comparison of results obtained by different methods, see Refs. 1–4). However, because of the local-spin-density approximation, the self-consistent spin-polarized calculations on bcc iron inevitably run into the difficulty of incorrectly predicting the relative stability of the ferromagnetic (FM) bcc phase with respect to the nonmagnetic (NM) fcc phase.

A way out of this deadlock could be to introduce into the theory an adjustable parameter in order to make calculations more consistent with experimental observations. Therefore, we have chosen to calculate the equilibrium magnetic moments as well as the magnetic contributions to the ground-state energies of iron using the Stoner model of itinerant ferromagnetism,⁵ rather than performing the spin-polarized calculations.

The Stoner exchange parameter, I , can then serve as the adjustable parameter. Using this approach, the analysis of metamagnetic behavior of the fcc iron phase,⁶ the structural properties of the bcc and fcc phases,⁷ and the energetics of the bcc-fcc Bain lattice deformation⁸ were performed recently.

In this short paper we will summarize some interesting results^{6–8} on the magnetic properties of iron and the role of FM effects in the iron phase stability.

We used the linear muffin-tin orbital^{9–11} (LMTO) method with the so-called combined-correction term,^{9–11} the Madelung electrostatic correction,¹² and the exchange-correlation functional of von Barth and Hedin.¹³ Also, the frozen-core approximation was used.¹⁴

II. bcc AND fcc MODIFICATIONS OF IRON

The Stoner parameter, I , was adjusted (enhanced by a factor 1.075 with respect to its values as calculated from the

linear-response theory¹⁵) in order to reproduce the experimental equilibrium Wigner–Seitz (WS) radius $s = 2.661$ a.u. for the FM bcc phase. No other adjustment of any parameters was made.

Figure 1 shows the plots of the total energies versus s for NM and FM phases of both bcc and fcc iron. As one can see, the FM phase in bcc iron has the lowest energy. The NM bcc phase was always believed to be metastable: having a higher energy, but corresponding to a local energy minimum. However, the unexpected result is that the NM bcc phase is unstable with respect to spontaneous magnetization for all volumes considered!

This result once again demonstrates the importance of distinguishing a “paramagnetic” phase from a zero spin “nonmagnetic” one. This has been stressed in the literature.¹⁶ Our point is that the nonmagnetic phase in iron is not a good model for the paramagnetic phase: the former is simply unstable!

The fcc phase is metamagnetic; in a constant-volume regime there are three stable ferromagnetic phases: one high-spin one and two low-spin ones.^{6–8}

Unfortunately, all the detailed calculated information on the FM fcc phase is not of much physical relevance since the latter turns out to be unstable with respect to tetragonal shear deformation.

III. TETRAGONAL SHEAR DEFORMATION

Upon imposing homogeneous tetragonal deformation a continuous transition is possible between the bcc ($c/a = 1$) and fcc phases ($c/a = \sqrt{2}$) (the so-called Bain deformation¹⁷). At low temperatures and moderate positive pressures, bcc iron is FM, while fcc iron is paramagnetic. Thus somewhere along the deformation path the ferromagnetism shall disappear. From an intuitive point of view, one could expect that along this path the energy (or enthalpy) plots of

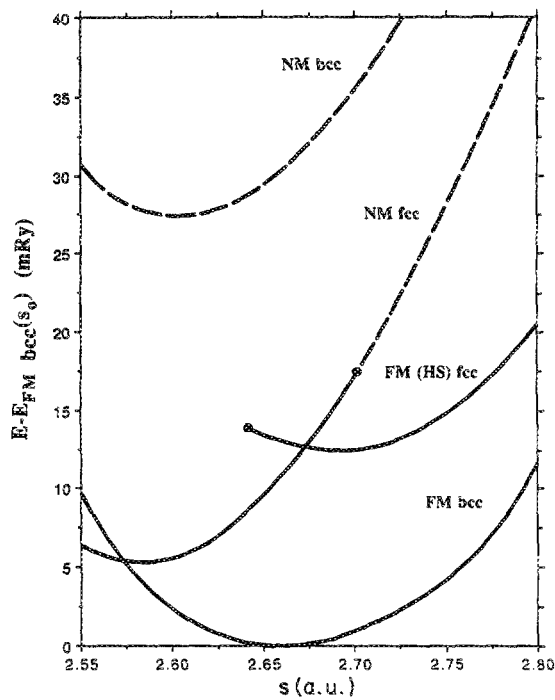


FIG. 1. Total energies of fcc and bcc phases of iron vs WS radius s . For the FM fcc phase only the energy of the high-spin (HS) states is shown. The dashed lines correspond to the states unstable with respect to spontaneous magnetization. The solid circles here and in other figures show the borders of stability.

both the NM and FM phases would have double-well shapes with minima at the bcc and fcc states and an intermediate smooth maximum at $1 < c/a < \sqrt{2}$.

Unexpectedly, the calculated picture is quite different. Figure 2 shows our results for three pressures: 140, 0, and -120 kbar. At 140 kbar the FM bcc and NM fcc phases are almost at equilibrium [the exact equilibrium takes place at $P_0 = 145$ kbar (Ref. 7 and 8)]. Though the NM bcc phase is unstable with respect to spontaneous magnetization, we still could expect that, disregarding the magnetic instability, it should correspond to a local enthalpy minimum along the c/a path. Instead, at all pressures, the NM bcc enthalpies have maxima: e.g., the NM bcc phase is also unstable with respect to tetragonal (shear) deformation. The FM contri-

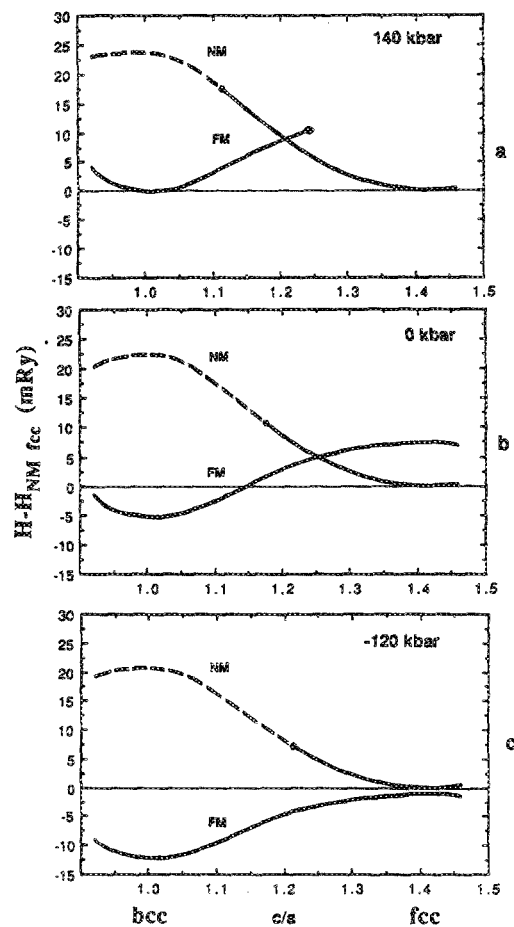


FIG. 2. Enthalpy plots along the Bain path for iron at three pressures.

bution stabilizes the tetragonal phases near the bcc region with an enthalpy minimum at $c/a = 1$. However, at high pressures, approaching the fcc region, ferromagnetism disappears and the FM solution does not correspond to an extremum (either a minimum or a maximum) of energy (or enthalpy). At lower pressures, however, where the FM solution does exist, the FM fcc phase corresponds to an enthalpy maximum. This simply means that the FM fcc phase is unstable with respect to tetragonal deformation, and therefore cannot exist.

TABLE I. Magnetic energy coefficients for different c/a . The footnotes denote the WS radii at which FM solutions disappear.

c/a	E_0	E_1 (10^4)	E_2 (10^6)	E_3 (10^7)	E_4 (10^7)	E_5 (10^8)
bcc	-31.008 28	1.449 390	-0.424 209 8	0.460 997 3	-2.210 560	0.395 594 6
1.08	-26.275 35	1.110 330	-0.328 110 1	0.358 840 1	1.728 155	0.310 270 0
1.12	-21.128 88	0.696 992 7	-0.203 802 6	0.219 410 1	-1.037 026	0.182 553 4
1.16	-15.660 03	0.595 340 1	-0.173 001 3	0.184 534 6	-0.862 489 8	0.150 027 8
1.20 ^a	-11.099 38	1.565 801	-0.458 232 5	0.497 844 2	-2.387 379	0.427 583 0
1.24 ^b	-7.933 51	3.749 784	-1.083 036	1.167 353	-5.572 479	0.995 288 9
1.32 ^c	-4.301 64	1.635 138	-0.460 035 7	0.481 019	-2.208 583	0.378 994 2
fcc ^d	-4.671 38	-6.937 274	2.030 991	-2.232 259	10.907 32	-1.997 477

^a 2.555 a.u. ^c 2.636 a.u.

^b 2.584 a.u. ^d 2.643 a.u.

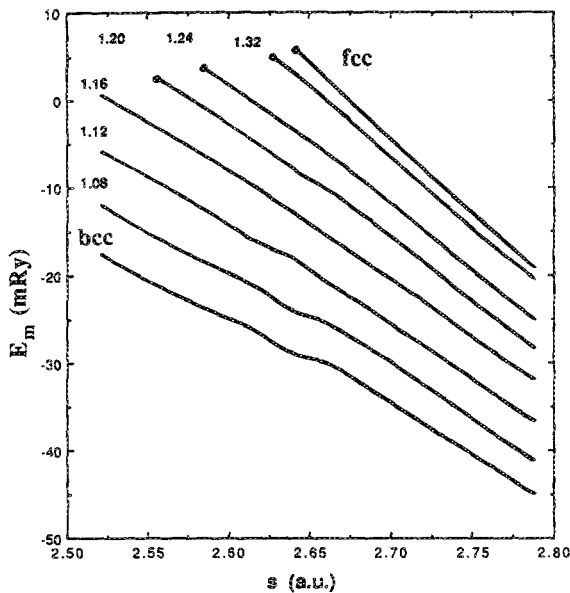


FIG. 3. Ferromagnetic contributions E_m vs s for different c/a . Solid circles indicate the points where FM phases cease to exist, i.e., do not correspond to either a minimum or a maximum of energy (see footnote in Table I).

This is an important new result. In the past, in order to explain the thermodynamics of fcc iron, a two-spin model was postulated.^{18,19} It was proposed that a mixture of two magnetic states—high-spin FM and low-spin antiferromagnetic (AFM)—could exist in fcc iron. We have found, however, that a homogeneous FM state in fcc iron is unstable. An AFM state can exist and has been observed experimentally at low temperatures.²⁰ As for the FM fcc phase, it has been observed as precipitates in Cu-Au alloys,²¹ and thin fcc films grown epitaxially on Cu surfaces were reported to be FM.²² In both cases finite-size effects could be responsible for the relative stability of the FM fcc phase.

Thus, going along the Bain path from bcc to fcc, first the FM bcc phase is stable, but near $c/a = 1.2$ a first-order phase transition occurs, and at higher c/a the NM face-centered-tetragonal phase is stable. As a result, the enthalpy plot is not a smooth double-well curve, but has a cusp.

In our calculations, the FM contributions to the total energy were approximated (with a rms of ≈ 0.03 mRy) by the five-term function

$$E_m(c/a, s) - E_0 = E_1 + E_2/s^2 + E_3/s^4 + E_4/s^6 + E_5/s^8,$$

where E_m is in mRy.

As an aid to the development of improved interatomic potentials for iron, in Table I we present the quantities $E_0 - E_5$ for a few values of c/a . Figure 3 plots E_m versus s for the same c/a values. E_m can be added to the nonmagnetic part of the energy modeled by simple interatomic potential functions.

IV. CONCLUSIONS

The suggested procedure of using the Stoner model and treating I as an adjustable parameter enabled us to calculate, for the first time, structural properties of fcc and bcc iron in good agreement with experiment. The results shed new light on the magnetic properties of iron. We would like to once again stress that the Stoner model in combination with reliable nonmagnetic calculations allows one to perform a detailed analysis of structural and magnetic properties of crystals.

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- ¹ K. B. Hathaway, H. J. F. Jansen, and A. J. Freeman, *Phys. Rev. B* **31**, 7603 (1985).
- ² V. L. Moruzzi, *Phys. Rev. Lett.* **57**, 2211 (1986).
- ³ V. L. Moruzzi, P. M. Marcus, K. Schwarz, and P. Mohn, *Phys. Rev. B* **34**, 1784 (1986).
- ⁴ H. J. F. Jansen and S. S. Peng, *Phys. Rev. B* **37**, 2689 (1988).
- ⁵ E. C. Stoner, *Proc. R. Soc. London, Ser. A* **169**, 339 (1939).
- ⁶ G. L. Krasko, *Phys. Rev. B* **36**, 8565 (1987).
- ⁷ G. L. Krasko, *Solid State Commun.* **70**, 1099 (1989).
- ⁸ G. L. Krasko and G. B. Olson, *Phys. Rev. B* **40**, 11536 (1989).
- ⁹ O. K. Andersen, O. Jepsen, and D. Gloetzel, in *Highlights of Condensed Matter Theory*, edited by F. Bassani, F. Fumi, and M. P. Tosi (North-Holland, New York, 1985).
- ¹⁰ O. K. Andersen, in *Electronic Structure of Complex Systems*, edited by P. Phariseau and W. M. Timmerman (Plenum, New York, 1984), pp. 11–65.
- ¹¹ H. L. Skriver, *The LMTO Method* (Springer, Berlin, 1984).
- ¹² D. Gloetzel and O. K. Andersen (unpublished); N. E. Christensen, *Phys. Rev. B* **32**, 207 (1985); H. L. Skriver, *ibid.* **31**, 1909 (1985).
- ¹³ U. von Barth and L. Hedin, *J. Phys. C* **5**, 1629 (1972).
- ¹⁴ U. von Barth and C. D. Gelatt, Jr., *Phys. Rev. B* **21**, 2222 (1980).
- ¹⁵ J. F. Janak, *Phys. Rev. B* **16**, 255 (1977).
- ¹⁶ J. Hubbard, *Phys. Rev. B* **19**, 2626 (1979); **20**, 4584 (1979); H. Hasegawa and D. G. Pettifor, *Phys. Rev. Lett.* **50**, 130 (1983).
- ¹⁷ E. C. Bain, *Trans. Am. Inst. Min. Metall. Eng.* **70**, 25 (1924).
- ¹⁸ L. Kaufman and H. Bernstein, *Computer Calculations of Phase Diagrams* (Academic, New York, 1970).
- ¹⁹ K. G. Tauer and R. J. Weiss, *Bull. Am. Phys. Soc.* **6**, 125 (1961); L. Kaufman, E. V. Clougherty, and R. J. Weiss, *Acta Metall.* **11**, 323 (1963); R. J. Weiss, *Proc. R. Soc. London* **82**, 281 (1963).
- ²⁰ C. Abrahams, L. Guttman, and J. S. Kasper, *Phys. Rev.* **127**, 2052 (1962); G. Johnson, M. B. McGirr, and D. A. Wheeler, *Phys. Rev. B* **1**, 3208 (1970).
- ²¹ U. Gonser, R. Krischel, and S. Nasu, *J. Magn. Magn. Mater.* **15-18**, 1145 (1980).
- ²² J. G. Wright, *Philos. Mag.* **24**, 217 (1971); U. Gradmann, W. Kümmerle, and P. Tillmanns, *Thin Solid Films* **34**, 249 (1976); R. F. Willis, J. A. C. Bland, and W. Schwarzacher, *J. Appl. Phys.* **63**, 4051 (1988).