Influence of the local-spin-density correlation functional on the stability of bcc ferromagnetic iron

D. Singh
Naval Research Laboratory, Washington, D.C. 20375-5000

D. P. Clougherty
Department of Physics, University of California, Santa Barbara, California 93106

J. M. MacLaren
Department of Physics, Tulane University, New Orleans, Louisiana 70118

R. C. Albers
Theoretical Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545

C. S. Wang
Department of Physics and Astronomy, University of Maryland, College Park, Maryland 20472
(Received 22 April 1991)

The influence of local-spin-dependent correlation effects on the predicted stable ground-state phase of iron is reexamined with use of general-potential linearized augmented-plane-wave calculations. Differences in the form of the Vosko-Wilk-Nusair (VWN) local-spin-density functional used in previous studies are noted, since in previous studies significant additional approximations were made with respect to those of Vosko, Wilk, and Nusan [Can. J. Phys. **58**, 1200 (1980)] and of MacLaren, Clougherty, and Albers [Phys. Rev. B **42**, 3205 (1990)]. While the results of previous linear muffin-tin orbital calculations using the VWN functional predict a bcc ferromagnetic ground state, the present calculations show that the VWN spin-correlation effects fail to stabilize a bcc ground state. Considerable sensitivity to the form of the spin interpolation is found.

The local-spin-density approximation (LSDA) has had remarkable success in the prediction of ground-state properties of many condensed-matter systems.[1] Elastic constants, lattice constants, and ground-state crystal structures in close agreement with experimentally determined values all attest to the utility of the LSDA. There are cases, however, where the LDA is known to be inadequate, for example calculating cohesive energies of solids. However, this problem is usually attributed to errors in the atomic reference calculation. Perhaps the most notable exception of a paramagnetic calculation in the solid state that has a significant error is in the prediction of lattice constants for the alkali metals Li, Na, K, and Cs.[1,2] The calculated values underestimate experimental values by between 3% and 6%, a factor that may be attributable to the large compressibility of the alkali metals. Results for some magnetic transition metals such as Fe and Cr show significantly worse agreement in properties such as the bulk modulus and lattice constant when compared to experiment than do nonmagnetic transition metals. In the case of Fe, full-potential calculations predict a fcc ground state.[3] This failure to predict the correct ground state for Fe has been attributed to the LSDA and to the neglect of nonlocal corrections to exchange and correlation in the LSDA. The inclusion of nonlocal effects through the generalized-gradient expansion stabilized the bcc ferromagnetic phase.[4] In a recent paper,[5] linear muffin-tin orbital (LMTO) calculations for Fe were performed using the local-spin-dependent potential[5,6] derived from the Vosko-Wilk Nussair (VWN) form for the correlation energy.[7] We wish to stress here that in the VWN functional there are two interpolations: one to fit a simple functional form for the correlation energy as a function of density to the Monte Carlo data of Ceperley and Alder,[8] and the second to describe the correlation energy as a function of the degree of spin polarization of the electron gas. An alternative density interpolation was suggested by Perdew and Zunger[9] (PZ), and this combined with the VWN spin interpolation was the form of the VWN functional used in the LMTO calculations in Ref. 5. The results of those LMTO calculations for Fe showed that the detailed form of the spin interpolation was important and that with the PZ density interpolation, the von Barth–Hedin (vBH) (Ref. 10) spin scaling predicted a fcc paramagnetic ground state while the VWN spin scaling predicted the observed bcc ferromagnetic crystal as that of lower total energy. This conclusion was also reached with the VWN density interpolation. However, the small value of the energy difference between bcc and fcc Fe obtained with the correct VWN spin interpolation is probably similar to intrinsic errors in the LMTO approach. The results of that study are included in Table I along the full-potential calculations. Thus the LMTO results are suggestive that the ground state of Fe can be obtained with an accurate local-spin-density potential, rather than conclusive. The full-potential calculations reported here, however, show that the fcc ground state is predicted with the VWN spin in-

terpolation.

To complement this earlier work we present, in this Brief Report, the results of general-potential linearized augmented-plane-wave (LAPW) calculations for bulk Fe using the different local-spin-density functionals discussed above. The LAPW technique has been discussed in detail elsewhere.[11] Accordingly only those details of the calculation particular to the present study are discussed. The calculations were performed fully self-consistently with a muffin-tin radius $R_{MT}=2.0$ a.u. (note, this is a general potential method—no shape approximations are made in either the charge density or potential). The basis-set sizes were determined by plane-wave cutoffs of $K_{max}=9.0/R_{MT}$. The Brillouin-zone samplings were performed using sets of 40 and 60 special **k** points[12] for the bcc and fcc structures, respectively. Convergence was accelerated by broadening states near the Fermi level with an artificial Fermi-Dirac distribution of width 1 mRy. This temperature broadening introduces errors in the total energy of about 0.01 mRy, i.e., considerably smaller than the effects of other approximations in the calculation. Convergence tests were performed using sets of 240 and 408 **k** points for the bcc and fcc structures, respectively. Based on these, it was determined that the calculations were converged to better than 1 mRy, with respect to Brillioun-zone sampling and basis-set size. The calculations were carried out as much in parallel as possible for the different functionals. Total energies were calculated for five lattice parameters between 4.9 and 5.3 a.u. for the paramagnetic bcc structure, five lattice parameters between 5.0 and 5.4 a.u. for the magnetic bcc structure, and five lattice parameters between 6.2 and 6.7 a.u. for the nonmagnetic fcc structure. The energies were then fitted to the Murnaghan equation of state[13] in order to determine the static properties of these phases.

In order to avoid any ambiguity about the form of the local spin potential, we state briefly the differences in the form of the potential used in this work and that used in previous LAPW calculations. In the previous calculations the true VWN spin-polarized energy functional was approximated[7] by assuming that the factor $[1+\beta(r_s)\zeta^4]$ appearing in the spin-dependent correlation energy [Eq. (2) of Ref. 5] was unity. This oversimplifies the resulting expressions for the potentials [Eq (3) of Ref. 5], which are just the functional derivatives of the spin-polarized exchange-correlation energy. Since this is equivalent to setting β to 0 in this factor, it results effectively in a vBH-like spin interpolation for correlation. Note that in the limit that β goes to zero the spin-polarization dependence (ζ) of the VWN spin form becomes the same as that of vBH. Thus, previous calculations did not really test the effect of spin interpolation on the determination of the ground state; only the sensitivity of the ground state to the *charge-density* interpolation.

The results presented here correct that deficiency and are summarized in Table I along with the LMTO results.

TABLE I. Summary of LAPW and LMTO total energies (mRy/atom) of the bcc state. The energies are quoted with respect to the relevant nonmagnetic fcc structure.

LDA	Phase	Spin interpolation	LMTO[a]	LAPW
CA-PZ	ferro	VWN	−1.9	4.2
CA-PZ	ferro	vBH	2.9	7.7
vBH	ferro	vBH	1.2	4.1
CA-PZ	para			25.9
vBH	para			25.9

[a]J. M. MacLaren, D. P. Clougherty, and R. C. Albers, Phys. Rev. B **42**, 3205 (1990).

The main conclusion of the new LAPW calculations is that, in contrast to the LMTO work, the fcc phase is the one with the lowest total energy. The correct VWN spin interpolation does provide a 1-mRy stabilization compared with previous approximate VWN potentials and a 3-mRy stabilization compared with the vBH spin interpolation. Both the LMTO and LAPW calculations produce the same trends, however in the latter it is insufficient to produce a bcc ferromagnetic ground state, as was found in the LMTO calculations, because of the larger energy separation between fcc and bcc phases. A comparison of these two sets of calculations provides an approximate estimate for the error due to the atomic-sphere approximation (ASA). Based upon differences between the present LAPW and LMTO total-energy results with the vBH functional for fcc and bcc structures, we estimate an ASA error of about 4 mRy. This is in agreement with previous estimates of Jansen and Peng.[14] To conclude, we have shown that while none of the functionals tested yields a correct ordering of phases for Fe, there is considerable sensitivity in the energy difference to the particular functional used. We note that since the CA data were only obtained for a small number of r_s values (2, 5, 10, 20, 50, and 100), it is possible that fitted functionals could be improved upon in replicating the true homogeneous electron-gas correlation energy. The two popular density fits to the CA data by PZ and VWN produce differences[15] in the total correlation energy of about 8 mRy/atom. Therefore, it may still be possible that the correct ground state for Fe may be obtained within the LSDA, if more accurate density and spin interpolation formulas were to become available. It is clear that the better spin interpolation does tend to stabilize the ferromagnetic ground state and that possible improvements to this may further stabilize the magnetic state.

We thank J. Perdew and J. Callaway for useful discussions. This work is partially supported by the Office of Naval Research and by NSF Grant No. DMR-8901453. The LAPW calculations were performed at the Cornell National Supercomputer Facility.

[1]V. L. Moruzzi, J. F. Janak, and A. R. Williams, *Calculated Electronic Properties of Metals* (Pergamon, New York, 1978); M. Yin and M. L. Cohen, Phys. Rev. Lett. **45**, 1004 (1979); G. B. Bachelet, H. S. Greenside, G. A. Baraff, and M. Schlüter, Phys. Rev. B **24**, 4745 (1981).

[2]R. Wyckoff, *Crystal Structures* (Interscience, New York, 1963).

[3]C. S. Wang, B M. Klein, and H. Krakauer, Phys. Rev. Lett. **54**, 1852 (1985); H. J. F. Jansen, K. B. Hathaway, and A. J. Free-

man, Phys. Rev. B **30**, 6177 (1984); K. B. Hathaway, H. J. F. Jansen, and A. J. Freeman, *ibid.* **31**, 7603 (1985).

[4]P. Bagno, O. Jepsen, and O. Gunnarsson, Phys. Rev. B **40**, 1997 (1989); D. J. Singh, W. E. Pickett, and H. Krakauer, *ibid.* **43**, 11 628 (1991).

[5]J. M. MacLaren, D. P. Clougherty, and R. C. Albers, Phys. Rev. B **42**, 3205 (1990).

[6]We would like to thank J. Perdew for pointing out that a derivation of the exchange-correlation potentials, which leads to equivalent results to those published in Ref. 3., can be found in Phys. Rev. B **24**, 4264 (1981). It should also be noted that Painter's parameter A for ε_c^P in Table I should read 0.062 181 4 to be consistent with Ref. 4.

[7]S. H. Vosko, K. Wilk, and N. Nusair, Can. J. Phys. **58**, 1200 (1980).

[8]D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. **45**, 566 (1980); D. M. Ceperley, Phys. Rev. B **18**, 3126 (1978).

[9]J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).

[10]U. von Barth and L. Hedin, J. Phys. C **5**, 1629 (1972).

[11]O. K. Andersen, Phys. Rev. B **12**, 3060 (1975); D. R. Hamann, Phys. Rev. Lett. **42**, 622 (1979); E. Wimmer, H. Krakauer, M. Weinert, and A. J. Freeman, Phys. Rev. B **24**, 864 (1981); S.-H. Wei and H. Krakauer, Phys. Rev. Lett. **55**, 1200 (1985); S.-H. Wei, H. Krakauer, and M. Weinert, Phys. Rev. B **32**, 7792 (1985).

[12]A. Baldereschi, Phys. Rev. B **7**, 5212 (1973); D. J. Chadi and M. L. Cohen, *ibid.* **8**, 5747 (1973); H. J. Monkhorst and J. D. Pank, *ibid.* **13**, 5188 (1976); **16**, 1748 (1977).

[13]F. D. Murnaghan, Proc. Natl. Acad. Sci. U.S.A. **30**, 244 (1944).

[14]H. J. F. Jansen and S. S. Peng, Phys. Rev. B **37**, 2689 (1988).

[15]J. M. MacLaren (unpublished).